



Osama Shahin Elzoubi

Exploiting the elastic properties of metallic glass thin foils:
the undulatory mechanical response upon loading
under geometric confinement

School of Aerospace, Transport and Manufacturing
PhD in Manufacturing

PhD
Academic Year: 2019 - 2023

Supervisor: Konstantinos Georgarakis
Associate Supervisor: Konstantinos Salonitis
Associate External Supervisor: Nikolaos Panagiotopoulos

June 2023



School of Aerospace, Transport and Manufacturing

PhD

Academic Year 2019 - 2023

Osama Shahin Elzoubi

Exploiting the elastic properties of metallic glass thin foils:
the undulatory mechanical response upon loading
under geometric confinement

Supervisor: Konstantinos Georgarakis

Associate Supervisor: Konstantinos Salonitis

Associate External Supervisor: Nikolaos Panagiotopoulos

June 2023

This thesis is submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

© Cranfield University 2023. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

ABSTRACT

A peculiar mechanical response was recently observed for metallic glass thin foils in confined geometries under normal loading. In particular, when an arc-shaped metallic glass foil is subjected to normal loading, it deforms elastically, changing its shape by progressively increasing the number of formed sinusoidal arcs. This mechanical response type is called undulatory behaviour and results from a combination of successive elastic bending and buckling events occurring on the foil. This behaviour is reversible and repeatable as long as the deformation of metallic glass foils remains within the elastic deformation limit for metallic glasses ($< 2\%$ strain) and can be exploited for developing novel types of nonlinear springs.

The undulatory behaviour of metallic glasses was first reported in 2016 and has been very little studied. This project aims to explore the limitations of studying the mechanism and the underlying phenomena associated with this behaviour and exploit its potential for engineering applications. More specifically, the undulatory behaviour for three different metallic glass systems (i.e. Fe-Cr-Si-B and Ni-Fe-Si-B-Mo and Ni-B-Si) with varying thicknesses of foil in the range from 19 – 40 μm was studied, and various initial set-up geometries were investigated. Specific focus was given to understanding the mechanism of the undulatory behaviour, establishing some spring design principles and exploring the cycling fatigue life of the glassy foils.

The undulatory behaviour involves elastic deformation, buckling and post-buckling phenomena occurring in a repeatable sequence. Buckling plays a significant role in the mechanism of undulatory behaviour. The required load for buckling was approached using the Euler's for buckling. The standing wave was shown to be able to describe the sequence of the undulatory response but only for the waveforms with perfect sinusoidal arcs. The parameters of the initial arc's geometry set-up, such as the boundary length (chord), amplitude, and foil thickness enable the tuning of the undulatory behaviour and offer capabilities for designing spring-type devices with desirable characteristics that can efficiently operate in different load ranges.

Under cyclic loading the glassy foils endured between 19×10^3 to 225×10^3 cycles, depending on load/strain parameters, foil thickness and alloy compositions, typically higher than conventional low cycle springs. Crack initiation during cyclic loading was found to be associated with surface defects and side edges of the foils. This unique mechanical response of metallic glass foils makes them a promising material for a wide range of applications, contributing to being exploited for the enormous potential for designing novel types of micro-flat springs using the exceptional mechanical and elastic properties of metallic glass foils.

Keywords:

metallic glass foils; undulatory behaviour; buckling; flat micro-springs

ACKNOWLEDGEMENTS

This work would not have been possible without the support of the Libyan Ministry of Higher Education & Scientific Research support via Libyan Academic Attaché – London, United Kingdom.

I am most grateful to my supervisor, Dr. Konstantinos Georgarakis, for his intellectual and emotional support throughout my PhD studies. He has taken me from my lack of knowledge of metallic glass and introduced me to a new world. Performing experiments with him left me with pleasure and excitement, and I hope to retain this enthusiasm in future research endeavours. His encouragement and understanding of my situation enabled me to be here today, about to begin my academic career. His patience in explaining the most obscure concepts, his ability to help me view results in a whole new light, and his ability to teach me how to think independently are very much appreciated. He has shown me wisdom and care even on the rainiest days. My sincere thanks go to him for all that he has done for me over the years.

Thanks to Dr. Nikolaos Panagiotopoulos for his guidance and recommendation, and to Prof. Konstantinos Salonitis and Dr. Martin Stiehler, for their keenness and support for my study. Dr. Claudiu Giusca gave me help with surface analysis equipment and his support. A big thanks to Dr. David Ayre who is in charge of the thermal analysis equipment and his support.

It would not have been possible for me to accomplish my work without the collaboration and support of many people. I owe a great deal of gratitude to my technicians Dr. Andrea Giampiccolo, and Jarryd Braithwaite, for their help in mechanical testing, and to Christine Kimpton, for her help in SEM and XRD testing. I appreciate all of the members of the laboratories at Cranfield University, my colleagues and friends. Thank you so much to librarian Emma Turner for all the help and guidance she provided.

Finally, my deepest thanks and appreciation go out to my parents and my wife for their support and encouragement. Having their patience and support has enabled me to reach where I am today.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS.....	iii
LIST OF FIGURES	viii
LIST OF TABLES	xvi
LIST OF EQUATIONS.....	xviii
LIST OF ABBREVIATIONS	xx
1 Introduction.....	21
1.1 Research Background	21
1.2 Research Aim and Objectives.....	23
1.3 Research Motivation	23
1.4 Research Scope and Limitations	24
1.5 Contribution to Knowledge.....	25
1.6 Thesis Structure.....	26
1.7 Publications	27
2 Literature review	28
2.1 Introduction	28
2.2 Metallic glass history.....	29
2.3 Formation of glassy state	33
2.4 Synthesis of metallic glass.....	35
2.4.1 Melt-spinning technique	35
2.4.2 Other methods to produce metallic glass	37
2.5 Mechanical properties of metallic glass	38
2.6 Fe-based metallic glasses	42
2.6.1 Development history of Fe-based MGs	42
2.6.2 Structure and mechanical properties.....	45
2.6.3 Applications of Fe-based bulk glassy alloys	49
2.7 Ni-based metallic glasses	52
2.8 Ni-Fe-based metallic glasses.....	55
2.9 Buckling of metallic glasses	59
2.10 Undulatory elastic behaviour of metallic glasses	64
2.11 Fatigue on metallic glasses.....	78
2.11.1 Fatigue crack initiation growth.....	79
2.11.2 Fatigue limit of metallic glasses.....	80
2.11.3 Fatigue crack initiation.....	82
2.12 Springs.....	84
2.12.1 Spring types and applications	85
2.12.2 Metallic glasses spring applications	88
3 Research Methodology	91
3.1 Introduction	91
3.2 Materials	91

3.2.1 Fe-based metallic glass foils	92
3.2.2 NiFe-based metallic glass foils	92
3.2.3 Ni-based metallic glass foils	92
3.3 Experimental method to explore undulatory behaviour	92
3.3.1 Method	92
3.3.2 Set-up.....	94
3.3.3 Structure characterisation techniques of MG foils	97
3.4 Experimental method to explore fatigue life under load cycling	97
3.4.1 Method and Set-up.....	97
3.4.2 Characterisation techniques of MG foils.....	100
4 Undulatory elastic behaviour of metallic glass foils of fully amorphous alloy	103
4.1 Introduction	103
4.2 Experimental details.....	Error! Bookmark not defined.
4.3 Results and discussion	104
4.3.1 Structure.....	104
4.3.2 Undulatory behaviour	105
4.3.3 Estimation of local strain	110
4.3.4 Loading/unloading rate effects	113
4.3.5 Mechanical response of crystalline materials	114
4.3.6 Mechanical response of superelastic alloy	116
4.4 Conclusions	117
5 Undulatory elastic behaviour of partially crystalline ($\text{Ni}_{78}\text{Si}_8\text{B}_{14}$) metallic glass foils.....	119
5.1 Introduction	119
5.2 Experimental details.....	Error! Bookmark not defined.
5.3 Results and discussion	119
5.3.1 Structural characterisation.....	119
5.3.2 Measurements of crystal volume fraction	120
5.3.3 Elastic undulatory behaviour	123
5.3.4 The effect of thickness on the undulatory behaviour	128
5.3.5 Estimation of local strain during arc formation.....	130
5.3.6 Undulatory behaviour of four metallic glass foils	132
5.4 Conclusions	134
6 Mechanism of the undulatory behaviour and spring design	136
6.1 Introduction	136
6.2 Analysis of perfect sinusoidal waveforms	136
6.3 Mechanism of undulatory behaviour	142
6.4 Buckling phenomena	144
6.4.1 Boundary conditions.....	146
6.4.2 Buckling analysis of the glassy foils during undulatory behaviour ..	148
6.4.3 Working range of spring design.....	156

6.5 Conclusions	162
7 Fatigue behaviour of metallic glass foils	165
7.1 Introduction	165
7.2 Experimental details.....	Error! Bookmark not defined.
7.3 Results and discussion	166
7.3.1 Cyclic lifetime tests of Fe-based metallic glass foils	166
7.3.2 Fatigue behaviour of other metallic glass foils.....	173
7.3.3 Cyclic fatigue for pre-buckling (low strain amplitude)	177
7.3.1 Characteristic features of fatigue failure of metallic glass foils	182
7.3.2 Surface roughness of Fe-based glassy foil	189
7.3.3 Surface roughness analysis of Fe-based glassy foil	192
7.3.4 Surface analysis of NiFe-based glassy foil.....	193
7.3.5 Surface analysis of Ni-based glassy foil.....	195
7.3.6 Suggestions to improve the fatigue property of metallic glass foils	201
7.4 Conclusions	204
8 Conclusions and future work	207
8.1 General conclusions	207
8.2 Future work recommendations	209
REFERENCES.....	211

LIST OF FIGURES

Figure 1-1: a) initial arc-shaped of metallic glass foil; b) assembly of snapshots from the undulatory behaviour with images of perfect sinusoidal waveforms.	22
Figure 2-1: Diagram of a) amorphous atomic structure; b) crystalline structure [6].	29
Figure 2-2. Different BMG systems with discovered years against the maximum diameter [6].	30
Figure 2-3. MG critical casting thickness versus discovery year [14].	31
Figure 2-4. Toughness versus strength for conventional engineering materials, bulk metallic glasses, and metallic glass composites [8].	32
Figure 2-5. Mechanical properties for over 1500 metallic alloys compared to metallic glasses [18].	33
Figure 2-6. Transition states of metallic glasses formation [23].	34
Figure 2-7. Illustration of the melt-spinning process [26].	36
Figure 2-8. Amorphous metal alloys combine higher strength than crystalline metal alloys with an elasticity of polymers [14].	39
Figure 2-9. Strength and strain limit of Cu-Zr-based MGs of different sizes [38].	40
Figure 2-10. Comparison between the elastic modulus of MGs and their solvent metals [41]	41
Figure 2-11: a) Typical XRD patterns for Fe-Cr-Si-B-C as built rotor, powder and spun ribbon [67]; b) DSC curves for the $\text{Fe}_{73}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_5\text{B}_4$ rods for different diameters [68].	44
Figure 2-12. Anticorrosive applications of Fe-based glassy alloy coatings [68].	51
Figure 2-13. SEM images; a) proprietary micro metallic punch; b) die; c) micro gear and punch [85][68].	52
Figure 2-14. X-ray diffraction patterns of Ni-Si-B alloy [90].	53
Figure 2-15. DSC thermograms of Ni-Si-B alloy [90].	54
Figure 2-16. XRD patterns of the $\text{Ni}_{40}\text{Fe}_{40}(\text{BSi})_{19}\text{Mo}_1$ ribbons were then annealed for 2 hours at different temperatures [93].	56
Figure 2-17. DSC curves of the $\text{Ni}_{38}\text{Fe}_{40}\text{B}_{18}\text{Mo}_4$ (sample 1), $\text{Fe}_{38}\text{Ni}_{35}\text{Mo}_4\text{Si}_5\text{B}_{18}$ (sample 2), and $\text{Fe}_{39}\text{Ni}_{36}\text{Mo}_2\text{Si}_5\text{B}_{18}$ (sample 3) alloys with a heating rate of 10 K/min [94].	56
Figure 2-18. Stress-strain curve of 2 mm diameter BMG alloy rod [97].	58

Figure 2-19. Typical curve of buckling states of a column [101].	60
Figure 2-20: a) Buckling load P_{cr} of Cu NW@CNT versus $1/L^2$, where L refers to Euler length of NW@CNT; b) same relation with CU@CNT (14,0) and (16,0) versus $1/L^2$.	62
Figure 2-21. Assembly of waveforms for an arc-shaped MG foil formed under load [1].	66
Figure 2-22. The maximum local strain on the Fe-based MG foil versus the number of arcs for different aspect ratios [1].	67
Figure 2-23: a) Load-displacement curve for the Fe-based for different boundary length L values; b) spring's rate k as a function of the number of arcs for various boundary conditions of L ; c) maximum applied normal load on the foils with sinusoidal arcs versus the number of arcs for different foil width [2].	69
Figure 2-24. An electromechanical switch exploiting the undulatory behaviour of MG foils [1].	70
Figure 2-25. Schematic of the electrical wiring for the automatic filling of an aquarium using a mechanical response of an MG foil as an electromechanical switch [117].	71
Figure 2-26: a) Shaped $Pd_{82}Si_{20}$ glassy tape showing double bending ductility; b) example of MG foil with complex shaping [127].	72
Figure 2-27. Front-view snapshots of the shaped MG foil: a) Free-standing pre-shaped MG foil; (b) elastic deformation at the maximum load when still functioning as a conventional wave spring; (c) the undulatory behaviour in which further loading leads to elastic multiplication of the number of arcs in the waveform and to an increase in the load capacity [118].	73
Figure 2-28. Load as a function of displacement during loading and unloading of the linear wave spring made by pre-shaping an MG foil. The transition zone is characteristic of MG foils, and corresponds to the undulatory behaviour in which additional arcs are generated (Fig. 2-26c) [118].	73
Figure 2-29: a) and b) side view of wave springs with the maximum shaping factor achievable for (a) $T_a < T_{embrit}$ (plastic) and (b) $T_a > T_{embrit}$ (brittle); c) and d) the corresponding 450 views; e) and f) the corresponding top views [118].	74
Figure 2-30: a) initial arc-shaped MG foil; b) load-displacement curve for L30h10W25 condition [119].	75
Figure 2-31: Present schematic of the arc-shaped MG foil in (x,y) plane with model parameters [119].	75
Figure 2-32: a) undulatory behaviour of MG foil with the corresponding curvature radius R_i ; b) the radius curvature R versus amplitude h [119].	77

Figure 2-33: a) numerical results presenting the profiles of foil deform; b) intermediate stage of undulatory behaviour for metallic glass foil [119].	77
Figure 2-34. Fatigue-crack-growth rates (da/dN) against the stress-intensity factor range (ΔK) [138].	80
Figure 2-35. The fatigue life of $Zr_{41}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [4].	81
Figure 2-36: An SEM image shows the crack was initiated by defects created during sample preparation, and many shear bands formed around the crack tip [2].	83
Figure 2-37: a) The linear spring is the most common spring type; b) the force of a non-linear spring varies nonlinearly with deflection.	85
Figure 2-38. Shows helical or coil spring types, made from wire coiled as a helix [153].	86
Figure 2-39. Types of disc springs with a round-shaped conical disc [153].	87
Figure 2-40. Load-displacement of non-linear spring function and strain energy absorption rate [154].	88
Figure 2-41. Conical spring microactuator, fundamental structure and micrographs [156].	89
Figure 2-42: a) Selection of inner and outer diameter for MG annular wave springs [118]; b) spiral shape spring made of $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$ glassy alloy [26][160]; c) helical springs of $Zr_{55}Cu_{30}Al_{10}Ni_5$ glassy wire alloy [26].	90
Figure 3-1. Specimen of MG foil set-up, including parts attached to a machine.	94
Figure 3-2. An Instron compression machine enclosing the MG foil between custom-made fixtures.	95
Figure 3-3. Foil and deformed shape to estimate local strain.	96
Figure 3-4. Analysis of local strain measurements to estimate MG foil deformation	96
Figure 3-5. Shows the cycle fatigue device with a stepper motor and pushing plates at the other end.	98
Figure 3-6. Plastic support where the specimen (MG foil) is placed and secured with stainless steel fixing clamps.	99
Figure 3-7. A Schematic of foil dimensions for 31 measurements taken along the foil width.	101
Figure 4-1: a) Initial arc-shaped of MG foil; b) harmonic undulatory response of arc shaped of MG foil	104
Figure 4-2. X-ray diffraction pattern of the metallic glass foils.	105

Figure 4-3. DSC thermograms for the metallic glass foils.	105
Figure 4-4: a) Load-displacement curves for ten cycles loading/unloading of a foil; b) load-displacement curves on three different samples of Fe-based metallic glass foils.....	106
Figure 4-5. Load-displacement curves upon loading for the NiFe-based (25 μm thick, blue) metallic glass foil compared to the Fe-based (19 μm thick, red) one for $L=20\text{mm}$ and $h_1=5\text{mm}$	107
Figure 4-6: a) Load-displacement curves for the NiFe-based (25 μm thick) metallic glass foil for boundary distance L values in the range of 20 –50 mm and h_1 to L ratio $h_1/L=0.25$; b) Load-displacement curves for the Fe-based (19 μm thick) metallic glass foil.....	109
Figure 4-7: a) Maximum applied normal load on the foils with n_i sinusoidal arcs just before the formation of the $n_i +1$ arc versus the number of arcs for the Fe-based and NiF-based metallic glass foils for set-ups with boundary distance L values in the range of 20 –50 mm and h_1 to L ratio $h_1/L=0.25$; b) the spring constants as calculated in the quasi-linear segments of the load- displacement curves Values for $L=40\text{ mm}$ were omitted for the clarity of the graphs.....	110
Figure 4-8: a) Assembly of snapshots from the undulatory response of a metallic glass foil with images of waveforms with perfect sinusoidal shaped arcs; b) assembly of snapshots from the undulatory response with images of waveforms with perfect sinusoidal shaped arcs (R_2 and R_4) and distorted arcs (R_3); and c) load-displacement curve of the undulatory response for the Fe- based foil.	111
Figure 4-9: Maximum local strain on the foils a) at waveforms with perfectly shaped sinusoidal arcs (equivalent to R_2 and R_4 in the example of Figure 4- 8b); b) at waveforms with distorted arcs, just before the formation of a new (n_i+1) arc (equivalent to R_3 in the example of Figure 4-8b).....	112
Figure 4-10: a) Representative load-displacement of the Fe-based MG with 19 μm thickness at different applied loading rates; b) The typical load vs number of arcs at various equivalent loading rates.....	114
Figure 4-11: a) Mechanical response of arc-shaped stainless-steel foil (adapted from [1]); b) load-displacement curve upon loading for stainless-steel crystalline foil; c) image of plastic deformation that is created after testing on the stainless-steel foil.	115
Figure 4-12: a) load-displacement curves of a NiTi foil; b) harmonic undulatory response of arc-shaped of NiTi foil; c) image of plastic deformation that is created after testing on the Nitinol foil.	117
Figure 5-1. X-ray diffraction patterns of metallic glass foils, for two thicknesses.	120

Figure 5-2. DSC thermograms of the metallic glass foils, for two thicknesses.	120
Figure 5-3: a) and b) the relative areas of the deconvoluted amorphous and crystalline peaks in the XRD diffraction pattern of the MG foil with a thickness of 25 μm ; c) and d) for MG foil with a thickness of 40 μm	122
Figure 5-4. Percentage of crystallinity of $\text{Ni}_{78}\text{Si}_8\text{B}_{14}$ MG of different thicknesses calculated from XRD patterns obtained from the wheel and air side.	123
Figure 5-5: a) Front view of initial arc-shaped metallic glass foil; b) harmonic undulatory behaviour response of arc-shaped metallic glass foil.....	124
Figure 5-6: Load-displacement curves for ten cycles of loading/unloading Ni-based metallic glass foil of a) 25 μm thickness; and b) 40 μm thickness.	125
Figure 5-7. Load-displacement curves for loading of Ni-based metallic glass foil with $L=20$ mm and $h_1=5$ mm for foil of 25 μm thick (red), and 40 μm thick (blue) for $L=20$ mm and $h_1=5$ mm.....	126
Figure 5-8: Load-displacement curves for Ni-based metallic glass foil for boundary length L values 20, 30 and 50 mm: a) 25 μm thickness and aspect ratio $h_1/L=0.25$; and b) 40 μm thickness and aspect ratio $h_1/L=0.25$	127
Figure 5-9: a) Maximum applied normal load on the foils with n_i sinusoidal arcs just prior to the formation of n_i+1 arcs versus the number of arcs; b) the spring rates (k) are calculated in the quasi-linear segments of the load-displacement curves. Both for Ni-based metallic glass foils with 25 μm and 40 μm thicknesses and set-up with boundary distance L values 20, 30, 40 and 50 mm, and $h_1/L=0.25$. In 5-9 (b) values for $L=40$ mm were omitted for the clarity of the graphs.	128
Figure 5-10. Undulatory behaviour for Ni-based metallic glass foils of 25 μm and 40 μm thicknesses.....	129
Figure 5-11: a) assembly of snapshots of the undulatory response with images of waveforms with sinusoidal shaped arcs (R_2 and R_4) and distorted arc (R_3); b) load-displacement curve with an undulatory response for the Ni-based foil; and c) maximum local strain on the foils, just prior to the formation of a new (n_i+1) arc.....	132
Figure 5-12. Load-displacement curves for Ni-based metallic glass foils (25 μm thick, blue) and (40 μm thick, red) NiFe-based and Fe-based foils (25 μm and 19 μm , olive and black, respectively) for $L=20$ mm and $h_1=5$ mm.	133
Figure 6-1: a) Harmonic undulatory response of arc-shaped metallic glass foil for $L=50$ mm; b) sinusoidal arc formation as calculated from the standing wave equation, where red refers to simulation only.	138
Figure 6-2. Arc amplitude as a function of number of arcs for three boundary lengths.....	139

Figure 6-3. Modelling sinusoidal arcs generated by standing wave for L ratio ($h_i/L=0.25$) a) boundary length $L=20\text{mm}$; b) boundary length $L=30\text{ mm}$. .	140
Figure 6-4. Modelling sinusoidal arcs generated according to the standing wave equation for $h_i/L=0.25$, a) boundary length $L=15\text{ mm}$; b) boundary length $L=25\text{ mm}$	141
Figure 6-5. Modelling of the experimentally formed waveforms for two metallic glass foils of thicknesses a) $25\text{ }\mu\text{m}$; b) $40\text{ }\mu\text{m}$	142
Figure 6-6: a) Assembly of snapshots from the undulatory behaviour with images of perfect sinusoidal shaped waveforms; b) assembly of snapshots of the transition from 1 to 2 perfect sinusoidal shaped arcs, where (i,ii and iii) are intermediate stages in the undulatory behaviour.	143
Figure 6-7. Beam element under applied load pre- and post-buckling.	145
Figure 6-8. Buckling analysis of flat section during applied load.	145
Figure 6-9. Sketch of the rectangular beam with dimensions.	146
Figure 6-10: a) Theoretical design condition values suitable for a variety of structural members [166]; b) Buckling mode on metallic glass foil for fixed ends.....	147
Figure 6-11: a) Critical load versus $1/(\text{Euler length})^2$ for different thicknesses foil for $L=20\text{ mm}$; b) critical load versus $1/(\text{Euler length})^2$ for different thicknesses foil for $L=50\text{ mm}$	151
Figure 6-12: Effect of the Young's modulus a) the variation of the critical buckling load at $L=20\text{ mm}$ for different metallic glass foils when thickness is kept constant; b) variation of the critical buckling load at $L=50\text{ mm}$ for different metallic glass foils when thickness is kept constant ($25\text{ }\mu\text{m}$ thick).	153
Figure 6-13. Critical load P_{cr} as a function of applied load for glassy foils a) boundary length $L=20\text{ mm}$; b) boundary length $L=50\text{ mm}$	155
Figure 6-14: Measured applied load (N_i) where buckling occurs for a) different foil thicknesses of the same materials; and b) different foil thicknesses and different MG foil.	156
Figure 6-15: a) curved beam bending shows areas of compression and tension; b) maximum strain on arc-shaped MG foil.	159
Figure 6-16: Maximum local strain of waveforms with distorted arcs, just before the formation of a (n_i+1) new arc, equivalent to $(P_{cr}=P)$ critical buckling load a) for Ni-based with $25\text{ }\mu\text{m}$, the transition from 5 to 6 arcs more than 1.25 mm diameter; b) for Ni-based with $40\text{ }\mu\text{m}$, the transition from 4 to 5 arcs more than 2 mm for curvature diameter.....	160
Figure 6-17. Spring length as a function of foil thickness.	162

Figure 7-1: a) Cycles to failure of metallic glass foils during fatigue tests and the corresponding load as a function of the maximum number of arcs; b) strain developed of foil deformation during the formation of additional arcs.....	167
Figure 7-2. A perfect sinusoidal arc-shaped cyclic loading is used to measure fatigue life.	169
Figure 7-3: a) cycles to failure for three conditions of MG foils; b) strain amplitude versus cycles to failure on three conditions of Fe-based metallic glass foils; c) working range for fatigue test versus cycles to failure of Fe-based metallic glass foils; d) strain developments with distorted arcs during cycles loading.	172
Figure 7-4: For three glassy foils with $L = 20$ mm and $h_1 = 5$ mm: a) cycles to failure as a function of the number of arcs for three different metallic glass foils; b) cycles to failure as a function of applied strain.	174
Figure 7-5: a) Schematic diagram of cyclic loading of metallic glass foils from initial arc-shaped to 2 sinusoidal arcs; b) cyclic loading for one cycle, showing stress cycle points for initial single arc, distorted shape due to increasing applied load, two arcs, distorted shape due to decreasing applied load, and finally to a single arc.	180
Figure 7-6. Fatigue behaviour in terms of the applied strain range; a) cycle loading for $\text{Fe}_{76.10}\text{Cr}_{2.48}\text{Si}_{4.51}\text{B}_{16.91}$ foil in current study; b) cycle to failure for $\text{Fe}_{69.5}\text{Cr}_8\text{Si}_{7.5}\text{B}_{15}$ glassy wire [82].	181
Figure 7-7. Types of cracks of NiFe-based foil during cyclic loading; a) interior crack; b) crack at foil edge.....	183
Figure 7-8. Crack propagation into NiFe-based MG foil during cyclic loading	184
Figure 7-9: (a) SEM of crack initiation location of Fe-based metallic glass on the crack surface for 3 sinusoidal arcs at 9900 cycles; (b) foil sample for the same foil.....	185
Figure 7-10: a) SEM of Crack initiation of Fe-based MG foil failed after 930 cycles within the cyclic loading range for 5 sinusoidal arcs with $L = 20$ mm; b) same foil sample after it had failed.	185
Figure 7-11: a) illustration of shear band at the bottom crack on the damage evolution after 930 cycles; b) shear band at the top crack evolution after 9900 cycles.....	186
Figure 7-12: Showing crack initiation at tension-compression reversal to compression-tension: a) MG foil formed into two sinusoidal arcs, demonstrating a crack site at position of maximum compression-tension; b) same foil showing initial arc-shape indicating crack site at tension-compression; c) schematic of formation of two arcs.	187
Figure 7-13. SEM image shows the cast edge of the metallic glass foil.	188

Figure 7-14. Schematic diagram of undulatory behaviour; a) stress cycle before buckling (before new arc begins); b) stress cycle from one arc to two arcs, indicating the crack location in both cases.....	189
Figure 7-15: a) the wheel-side of the $\text{Ni}_{78}\text{B}_{14}\text{Si}_8$ glassy foil, which is in contact with the compression plate during cyclic loading; b) the air-side of the same foil, but this surface is in contact with the base.	190
Figure 7-16: a) A profile measurement extracted from a 3D surface topography of Fe-based MG on wheel-side, where the black line represents the 2D profile extracted; b) 2D profile extracted.....	191
Figure 7-17: a) A profile measurement extracted from a 3D surface on air-side foil of the Fe-based MG foil as-cast, where the black line represents the 2D profile extracted ; b) 2D profile extracted.	192
Figure 7-18: a) Profile measurement extracted from a 3D surface of NiFe-based on wheel-side; b) 2D profile extracted.	194
Figure 7-19: a) Profile measurement extracted from a 3D surface topography of NiFe-based on air-side foil as-cast; b) 2D profile extracted measurement.	194
Figure 7-20: a) Profile measurement extracted from a 3D surface topography of Ni-based MG on wheel-side; b) 2D profile extracted.	196
Figure 7-21: a) Profile measurement extracted from 3D surface topography of Ni-based MG foil on the air-side as-cast; b) 2D profile extracted.	196
Figure 7-22. Stress concentration in a beam with two grooves loaded in bending.	198
Figure 7-23. Stress concentration factor K_t for a notched beam in tension [176].	199
Figure 7-24. Stress concentration factor k_t for a notched plate in transverse bending [177].....	200
Figure 7-25. Maximum applied load versus initial load /or stress for leaf spring [179].....	203

LIST OF TABLES

Table 2-1. An overview of some methods used to produce glassy and amorphous metals [28].	38
Table 2-2. Fe-based BMGs development with traditional manufacturing processes to date [68].	45
Table 2-3. Mechanical properties of Fe-based bulk metallic glasses as-cast rod from the literature [56].....	47
Table 2-4. Mechanical properties of Fe-based BMGs from the literature [59]. .	47
Table 2-5. Young's modulus values of Fe-based MG as-cast wire [82].....	48
Table 2-6. Static mechanical properties of Fe-based glassy alloy wires (HV, Vickers hardness; σ_f , fracture stress; ϵ_f , fracture strain) [83].....	49
Table 2-7. Applications field of Fe-based BMGs type and their responding characteristic [76].	50
Table 2-8. Crystallisation and peak temperatures of the Ni-Si-B alloys studies by DSC analysis [91].	55
Table 2-9. Thermal properties of glassy Ni-Fe-based alloys [96].	57
Table 2-10. Thermal and mechanical properties of Ni-Fe-based metallic glass alloys.	58
Table 2-11. Mechanical properties of different spring materials [152].	87
Table 3-1. Experimental design for metallic glass foils during cyclic loading..	100
Table 5-1. The crystalline volume fraction of Ni-based metallic glass foils.....	122
Table 5-2. Undulatory behaviour specimen data for Ni-based metallic glass foils of 25 μm and 40 μm thicknesses.....	130
Table 6-1. Experimental data for undulatory behaviour for three lengths ($L=20$, 30 and 50 mm).	137
Table 6-2. Dimension and materials used for the present analytical model in the parametric study.	144
Table 6-3. Work range of metallic glass foil spring for boundary length $L=20$ mm	157
Table 6-4. Work range of metallic glass foil spring for boundary length $L=30$ mm.	157
Table 6-5. Work range of metallic glass foil spring for boundary length $L=50$ mm.	158

Table 7-1. Summary of experimental results and details of fatigue endurance limit for Fe-based glassy foil (N_f , cycles to failure; STD standard deviation)...	170
Table 7-2. Deformation of radius curvature for Ni-based foils of undulatory response for two thicknesses.	175
Table 7-3. Comparison of strain deformation on arc curvature between NiFe-based and Ni-based foil.	176
Table 7-4. Summary of experimental results for fatigue endurance limit in terms of number of cycles, strain and load for three MG foils of length 20 mm with 2 arcs (N_f , cycles to failure; STD standard deviation).	177
Table 7-5. Comparison between two different operating of cyclic loading of Fe-based glassy foil	178
Table 7-6. Types of crack initiation of metallic glass foils during cyclic loading.	183
Table 7-7. Surface roughness parameters of Fe-based metallic glass foil for scan area of $0.8 \times 0.8 \text{ mm}^2$	192
Table 7-8. Surface parameters of NiFe-based metallic glass foil for scan area of $0.8 \times 0.8 \text{ mm}^2$	195
Table 7-9. Surface parameters of Ni-based metallic glass foil for scan area of $0.8 \times 0.8 \text{ mm}^2$	197
Table 7-10. The parameters used to calculate stress concentration of metallic glass foils with different surface defects.	200
Table 7-11. Force ranges and fatigue limit requirements in MG foils for spring applications.....	202
Table 7-12. Fatigue life requirements of spring applications.	204

LIST OF EQUATIONS

(2-1)..... 65

(2-2)..... 66

(2-3)..... 74

(2-4)..... 76

(2-5)..... 76

(2-6)..... 76

(2-7)..... 79

(3-1)..... 93

(3-2)..... 96

(5-1)..... 121

(6-1)..... 136

(6-2)..... 138

(6-3)..... 146

(6-4)..... 146

(6-5)..... 148

(6-6)..... 148

(6-7)..... 148

(6-8)..... 149

(6-9)..... 149

(6-10)..... 149

(6-11)..... 149

(6-12)..... 150

(6-13)..... 150

(6-14)..... 150

(6-15)..... 150

(6-16)..... 152

(6-17)..... 152

(6-18)..... 152

(6-19).....	152
(6-20).....	153
(6-21).....	154
(6-22).....	154
(6-23).....	154
(6-24).....	154
(6-25).....	154
(6-26).....	158
(6-27).....	160
(6-28).....	161
(6-29).....	161
(6-30).....	161
(7-1).....	197

LIST OF ABBREVIATIONS

MG	Metallic glass
BMG	Bulk metallic glass
GFA	Glass forming ability
R	Radius of arc curvature
W	Width of the foils
L	Distance between fixation points
h	Amplitude
d	Thickness of the foil
ε	Strain
k	Spring rate
K	Deflection value of boundary conditions
L_e	Actual unsupported length of the foil (Euler length)
I	Second moment of inertia
P_{cr}	Critical buckling load
K_t	Stress concentration factor
V	Voltage
N	Applied load

1 Introduction

1.1 Research Background

An interesting technologically attractive behaviour, namely the undulatory behaviour of metallic glass foils, has been recently discovered [1]. This behaviour occurs when a load is applied to an arc-shaped metallic glass ribbon with an arc shape, which results in the ribbon forming additional sinusoidal arcs, see Figure 1. Once the applied load is removed, the ribbon returns to its original position, exhibiting a reversible wavy elastic response. When forming a new waveform, all arcs have a perfect sinusoidal shape. With increasing load, however, the shape of the arcs becomes distorted until the load reaches a sufficient level to cause the formation of an additional arc [1][2]. This discovery has opened up a new domain of possibilities in the field of materials science and engineering. Metallic glasses, characterised by their disordered atomic structure, have long been of interest due to their unique combination of mechanical properties, such as high strength and exceptionally large elastic deformation range of ~2% strain before the start of plastic deformation [3], the undulatory behaviour has not been observed in conventional crystalline metals. However, this newfound undulatory behaviour adds a novel extent to their already remarkable series. This reversible phenomenon has a wide range of implications beyond scientific curiosity. Engineers and designers alike are enthusiastic to investigate the practical applications of metallic glass foils with undulating properties. As a result of wavy and controlling these self-organising patterns, innovative technologies are possible, from advanced damping systems in aerospace engineering to flexible and adaptive structures in consumer electronics, and be applicable in spring systems, as an electromechanical switch in MEMs or in shock-absorbing devices.

The aim of this project is to investigate the mechanisms underlying this undulatory behaviour of metallic glass foils, explore their extent and limitations and exploit their potential use in engineering applications. More specifically, the undulatory behaviour involves elastic deformation, bending and buckling of the metallic glass foils resulting in a change of the ribbon shape and the multiplication of sinusoidal arcs. Buckling is a mechanical instability because it involves a sudden and often

catastrophic failure of a structure under a compressive load and is usually an undesirable phenomenon. However, in this case, buckling is a functional part of the mechanism because the buckling mode of metallic glass foils behaves similarly to Euler-buckling, depending on the geometry and boundary conditions. The undulatory behaviour of the glassy foils has been examined for two amorphous alloys, (Fe-based) and (Ni-Fe based) in this project. Among the goals of this project is to show the extent to which this behaviour can be observed in various of glassy alloys and partially crystalline alloys (metallic glass composites). Developing a model to simulate the undulatory behaviour of the glassy foils able to predict the behaviour of foils with different properties and/or geometries is an important part of the project. Analysing and the understanding of mechanical undulatory behaviour mechanism is a critical part for predicting and developing wavy patterns of undulatory behaviour. Designing types of flat springs to predict undulatory behaviour is crucial in spring systems, where failure due to deformations can have severe consequences. Fatigue is a major concern for most engineering devices and applications [4]. However, the fatigue behaviour of metallic glasses has yet to be well understood. While the fatigue life of metallic glass foils undergoing a cyclic undulatory behaviour is relatively limited, it has been hypothesised that manufacturing defects on the surface or edge of the foils are responsible for forming fatigue cracks limiting the cycling lifespan. However, this hypothesis remains to be tested.

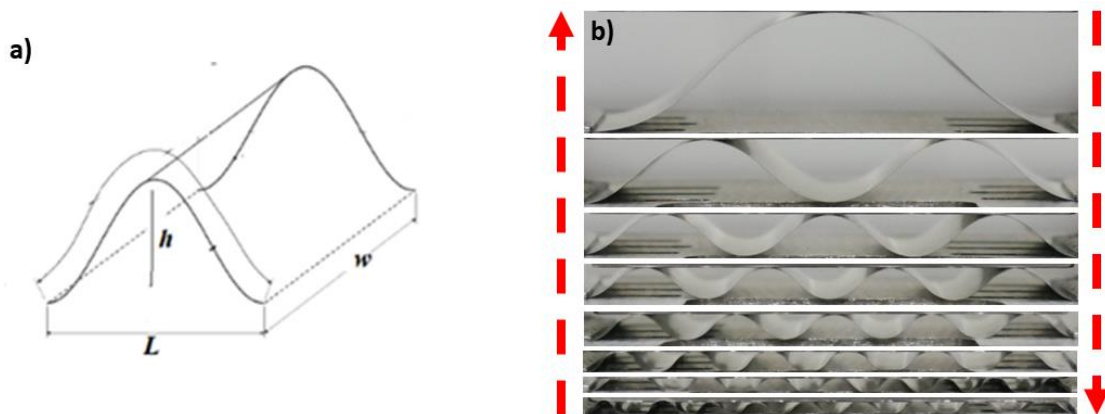


Figure 1-1: a) initial arc-shaped of metallic glass foil; b) assembly of snapshots from the undulatory behaviour with images of perfect sinusoidal waveforms.

1.2 Research Aim and Objectives

This project aims to investigate the undulatory behaviour for several metallic glass alloy foils, uncover the mechanism behind this behaviour and understanding the fatigue behaviour.

The main objectives of this project are:

1. Conduct a comprehensive literature review of the essential elements relevant to the project.
2. Investigate the effect of geometrical characteristics on the “flat spring-type set-up” such as the geometry of the initial arc; length:amplitude ratio on the undulatory behaviour in terms of applied load-displacement, the maximum number of arcs before plastic deformation, maximum localised loads, and local strain.
3. Investigate the impact of loading rate (i.e. crosshead speed) on the undulatory behaviour of the foils of various thickness, length boundaries and speed rates.
4. Investigate the effect of the foil thickness and materials properties (elastic modulus) on the undulatory behaviour of MG foils using different metallic glass foils.
5. Investigate the underlying mechanism of undulatory behaviour that leads to wavy elastic behaviour.
6. Investigate the fatigue behaviour of (amorphous and MG composite) under cycling loading and test the hypothesis that surface defects affect fatigue life.

1.3 Research Motivation

This research emphasises exploring the underlying mechanism of wavy elastic behaviour by studying mechanical performance for metallic glasses foils. Metallic glass is class of material can be used in many technological applications due to the excellent combination of characteristics such as high yield strength, elasticity, corrosion resistance, and excellent magnetic properties.

Developing a better understanding of the recently discovered undulatory behaviour of metallic glass foils will help the exploitation of the enormous potential

for designing novel types of hybrid micro-flat springs using the exceptional properties of metallic glass foils can be developed to achieve the results of this project, including damping or/springs and shock absorbance with diverse uses.

Developing the standing wave equation is a key success factor that facilitates knowledge of the unique undulatory behaviour of any metallic glass foils within the manufacturing sector by choosing the proper set-up of spring-type designing and arc multiplication needed in particular geometry for operational requirements. Therefore, spring-type devices with desirable characteristics can be designed by choosing the glassy alloy and foil thickness under cyclic loading based on the load ranges and fatigue life requirements. However, the load range and fatigue life for these MG foils depends on several parameters of set up like (boundary lengths L , foil thickness and number of sinusoidal arcs formation). Unless glassy foil exceeds its elastic limit of 2% strain during loading/unloading.

Furthermore, this work will contribute to the academic knowledge of metallic glasses and metallic glass composites relevant to the buckling of foils.

1.4 Research Scope and Limitations

The research focused on exploring the undulatory behaviour of metallic glass beyond what has been reported. From the literature, this behaviour is shown only for specific metallic glass foil. Due to this, the main research gap will focus on the mechanism of undulatory elastic behaviour of thin metallic glass foils. Hence, this work focuses on explaining the phenomena related to these transitions during undulatory behaviour. Another research gap comes from the literature. There has been little research on fatigue so far, and there are some interesting hypotheses about how fatigue develops. Following that, this work explores fatigue behaviour and fatigue behaviour for other metallic glass foils. This study involved the experimental mechanical investigation of three different metallic glass foils; Fe-based, NiFe-based and Ni-based glassy foils as workpiece material. For this project, the study involved for mechanical properties of materials, including conducting mechanical testing, and materials characterisation such as X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), nanoindentation test and Interferometer measurements of

surface roughness. In addition, fatigue tests were examined the fatigue performance of metallic glass foils by defined their lifespan under cyclic loading; cycles to failure were determined by applying different parameters for arc spring geometry.

Further, understanding the mechanisms underlying undulatory behaviour may provide useful insights for spring design applications.

1.5 Contribution to Knowledge

This work contributes significantly to the knowledge in the field of elastic behaviour of glassy foil in geometric confinement and, more specifically, to the recently discovered undulatory behaviour.

Firstly, this work shows the undulatory behaviour of a variety of metallic glass foils beyond the previous metallic glass composition shown in the literature. Indicating that this is universal behaviour for glassy foils rather than a behaviour shown for a specific glass. Furthermore, the undulatory behaviour was shown for partially metallic glass foils, thus opening the window for this behaviour to be exploited for metallic glass composite foils.

In addition, this work reveals in detail for first time the understanding mechanism of the undulatory behaviour, which includes further than the sinusoidal waveforms that the foils form under the application of load, a sequence of bending, buckling and post-buckling phenomena. The use of Euler's approach to analysing buckling occurring in the straight parts of the foils offers indeed new insights for understanding the undulatory behaviour. The work also clarifies that the limitations for this behaviour should be exported in relation with the max strains at the deformed/distorted waveforms rather than the perfect sinusoidal waveforms that were previously thought.

Furthermore, this work explored in detail the limitations for the undulatory behaviour as set by the fatigue life during load cycling tests for a variety of metallic glass foils. The findings indicate a correlation between fatigue crack initiation with surface defects of the foils and thus suggest that improving surface quality could reduce defects and potentially lead to an increase in fatigue life of the foils.

1.6 Thesis Structure

Thesis has been structured into eight chapters which are given below:

Chapter 1 covers the research introduction which includes research background, aim and objectives. This chapter also clearly mentions the motivation and contribution to knowledge.

Chapter 2 outlines a critical literature review which helps to understand mechanical behaviour of metallic glass foils, manufacturing methods, mechanical properties and different metallic glass alloys. An extensive literature review has been performed to summarise published research work in the field of undulatory behaviour of metallic glass foils and fatigue behaviour. The research gaps are also identified. Also, study springs and springs application types.

Chapter 3 presents the research methodology adopted to achieve the research aim and objectives. This chapter presents different experimental methods that have been used to gain an understanding of elastic undulatory behaviour.

Chapter 4 studies mechanical response of Fe-based and NiFe-based glassy foils. Results show that undulatory behaviour exhibits remarkable repeatability.

Chapter 5 studies the undulatory behaviour of partially crystalline system (Ni-B-Si) alloy. It contributes to the understanding of the undulatory mechanical response and clarifies the operational limitations imposed by local deformation.

Chapter 6 studies the mechanism of the undulatory behaviour, proposing an analytical model of the undulatory behaviour using buckling analysis to describe the mechanical response of an arc-shaped MG foil subjected to load.

Chapter 7 presents the studies on the fatigue life of metallic glasses, cyclic lifetime, fatigue life characteristics, fatigue analysis and suggestions for improvement of fatigue life of MG foil.

Finally, in Chapter 8 the research findings are highlighted along with the conclusions. Furthermore, research limitations and recommendations for future work have been pointed out.

1.7 Publications

a) Conference presentations:

1. Euromat 2021 conference, 13-17 September, 2021, Germany.
On the mechanical response of metallic glass foils (online oral presentation)
Shahin Elzoubi O, Stiehler M, Georgarakis K, (2021).
2. Future materials conference 2021, 13 December 2021, Birmingham, UK.
Exploiting the elastic properties of metallic glasses (oral presentation)
Shahin Elzoubi O, Stiehler M, Georgarakis K, (2021).
3. 11th International Conference on Through-life Engineering Services – TESConf2022, , Cranfield, UK, November 2022
On the undulatory behaviour of metallic glass foils: a novel spring-type behaviour (oral presentation)
Shahin Elzoubi O, Panagiotopolous NT, Stiehler M, et al., (2022).
4. RQ17 & ISMANAM27 Warsaw, Poland, Aug 2023
Understanding the undulatory behaviour of metallic glasses (poster)
O Shahin Elzoubi, N Panagiotopolous, M Stiehler, K Salonitis, K Georgarakis.

b) Conference paperps:

1. Shahin Elzoubi O, Panagiotopolous NT, Stiehler M, et al., (2022) On the undulatory behaviour of metallic glass foils: a novel spring-type behaviour.
In: Proceedings of the 11th International Conference on Through-life Engineering Services – TESConf2022, Cranfield, Nov 2022, Paper number 7682. URI: <https://dspace.lib.cranfield.ac.uk/handle/1826/18681>

c) Journal papers (under preparation):

1. On the mechanical response of metallic glass foils in geometry confinement: understanding the undulatory behaviour of metallic glasses, to be submitted to Mater. Sci Engin A.
2. Fatigue crack initiation in metallic glass foils under cycling loading in confined geometry, to be submitted to, Journal of Alloys and Compounds.

2 Literature review

2.1 Introduction

Bulk metallic glasses gained significant interest from the materials research community following innovation in the 1980s and 1990s. Various water cooling and casting processes enabled some alloys to produce bulk metallic glasses up to 80 mm due to their high glass-forming ability (GFA). This material has a unique deformation mechanism because it has no long-range ordered structure. This lack of order gives metallic glasses unique mechanical and physical properties, such as high strength, high corrosion resistance, good wear resistance and large elastic deformation. The purpose of this chapter is to describe metallic glasses, their formation mechanism, GFA, structure, mechanical properties and the manufacturing process of metallic glass in ribbon form. A particular emphasis is given to Fe-based and Ni-based metallic glass alloys, also studies springs and different types of metallic glass springs.

2.2 Metallic glass history

Metallic glasses (MGs) are a unique metallic material class of materials that do not display long-range order. Their amorphous nature, lack of dislocation, and grain boundaries are quite different from conventional crystalline materials, see Figure 2-1[5]. Metallic glasses characterised by a representative size of over 1 mm are called bulk metallic glasses (BMGs).

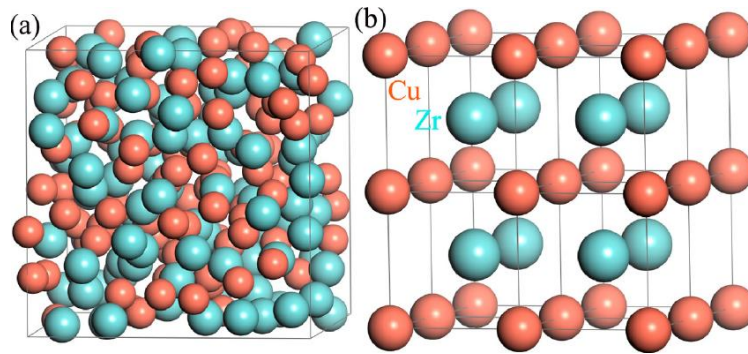


Figure 2-1: Diagram of a) amorphous atomic structure; b) crystalline structure [6].

In 1960 the first synthesis of an amorphous phase was achieved using the rapid solidification of an Au-Si system [7]. Only thin ribbons (typically $<100\text{ }\mu\text{m}$) could be produced initially due to the rapid quenching levels required among $10^3 - 10^6\text{ K/s}$. Since then, many amorphous alloys have been synthesised using different fast quenching techniques from liquid or vapour to avoid crystallisation at early binary structures [8]. However, amorphous alloys are less than $100\text{ }\mu\text{m}$ thick, which limits their potential uses [9].

The ternary Pd-Cu-Si alloy was found to form a metallic glass in bulk form for the first time in 1974 by Chen [10], who used a cylindrical sample ranging from 1 mm to 3 mm in diameter with various centimetres in length, using a critical cooling rate below 10^3 K/s . Further studies of BMGs in the different alloy systems occurred during the 1980s to develop a fundamental understanding of their structure, mechanical, magnetic and chemical properties. Also explored were their atomic and electronic transport properties and their low-temperature behaviour.

Inoue and his group at Tohoku University, Japan, developed several multicomponent BMGs based on common metallic elements with low critical cooling rates in the late 1980s. This group found that La-Al-Ni and La-Al-Cu alloys showed exceptional glass-forming abilities [11]. Moreover, in the early 1990s, this group fabricated BMGs of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ via water quenching, achieving diameters reaching 16 mm. In addition, molten alloys of $Zr_{55}Al_{10}Ni_5Cu_{30}$ were cast into copper moulds with an outer diameter of 16 mm [12]. The same group introduced a new family of bulk metallic glasses in 1997, consisting of Pd–Cu–Ni–P. This new bulk metallic glass shows high glass forming ability (GFA) and a casting diameter of up to 72mm [13]. Importantly, this innovation sparked significant interest in BMG compositions based on several non-noble metals. The numerous quaternary BMGs were developed using Zr-Fe-Ni-Co-Cu-Ti-Mg compositions and based on many noble metals, with a wide range of mechanical and physical properties due to their excellent glass-forming ability.

Figure 2-2 shows the maximum BMG diameter achieved and the year of their discovery. Bulk metallic glass was primarily motivated by an interest in disordered materials and their structural and functional potential applications at the beginning of the 21st century. Figure 2-3 shows the date of discovery of BMGs against their critical casting thickness [14].

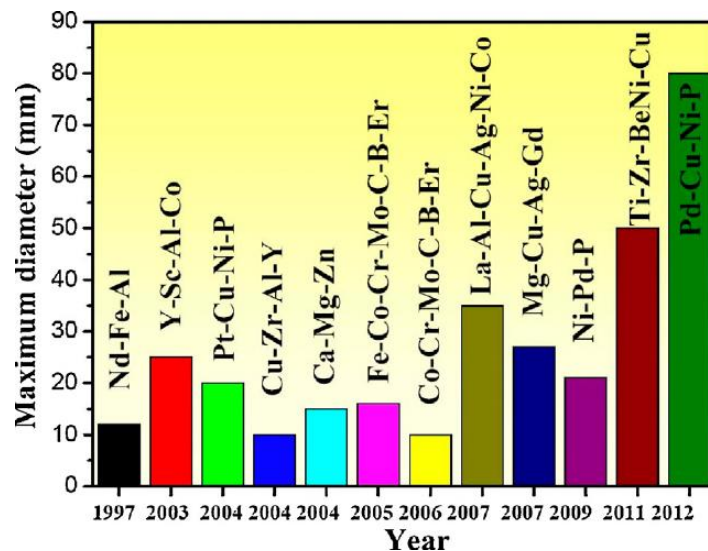


Figure 2-2. Different BMG systems with discovered years against the maximum diameter [6].

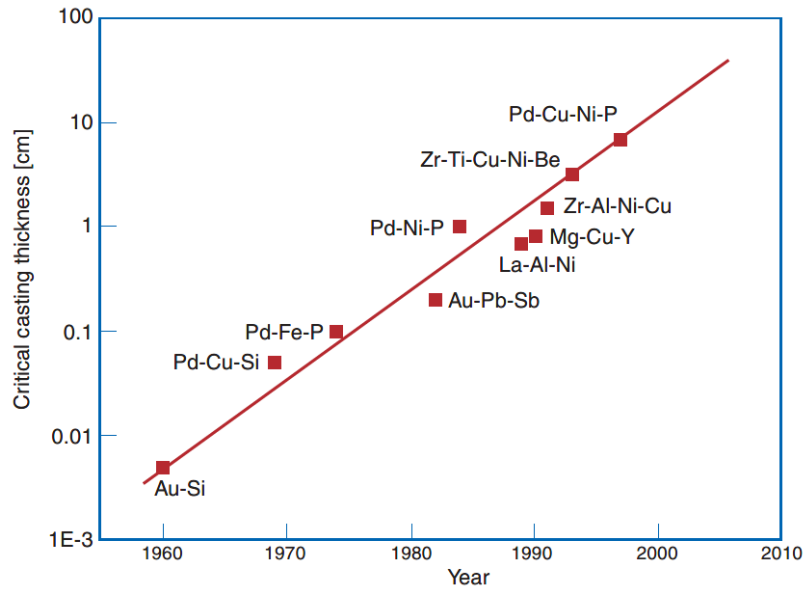


Figure 2-3. MG critical casting thickness versus discovery year [14].

Generally, BMGs can exhibit exceptional combinations of mechanical properties that make them attractive for a wide range of mechanical engineering applications. Metallic glasses have an exceptionally high yield strength of up to 5 GPa, and a higher limit to the elastic strain, up to 2%, significantly higher than many crystalline metals. Compositions of BMG can combine outstanding strength and toughness relationships that other metals cannot achieve, even though fracture toughness values can range from highly brittle to very tough, see Figure 2-4 [1][8][15].

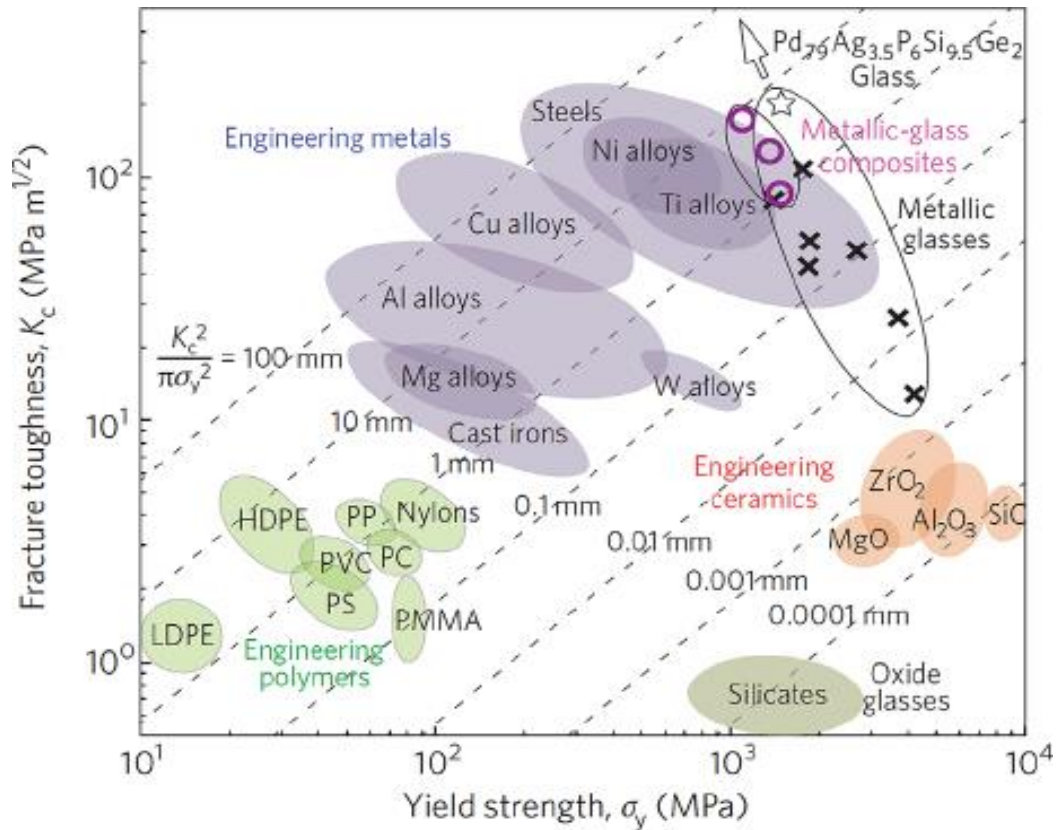


Figure 2-4. Toughness versus strength for conventional engineering materials, bulk metallic glasses, and metallic glass composites [8].

Due to the high interest in metallic glasses, their mechanical properties have been extensively reviewed. There are over 1500 metals, alloys, and metal–matrix composites, as shown in Figure 2-5. The ellipses on chart type identify the values associated with specific materials and groups. MGs exhibit high mechanical strength exceeding 5 GPa and yield strain of store and release elastic energy, which is applied for spring applications. Compared to even the strongest crystalline materials, BMGs are a promising new class of structural materials. However, some problems are associated with the absence of work hardening and restricted flexibility. Obviously, BMGs cannot be classified according to the crystallographic described slip-systems of polycrystalline metals. High-yield stresses are possible in BMGs because of the non-existence of dislocation-mediated slip; the results relate more closely to the theoretical limits than those obtained with their crystalline counterparts, see Figure 2-5 [15][16][17][18].

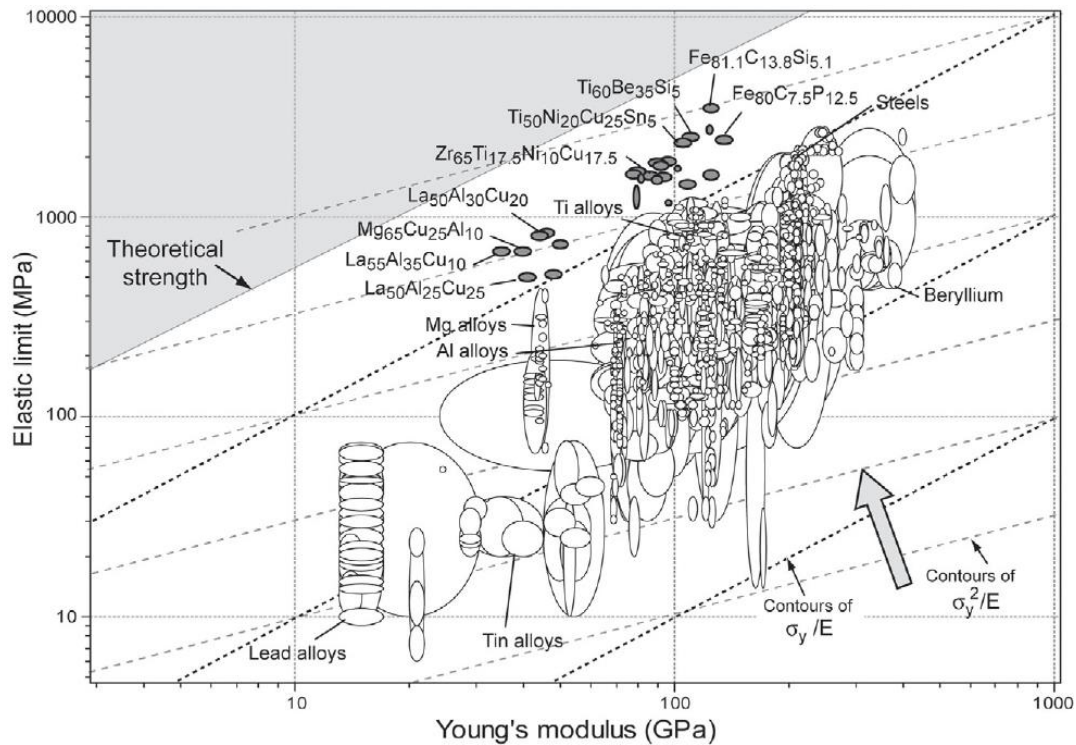


Figure 2-5. Mechanical properties for over 1500 metallic alloys compared to metallic glasses [18].

2.3 Formation of the glassy state

Many researchers have investigated the formation of metallic glasses. Metallic glass is an amorphous solid structure formed by continuous cooling from the liquid state.

Glasses are fundamentally frozen liquid that is made by quenching high-temperature melts. A liquid usually crystallises when it reaches temperature below its melting (T_m) or liquidus temperatures (T_l) to preserve its amorphous nature. To achieve this, the needs to be decreased the temperature sufficiently quickly. Therefore, the liquid is frozen by undergoing the glass transition temperature, T_g , before crystals can nucleate and grow [18][19][20][22].

When an undercooled liquid is quenched rapidly, its viscosity increases dramatically and constantly, comparable to a crystalline solid. Therefore, the atoms cannot diffuse and arrange themselves due to insufficient time, as illustrated in Figure 2-6.

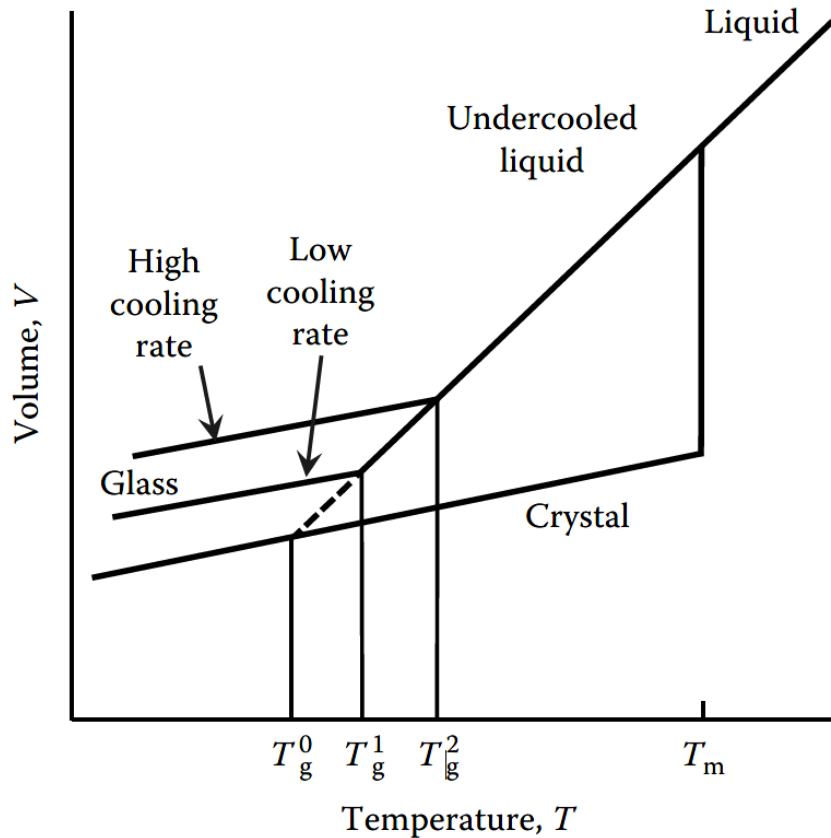


Figure 2-6. Transition states of metallic glasses formation [23].

Figure 2-6 shows the specific volume (V) of a typical liquid as a function of temperature. A liquid may crystallise at T_m when cooled from a high temperature. During first-order phase transitions, the specific volume typically decreases (water is a notable counterexample). Supercooled liquids are liquids that get below T_m without crystallising. Supercooled liquids in specific volumes and other thermodynamic properties can be extrapolated to lower temperatures from their properties above T_m .

As the temperature of a supercooled liquid decreases, its viscosity increases, causing the constituent atoms to move significantly slower than before. At temperatures below a certain threshold, the atoms move so slowly that they cannot undergo significant rearrangement before reaching even lower temperatures. Glass-forming ability (GFA) suppresses crystallisation in favour of forming a glassy phase upon solidification [21][23].

2.4 Synthesis of metallic glass

Metallic glasses were produced by speedily solidifying metallic melts at cooling rates of around 10^6 K/s. Due to its exceptional mechanical, chemical, and magnetic properties, various techniques have been developed for obtaining different sizes and shapes of MGs in a glassy form (ribbons, wires, powders, etc.) [24][25]. However, the need for significant size sheets for various applications in commercial settings led to the creation of the planar flow casting technique. This method enables the production of solidified sheets with a minimum width of 30 cm. The investigation for bulk glass alloys for industrial applications eventually concluded with the reveal of bulk metallic glasses (BMGs). BMGs were produced at relatively slow solidification rates of around 10^3 K s⁻¹ or lower. The study looks briefly at the criteria for rapid solidification processing (RSP) and the essential methods for fabricating solidification ribbons quickly. Many BMGs researchers still use the melt-spinning method to manufacture ribbons and study their characteristics and crystallisation behaviour [26].

2.4.1 Melt-spinning technique

Several approaches have been developed to produce amorphous alloys. This section will focus on melt-spinning because it is more relevant to this research and is a standard method to make ribbons, enabling a variety of ribbons with different specifications to be studied in this work, such as foil thickness and composition.

The glass is produced by a rapid cooling rate of liquid to avoid crystallisation. The critical cooling rate for conventional oxide glasses is so low that it is not a significant parameter in production [27]. However, critical cooling rates are usually high for MGs [27][28].

Melt spinning is the most widely used technique for producing solidified ribbons, wires, and filaments continuously and quickly. Since the 1970s, this technique has contributed significantly to the development of Rapid Solidification Processing (RSP) technology. [29].

In the melt-spinning process, molten metal is expelled through a small hole [24][25][29]. It is then ejected to a fast-rotating copper wheel by pressurisation through a fine nozzle. Each parameter can be tuned precisely for the required ribbon width, shape and thickness [29]. A diagram of the melt-spinning cycle is shown in Figure 2-7.

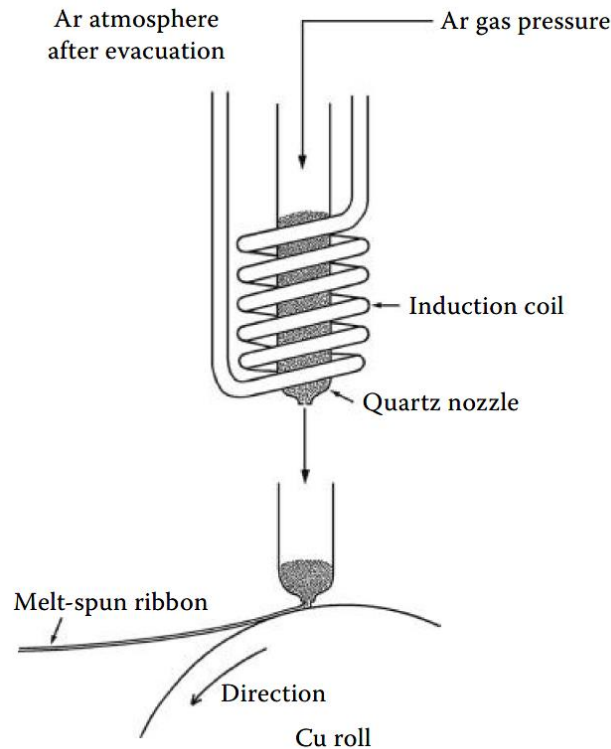


Figure 2-7. Illustration of the melt-spinning process [26].

The crucible material is selected based on its chemical compatibility with the melt, ability to handle temperatures, thermal shock resistance, low thermal conductivity and porosity.

The nozzles in cross-section are usually circular and range between 50 and 1250 μm in diameter. Moreover, the nozzles are manufactured from a suitable refractory material whose exact nature depends on the metal that must be addressed [29]. The ejection pressures are usually from 5-70 kPa, according to the desired melting rate. Higher ejection pressures lead to improved feeding patterns and better thermal transmission between the melt puddle and substrate.

Melt-spinning wheels were made of various materials, such as copper, steel, chromium and molybdenum, although the most popular material is copper. The main objective of the wheel is to draw out the heat from ribbons and would be better quickly, whilst allowing the puddle to wet the wheel and form ribbon. A key parameter to determine the ribbon thickness is wheel speed; a thinner ribbon is obtained as long as the wheel rotates faster. For instance, a ribbon of 37 μm thickness obtained from an alloy of $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ cast on a 250 mm diameter copper wheel rotating at a tangential velocity of 26.6 m s^{-1} . In contrast, at a speed of 46.5 m s^{-1} , the ribbon thickness was only 22 μm [26][29].

The solidification rates accomplished in this process are usually about 10^5 – 10^6 K/s. Typical ribbons measurements are approximately 2 to 5 mm wide and 20 – 50 μm thick [29]. Due to high solidification rates, this technique should allow producing most alloys of suitable composition in the glassy state. The downside is that the thickness of the section is restricted. In order to increase the width of ribbons, however, there is a planar flow casting process that uses nozzles with a rectangular cross-section, which can have a cross-section of up to 30 cm. Sometimes more than one nozzle may also be used to overlap the melt puddle with the ribbon to raise the width of the ribbon [24][30].

2.4.2 Other methods to produce metallic glass

Other methods of quickly cooling liquid are also available. For example, a molten alloy jet may be ejected into a stream of water to produce wire. The cooling rate plays an important role comparable with melt spinning, and the interest is in the product forms. Pulsed laser quenching is another example in which an incident laser beam with a short duration melts a thin surface layer ($\sim 100 \text{ nm}$). The melted surface lays on a significant cold substrate being cooled extremely rapidly at 10^{14} K s^{-1} [28][31].

Table 2-1 summarises the techniques used in the production of amorphous alloys. There are also other ways to produce metallic glasses besides the rapid quenching of a liquid. These techniques are based on the deposition of vapour (evaporation or sputtering) or solution (electrodeposition or electro-lower repositioning). They can be regarded as fast liquids by forming a solid when the

mobility of atoms is decreased rapidly. Therefore, several techniques are based on an amorphous phase formation within a solid-state.

There are other techniques for producing an amorphous phase in which the only energy input is thermal annealing. As was first demonstrated by Schwarz and Johnson [32], certain combinations of crystalline elemental metals react in a solid state to produce an amorphous phase. A further type of amorphisation, rarely observed, is the transformation of a supersaturated solid solution.

Table 2-1. An overview of some methods used to produce glassy and amorphous metals [28].

	Method
Melt-spinning, planar flow casting	<i>Rapid liquid cooling</i>
Atomization	
Wire formation in water	
As a surface treatment	
	Scanned laser or electron beam
	Pulsed laser beam
	<i>Undercooling of clean liquids</i>
Emulsion technique	<i>Physical vapor deposition</i>
Fluxing	
Solidification in free fall	
Evaporation	<i>Chemical methods</i>
Sputtering	
Electroless deposition	
Electrodeposition	
Precipitation	<i>Irradiation</i>
Hydrogenation	
By light or heavy ions	
By electrons	
By neutrons	<i>Mechanical methods</i>
Ion implantation	
Ion mixing	
Grinding	<i>Reactions</i>
Mechanical alloying	
Solid-state reaction of elements	
Decomposition of crystalline solid solution	

2.5 Mechanical properties of metallic glass

The mechanical properties of metallic glasses play a significant role in many applications. Their disordered atomic and dislocation-free structures make them

ideal engineering materials for mechanical and chemical applications [33][34][35][36]. Metallic glasses are usually deformed elastically, then plastically deformed, and eventually destroyed on applied loading catastrophically. Compared to crystalline materials, metallic glasses typically show a higher strength with large elastic deformation of 2% strain, as shown in Figure 2-8 [14][28][37].

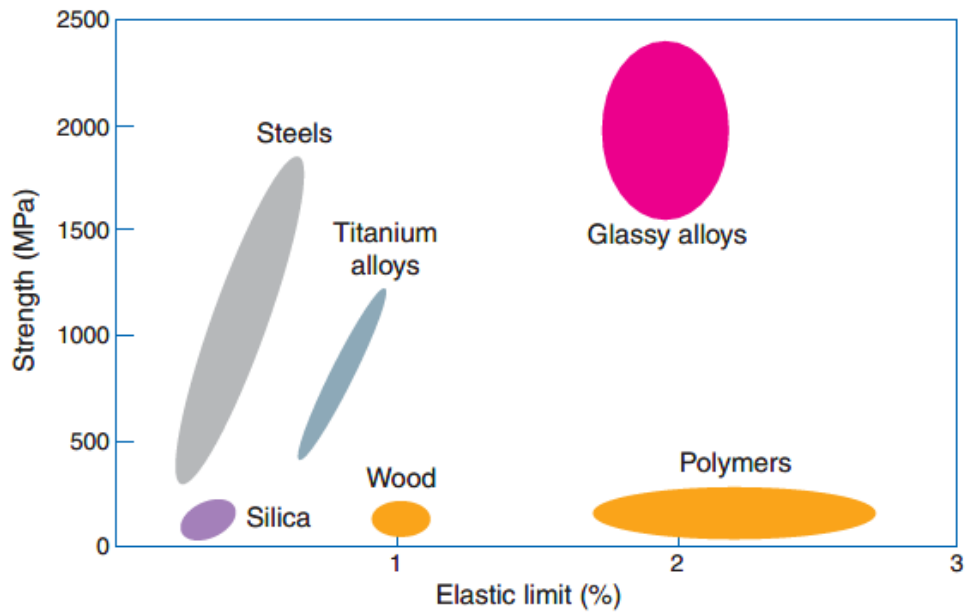


Figure 2-8. Amorphous metal alloys combine higher strength than crystalline metal alloys with an elasticity of polymers [14].

As the size of metallic glasses decreases to the nanoscale or sub-micron scale, their mechanical properties, such as yield strength and elastic strain, show an upward tendency, see Figure 2-9 [38][39]. Upon reducing dimension to the nanoscale, the strength corresponding to the elastic strain limit of bulk metallic glasses is twice their strength. At the same time, the strength of micro-scaled bulk metallic glasses rises to three times the elastic strain, in line with the ideal elastic limit of metallic glasses. In a three-section comparison by Ashby and Greer, thousands of metals and alloys were described quantitatively by their mechanical properties [18]. Compared to conventional crystalline materials, metallic glasses

have a greater elastic strain, a higher capacity for storing elastic energy, and a higher toughness.

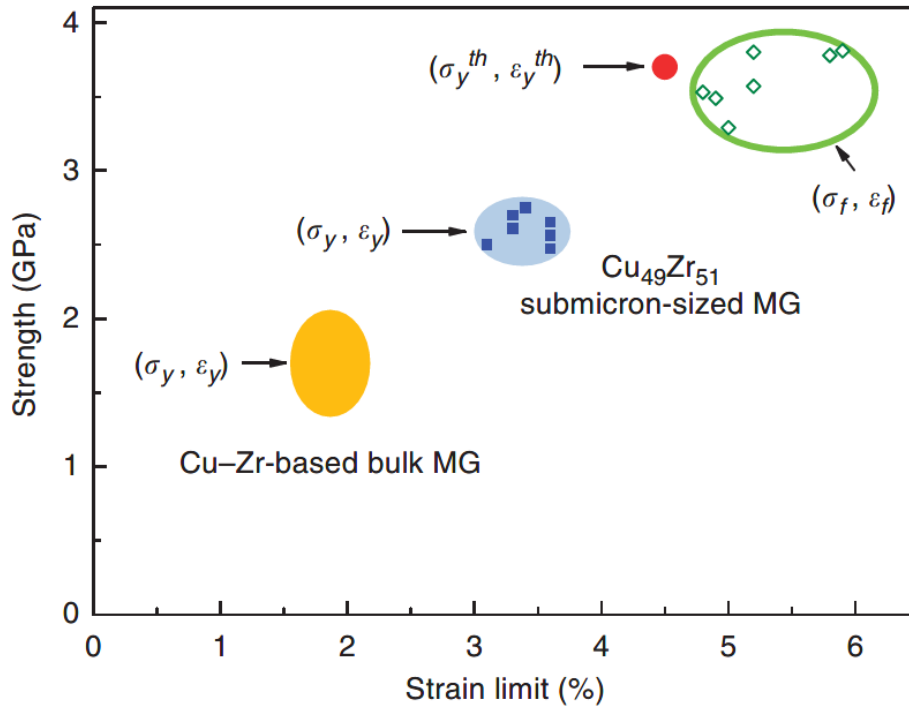


Figure 2-9. Strength and strain limit of Cu-Zr-based MGs of different sizes [38].

It is found that elastic moduli of BMGs are correlated with various mechanical properties, glass transition temperatures, melting temperatures, and even liquid fragility. This was discovered by summarising and comparing the related experiments data from different BMG families [40]. It was found that Young's modulus E is linearly related to fracture tensile strength σ for BMGs ($E/\sigma \approx 50$). It is shown in about 30 BMGs that a similar relationship exists between shear stress at yielding T_Y and shear modulus G : $T_Y = Y_c G$, $Y_c = 0.0268$.

These connections better explain the composition of glass, its nature, and its impact on physical properties. Elastic modulus on applied stress (i.e. strain resistance) may be known as the material's strain response [41][42]. As such, it represents the intrinsic stiffness of atomic bonding. The elastic modulus of several MGs was found to be virtually the same as that of their solvents by Dong et al. [41], as shown in Figure 2-10. Therefore, MG elastic modulus is determined mainly by solvent metals, which control the solvent's overall rigidity. It is

interesting because, typically, the base element only makes up about half of those glasses [41][43].

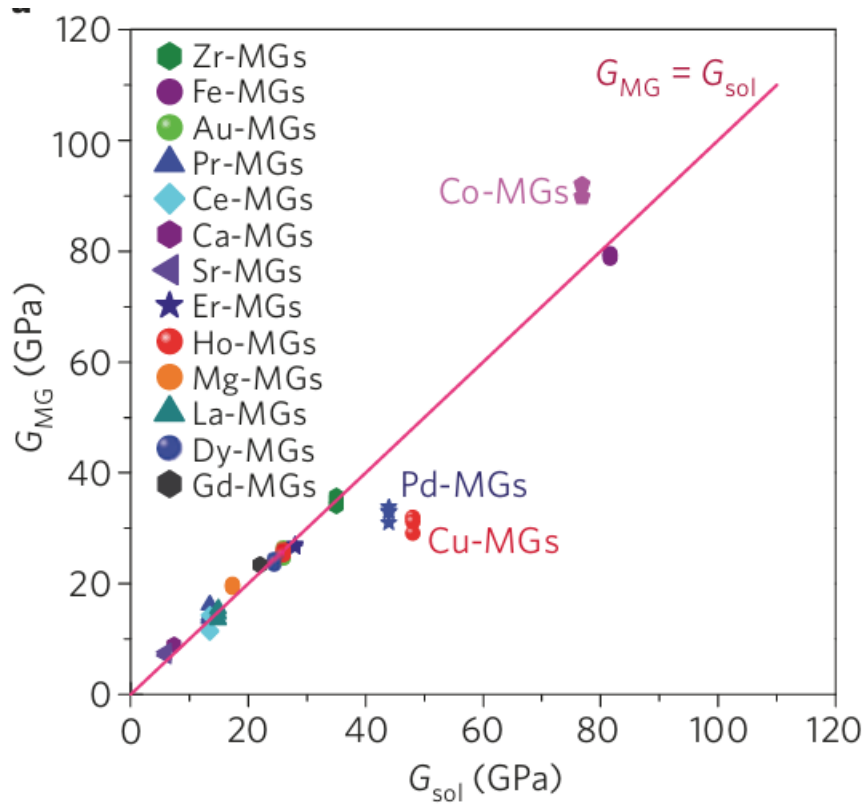


Figure 2-10. Comparison between the elastic modulus of MGs and their solvent metals [41]

Mechanical behaviour during plastic deformation is based on extrinsic and intrinsic factors [4]; [33]; [44]; [45]; [46], in addition to testing conditions (such as strain rate, testing temperature, machine stiffness, and the aspect ratio of the specimen etc.). During the test temperature or strain rate change, metallic glasses go from brittle to ductile [47]; [48]. The formation of multiple shear bands is favoured by increasing machine stiffness, which further influences the behaviour of metallic glass deformation [49]. Metallic glasses become increasingly plastic with a decreasing aspect ratio sample from 2 to 0.5 [50]. Amorphous phases are characterised by their intrinsic characteristics, such as their sizes and heterogeneous precipitation patterns [4][33]. Therefore, inclusion in the glassy system of the structural heterogeneities would affect the formation

and spread of shear bands and alter the mechanical stability of the samples further during loading [44][45].

2.6 Fe-based metallic glasses

Iron availability in the Earth's crust makes it a less expensive raw material, and the outstanding mix of physical, chemical, and mechanical qualities makes Fe-based alloys the most significant of these BMGs in terms of commercial importance. Tohoku University's Inoue group reported the discovery of the first Fe-based BMG in 1995 [51][52]. Fe-based BMGs alloys demonstrated soft magnetic properties and high glass-forming ability (GFA) [53].

Fe-based bulk metallic glasses offered great potential for engineering applications, due to their high strength, good magnetic softness, and relatively the less-expensive [54][55][56][57]. Although the Fe-based BMGs are relatively ductile, they rarely exhibit plastic strain when deformed at room temperature. This behaviour is significantly different from non-ferrous BMGs [56][58][59][60]. Many non-ferromagnetic Fe-based BMGs showed fracture strength of up to 4 GPa [61][62][63][64][59]. The Fe-Mn-Cr-C-B amorphous steels, developed at the University of Virginia and further improved by numerous groups to form BMGs exceeding 10 mm in thickness, are however brittle [52][59][62][64]. Several studies report that the Fe-based BMGs' fracture strength for soft magnetic applications ranges from 2.8 to 4.2 GPa [59]. However, these findings need more information to determine whether composition influences the deformation behaviour of Fe-based BMGs.

2.6.1 Development history of Fe-based MGs

In 1967 Duwez and his co-authors developed the first amorphous alloy of the Fe-family, which contains Fe-P-C. The typical form of Fe-based MGs is usually in ribbons, powders or wires shape. They are produced by rapid quenching levels required up to 10^6 K/s [19]. The Fe-based MGs became more interesting for energy saving. Their soft magnetic properties, production cost, and lower core loss introduce high-performance soft magnetic materials. Popular

commercialised amorphous alloys, Fe-Co-P-B and Fe-Co-Si-B are provided via METGLAS.

FINEMET alloy was discovered by Yoshizawa et al. in 1988, which has soft magnetic properties and is a composition of Fe-Si-B. It is come up by annealing treatments and adding Cu and Nb alloying to obtain a significant development. Subsequently, the NANOPERM alloys family were developed from Fe-Zr-B, Fe-Hf-B and Fe-M-B-Cu ($M = \text{Ti, Zr, Hf, Nb, or Ta}$) MGs. Afterwards, nanocrystalline alloys (Fe, Co)-M-B-Cu ($M = \text{Nb, Hf, or Zr}$) were invented and named HITPERM alloys. Presently, these commercial FINEMET, NANOPERM, and HITPERM alloys possess excellent soft magnetic properties, leading to extensive utilises in industries [65].

In 1995, Inoue and his group at Tohoku University, Japan, achieved success in improving many multicomponent BMGs, comprising mostly popular metallic elements with lower critical cooling rates ($\leq 10^3 \text{ K/s}$), and the first Fe-based MGs is $\text{Fe}_{73}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_5\text{B}_4$ [66]. Figure 2-11a exhibits the XRD patterns of the Fe-Si-Cr-B-C amorphous alloys in three forms (as built rotor, powder and ribbon) [67]. A broad perfect halo peak around 2θ at 44° is noticed on XRD patterns, showing their amorphous nature. The results confirm that those samples do not contain a crystalline phase. DSC curves of $\text{Fe}_{73}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_5\text{B}_4$ rods for various diameters, manufactured by injection casting are shown in Figure 2-11b [68]. As-cast rods and as-spun ribbons exhibit no significant differences in glass transition or crystallisation onset temperature, indicating their amorphous nature.

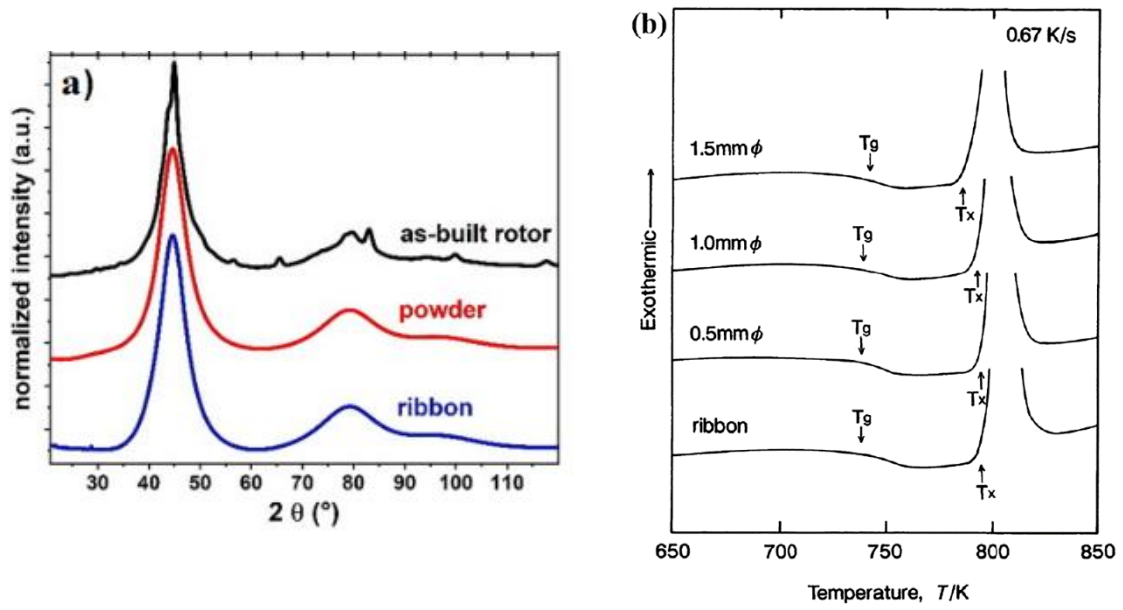


Figure 2-11: a) Typical XRD patterns for Fe-Cr-Si-B-C as built rotor, powder and spun ribbon [67]; b) DSC curves for the $\text{Fe}_{73}\text{Al}_5\text{Ga}_2\text{P}_{11}\text{C}_5\text{B}_4$ rods for different diameters [68].

Later on, a large-scale study manufactured a series of Fe-based MGs for ranging in critical diameter from 1mm to 6 mm, as following Fe-(Nb, Cr, Mo)-(Al, Ga)-(P, B, C) [69], Fe-Co-(Zr, Hf, Nb)-(Mo, W)-B [70], Fe-Co-Nd-Dy-B [71], Fe-Co-Ga-(P, C, B) [72], Fe-(Co, Cr, Mo, Ga)-(P, C, B) [73], Fe-Ni-P-B [74], and Fe-B-Si-(Zr, Nb) [55] were manufactured between 1 and 6 mm in diameter. Researchers have made efforts to enhance the GFA of Fe-based alloys, and in 2013, $(\text{Fe}_{0.8}\text{Co}_{0.2})_{47}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{TM}_3$ alloy achieved a maximum size of complete glass formation of 18 mm [75][76].

Table 2-2. Fe-based BMGs development with traditional manufacturing processes to date [68].

System	Alloys	D_c (mm)	Preparing methods	Discovery Year
Fe-based	(Fe _{0.8} Co _{0.2}) ₄₇ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Tm ₃	18	copper mold casting	2013
	(Fe _{0.8} Co _{0.2}) ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Tm ₂	16	copper mold casting	2013
	(Fe _{0.6} Co _{0.4}) ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Tm ₂	16	copper mold casting	2013
	Fe ₄₃ Co _{4.5} Cr _{16.5} Mo _{16.5} C ₁₄ B ₄ Y _{1.5}	10	copper mold casting	2013
	Fe _{43.7} Co _{7.3} Cr _{14.7} Mo _{12.6} C _{15.5} B _{4.3} Y _{1.9}	10	copper mold casting	2008
	Fe ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Tm ₂	10	copper mold casting	2008
	Fe ₄₁ Co ₇ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Y ₂	16	copper mold casting	2005
	(Fe _{44.3} Cr ₅ Co ₅ Mo _{12.8} Mn _{11.2} C _{15.8} B _{5.9}) _{98.5} Y _{1.5}	12	copper mold casting	2004
	(Fe _{44.3} Cr ₁₀ Mo _{13.8} Mn _{11.2} C _{15.8} B _{5.9}) _{98.5} Y _{1.5}	12	copper mold casting	2004
	Fe ₄₈ Cr ₁₅ Mo ₁₄ Er ₂ C ₁₅ B ₆	12	copper mold casting	2004
	Pd _{42.5} Cu ₃₀ Ni _{7.5} P ₂₀	80	water quenching	2012
	Pd ₄₀ Cu ₃₀ Ni ₁₀ P ₂₀	72	water quenching	1997
Pd-based	Pd ₄₀ Ni ₄₀ P ₂₀	10	fluxing	1984
	Zr ₄₆ Cu _{30.14} Ag _{8.36} Al ₈ Be _{7.5}	73	copper mold casting	2011
	Zr _{41.2} Ti _{13.8} Cu _{12.5} Ni ₁₀ Be _{22.5}	12.6	copper mold casting	1993
Zr-based	Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{17.5}	16	water quenching	1993
	(Ti _{36.1} Zr _{33.2} Ni _{5.8} Be _{24.9}) ₉₁ Cu ₉	50	water quenching	2010
	Ti ₄₀ Zr ₂₅ Cu ₁₂ Ni ₃ Be ₂₀	14	copper mold casting	2005
Ti-based	(Ti ₄₁ Zr ₂₅ Be ₂₈ Fe ₆) ₈₅ Cu ₁₅	15	copper mold casting	2013
	(La _{0.5} Ce _{0.5}) ₆₅ Al ₁₀ (Co _{0.6} Cu _{0.4}) ₂₅	32	copper mold casting	2009
	(CeLaPrNd) ₆₅ Co ₂₅ Al ₁₀	15	copper mold casting	2006
La-based	Cu ₃₄ Pd ₂ Zr ₄₈ Ag ₈ Al ₈	30	copper mold casting	2007
Ce-based	Cu ₄₆ Zr ₄₂ Al ₇ Y ₅	10	copper mold casting	2004
Cu-based	Cu ₄₉ Hf ₄₂ Al ₉	10	copper mold casting	2006
Mg-based	Mg _{59.5} Cu _{22.9} Ag _{6.6} Gd ₁₁	27	copper mold casting	2007
	Mg ₅₄ Cu _{26.5} Ag _{8.5} Gd ₁₁	25	copper mold casting	2005
	Mg ₆₅ Cu _{7.5} Ni _{7.5} Zn ₅ Ag ₅ Y ₅ Gd ₅	14	copper mold casting	2005
	Y ₃₆ Sc ₂₀ Al ₂₄ Co ₂₀	25	water quenching	2003
Y-based	Ni ₅₀ Pd ₃₀ P ₂₀	21	copper mold casting	2009
Ni-based	Pt _{42.5} Cu ₂₇ Ni _{9.5} P ₂₁	20	water quenching	2004
Pt-based	Nd ₆₀ Fe ₃₀ Al ₁₀	12	copper mold casting	1996
Nd-based	Ca ₆₅ Mg ₁₅ Zn ₂₀	15	copper mold casting	2004
Ca-based	Ca ₅₈ Mg ₁₈ Zn ₁₂ Cu ₁₂	10	copper mold casting	2006
Co-based	Co ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Er ₂	10	copper mold casting	2006
	Hf ₄₇ Cu _{29.25} Ni _{9.75} Al ₁₄	10	copper mold casting	2008
Hf-based	(Sm _{0.32} La _{0.3} Al _{0.14} Ni _{0.12} Cu _{0.12}) ₉₇ Fe ₃	10	copper mold casting	2010
Sm-based	Au ₄₉ Ag _{5.5} Pd _{2.3} Cu _{26.9} Si _{16.3}	5	copper mold casting	2005
Au-based	Pr ₆₀ Cu ₂₀ Ni ₁₀ Al ₁₀	5	copper mold casting	2003
Pr-based	Zn ₄₀ Mg ₁₁ Ca ₃₁ Yb ₁₈	2	copper mold casting	2010
Zn-based	Al _{85.5} Ni _{9.5} La ₅	1	copper mold casting	2009
Al-based				

2.6.2 Structure and mechanical properties

G. Savva et al. 1987, reported the effect of crystallinity, metal and metalloid (Si and B) composition on the corrosion behaviour of Fe-based BMG wires [77]. The corrosion resistance is decreased of Fe₆₇Cr₈Si₁₀B₁₅ (at%) in crystallisation anneals. Chromium content (5-7%) exhibited the highest negative film constancy of Fe_{70-x}Cr_xSi₁₅B₁₀ glassy alloys. The corrosion resistance of Fe-Cr-Si-B alloys will increase as the Si:B ratio is increased from 0.4 to 1.5.

A glassy alloy rod with 0.5 mm in diameter was made using a copper mould casting method by adding a little amount of B (1.5 at.%) to commercial FC20 alloy (Fe_{80.75}C_{13.8}Si_{5.1}Mn_{0.18}P_{0.15}S_{0.02}) [76][78][79]. The mechanical properties of Fe-

based metallic glass alloys below 780 K exhibited high tensile fracture strength of 3480 MPa, Young's modulus E is 125 GPa, and hardness HV is 970. With increasing annealing, these properties increased to 8540 MPa, E 135 GPa, and 1120 hardness before crystallisation at 680 K. The alloy rod still shows high yield strength and tensile elongation exceeding 10%, even after crystallisation to bcc-Fe and $Fe_3(C,B)$ phases. FC20 alloy containing 1.5 at.% of B has good mechanical properties and a simple production method, making it a promising material for structural Fe-based materials [76][80].

Non-ferromagnetic amorphous steel alloy of Fe-based BMGs showed fracture strengths of 3000-4000 MPa, according to Ponnambalam et al. [61] and Inoue et al. [81]. Fe-based MG alloys with a diameter of up to 4 mm were cast in injection. Young's modulus and bulk modulus are 210 and 190 GPa, respectively.

Inoue et al., 2004, found another interesting result indicating the possibility of using such alloys as structural materials is the formation of bulk glassy alloys of Fe-based with diameters up to 5 mm using copper mould casting with additions of Co, leading to a decrease in glass transition temperature (T_g) from 1475 K to 1395 K [81]. The bulk glassy alloys display distinct high strength reaching 4250 MPa, Young's modulus (E) between 190 to 210 GPa, a plastic strain of 2.5% and Vickers hardness HV of 1220.

According to M. Stoica, et al. 2005, Fe-based MG with a cross-section of 2x2 mm² and a length of 30 mm was cast in a copper mould, and the Vickers hardness of the samples increased from 885 to 902 with increased annealing [56]. The bulk amorphous alloys exhibit a different fracture behaviour than Zr-based MG, and fractures propagate in diffuse directions with irregular fracture patterns on the surface. The deformation data are listed in Table 2-3. Mechanical properties of Fe-based bulk metallic glasses as-cast rod from the literature [56]., along with some literature values for other Fe-based bulk glassy alloys.

Makino. A, et al. 2009, reported exciting results for the diameter of rods specimen 2.5 mm of Fe-based MG by adding (0.1 – 1.5 at.%) Cu, which can considerably improve the ductility [57]. The BMGs alloys exhibited a tensile strength of 3.3

GPa, and a plastic strain of 3.1% in compression and multiple shear bands were shown near the fracture surface of the rod specimen.

Table 2-3. Mechanical properties of Fe-based bulk metallic glasses as-cast rod from the literature [56].

Type and composition	σ_y (GPa)	ε_y (%)	σ_f (GPa)	ε_f (%)	ε_{pl} (%)	E (GPa)	HV
Bar 2×2 mm as-cast Fe _{65.5} Cr ₄ Mo ₄ Ga ₄ P ₁₂ C ₅ B _{5.5}	2.82	1.76	2.84	1.91	0.15	161	885
Bar 2×2 mm annealed Fe _{65.5} Cr ₄ Mo ₄ Ga ₄ P ₁₂ C ₅ B _{5.5}	2.84	1.60	2.84	1.63	0.03	177	902
Rod ϕ 1.5 mm as-cast (Fe _{0.75} B _{0.15} Si _{0.1}) ₉₆ Nb ₄ [8]	3.16	1.8	3.250	2.2	0.4	175	1060
Rod ϕ 2 mm as-cast Fe ₇₇ Ga ₃ P _{9.5} C ₄ B ₄ Si _{2.5} [8]	2.98	1.9	3.16	2.2	0.3	182	870
Rod ϕ 2 mm as-cast Co ₄₃ Fe ₂₀ Ta _{5.5} B _{31.5} [9]	5.18	0.02	5.185	0.02		268	
Rod ϕ 2 mm annealed Co ₄₃ Fe ₂₀ Ta _{5.5} B _{31.5} [9]	5.33	0.02		0.03	0.01	268	
Rod ϕ 2 mm as-cast FC20+0.4 wt.% B [10]			3.48			125	970
Rod ϕ 0.5 mm annealed FC20+0.4 wt.% B [10]	1.42		1.53		9		1120
Rod ϕ 12 mm Fe ₄₈ Cr ₁₅ Mo ₁₄ Er ₂ C ₁₅ B ₆ [11]	~4					200	~1200
Rod ϕ 12 mm (Fe _{44.3} Cr ₅ Co ₅ Mo _{12.8} Mn _{11.2} C _{15.8} B _{5.9}) _{98.5} Y _{1.5} [12]	~3					257	1224

Table 2-4. Mechanical properties of Fe-based BMGs from the literature [59].

Alloy	D (mm)	T_g (°C)	T_x (°C)	T_1 (°C)	σ_y (GPa)	σ_f (GPa)	ϵ_{pl} (%)	G (GPa)	K (GPa)	E (GPa)	ν
Fe ₆₅ Mo ₁₄ C ₁₅ B ₆	1.5	516	570	1145	3.4	3.8	0.6	73	195	195	0.334
(Fe _{0.9} Co _{0.1}) _{64.875} Mo ₁₄ C ₁₅ B ₆ Er _{0.125}	2	508	569	1130	3.7	3.95	0.5	73	178	193	0.319
(Fe _{0.9} Co _{0.1}) _{64.75} Mo ₁₄ C ₁₅ B ₆ Er _{0.25}	3	509	570	1126	3.6	3.9	0.45	73	175	193	0.317
(Fe _{0.9} Co _{0.1}) _{64.5} Mo ₁₄ C ₁₅ B ₆ Er _{0.5}	4	517	572	1130	3.7	4.1	0.55	73	175	192	0.317
(Fe _{0.9} Co _{0.1}) _{64.25} Mo ₁₄ C ₁₅ B ₆ Er _{0.75}	4	508	565	1121	...	4.0	0	73	176	193	0.317
(Fe _{0.9} Co _{0.1}) ₆₄ Mo ₁₄ C ₁₅ B ₆ Er ₁	3.5	503	557	1125	...	4.0	0	73	177	196	0.317
(Fe _{0.9} Co _{0.1}) ₆₃ Mo ₁₄ C ₁₅ B ₆ Er ₂	1.5	494	536	1142							
(Fe _{0.8} Co _{0.2}) ₆₅ Mo ₁₄ C ₁₅ B ₆	2	502	565	1119							
(Fe _{0.8} Co _{0.2}) _{64.75} Mo ₁₄ C ₁₅ B ₆ Er _{0.25}	3	506	571	1122							
(Fe _{0.8} Co _{0.2}) _{64.5} Mo ₁₄ C ₁₅ B ₆ Er _{0.5}	4	506	573	1120							
(Fe _{0.8} Co _{0.2}) ₆₄ Mo ₁₄ C ₁₅ B ₆ Er ₁	3.5	499	555	1119							
(Fe _{0.7} Co _{0.3}) ₆₅ Mo ₁₄ C ₁₅ B ₆	1.5	503	565	1101							
(Fe _{0.7} Co _{0.3}) _{64.75} Mo ₁₄ C ₁₅ B ₆ Er _{0.25}	2.5	504	569	1107							
(Fe _{0.7} Co _{0.3}) _{64.5} Mo ₁₄ C ₁₅ B ₆ Er _{0.5}	3	505	571	1110							
(Fe _{0.7} Co _{0.3}) ₆₄ Mo ₁₄ C ₁₅ B ₆ Er ₁	3	497	553	1112							
Fe ₆₁ Cr ₄ Mo ₁₄ C ₁₅ B ₆	2	527	580	1160							
Fe ₅₉ Cr ₆ Mo ₁₄ C ₁₅ B ₆	1.5	533	585	1163	3.8	4.4	0.8	77.4	188	204	0.319
Fe ₆₀ Cr _{7.5} Mo ₁₄ C ₁₅ B ₆	1.5	556	601	1210	...	4.17	0	82	204	217	0.322
Fe _{60.5} Cr ₄ Mo ₁₄ C ₁₅ B ₆ Er _{0.5}	3	530	586	1168	...	4.0	0	76.6	184	202	0.318
Fe ₆₃ Mo ₁₄ C ₁₅ B ₆ Er ₂	3	504	546	1150	...	4.0	0	77.8	178	204	0.31
Fe ₅₅ Cr ₈ Mo ₁₄ C ₁₅ B ₆ Er ₂	>4				...			80	180	209	0.31
Fe ₄₈ Cr ₁₅ Mo ₁₄ C ₁₅ B ₆ Er ₂	12	570	620	1170	...	4.2	0	81	195	213	0.317

Verduzco et al. [82] studied the fatigue behaviour of Fe-Cr-Si-B glassy wires using an apparatus for testing double pulleys with controlled strains. It was found that the Fe_{69.5}Cr₈Si_{7.5}B₁₅ glassy wire had a superior fatigue performance under higher cycle conditions than the HT steel wire in terms of strain. After partially substituting Fe with Cr, the fatigue life of glassy wires improved. The difference

in elastic modulus for $\text{Fe}_{77.5-x}\text{Cr}_x\text{Si}_{7.5}\text{B}_{15}$ wires was measured from the nanoindentation test in the Material Science and Metallurgy department at Cambridge University, and the E values are given in Table 2-5. Young's modulus values of Fe-based MG as-cast wire [82].

Table 2-5. Young's modulus values of Fe-based MG as-cast wire [82].

Alloy	Young's modulus, E (GPa)
$\text{Fe}_{78}\text{Si}_{10}\text{B}_{12}$	156 ^a
$\text{Fe}_{74.5}\text{Cr}_{3.5}\text{Si}_{10}\text{B}_{12}$	156 ^a
$\text{Fe}_{71.75}\text{Cr}_{6.25}\text{Si}_{10}\text{B}_{12}$	157 ^a
$\text{Fe}_{70}\text{Cr}_8\text{Si}_{10}\text{B}_{12}$	158 ^a
$\text{Fe}_{77.5}\text{Si}_{7.5}\text{B}_{15}$	159 ^b
$\text{Fe}_{69.5}\text{Cr}_8\text{Si}_{7.5}\text{B}_{15}$	157 ^b

Moreover, another study on the mechanical properties of Fe-Cr-Si-B metallic glass wires has been investigated by Olofinjana et al. [83]. A 10 (at.%) Cr substitution in the as-cast metallic glass wire caused a relatively slow increase in static strength (3000 - 3800 Pa and HV= 900 - 1080). Therefore, the substitution of Cr for Fe significantly improved the fatigue strength of Fe-Si-B at lower concentrations than before reported [83]. The results of the microhardness and tensile test for Fe-Cr-Si-B glassy wires samples are given in Table 2-6. Static mechanical properties of Fe-based glassy alloy wires (HV, Vickers hardness; σ_f , fracture stress; ϵ_f , fracture strain) [83].

Table 2-6. Static mechanical properties of Fe-based glassy alloy wires (HV, Vickers hardness; σ_f , fracture stress; ϵ_f , fracture strain) [83].

Alloy composition	H_v	σ_f ± 10 (MPa)	ϵ_f (%)	H_v/σ_f^a
Fe ₇₅ Si ₁₀ B ₁₅	1035 $\pm$ 10	3510	1.6	2.88
Fe ₇₃ Cr ₂ Si ₁₀ B ₁₅	1040 $\pm$ 5	3550	1.3	2.87
Fe ₇₁ Cr ₄ Si ₁₀ B ₁₅	1030 $\pm$ 6	3690	1.1	2.73
Fe ₆₉ Cr ₆ Si ₁₀ B ₁₅	1076 $\pm$ 15	3710	1.0	2.84
Fe ₆₇ Cr ₈ Si ₁₀ B ₁₅	1110 $\pm$ 5	3830	1.0	2.84
Fe _{77.5} Si _{7.5} B ₁₅	986 $\pm$ 7	3180	2.6	3.03
Fe _{75.5} Cr ₂ Si _{7.5} B ₁₅	1017 $\pm$ 5	3320	2.6	3.0
Fe _{73.5} Cr ₄ Si _{7.5} B ₁₅	1004 $\pm$ 5	3320	2.6	2.93
Fe _{71.5} Cr ₆ Si _{7.5} B ₁₅	1000 $\pm$ 7	3470	2.5	2.81
Fe _{69.5} Cr ₈ Si _{7.5} B ₁₅	1006 $\pm$ 5	3550	2.5	2.77
Fe _{67.5} Cr ₁₀ Si _{7.5} B ₁₅	1020 $\pm$ 5	3550	1.7	2.81

^a σ_f converted to kg mm⁻².

2.6.3 Applications of Fe-based bulk glassy alloys

Besides their strength and hardness, Fe-based glassy alloys also present large elastic deformation, corrosion resistance, and softer magnetic [68]. In recent years, these new materials have significantly contributed to industrial applications, such as soft magnetic materials, wear- and corrosion-resistant coatings, biomedical materials, precision gears, etc. A list of applications for Fe-based BMGs can be found in Table 2-7. This table summarises the fields for which glassy type alloys have been developed in Japan. This list represents an extensive range of applications. The most recent applications of Fe-based BMGs are summarised in the below section.

Table 2-7. Applications field of Fe-based BMGs type and their responding characteristic [76].

Application fields	Characteristic
Structural materials	High strength, high hardness, high fracture strength
Sensor materials	High magnetostriction, giant magneto-impedance effect
Spring materials	High fatigue strength
Sporting goods materials	High strength and large elastic elongation limit
Wear resistant coating materials	High wear resistance
Corrosion resistant materials	High corrosion resistance
Magnetic materials	Excellent soft-magnetic properties, high electrical resistivity
Micro-technology materials	Micro-formability, transferability
Nano-technology materials	Nanoscale imprintability
Data storage materials	
Biomedical materials	Biocompatibility, high wear and corrosion resistance
Fuel cell separator materials	

2.6.3.1 Soft magnetic application

The characteristics of Fe-based BMGs make them the best choice for soft magnetic materials, as they have a high saturation magnetisation, a low coercive force, a low core loss, high permeability, and high electric resistance. They are widely used in inductors, linear actuators, sensors, and as a component material for radio-frequency identification systems. Fe-based BMGs display intrinsic technical advantages in this field, and now LIQUALLOY, which consists of Fe-Cr-(P, Si)-(B, C) and SENNTEX, which is Fe-Cr-Nb-(P, Si)-B, is used for induction cores. Moreover, linear actuators of this type are best fitted with soft-magnetic Fe-based BMGs [68].

Fe-based glassy alloys have excellent permeability, low magnetic loss, and fast flux reversal compared to other soft magnetic materials. Fabrication techniques and post-fabrication heat treatments can also achieve a unique magnetic domain structure. In this respect, Fe-based glassy alloys are more suitable for sensor applications, including position, magnetic field, fluxgate, current, magnetoelastic, temperature, and electronic article surveillance [68][84].

2.6.3.2 Corrosion-resistance and wear-resistance coatings

Fe-based glassy alloys exhibit distinctive physical and chemical properties depending on their microstructure and composition [68]. For example, the screw of a water injection pump, super pressure ball valves, and blade wheels exhibit those components with Fe-based amorphous coatings, see Figure 2-12. Fe-

based glassy alloys can be formed easily into complex shapes due to their viscous flow behaviour. The SEM images in Figure 2-13 show a proprietary micro metallic die and micro gear manufactured by Yodoshi [85]. Fe-based BMGs, however, possess greater strength, modulus, and corrosion resistance than conventional stainless steels, making them ideal for biomedical applications [68]. Despite challenges like poor plasticity at room temperature, Fe-based BMGs have many potential applications. It is foreseeable that with constant efforts, such a unique type of material will be investigated increasingly more significantly in the future.



Figure 2-12. Anticorrosive applications of Fe-based glassy alloy coatings [68].

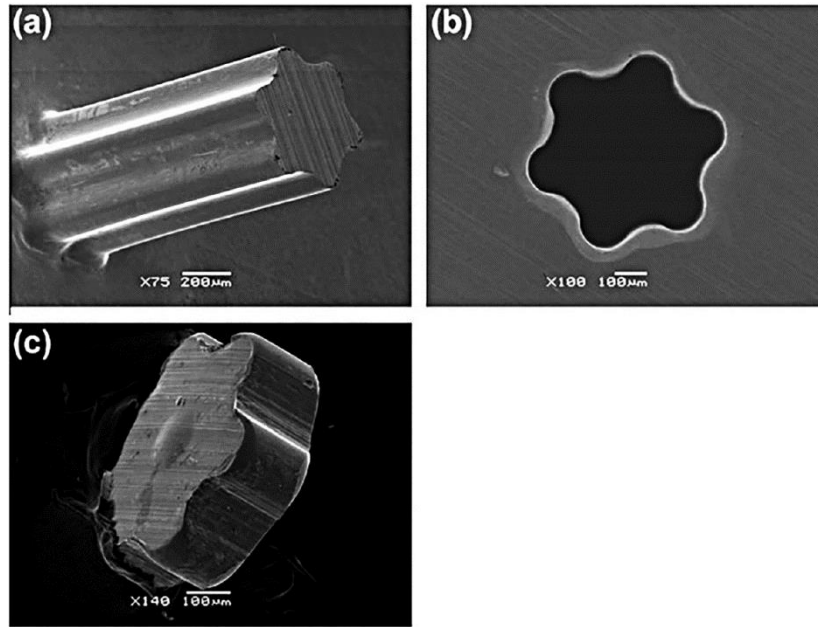


Figure 2-13. SEM images; a) proprietary micro metallic punch; b) die; c) micro gear and punch [85][68].

2.7 Ni-based metallic glasses

Amorphous and nanocrystalline alloys display many properties not found in crystalline counterparts because of the non-existence of long-range periodicity. Due to their excellent soft magnetic properties, these alloys (especially ferromagnetic ones) have considerable interest in many technical fields. Compared to crystalline materials, these materials are characterised by higher electrical conductivity and hysteresis loss. Therefore, due to their higher resistance to wear, impact, corrosion, and oxidation at high temperatures, Ni-based alloys can be used in the glass sector [28][18][36][43]. 3-dimensional (3D) thin-walled honeycomb-like structures like heat exchangers, boilers, co-generators, and heat recovery units are frequently produced using a Ni-based amorphous alloy with brazing. Therefore, Ni-based amorphous alloys ($\text{Ni}_{78}\text{Si}_8\text{B}_{14}$) possess excellent castability, wettability, and flowability [86].

Inoue and his colleagues examined Ni-based amorphous alloys for $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ and $\text{Ni}_{78}\text{P}_{12}\text{B}_{10}$ alloys containing up to 2% Al or Zr were prepared by the melt-spinning method [87]. The mechanical properties of $\text{Ni}_{78}\text{P}_{12}\text{B}_{10}\text{Al}_1$ wire exhibited tensile fracture elongation of 2.4% and fracture strength of 2170 MPa, while $\text{Ni}_{75}\text{Si}_8\text{B}_{17}\text{Al}_1$

wire exhibited fracture elongation of 2.9% and high tensile fracture strength of 2730 MPa. Ni-based glassy alloys exhibit a fatigue limit; the fatigue limit for Ni-based wires is 1.4 to 2.3 times higher than the Ni-based ribbons form. Later on, Inoue et al., 2002 reported that Ni-based BMG rod samples with up to 3 mm in diameter and 1 mm thickness were using a copper mould casting method [88]. The Ni-Nb-Ti-Zr base system exhibited fracture elongation of 2.4% and tensile fracture strength of 3010 MPa. Additionally, DSC curves of $\text{Ni}_{53}\text{Nb}_{20}\text{Ti}_{10}\text{Zr}_8\text{Co}_6\text{Cu}_3$ alloy show the glass transition temperature (T_g) is 846 K and the crystallisation temperature (T_x) is 897 K, respectively. In the studies that followed, Choi-Yim et al. constructed Ni-Nb-Sn-(B,Fe,Cu) BMGs with up to 3mm in diameter, and predicted that this Ni-based BMG would exhibit high strength of 3000 to 3800 MPa with high Vickers hardness ($\text{HV} \sim 1000\text{-}1280 \text{ kg/mm}^2$) [89].

Yue et al. [90] showed XRD patterns of Ni-B-Si alloy grown by magnetron sputtering, Figure 2-14. The phase structure contained the Ni phase, including Ni_3B and Ni_3Si .

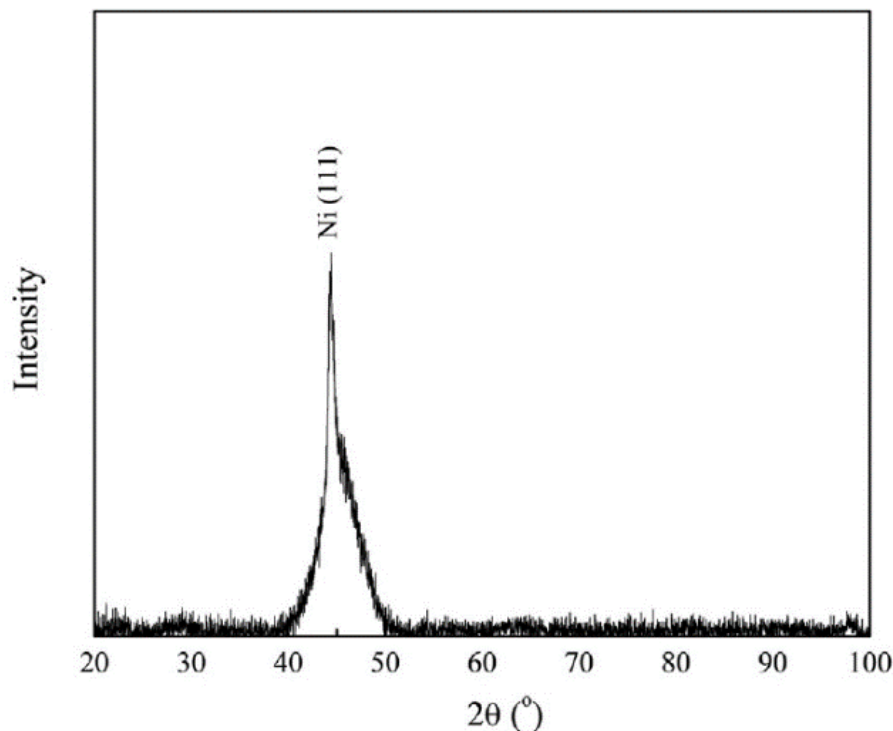


Figure 2-14. X-ray diffraction patterns of Ni-Si-B alloy [90].

However, only a sharp peak at $2\theta \approx 45^\circ$ indicates that this alloy is a mixture of amorphous and crystalline phases, while those of boride and silicide (Ni_3B and Ni_3Si) have entirely disappeared [90]. Furthermore, a similar behaviour was observed with a high Ni-content alloy ($\text{Ni}_{80}\text{Si}_{10}\text{B}_{10}$) ribbon formed by rapid solidification [91].

Moreover, the crystallisation process of the Ni-B-Si as-magnetron sputtering film was measured by the DSC as shown in Figure 2-15. The film's non-crystalline structure was clearly recrystallised at 501.13°C , which is considered a typical crystallisation temperature and average enthalpy change of 25.21 J/g [90].

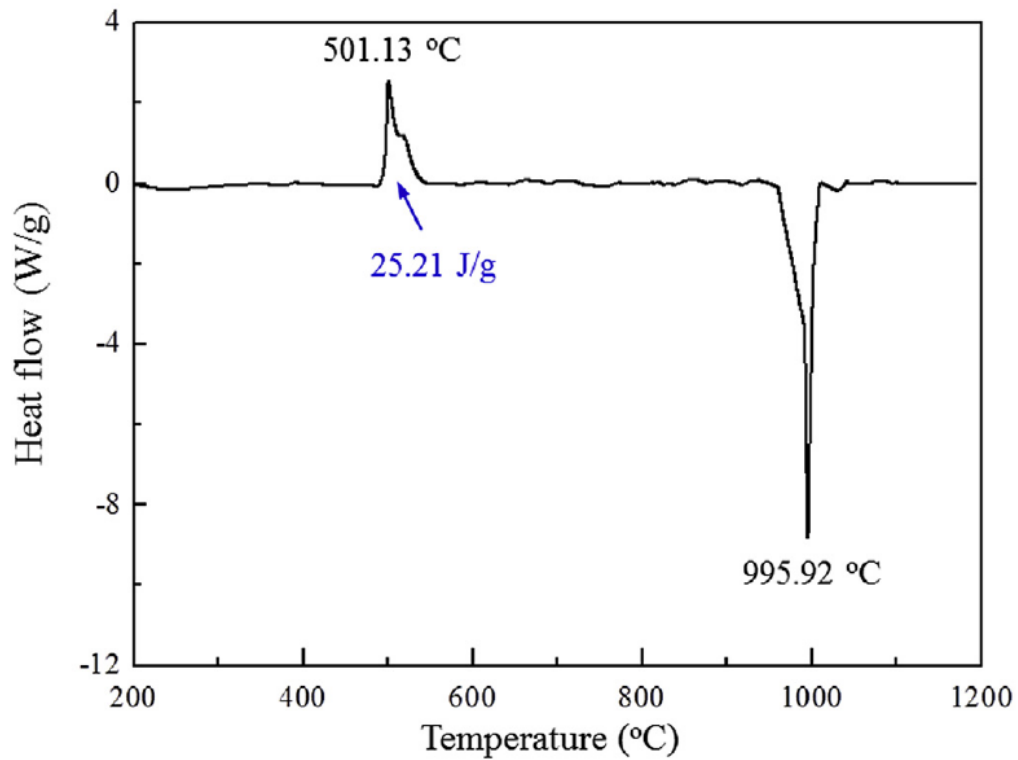


Figure 2-15. DSC thermograms of Ni-Si-B alloy [90].

Donald et al. [92] 1980, claimed that the effect of metal and metalloid (Si and B) composition on the crystallisation temperature of Ni-based glassy alloys was produced by the melt-spinning method [92]. Ni-Si-B exhibited the highest crystallisation temperature (T_x) among all the glassy alloys tested, occurring

between 32 and 38 at% metalloids. However, the real value of T_x is determined by the Si:B ratio.

Ipatov. M., et al. [91] reported that the higher Ni content alloy exhibits a single crystallisation exothermic peak at about 790 K in the crystallisation process of Ni-B-Si alloys [91]. Notably, the single crystallisation exothermic peak divides into three crystallisation exothermic peaks with decreased Ni content. The onset temperatures: first, second and third exothermic peaks are referred to as T_{x1} and T_{x2} and the temperature peaks T_{p1} , T_{p2} and T_{p3} , respectively, are listed in Table 2-8.

Table 2-8. Crystallisation and peak temperatures of the Ni-Si-B alloys studies by DSC analysis [91].

Sample	T_{x1} (K)	T_{p1} (K)	T_{x2} (K)	T_{p2} (K)	T_{p3} (K)	ΔH_C (J/g)
Ni ₇₅ Si ₁₅ B ₁₀	671.5	688.2	766.3	772.9	799.7	442.8
Ni ₈₀ Si ₁₀ B ₁₀	773.7	793.1	–	–	–	318.0

2.8 Ni-Fe-based metallic glasses

Investigating the relationship between the formation of Ni and Fe-based metallic glasses and their crystallisation phases is critical. Figure 2-16 shows x-ray diffraction data for a thin ribbon with Ni content for Ni₄₀Fe₄₀(BSi)₁₉Mo₁ alloys 25 μ m thick and 25 mm wide were prepared using the melt spinning method. Saiseng et al. [93] reported that among the temperature ranges considered, three phases have been observed: firstly, an amorphous phase that annealed at 350 °C and 400 °C. Secondly, a phase containing (-Fe and (-Fe(Si) nanocrystallites annealed at 450 °C, 475 °C and 500 °C. Finally, ribbons are crystallites in a phase without any (-Fe and (-Fe(Si) above 550 °C [93].

Figure 2-17 shows the DSC curves of the Ni₃₈Fe₄₀B₁₈Mo₄ (sample 1), Fe₃₈Ni₃₅Mo₄Si₅B₁₈ (sample 2), and Fe₃₉Ni₃₆Mo₂Si₅B₁₈ (sample 3) metallic glass alloys in melt-spinning ribbon forms [94].

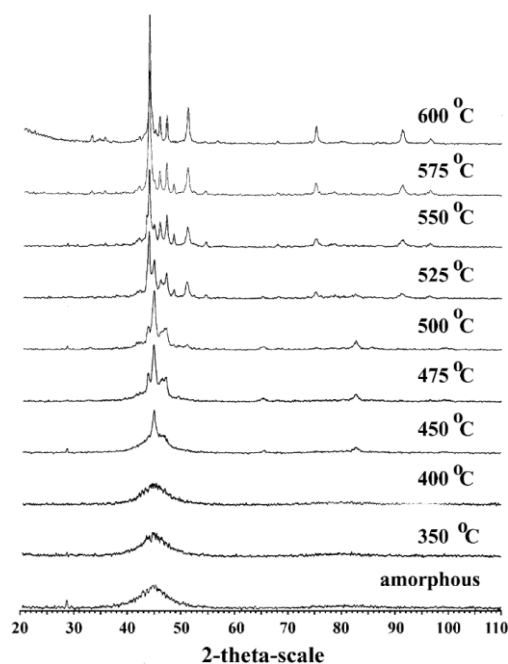


Figure 2-16. XRD patterns of the $\text{Ni}_{40}\text{Fe}_{40}(\text{BSi})_{19}\text{Mo}_1$ ribbons were then annealed for 2 hours at different temperatures [93].

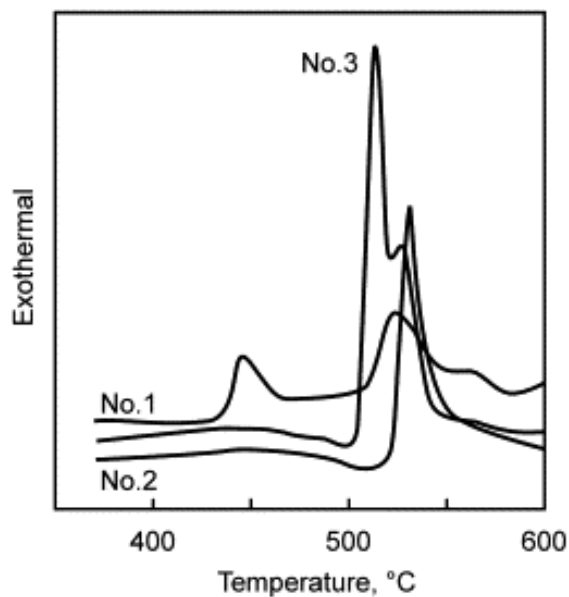


Figure 2-17. DSC curves of the $\text{Ni}_{38}\text{Fe}_{40}\text{B}_{18}\text{Mo}_4$ (sample 1), $\text{Fe}_{38}\text{Ni}_{35}\text{Mo}_4\text{Si}_5\text{B}_{18}$ (sample 2), and $\text{Fe}_{39}\text{Ni}_{36}\text{Mo}_2\text{Si}_5\text{B}_{18}$ (sample 3) alloys with a heating rate of 10 K/min [94].

He et al. [94] found that the crystallisation process of the $\text{Ni}_{38}\text{Fe}_{40}\text{B}_{18}\text{Mo}_4$ (sample 1), exhibited two exothermic peaks ($T_{x1}= 435\text{ }^{\circ}\text{C}$ and $T_{x2}= 505\text{ }^{\circ}\text{C}$). Also, a similar result for (sample 3) $\text{Fe}_{39}\text{Ni}_{36}\text{B}_{18}\text{Si}_5\text{Mo}_2$ glassy alloy presented two separated exothermic peaks, $T_{x1}= 505\text{ }^{\circ}\text{C}$ and $T_{x2}= 520\text{ }^{\circ}\text{C}$. However, the $\text{Fe}_{38}\text{Ni}_{35}\text{B}_{18}\text{Si}_5\text{Mo}_4$ alloy (sample 2) exhibited only one sharp exothermic peak, $T_x= 552\text{ }^{\circ}\text{C}$. It was found that a single FCC crystalline phase structure cannot be formed in the amorphous matrix of $\text{Fe}_{38}\text{Ni}_{35}\text{Mo}_4\text{Si}_5\text{B}_{18}$ and $\text{Fe}_{39}\text{Ni}_{36}\text{Mo}_2\text{Si}_5\text{B}_{18}$ samples when several crystalline phases, such as Fe–B compounds and $\alpha\text{-(Fe, Ni)}$, precipitate almost simultaneously by annealing [94].

Ni-Fe-based glassy alloys were prepared by roller quenching, and their mechanical and thermal properties are influenced by Fe content [95]. The maximum tensile strength of 1586 MPa was obtained for the Ni-Fe-based glassy alloys. According to findings, the ratio of Ni to Fe and P, B, C, Si, and Al content impacts the glass transition temperature of Ni-Fe-P-B-Si-Al alloys [96]. The thermal properties of selected amorphous Ni-Fe alloys and the glass transition temperature T_g are listed in Table 2-9.

Table 2-9. Thermal properties of glassy Ni-Fe-based alloys [96].

	$T_g(\text{K})$	$T_c(\text{K})$	$T_{cm}(\text{K})$	ΔC_p	ΔH_c
$\text{Fe}_{75}\text{P}_{15}\text{C}_6\text{Al}_4$	713	727	744	6.0	1 300
$\text{Fe}_{76.6}\text{P}_{14.2}\text{C}_{1.2}\text{B}_{4.8}\text{Al}_{3.2}$	720	730	746	4.0	1 060
$\text{Fe}_{77}\text{P}_{17}\text{C}_4\text{Al}_4$	714	724	738	6.2	1 260
$\text{Fe}_{38.5}\text{Ni}_{38.5}\text{P}_{18}\text{B}_2\text{Al}_3$	682	699	713	4.6	1 170
$\text{Fe}_{38.5}\text{Ni}_{38.5}\text{P}_{14}\text{B}_6\text{Al}_3$	688	707	721	4.8	1 130
$\text{Fe}_{38.5}\text{Ni}_{38.5}\text{P}_{14}\text{B}_6\text{Si}_3$	708	722	738	5.3	1 160
$\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$	663	673	700	4.5	1 010
$\text{Fe}_{37.5}\text{Ni}_{37.5}\text{P}_{16}\text{B}_6\text{Al}_3$	701	714	724	5.0	1 050
$\text{Ni}_{75.3}\text{P}_{16}\text{B}_{5.7}\text{Al}_3$	693	710	723	5.5	800
$\text{Fe}_{29}\text{Ni}_{49}\text{P}_{14}\text{B}_6\text{Al}_2$	676	704	722	4.7	930
$\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$	643	684	708	3.86	924

According to Inoue et al. (2006), substituting Fe for Ni improves mechanical properties and increases GFA. An arc furnace method and an argon atmosphere

produced Ni-based BMG rods up to 3 mm in diameter [81][97]. The mechanical properties of $[(\text{Ni}_{1-x}\text{Fe}_x)_{75}\text{B}_{20}\text{Si}_5]_{96}\text{Nb}_4$ alloy system display the highest values for Ni-based BMG: a super high fracture strength of 3680-3840 MPa, a plastic strain of about 2% and Young's modulus of 172-186 GPa. Figure 2-18 shows a true stress-strain curve of the $[(\text{Ni}_{1-x}\text{Fe}_x)_{75}\text{B}_{20}\text{Si}_5]_{96}\text{Nb}_4$ metallic glass rod with a diameter of 2 mm.

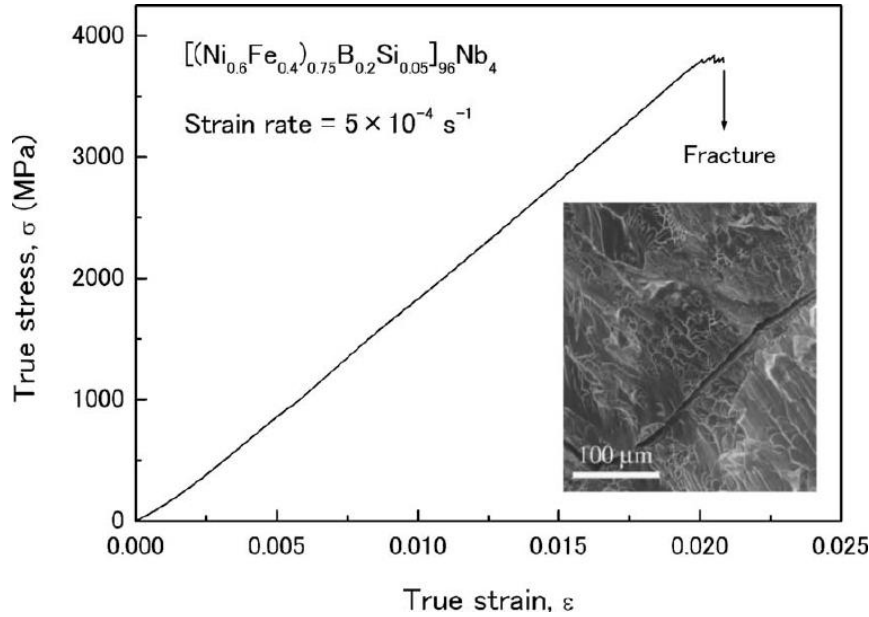


Figure 2-18. Stress-strain curve of 2 mm diameter BMG alloy rod [97].

Table 2-10 summarises the thermal and mechanical properties of Ni-Fe-based bulk glassy alloys. The highest fracture strength has been reported on $[(\text{Ni}_{60}\text{Fe}_{40})_{75}\text{B}_{20}\text{Si}_5]_{96}\text{Nb}_4$, which is 3836 MPa.

Table 2-10. Thermal and mechanical properties of Ni-Fe-based metallic glass alloys.

Alloy	Diameter ϕ (mm)	Thermal stability							Mechanical properties			
		T_g (K)	ΔT_x (K)	T_m (K)	T_l (K)	$T_m - T_l$ (K)	T_g/T_l	$T_x/(T_g + T_l)$	HV	E (GPa)	σ_y (MPa)	σ_f (MPa)
$(\text{Ni}_{0.75}\text{B}_{0.2}\text{Si}_{0.05})_{96}\text{Nb}_4$	0.5	770	25	1275	1446	171	0.532	0.359	972	...	...	...
$[(\text{Ni}_{0.9}\text{Fe}_{0.1})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$	1	762	33	1243	1408	165	0.541	0.366	1053	...	...	...
$[(\text{Ni}_{0.8}\text{Fe}_{0.2})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$	2	755	40	1232	1381	149	0.547	0.372	1082	172	3598	3683
$[(\text{Ni}_{0.7}\text{Fe}_{0.3})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$	2.5	750	45	1237	1356	120	0.553	0.377	1106	179	3668	3756
$[(\text{Ni}_{0.6}\text{Fe}_{0.4})_{0.75}\text{B}_{0.2}\text{Si}_{0.05}]_{96}\text{Nb}_4$	3	745	50	1232	1348	116	0.553	0.380	1130	186	3778	3836

Another interesting result of Ni-Fe-based BMG indicates that possibility as structure materials, $\text{Fe}_{80}\text{-Ni}_x\text{P}_{14}\text{B}_6$ BMG rods up to 2.5 mm in diameter are formed by the J-quenching technique [98]. By increasing the Ni content to $x=50$, the BMG rods exhibit significant plastic strain of $\text{Fe}_{30}\text{-Ni}_{50}\text{P}_{14}\text{B}_6$ BMG up to 11.7% before fracture and corrosion-resistant. However, the magnetisation of $\text{Fe}_{80}\text{-Ni}_x\text{P}_{14}\text{B}_6$ decreases as Ni content increases from $x=20$ to $x=50$.

2.9 Buckling of metallic glasses

Over the last decade, the study of structure elastic stability has experienced a paradigm shift in mechanics that has revived the popularity of elastic instabilities of many kinds, including snapping, buckling, creasing, crumpling, phase transition, and cavitation [99][100]. Among these phenomena, buckling has been known for centuries ever since Leonhard Euler formulated an equation for calculating the critical buckling of a column. Therefore, special design modifications are usually required to avoid such a phenomenon, but new and emerging applications consider it beneficial. It has recently attempted to transform buckling from a negative to a positive effect.

Buckling is a form of mechanical instability that often causes the failure of a structure, but the bulking phenomenon in metallic glass foils contributes to undulatory behaviour. The expression “buckling” refers to a phase of deformation in which a structure undergoes high stress and abrupt changes in shape when the load (P) exceeds a critical value (P_{cr}). A model case of buckling occurs when the ends of a long, thin elastic beam are pressed in opposite directions to one another (see Figure 2-19). Under a light load, the load is applied over the beam in the direction of the axis while maintaining its linear shape, as can be seen in Figure 2-19b.

In this case, the strain energy is proportional to the square of the axial movement. However, once the load passes a critical threshold, the beam will bend archwise (Figure 2-19c), leading to a significant deviation from the square law regarding the change in the association between the strain energy and the displacements [101]. As well as axial compression, bending and torsion forces contribute to the buckling behaviour of elastic beams, and these impacts are highly related to the

geometric and material parameters of the buckled patterns. The most interesting finding is that the elastic deformation of structure pipe-in-pipe cross-sections can be induced using hydrostatic pressure [101]. Pipe-in-pipe applications (i.e., a pipe inserted inside another pipe) have advantages for use in offshore oil and gas manufacturing systems in civil engineering [101][102].

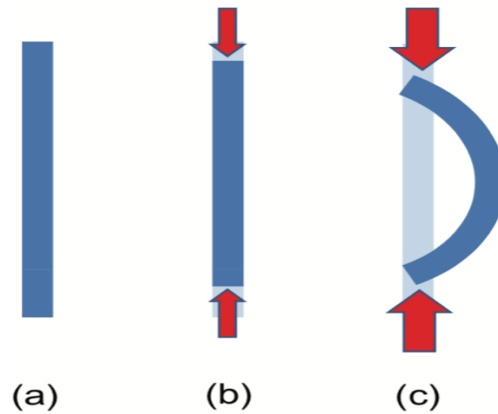


Figure 2-19. Typical curve of buckling states of a column [101].

These considerations regarding macroscopic elastic objects have prompted researchers to examine the buckling patterns attained in carbon nanotubes. The similarities and differences between macroscale buckling and macroscopic patterns are complicated because of the latter's nanometric scale. This complexity has been the impetus behind much of the research into buckling analysing carbon nanotubes under various loading conditions, including axial compression, radial compression, bending, torsion, and multiple combinations of these [103][104][105]. A wide range of studies has been driven mainly by the geometric reversibility of nanotubes versus mechanical deformation and the essential effects of buckling on physical properties. For example, cylindrical shapes are reversible without damaging the atomic structure permanently during unloading. Carbon nanotubes also show high fatigue resistance and, therefore, mechanical energy storage with extremely high energy density [101][106].

Mechanical instabilities, like Euler buckling and shell buckling, can occur with macroscopic tubes and/or columns under axial compression. Hsao et al. [107] reported that atomic force microscopy experiments using cyclic loading compressing large strains to individual multiwall carbon nanotubes revealed buckling instabilities. This study demonstrates that distinct elastic buckling and post-buckling phenomena are observed reproducibly and can be attributed to Euler, asymmetric shell buckling (i.e., kinking), and symmetric shell buckling. As a result, both buckling behaviours exhibit sharp drops in load with increasing axial strain, resulting in negative stiffness when initial post buckling occurs.

In an investigation of individual multiwalled carbon nanotubes (MWCNT), Kuzumaki et al. [108] used nanoprobe manipulation methods to study their nanoscale mechanics in a transmission electron microscope (TEM). It was found that MWCNT buckled like deformation, and Young's modulus of the MWCNT was estimated at 1.1 TPa. However, MWCNTs showed structural defects caused by the deformation of CNTs above their elastic limit, resulting in local plastic deformation.

Molecular dynamics simulations were conducted by Ajori et al [109] to investigate the effects of nanowire (NW)/carbon nanotube (CNT) reinforcement on the buckling behaviour of metallic glass matrix nanocomposites (MGMNCs). Under axial compression, metallic glass alloys containing (Cu and Zr) with a higher Cu percentage exhibited the best buckling behaviour. Adding NW to the metallic glass alloys negatively affects the buckling behaviour, whereas adding CNT and NW-encapsulated CNT increase the buckling load and strain significantly. In addition, filled CNTs are the most effective nanofiller for amending metallic glass buckling behaviour. Moreover, with increasing nanofiller size, critical force and critical strain increase [109].

The molecular dynamics approach combined with continuum mechanics is employed to predict the compressive mechanical properties of copper nanowires encapsulated in carbon nanotubes (NW and CNTs), to obtain copper nanowires with helical structures, and the simulated annealing method was employed [110]. As compared to the corresponding CNTs, NWs and CNTs can withstand higher

buckling loads. It is shown through strain energy curves that the interaction between atoms during the compressive process can be predicted. In this model, NWs and CNTs with different diameters and lengths can be evaluated for their mechanical properties, including the critical buckling load P_{cr} and Young's modulus. However, Sun et al. [110] found that not all composites have greater maximum strengths than the corresponding carbon nanotube composites. Moreover, critical buckling load showed linear fitting with the Euler formula when the aspect ratio of the composite exceeds a certain value, as shown in Figure 2-20. The study has also revealed that Young's modulus of NW and CNT depends more on its radius than its length [110].

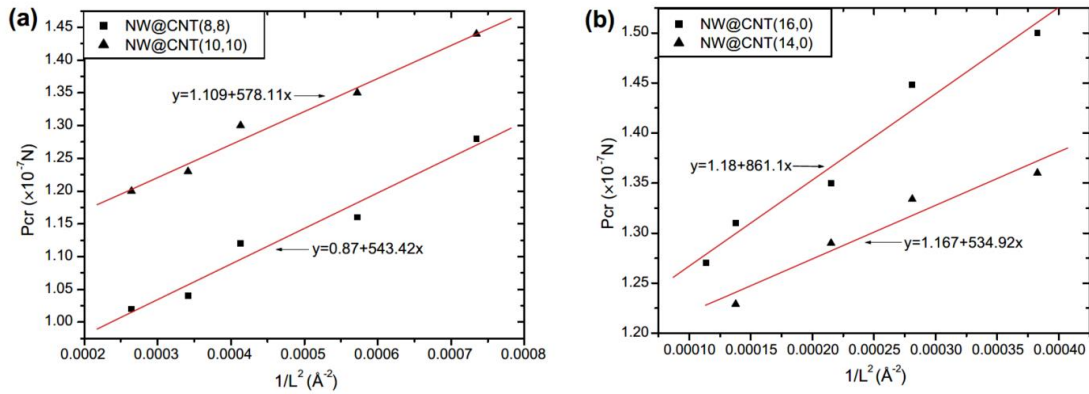


Figure 2-20: a) Buckling load P_{cr} of Cu NW@CNT versus $1/L^2$, where L refers to Euler length of NW@CNT; b) same relation with CU@CNT (14,0) and (16,0) versus $1/L^2$.

Wachter et al. [111] examined the buckling in $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ metallic glass nanowires with different slenderness ratios by molecular dynamics simulations, which were subjected to uniaxial compressive loading tests. According to the modified Euler theory of buckling, values were found for the surface elastic modulus and residual surface stress, versus the slenderness ratio for two nanowire diameters. Due to its nanometric size, $\text{Cu}_{45}\text{Zr}_{45}\text{Al}_{10}$ metallic glass becomes stiffer and exhibits a lower Young's modulus than bulk samples [111].

Demetriou et al. [112] pointed out the mechanical behaviour of open-and closed cell metallic glass foams by conducting standard mechanical testing procedures. Based on real-time X-ray microtomography, this study found that the percolation of local elastic membrane-buckling instabilities causes nonlinear yielding of metallic glass foam. The shear stability of metallic glass foams with various porosities and different base materials was limited to 3.6 % strains. Therefore, the shear stability of metallic glasses at zero temperature reveals a link between floppy modes in a glass and buckling instabilities in stochastic cellular structures [112].

Another interesting result, Wang et al. [113] reported uniaxial compression tests of slender metallic glass $\text{Zr}_{52.5}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}\text{Ti}_5$ (at. %) bars. It was found that the Zr-based metallic glass bars tend to buckle elastically or plastically rather than yield or fracture as long as their slenderness ratio exceeds a critical value. Unlike elastic buckling, plastic buckling imparts a benign failure mode to metallic glass, preventing catastrophic fractures from occurring. Wang et al. [113] asserted that plastic buckling is safer and more reliable than brittle fracture in BMG applications.

Meduri et al. [114] reported the thickness effect of metallic glass supercooled liquids on template-based embossing. It was found that thick samples fail to describe the process based on the existing embossing theory developed, particularly if the thickness of metallic glass becomes similar to the template cavity diameter due to the increased flow resistance at the cavity entrance, supercooled liquid buckles instead of filling. Therefore, Meduri et al. suggested that the thickness-dependent buckling of metallic glass could be exploited in manufacturing hollow metal structures for many emerging applications [114].

Chen et al. [115] studied the buckling deformation behaviour arising at nanopillars of the Zr-based metallic glass using a transmission electron microscope (TEM) nanoindenter to conduct compression tests. At a compression depth of 120 nm, buckling was found to occur as semi-homogeneous deformation. However, Zr-based metallic glass still exhibits amorphous microstructures in the buckling region. Due to this, no phase transformations were involved in the deformation

mechanism of Zr-based metallic glass, and deformation only occurred by the propagation of shear bands [115].

According to Jin-Feng et al. [116], laser patterning forms 3D biomimetic structure of metallic glass ribbon, Blooming, closing, and reversing metallic *Mimosa pudica*. An applied magnetic field can control this process or manually reshape it. Due to changes in density and/or elastic modulus, composite materials buckle within their elastic limit and obey the minimum elastic energy criterion due to residual stress and elastic distortion energy. They also provide a programming route for constructing metallic glass buckling structures. It also sheds light on materials that need automatic functions for robotics, electronic devices, and medical devices, such as vessel scaffolds and vascular filters, which can expand and contract through contactless [116].

In a recent interesting development, Panagiotopoulos et al. [1] reported that thin metallic glass foils exhibit a mechanical response under applied load on top of an elastically shaped arc. It was obvious that the undulatory behaviour mechanism of metallic glass foils is caused by buckling behaviour. Due to this, buckling behaviour is a functional part of the mechanism of undulatory behaviour, resulting in changes in the shape of MG foil and the multiplication of sinusoidal arcs. Therefore, they asserted that undulatory behaviour in thin metallic glass foils is attributed to buckling phenomena. Thus, the undulatory behaviour of metallic glass foils resulting from buckling phenomena can be potentially helpful for a wide range of emerging applications [2][1][117][118][119].

2.10 Undulatory elastic behaviour of metallic glasses

In recent years, a few studies have reported on the elastic behaviour of metallic glass (MG) foils for a range of engineering applications [2][1]. In this regard, metallic glass foils, or amorphous metals, are a new class of materials that have attracted a wide range of technological fields for use as components in, for example, micro-electro-mechanical systems (MEMS) and nano-electro-mechanical systems (NEMS), micro flat springs, and electromechanical switches [2][1][120][54][121][122][123]. Metallic glass foils are valued due to their mechanical properties, which include a high strength of greater than 5 GPa, good

fracture toughness, excellent wear, corrosion resistance, and high elastic deformation of 2% strain [54][18][124][125][126]. Combining such properties makes metallic glasses ideal for applications requiring a high density of elastic energy.

Unlike crystalline metals, metallic glasses have no periodic lattice with glide planes on which mobile dislocations can cause flow. An elastically arc-shaped thin metallic glass foil is loaded and exhibits a unique reversible sinusoidal mechanical response due to its exceptional properties [2][1]. The undulatory behaviour of Fe-Cr-B-Si metallic glass foils was shown for the first time by Panagiotopoulos et al. [1]. This behaviour occurs when a load is applied to a metallic glass foil with an arc shape, resulting in the foil forming additional sinusoidal arcs only when the aspect ratio ($h_1/L \leq \frac{1}{2}$), as seen in Figure 2-21. The foil returns to its initial shape once the applied load is released, exhibiting a reversible wavy elastic response. At the moment of the formation of an additional arc-shaped undulation, all arcs have a perfect sinusoidal shape. With increasing load, the shape of the arcs becomes distorted until the load reaches a sufficient level to cause the formation of an additional arc [2][1]. Under normal load, Panagiotopoulos et al. [1] found that the standing wave formula can be used to describe the undulatory behaviour of metallic glass foil:

$$y^2(x) = A \sin^2\left(n \frac{2\pi}{\lambda_{fundamental}} x\right) \quad (2-1)$$

Where A is the arc amplitude h_i , n refers to the harmonic number of the formed waves, and $\lambda_{fundamental}$ is the fundamental wavelength.

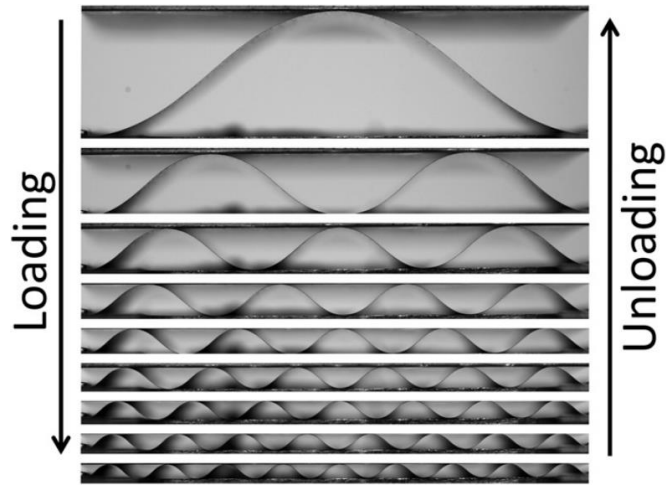


Figure 2-21. Assembly of waveforms for an arc-shaped MG foil formed under load [1].

Figure 2-22 exhibits strain developments during the undulatory behaviour of metallic glass foil as a function of sinusoidal arcs, where these measurements have been taken for perfect sinusoidal arcs. The local strain (maximum strain) around the arcs for $L = 20$ mm in different aspect ratios was measured using the following Equation [127]:

$$\varepsilon = \frac{d}{2R} \quad 2-2)$$

Where d refers to the foil thickness and R is the radius of curvature. The maximum elastic strain should be below 2% to avoid plastic deformation.

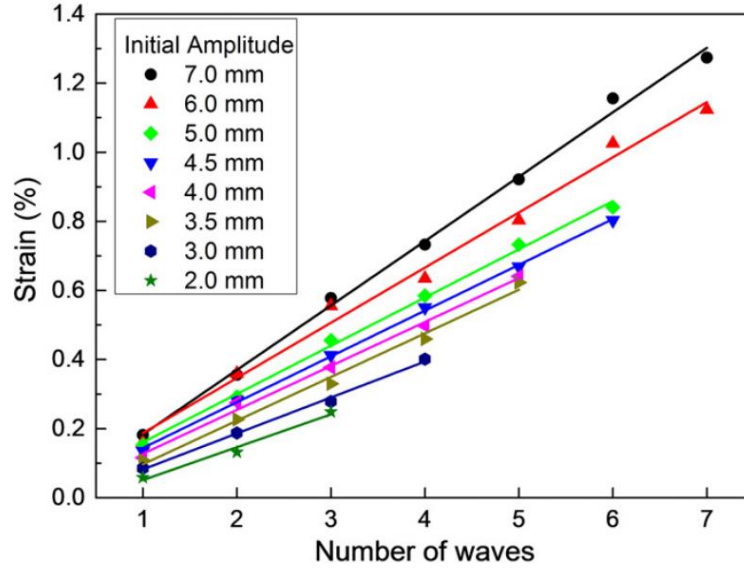
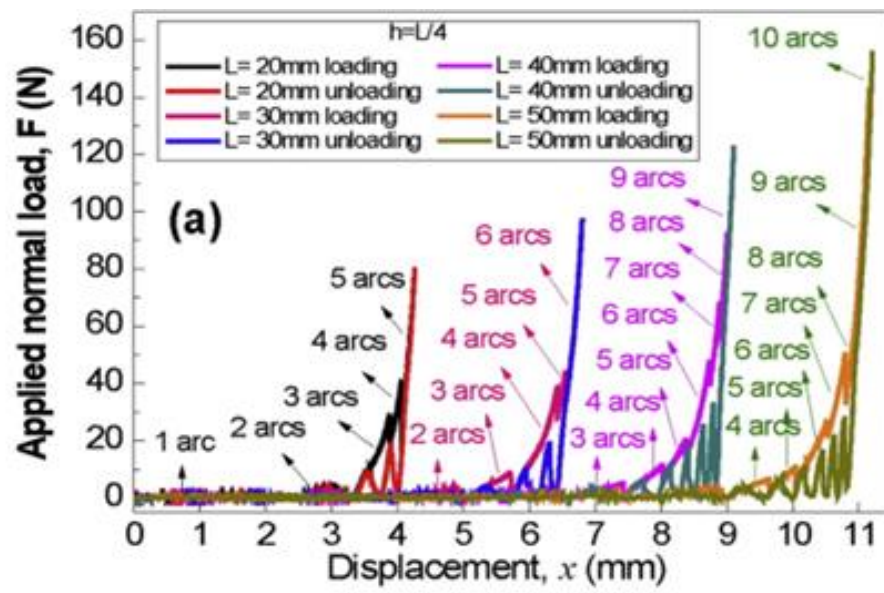
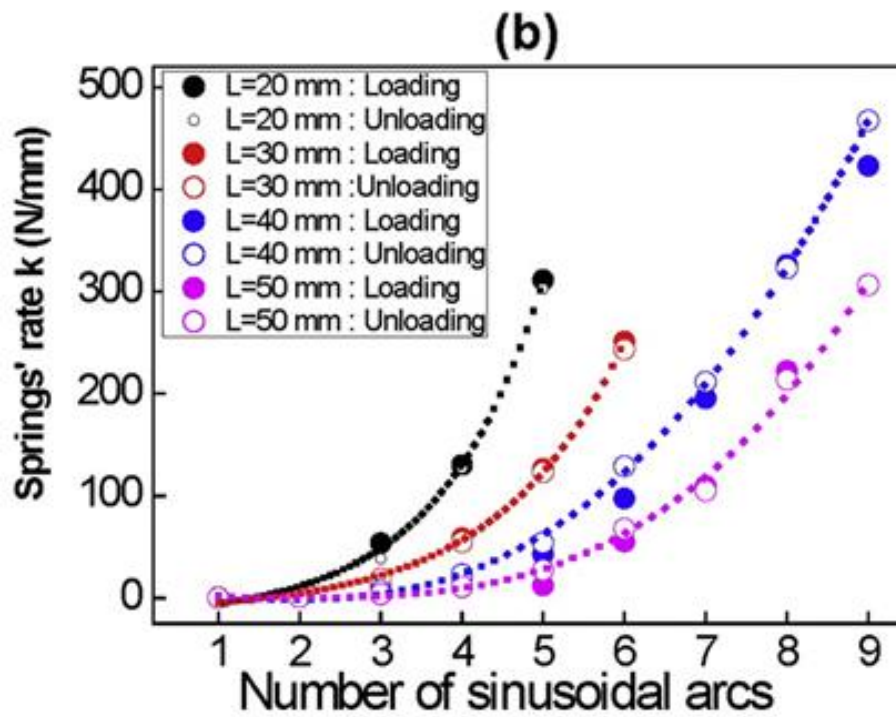


Figure 2-22. The maximum local strain on the Fe-based MG foil versus the number of arcs for different aspect ratios [1].

Yousfi et al. [2] systematically found that the exponential of the form can describe the relationship between the load-displacement curve: $F = \alpha \exp(\beta x)$, where α and β are constant. At the same time, x is the displacement at a specific value of load-displacement, as shown in Figure 2-23(a). The drops in load are related to the change in the number of the formed sinusoidal arcs when showing discontinuous values of load and displacement. In contrast, increments between $(n+1)$ and (n) show a quasi-linear trend. Therefore, the slope between these intervals is referred to as spring's rate, see Figure 2-23(b). Therefore, the non-linear load versus displacement response allows metallic glass foils to act as a non-conventional spring with variable equivalent spring constants at different ranges of applied load [2][1].

Furthermore, the initial geometry of the sinusoidal arc is easily configurable to adjust the mechanical response of the foils on the load-displacement curves (amplitude h , length L , and width W). Also, metallic glass foil selection (elastic modulus) and foil thickness can affect mechanical response. However, the initial geometries with lower L values show a steeper load increase than those with higher L values. However, the higher L values show a maximum number of arcs before plastically deforming compared to small L values, see Figure 2-23(c) [2][1].



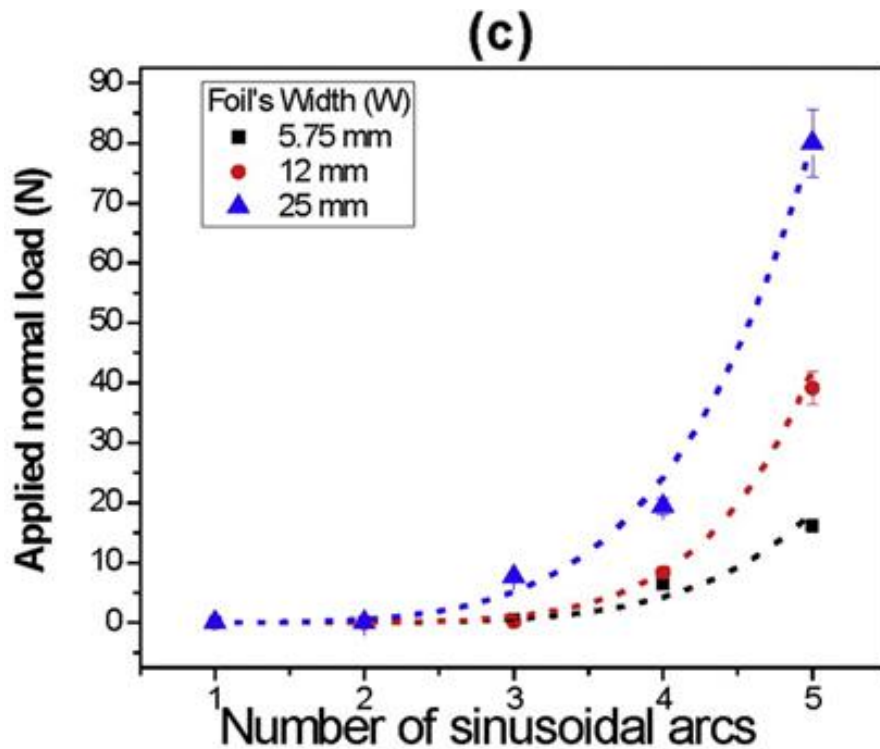


Figure 2-23: a) Load-displacement curve for the Fe-based for different boundary length L values; b) spring's rate k as a function of the number of arcs for various boundary conditions of L ; c) maximum applied normal load on the foils with sinusoidal arcs versus the number of arcs for different foil width [2].

Consequently, vitrified alloys have been proposed for spring material with enhanced properties, functioning as a flat spring with multiple spring rates [3][5]. Panagiotopoulos et al. [1] proposed an electromechanical switch that exploits the undulatory behaviour of metallic glass foils to operate a flat spring with a specific spring rate k . Figure 2-24 shows that the linear actuator stopped applying load and pulled back when 5 sinusoidal arcs were formed. Then metallic glass foil was pushed back the plate, causing a decrease in the number of arcs, which behaves as spring. Subsequently, the linear actuator is restarted again when 2 sinusoidal arcs are formed using a different electric circuit [1].

By their linear contact position, electromechanical switches manufactured from metallic glass foils can take advantage of undulatory behaviour in practical applications, such as an alarm device or an automatic aquarium filler, for example [117]. Figure 2-25 exhibits a schematic for the electric aquarium's wiring,

including an automatic device to fill the tank when needed. The concept is to place a sensor on the glass wall with well-defined high and low levels. The sensor acts as a switch to operate the motor pump (M-P) and uses an Arduino card (electronic card) to control the system. Whenever the water level in the aquarium exceeds the standard value (aquarium filled), the float is in the up position off, and the pump will not run. However, a signal from sensor S1 will be sent to the electronic card once the water reaches level 1. After that, the motor starts rotating from initial arc-shaped to 3 formed sinusoidal arcs. The metallic glass foil deformed elastically during loading from 1 to 2 sinusoidal arcs, making the first linear contact position (blue point in Figure 2-25). This contact position makes the pump on, and filling starts by sending a signal to the electronic card. A continuous filling is carried out until the development of 3 sinusoidal arcs end of displacement is achieved (red point in Figure 2-25); another command will be sent to the electronic card to turn on the motor (M) in the second rotation sense. Finally, an electronic signal card will be sent to motor (M), returning to its original position, and filling stops.

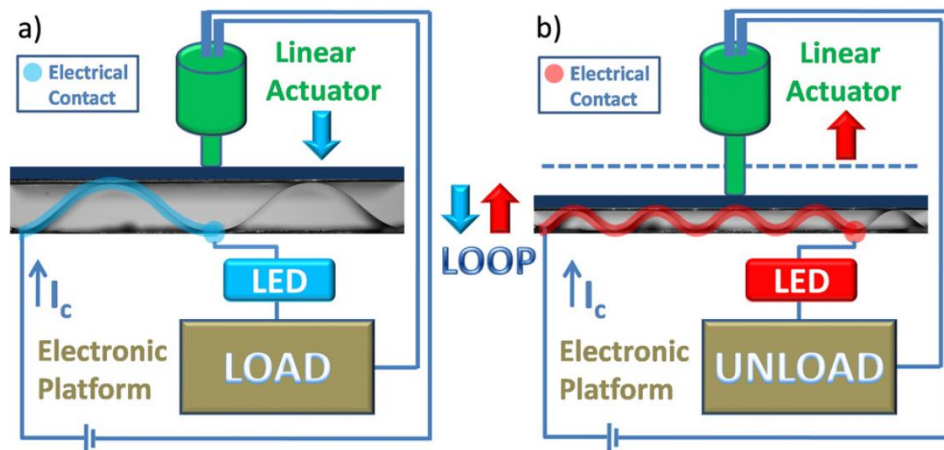


Figure 2-24. An electromechanical switch exploiting the undulatory behaviour of MG foils [1].

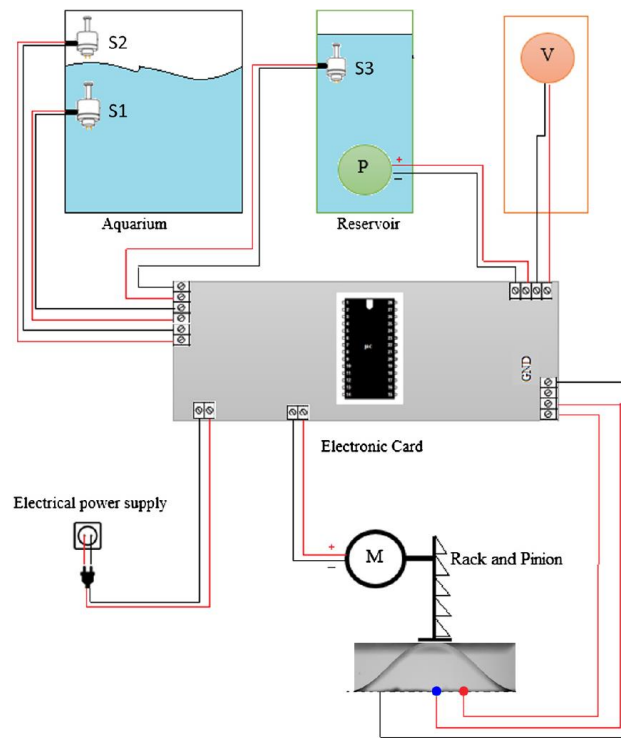


Figure 2-25. Schematic of the electrical wiring for the automatic filling of an aquarium using a mechanical response of an MG foil as an electromechanical switch [117].

Aljerf et al. [127] found that a metallic glass foil can be formed into complex shapes without embrittlement using thermo-elastic processing (TEP). Aljerf et al. found that glass alloy tapes, including $\text{Fe}_{83}\text{B}_{17}$, $\text{Co}_{80}\text{B}_{20}$ and $\text{Pd}_{82}\text{Si}_{18}$, ternary $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$ and $\text{Cu}_{60}\text{Zr}_{30}\text{Al}_{10}$ and more complex quaternary alloys for metal-metalloid and metal-metal types such as $\text{Zr}_{70}\text{Ni}_{16}\text{Cu}_6\text{Al}_8$ and $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$ can be shaped without embrittlement within their elastic limit. However, only the $\text{Pd}_{42.5}\text{Cu}_{30}\text{Ni}_{7.5}\text{P}_{20}$ glassy alloy became brittle after shaping. Figure 2-26 shows ductile metallic glass ribbons in complex shaping undergoing 180° bending without cracking before and after shaping [127].

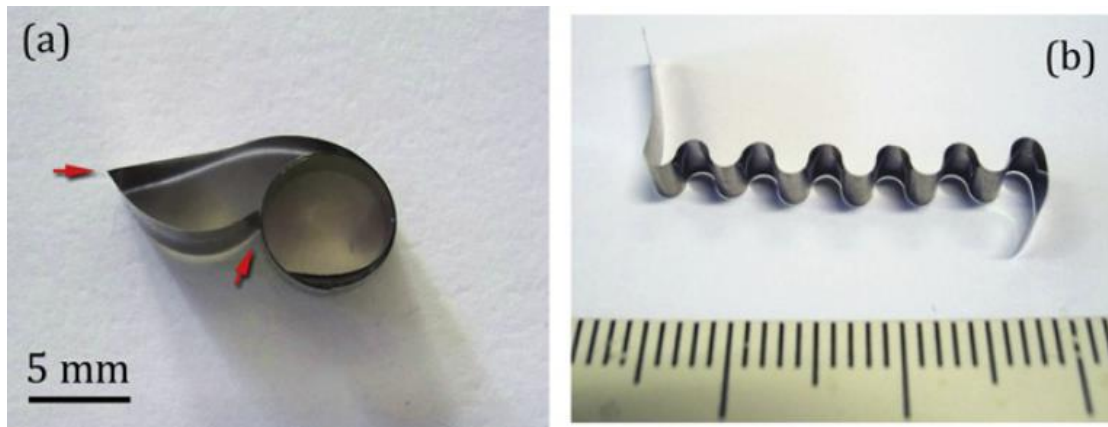


Figure 2-26: a) Shaped Pd₈₂Si₂₀ glassy tape showing double bending ductility; b) example of MG foil with complex shaping [127].

Aljerf et al. [127], reported that the Taub approach had been used for TEP, leading to complete shaping without thermal embrittlement for glassy Fe_{81.5}B_{14.5}Si₄. The Taub approach is based on the free-volume model of structural relaxation [128][129]. However, the model applies to other metallic glasses as well. Therefore, metallic glasses can be used as spring applications [127].

Panagiotopoulos et al. [118] found that metallic glass behaves shaped into linear and annular wave springs using TEP under applied load up to 140 N with 5 sinusoidal arcs within the elastic region. Consequently, further loading up to 270 N results in doubling the number of sinusoidal arcs from (5 to 9 sinusoidal arcs), as seen in Figure 2-27. Once the unloading occurs, the sinusoidal arcs with double waveform return to their original shape, showing a unique undulatory behaviour. Due to this elastic strain limit of 2% in metallic glass, reversibility is attained. In addition, the load-displacement curve for metallic glass foil, loaded to 140 N, obtained the maximum stored elastic energy of 26.6 mJ in the first wave spring production. During the transition zone, the foil elastically deforms, which induces the buckling of additional arcs leading to a drop in load. Meanwhile, elastic energy is also stored. However, when additional arcs on the waveform, it becomes a different flat spring with a higher load capacity than 270 N and a higher spring rate (~1780 N/mm) than the initial configuration. Therefore, the maximum total elastic energy stored in the metallic glass wave spring with the higher

number of waveforms reaches 39 mJ during loading compared to less energy stored on unloading, as shown in Figure 2-28. Consequently, the energy storage capacity of Fe-based MG foils, either in linear or annular form, can be up to 2600 kJ/m³, higher than that in conventional springs [118].



Figure 2-27. Front-view snapshots of the shaped MG foil: a) Free-standing pre-shaped MG foil; (b) elastic deformation at the maximum load when still functioning as a conventional wave spring; (c) the undulatory behaviour in which further loading leads to elastic multiplication of the number of arcs in the waveform and to an increase in the load capacity [118].

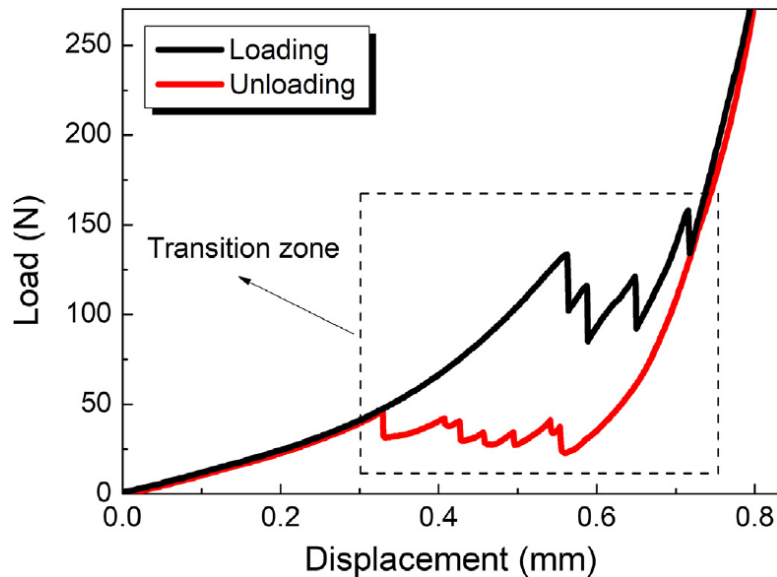


Figure 2-28. Load as a function of displacement during loading and unloading of the linear wave spring made by pre-shaping an MG foil. The transition zone is characteristic of MG foils, and corresponds to the undulatory behaviour in which additional arcs are generated (Fig. 2-26c) [118].

Moreover, metallic glass wave springs in linear form can support about 2.5×10^5 times their weight, and annular wave springs can support about 1.3×10^6 times their weight. For example, Figure 2-29 shows annular wave springs formed by TEP of Fe-based metallic glass foils. The appropriate working regime of these metallic glass wave springs is to be operated with maximum load sustainable by the initial waveform. However, the hysteresis in the transition zone causes significant energy dissipation during loading/unloading. Therefore the undulatory behaviour is significant in providing an essential fail-safe mechanism in case of overload [118].

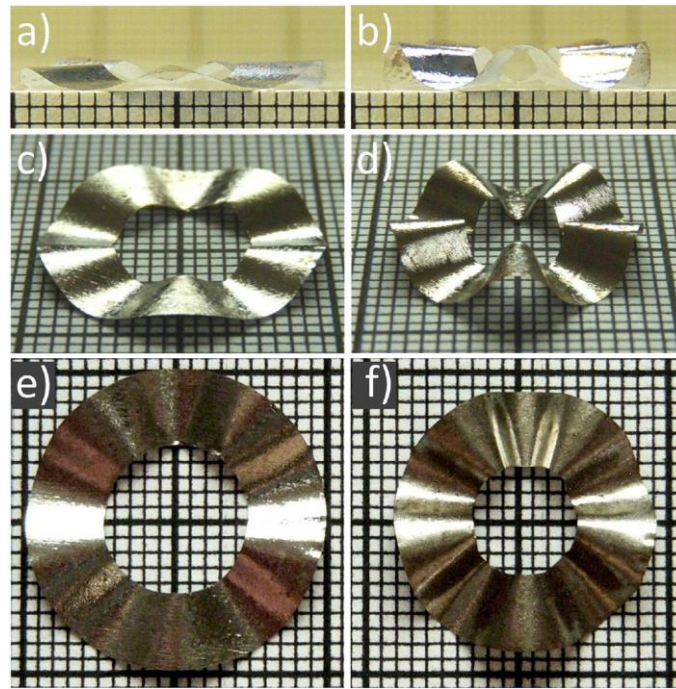


Figure 2-29: a) and b) side view of wave springs with the maximum shaping factor achievable for (a) $T_a < T_{mbrit}$ (plastic) and (b) $T_a > T_{mbrit}$ (brittle); c) and d) the corresponding 450 views; e) and f) the corresponding top views [118].

Yousfi et al. [119] suggested a model to predict the wavy elastic behaviour of arc-shaped thin MG foils during a reversible sinusoidal mechanical response. The concept of this model is based on the specific geometrical condition of the arc-shape of thin foil of metallic glass, where is following Equation is used [119]:

$$\frac{L^2}{4} + h_1^2 = \frac{L_t^2}{4} \quad 2-3)$$

The Pythagorean theorem has been used where L_t is the total length of the foil, where they assumed the bent of half foil equal to a rectangle triangle. Due to this, the undulatory behaviour of thin foil is symmetric and then considered as a thin-walled beam, as shown in Figure 2-30. Figure 2-31 shows the arc-shaped foil, including all model parameters. Therefore, the angle θ continuously changes during undulatory behaviour and is the main parameter for tracing the wavy elastic behaviour [119].

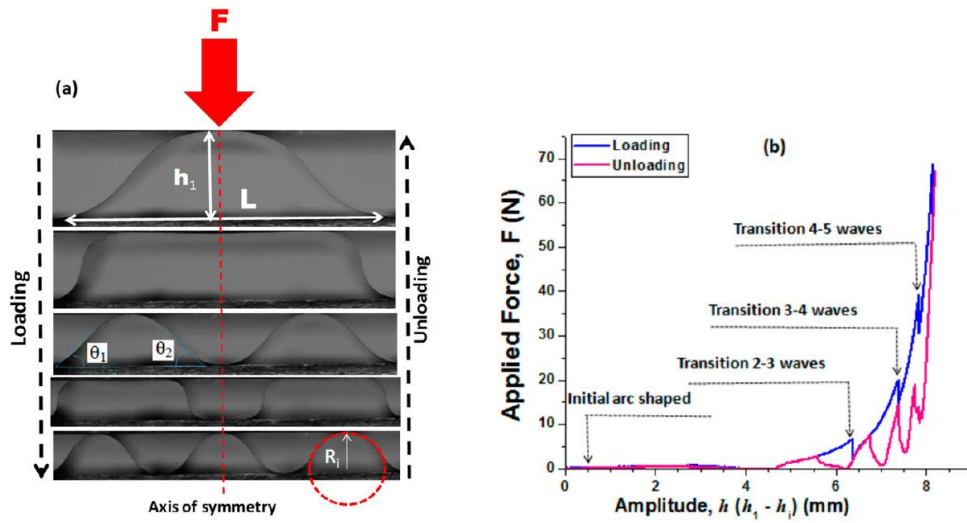


Figure 2-30: a) initial arc-shaped MG foil; b) load-displacement curve for L30h10W25 condition [119].

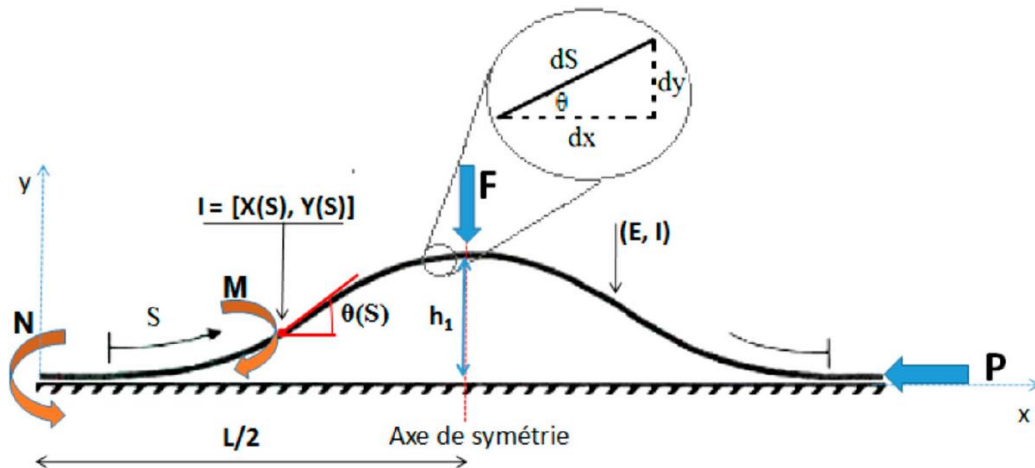


Figure 2-31: Present schematic of the arc-shaped MG foil in (x, y) plane with model parameters [119].

The undulatory behaviour induced by buckling phenomena, the Bernoulli-Euler theory is used at the bending moment (flattening area) induced by the curvature given by:

$$EI \frac{d\theta}{ds} = M \quad 2-4)$$

Where θ is the bending rotation angle of the arc-shaped foil at each curvilinear abscissa S in the plane (x,y) , E refers to Young's modulus, and I is the moment of inertia.

The derivative Equation (2-13) can be given in Equation (2-14) which is the evolution θ angle during applied load on the foil (undulatory behaviour).

$$\frac{d^2\theta}{d^2S} = -\frac{P}{EI} \sin(\theta) + \frac{F}{EI} \cos(\theta) \quad 2-5)$$

Therefore, the correlation between the θ and radius R_i through the wavy elastic behaviour can be described by the following linear Equation:

$$R = nh - m \quad 2-6)$$

An example of how the amplitude h_i changes with amplitude R_i during loading can be seen in Figure 2-32 using the model parameters n and m obtained from the experiment [119].

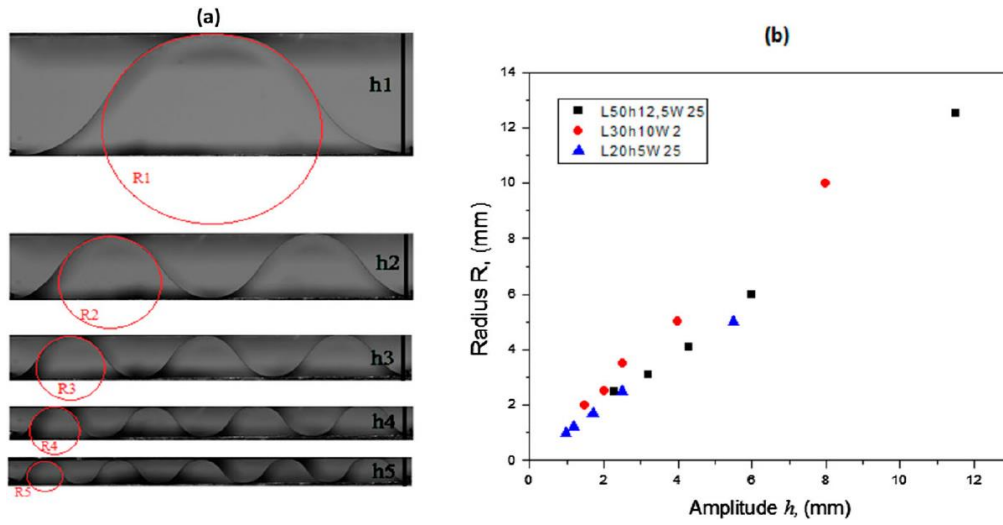


Figure 2-32: a) undulatory behaviour of MG foil with the corresponding curvature radius R ; b) the radius curvature R versus amplitude h [119].

Yousfi et al. [119] showed that the numerical code in MATLAB software is entirely compatible with experimental results. Accordingly, the obtained results based on a numerical solution of the constitutive equations of the model are in good agreement with experimental results, as shown in Figure 2-33.

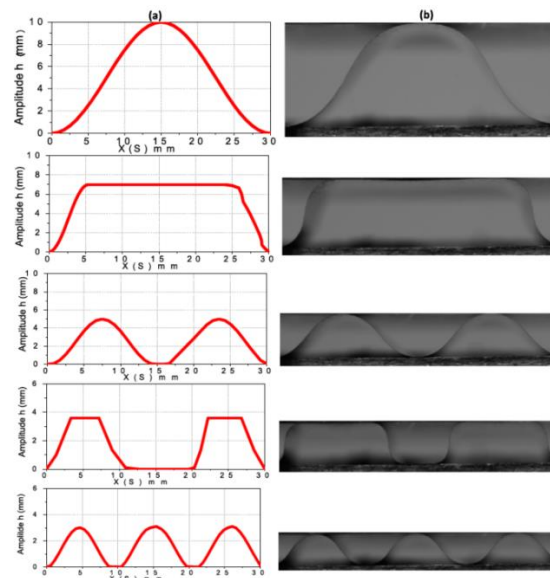


Figure 2-33: a) numerical results presenting the profiles of foil deform; b) intermediate stage of undulatory behaviour for metallic glass foil [119].

Furthermore, Yousfi et al. [130] suggested that numerical modelling could estimate the maximum number of sinusoidal arcs of an arc-shaped metallic glass foil before plastic deformation occurs. In this study, Abaqus software was used to simulate the undulatory behaviour of MG foils using a similar linear equation to the one proposed in [119] for the evolution of the radius of arc curvature, R_i , against amplitude, h_i , associated with a strain equation (6) to measure maximum strain around arc formation, which can trace elastic undulatory behaviour caused by the applied load of an arc shaped foil [130].

Elastic undulatory behaviour is related to the exceptionally (for metal) extensive elastic deformation range of metallic glasses. In other words, wavy elastic patterns of MG foils must be within the elastic range of metallic glass of 2% strain. However, elastic undulatory behaviour is an underlying mechanism that involves elastic deformation, bending and buckling occurring sequentially, resulting in changes in the shape of MG foil and the multiplication of sinusoidal arcs. Although buckling, as a form of mechanical instability, is often related to the failure of a structure and is usually an undesirable phenomenon. Despite this, as mentioned before, buckling behaviour is an essential part of the undulatory mechanism.

2.11 Fatigue on metallic glasses

Fatigue is a form of failure occurring in structures under dynamic and fluctuating stresses. For example, fatigue failure could occur in bridges, aircraft, and machine components. Under these stresses, failure can occur considerably below the tensile or yield strength for a static load at a stress level. The term fatigue is used because it usually happens after a long period of repeated stress or strain cycling. Furthermore, fatigue failure is catastrophic and intrinsic, occurring very suddenly and without warning [131].

Fatigue of amorphous metals was not widely studied until relatively recently, mainly because of the lack of sufficiently large specimens for testing.

The fatigue behaviour of BMGs has been widely studied for different types of BMGs. For example, Zr, Fe, and Cu-based BMGs with various loading approaches, including three-point-bending, four-point-bending, and tension–

tension approaches. However, these findings indicate a significant difference in fatigue limits and lifespan between BMG alloys [132][133]; [134]; [135]; [136]; [137].

A significant difference between fatigue results in bulk metallic glasses can be attributed to several factors, including material composition, material quality, sample geometry, the chemical environment, the surface state, temperature, cyclic loading, mean stress, and residual stress [138]; [139]. Recent research has shown that fatigue cracks growth behaviour is similar to those in other high-strength alloys. However, for reasons that are not well known, the fatigue behaviour of amorphous alloys tends to be slightly different from crystalline alloys. The complicated situation is due to specimen geometry and preparation variations, as the findings vary from different testing groups [4].

2.11.1 Fatigue crack initiation growth

As with crystalline alloys, steady-state fatigue crack growth occurs according to the Paris equation in rapidly solidified metallic glass wires and ribbons [140]; [141]; [142].

$$\frac{da}{dN} = \Delta K^M \quad 2-7)$$

Where a is the crack length, N is the number of cycles, ΔK is the stress intensity range, and M is a constant for a given material. Amorphous alloys also show a fatigue threshold ΔK_{TH} below which fatigue cracks do not propagate; typical values are $\Delta K_{TH} = 1 - 5 \text{ MPa m}^{1/2}$, again comparable to many crystalline alloys.

Another similarity is the observation of fatigue striations on the fracture surface, which can associate their distancing with the measured growth rate of fatigue cracks [142]. Amorphous alloys exhibit fatigue cracks quite similar to crystalline alloys, as plastic deformation is permanently involved, repeatedly blunting and resharpening the crack tip [133].

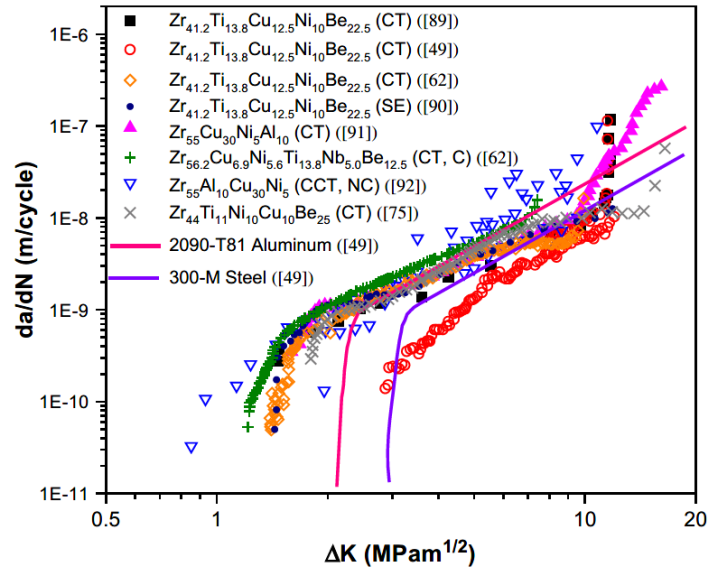


Figure 2-34. Fatigue-crack-growth rates (da/dN) against the stress-intensity factor range (ΔK) [138].

Wang et al., [138] found that the fatigue crack growth rates of the Zr-based BMGs and composites could be comparable with conventional crystalline alloys, as shown in Figure 2-34.

In the Paris system, the exponent M of ductile crystalline alloys and Zr-based BMGs are typically between 1-3. The fatigue cracks growth rates of Zr-based BMGs and composites are similar to those of conventional crystalline alloys, such as ultrahigh-strength steel (300M) and age-hardened aluminium alloy (2090-T81). However, the ΔK values of crystalline alloys are usually higher than Zr-based BMGs. Therefore, Zr-based BMGs are much less than crystalline alloys as fatigue-fracture hardness begins to spread unstable fatigue-cracking [143]. This feature might be behind BMG failure, which occurs after several loading cycles, leading to crack initiation.

2.11.2 Fatigue limit of metallic glasses

Many crystalline alloys display a fatigue limit of about 40% of the tensile strength lower than a stress amplitude S which the material can be cycled permanently without failure [144]. Currently, research Zr-based MGs show different performances, with some classes having fatigue limits of 5% of the tensile

strength [133]; [134]; [144]. However, Liaw and his colleagues reported values between 15–25% of the tensile strength [145]. The S-N curve of two classes of MGs with a four-point stress and strain geometry is shown in Figure 2-35 [145]. Menzel and Dauskardt also quantify fatigue life, suggesting that the cracks nucleate early and increase at levels consistent with "long" fatigue cracks [134].

Liaw et al. indicated that a smaller volume of specimens is less likely to have a defect that induces fatigue crack initiation. Therefore, one would expect these specimens to show higher fatigue limits. Nevertheless, cracks of fatigue seem easy to initiate. There are some residual stresses of BMG specimens arising from the difference in cooling rates between the interior and exterior of the casting process. Thus, residual stresses will affect fatigue life [144]; [146]. The structural relaxation may also change because of various cooling rates.

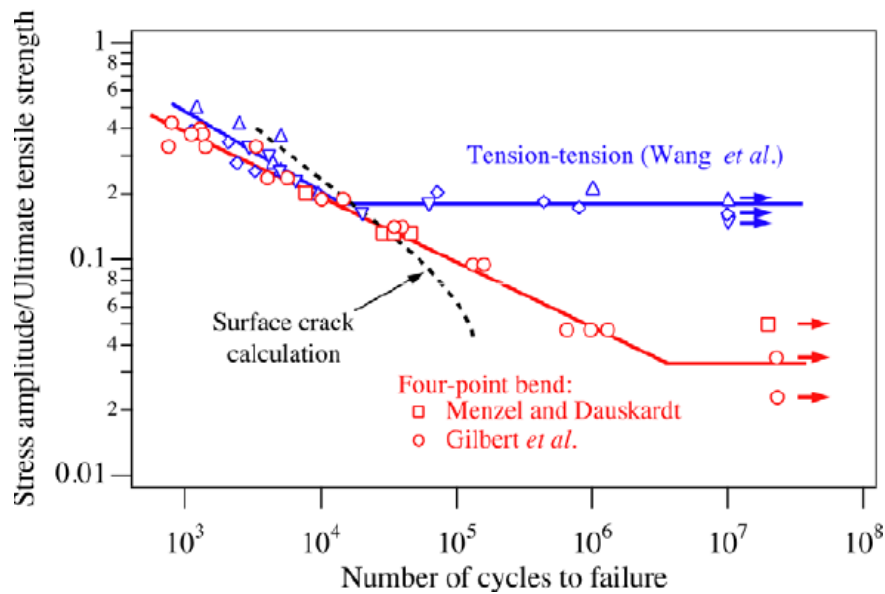


Figure 2-35. The fatigue life of $\text{Zr}_{41}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ [4].

Launey et al., investigated specimens taken from thick plates 4.8 mm, and 2.6 mm, respectively, showing that the specimen 4.8 mm thick had a higher fatigue limit twice, compared to the specimen with a thick of 2.6 mm. Therefore, it is attributed to structural relaxation in the thick plate because of the slower cooling rate [147].

Wang et al., [148] studied the fatigue behaviour of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ monolithic bulk metallic glass and $\text{Zr}_{56.2}\text{Ti}_{13.8}\text{Nb}_5\text{Cu}_{6.9}\text{Ni}_{5.6}\text{Be}_{12.5}$ bulk metallic glass containing crystalline phase. They found that the tension-tension fatigue of the Zr-based composite is comparable with the previous four-point-bend results reported by Gilbert et al. However, the monolithic BMG had a longer fatigue life compared to the monolithic BMG used in four-point-bend fatigue. Fatigue crack initiation is characterised by casting defects in the fracture morphology. In addition, the Zr-based BMG shows a higher fatigue lifetime than the Zr-based BMG composite.

Finally, there may also be other consequences, such as the surface finish of the specimens may be affected, composition differences and oxide surface layer formation [4]. This field requires additional research to understand the effects of residual stresses, relaxation and surface preparation, and careful attention should be given to them.

2.11.3 Fatigue crack initiation

Recently, Menzel and Dauskardt investigated how fatigue cracks initiate on the surface of fatigue specimens. After just a few loading cycles, it was observed that a shear band initiates first, and the direction of the maximum stress is oriented at around 49° [134]. That compares with high cycle fatigue in crystalline metals, which often account for 80% of fatigue life by crack nucleation. The lack of a microstructure impedes fatigue crack propagation in amorphous alloys [144].

The importance of initiating fatigue cracks suggests two ways to manage fatigue failure in amorphous alloys. First, adding a microstructure will restrict the growth of small fatigue cracks by making a composite, improving fatigue efficiency. A second way to boost fatigue efficiency could be to add residual compressive stresses on the surface, as recently done in the shot peening [149].

It is supposed that compressive stresses will likely impede the process of surface shear bands transforming to mode I crack and the small cracks' growth. It is essential to note in this regard that for at least part of the loading process, in compression-compression loading, specimens have a much higher fatigue limit

than those under tensile loading. [134]. This study shows that maintaining the part surface component in a non-tensioned state will dramatically enhance the fatigue resistance of amorphous alloys.

Gilbert et al.,[133] reported that the behaviour of fatigue cracking propagation in Zr-based BMGs was generally found to be like certain crystalline alloys. However, the lifetimes of Zr-based BMGs showed lower stress-life fatigue findings compared to the crystalline alloys. Therefore, the crack initiation could be quickly initiated in BMGs, due to the absence of grain boundary. During cyclic loading, fractures in BMGs were observed to initiate from casting defects, such as porosities, inclusions, or surface flaws, such as polishing scratches [145].

On the other hand, other studies reported that fatigue cracks are initiated from shear bands. Some researchers indicated that shear bands of formation and propagation are related to free volume theory, resulting in fatigue behaviour in BMGs [134]; [150].

Yousfi et al., [2] showed that the fatigue lifespan of Fe-based metallic glass foil, a 100 mg thin (19 microns) arc-shaped foil bearing cycling loads up to 30 N (~3 kg) was found to be higher than 5000 cycles, comparable (or better) than conventional low cycle springs. The authors argued that surface or edge defects generated during the manufacturing process induced the formation of fatigue cracks. They suggested that improving the surface quality of MG foils may significantly increase the cycling lifespan, as shown in Figure 2-36. However, this hypothesis remains yet to be proven.

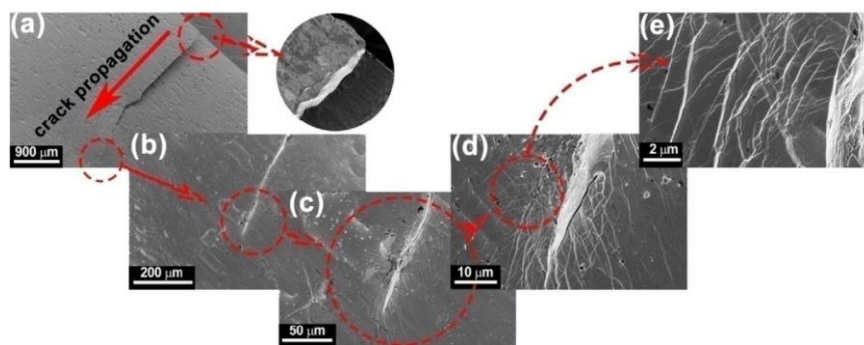


Figure 2-36: An SEM image shows the crack was initiated by defects created during sample preparation, and many shear bands formed around the crack tip [2].

2.12 Springs

A spring is a component that stores mechanical energy and releases it when subjected to an external force. It absorbs shock and vibration, maintains a force between two objects, and stores energy. Springs are typically made of metal and come in various shapes and sizes, including coil springs, leaf springs, and torsion springs. They are used various applications, including automotive suspension systems, mechanical watches, and household appliances. The behaviour of a spring is determined by its material properties, geometry, and the conditions under which it is used, such as its load, temperature, and rate of loading. Springs are widely used in various applications due to their ability to store and release energy. Figure 2-37 shows that most of these springs display linear behaviour when loaded, but can also be non-linear with constant force springs. Springs are often used in dynamic loading conditions from repeated or fatigue loading from varying amplitude stress cycles. However, they can also be used under static loading conditions at normal temperatures, static loading conditions at elevated temperatures, or repeating static loading conditions. Passive energy storage is excellent for springs because of their variability [151].

Non-linear springs exist in many forms and have a wide variety of applications. A non-linear spring is a compliant mechanism with a non-linear load-displacement function, as Figure 2-37b shows.

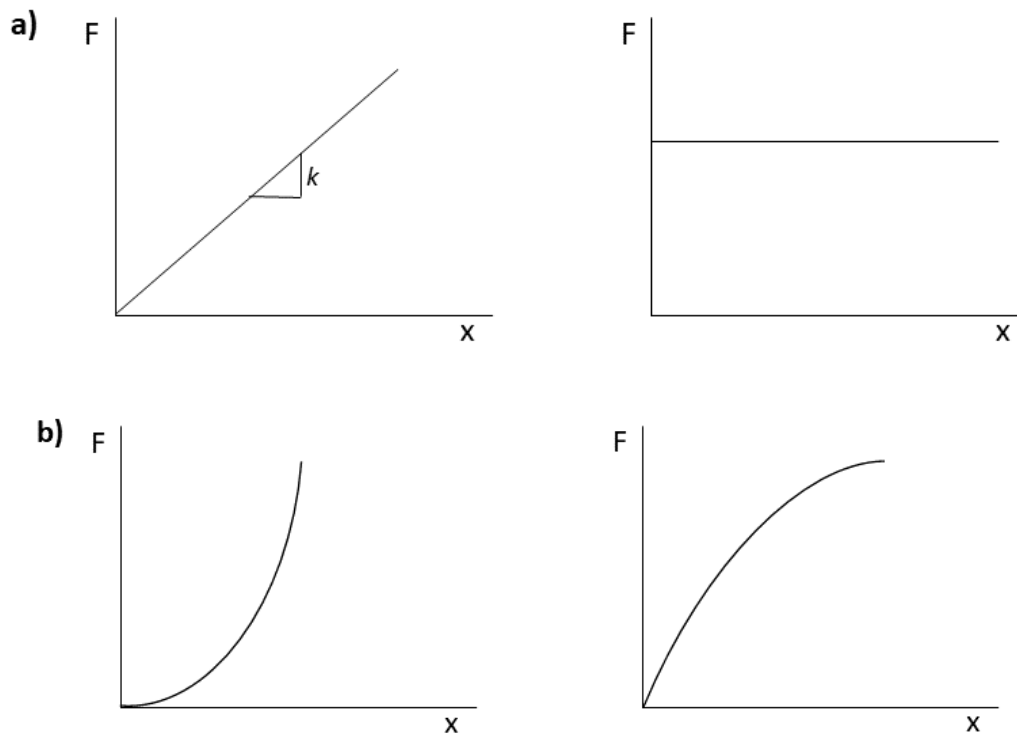


Figure 2-37: a) The linear spring is the most common spring type; b) the force of a non-linear spring varies nonlinearly with deflection.

2.12.1 Spring types and applications

Spring can be classified into several types, with its characteristics and purposes. According to their construction and applied force, these springs can be classified.

Figure 2-38 shows a helical or/and coil spring, used in various applications, including suspension systems, automotive engines and mechanical devices that require storing and releasing energy. The spring compresses or stretches the helix, storing potential energy released when the spring returns to its original shape. The amount of force a helical spring can exert is determined by its stiffness or spring constant, a function of its wire diameter, coil diameter, and the number of coils. Therefore, there are different types of helical springs, including compression springs, tension springs, extension springs, spiral springs and torsion springs, each designed to work in a specific way to provide the desired function [152].

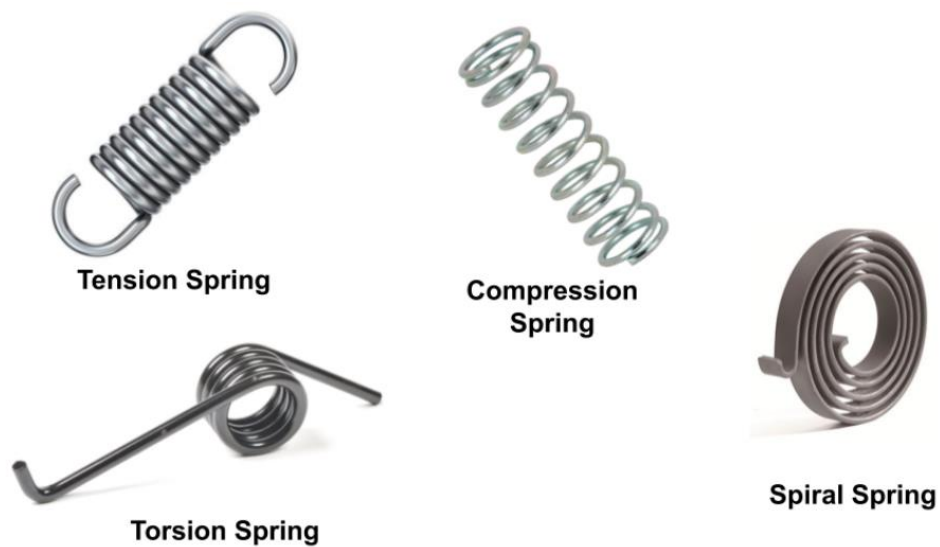


Figure 2-38. Shows helical or coil spring types, made from wire coiled as a helix [153].

Figure 2-39 presents a disc spring, also known as a Belleville spring, conical spring shaped like a washer or a disc. This kind of spring consists of conically shaped discs stacked on each other. When a load is applied, the spring compresses and the disc stack flattens out, allowing it to absorb and distribute the load. Because of their conical shape, disc springs provide a higher load capacity than other types of springs of the same size and thickness. Disc springs are commonly used in bolted connections, valves, and various types of machinery, including automotive and aerospace applications [152]. They are also used in high-pressure applications, such as hydraulic systems, to help absorb shock and vibration. However, disc springs come in various shapes, including Belleville springs, wave springs, curved springs and slotted disc springs. Table 2-11 shows common spring materials listed according to their typical properties.

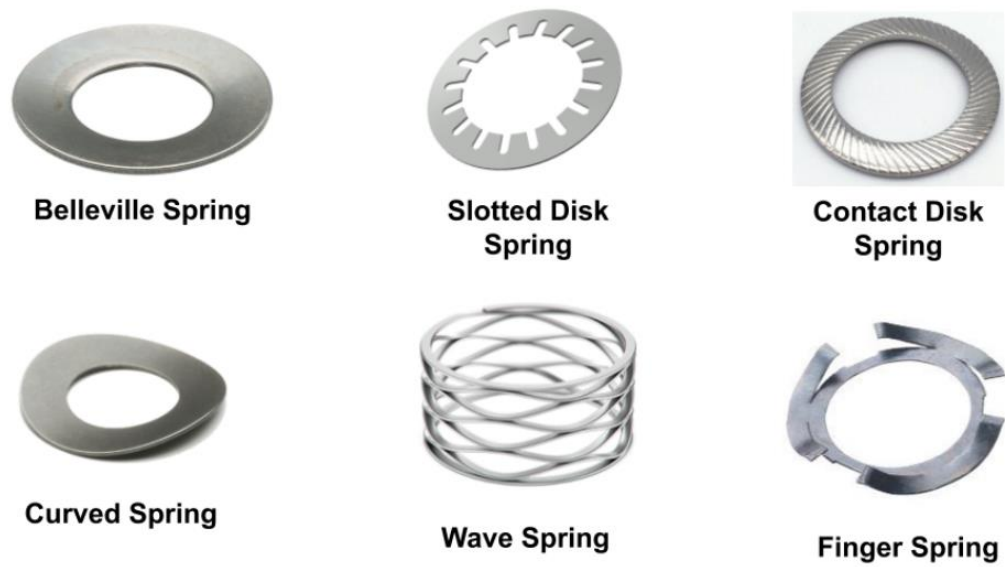


Figure 2-39. Types of disc springs with a round-shaped conical disc [153].

Table 2-11. Mechanical properties of different spring materials [152].

Material	Young's modulus (GPa)	Modulus of rigidity (GPa)	Density (kg/m ³)	Maximum service temperature (°C)
Music wire	207	79.3	7860	120
Hard drawn wire	207	79.3	7860	150
Oil tempered	207	79.3	7860	150
Valve spring	207	79.3	7860	150
Chrome vanadium alloy steel wire	207	79.3	7860	220
Chrome silicon alloy steel wire	207	79.3	7860	245
302 stainless steel	193	69	7920	260
17-7 PH stainless steel	203	75.8	7810	315
Phosphor bronze (A)	103	43.4	8860	95
Silicon bronze (A)	103	38.6	8530	95
Silicon bronze (B)	117	44.1	8750	95
Beryllium copper	128	48.3	8260	205
Inconel 600	214	75.8	8430	320
Inconel X750	214	79.3	8250	595
AISI 1050	207	79.3	7860	95
AISI 1065	207	79.3	7860	95
AISI 1074	207	79.3	7860	120
AISI 1095	207	79.3	7860	120

2.12.2 Metallic glasses spring applications

Metallic glass springs represent a novel category of springs, harnessing their amorphous structure and distinctive attributes. Metallic glass springs are still a relatively new technology. They have already found use in various applications, including precision instruments, medical devices and aerospace components. Their unique properties make them ideal for applications where traditional metal springs are unsuitable due to strength, corrosion resistance and elasticity limitations.

Spring's strain energy absorption rate is also determined by its load-displacement function since the integral is equal to the strain energy of the spring, see Figure 2-40. Load-displacement of non-linear spring function and strain energy absorption rate [154]. [154]. The performance of bandpass filters can be improved using non-linear hardening and softening springs in micromechanical systems (MEMS) [155]. Figure 2-41 shows an example of a spring actuator [156]. Therefore, metallic glass thin foils will be useful in this kind of application; this implies the components and devices will be small, particularly micro-electro-mechanical systems (MEMS).

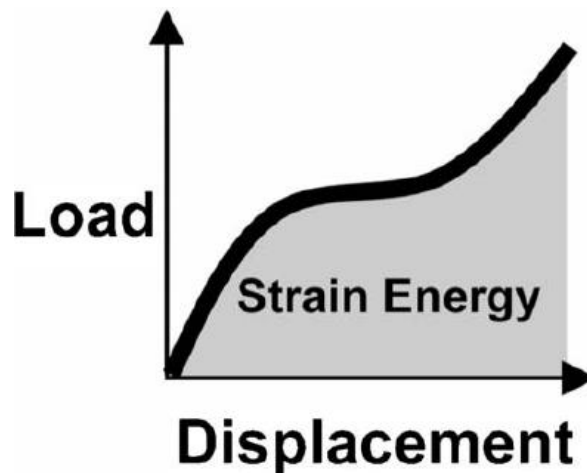


Figure 2-40. Load-displacement of non-linear spring function and strain energy absorption rate [154].

Thin metallic components of different shapes and designs, including waves, coil, and flat springs, are of interest to applications in sensors and actuators, as shown

in Figure 2-41 of MEMS devices [123][157][158]. The range of materials used can be broadened, and metallic glass foils are of a particular material to be considered. Shock absorbers depend on non-linear springs, and robotic joints generate non-linear elastic relations as a quadratic spring. They are used to create a passively compliant robot joint with a series-elastic actuator [159]. Therefore, many applications take advantage of spring rate, a class of nonlinear springs. Since load-displacement functions differ, spring configurations must be modified for each non-linear spring application. Figure 2-42 illustrates metallic glass foils for non-linear spring applications, such as annular waves, coils, and helical springs.

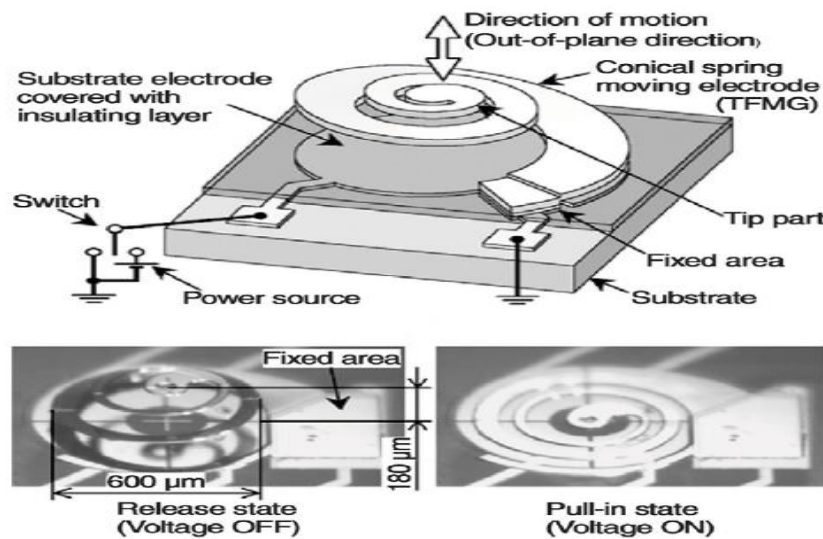


Figure 2-41. Conical spring microactuator, fundamental structure and micrographs [156].

Wave annular spring exhibit remarkably high in terms of stored elastic energy values per unit volume of material-assisted load and stored energy per unit weight. Therefore, the use of MG foils can increase these values significantly. Thus, deposition methods in MEMS device manufacturing can achieve more property changes for springs for thinner foils [118].

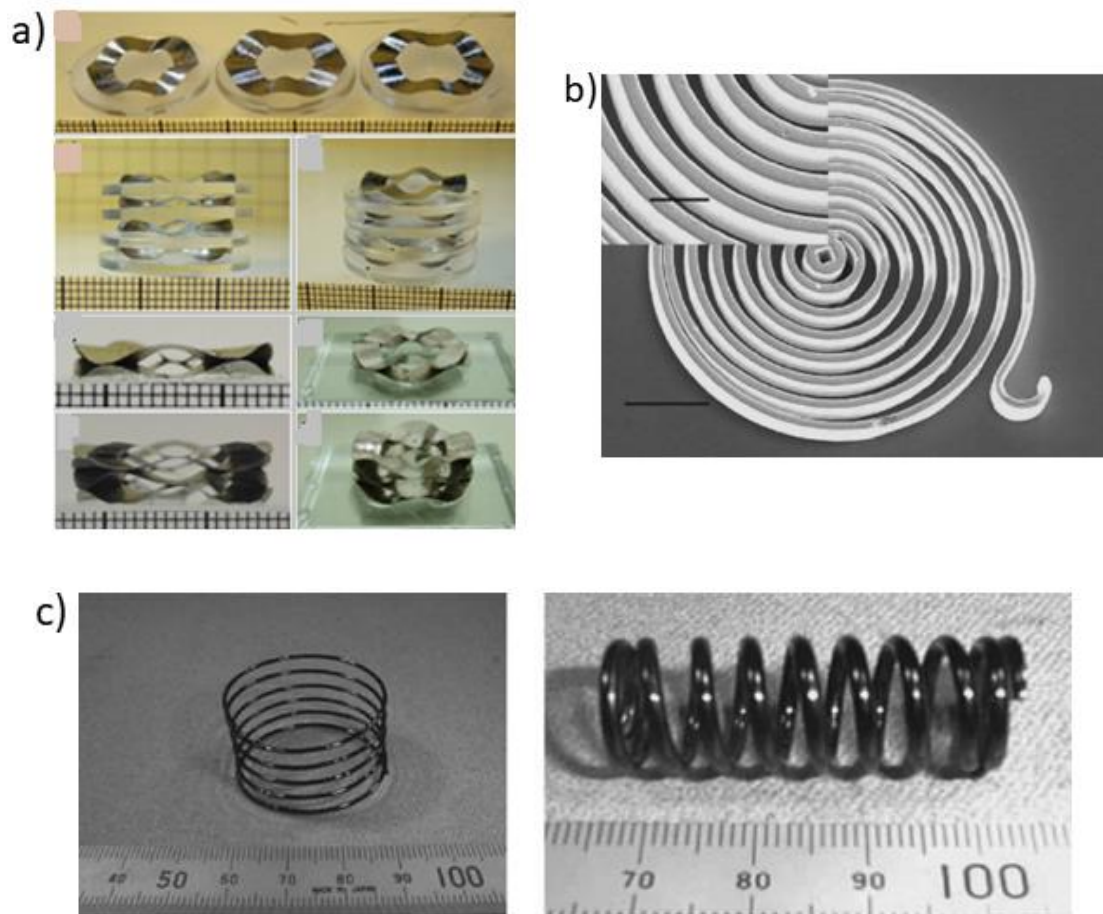


Figure 2-42: a) Selection of inner and outer diameter for MG annular wave springs [118]; b) spiral shape spring made of $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ glassy alloy [26][160]; c) helical springs of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ glassy wire alloy [26].

3 Research Methodology

3.1 Introduction

This chapter presents the different experimental techniques that we used for each step. The experimental work goes through three essential stages: i) the mechanical response of metallic glass foils of different compositions and partially crystalline metallic glass foils under applied load; ii) the selection and preparation of samples for mechanical tests (undulatory behaviour and fatigue test); iii) structural analysis by characterisation techniques.

3.2 Materials

The materials used in this work are commercially available in ribbon form for different quantities and dimensions, but with a standard width of 25 mm, they are sold as roll packages. In this project, three materials were selected with different compositions and thicknesses. The main reason for choosing these materials is to examine the effect of geometrical characteristics of metallic glass foils such as the geometry of the initial arc, length/amplitude, and thickness of the foils on the elastic undulatory behaviour in terms of applied load-displacement, maximum number of arcs before plastic deformation, local strain and cycle lifetime during loading/unloading cyclic of these foils for selected materials.

Fe-based glassy foils are the primary amorphous alloy used in this project since it is the first foil shown in the literature to exhibit undulatory behaviour. This research builds upon existing literature and uses a different amorphous glassy alloy with a different thickness, namely NiFe-based metallic glass foils. Moreover, the third material, Ni-based metallic glass foils has been selected because these foils are partially crystalline with MG composition and have two different thicknesses. Therefore, these materials were chosen in this research to investigate the mechanical performance of thin foil metallic glass and its estimate of undulatory behaviour using a variety of glassy foils. In addition, these materials were selected to examine the fatigue limit undergoing cyclic loading/unloading.

3.2.1 Fe-based metallic glass foils

The main Fe-based glassy foil commercially available was used for this project with a nominal composition of $\text{Fe}_{76.10}\text{Cr}_{2.48}\text{Si}_{4.51}\text{B}_{16.91}$ (at.%) foil with a thickness of 19 μm and width of 25 mm. The mechanical properties of Fe-based metallic glass alloy exhibited Young's modulus E around 150 GPa as measured by nanoindentation, which depends on the difference of compositions and mechanical strength of about 3320 MPa as measured by tensile test [82].

3.2.2 NiFe-based metallic glass foils

NiFe-based metallic glass foils have been used in this project, commercially available from Goodfellow, with a composition of $\text{Ni}_{40}\text{Fe}_{40}(\text{SiB})_{19}\text{Mo}_1$ (at.%) with a thickness of 25 μm and width of 25 mm.

3.2.3 Ni-based metallic glass foils

The third material selected for this project is $\text{Ni}_{78}\text{B}_{14}\text{Si}_8$ (at.%) metallic glass foils commercially available from the Goodfellow company. However, these foils have been chosen with two different thicknesses of 25 μm and 40 μm for research purposes and have a similar width of 25 mm. The mechanical properties, such as tensile strength between (1.5 to 2) GPa, and Young's modulus is about 150 GPa [161].

3.3 An experimental method to explore undulatory behaviour

3.3.1 Method

The metallic glass foils were placed on a base with fixation clamps on both foil ends for a specific length L refers to horizontal boundary length, and the height of arc curvature between the top of the arc and bottom of the base refers to amplitude h , as shown in Figure 3-1. However, this project has only used the aspect ratio ($h=L/4$). This aspect ratio for harmonic motion is a significant parameter for the undulatory response of metallic glass foils. Equation (3-1) was proposed to achieve wavy elastic behaviour by Panagiotopoulos et al [1].

$$\frac{h_1}{L} \leq \frac{1}{2} \quad \text{3-1)}$$

The metallic glass foil samples were cut to a specific length depending on the aspect ratio of amplitude to boundary length ($h:L$) using ceramic scissors to avoid defects as much as possible along the foil cutting.

The rectangular-shaped metallic glass foil samples were cut and prepared to meet the required dimensions. These samples have a width of 25 mm, but different thicknesses. The mechanical testing was conducted in an Instron machine. The most used loading rate of the test machine was 1 mm/min, but also different loading rates of 10 mm/min and 100 mm/min were examined. Four parameters were selected for these experiments: boundary lengths L , amplitude h , thickness d and material types.

Furthermore, other parts have been manufactured for this custom test; four parts have been attached to the top of the Instron machine (loading plate) when pushed down, as shown in Figure 3-1. In addition, flat based is used to fix the specimen. Two fixtures contain scales to attach the loading plate and a high-speed camera for recording.

Moreover, the metallic glass foils exhibit two different surface finishing and topography: wheel side and air side. Therefore, the metallic glass foils were always placed in the same direction for entire tests. There was a preference to put the air side towards the base and the wheel side towards the loading plate to reduce friction between the base and specimen due to the air side's better surface finish.

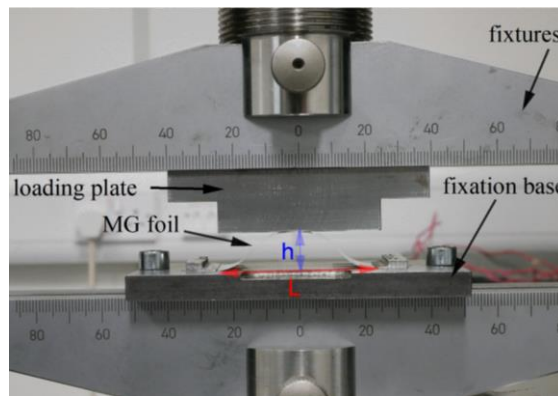


Figure 3-1. Specimen of MG foil set-up, including parts attached to a machine.

The metallic glass foils were inspected before mechanical or fatigue testing to check if any defects could be seen on these samples. These defects are produced by either the manufacturing process or the storage method at the supplier. Typically, these defects appear as lines running along the length of the foil or as dent marks. Due, however, to potential impacts on the mechanical performance and/or concerns over the early failure of these foils during cyclic loading, the foils with defects on the surface (visual defects) were not tested.

3.3.2 Set-up

An Instron 825 compression machine was employed for mechanical testing by applying load on the top of the arc-shaped foils, as shown in Figure 3-2. A piece of foil was placed between two fixtures (top and bottom). A measuring scale was then attached to the loading frame and adjusted to align the top foil to a zero reading on the scale. The load increase at a rate of 1 mm/min. The position of the top plate when it was in contact with the top foil was measured on the scale and recorded. The foil started bending and buckling to create a new arc as the load increased. Once the load was released, the foil snapped to its original shape and returned to the initial back position (zero).

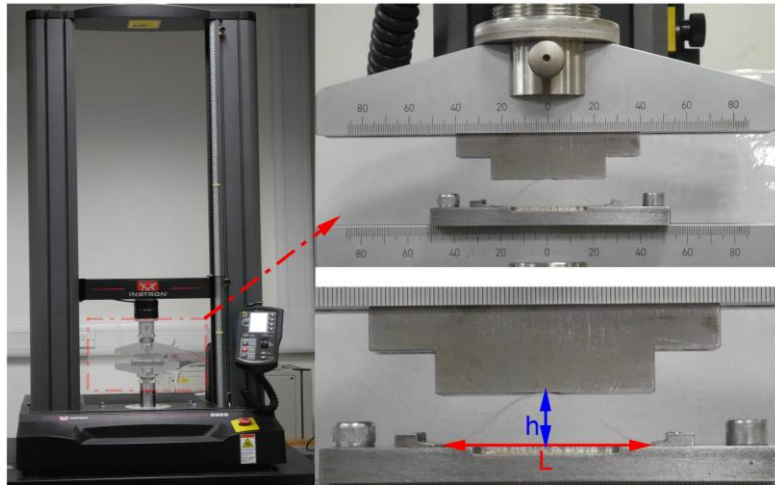


Figure 3-2. An Instron compression machine enclosing the MG foil between custom-made fixtures.

Compression tests following a specific protocol, as shown in Figure 3-2, measured load-displacement curves. An arc-shaped foil must be perfectly aligned, especially with significant boundary lengths, for alignment to be perfect. Mechanical properties such as elastic and plastic deformation and local strains are directly measured from the load-displacement curve by analysing images to measure local strains.

A Panasonic DMC-G7 camera was used to record the loading/unloading process. The obtained images were used to analysis of local strains on the foils. The captures of arc curvature were used for measuring local strain to find elastic and plastic deformation regions during undulatory behaviour. Load-displacement curves were recorded for foils using initial arc length L values ranging from 20 to 50 mm, initial arc amplitude h in of 5 to 12.5 mm range and a constant ratio of $L/h=4$.

The local strain was measured using Equation (3-2); the pre-test takes arc-shaped with a bit strain representing the initial arc shape. Therefore, in this case, the maximum local strain shows in compression at a bottom radius of curvature and tension mode at the top arc curvature. However, the strain is distributed

inhomogeneously on the foil surface. Consequently, the Equation below is derived based on the bending behaviour of the foil, as shown in Figure 3-3.

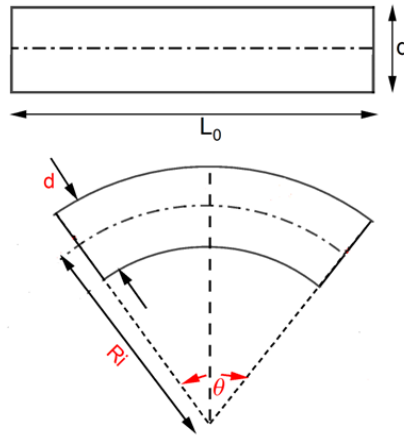


Figure 3-3. Foil and deformed shape to estimate local strain.

Aljerf et al. [127] measured the local strain to find the elastic deformation limit of sinusoidal undulation for metallic glass foils of 2% strain. As the foil undergoes deformation and bending phenomena, the strain is not homogeneously distributed; it becomes maximum locally at positions that exhibit the highest bending or the smallest radius of curvature. Therefore, the maximum local strain is estimated to occur before the foil snaps, as shown in Figure 3-4.

$$\varepsilon = \frac{d}{2R_i} \quad (3-2)$$

The d refers to foil thickness, and R_i is the radius of curvature.

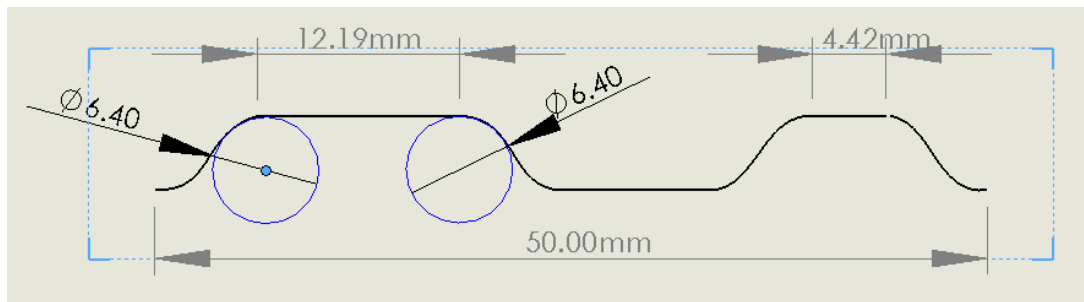


Figure 3-4. Analysis of local strain measurements to estimate MG foil deformation

Therefore, all the cases of an aspect ratio of amplitude:length chosen in our work follow this principle, which always follows Equation (3-2) to the estimate maximum number of arcs and ensure the undulatory behaviour of metallic glass foils still within elastic deformation.

3.3.3 Structure characterisation techniques of MG foils

After testing the undulatory behaviour of metallic glass foils used characterisation techniques to examine the samples as follows:

3.3.3.1 X-ray diffraction (XRD)

The structure of metallic glass foils was examined by X-ray diffraction. X-ray diffraction measurements were employed to characterise the structure of the foils using Siemens D5005 with $\text{CuK}\alpha$ radiation with beam length ($\lambda_{\text{Cu}} = 1.5406$) in the 2θ range of 20° to 90° . X-ray diffraction was conducted on the air and wheel sides to examine the structure on both foil surfaces to calculate volume fraction crystallinity.

3.3.3.2 Differential scanning calorimetry (DSC)

The glass transition (T_g) and crystallisation temperature (T_x) of metallic glass foils were examined by differential scanning calorimetry (DSC). DSC using a TA instrument Q200 was employed to investigate the thermal stability of the foils. The measurements were performed in an argon atmosphere using a heating rate of 20°C/min up to 550°C using standard aluminium pans. The weight of each sample was scaled and should be over 5 mg.

3.4 An experimental method to explore fatigue life under load cycling

3.4.1 Method and Set-up

In this project, to obtain accurate cyclic loading/unloading, a custom device fatigue test was used to evaluate the tension-compression fatigue life of loading and unloading MG foils at room temperature. This device contains a stepper

motor that is a releasable linear actuator with an input voltage of 5.6 V, a maximum load of 58 N and an extension bar up to 10 mm and nominal power of 5 W, a performance speed of 150 mm/min (those specifications are taken from the manufacturer company). This device is controlled by an Arduino card (electronic card) for a specific displacement to perform cyclic fatigue. The specimen of metallic glass foil is placed between the back wall of the device and in the front loading (pushing) plate attached to a sliding rail, as shown in Figure 3-5. Due to the displacement limitation on this device, the number of arcs was selected based on the extension bar for all boundary conditions used in cyclic fatigue.

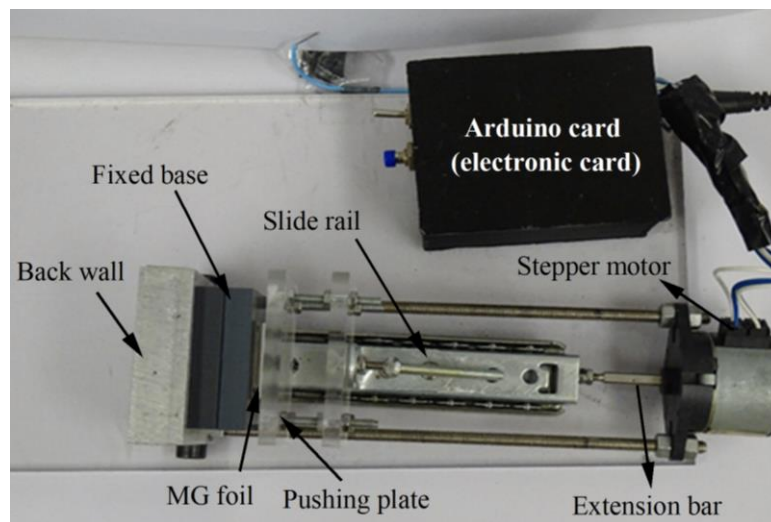


Figure 3-5. Shows the cycle fatigue device with a stepper motor and pushing plates at the other end.

To ensure the constrained MG foil is compressed with an equal load through loaded and unloaded, the specimen (MG foil) must be perpendicular to the pushing (loading) plates. The metallic glass foil was adjusted during pre-testing by controlling the distance of the motor (displacement). The cyclic fatigue device applied load on the foils which undergo undulatory deformation up to the number of cycles, after which cracking was observed, thus, defining the failure point. The failure was identified by the inability of the metallic glass foil to repeat undulatory

behaviour (noticing a difference in geometry behaviour during cyclic fatigue). However, each fatigue cycle is defined as loading/unloading, taking 2 seconds.

Samples were tested at various boundary lengths L in a range from 20 to 50 mm with an amplitude of initial arc shape of $L/4$. Testing was conducted until the sample failed or until the initial crack occurred.

The specimen (foil) was placed on the plastic plate with dimensions of 45 mm wide, 45 mm long and 8 mm thick, as shown in Figure 3-6. This plate was machined with good surface finishing to minimise surface effects during fatigue tests, made from plastic material and two clamps used made from stainless steel.

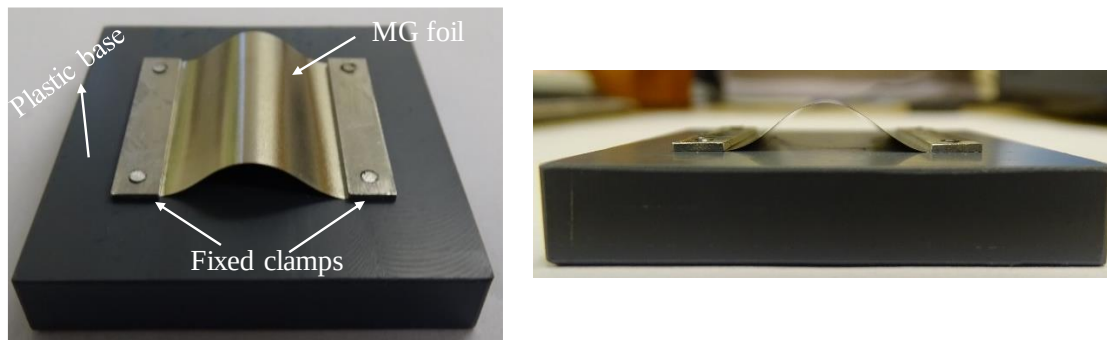


Figure 3-6. Plastic support where the specimen (MG foil) is placed and secured with stainless steel fixing clamps.

Fe-based glassy foil samples were tested at various boundary lengths L ranging from 20 to 50 mm each with an aspect ratio of $L/4$ for the initial arc shape (multiple sinusoidal arcs are generated during a load cycle). NiFe-based and Ni-based glassy foils were tested with boundary length $L = 20$ mm with the same aspect ratio of the initial arc, $L/4$. Table 3-1 presents the dimensions of the metallic glass foils investigated in this study.

Testing continued until the sample failed or until an initial crack was observed. After the samples were cycled to failure, they were removed and stored. The fracture surfaces of selected specimens were examined using a Tescan VEGA 4 SEM to aid the analysis of the fatigue and fracture mechanism.

Table 3-1. Experimental design for metallic glass foils during cyclic loading.

MG foil	Thickness	Boundary lengths	Cyclic loading operation
Fe-based MG	19 μm	$L = 20 \text{ mm}$	(2,3,4 and 5) arcs
Fe-based MG	19 μm	$L = 30 \text{ mm}$	(3,4,5 and 6) arcs
Fe-based MG	19 μm	$L = 50 \text{ mm}$	(4,5,6,7 and 8) arcs
NiFe-based MG	25 μm	$L = 20 \text{ mm}$	(2,3 and 4) arcs
Ni-based MG	25 μm	$L = 20 \text{ mm}$	(2, 3 and 4) arcs

3.4.2 Characterisation techniques of MG foils

After the samples were cycled to failure, they were removed and stored to examine the failure of MG foils as follows:

3.4.2.1 Scanning electron microscopy (SEM)

The surface metallic glass foil specimens subjected to cyclic fatigue testing were analysed by SEM analysis, obtaining valuable information about the surface morphology, and fracture mechanisms of the samples after mechanical cycling. SEM measurements were employed to characterise the foils' topography and crack initiation sites. They were also carried out at different magnifications to examine the shear band and evolution of crack initiation in a Tescan VEGA 4 SEM.

3.4.2.2 Interferometer measurements

The metallic glass foils used in this research have two sides with different topography. One side was in contact with a gaseous atmosphere, and the other was with the copper wheel during manufacturing.

The surface roughness was measured using a Taylor Hobson Precision Interferometer CCI. A series of measurements across the width of the foil of 25 mm, on the two sides, were taken with an interspacing of 0.4 mm between each measurement. The areas measured were $0.8 \times 0.8 \text{ mm}^2$, with a total number of measurements being 31 along the foil width, as shown in Figure 3-7. After

measurement, levelling was applied and line profiles were extracted for evaluation. The line profiles were filtered (Gaussian) with a cut-off of 0.025 mm to eliminate the noise in the measurement. The primary profile (P-profile) parameters P_a (arithmetic mean height), P_q (root-mean-square) and P_t (total height) were extracted from the profiles. Since surfaces in their functional state can be better understood through three-dimensional techniques, areal parameters were extracted from the 3D surface map measured. The kurtosis (S_{ku}) and skewness (S_{sk}) were used to evaluate the peaks and valleys on the surface.

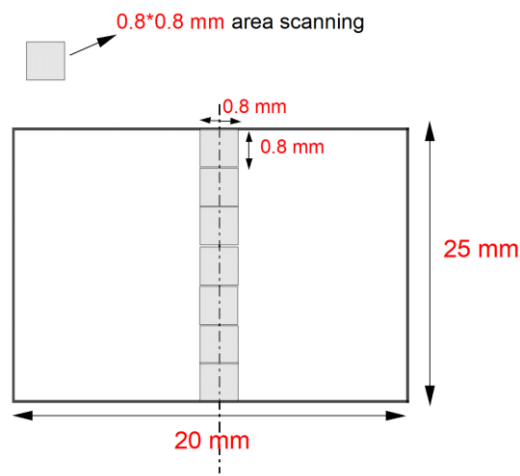


Figure 3-7. A Schematic of foil dimensions for 31 measurements taken along the foil width.

4 Undulatory elastic behaviour of metallic glass foils of fully amorphous alloy

4.1 Introduction

This chapter presents a pioneering investigation into the undulatory behaviour of Ni-Fe-Si-B-Mo metallic glass foils for the first time, and compare with that of the previously reported Fe-Cr-Si-B foil, using a similar methodology as the one proposed in [1] and using a similar experimental set up, as shown in Figure 4-1. In this chapter, the undulatory behaviour of a Ni-Fe-Si-B-Mo metallic glass foil has been systematically studied and to draw insightful comparisons with the behaviour observed in Fe-Cr-Si-B foil. Thus, the aim of this chapter is to shed light on the variations in the undulatory behaviour of amorphous glassy alloys with different thickness foil and see how different mechanical responses between those foils. This chapter also examined and compared crystalline and superalloy foils on undulatory behaviour. Several key factors influence the undulatory behaviour observed in these metallic glass foils. These factors encompass the alloy compositions, characterised by differences in their elastic and mechanical properties, as well as variations in foil thickness and the initial geometric parameters of the sinusoidal arcs. These geometric parameters include the boundary horizontal length denoted as (L) and the amplitude of the arcs (h). Together, these variables contribute to the diverse and intricate manifestations of undulatory behaviour observed in these foils.

In essence, this chapter serves as an exploration into the undulatory behaviour of a novel amorphous glassy alloy, the Ni-Fe-Si-B-Mo metallic glass foil, while drawing comparisons to previously studied materials. This investigation aims to unravel the complexities of undulatory behaviour dynamics influenced by alloy compositions, foil thickness, and geometric parameters, a pursuit that promises to enrich our understanding of this intriguing phenomenon.

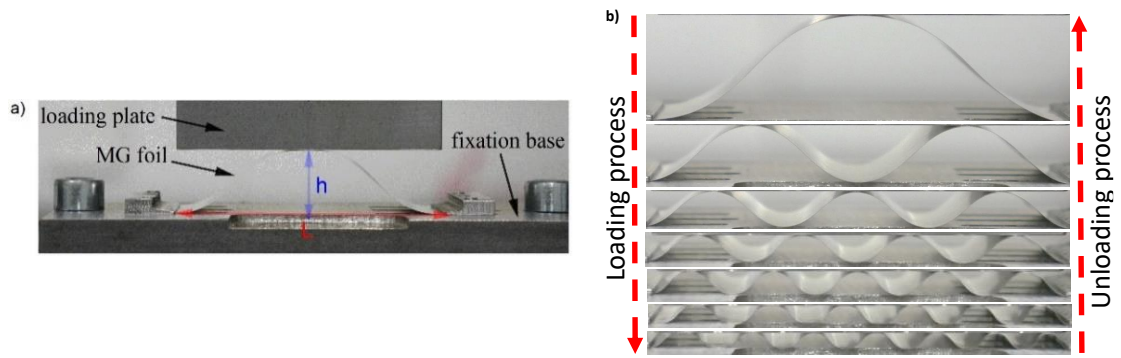


Figure 4-1: a) Initial arc-shaped of MG foil; b) harmonic undulatory response of arc shaped of MG foil

4.2 Results and discussion

4.2.1 Structure

Figure 4-2 show X-ray diffraction patterns taken from the $\text{Fe}_{90.65}\text{Cr}_{2.75}\text{Si}_{2.7}\text{B}_{3.9}$ and $\text{Ni}_{40}\text{Fe}_{40}(\text{SiB})_{19}\text{Mo}_1$ melt spun foils with 19 μm and 25 μm thickness, respectively. Both patterns exhibit only broad-diffuse peaks (around 44° in 2-theta angle) indicating their amorphous nature. Figure 4-3 presents DSC thermograms of the two amorphous materials studied in this work. For the $\text{Fe}_{90.65}\text{Cr}_{2.75}\text{Si}_{2.7}\text{B}_{3.9}$ ribbon, an exothermic peak with onset at $T_x = 520^\circ\text{C}$ is observed, corresponding to the crystallisation of the amorphous phase. For the $\text{Ni}_{40}\text{Fe}_{40}(\text{SiB})_{19}\text{Mo}_1$ alloy, crystallisation occurs at about 455°C , whereas a second crystallisation reaction occurs around 525°C .

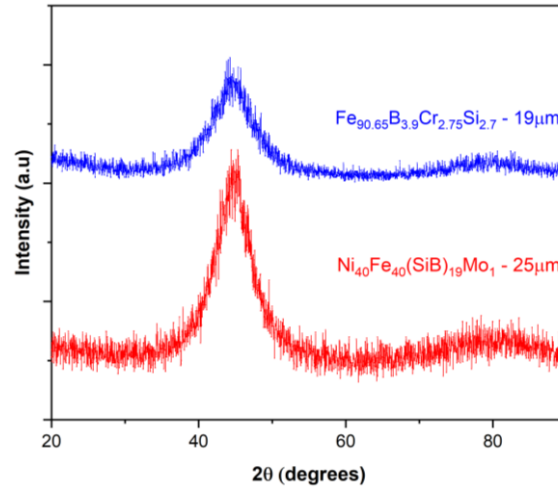


Figure 4-2. X-ray diffraction pattern of the metallic glass foils.

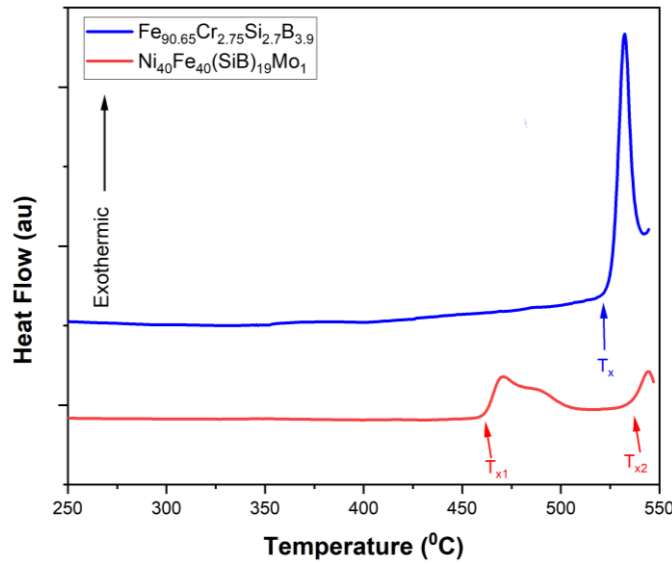


Figure 4-3. DSC thermograms for the metallic glass foils.

4.2.2 Undulatory behaviour

Mechanical loading was applied on the top of arc-shaped Fe-based and NiFe-based foils as shown in Figure 4-1. Upon loading, the foils deform elastically up to a specific value of load or displacement, followed by a change in their shape leading to a successive increase of the number of sinusoidal arcs, Figure 4-1b. Figure 4-4a presents the load versus displacement for the Fe-based MG foil with boundary distance $L=20$ mm, amplitude of the initial arc $h_1=5$ mm (aspect ratio $h_i=L/4$), Figure 4-1a. As expected, the results in Figure 4-4a indicate a similar

undulatory behaviour with that shown by Panagiotopoulos, et al [1]. During loading, the load-displacement curves can be overall described by exponential relations of the type $F = \alpha * \exp(\beta x)$, where α and β are constants (depend on the initial arc geometry and materials) and x is the displacement. The discontinuities, represented by (small) but sharp load decreases, occur at the time of the formation of additional arcs. In between these abrupt drops in load, one could approach the segments of the curve as quasi-linear, with the slopes considered equivalent the spring rate k according to Hooke's law. Overall, due to the undulatory behaviour, arc-shaped metallic glass foils subjected to loading conditions as shown in Figure 4-1, operate as non-linear flat springs with variable spring's rates [2].

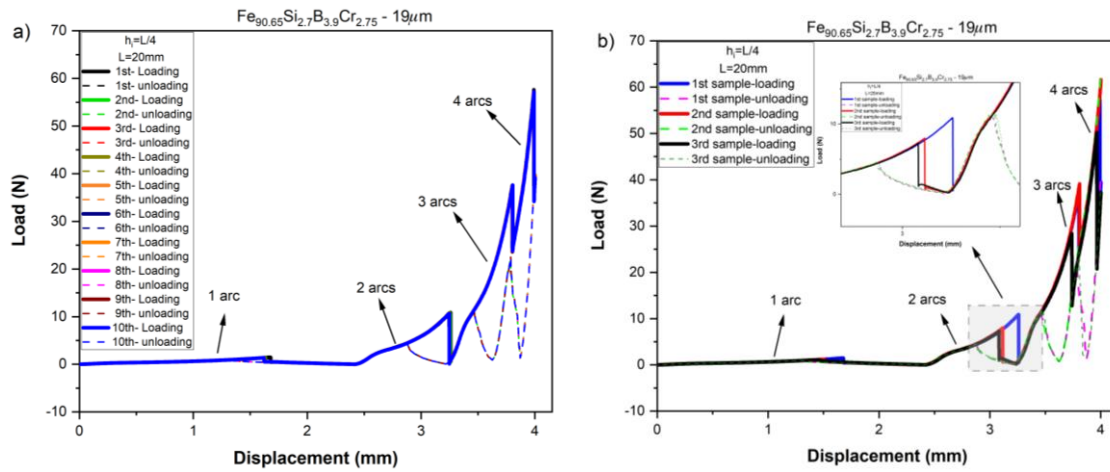


Figure 4-4: a) Load-displacement curves for ten cycles loading/unloading of a foil; b) load-displacement curves on three different samples of Fe-based metallic glass foils.

Figure 4-4a shows ten (10) successive loading cycles for the same foil to follow the exact same path, highlighting the repeatability of the undulatory behaviour. During unloading, the load-displacement path shows a hysteresis compared to the loading path, but yet identical for all unloading cycles; returning however to the exact initial shape and position as the initial sinusoidal arc.

Figure 4-4b shows the load displacement response of three samples of the same material (Fe-based foil) and same initial arc geometry. The three samples follow

essentially the same path showing the same behaviour as expected, confirming the repeatability of the process. Some minor variations at the position when the sharp load drop starts in some cases can be observed, whereas the paths exactly coincide again when loading resumes, as shown in the insert of Figure 4-4b.

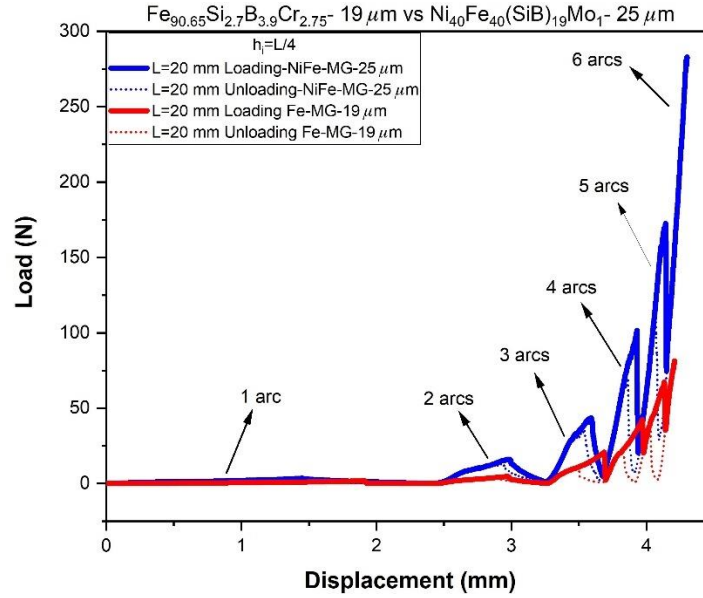


Figure 4-5. Load-displacement curves upon loading for the NiFe-based (25 μm thick, blue) metallic glass foil compared to the Fe-based (19 μm thick, red) one for $L=20\text{mm}$ and $h_1=5\text{mm}$.

Figure 4-5 presents the load-displacement curve upon loading for an arc-shaped NiFe-based (25 μm thick) metallic glass foil -for the first time- in comparison with the Fe-based one (19 μm thick) for $L=20\text{mm}$ and $h_1=5\text{mm}$. A similar behaviour can be observed for the two amorphous foils, as expected, where the load increases quasi-exponentially with increasing distance. The arc multiplication occurs at about the same displacement values for both foils, but clearly, the NiFe-based foil exhibits higher load values compared to the Fe-based one. For example, the transition from 2 to 3 arcs the NiFe-based foil requires around 16 N whereas for the thinner Fe-foil only 5 N while the transition from 4 to 5 arcs requires 100 N compared with Fe-based MG foil that requires 42 N. For higher order transitions the load differences are even higher. This indicates that with the appropriate choice of the thickness of the foils as well as the metallic glass alloy –in terms of Young’s modulus – one can effectively design non-linear flat spring

type devices with desirable mechanical response. Further work is discussed in Chapter 5 to study the effect of foil thickness on the mechanical undulatory response of the metallic glass foils.

Focusing on the unloading cycle, again, a “hysteresis” is observed in the unloading cycle, in both cases, while the foil returns to the initial position and resuming the initial sinusoidal arc shape. Obviously, the hysteresis that occurs during unloading can contribute to the energy dissipated, and altering its mechanical response, as can be seen in unloading path in Figure 4-4b. Consequently, hysteresis during the unloading process is primarily due to stress relaxation during unloading, where the stress or/load decreases at a slower rate than during loading. According to Panagiotopoulos, storage energy is returned to the system after unloading and is significantly less than the energy expended by loading. Further, metallic glass linear wave springs with waveform multiplication reach 39 mJ [118]. The difference between the energy expended and the energy returned is often referred to as energy loss or energy dissipation. This can result from various factors, including the release of stored internal stresses. Stress relaxation contributes to hysteresis by causing the stress-strain (load-displacement) curve during unloading to deviate from the loading curve. However, controlling these factors causing hysteresis is essential for engineering applications involving metallic glass foils.

Figure 4-6a and Figure 4-6b depicts the load-displacement curves for boundary distance L values in the range of 20 –50 mm and h_1 to L ratio $h_1/L = 0.25$ for NiFe-based (25 μm thick) and the Fe-based glassy foils respectively. Spring type set-ups with higher L values can reach higher number of arcs (while still within the elastic deformation limit of 2% for the metallic glass foils) as well as higher load and displacement values. Thus, the geometry and size of the initial sinusoidal arc gives of course another design tool to tune the range of the mechanical responses of these types of spring-type set-ups or devices.

Figure 4-7a shows the load required to induce the transition from n_i sinusoidal arcs to the $n_i + 1$ arc versus the number of arcs for the Fe-based and NiFe-based metallic glass foils with initial arc geometry defined by L values in the range of 20

–50 mm and initial amplitude h_1 to L ration $h_1/L = 0.25$. Comparing the two foils, the load for the NiFe-based foils is higher than those for the thinner Fe-foils as inferred from Figure 4-6a and Figure 4-6b. Comparing the initial boundary length L , higher L values lead to lower load for the same number of arcs. However, the glassy foil set-ups with higher L values can allow the formation of higher number of arcs while remaining in the region of elastic deformation of the metallic glass foils and thus able to reach considerably higher load values.

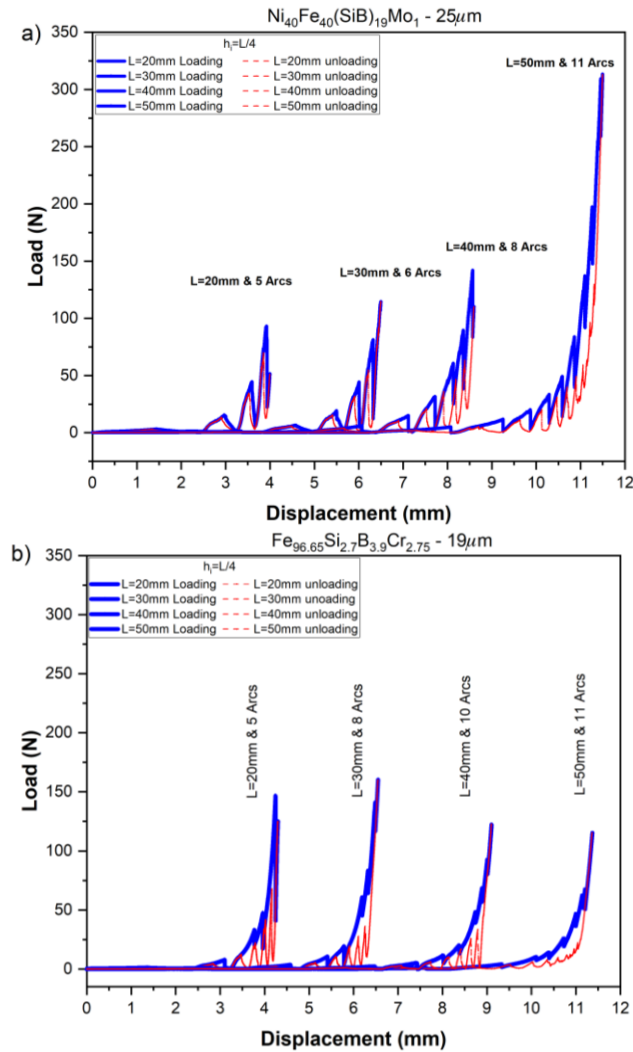


Figure 4-6: a) Load-displacement curves for the NiFe-based (25 μm thick) metallic glass foil for boundary distance L values in the range of 20 –50 mm and h_1 to L ration $h_1/L = 0.25$; b) Load-displacement curves for the Fe-based (19 μm thick) metallic glass foil.

Figure 4-7b shows the calculated spring rate versus the number of arcs for different boundary lengths (L) for both type of glassy foils. Similarly, the spring rate k values show exponential increase with the increase of the number of arcs. For initial foil set-up with higher L values this increase of is more gradual in the beginning but can reach higher number arcs and higher k values. Furthermore, the NiFe-based MG foils exhibit higher k values compared to the thinner Fe-based alloy. Characteristically, for the Ni-Fe based MG foil at $L=50$ mm, the estimated spring rate range from about 1 to 1600 N/mm depending on the number of the formed arcs, and the horizontal boundary conditions L . Thus, the NiFe-based MG foil is shown higher load values and spring rate values mainly due to its higher thickness compared to Fe-based MG foil.

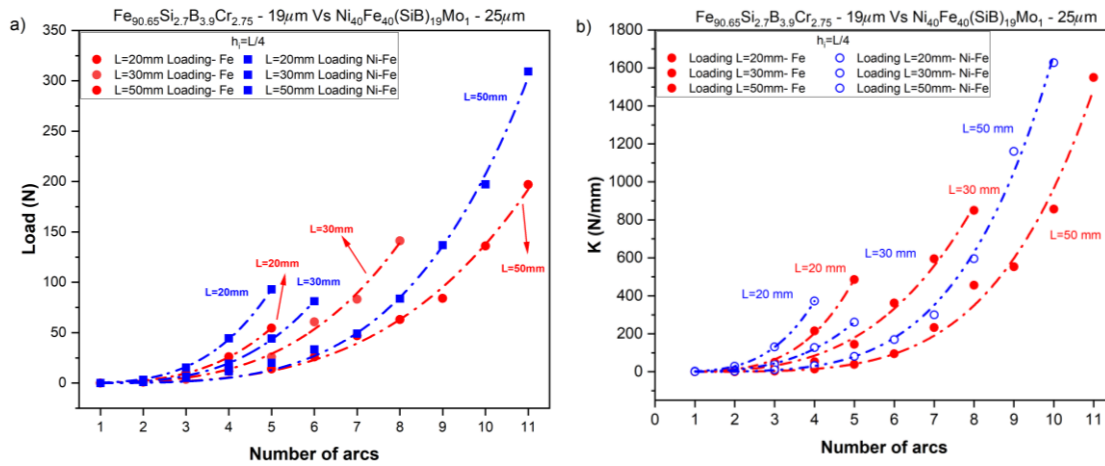


Figure 4-7: a) Maximum applied normal load on the foils with n_i sinusoidal arcs just before the formation of the $n_i + 1$ arc versus the number of arcs for the Fe-based and NiFe-based metallic glass foils for set-ups with boundary distance L values in the range of 20 –50 mm and h_1 to L ratio $h_1/L = 0.25$; b) the spring constants as calculated in the quasi-linear segments of the load-displacement curves. Values for $L = 40$ mm were omitted for the clarity of the graphs.

4.2.3 Estimation of local strain

For the undulatory behaviour to remain reversible and repeatable, plastic deformation must be avoided. Thus, the strain must always remain below 2% which is the limit of elastic deformation in metallic glasses. As the foil undergoes deformation and bending phenomena, the strain is not homogeneously

distributed in the foil; it rather becomes maximum locally at positions that exhibit “highest bending” or the smallest radius of curvature. Previously considered [1] the local strains at the waveforms with perfectly shaped sinusoidal arcs, as shown in Figure 4-8a. However, a close observation of the evolution of the foil’s geometry Figure 4-8b, reveals that the radius of curvature is smallest just before the formation of a new (n_i+1) arc (R_3 in Figure 4-8b) rather than when an additional arc is formed see R_2 and R_4 in Figure 4-8b and thus the strain needs to be primarily considered at this step of the shape evolution of the foil. These states of the foil’s shape evolution are indicated in the load displacement curve of Figure 4-8c. Thus, between R_3 and R_4 the transition from two to three arcs occurs accompanied by a drop in load.

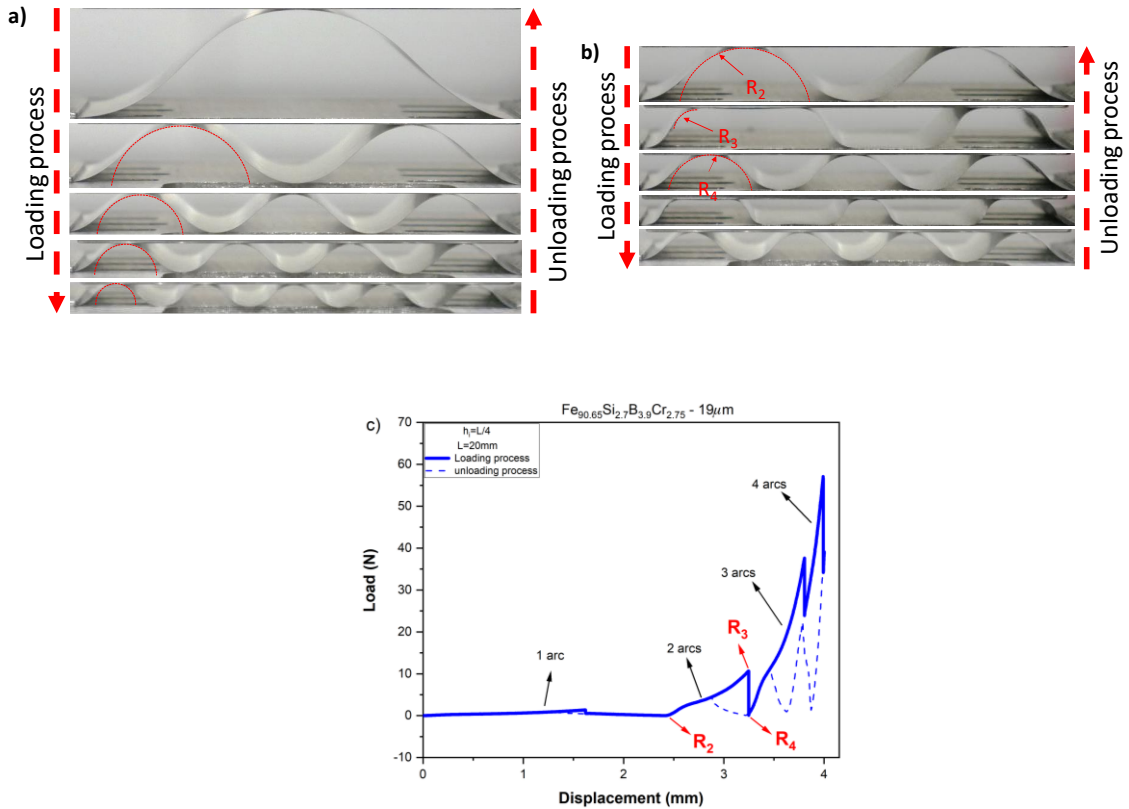


Figure 4-8: a) Assembly of snapshots from the undulatory response of a metallic glass foil with images of waveforms with perfect sinusoidal shaped arcs; b) assembly of snapshots from the undulatory response with images of waveforms with perfect sinusoidal shaped arcs (R_2 and R_4) and distorted arcs (R_3); and c) load-displacement curve of the undulatory response for the Fe-based foil.

Figure 4-9a presents the local strain on the foils at the steps where perfect sinusoidal arcs are formed, equivalent to R_2 and R_4 in Figure 4-8b for the NiFe metallic glass foil with a variety of initial boundary lengths between $L=20$ mm and $L=50$ mm. Figure 4-9b presents the estimated local strains foils at the steps of maximum distortion, equivalent to R_3 in Figure 4-8b for similar conditions as in Figure 4-9a. In both cases and all represented measurements, the local strain remains below the 2% limit of elastic deformation.

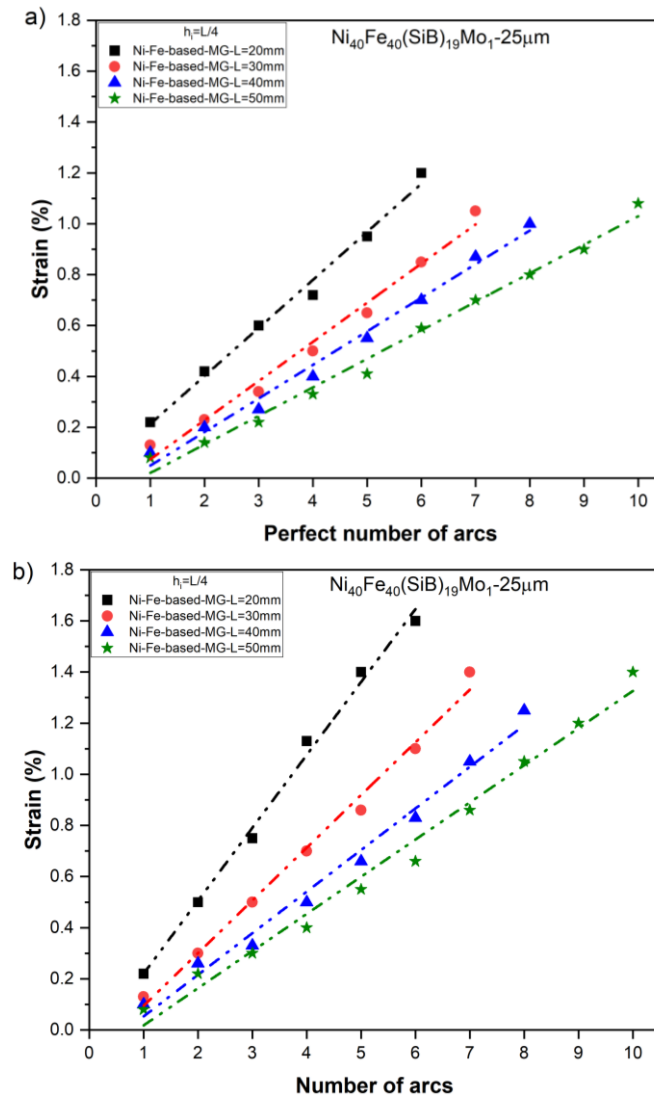


Figure 4-9: Maximum local strain on the foils a) at waveforms with perfectly shaped sinusoidal arcs (equivalent to R_2 and R_4 in the example of Figure 4-8b); b) at waveforms with distorted arcs, just before the formation of a new (n_i+1) arc (equivalent to R_3 in the example of Figure 4-8b).

The results confirm previous observations on a different alloy system on one hand and on the other hand, uncover the remarkable repeatability of the undulations under cycling conditions. Overall, the work significantly contributes to the understanding of the recently discovered undulatory mechanical response and clarifies the operational limitations imposed by local deformation.

4.2.4 Loading/unloading rate effects

Figure 4-10a shows three (3) loading rates of load-displacement curves for the same foil to prove their mechanical response, indicating the same undulatory behaviour. However, the loading path exhibits minor variations in load values at a new arc formation due to the impact of various loading rates on the undulatory behaviour of metallic glass foils. For example, for a 1 mm/min loading rate the highest load value for a new arc to be formed is bigger compared to 100 mm/min loading rate. Therefore, a high loading rate will change the arc curvature geometry faster than the normal speed loading rate (1 mm/min), resulting in arc formation at less load values. During unloading, the load-displacement curves follow the same identical path for all unloading rates to return to their initial sinusoidal arc.

Figure 4-10b shows the load versus the number of arcs response of three loading rates of the same material (Fe-based foil) and the same aspect ratio ($h_f=L/4$) for $L=20$ mm. All three loading rates are generally consistent, indicating that undulatory behaviour can be reproduced when loading rates differ. Although, in the same cases, some minor variations in load can be observed at the point where the new arc is generated. Thus, the different loading rates do not result in different undulatory behaviour during loading/unloading and the same maximum number of sinusoidal arcs are always achieved. In other words, the loading/unloading curve follows a similar path for each sinusoidal arc regardless of load rates.

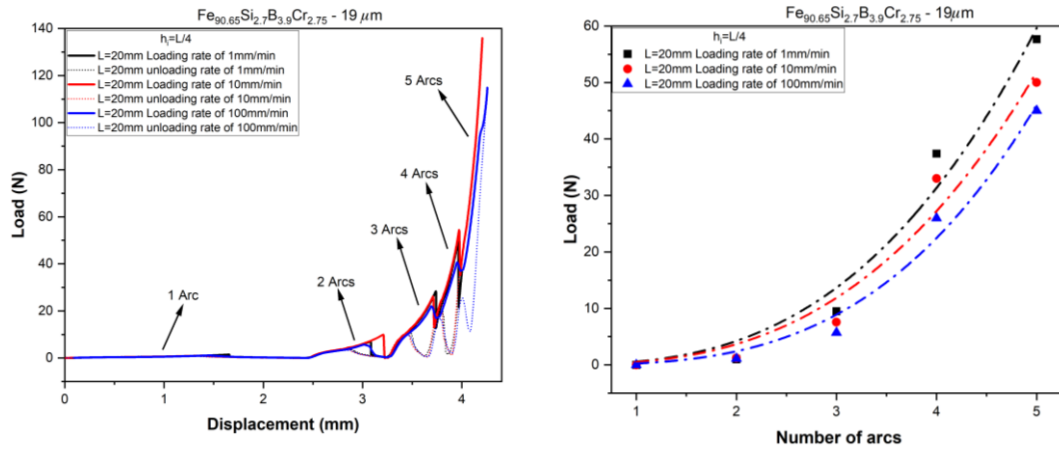


Figure 4-10: a) Representative load-displacement of the Fe-based MG with 19 μm thickness at different applied loading rates; b) The typical load vs number of arcs at various equivalent loading rates.

4.2.5 Mechanical response of crystalline materials

The mechanical response for crystalline materials has been tested before by Panagiotopoulos et al. [1]. Therefore, to evaluate whether crystalline materials can exhibit undulatory behaviour, similar tests were carried out using crystalline foil made of stainless steel with a thickness of 20 μm and width of 25 mm to investigate the ability of mechanical response. Mechanical loading was applied on the top of an arc-shaped stainless-steel foil, as shown in Figure 4-11a. Figure 4-11b shows the load-displacement curve upon only one loading/unloading cycle for an arc-shaped stainless-steel foil (20 μm) for $L = 20$ mm and $h_1 = 5$ mm. Upon loading, the foil starts to deform, followed by a change in shape from 1 to 2 sinusoidal arcs, but clearly, the stainless-steel foil exhibits higher load values compared to glassy foils within the same thickness. During the transition from 2 to 3 arcs, arc curvature geometry becomes unsymmetrical, indicating plastic deformation. Unloading shows a slow snapback, but the foil does not return to its initial arc-shaped due to permanent plastic deformation.

Compared to amorphous foil, crystalline foil shows different behaviour due to plastic deformation that occurs when the foil begins to deform from 1 to 2

sinusoidal arcs. Therefore, crystalline alloys exhibit limited elastic deformation between (0.2 - 0.5) %, which limits the crystalline foils' ability to exhibit mechanical response and makes them more likely to deform plastically in the early stage without multiplication of the initial arc.

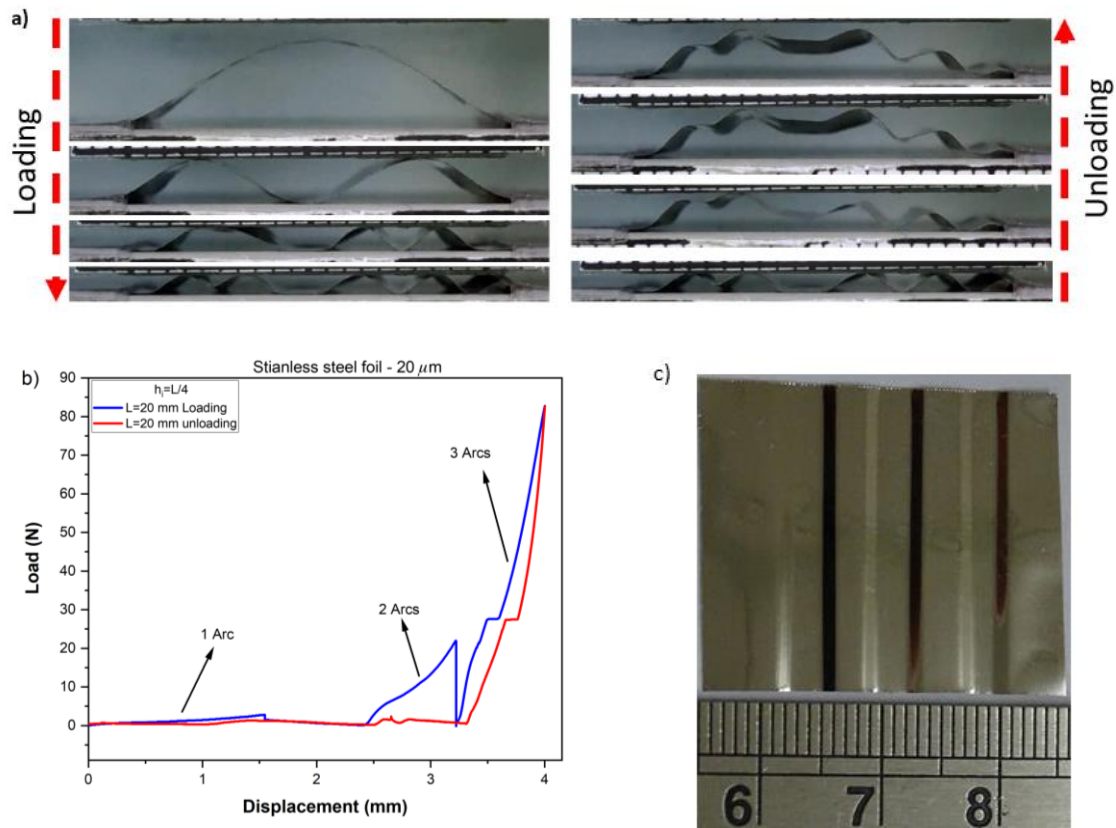
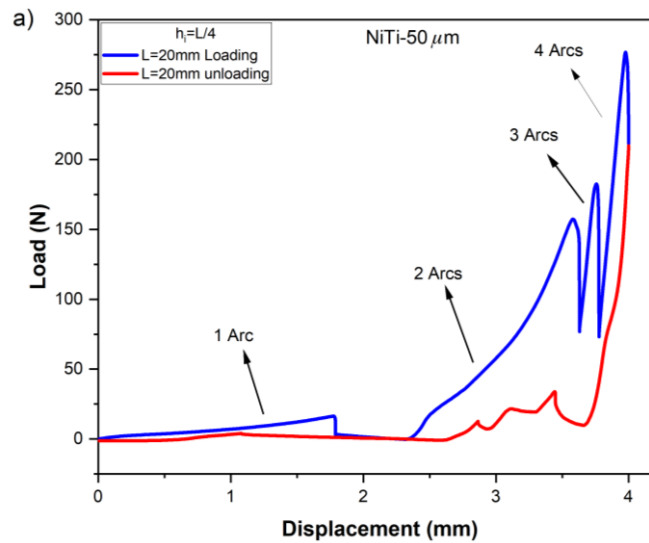


Figure 4-11: a) Mechanical response of arc-shaped stainless-steel foil (adapted from [1]); b) load-displacement curve upon loading for stainless-steel crystalline foil; c) image of plastic deformation that is created after testing on the stainless-steel foil.

Figure 4-11c shows stainless steel foil after load-displacement testing for visual defects caused by plastic deformation under applied load. The associated deformation occurred due to the limited ability of crystalline foil to deform elastically. These plastic deformation signs would usually present themselves as a crease line or as an indent in the material.

4.2.6 Mechanical response of superelastic alloy

The undulatory behaviour of Ni-Ti foil has been tested for the first time. A similar geometry set-up is used for testing the mechanical response for Ni-Ti foil of 50 μm thickness with boundary distance $L=20$ mm, the amplitude of the initial arc $h_1=5$ mm $h_1=L/4$ (aspect ratio $h_1/L=0.25$), as shown in Figure 4-12. The results in Figure 4-12a indicate that the foil deforms elastically from the initial arc to 2 arcs and then deforms plastically for more sinusoidal arcs. However, the arc geometry is not symmetric (not perfect shape), and the arc geometry changes from 2 arcs as the load increases to form up to 4 arcs. During unloading, the load-displacement curve shows load drop compared to the loading path but returns to its initial shape with minor signs of plastic deformation. These plastic deformations were observed on the Ni-Ti foil, similar to a crease line along the foil. Therefore, superelastic alloys show a different behaviour, unlike those seen in metallic glass foils and could be exploited for particular applications, such as a medical application.



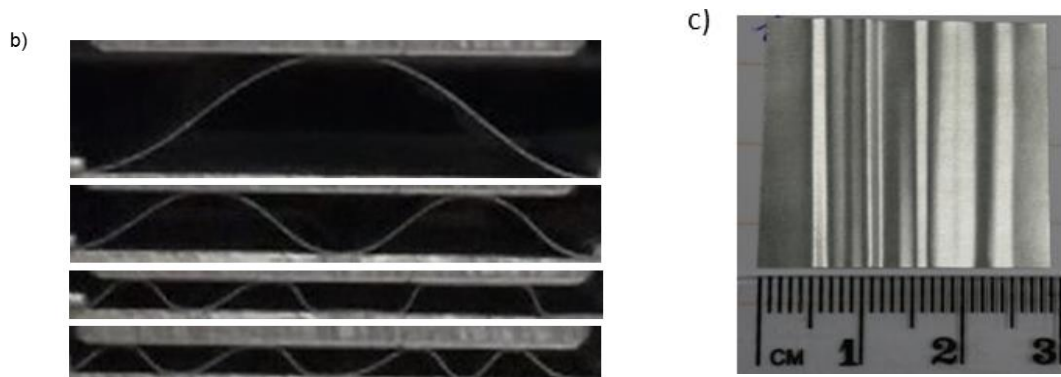


Figure 4-12: a) load-displacement curves of a NiTi foil; b) harmonic undulatory response of arc-shaped of NiTi foil; c) image of plastic deformation that is created after testing on the Nitinol foil.

4.3 Conclusions

The undulatory behaviour of metallic glass foils was investigated for Ni-Fe-based and Fe-based alloy foils of different thicknesses. For both alloys, the initially arc shaped foils deform elastically creating harmonic wavy patterns, in a reversible and repeatable manner, similar to a non-linear spring-type behaviour. The results indicate that the thickness of the foils as well as the choice of the glassy alloy, affect the load required for the transition from a lower order (n_i arcs) to higher order (n_i+1 arcs) waveform.

The initial geometry of the formed sinusoidal arc, like the boundary length L and initial amplitude h also influence the load and displacement response of the foils and thus can be used for tuning the spring-type behaviour of the set-up. The thicker Ni-Fe-based foils showed higher load for the same distance (or number of arcs formed) and higher spring rate values compared to the thinner Fe based foils. Under the conditions examined in this study, the foils always remain in the elastic deformation region. Remaining consistently always below this elastic limit (2% strain for metallic glasses) is critical for the reversibility of this behaviour.

5 Undulatory elastic behaviour of partially crystalline (Ni₇₈Si₈B₁₄) metallic glass foils

5.1 Introduction

In this chapter, the undulatory behaviour of Ni-B-Si MG foils is reported for the first time, showing that compositions of glassy foils are partially crystalline composites of up to 16 % crystalline volume. Among the factors that influence undulatory behaviour are alloy composition (due to differences in mechanical properties), foil thickness (d), boundary horizontal dimensions (length L and width W), and aspect ratio of the arc height and L , h_1/L of the initial spring set-up geometry. The undulatory elastic behaviour of two thicknesses of a Ni-B-Si metallic glass foil has been systematically studied and compared by finding out the effect of foil thickness on the undulatory behaviour. Thus, this chapter aims to show the undulatory behaviour of different metallic glass compositions for partially crystalline and compared to fully amorphous, as reported in the previous chapter.

5.2 Results and discussion

5.2.1 Structural characterisation

Figure 5-1 shows XRD patterns for Ni₇₈Si₈B₁₄ melt spun foils with 25 μm and 40 μm thicknesses. Both patterns exhibit extremely sharp peaks around 44° in the 2-theta angle, indicating the presence of a crystalline phase. These sharp peaks correspond to Ni metastable phase, which has a face-centred cubic structure at the diffraction plane (111). Figure 5-2 presents DSC thermograms of the semi-amorphous material used in this work. For the Ni₇₈Si₈B₁₄ foil with 40 μm thickness, an exothermic peak with onset at $T_x = 478^\circ\text{C}$ is observed, corresponding to the crystallisation of the amorphous phase. Similarly, the Ni₇₈Si₈B₁₄ foil of 25 μm thickness exhibits an exothermic peak at $T_x = 485^\circ\text{C}$, again corresponding to the crystalline, amorphous phase.

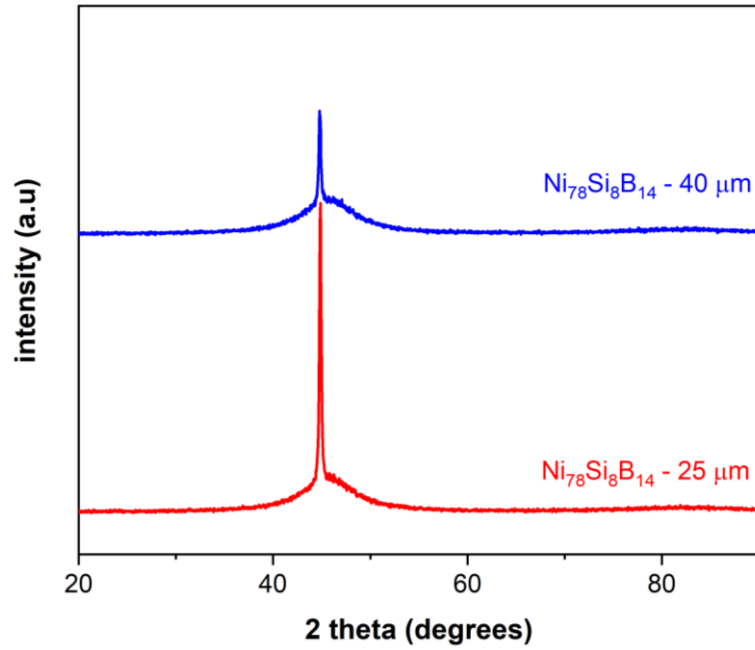


Figure 5-1. X-ray diffraction patterns of metallic glass foils, for two thicknesses.

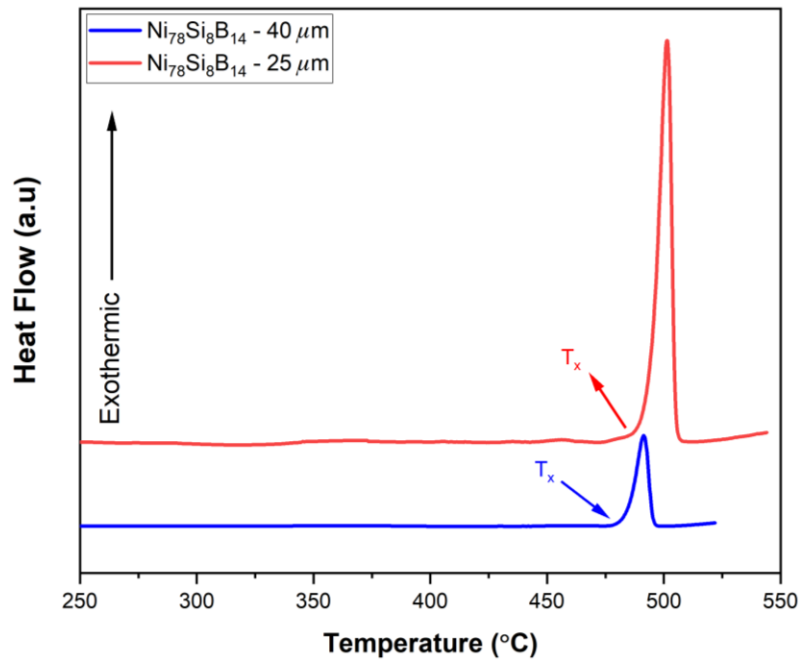


Figure 5-2. DSC thermograms of the metallic glass foils, for two thicknesses.

5.2.2 Measurements of crystal volume fraction

Quantification of the change in amorphous content, change is determined from the changes in diffraction patterns shown in Figure 5-3. The area of the

amorphous and crystalline peaks can be determined by integration, and the crystalline nanocrystalline volume fraction calculated [162][163]:

$$\phi_s = \frac{A_c}{A_c + A_a} \quad \text{5-1)}$$

Where ϕ_s is the volume fraction of precipitated Ni, A_c is the total integrated area corresponding to the crystalline phase, and A_a is the total integrated area corresponding to the amorphous phase.

These results are presented in Table 5-1 and imply the evolution of a larger crystalline volume fraction of Ni due to the sharp peak showed in x-ray diffraction for the foils tested, reaching as high as 53.55% in specimens on the air side. A smaller crystalline volume fraction of Ni was calculated on the wheel side of all foils, in a range between 12.5% to 16.3%. The difference in crystalline volume fraction between the air side and the wheel side of a thin ribbon of a Ni-Si-B glassy alloy can be attributed to the cooling rate and solidification process experienced by the alloy during its formation through rapid quenching, typically in a process called melt spinning or ribbon casting. However, in melt spinning or ribbon casting, the molten alloy is rapidly cooled to form a thin ribbon. The cooling rate varies across the thickness of the ribbon. Therefore, in case of melt spinning, the side of the ribbon that is in contact with the wheel (wheel side) experiences much faster cooling rates compared to the side exposed to the air (air side). This difference in cooling rates has a significant influence on the structure of the alloy.

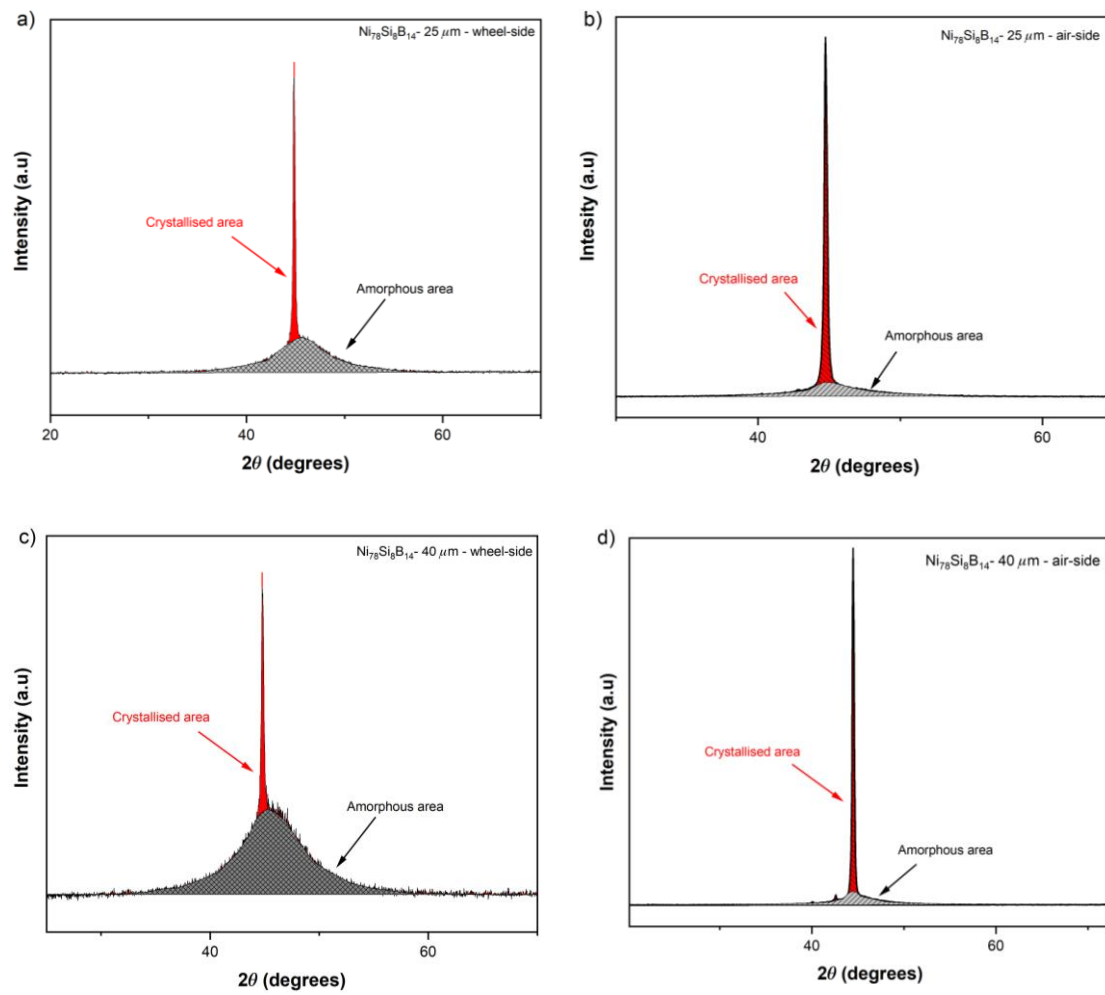


Figure 5-3: a) and b) the relative areas of the deconvoluted amorphous and crystalline peaks in the XRD diffraction pattern of the MG foil with a thickness of 25 μm ; c) and d) for MG foil with a thickness of 40 μm .

Table 5-1. The crystalline volume fraction of Ni-based metallic glass foils

<i>Thickness</i>	<i>2θ</i>	<i>Ni- Crystal Plane</i>	<i>Crystallinity ratio</i>
40 μm -wheel	44.50	(111)	12.57%
40 μm -air	44.50	(111)	53.55%
25 μm -wheel	44.50	(111)	16.35%
25 μm -air	44.50	(111)	43%

Figure 5-4 presents the percentage of volume fraction of precipitation nanocrystals on both sides of MG foils in an area integrated with amorphous and crystallinity peaks. Clearly, the crystallinity area of metallic glass foil on the air side is significantly larger than that on the wheel side in both thicknesses.

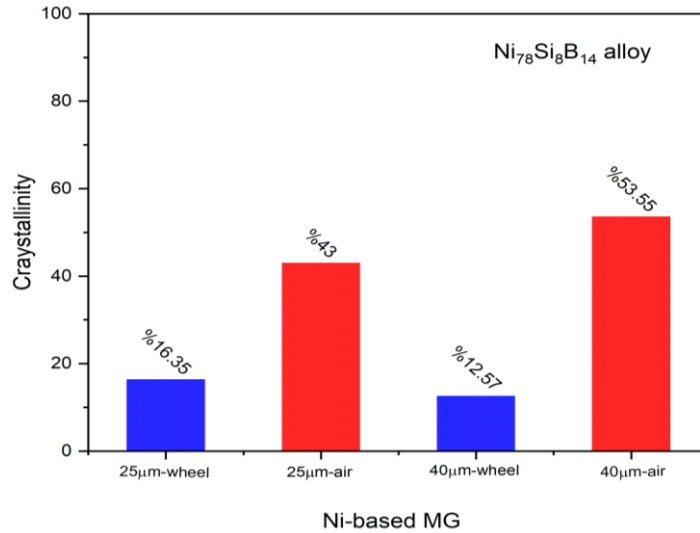


Figure 5-4. Percentage of crystallinity of Ni₇₈Si₈B₁₄ MG of different thicknesses calculated from XRD patterns obtained from the wheel and air side.

5.2.3 Elastic undulatory behaviour

Metallic glass foils with partially crystalline composites have been studied for the first time. Mechanical loading was applied to the top of the arc-shaped Ni-based foil, as shown in Figure 5-5. Ni-based foils showed the same loading behaviour as NiFe and Fe-based foils, showing an increase in sinusoidal arcs as their shapes changed, see Figure 5-5b.

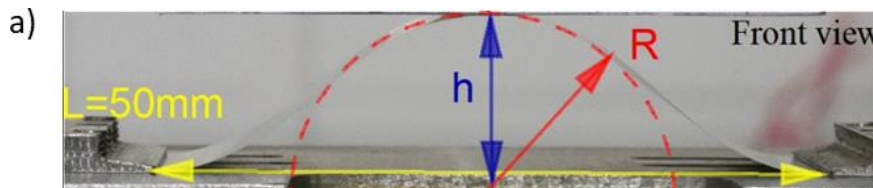




Figure 5-5: a) Front view of initial arc-shaped metallic glass foil; b) harmonic undulatory behaviour response of arc-shaped metallic glass foil.

Figure 5-6 presents the load versus displacement for the Ni-based MG foil with boundary distance $L=20$ mm, the amplitude of the initial arc $h_1 = 5$ mm for a constant aspect ratio of ($h_1=L/4$), as shown in Figure 5-5a.

Figure 5-6a shows ten successive loading cycles for a single Ni-based MG foil with a thickness of $25\ \mu\text{m}$ and it is seen that, typically, each cycle follows the same path, indicating its undulatory behaviour is repeatable and reversible. However, in the first loading cycle the path differs slightly from the others, and the load values to form 2 and 3 arcs are slightly higher. During unloading, the load-displacement curve follows an identical path for all unloading cycles, showing hysteresis but returning to its initial shape of a sinusoidal arc.

Figure 5-6b shows ten successive loading/unloading cycles for the same foil composite, but of thickness of $40\ \mu\text{m}$. This foil sample's mechanical response and undulatory behaviour follow the same pattern as the thinner foil, especially in first cycle loading, where load values are slightly higher for the step in arc

formation from 1 to 2 and 2 to 3 arcs. Again, during unloading, the mechanical response of the load-displacement follows the same path for all cycles.

The upward trend of the load-displacement curves indicates that an exponential relationship results from the loading process, as shown in Figure 5-6. It is seen that it is only at specific displacements that discrete discontinuities, appear characterised by a sharp decrease in load. According to Hooke's law, the gradients between these abrupt decreases in load could be viewed as quasi-linear, equivalent to the spring rate (k). Consequently, the undulatory behaviour of arc-shaped metallic glass foils subjected to loading conditions, as shown in Figure 5-5, functions as non-linear flat springs with variable spring rates [1][2].

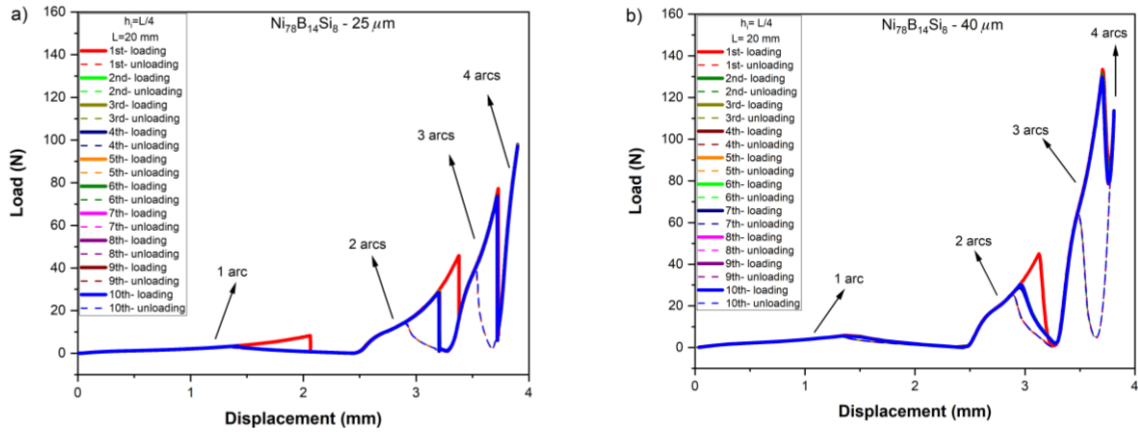


Figure 5-6: Load-displacement curves for ten cycles of loading/unloading Ni-based metallic glass foil of a) $25 \mu\text{m}$ thickness; and b) $40 \mu\text{m}$ thickness.

For the first time, this work reports the load-displacement response for two samples of the same Ni-based foil and initial arc geometry ($L = 20$ mm and $h_1 = 5$ mm) but different thicknesses: $25 \mu\text{m}$ and $40 \mu\text{m}$, see Figure 5-7. Similar behaviour can be observed for both foils. As the displacement increases, the number of arcs increases, and the load increases quasi-exponentially. At a specific displacement, the number of arcs increases by one at the same values of the loads for both foils, though at a slightly higher load value for the thicker foil. For example, the transition from 2 to 3 arcs occurs at around 80 N for the thicker foil, compared to 50 N for the thinner foil. For the transition from 4 to 5 arcs, the

thicker foil required 354 N, whereas the thinner foil required 187 N. Therefore, the undulatory behaviour is significantly affected by the thickness of the foils, and the foil thickness must be considered in the design of spring-type devices to ensure the desired mechanical response. Hysteresis is again observed during the unloading cycle; in both cases, the foil snaps-back to its initial position and resumes the initial sinusoidal arc shape.

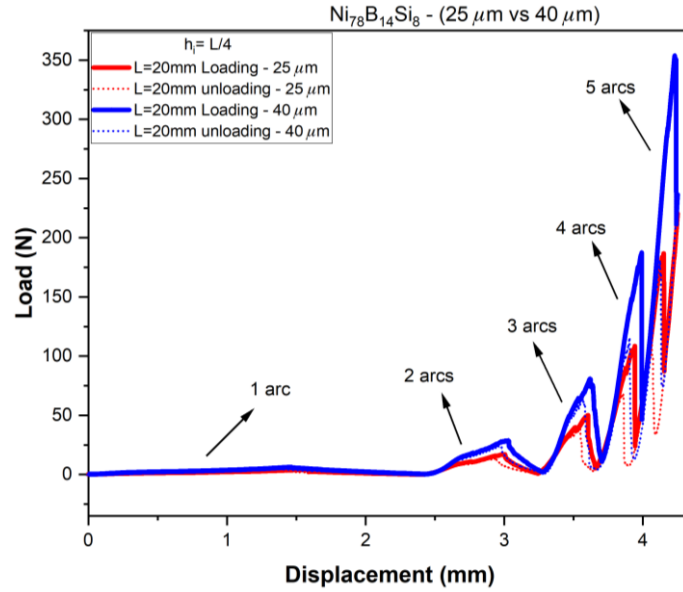


Figure 5-7. Load-displacement curves for loading of Ni-based metallic glass foil with $L = 20$ mm and $h_1 = 5$ mm for foil of $25 \mu\text{m}$ thick (red), and $40 \mu\text{m}$ thick (blue) for $L = 20$ mm and $h_1 = 5$ mm.

Figure 5-8 presents the load-displacement curves for Ni-based MG foils for three boundary distances, $L = 20, 30$ and 50 mm, with 25 and $40 \mu\text{m}$ foil thicknesses, with an aspect ratio of $h_1/L = 0.25$. The arrangements with greater L values provided more sinusoidal arcs within MG foils' 2% elastic deformation limit. Moreover, the load value for the same displacement is higher for the thicker foils. The load-displacement confirms that the thickness of the foil and its geometry spring-setup parameters of the initial arc shape must be considered when designing spring type devices for a desired mechanical response, as shown in Figure 5-8.

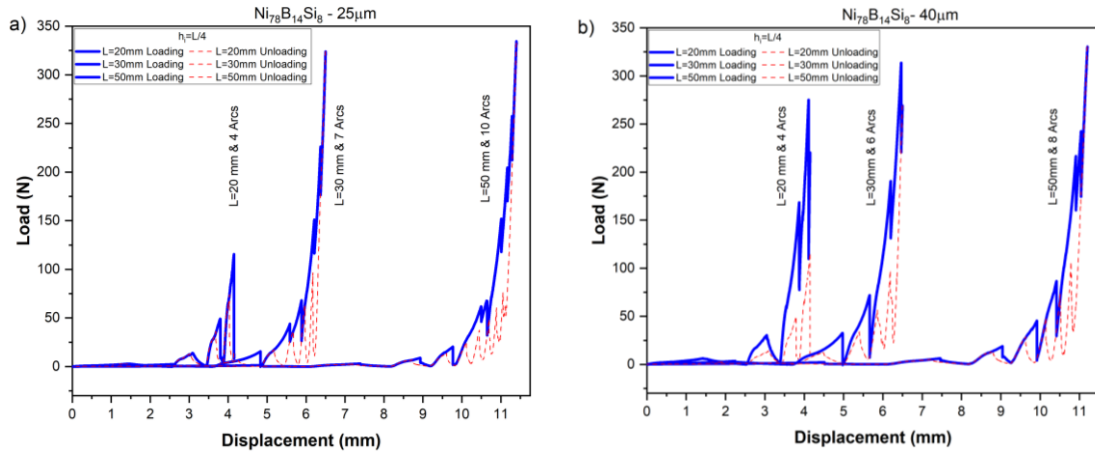


Figure 5-8: Load-displacement curves for Ni-based metallic glass foil for boundary length L values 20, 30 and 50 mm: a) 25 μm thickness and aspect ratio $h_1/L = 0.25$; and b) 40 μm thickness and aspect ratio $h_1/L = 0.25$.

Figure 5-9a shows the load required to induce the transition from n_i sinusoidal arcs to $(n_i + 1)$ arcs versus the number of arcs for Ni-based MG foils with initial arc geometry defined by L values of 20, 30, 40 and 50 mm and initial ratio $h_1/L = 0.25$. Comparing the two thicknesses of the Ni-based MG foils, the load to trigger the transition from n_i to $(n_i + 1)$ arcs is greater for the thicker foil, as shown in Figure 5-6 and Figure 5-7. Figure 5-9a also shows that the longer the initial boundary length, L , the lower the load required to produce arcs. The longer the length of the MG foil, however, the greater number of arcs that can be formed within an elastic deformation of 2% strain, thus, being able to reach considerably higher load values.

Figure 5-9b shows the calculated spring rates of both thicknesses of glassy foil versus the number of arcs for different boundary lengths (L). The spring rate value gradually increases for a given length as the number of arcs increases. In all cases, the higher the L values, the more gradual the initial increase in the k value, but the higher the final value of k due to the greater number of arcs produced. As expected, the thicker Ni-based foils exhibit higher k values than the thinner ones. Consequently, for the Ni-based foil of 40 μm thickness and $L = 50$ mm, the predicted spring rates range between 1 to 1800 N/mm based on the number of arcs formed and the horizontal boundary conditions in which L is used. Therefore,

the Ni-based MG foil of 40 μm thickness shows higher load and spring rate values due to its greater thickness compared to the Ni-based MG foil of 25 μm .

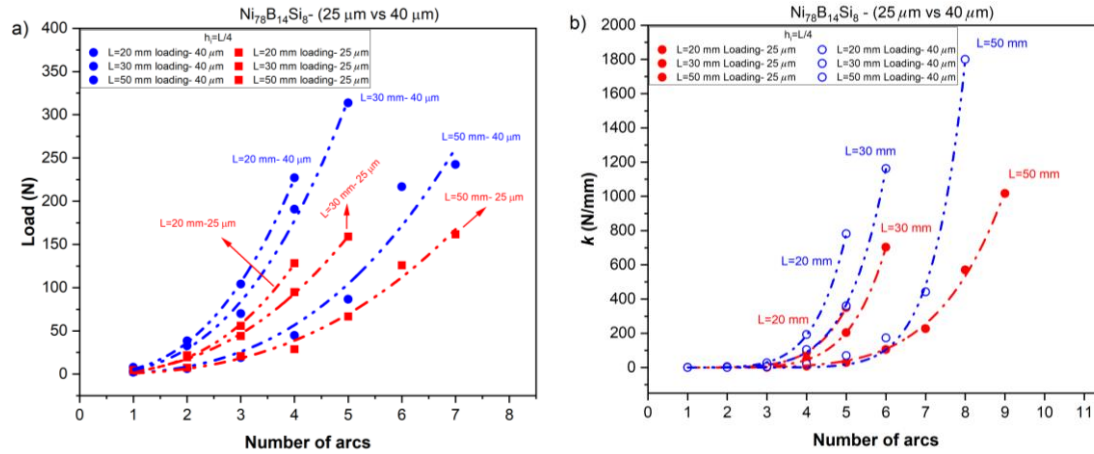


Figure 5-9: a) Maximum applied normal load on the foils with n_i sinusoidal arcs just prior to the formation of $n_i + 1$ arcs versus the number of arcs; b) the spring rates (k) are calculated in the quasi-linear segments of the load-displacement curves. Both for Ni-based metallic glass foils with 25 μm and 40 μm thicknesses and set-up with boundary distance L values 20, 30, 40 and 50 mm, and $h_1/L=0.25$. In 5-9 (b) values for $L=40$ mm were omitted for the clarity of the graphs.

5.2.4 The effect of thickness on the undulatory behaviour

In this section, the effect of the thickness on the undulatory behaviour of MG foils is investigated using the two foils of 25 μm and 40 μm thickness. The through-thickness behaviour is assumed to be purely elastic. The load-displacement curve, Figure 5-10, shows significantly different behaviour for the two foil thicknesses. The load value of the two foils is here defined just before forming a new (n_i+1) arc. The corresponding load values of the two foils are selected where buckling occurs at the peak points of the load-displacement curve.

The load-displacement curves of two foils are shown in Figure 5-10, where the red and blue curves are for the 25 μm and 40 μm thickness, respectively. The thinner foil reaches the formation of a new (n_i+1) arc at a lower load because the thinner foil requires less load to deform compared to thicker foil. It is seen that, as expected, increasing the thickness increases the load required to deform the

foil. Increasing the thickness increases the resistance to deformation of the arc shape. During the loading process the increase in displacement shows a similar pattern for both thicknesses, but the greater thickness requires a greater load for a given displacement. The effect of thickness on the undulatory behaviour will be further discussed in Chapter 6, regarding the critical load required for buckling. The relevant dimensions and specimens used to define each sinusoidal arc of the specimen foils are listed in

Table 5-2, where the maximum load values and maximum displacement of the foil when the arc form are also given. Therefore, the effect of foil thickness on the undulatory behaviour that changes mechanical performance is determined mainly by the required applied load to buckle foil.

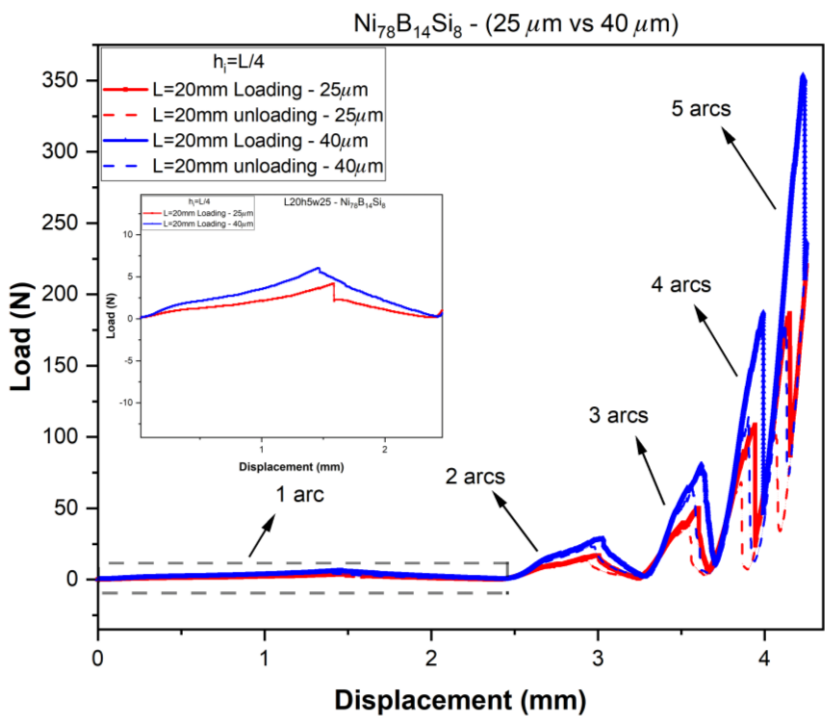


Figure 5-10. Undulatory behaviour for Ni-based metallic glass foils of 25 μm and 40 μm thicknesses.

Table 5-2. Undulatory behaviour specimen data for Ni-based metallic glass foils of 25 μm and 40 μm thicknesses.

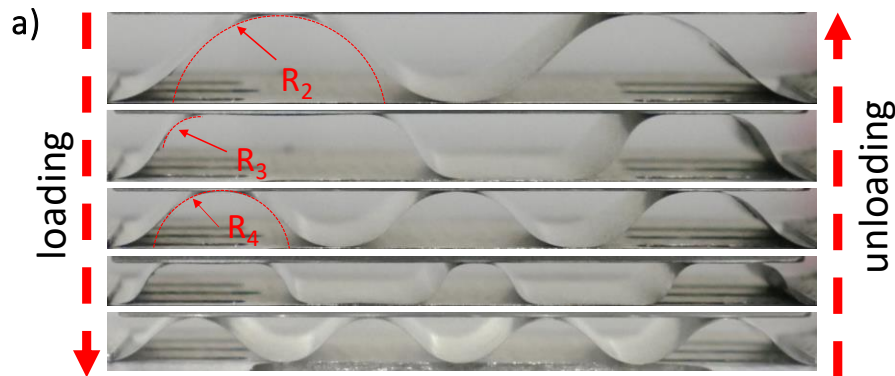
		Load values (N)		Displacement (mm)		Spring constant (N/mm)	
		25 μm <i>thick</i>	40 μm <i>thick</i>	25 μm <i>thick</i>	40 μm <i>thick</i>	25 μm <i>thick</i>	40 μm <i>thick</i>
Sinusoidal arc	Width (w) mm						
1	25	3.3	5.8	1.35	1.4	2.5	4.5
2	25	28	30	3.0	2.95	16	23
3	25	82	103	3.7	3.6	145	192
4	25	123	234	3.95	3.96	441	780

5.2.5 Estimation of local strain during arc formation

Plastic deformation should be avoided to maintain reversible and repeatable undulatory behaviour of MG foils. Therefore, the strain must remain below the 2% elastic deformation limit. As described above, the foil is subjected to applied load leading to deformation and bending phenomena, resulting in an inhomogeneous strain distribution. At positions exhibiting the greatest bending or the smallest radius of curvature, the strain reaches its maximum local value. In previous work [164], we found that estimates of local strain in foils must be taken at the points of maximum distortion marked with an R in Figure 5-11a. These states in the evolution of the foil shape are shown as R₂, R₃ and R₄, on the load-displacement curve in Figure 5-11b. A drop in load accompanies, the transition from two to three arcs, see the transition from R₃ to R₄.

Figure 5-11c presents the measured local strain in the Ni-based foils at the points of maximum distortion when a new arc is engendered, equivalent to the transition

from R_3 to R_4 in Figure 5-11a. The foils have $40\text{ }\mu\text{m}$ and $25\text{ }\mu\text{m}$ thicknesses, with initial boundary lengths of $L=20, 30, 40$ and 50 mm . The thinner foil presented with less local deformation strain for all lengths than the thicker foil. Thus, the thicker foil exhibited greater local strain in all conditions, reaching and exceeding the elastic deformation limit (2%) in all cases before the thinner foil. Closer observation shows that for all cases of Ni-based foils with $25\text{ }\mu\text{m}$ thickness, the local strain remains within the elastic deformation limit of 2%. On the other hand, the foils with $40\text{ }\mu\text{m}$ thickness entered the plastic region for all three lengths shown, specifically for $L=20, 30$, and 50 mm ; the thicker foil began to deform plastically from 5, 7 and 11 sinusoidal arcs, respectively. Consequently, the maximum permitted number of sinusoidal arcs can be estimated by measuring the local strain maintained below the elastic deformation limit of MG foils. The local strain estimation method for the pre-buckling shape of the load-displacement curve is consistent with the experimental analysis, which estimates the operating range of undulatory behaviour in MG foils.



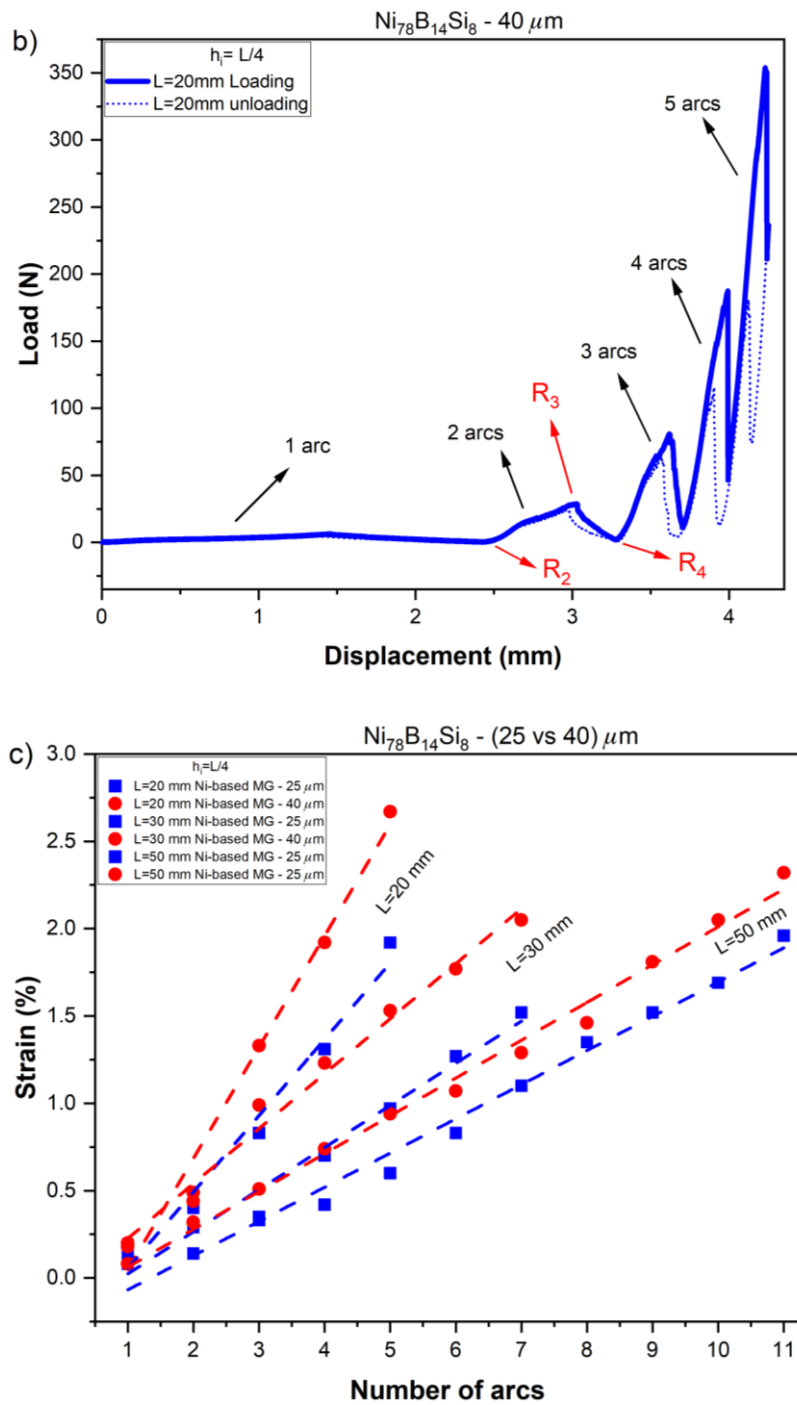


Figure 5-11: a) assembly of snapshots of the undulatory response with images of waveforms with sinusoidal shaped arcs (R_2 and R_4) and distorted arc (R_3); b) load-displacement curve with an undulatory response for the Ni-based foil; and c) maximum local strain on the foils, just prior to the formation of a new (n_i+1) arc.

5.2.6 Undulatory behaviour of four metallic glass foils

This study of the undulatory behaviour of MG foils includes materials not previously investigated. Figure 5-12 shows the load displacement response of four samples of three materials: Fe-based glassy foil with 19 μm thickness, NiFe-based glassy foil with 25 μm thickness and the two Ni-based glassy foils of 25 μm and 40 μm thickness, for the same initial arc geometry. Similar behaviour patterns are observed for the four glassy foils. When the load increases, the displacement increases quasi-exponentially. Clearly, the Ni-based foil with greater thickness exhibits higher load values compared to the other glassy foils. For example, for the transition from 4 to 5 arcs, the Ni-based foil with 40 μm and 25 μm thicknesses required about 187 N and 108 N, respectively. The NiFe-based foil (25 μm thick) and Fe-based foil (19 μm thick) required 100 N and 42 N, respectively. Due to differences in foil thickness, there is some variation in the position of the sharp load drop, but the paths precisely coincide again when loading resumes.

The load-displacement curves confirm by observation the repeatability of undulatory behaviour under cyclic loading of the different glassy alloys. However, the arc multiplication of these MG foils shows the same displacement values but Fe-based MG foil exhibit displacement values that differ only slightly at the sharp load drop position compared to other MG foils. These minor variations in displacement values are due to set-ups of MG foils arc-shaped. The results clearly indicate that spring-type applications can effectively utilise the unique behaviour of glassy alloys. By selecting the appropriate glassy alloy and adjusting the foil's thickness, it is possible to control the mechanical response of the foil when subjected to a load. Thus, this capability allows for designing spring-type devices with specific characteristics efficiently functioning across various load ranges.

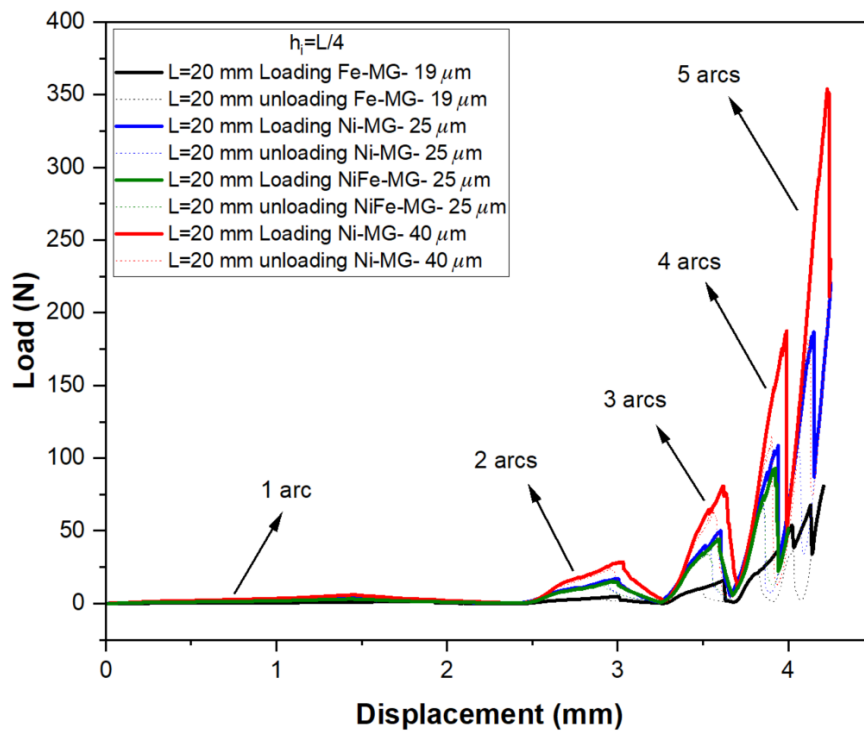


Figure 5-12. Load-displacement curves for Ni-based metallic glass foils (25 μm thick, blue) and (40 μm thick, red) NiFe-based and Fe-based foils (25 μm and 19 μm , olive and black, respectively) for $L=20$ mm and $h_1=5$ mm.

5.2.7 Effect of mechanical strength

The mechanical strength of crystalline and amorphous metals differs significantly due to their distinct atomic structures. Crystalline metals have a highly ordered atomic structure characterised by repeating and organised patterns of atoms in a lattice. This regular atomic arrangement allows for the propagation of dislocations, which contribute to the metals' plastic deformation. The presence of grain boundaries, defects, and crystallographic planes can influence their mechanical properties. On the other hand, amorphous metals or metallic glasses, lack a regular crystalline structure. They have a disordered, non-periodic atomic arrangement resembling that of liquids. Therefore, this disordered atomic structure makes it more difficult for dislocations to move through the material, which contributes to their high strength.

In addition, amorphous metals often have higher strength and hardness compared to their crystalline counterparts. Their lack of crystalline defects and

grain boundaries minimises dislocation movement, leading to high strength and resistance to plastic deformation. Thus, the mechanical response of Ni-based glassy alloy might be caused by the strengthening effect of crystalline phases. However, these partially crystalline foils exhibit the same undulatory behaviour as the amorphous glassy foils. Also, it can be seen that Ni-based shows a maximum strength range from 1.5 to 2 GPa, which is less than Fe-based glassy alloys with 3.3 GPa.

As can be seen from the mechanical properties, the presence of a small amount of up to (15%) in partially crystalline foil does not affect mechanical response performance, indicating that a small amount of crystals embedded in the amorphous would not deteriorate the mechanical properties of the metallic glass foils as long as still within elastic deformation of 2% strain. Load-displacement curves for undulatory behaviour must have strains less than 2%. As a result, the mechanical strength of these materials does not affect their mechanical behaviour. Thus, mechanical strength does not affect undulatory behaviour in mechanical terms. However, if the volume fraction of crystalline phases in the amorphous alloy is too high, the part will become very brittle. The choice between partially crystalline and amorphous alloys depends on the specific requirements of the application and the desired combination of mechanical properties.

5.3 Conclusions

The undulatory behaviour of partially crystalline Ni-based MG foils with two different thicknesses was investigated and compared with fully amorphous Fe-based and NiFe-based foils examined in Chapter 4. Interestingly partially crystalline MG foils showed undulatory behaviour like the fully amorphous ones. It was found that increasing the foil thickness resulted in a significant increase in both load and local strain. The series of undulatory mechanical responses and elastic properties revealed the presence of reversible and repeatable mechanical responses that can be exploited as flat springs with multi-spring rates. The geometry of the initial arc-shape such as the boundary length L and amplitude h , impacts the foils' load-displacement. The Ni-based foil with 40 μm thickness exhibited higher load and spring rate values for the same number of sinusoidal

arcs formed compared to the thinner foil with 25 μm thickness. Moreover, the results revealed that the present amount of crystallinity found in MG foils does not cause any effects on the undulatory behaviour as long as local strains remain within the elastic region limits of 2% strain.

6 Mechanism of the undulatory behaviour and spring design

6.1 Introduction

In the previous chapter, partially crystalline metallic glass foils exhibited undulatory behaviour and were compared to fully amorphous alloys. While the effect of foil thickness on undulatory behaviour was reported, the mechanism that causes undulatory elastic behaviour needs to be investigated and understood. The mechanism driving the undulatory behaviour of metallic glass foils is attributed to buckling phenomena. However, buckling phenomena have been studied in depth. Thus, this chapter's primary motivation is to explain the underlying mechanisms of undulatory behaviour, part of which will be an investigation of the hypothesis that buckling phenomena lead to undulatory behaviour.

6.2 Analysis of perfect sinusoidal waveforms

Panagiotopoulos. et al., [1] reported that arc-shaped metallic glass foils are sinusoidal arcs (harmonic), as shown in Figure 6-1a, which can be described by a modified expression of the standing waves formula as follows:

$$y^2(x) = A \sin^2\left(n \frac{2\pi}{\lambda_{fundamental}} x\right) \quad 6-1)$$

A similar approach is applied in this chapter to various tests and conditions, confirming that it can be helpful to model undulatory behaviour. The amplitude and displacement are considered to describe metallic glass foils in the shape of sinusoidal arcs, , but the applied load is not. The standing wave equation (Equation (6-1)) was used to describe the assembly of all waveforms in Figure 6-1a, which correspond to Ni-based (25 mm thick) metallic glass foil from 1 to 5 sinusoidal arcs for ($L= 50$ mm and $h_i= 12.5$ mm). As shown in Figure 6-1a, Equation (6-1) can very well simulate all the waveforms shown in Figure 6-1b. For the initial waveforms (*i*) in Figure 6-1a (initial arc), A_i corresponds to the initial amplitude, the amplitude of the arc for the $L=50$ mm long foil (12.5 mm) and “fundamental” corresponds to the fundamental wavelength, where $\lambda_{fundamental} = 2L$.

Table 6-1. Experimental data for undulatory behaviour for three lengths ($L=20$, 30 and 50 mm).

No.	Sinusoidal arc	Amplitude A (mm)			$\lambda_{fundamental}$ (mm)		
		$L=20$ mm	$L=30$ mm	$L=50$ mm	$L=20$ mm	$L=30$ mm	$L=50$ mm
i	1	4.75	6.5	12.5	40	60	100
ii	2	2.4	3.07	6.5	40	60	100
iii	3	1.62	2.38	4.5	40	60	100
v	4	1.35	2	3.5	40	60	100

iv	5	1.12	1.5	3	40	60	100
----	---	------	-----	---	----	----	-----

From observation, experimental errors are typically systematic errors caused by flaws in the setup or biases, the measured values for the amplitudes of the arcs were consistent with the standing wave model described by Equation (6-1), showing a good fit to model the undulatory behaviour of metallic glass foils. Thus, the standing wave equation can model undulatory behaviour as shown in the snapshots assembly in Figure 6-1b.

Theoretically, the number of waves in the standing wave equation (n) is unbounded. However, experimentally the maximum number of arcs in metallic glass foils is limited due to a plastic deformation limit of 2% strain, as discussed in Chapters 4 and 5 (see Figure 4-9 in Chapter 4). The model does not consider this limit, nor does it discuss the full range of mechanisms contributing to undulatory behaviour; it only describes the waveforms of perfect sinusoidal waveform and does not consider the load.

It was found that the amplitude A is a function of the number of sinusoidal arcs, which is described by the relation of the type as follows:

$$A = A_i x^c \quad \mathbf{6-2)}$$

Where A_i corresponds to the initial amplitude (12.5 mm) and (x) refers to the number of arcs. The relation is limited to an aspect ratio of ($h_1/L=0.25$).

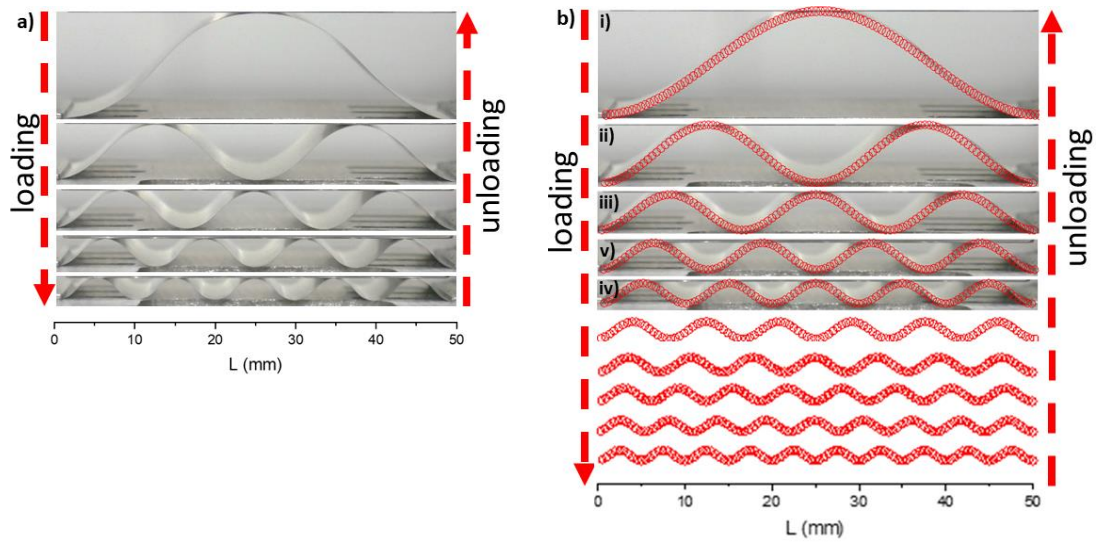


Figure 6-1: a) Harmonic undulatory response of arc-shaped metallic glass foil for $L=50$ mm; b) sinusoidal arc formation as calculated from the standing wave equation, where red refers to simulation only.

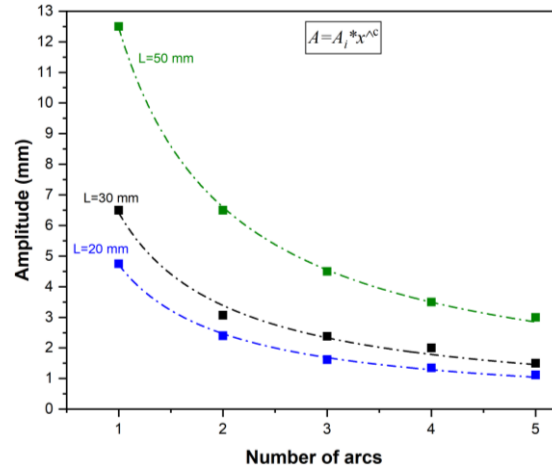


Figure 6-2. Arc amplitude as a function of number of arcs for three boundary lengths.

Figure 6-2 represents all boundary conditions with the aspect ratio of ($h_1/L=0.25$). From this, the value of the constant, c , which appears in Equation (6-2), is equal to (-0.92) .

To apply the standing wave equation to Figure 6-1b for $L = 50$ mm, it is first necessary to calculate the amplitude A of the arcs using Equation (6-2), assuming the aspect ratio remains the same at $h/L = 0.25$. The amplitude A_1 for the first waveform ($i = 1$) in Figure 6-1b is equal to 12.5 mm, then inserting $A_1 = 12.5$ mm into the standing wave equation (6-1), where n here is for the first initial arc and λ in this boundary length is constant of 100 mm, which identifies ($\lambda_{fundamental} = 2L$).

The same steps are repeated for the second waveform ($ii = 2$), considering the number of arcs formed and assuming that $A_i = 12.5$ is always the initial amplitude. We calculate A_2 for the second waveform (ii) in Figure 6-1b using Equation (6-2) and obtain a value of 6.5 mm, as shown in Table 6-1. Similarly for the remaining waveforms (i.e., *iii*, *iv* and *v*) in Figure 6-1b can be calculated by applying the same steps, taking into account changes in parameters such as amplitude and the number of arcs when implemented into the standing wave equation, keeping $\lambda_{fundamental} = 100$ mm.

The standing wave equation could also describe the undulatory behaviour for other boundary lengths considered ($L = 20$ to 50 mm) and specific aspect ratios. Figure 6-3 shows undulatory behaviour for boundary lengths ($L = 20$ and 30 mm), according to the standing wave formula. Table 6-1 presents values of the amplitude of the arcs with change in the number of arcs and $\lambda_{fundamental}$. Following the same procedure as for $L = 50$ mm, Equation (6-2) obtains amplitude values for each sinusoidal waveform and is then implemented into the standing wave formula, Equation (6-1).

Figure 6-3a presents waveforms of undulatory behaviour of Ni-based metallic glass foil of 25 μm thickness for $L = 20$ mm and $A_1 = 5$ mm. The waveforms model is identical to the amorphous foil's undulatory behaviour.

Figure 6-3b shows the waveforms of undulatory behaviour for the same material (Ni-based foil), but for $L = 30$ mm and $A_1 = 7.5$ mm for the initial arc geometry. The modelled waveforms follow the same geometric pattern as the metallic glass foil, confirming that the standing wave equation can be used to predict the waveforms

of the foils. This procedure can be extended to modelling the waveforms corresponding to the undulatory behaviour of cases not experimentally tested in this work.

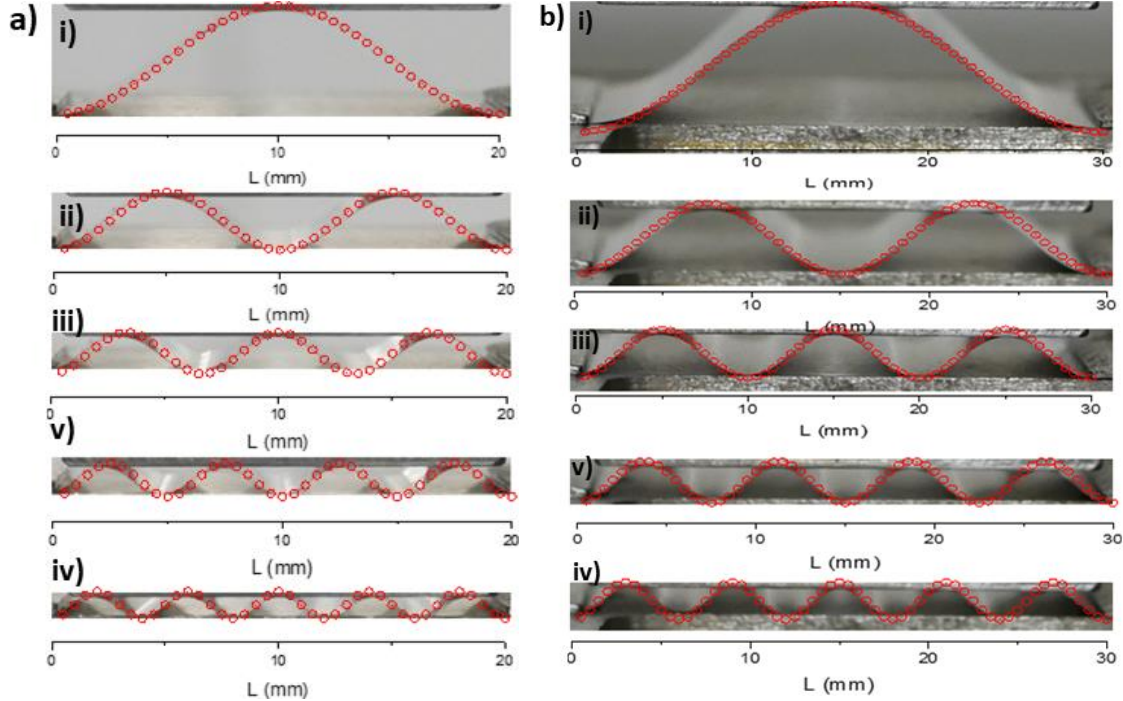


Figure 6-3. Modelling sinusoidal arcs generated by standing wave for L ratio ($h/L=0.25$) a) boundary length $L=20\text{mm}$; b) boundary length $L=30\text{ mm}$.

Figure 6-4a shows the predicted undulatory behaviour of boundary lengths, $L=15\text{ mm}$ with an initial amplitude $A_1=3.75\text{ mm}$, and an aspect ratio ($h/L=0.25$). The waveforms produced can be used to estimate the undulatory behaviour of metallic glass foils under these conditions without a running test. Figure 6-4b shows the simulated waveforms representing the undulatory behaviour for $L=25\text{ mm}$ and $A_1=6.25\text{ mm}$. While similar waveforms can be observed, the arc geometry is clearly different compared to those for $L=15\text{ mm}$ and $A_1=3.75\text{ mm}$.

However, while these two cases were not evaluated experimentally in this study, it is evident that the standing wave equation together with Equation 6-2 can be used to predict the undulatory behaviour of MG foils with initial amplitude, respecting the condition to obtain sinusoidal undulations, i.e. $h/L = 0.25$.

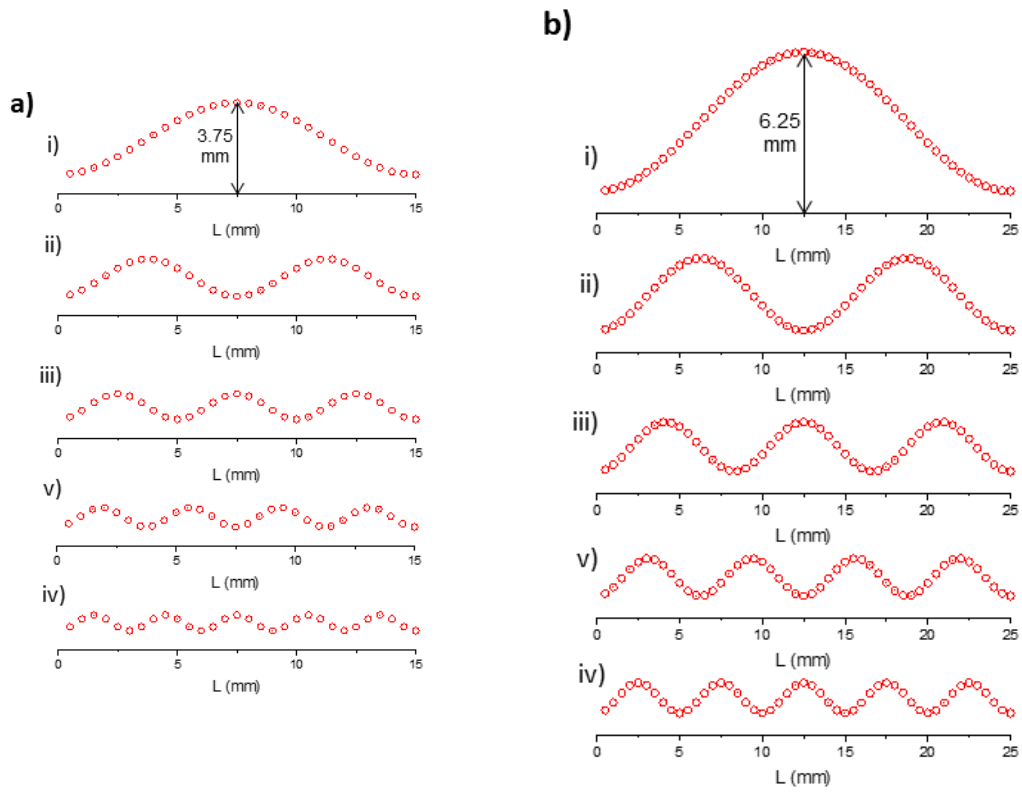


Figure 6-4. Modelling sinusoidal arcs generated according to the standing wave equation for $h/L=0.25$, a) boundary length $L=15$ mm; b) boundary length $L=25$ mm.

Further, the standing wave equation can be used to predict the undulatory behaviour for a variety of foil thicknesses. Figure 6-5 shows the waveforms of undulatory behaviour for an arc-shaped Ni-based ($25\text{ }\mu\text{m}$ thick) metallic glass foil. For comparison is a foil of the same material but different thicknesses ($40\text{ }\mu\text{m}$ thick), both for $L=50$ mm and $A_1=12.5$ mm. As expected, the two amorphous foils show a similar waveform, and the thickness does not effect on the geometry, as discussed in Chapters 4 and 5, confirming that the standing wave equation is the appropriate approach to model the waveforms of undulatory behaviour of metallic glass foils of different thickness and arc amplitude. Thus, the standing wave equation can be used to design different types of spring set-ups to ascertain the mechanical response based on the initial arc-shaped geometry and amplitude. However, it is significant to consider the limitations and constraints associated with the materials and manufacturing processes such as yield strength, fatigue

life and elastic modulus that used to make the spring. Understanding these limitations is crucial for ensuring that the spring performs as intended and remains safe and reliable in its application.

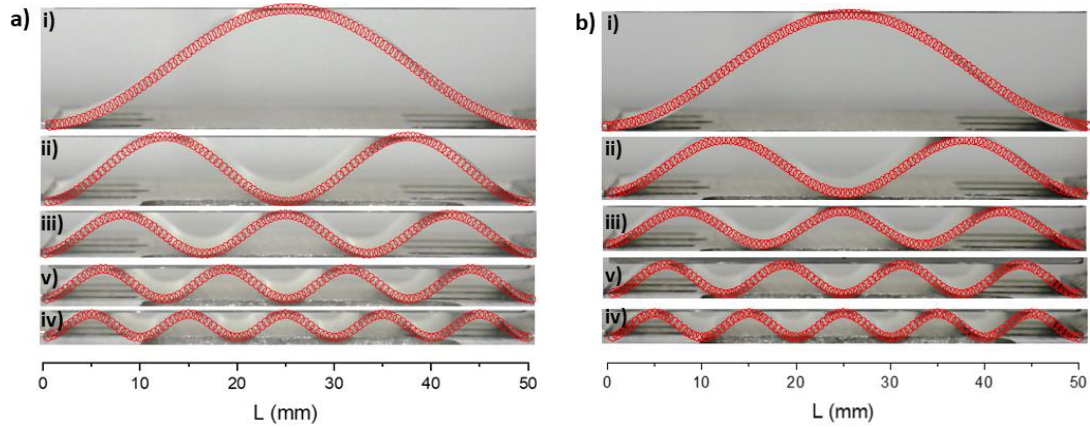


Figure 6-5. Modelling of the experimentally formed waveforms for two metallic glass foils of thicknesses a) 25 μm ; b) 40 μm .

6.3 Mechanism of undulatory behaviour

To understand the mechanism of undulatory behaviour, we must closely observe the shape changes of the foil under applied load.

Figure 6-6a shows an assembly of perfect sinusoidal arcs during undulatory behaviour.

Figure 6-6b shows a sequence of images indicating how the foil changes shape from 1 perfect sinusoidal arc to 2 perfect sinusoidal arcs. The mechanisms of undulatory behaviour involves elastic deformation, bending (flattening/stretching) and buckling of the metallic glass foils, which are the mechanisms that lead to an increase in the number of the sinusoidal arcs. This undulatory behaviour can be divided into three stages as shown in the transition from one to two perfect sinusoidal arcs, see Figure 6-6b;

- i) Bending / flattening,
- ii) Buckling, and
- iii) Post-buckling.

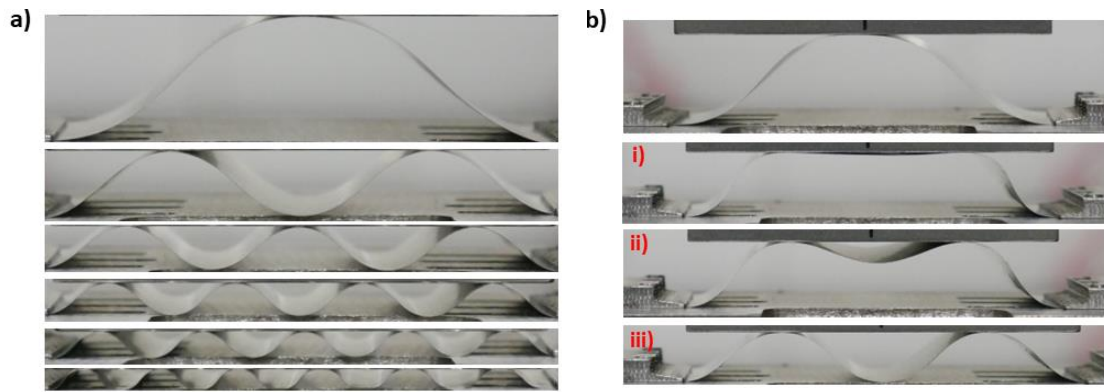


Figure 6-6: a) Assembly of snapshots from the undulatory behaviour with images of perfect sinusoidal shaped waveforms; b) assembly of snapshots of the transition from 1 to 2 perfect sinusoidal shaped arcs, where (i,ii and iii) are intermediate stages in the undulatory behaviour.

Upon loading, arc-shaped metallic glass foils deform elastically up to a specific value of load or displacement, this is followed by a distortion in the shape, a flattening of the arc (*i* in Figure 6-6b). When the foil reaches this load level, the shape of the foil becomes unstable, and that shape cannot carry any more load.

Pre-buckling refers to the flattening/bending where the applied load becomes critical ($P = P_{cr}$). Therefore, knowing the value of the elastic critical load (P_{cr}) is essential to determine the buckling resistance of the foil. The concept here is Euler buckling of a slender beam. The value of the critical load depends on the foil geometry and material stiffness (Young's modulus), but the strength of the material does not affect this critical theoretical value.

The foil will buckle when the applied load exceeds the critical load ($P > P_{cr}$). Under this condition, the shape of the foil changes, as can be seen in (ii) in Figure 6-6b. The initial stage of transition from one to two sinusoidal arcs, has only one flat section. In the case of multiple arcs, flat/or bending sections will exist at different points along the length. Euler's buckling theory suggests that a longer beam requires a lower uniaxial load to buckle. It is the longest flat section that buckles and forms a new ($n+1$) arc. However, for thin foils it is the boundary length conditions and the aspect ratio that are primarily responsible for the magnitude of the critical load.

With increase in displacement, post-buckling will occur just after the foil buckles to form a new (n_i+1) sinusoidal arc to complete the transition to the full sinusoidal shape representative of undulatory behaviour. In this case, post-buckling begins once the foil has begun to buckle, and ends in the new sinusoidal shape, see (iii) in Figure 6-6b. The details of the geometry and materials used for the model are given in Table 6-2.

Table 6-2. Dimension and materials used for the present analytical model in the parametric study.

<i>Length, L (mm)</i>	20	30	50
<i>Width, a (mm)</i>	25	25	25
<i>Thickness, d (μm)</i>	25	40	
<i>Height of arc, h (mm)</i>	5	6.5	12.5
Materials			
Ni ₇₈ B ₁₄ Si ₈		Fe ₄₀ Ni ₄₀ (BSi) ₁₉ Mo ₁	Fe _{90.65} B _{3.9} Cr _{2.75} Si _{2.7}
E (GPa)	150	E (GPa)	150

6.4 Buckling phenomena

Buckling mechanisms can be classified into elastic and inelastic. Upon removing the load, with elastic buckling the buckled structure returns to its original shape with no change in the cross-sectional area of the beams. On the other hand, inelastic buckling results in plastic deformation. A structure that buckles inelastically cannot return to its original shape upon unloading. This study focuses on the reversible deformation of metallic glass foil structures within the elastic limit, our focus is only on elastic buckling.

Among the most common and straightforward instability phenomena is Euler buckling, described in 1757 by Leonhard Euler, in which an elastic beam buckles under a sufficiently large compressive axial load [165]. This elastic buckling of a long slender beam subjected to an applied uniaxial load is illustrated in Figure 6-7.

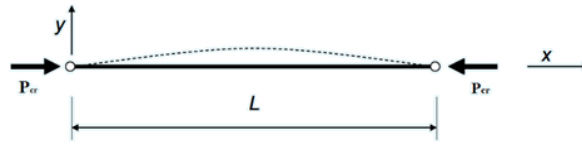


Figure 6-7. Beam element under applied load pre- and post-buckling.

The observed arc multiplication during the undulatory behaviour of glassy foils, as discussed in Chapters 4 and 5, is shown in Figure 6-1, which indicates that buckling of a thin section (flattened) foils is part of the undulatory behaviour mechanism. More specifically, most extended flattened sections can be considered to be possible buckling sources with formation of an additional arc.

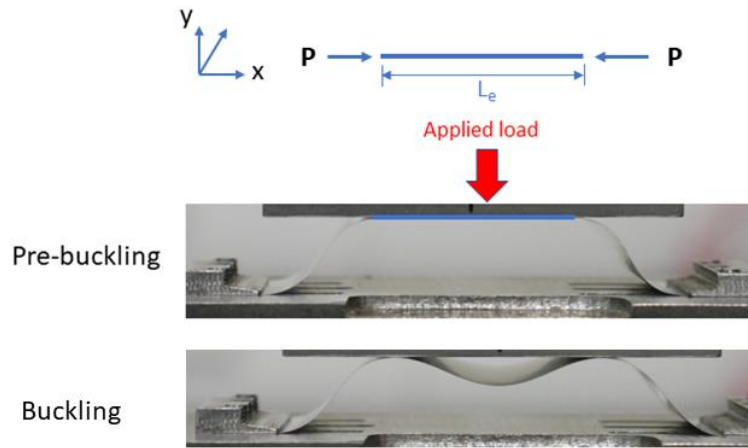


Figure 6-8. Buckling analysis of flat section during applied load.

The Euler formula is employed to find the critical buckling load (P_{cr}), with the effective length (L_e) for a buckling mode the longest flat section, see Section 6.3 and Figure 6-8. Equation (6-3) is the Euler formula used to analyse buckling behaviour:

$$P_{cr} = \frac{\pi^2 I E}{(KL_e)^2} \quad 6-3)$$

The elastic critical buckling load for flexural buckling, P_{cr} , is often referred to as the Euler load or critical buckling load. Where E is the Young's modulus of elasticity, K is a factor determined by the boundary conditions, L_e refers to the

actual unsupported length of the column/foil, and I is the second moment of area of the member about the minor axis, which is given by:

$$I = \frac{ad^3}{12} \quad 6-4)$$

Where a is the width of the foil and d is the thickness of the foil.

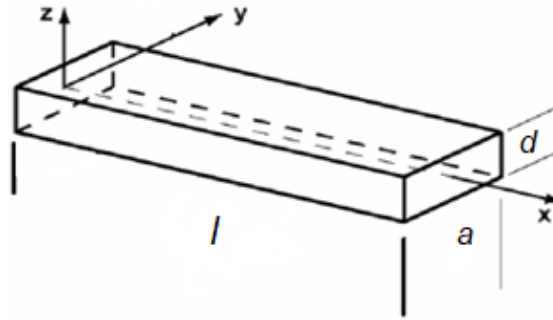


Figure 6-9. Sketch of the rectangular beam with dimensions.

An increasing applied normal load perpendicular to the foil (in the Xy plane) generates increasing reaction forces towards the ends of the flat section for a fixed-fixed boundary condition. The fixed-fixed boundary condition was selected because that is close to the manner in which the foils are fixed, see Section 6.4.1.

6.4.1 Boundary conditions

KL_e , is often referred to as the effective length or Euler length and is the length relevant for buckling.

Figure 6-10a presents K values from (0.7 to 1.0) suitable for fixed ends type structures and provides some general formulation on behaviour of various structural members [166]. The K value in our case is determined by the type of fixed boundary conditions with $K = 1$ for both ends pinned, $K = 0.5$ for both ends fixed and $K = 0.7$ for one end pinned, and one end fixed. However, post-buckling deflection characteristics for undulatory behaviour between pinned-pinned and fixed-fixed boundary conditions.

Therefore, the deflection characteristics of flat foil section fit the buckling profile of a fixed-fixed system with the undulatory behaviour of metallic glass foils showing a distinctive buckling mode when the effect of the geometric nonlinearity becoming decisive. Consequently, for the assumed fixed-fixed system, the K value is assumed to be $K = 0.5$, see Figure 6-10b.

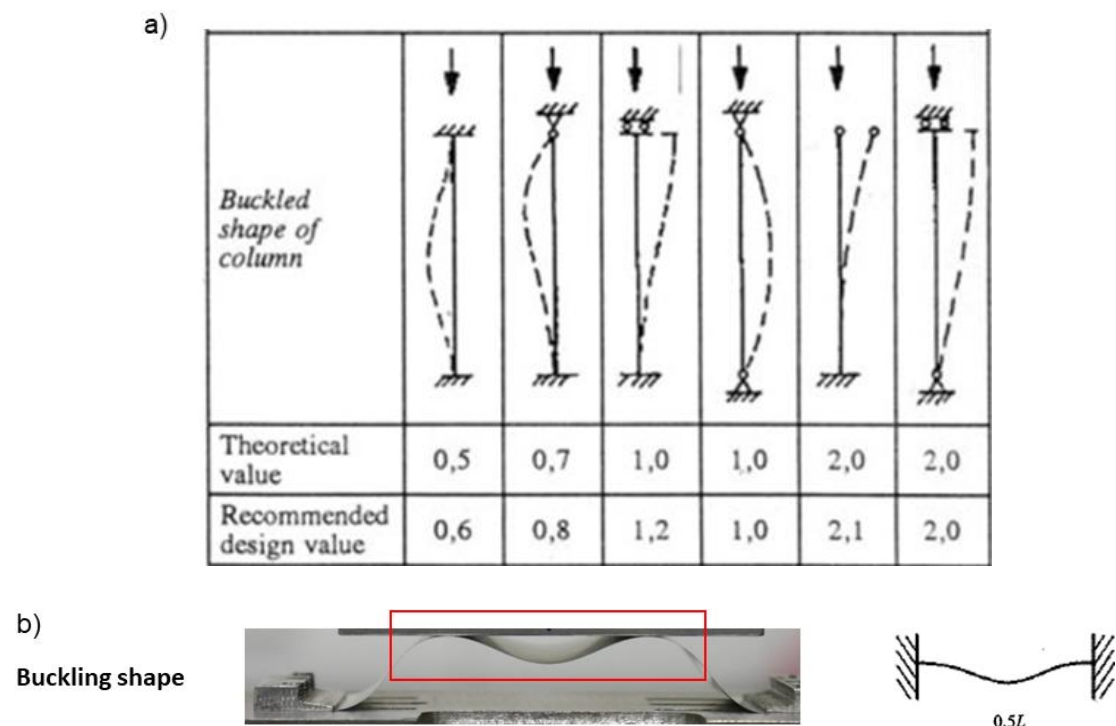


Figure 6-10: a) Theoretical design condition values suitable for a variety of structural members [166]; b) Buckling mode on metallic glass foil for fixed ends.

6.4.2 Buckling analysis of the glassy foils during undulatory behaviour

The analysis of buckling part on the undulatory behaviour uses an Euler formula to represent the distorted steps of buckling foils during undulatory behaviour. The three foil lengths, 20 mm, 30 mm and 50 mm, define the initial arc-shaped geometry of the MG foils and initial amplitude h_1 , where $h_1/L = 0.25$. The buckling phenomena during undulatory behaviour when a load is applied normally to the top of an arc-shaped MG foil, as shown in Figure 6-6b.

Predicting the critical buckling load of a thin foil under an applied load is a complex engineering problem that depends on various factors, including material

properties, geometry, boundary conditions, and loading conditions. Therefore, a combination of theoretical analysis and experimentation is often necessary to obtain reliable predictions for specific metallic glass foils of different thicknesses. In order to predict the critical buckling load of a thin foil under an applied load has been obtained for lengths of the same metallic glass foils of thicknesses 25 μm and 40 μm . The critical buckling load was calculated using the Euler formula Equation (6-3).

Therefore, the critical loads of the two metallic glass foils of the same material, 25 μm and 40 μm thick can be found by solving the two equations.

$$P_{cr1} = \frac{\pi^2 a_1 d_1^3 E}{12(KL_e)^2} \quad 6-5)$$

$$P_{cr2} = \frac{\pi^2 a_2 d_2^3 E}{12(KL_e)^2} \quad 6-6)$$

Where, the Young's modulus is the same for both foils 150 (GPa)

Both Equations (6-5) and (6-6) can be written in the form $P_{cr} = m(1/Le^2)$ to give a straight line plot with gradient m . For Equation (6-5) the gradient m_1 is:

$$m_1 = \frac{\pi^2 a_1 d_1^3 E}{12(K)^2} \quad 6-7)$$

And for Equation (6-6) the gradient m_2 is:

$$m_2 = \frac{\pi^2 a_2 d_2^3 E}{12(K)^2} \quad 6-8)$$

Hence, m_1 and m_2 can be found, and if we divide Equation (6-7) by Equation (6-8) we have:

$$\frac{m_1}{m_2} = \frac{\pi^2 a_1 d_1^3 E K^2}{K^2 \pi^2 a_2 d_2^3 E} \quad 6-9)$$

But the foils are of the same material so, $E_1 = E_2$ and the width is the same for both foils so $a_1 = a_2$, and hence:

$$\frac{m_1}{m_2} = \frac{d_1^3}{d_2^3} \quad 6-10)$$

The gradient m_i is a value that must be found by inspection from plotting the critical load as a function of Euler length.

We found, $m_1 = 192.8$ for Ni-based foil with 25 μm thickness and $m_2 = 789.6$ for Ni-based foil with 40 μm thickness.

It follows that a new gradient for the same foil material of the same width but different thickness, d_i , can be defined as:

$$m_i = \frac{m_1}{d_1^3} d_i^3 = \frac{m_2}{d_2^3} d_i^3 \quad 6-11)$$

Thus

$$\frac{m_1}{d_1^3} = \frac{\pi^2 a_1 E}{12 K^2} = \frac{m_2}{d_2^3} \quad 6-12)$$

The gradient of this line m_i is a value that must be found by inspection from plotting the critical load as a function of Euler length.

$$m_i = P_{cr} L_e^2 \quad 6-13)$$

Therefore, the buckling load for any gradient line can be found as follows:

$$P_{cr_i} = m_i \frac{1}{L_e^2} \quad 6-14)$$

The constant $\frac{\pi^2 a_1 E}{12K^2}$ in Equation (6-12) will have the value:

$$\frac{\pi^2 a_1 E}{12K^2} = 123.4 \times 10^6$$

Hence, Equation 6-10 can be put into the simple form:

$$m_i = 123.4 \times 10^6 d_i^3 \quad 6-15)$$

Equation (6-15) applies to all boundary conditions ($L=20$ mm, 30 mm, 40 mm, and 50 mm), but is limited to undulatory behaviour when the aspect ratio, $h_i = L/4$. Therefore, when analysing the buckling behaviour of metallic glass foils, it is essential to investigate the effect of both foil thickness and geometrical conditions. It is emphasised that the buckling analysis carried out thus far is only for understanding the mechanism of the undulatory behaviour of metallic glass foils.

6.4.2.1 Effect of foil thickness

Here the effect of the foil thickness on the buckling of the sinusoidal arcs is explored. Figure 6-11 shows that Ni-based foil has the highest buckling load, which increases as the thickness foil increases. The highest buckling load is obtained for 80 μ m foil, whereas the buckling loads are less as the thickness decrease, see Figure 6-11.

To determine the relationship between buckling load and Euler length, we plot P_{cr} against $(1/L_e^2)$, see Figure 6-11a. The first thing to notice is the straight line nature of the plots which is taken as strong confirmation of the arguments proposed above. As the thickness of a thin foil increases, the stiffness and buckling load increase accordingly. For boundary length, $L=20$ mm with an aspect ratio of $h_1=L/4$, the gradient found based on Euler formula is 123.4×10^6 . The values the

gradients observed for $L=20$ mm was for foil thicknesses of 1 nm, 10 μm , 25 μm , 30 μm , 40 μm , 50 μm and 80 μm representing high buckling load as long as foil thickness increased. Estimating the gradient for undulatory behaviour for the model under consideration occurs for pre-buckling of the foil on the load-displacement curve and was calculated using Equation 6-15.

For the longest boundary length, $L=50$ mm, the effect of the foil thickness can be seen in Figure 6-11b. A similar trend to that observed for $L=20$ mm was found.

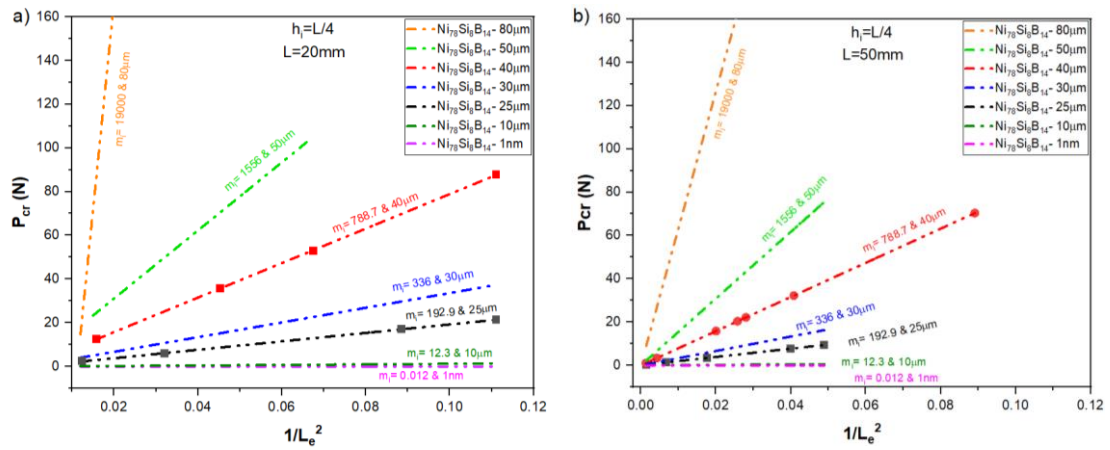


Figure 6-11: a) Critical load versus $1/(\text{Euler length})^2$ for different thicknesses foil for $L=20$ mm; b) critical load versus $1/(\text{Euler length})^2$ for different thicknesses foil for $L=50$ mm.

6.4.2.2 Effect of material type

The local buckling of thin foils of different materials is derived for the condition of constant of the foil. The validity of the results obtained from the solution for various materials. Considering foils of the same thickness but different Young's modulus Equation 6-9 becomes:

$$\frac{m_1}{m_2} = \frac{E_1}{E_2} \quad 6-16)$$

The gradient for a new material m_i can be depicted as follows:

$$m_i = \frac{m_1}{E_1} E_i \quad 6-17)$$

$\frac{m_1}{E_1}$ is a constant and equal to:

$$\frac{m_1}{E_1} = \frac{\pi^2 a_1 d_1^3}{12k^2} \quad \mathbf{6-18)}$$

Hence:

$$\frac{m_1}{E_1} = 1.285 \times 10^{-3}$$

Hence, Equation 6-17 can be re-written for constant thickness:

$$m_i = 1.285 \times 10^{-3} E_i \quad \mathbf{6-19)}$$

Note that Equation 6-18 applies to all boundary conditions; $L = 20$ mm, 30 mm, 40 mm, and 50 mm, with the characteristic buckling load for the undulatory behaviour based on the aspect ratio of ($h_1=L/4$).

Figure 6-12 shows excellent agreement between two results from critical buckling load as function of Euler length for both boundary conditions of undulatory behaviour. Accordingly, the derived equation is certainly capable of predicting the local buckling of material types with very high accuracy, which is extremely useful as it is a useful contribution to knowledge of the undulatory behaviour of arc-shaped MG foils. The effect of material type is initially examined by varying Young's modulus while keeping all other parameters (d , a) constant, as given in Table 6-2. As a result, we used the theoretical value to examine the effect of changing Young's modulus for the same foil thickness, of $25 \mu\text{m}$. Figure 6-12a and Figure 6-12b show that the critical buckling load increases linearly with the increase of Young's modulus for different values (i.e. 64 , 100 and 150 GPa).

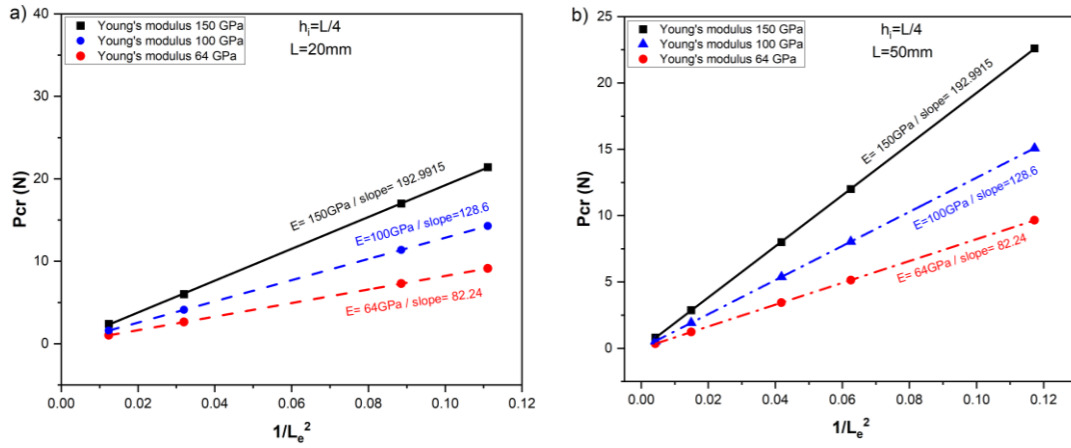


Figure 6-12: Effect of the Young's modulus a) the variation of the critical buckling load at $L=20$ mm for different metallic glass foils when thickness is kept constant; b) variation of the critical buckling load at $L= 50$ mm for different metallic glass foils when thickness is kept constant (25 μ m thick).

6.4.2.3 Applied load

In the previous sections, the thickness and the Young's modulus of the foils were found to influence critical buckling load. In this section, the critical buckling load will be used to determine the applied load in order to determine the relationship between critical load and applied load. Figure 6-13 shows a linear relationship between critical buckling load and the applied load (N_i). Thus, the critical load P_{cr} was found to be a function of the applied load, which could be described by a linear relation of the type $y = mx$, where m is the gradient can be calculated from Equation 6-14 is:

$$P_{cr_i} = n_i N_i = m_i \frac{1}{L_{e_i}^2} \quad 6-20)$$

Thus, the critical load as a function of applied load (N) for a given thickness can be stated as:

$$P_{cr_1} = \frac{\pi^2 a_1 d_1^3 E_1}{12 K^2} \left(\frac{1}{L_{e1}^2} \right) = n_1 N_1 \quad 6-21)$$

$$P_{cr2} = \frac{\pi^2 a_2 d_2^3 E_2}{12 K^2} \left(\frac{1}{L_{e2}^2} \right) = n_2 N_2 \quad 6-22)$$

We assumed that by using the same material of the same width, $E_1=E_2$ and $a_1=a_2$, and with Euler length the same ($L_{e1}=L_{e2}$), as shown in Section 6-2 (Figure 6-5). Hence, dividing (6-21) by (6-22) gives:

$$\frac{P_{cr1}}{P_{cr2}} = \left(\frac{d_1}{d_2} \right)^3 \left(\frac{L_{e2}}{L_{e1}} \right)^2 = \frac{n_1 N_1}{n_2 N_2} \quad 6-23)$$

Hence, equation 6-23 can be expressed as follows:

$$\left(\frac{d_1}{d_2} \right)^3 = \frac{n_1 N_1}{n_2 N_2} \quad 6-24)$$

If the constants n_i are identified, then it is possible to calculate critical load, P_{cr} , from the applied load N and vice versa, using:

$$P_{cr} = n_i N_i \quad 6-25)$$

Figure 6-13 shows the calculated critical load as a function of applied load for number of arcs for two boundary lengths ($L=20$ and 50 mm) for different types of glassy foils. The critical buckling load shows a linear increase with increase in applied load. The constant (n) for Ni-based glassy foil of $25 \mu\text{m}$ thickness with boundary length ($L=20$ mm) is around 0.15 . Further, the Ni-based glassy foil of $40 \mu\text{m}$ thickness for the same boundary length ($L=20$ mm) exhibits a higher (n) constant of around 0.318 .

To find the applied load for different foil thickness from Equation (6-24), was not possible due to there being two values unknown. As the applied load is not the same for different foil thicknesses.

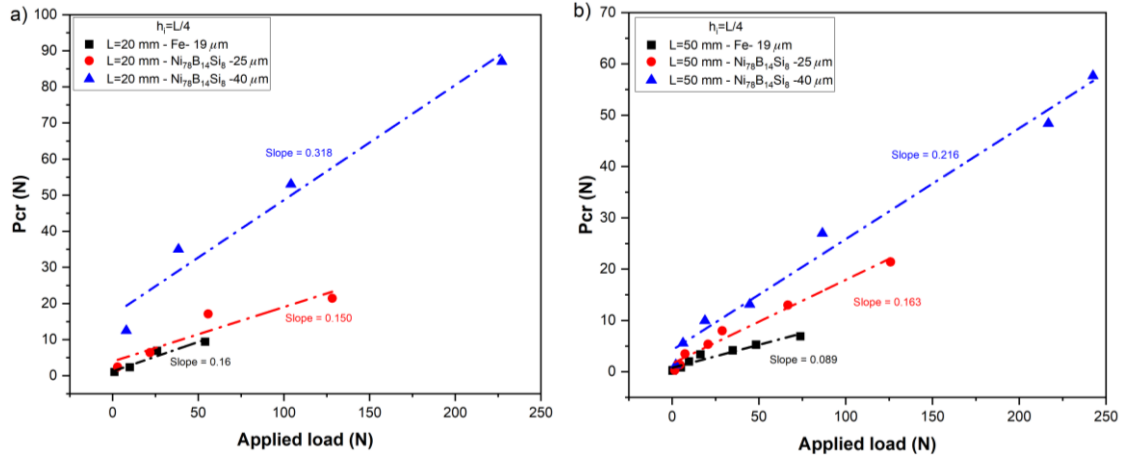


Figure 6-13. Critical load P_{cr} as a function of applied load for glassy foils a) boundary length $L=20$ mm; b) boundary length $L=50$ mm.

Figure 6-14a shows the calculated applied load (N_1) of Ni-based glassy foil of 25 μ m thickness versus applied load (N_2) of Ni-based glassy foil of 40 μ m thickness, each for boundary lengths $L=20$ mm. The applied load (N) values show a linear relationship between the applied loads with gradient 1.90. Similarly, Figure 6-14b shows the applied load for the Fe-based alloy of 19 μ m thickness versus applied load for the Ni-based alloy with 25 μ m, again with a boundary length of 20 mm. Again, we see a linear relationship, this time with gradient 1.87.

Thus, the gradient shows little variation with foil thickness. The applied load could not be estimated using Equation (6-24) due to the absence of constant values for different thicknesses of foil, so it was not able to estimate the applied load to each foil thickness unless one of the applied load measurement data is obtained to calculate the new applied load (N_i) for the new foil thickness.

Further work needs to be done to model the effect of the applied load on the undulatory behaviour of the metallic glass foils. However, the applied load on the Ni-based foils of 25 μ m and 40 μ m thickness, respectively were for similar conditions. In both cases of boundary lengths being tested, the applied load as a

function of number of arcs can be described by exponential relations of the type $F = \alpha x^\beta$. Where α and β are constants (depending on the foil thickness), and x is the number of arcs.

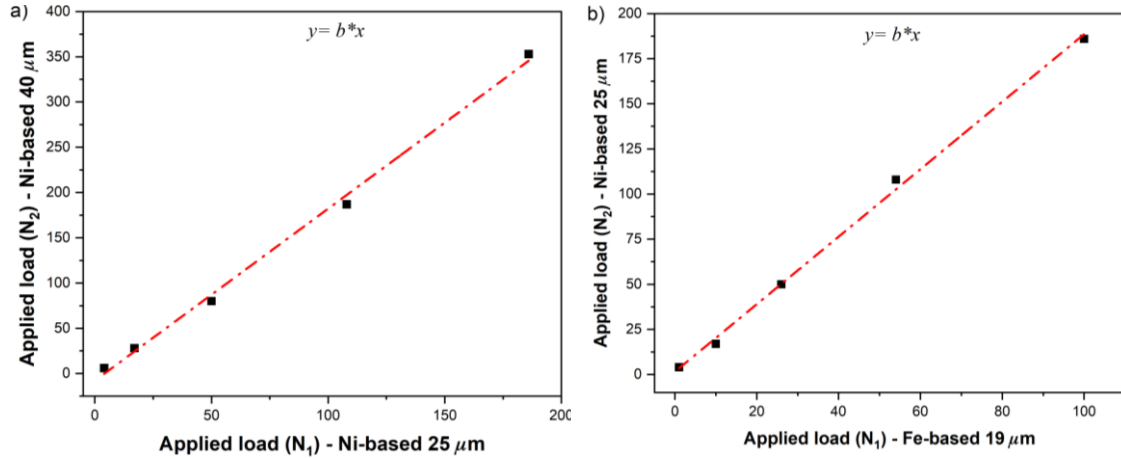


Figure 6-14: Measured applied load (N_i) where buckling occurs for a) different foil thicknesses of the same materials; and b) different foil thicknesses and different MG foil.

6.4.3 Working range of spring design

Design of compression springs (non-linear springs) require a number of considerations. As a first step in establishing a custom spring design, it is important to understand load, geometry, and thickness are essential considerations in setting up a customised spring design.

6.4.3.1 Compression spring

The dimensions, with load and displacement, determine the strain in the spring. When an arc-shaped spring is loaded, the metallic glass foil is strained in pre-buckling mode before a new arc forms. The strain is maximum at the transition from (n) to $(n+1)$ sinusoidal arcs; as the spring buckles, the load varies, producing a range of operational strains. Strain and applied load range govern the life of the spring. The higher the applied load range, the maximum local strain must be such as to provide a reasonable life.

In designing springs, the space allotted governs the geometrical limits, but the operating range of the spring is the most significant factor. These geometrical

limits, together with the applied load requirements, determine the strain level. To avoid costly design changes, the load/displacement range must be carefully considered to ensure that the spring works properly from the start. Table 6-3,

Table 6-4 and

Table 6-5 present the working load/displacement range for three metallic glass foils, along with the geometry of spring setup.

Table 6-3. Work range of metallic glass foil spring for boundary length $L=20$ mm

Metallic glass foil	Boundary lengths L	Amplitude h	Width w	Max-Working load (N)	Max-displacement (mm)
Fe-based	20	5	25	100	4.30
Ni-based- 25 μm	20	5	25	186	4.15
Ni-based- 40 μm	20	5	25	186	4.00
NiFe-based- 25 μm	20	5	25	170	4.15

Table 6-4. Work range of metallic glass foil spring for boundary length $L=30$ mm.

Metallic glass foil	Boundary lengths L	Amplitude h	Width w	Max-Working load (N)	Max-displacement (mm)
Fe-based	30	7.5	25	140	6.48
Ni-based- 25 μm	30	7.5	25	226	6.37
Ni-based- 40 μm	30	7.5	25	313	6.46
NiFe-based- 25 μm	30	7.5	25	114	6.5

Table 6-5. Work range of metallic glass foil spring for boundary length $L=50$ mm.

Metallic glass foil	Boundary lengths L	Amplitude h	Width w	Max-Working load (N)	Max-displacement (mm)
Fe-based	50	12.5	25	167	11.31

Ni-based- 25 μm	50	12.5	25	257	11.29
Ni-based- 40μm	50	12.5	25	330	11.20
NiFe-based- 25 μm	50	12.5	25	309	11.45

6.4.3.2 Compression spring set

When a load is applied normally on the top of an arc-shaped thin foil of metallic glass and released, the is supposed to return to its original shape, i.e., any displacement point should remain below an elastic deformation of 2% strain and any load within specified load limits. When a MG foil spring is made and then loaded, if the load on the foil generated a strain higher than 2%, the spring will not return to its original shape.

Therefore, the 2% strain is referred to as a set point in spring design and arc-shaped MG foils may deform plastically if this limit is exceeded during loading/unloading. In beam theory, the strain, ε , during curved beam bending is inversely proportional to the twice radius, which can be obtained as [127]:

$$\varepsilon = \frac{d}{2R} \quad \text{6-26)}$$

Figure 6-15 shows a beam being subjected to a load, resulting in bending of the beam. The stress and strain experienced at the neutral axis is zero, while the curved beam experienced maximum tension at the top and maximum compression at the bottom. The highest strain has the smallest radius of arc curvature, and the maximum strain occurs just before buckling and transition from (n) to ($n+1$) sinusoidal arcs. Maximum strains in metallic glass foils were found in these regions and these can be determined for metallic glass foils using Equation (6-26).

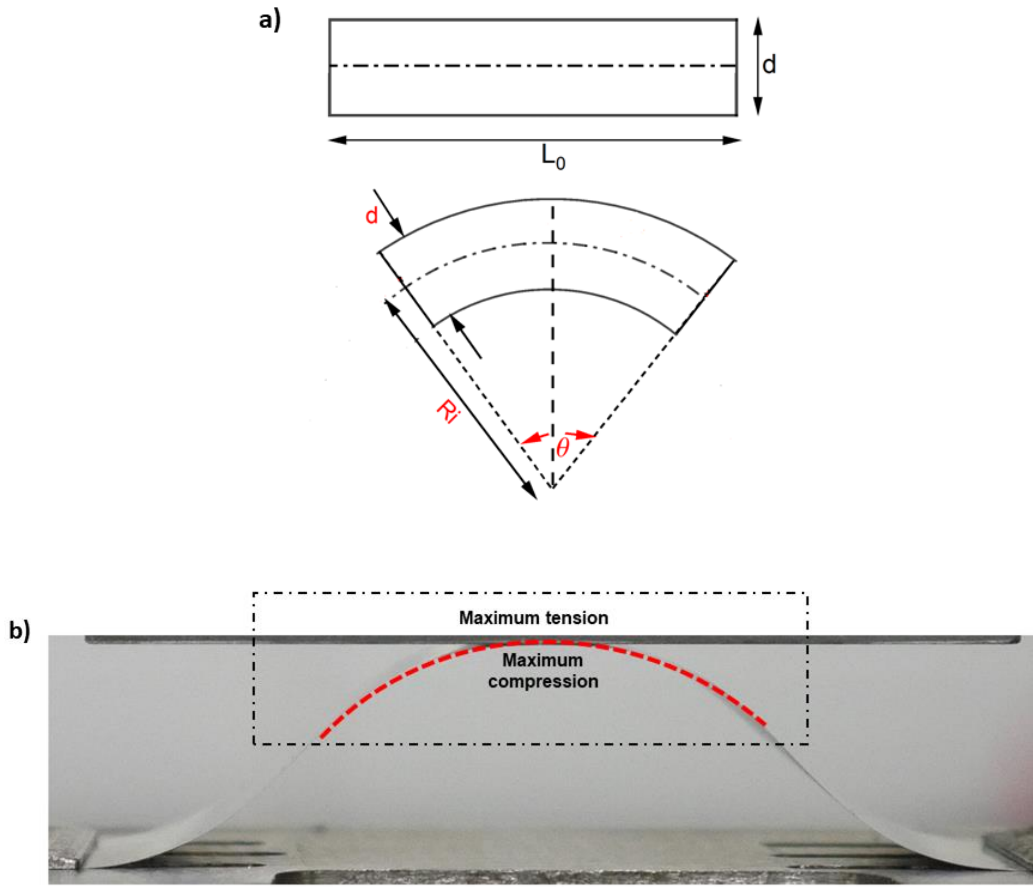


Figure 6-15: a) curved beam bending shows areas of compression and tension; b) maximum strain on arc-shaped MG foil.

6.4.3.3 Foil thickness

The results presented above show that the thickness of foils affects the load required for the transition from a lower order (n arcs) to a higher order (n_i+1 arcs). However, as stated above the strain is not uniformly distributed along the foil; it is a where the foil exhibits the smallest radius of curvature.

Figure 6-16 presents the diameter of curvature upon loading for an arc-shaped Ni-based metallic glass foil, 25 μm thick and a Ni-based foil, 40 μm thick. Both foils were long $L = 20$ mm with $h_1 = 5$ mm. By applying Equation (6-26) the local strain is estimated at the maximum distortion just prior to the formation of a new arc (n_i+1) which here is the transition from 5 to 6 sinusoidal arcs for the thinner foil, but from 4 to 5 arcs for the thicker foil. Therefore, for a deformation corresponding to the elastic limit of metallic glass ($\sim 2\%$) strain.

$$2R_{min} = \frac{d}{\epsilon} \quad 6-27)$$

Where R_{min} is the minimum radius of curvature.

For a given metallic glass foil, using Equation (6-26), we can estimate the maximum number of sinusoidal arcs at which we can expect undulatory behaviour for spring setup geometry while remaining the elastic region. The two metallic glass foils studied are shown in Figure 6-16 with thicknesses of 25 μm and 40 μm which give a minimum elastic radius of curvature of 0.625 and 1 mm, respectively. For this spring setup geometry, no bend with a radius greater than these values should produce plastic deformation. Note that in the figure it is the diameter of curvature that is presented. Here we consider how the mechanical response of the foil under loading is affected by the thickness, how the thickness of the foil governs the operating range of the spring design system.

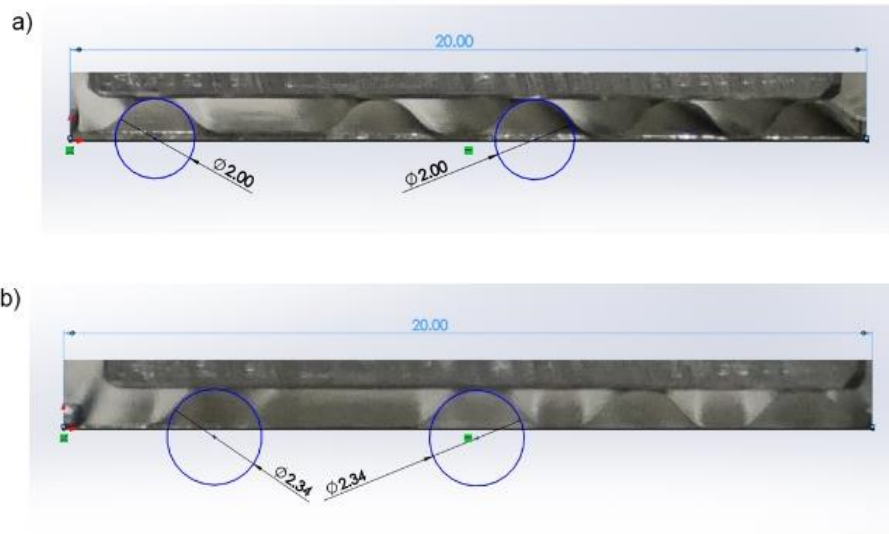


Figure 6-16: Maximum local strain of waveforms with distorted arcs, just before the formation of a (n_i+1) new arc, equivalent to $(P_{cr}=P)$ critical buckling load a) for Ni-based with 25 μm , the transition from 5 to 6 arcs more than 1.25 mm diameter; b) for Ni-based with 40 μm , the transition from 4 to 5 arcs more than 2 mm for curvature diameter.

6.4.3.4 Spring length

In the spring design, the length of the spring, L_{spring} , is a geometrical parameter that must be taken into account; a specific length of device can be designed based on the space in which the spring will operate, i.e., determining the maximum number of arcs for different thicknesses. The spring length would be a function of foil thickness using Equation (6-26). As we know, the maximum permitted elastic deformation of metallic glass foils is 2% strain and the minimum radius of curvature R_{min} should be equal to or greater than 25 times the foil thickness to remain in the elastic region, as can be depicted in equation (6-28).

$$R_{min} = 25d \quad 6-28)$$

Thus, the length of the spring L_{spring} can be calculated as follows:

$$L_{spring} = 2R_{min}n_i \quad 6-29)$$

Where R_{min} is the minimum radius of curvature and n_i is the number of arcs along the foil length. Substituting R_{min} for we have:

$$L_{spring} = 50dn_i \quad 6-30)$$

Where d is the foil thickness.

Figure 6-17 shows the spring length for different foil thicknesses. The thinner foils show a higher number of arcs compared to the thicker foils. Therefore, the maximum number of arcs can be estimated based on device length and foil thickness. Thus, we see in Figure 6-16, the $L = 20$ mm Ni-based foil of thickness $25 \mu\text{m}$ showed 6 sinusoidal arcs, while for thickness $40 \mu\text{m}$ the foil showed 5 sinusoidal arcs.

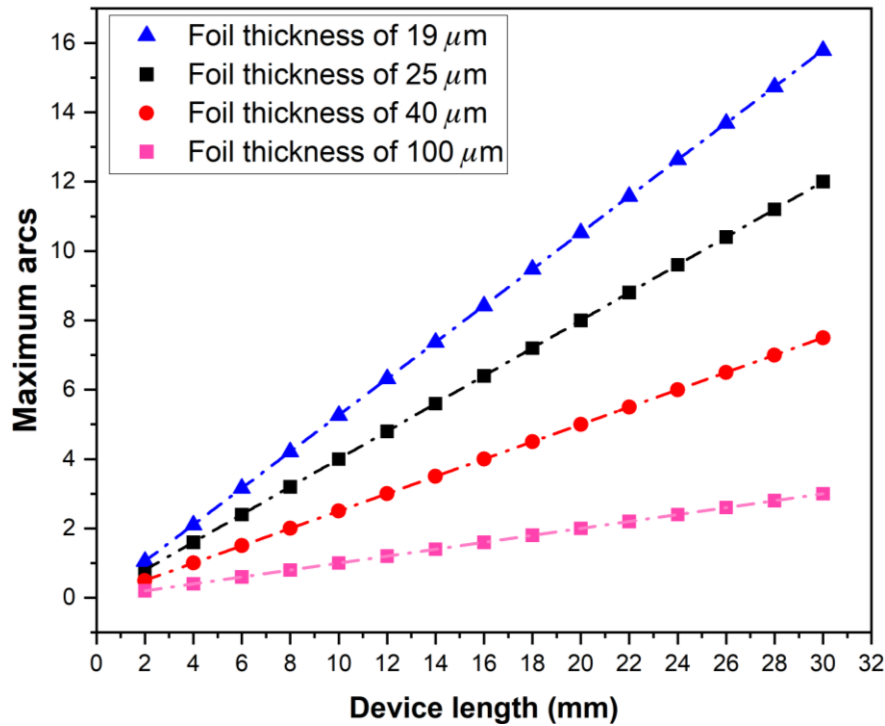


Figure 6-17. Spring length as a function of foil thickness.

However, there are additional design considerations that must be taken into account when designing spring, such as selecting the appropriate material (in terms of Young's modulus and thickness), the geometry setup of the spring (h and L), any work and overload requirements. In addition, fatigue cycle life is considered a significant factor in designing springs. More details on the fatigue cycle life of metallic glass foils can be found in Chapter 7.

6.5 Conclusions

The mechanism of undulatory behaviour and the pathway to arc multiplication were studied; the main phenomena occurring include bending, buckling and post-buckling in a repeatable manner. The Euler equation was used to analyse the buckling critical load during the undulatory behaviour. A modified expression of the standing wave equation was found to describe well the waveforms where the foil exhibits only perfect sinusoidal arcs. In constraint, it cannot describe waveforms with distorted shapes. Even though this Equation does not give information on the applied load within undulatory behaviour, it can still be a

valuable tool in designing any spring set-ups. Furthermore, it can generate unlimited waveforms of sinusoidal arcs as it does not restrict to metallic glass foils limitation of 2% strain. With increasing the foil's thickness, the required load cause bending and buckling to increase; however, plastic deformation would be reached earlier (in terms of the number of arcs) compared to thinner foil. Thicker metallic glass foils may have a higher resistance to buckling but can reach plastic deformation, indicated by shear band formation, at an earlier stage compared to thinner foils due to the increased volume available for shear band development.

7 Fatigue behaviour of metallic glass foils

7.1 Introduction

The fatigue life of metallic glass foils is limited as the cyclic loading can be performed with different combinations of process parameters which all affect the number of arcs formed, the thickness of foil, crack initiation, surface roughness and stress concentration during cyclic loading of metallic glass foils. Therefore, in the current chapter, the cyclic lifetime of metallic glass foils has been studied.

Fatigue resistance is a significant issue related to MGs as structural materials, which is very important for practical application. The stress-life (S-N) approach has been widely used in past decades to evaluate MG fatigue properties [167][134][147][168][2][169]. The early fatigue data of $\text{Fe}_{90.65}\text{B}_{3.9}\text{Cr}_{2.75}\text{Si}_{2.7}$ (wt. %) thin MG foil showed that the fatigue endurance limit for $L = 20$ mm with 3 sinusoidal arcs is around 7×10^3 cycles based on maximum strain, which is around 30 N applied load. Compared with another foil for a similar boundary length $L = 20$ mm the fatigue endurance limit with 4 sinusoidal arcs was 5×10^3 cycles [2]. The fatigue ratio is much lower than that in crystalline counterparts. In addition, the fatigue results of other metallic glass foils based on the number of waves of sinusoidal arcs formed also reveal the scatter of fatigue ratio, varying over a wide range from 7×10^3 to 1.5×10^3 cycles [2]. Due to various factors such as boundary conditions, thickness of the foil.

Metallic glass foils display lower fatigue ratios than predicted because of chemical composition [170], microstructure [147][171][172], loading modes [173][2], surface quality [2], and other concerns. The microstructure of MGs foil is an intrinsic factor determining its fatigue property. Clarifying fatigue failure mechanisms is the first step toward improving the fatigue performance of MGs ribbon. The plastic deformation media and failure origin of MG foils are localised shear bands. Additionally, shear bands make MG foils prone to fatigue damage and fracture.

Yousfi et al. reported two types of cracks in the fatigue limit of MG foils. The difference results from the microstructure change induced by the casting process

and defects on the surface of the specimen, leading to a significant difference in fatigue life [2]. The second type of crack induced by the cutting process of the foils, which is observed at the side edge of foils and shear step on the surface of the foils, is one of the main origins of fatigue crack initiation [2]. Yousfi et al. conducted loading/unloading cyclic fatigue experiments of Fe-based MG and observed shear banding morphologies near the fracture surface. The origin of fatigue crack initiation cannot be determined, however, because fatigue fractures may produce observed shear bands. Wang et al. carried out compression-compression tests on Zr-based MGs. They showed that fatigue cracks form and grow from the shear bands under maximum compressive cyclic stress, lower than the elastic limit, which shows that the shear band is the source of fatigue cracks at high stress levels [174].

In this chapter, systematically investigated metallic glass foils, including Fe-based, NiFe-based and Ni-based MG foils under cyclic loading using visual observation of fatigue behaviour. Thus, the primary aim of this chapter is to ascertain the fatigue life of metallic glass foils under cyclic loading conditions. Furthermore, it investigates the underlying mechanisms governing fatigue life, particularly in relation to crack formation, which ultimately culminates in failure.

7.2 Results and discussion

7.2.1 Cyclic lifetime tests of Fe-based metallic glass foils

The fatigue results for the Fe-based MG samples under loading/unloading cyclic tests are presented in Figure 7-1 with various boundary lengths L in the range of (20 to 50) mm for working load range of up to 80 N. The number of cycles to failure, the fatigue life, differs with the number of sinusoidal arc modes. The fatigue endurance limit of a boundary length of 20 mm with 3 sinusoidal arcs appears to be 8475 cycles compared 4210 and 1002 cycles for 4 sinusoidal arcs and 5 sinusoidal arcs, respectively. The results in Figure 7-1 indicate a similar fatigue life for Fe-based foil to that obtained by Yousfi, et al., [2].

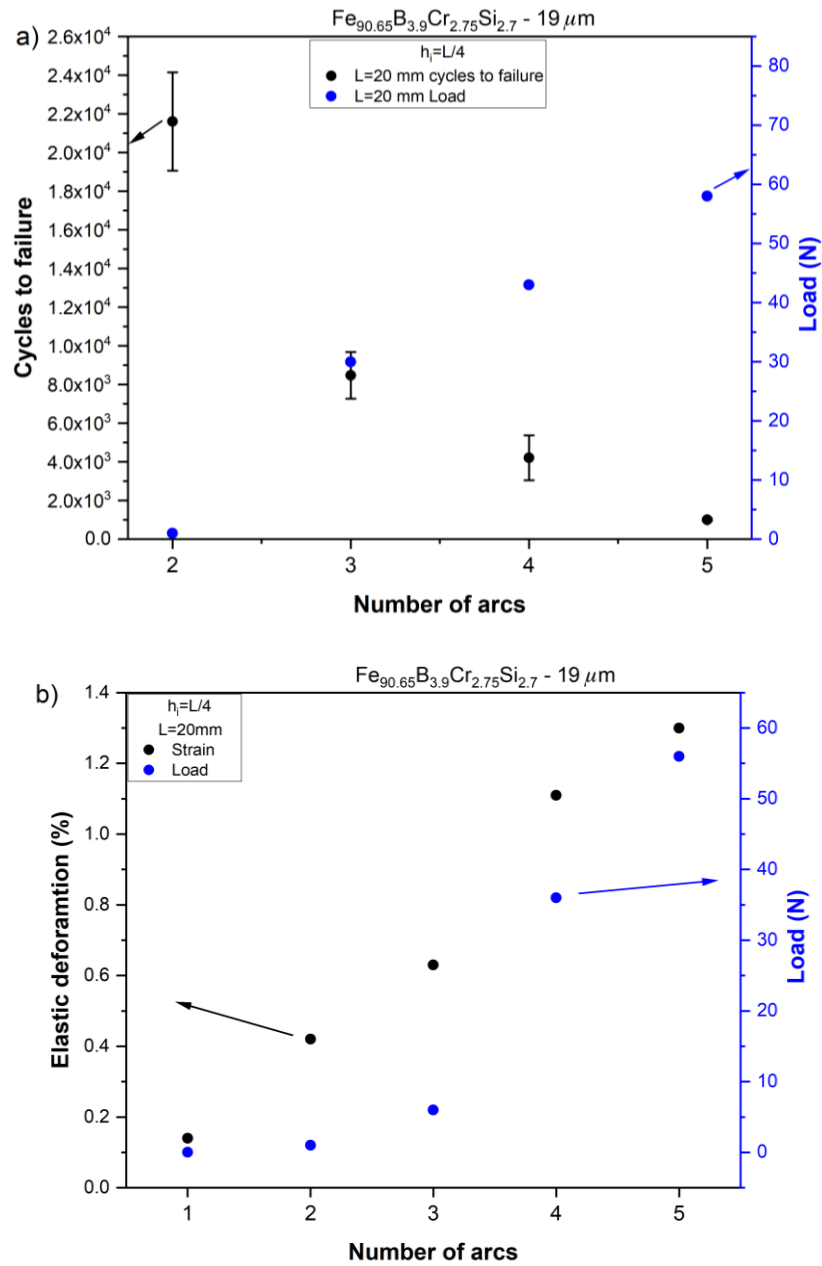


Figure 7-1: a) Cycles to failure of metallic glass foils during fatigue tests and the corresponding load as a function of the maximum number of arcs; b) strain developed of foil deformation during the formation of additional arcs.

The present study investigated the lifespan of Fe-based MG foil with boundary length of $L = 20$ mm, and number of sinusoidal arcs in the range from 2 to 5. The fatigue life with 2 sinusoidal arcs was 27075 continuous compression cycles to failure with a load of up to 1 N. The fatigue life for 3 sinusoidal arcs under the same conditions was 8475 cycles, for 4 sinusoidal arcs 4210 cycles, and for 5

sinusoidal arcs the number of cycles to failure was 1002. However, there was a significantly larger scatter in the results for 2 and 3 sinusoidal arcs, compared to 4 and 5 sinusoidal arcs.

The life cycles of a thin foil of MG can be plotted as a function of the maximum number of arcs, with the relationship between the number of arcs and cycles to failure expressed as maximum strain around arc formation, as shown in Figure 7-1. However, in the current study, tests to determine the fatigue life in terms of cycles of MG foils was carried out at various boundary lengths, $L=20, 30$ and 50 mm. It was found that the lifespan of MG foils for different boundary lengths follows the same relationship.

The cyclic loading range for fatigue life is measured assuming perfectly sinusoidal arcs. Cyclic loading from an initial single sinusoidal arc to 3 sinusoidal arcs, is shown in Figure 7-2, note that the local strains causing changes in the number of

arcs are taken at the point when the shape of the foil is distorting and about add an additional arc, see R_2 in Figure 7-2.

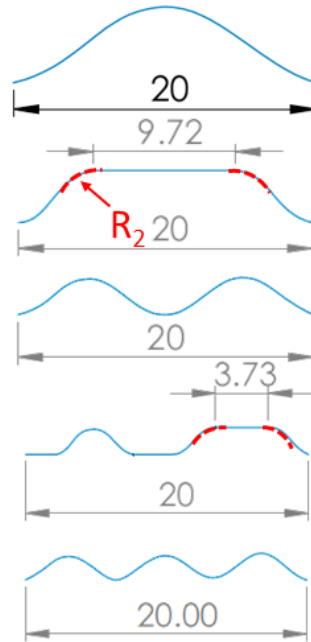


Figure 7-2. A perfect sinusoidal arc-shaped cyclic loading is used to measure fatigue life.

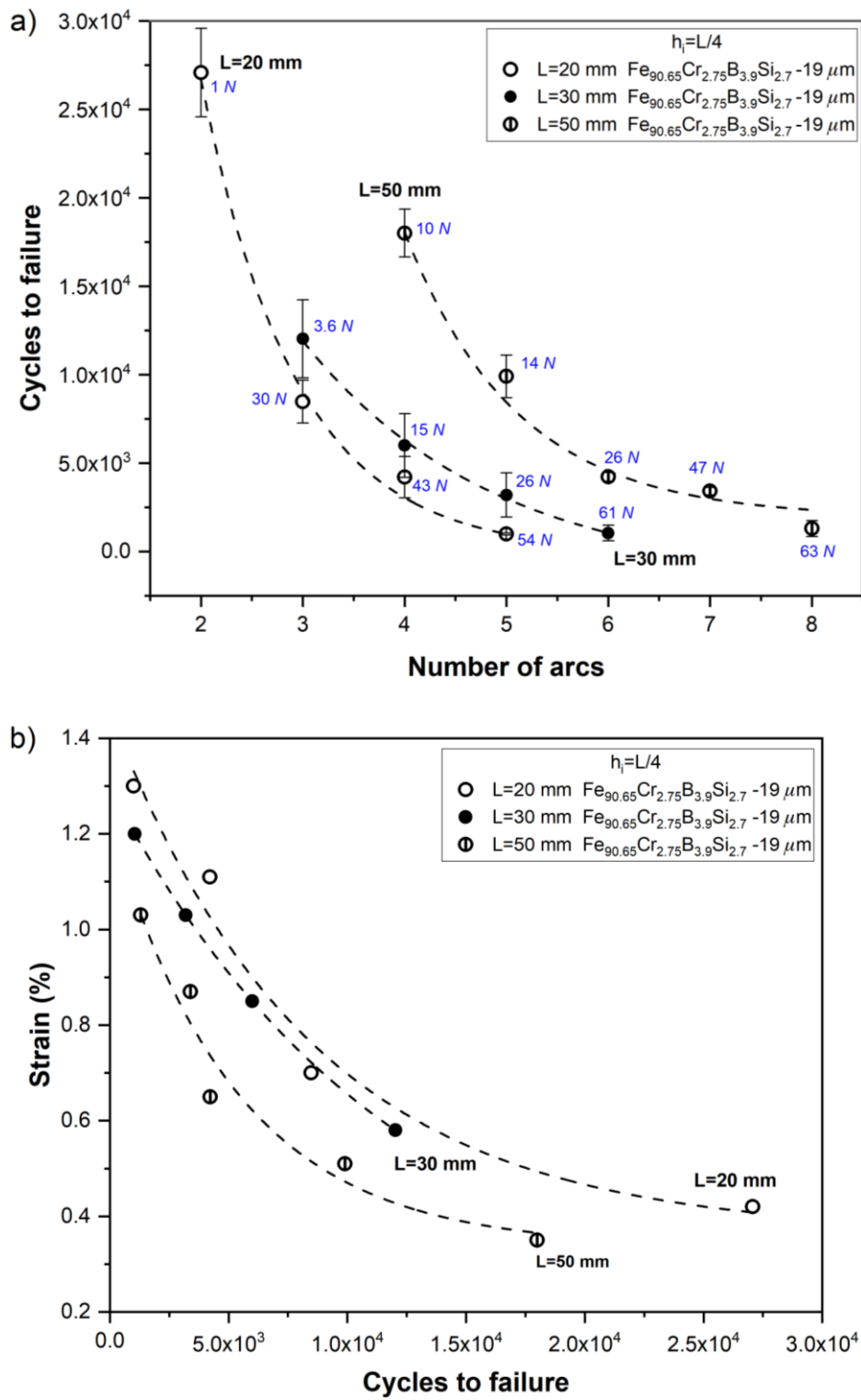
The cyclic loading to failure for Fe-based MG foil with boundary length $L=50$ mm with $h_f = L/4$ was conducted with 4, 5, 6, 7 and 8 arcs, see Figure 7-3a. The number of cycles to failure for 4 sinusoidal arcs, formed at a load of 10 N was 18000. For, 5, 6, 7 and 8 arcs formed at loads of 14, 26, 47 and 63 N respectively had lifespans of 9900, 4222, 3417 and 1300 cycles, respectively. The MG foils subject to higher strains caused by greater loading failed earlier than foils subject to lower strains. For instance, for foils of length $L=50$ mm, the strain increased from 0.35% to 1.03% when transformed from 4 to 8 arcs. Table 7-1 presents the fatigue endurance limit for Fe-based MG foils for three boundary lengths and a range of sinusoidal arcs.

Table 7-1. Summary of experimental results and details of fatigue endurance limit for Fe-based glassy foil (N_f , cycles to failure; STD standard deviation).

Sinusoidal arcs	Fe-based (19 μm)				
	Boundary lengths L (mm)	N_f	STD	Strain (%)	Load (N)
2	20	27075	2546	0.42	1
3	20	8475	1209	0.55	30
4	20	4210	1165	1.1	43
5	20	1002	54	1.3	57
3	30	10050	1700	0.65	3.65
4	30	7000	3827	0.85	15
5	30	4850	1899	1.03	26
6	30	1412	448	1.2	61
4	50	18000	1350	0.35	10
5	50	9900	1200	0.51	14
6	50	4222	255	0.65	26
7	50	3417	213	0.87	47
8	50	1300	458	1.03	63

Figure 7-3b presents cycles to failure versus strain amplitude for three lengths of Fe-based MG foil of the same width and thickness. It was found for all three lengths that the lower the strain the greater the number of cycles to failure, and vice versa. Figure 7-3c shows the cycles to failure as a function of applied load for the three samples of Fe-based MG. The three curves can be described by an exponential function of the type $F(x) = \exp(x)$, where x is the number cycles to failure, which depends on the initial arc geometry. It would be expected that different materials would follow different curves with the same general shape.

Figure 7-3d presents maximum local strain in the three foils at maximum distortion of the arc-shape for Fe-based MG foils as a function of the number of arcs.



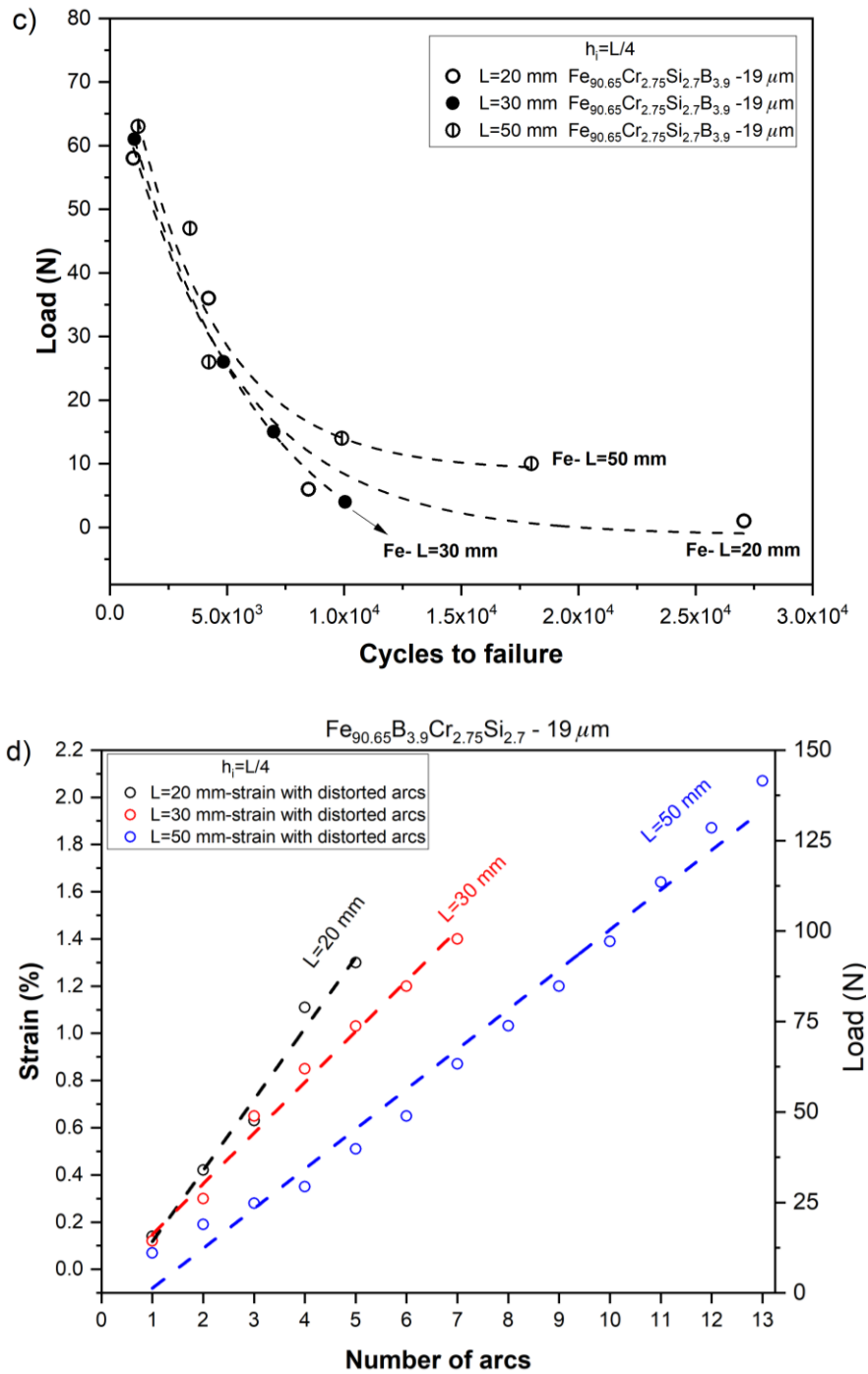


Figure 7-3: a) cycles to failure for three conditions of MG foils; b) strain amplitude versus cycles to failure on three conditions of Fe-based metallic glass foils; c) working range for fatigue test versus cycles to failure of Fe-based metallic glass foils; d) strain developments with distorted arcs during cycles loading.

7.2.2 Fatigue behaviour of other metallic glass foils

This project is the first to study Ni-B-Si, and Ni-Fe-B-Si-Mo foils of 25 μm thicknesses. For comparison corresponding data for the Fe-based foil (19 μm thick) and the Ni-B-Si, and Ni-Fe-B-Si-Mo foils are shown in Figure 7-6. Note that all three foils had $L = 20\text{ mm}$, $h_1 = 5\text{ mm}$ and aspect ratio $h_l = L/4$.

Figure 7-4a shows cycles to failure for the three MG foils. The result from cyclic loading for the Ni and NiFe-based foils are limited to 2, 3 and 4 arcs due to a constrained applied load, but the results for the Fe-based foil also includes 5 arcs. The number of cycles to failure for 2 arcs for all three materials, was 19.10×10^3 cycles for Ni-based foil and 25.80×10^3 cycles for NiFe-based foil. While the number of cycles to failure (at which crack initiation occurred) for 2 sinusoidal arcs of Fe-based foil was much higher compared to all glassy foils, about 27×10^3 cycles. Similar behaviour is observed for all three glassy foils, where the cycles to failure decrease quasi-exponentially with increasing strain. It is noted that the thinner Fe-based foil failed at a higher number of cycles than the thicker NiFe-based and Ni-based foils, 8.47×10^3 cycles, compared to 6.75×10^3 and 5.07×10^3 cycles, respectively for 3 arcs. However, increasing the load to form 4 arcs, cracking initiation was observed in all three foils at a much lower number of cycles, 546 for the Ni-based foil, 840 for the NiFe-based foil and 4.21×10^3 for the Fe-based foil. For example, the cyclic loading for 2 sinusoidal arcs for Fe-based foil requires around 1 N while the NiFe-based foil for the same arc formation requires 3 N, but clearly, the Ni-based foil exhibits higher load values about 5 N. This indicates that the appropriate choice of foil thickness can effectively cyclic life with desirable load ranges, a valuable tool in designing any type of spring set-ups.

As the number of arcs increases the relative differences between the foils becomes clearer, with the NiFe-based and Ni-based foils failing at a significantly lower number of cycles than the Fe-based foil. This suggests that the cycle life of MG foils could depend on the thickness of the foil as well as the alloy composition.

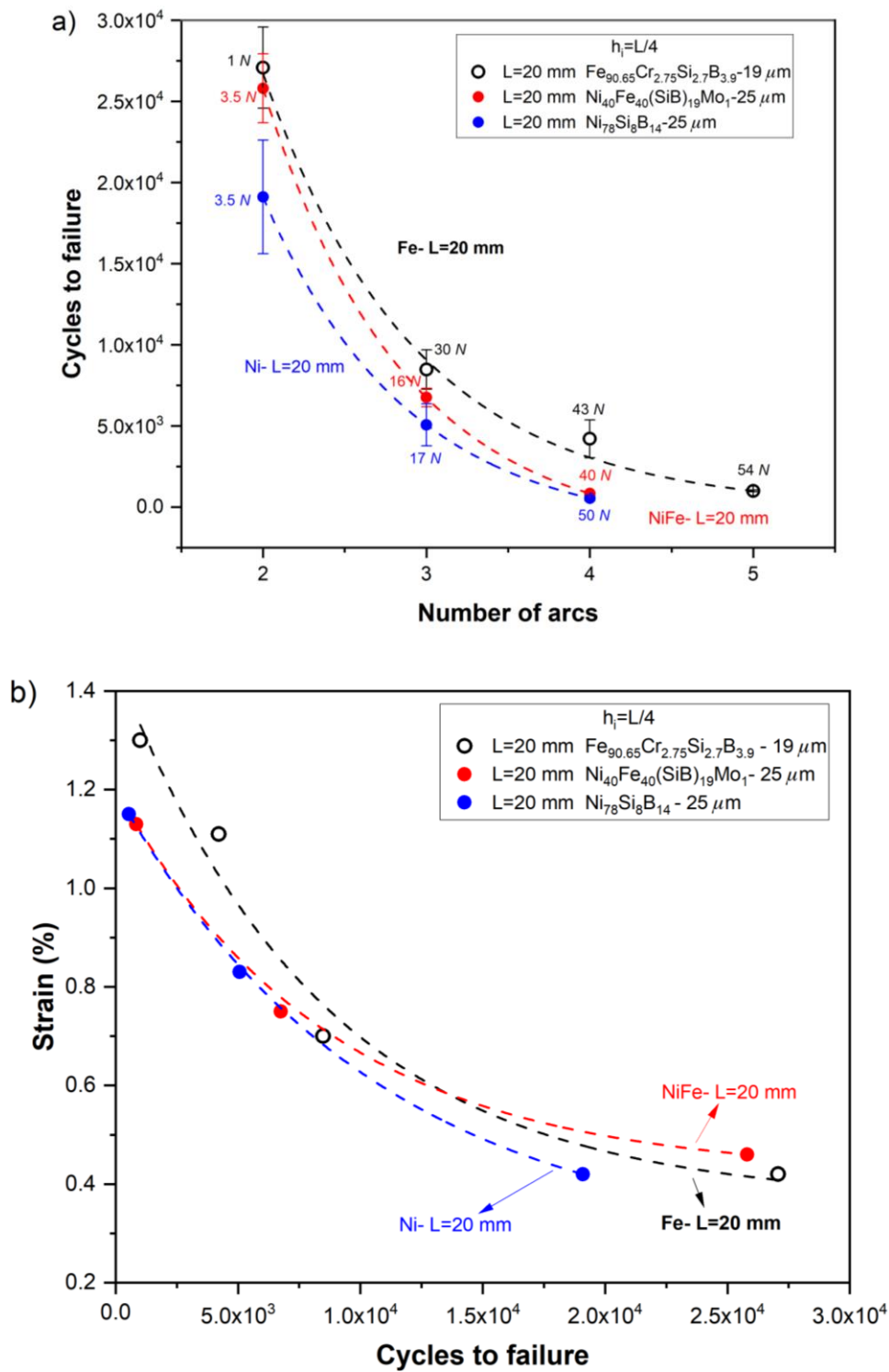


Figure 7-4: For three glassy foils with $L=20$ mm and $h_1=5$ mm: a) cycles to failure as a function of the number of arcs for three different metallic glass foils; b) cycles to failure as a function of applied strain.

Figure 7-4b shows local strain versus cycles to failure for three glassy foils for an arc-shaped NiFe-based (25 μm thick) metallic glass foils and Ni-based (25 μm thick) glassy foils for the first time. For failure to occur, the strain values for all three foils are similar, though the strain at failure of the Fe-based foil is consistently slightly larger than the other two. As expected, for higher strains, the number of cycles to failure is much smaller. However, a close observation of the evolution of the foil's geometry figure 7-4b, reveals that the radius of curvature of different foils just before the formation of a new (n_i+1) arc. In the Table 7-2 shows the comparison between two foils of Ni-based with thickness of 25 and 40 μm , respectively. The results show that the Ni-based foil of 40 μm exhibits higher load and deformation values compared to the Ni-based foil of 25 μm for the same arc formation. For example, for the transition from 1 to 2 arcs, the Ni-based foil with 40 μm thick required about 5.8 N and elastic deformation of 0.56% strain. While the Ni-based foil with 25 μm thick required a load of about 4.2 N and a deformation of 0.42% strain. Therefore, the radius of curvature of thicker foil presented higher deformation of strain compared to thinner foil.

Table 7-2. Deformation of radius curvature for Ni-based foils of undulatory response for two thicknesses.

Sinusoidal arcs	Ni-based (25 μm)		Ni-based (40 μm)	
	Load (N)	Strain (%)	Load (N)	Strain (%)
Transition from (1 to 2)	4.2	0.42	5.8	0.56
Transition from (2 to 3)	28	0.9	30	1.3
Transition from (3 to 4)	82	1.35	103	1.85
Transition from (4 to 5)	123	1.8	234	2.6

In addition, the effect of composition alloy on fatigue life for metallic glass foils Table 7-3 presents results of Ni-based foil with 25 μm thickness compared to fatigue results for NiFe-based foil with 25 μm . The fatigue performance of NiFe-based in terms of cycles to failure is higher compared to Ni-based foil for the same number of arc formation. As can be seen in Figure 7-4b, the deformation of radius of curvature for both foils are quite similar, but clearly, cycles to failure are different. For example, the NiFe-based with 25 μm thickness for the transition from 1 to 2 arcs required load of 3 N and strain on radius of curvature was 0.42%. While the Ni-based with 25 μm for the same transition required load of 4.2 N and strain on radius of curvature was 0.42% similarly to NiFe-based. In this case, the cycle life of metallic glass foils is affected by alloy compositions. Table 7-4 presents the fatigue endurance limits in terms of number of cycles, strain and load for three foils with sinusoidal arcs formation.

Table 7-3. Comparison of strain deformation on arc curvature between NiFe-based and Ni-based foil.

Sinusoidal arcs	NiFe-based (25 μm)			Ni-based (25 μm)		
	Load (N)	Strain (%)	Cycle to failure	Load (N)	Strain (%)	Cycle to failure
Transition from (1 to 2)	3.2	0.42	25800	4.2	0.42	19100
Transition from (2 to 3)		0.9	6750	28	0.9	5070
Transition from (3 to 4)		1.35	840	82	1.35	546
Transition from (4 to 5)		1.8	-	123	1.8	-

Table 7-4. Summary of experimental results for fatigue endurance limit in terms of number of cycles, strain and load for three MG foils of length 20 mm with 2 arcs (N_f , cycles to failure; STD standard deviation).

Sinusoidal arcs	Fe-based (19 μm)				NiFe-based (25 μm)				Ni-based (25 μm) partially crystalline			
	N_f	STD	Strain (%)	Load (N)	N_f	STD	Strain (%)	Load (N)	N_f	STD	Strain (%)	Load (N)
1 (distorted)	225900	21250	0.42	1	-	-	-	-	-	-	-	-
2	27075	2546	0.42	1	25800	2121	0.46	3.2	19100	2523	0.46	4.2
3	8475	1209	0.55	9	6750	574	0.7	16	5070	1301	0.9	30
4	4210	1165	1.1	30	840	107	1.2	40	546	155	1.35	50
5	1002	54	1.3	57	-	-	-	-	-	-	-	-

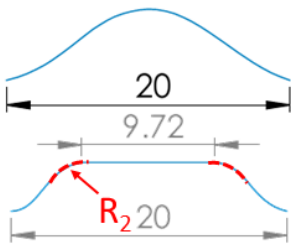
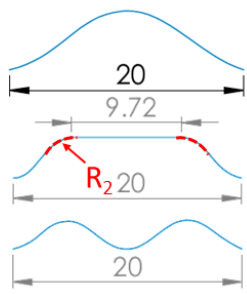
7.2.3 Cyclic fatigue for pre-buckling (low strain amplitude)

For a long fatigue life of metallic glass foils, the strain must be below 2%. Thus, fatigue life tests were carried out on the MG foil subjected to low strain. In this case, the cyclic loading ranged from a single initial arc-shaped just prior to the initiation of 2 sinusoidal arcs and just before the new arc is formed (n_i+1), as shown in Table 7-5.

Table 7-5 shows the cycles to failure of $\text{Fe}_{76.10}\text{Cr}_{2.48}\text{Si}_{4.51}\text{B}_{16.91}$ MG foil for $L = 20$ mm and $h_1 = 5$ mm at low strain, 0.42% corresponding to the initiation of a second arc and the completion of that arc. The fatigue performance increases with decrease in applied strain. The fatigue life of amorphous alloys in terms of cycles to failure is higher at lower strains. For example, the Fe-based metallic glass foils failed after 225900 cycles without buckling and one arc transitioning into just before two arcs are formed. Crack initiation, in this case, occurred at the sites of maximum local strain, where the sinusoidal arcs are distorted, (R_2 in Table 7-5), at about 0.42% strain. The fatigue life, in this case, is about 8 times higher than

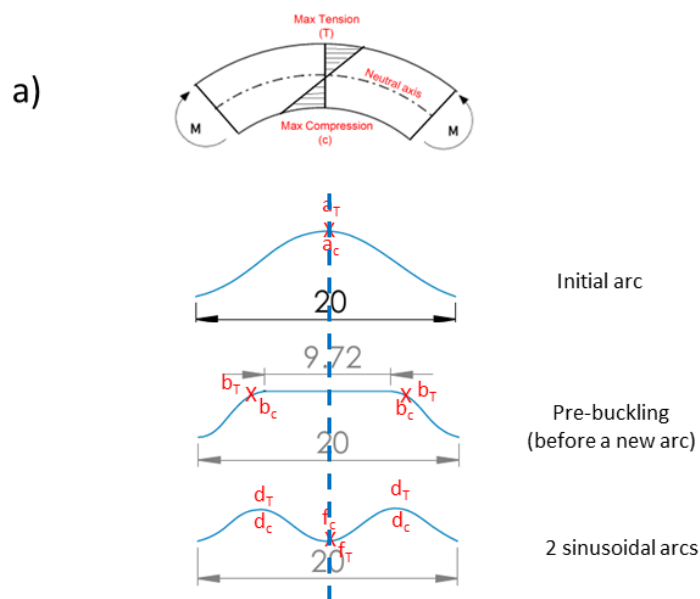
with two sinusoidal arcs of the same foil, see Table 7-5. Obviously, the number of arcs plays an important role in determining the fatigue life of metallic glass foils.

Table 7-5. Comparison between two different operating of cyclic loading of Fe-based glassy foil

Description	Case 1 (1 to just before a new arc is formed n_i+1)	Case 2 (1 to 2 fully perfect shaped)
Schematic		
Maximum strain	0.42%	0.42%
Cycles to failure	225900	27075

Tension-compression fatigue is a common form of fatigue, as for example, in vibration of aircraft wings. For metallic glass foils, the number of cycles has been shown to be limited due to tension-compression fatigue caused by undulatory behaviour of the disturbance. The effect of tension-compression fatigue, and the maximum strain on the fatigue performance can be explained in terms of the forming of sinusoidal arc. Figure 7-5 shows a schematic diagram of the tension-compression cycles produced by undulatory behaviour. The strain in the cross-section at position 'a' represents tension along the outer surface of the foil and compression along the interior surface of the foil. The foil surface instantly attains its maximum tension and compression strain ($\sigma_{\max}$) at position *b*. Position *b* shows this strain just before a new arc forms (n_i+1). After the point marked X reaches position *d*, the strain drops immediately to minimum strain ($\sigma_{\min}$), and this is accompanied by the formation of an additional sinusoidal arc. In position *f*, where point *f* is equivalent to point *a* on the initial curve, point X flips from tension-compression to compression-tension. After that, at this point *f*, the process is then reversed with multiple arc formations.

Figure 7-5a shows that as metallic glass foils undergo deformation and bending, the strain is inhomogeneously distributed in the foil, where compression occurs at the bottom of the foil and tension on the top, so the foil experience varying compression and tension due to the undulating nature of the applied load. However, tension-compression phenomena along foil reverse during the undulatory behaviour. For example, in one cyclic loading when the foil shape goes from 1 to 2 arcs, it experiences maximum strain just before forming the second (n_i+1) arc. See points 'b' in Figure 7-5a, which refer to the pre-buckling stage. Post-buckling, with the new shape (2 arcs), the maximum strain is less than pre-buckling. In this case, both sides of the foil experience a double stress at different parts of the cycle loading (tension-compression). Thus, it has been found that the loading over one cyclic is constrained due to the double stress of more than one maximum strain from different sides of the foil. The tension-compression fatigue with undulatory behaviour can be seen in the schematic in Figure 7-5b.



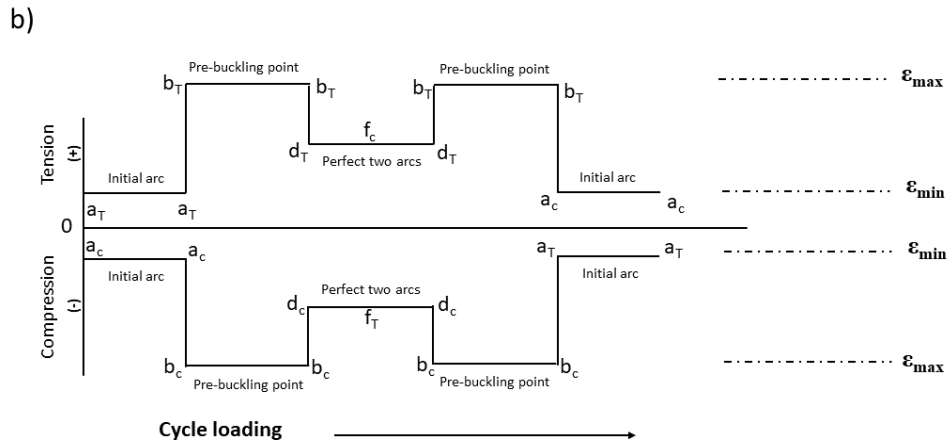


Figure 7-5: a) Schematic diagram of cyclic loading of metallic glass foils from initial arc-shaped to 2 sinusoidal arcs; b) cyclic loading for one cycle, showing stress cycle points for initial single arc, distorted shape due to increasing applied load, two arcs, distorted shape due to decreasing applied load, and finally to a single arc.

In cyclic loading, the undulatory behaviour can impart tension-compression bending stresses along the foil, as explained above. The present tests found that buckling phenomena leading to undulatory behaviour may affect the fatigue performance of glassy foils by causing reverse bending fatigue. This means that during cyclic loading, the local strain on the foil flips from tension to compression in each sinusoidal arc formed due to the undulatory behaviour, see the results previously mentioned for cycle fatigue of Fe-based at low strain amplitude. For example, the Fe-based foils show maximum tension-compression just before buckling occurs, then the maximum tension-compression as the buckling finishes with the production of two sinusoidal arcs. Thus, the material experiences a double fatigue cycle due to the two maximum stress that occur, pre-buckling and post-buckling.

However, under low cycle fatigue conditions, Fe-based foil outperformed the other two amorphous alloy foils when the data are expressed in terms of strain or number of sinusoidal arcs formed. In Figure 7-6a, it can be seen that fatigue life for amorphous alloy foils is generally similar at low strain ranges, but that the lifespan of Fe-based foil is superior to that of other glassy foils tested in this study.

This is due at least in part to the different MG compositions of the three foil types, as well as the thickness differences between foils.

Verduzco, et al., [82] found that $\text{Fe}_{69.5}\text{Cr}_8\text{Si}_{7.5}\text{B}_{15}$ glassy wire had superior fatigue performance in terms of applied strain range compared to HT steel wire of diameter 245 μm under high cycle. For Fe-Cr-Si-B glassy wire, using a double pulley fatigue machine, the minimum strain range that could be obtained was 0.5%, leading to failure after 10^7 cycles, Figure 7-6b [82].

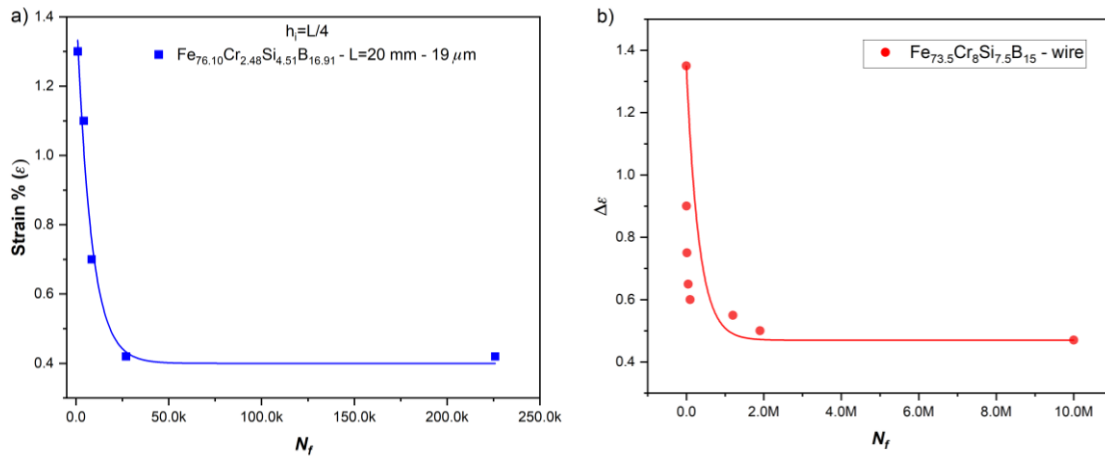


Figure 7-6. Fatigue behaviour in terms of the applied strain range; a) cycle loading for $\text{Fe}_{76.10}\text{Cr}_{2.48}\text{Si}_{4.51}\text{B}_{16.91}$ foil in current study; b) cycle to failure for $\text{Fe}_{69.5}\text{Cr}_8\text{Si}_{7.5}\text{B}_{15}$ glassy wire [82].

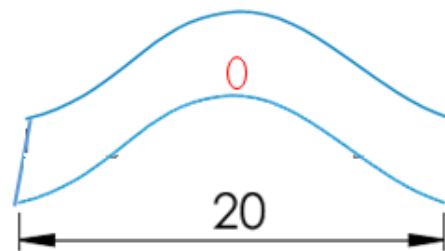
It has been shown that for any constant mean cyclic loading, the fatigue life of all metallic glass foils decreases with increasing number of sinusoidal arcs under all boundary conditions due to increased load/strain as long as the increased number of arcs. These results are broadly consistent with a study carried out by Yousfi et al. [2], whose results were given only as a function of cycles to failure and with experiments were performed with only one value of boundary length, $L = 20 \text{ mm}$. However, to understand the effect of undulatory behaviour on the fatigue life of metallic glass foils, the results are given as a function of a strain range rather than load range.

7.2.1 Characteristic features of fatigue failure of metallic glass foils

After fatigue testing, the foils were examined with a high-resolution SEM to better understand failures. Interestingly, crack initiations occurred at higher stress levels regardless of tension or compression on the surface. Two kinds of crack initiation mechanisms in metallic glass foils were observed after cyclic loading tests as shown in Figure 7-7.

Figure 7-7a indicates that the crack initiation site occurs in the interior of the specimen at a high strain level and propagates out to the surface. It was observed that such cracks were always initiated at defects.

The second type of crack was observed to consistently occur at the side edge of the foil specimen at high strain levels. Figure 7-7b shows that the micro-crack propagated rapidly, leading to failure. At high strain levels, crack initiation occurs at the side edge of this type of crack. Due to the late capture of cycles to failure, cracks at the edge are not considered as crack initiation since the majority of crack initiation occurred on the interior surface. Table 7-6 shows the characteristic types of crack initiations, including pictures of metallic glass foils used in this study.



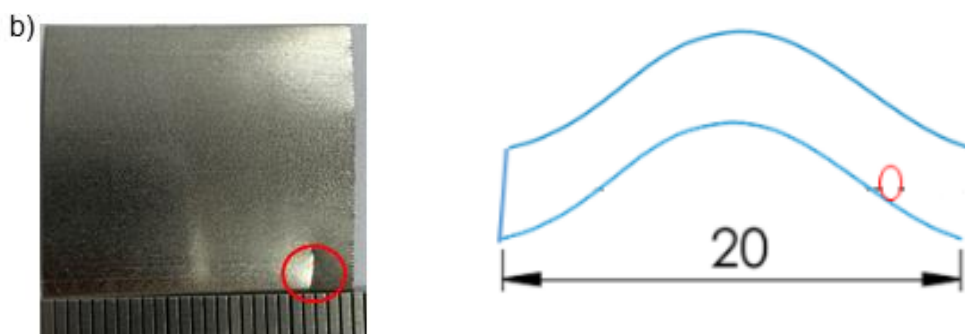
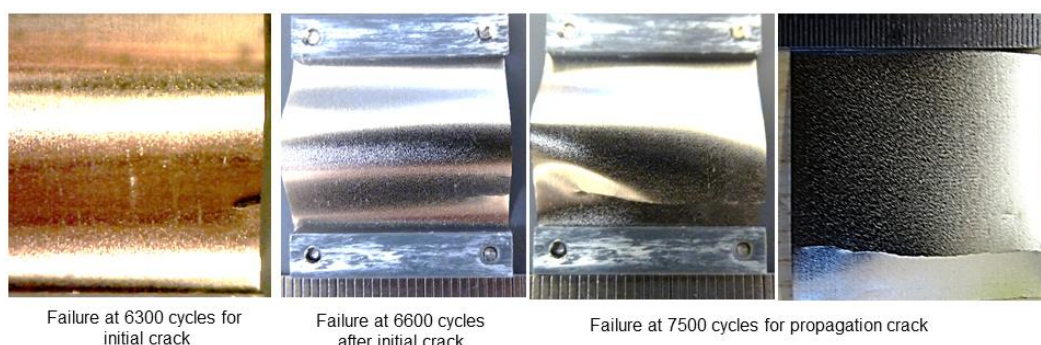


Figure 7-7. Types of cracks of NiFe-based foil during cyclic loading; a) interior crack; b) crack at foil edge.

Table 7-6. Types of crack initiation of metallic glass foils during cyclic loading.

MG foil	Crack type I (interior surface)	Crack type II (at foil edge)
Fe-based	75%	25%
NiFe-based	75%	25%
Ni-based	100%	-

Figure 7-8 shows the crack initiation in NiFe-based foil at 6300 cycles, which continued to propagate so long as the cyclic loading continued. Note crack length at 6600 cycles, and after 7500 cycles, it is seen that the crack had increased its length, deeper into the foil such that the foil was nearly split into two pieces.



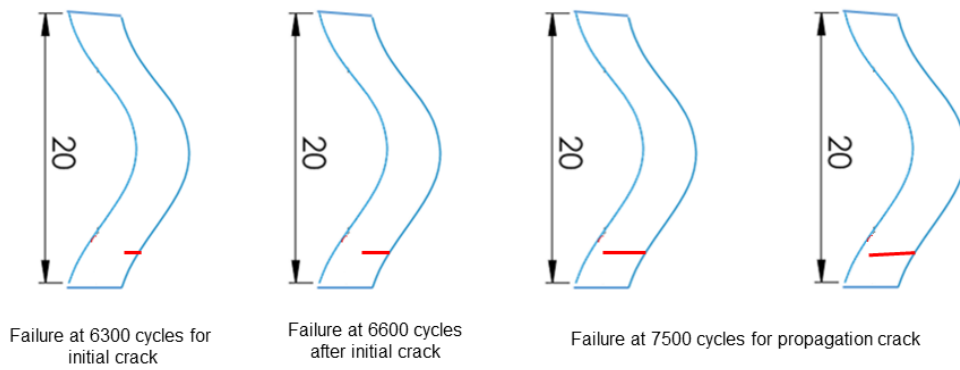


Figure 7-8. Crack propagation into NiFe-based MG foil during cyclic loading

Figure 7-9a shows an SEM image of crack initiation in Fe-based metallic glass foil after 9900 cycles. Figure 7-9b shows the Fe-based foil sample failed after 9900 cycles, where cyclic loading was for 3 sinusoidal arcs. From the results, the initiation site occurred as marked with a red circle, in the interior of the foil near the middle of the surface. Crack initiation on the surface began from the interior of the sample. However, with increasing number of load cycles the crack stops growing inside the sample and extends toward the edge until a fracture occurs, as shown in Figure 7-9a.

Looking closely at the point of crack initiation in Figure 7-9a, initially, cracks propagate in a straight line following their initiation, the direction of propagation is in both directions perpendicular to the direction of application of the load. The crack likely originated due to an embedded defect and propagated towards the outer face of the foil, in the direction of increasing strain and, as the number of cycles increased with multiple arc formations, fracture occurred.

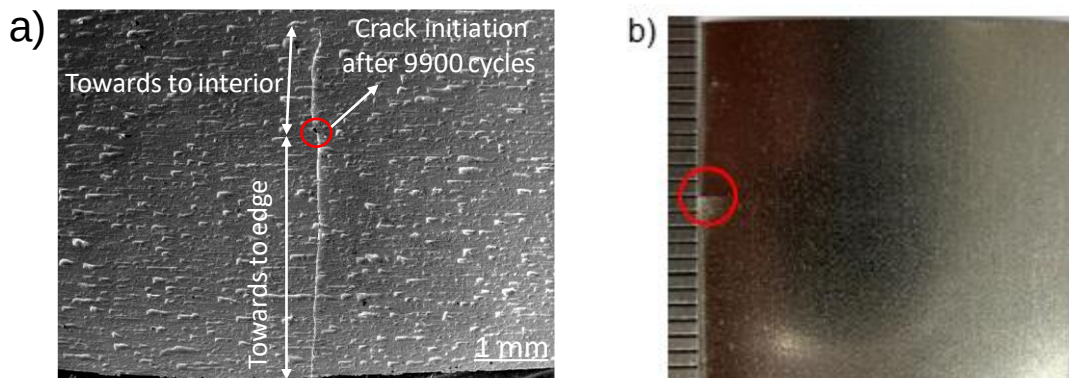


Figure 7-9: (a) SEM of crack initiation location of Fe-based metallic glass on the crack surface for 3 sinusoidal arcs at 9900 cycles; (b) foil sample for the same foil.

Figure 7-10a shows an SEM image of a Fe-based metallic glass foils, while Figure 7-10b presents the Fe-based metallic glass foil under cyclic loading with 5 sinusoidal arcs where deformation was induced after 930 cycles. As a result, the maximum strain at the origin of the crack can be used as a parameter to indicate the number of cycles to failure and the foil's likely lifespan. It was found that for foils of length 20 mm, the strain value for 2 sinusoidal arcs was 0.42% and for 5 arcs was more than three times as great, 1.3%. Failure in the former occurred after 27075 cycles and in the latter after 930 cycles.

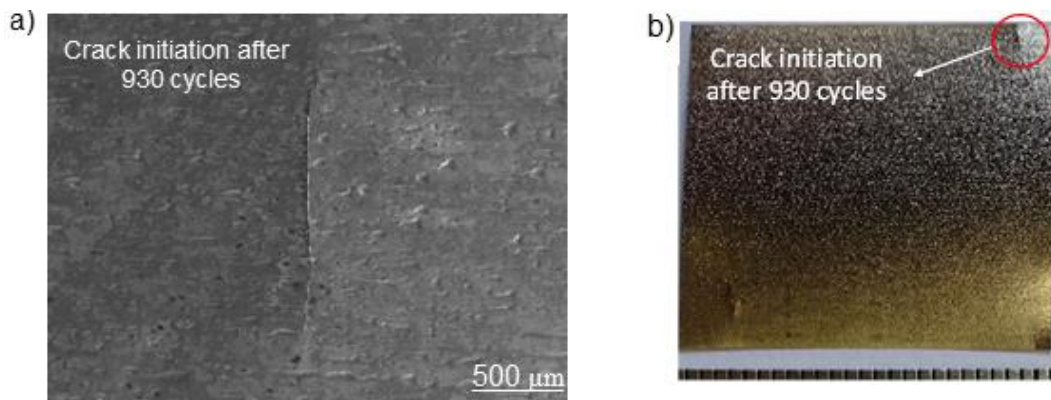


Figure 7-10: a) SEM of Crack initiation of Fe-based MG foil failed after 930 cycles within the cyclic loading range for 5 sinusoidal arcs with $L=20$ mm; b) same foil sample after it had failed.

Furthermore, the main crack propagation is in the shear band, which is present on both sides of the crack, as shown in Figure 7-11. Shear bands were also observed in other and samples, including NiFe-based and Ni-based foils, and exhibited similar cracking and shear banding phenomena. The shear band and cracking observed in this study are significant mechanisms of damage for metallic glass foils subjected to cyclic loading. Rapid crack growth occurs at the tip of the fatigue crack once a shear band forms at the crack tip, as shown in Figure 7-11. In order to gain a deeper understanding of the crack initiation, during cyclic

loading we regularly interrupted testing and, using the SEM, examined the original site of the crack and along the crack length for maximum strain.

The strain level for shear band which is at the maximum local strain at the crack tip, can be used to represent the resistance to cracking by the shear band during fatigue crack propagation. Note that the number of cycles to failure, i.e., to fatigue crack initiation, was measured through the maximum local strain, whether in compression or tension during the undulatory behaviour. The sinusoidal arcs produced during loading/unloading show different tension and compression sites along the foil; it would be expected that the cracks occur where the maximum strain is applied.

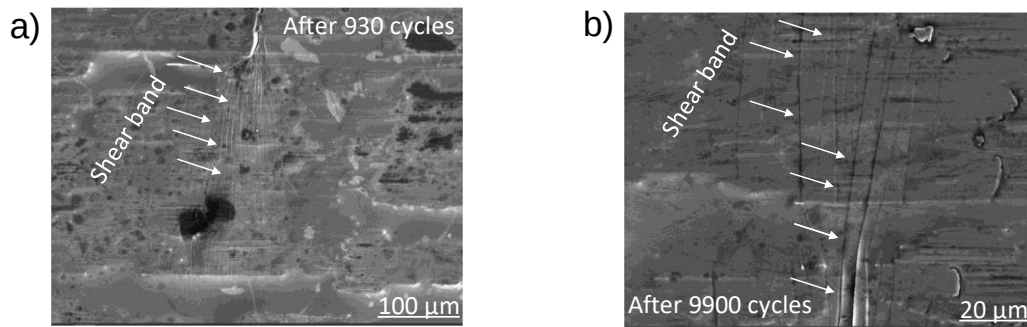
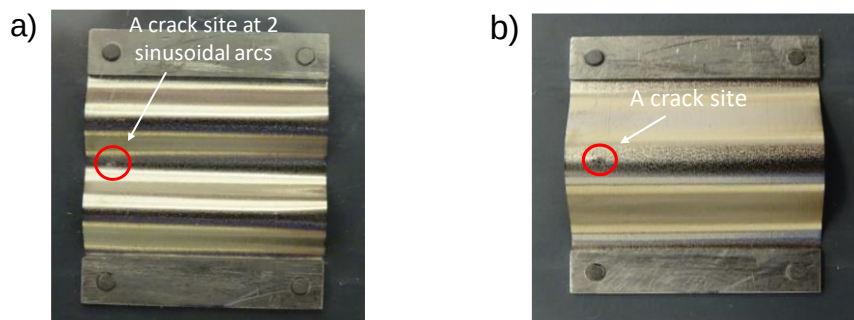


Figure 7-11: a) illustration of shear band at the bottom crack on the damage evolution after 930 cycles; b) shear band at the top crack evolution after 9900 cycles.

For example, Figure 7-12 shows that the crack site had maximum tension-compression for the initial single arc, this was converted to compression-tension as 2 arcs were formed.



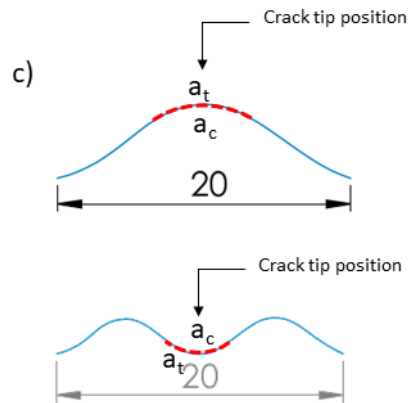


Figure 7-12: Showing crack initiation at tension-compression reversal to compression-tension: a) MG foil formed into two sinusoidal arcs, demonstrating a crack site at position of maximum compression-tension; b) same foil showing initial arc-shape indicating crack site at tension-compression; c) schematic of formation of two arcs.

However, another potential failure is related to the casting process at the foil's edges, as shown in Figure 7-13. Micro-casting defects are generated by the spinning cast manufacture of those foils, the condition of the copper roller, and the gaseous atmosphere used [175]. These types of defects are observed at the side edge of metallic glass foils starting from micro-notches, which are created during the cutting process of the foils [2]. Due to the high-stress level concentration produced at the tip of a defect, it is a conducive site for crack initiation. However, it was found not only that the crack initiation occurred around 3 mm away from these edges but also that some cracks began life in the middle of the surface interior.

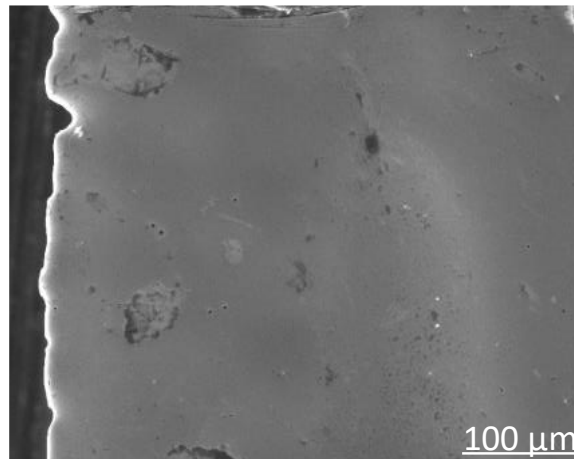


Figure 7-13. SEM image shows the cast edge of the metallic glass foil.

Another concern is to avoid early failure due to misalignment when setting up the foil in an arc-shape on the base. A pre-test was carried out in each case to ensure the base holder base was fully aligned with the pushing plate since misalignment would cause more concentrated stress in some areas of the foil than others during cyclic loading, resulting in a slight twist giving the sinusoidal arcs a different arc curvature shape, resulting in higher stress and strain and earlier failure due to a smaller radius of curvature.

Further, this study found that another potential cause of early failure is the thickness of the foil. Ni-based and NiFe-based MG foils have similar thicknesses but different compositions, the results for fatigue cracks compared to thinner Fe-based MG foils showed a high lifespan for fatigue. Foil thickness influences fatigue life during cyclic loading due to the different stress and strain values that occur for different foil thicknesses. Whether crack growth initiates from defects on the surface or shear events, it always is initiated in areas of the foil that are subjected to maximum stress loading. While these metallic glass foils are considered to have a low fatigue life overall based on their observed cyclic lifetimes, that could be useful for some engineering applications.

In addition, the apparently better fatigue life performance of metallic glass foils (expressed in terms of strain range), indicated by the present tests, arises from the higher maximum local strain of arc-shapes during undulatory behaviour.

However, thinner Fe-based foils clearly have better fatigue performance than other glassy foils in the same applied strain range. As a result, the crack site appeared just where maximum localised strain occurred just before a new arc was formed (n_i+1). As shown in Figure 7-14, the crack site is precisely at the same site when two perfect sinusoidal arcs formed under cyclic loading resulting in double stress, either compression-compression or tension-tension.

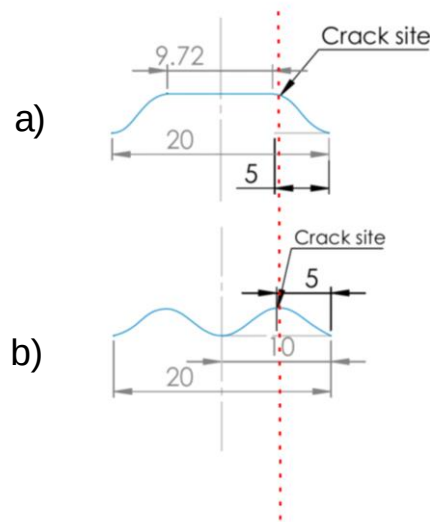


Figure 7-14. Schematic diagram of undulatory behaviour; a) stress cycle before buckling (before new arc begins); b) stress cycle from one arc to two arcs, indicating the crack location in both cases.

7.2.2 Surface roughness of Fe-based glassy foil

The metallic glass foils are manufactured by melt-spinning methods and these foils have two surfaces, one surface called air-side and the other wheel-side. The fatigue tests of metallic glass foils were conducted with wheel-side surface in contact with the pushing plate and the air-side surface towards the base. The crack initiation was carefully observed on both sides to identify which was more susceptible to fatigue cracking. The metallic glass foils on the wheel-side show more apparent signs of shear banding where the fatigue crack develops compared to the air-side.

All metallic glass foils have different topographical characteristics on their two sides, as shown in Figure 7-15.

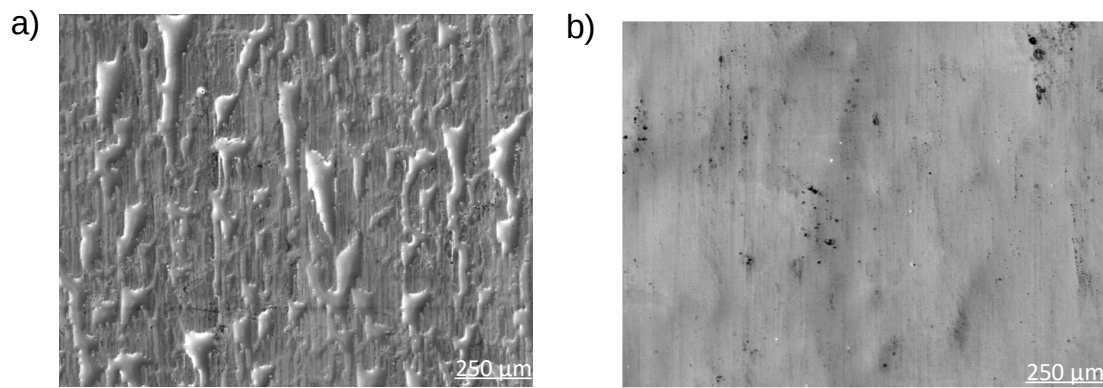


Figure 7-15: a) the wheel-side of the $\text{Ni}_{78}\text{B}_{14}\text{Si}_8$ glassy foil, which is in contact with the compression plate during cyclic loading; b) the air-side of the same foil, but this surface is in contact with the base.

A Taylor Hobson Precision Interferometer was used to measure the roughness of both sides of metallic glass foils in the direction perpendicular to the casting. Due to abnormal early failure of these MG foils under cyclic loading, the surface roughness of both sides of the foil was compared to determine whether it might have had an effect on the failure or not. Several measurements were taken on each side of the samples for the same scanning area. Figure 7-16 shows the extracted profile (primary profile) of the copper roller side (wheel-side), while Figure 7-17 shows the extracted profile for the air-side. In the vertical black line, the analysis direction is along the foil from which a profile is extracted. It can be seen that the maximum value of valley depth on the wheel-side is $7.3 \pm 0.14 \mu\text{m}$, which appears slightly greater than those on the air-side (depth = $6.76 \pm 0.45 \mu\text{m}$). The former could be due to unevenness of the roller surface and the latter could be attributed to the presence of surface defects distributed across the foil surface.

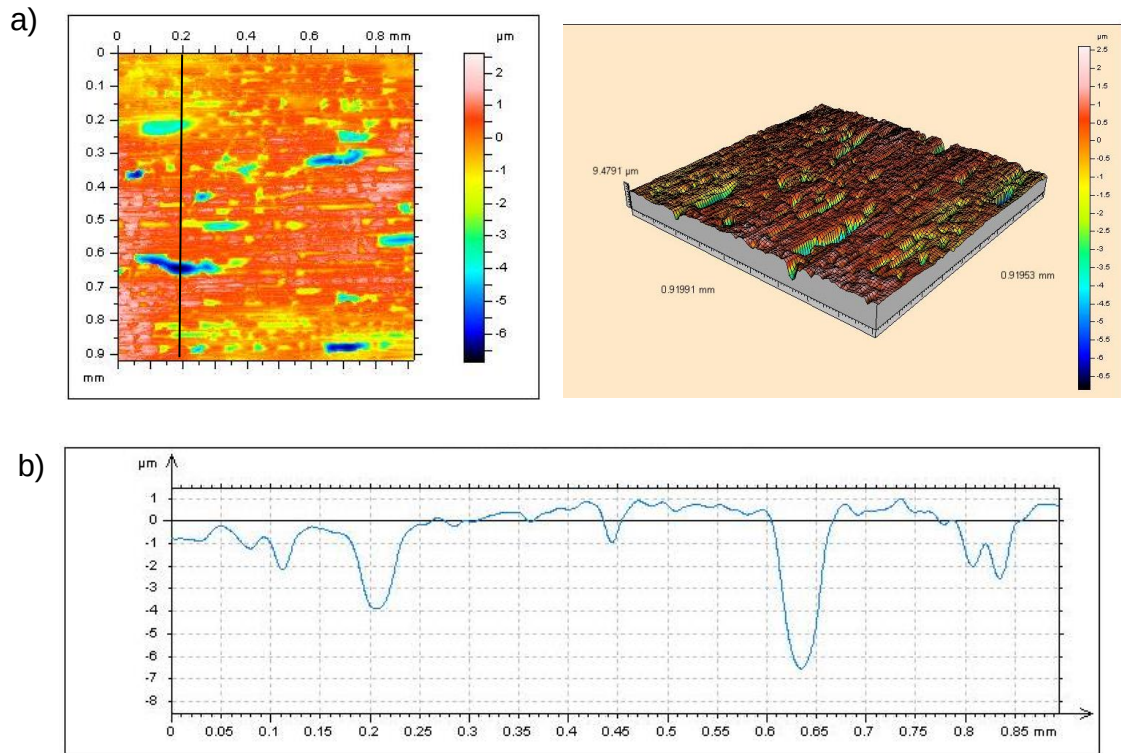
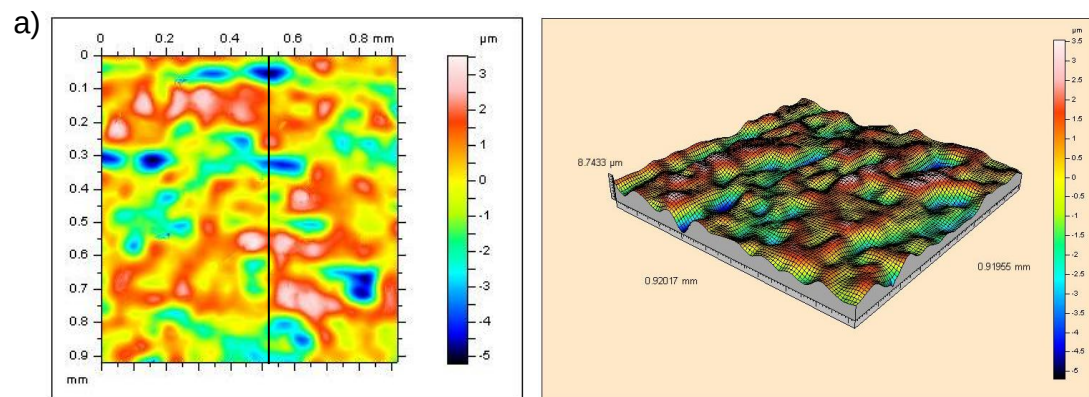


Figure 7-16: a) A profile measurement extracted from a 3D surface topography of Fe-based MG on wheel-side, where the black line represents the 2D profile extracted; b) 2D profile extracted.

All metallic glass foils showed a higher surface roughness on wheel-side than that along the direction of casting. Due to the dip in the MG foil in the direction of casting, the profile taken in that direction may not have shown the true roughness profile.



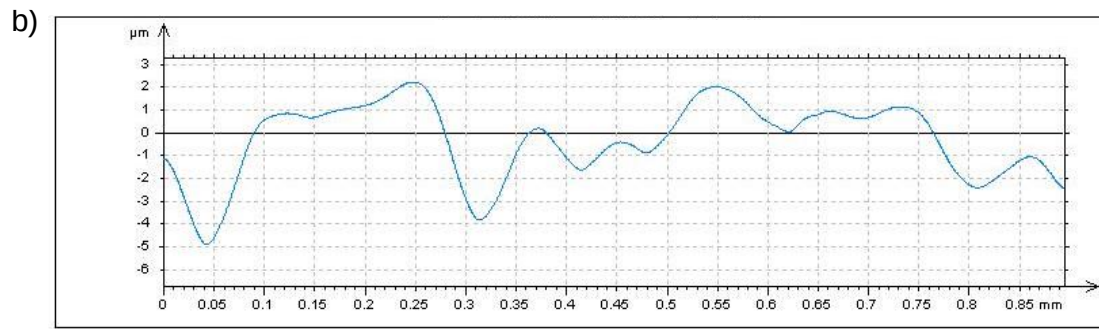


Figure 7-17: a) A profile measurement extracted from a 3D surface on air-side foil of the Fe-based MG foil as-cast, where the black line represents the 2D profile extracted ; b) 2D profile extracted.

7.2.3 Surface roughness analysis of Fe-based glassy foil

In order to improve fatigue life in metallic glass foils, it is essential to evaluate the surface roughness parameters. The MG foils surface topographical parameters studied include the total height, root mean square roughness and roughness average. Total height, P_t , measures the vertical distance between the highest peak and deepest valley on the surface. P_q refers to the root mean square roughness within the sampling area, which corresponds to the standard deviation of the height distribution. The average roughness P_a represents the average height of the sampled area and shows the general variation in height. Skewness S_{sk} and Kurtosis S_{ku} measure the topography of height distribution of the sample from the mean surface level. The values of the roughness parameters for metallic glass foils are given in Table 7-7.

Table 7-7. Surface roughness parameters of Fe-based metallic glass foil for scan area of 0.8x0.8mm².

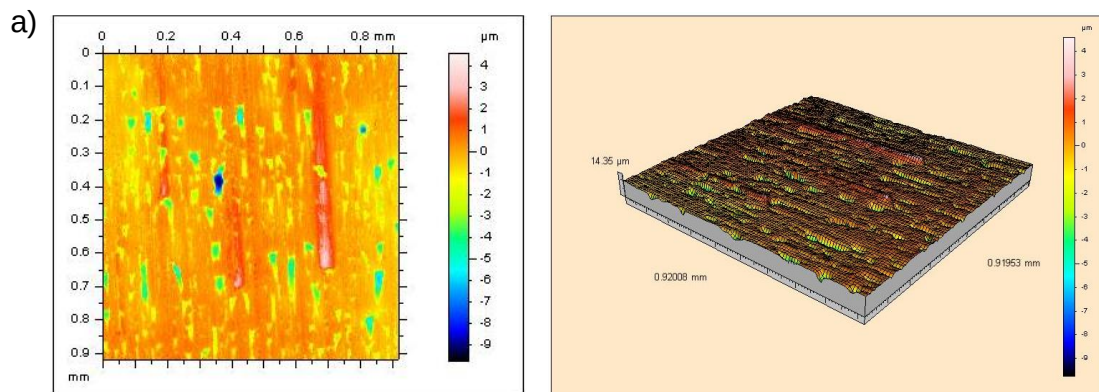
Roughness parameters	Wheel-side	Air-side
Total hight, P_t	$7.3 \pm 0.14 \mu\text{m}$	$6.76 \pm 0.45 \mu\text{m}$
Root mean square, P_q	$1.35 \pm 0.08 \mu\text{m}$	$1.51 \pm 0.22 \mu\text{m}$
Roughness average, P_a	$0.98 \pm 0.14 \mu\text{m}$	$1.17 \pm 0.25 \mu\text{m}$
Skewness, S_{sk}	-1.95 ± 0.33	-0.73 ± 0.44
Kurtosis, S_{ku}	8.22 ± 2.62	3.86 ± 1.40

From the listed in Table 7-7, the kurtosis value of 8.22 ± 2.62 suggests the height distribution has a few extreme peaks in the wheel-side of the foil. In contrast, the air-side sample shows a more evenly distributed surface with a smaller number of not-so-high peaks as shown by the Kurtosis values of 3.86 ± 1.40 , which is bigger than 3. Both surfaces of these foils have a negative skewness value, indicating that they possess surface valleys and peaks on their surfaces. The P_a value increased from $0.98 \pm 0.14 \mu\text{m}$ on the wheel-side foil samples to more than $1.17 \pm 0.25 \mu\text{m}$ in the air-side foil samples. The P_q value was $1.35 \pm 0.08 \mu\text{m}$ for the wheel-side and $1.51 \pm 0.22 \mu\text{m}$ for the air-side foil samples. Overall, that the wheel-side has higher peaks compared to the air-side. However, all those values presented are averages of several measurements taken on the specimen, and the results shown in the figures are one of these measurements.

7.2.4 Surface analysis of NiFe-based glassy foil

Figure 7-18 shows the extracted profile of NiFe-based metallic glass foil on wheel-side, it is seen that the total height is $7.90 \pm 1.55 \mu\text{m}$.

The air-side of the NiFe-based MG foil has a total height of $3.03 \pm 0.61 \mu\text{m}$. Comparison of FiguresFigure 7-18 andFigure 7-19 shows the air-side has fewer, smaller amplitude peaks and troughs compared to wheel-side. The values of the roughness parameters for NiFe-based metallic glass foil are reported in Table 7-8.



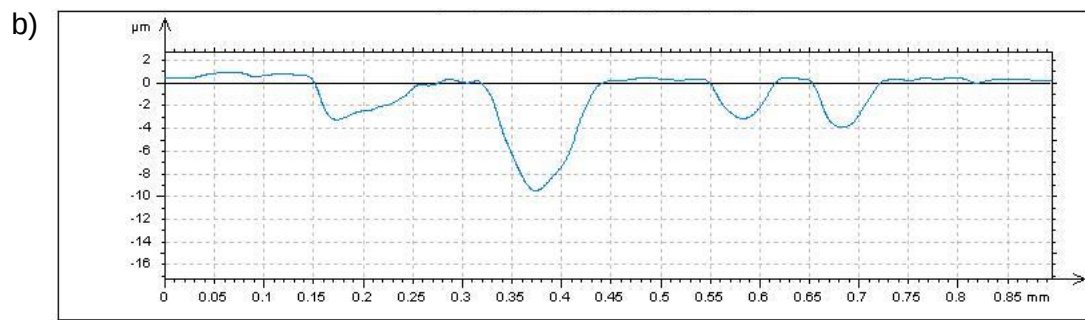


Figure 7-18: a) Profile measurement extracted from a 3D surface of NiFe-based on wheel-side; b) 2D profile extracted.

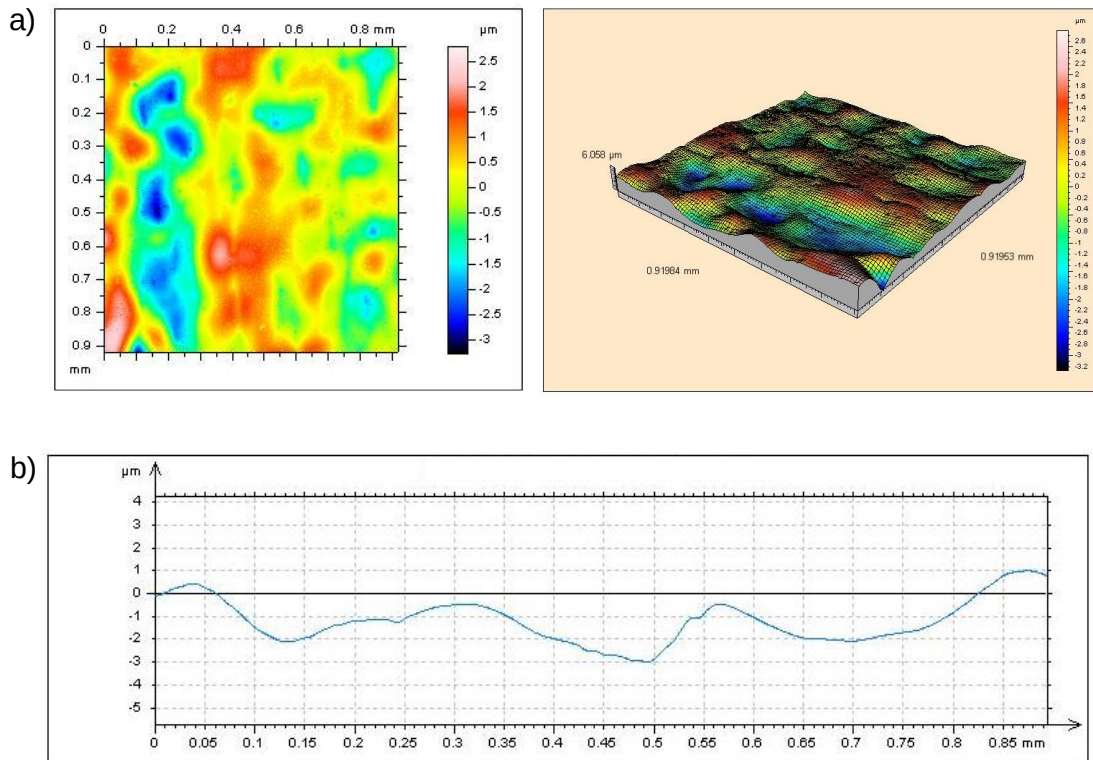


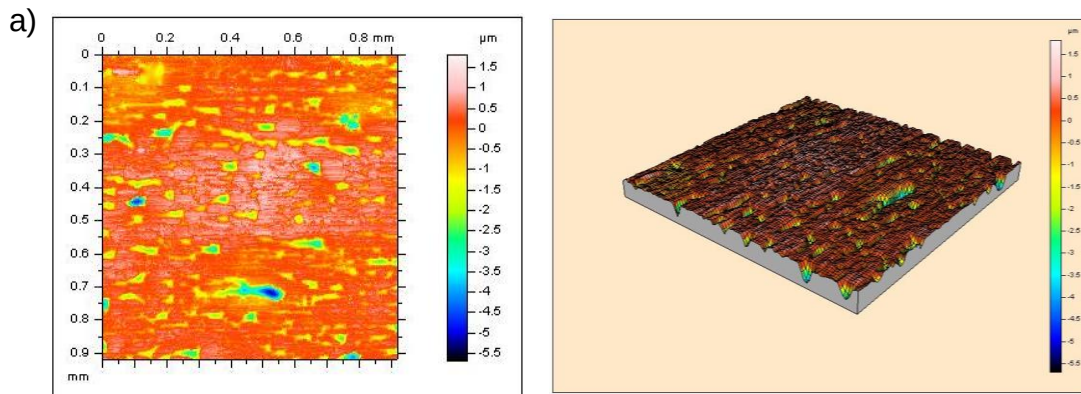
Figure 7-19: a) Profile measurement extracted from a 3D surface topography of NiFe-based on air-side foil as-cast; b) 2D profile extracted measurement.

Table 7-8. Surface parameters of NiFe-based metallic glass foil for scan area of 0.8x0.8 mm².

Roughness parameters	Wheel-side	Air-side
Total height, P_t	$7.90 \pm 1.55 \text{ } \mu\text{m}$	$3.03 \pm 0.61 \text{ } \mu\text{m}$
Root mean square, P_q	$1.65 \pm 0.52 \text{ } \mu\text{m}$	$0.75 \pm 0.15 \text{ } \mu\text{m}$
Roughness average, P_a	$1.14 \pm 0.50 \text{ } \mu\text{m}$	$0.62 \pm 0.13 \text{ } \mu\text{m}$
Skewness, S_{sk}	-2.31 ± 0.04	-0.41 ± 0.09
Kurtosis, S_{ku}	7.12 ± 2.42	3.13 ± 0.20

7.2.5 Surface analysis of Ni-based glassy foil

Figure 7-20 shows the extracted surface profile of Ni-based metallic glass foil on wheel-side. While Figure 7-21 shows the extracted surface profile from air-side for the same foil. The values of total height appear quite similar, on the wheel-side it is $5.10 \pm 0.59 \text{ } \mu\text{m}$, while on the air-side it is $5.68 \pm 0.57 \text{ } \mu\text{m}$. The values of the roughness parameters for Ni-based MG foils are reported in Table 7-9. From the values given, it is concluded that greatest number of defects on the surface of the foil is likely to be due to air pockets. These observations are consistent for all MG foils studied.



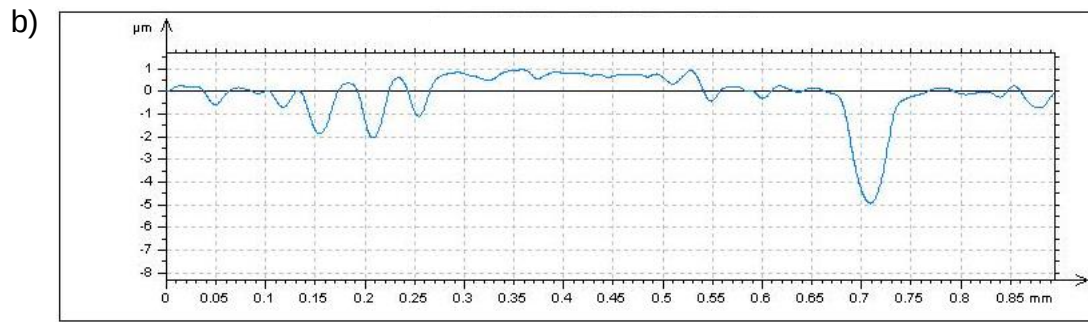


Figure 7-20: a) Profile measurement extracted from a 3D surface topography of Ni-based MG on wheel-side; b) 2D profile extracted.

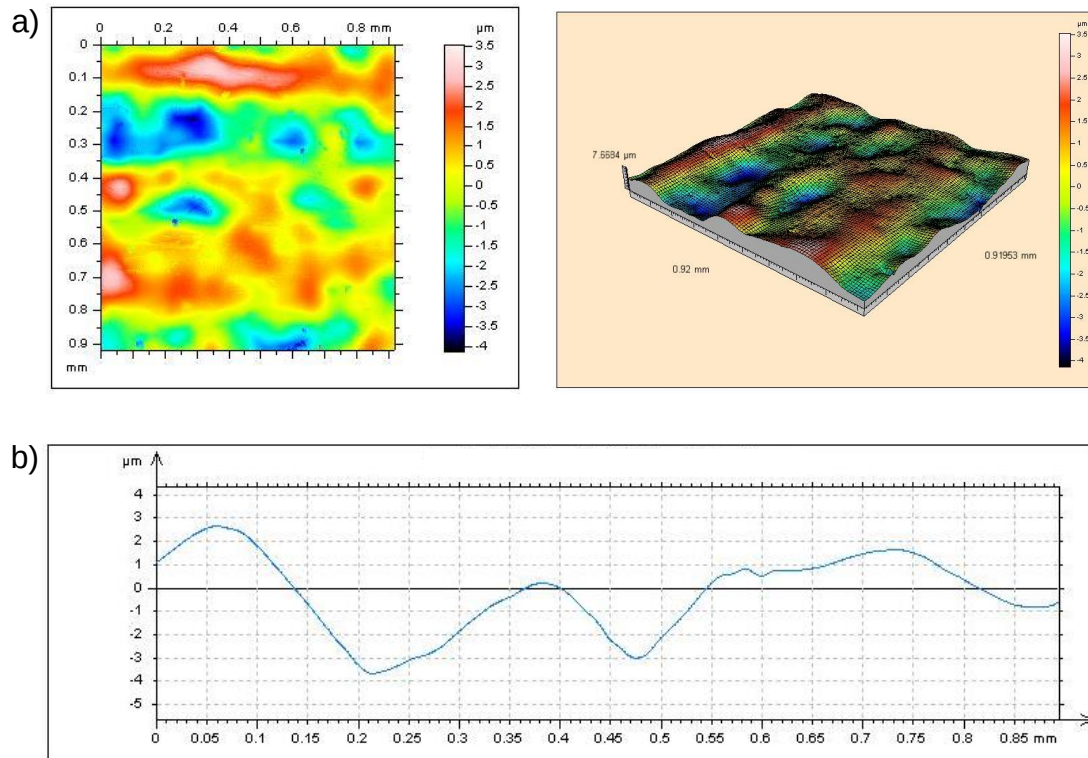


Figure 7-21: a) Profile measurement extracted from 3D surface topography of Ni-based MG foil on the air-side as-cast; b) 2D profile extracted.

Table 7-9. Surface parameters of Ni-based metallic glass foil for scan area of 0.8x0.8 mm².

Roughness parameters	Wheel-side	Air-side
Total height, P_t	5.10 ±0.59 μm	5.68 ±0.57 μm
Root mean square, P_q	0.88 ±0.10 μm	1.30 ±0.26 μm
Roughness average, P_a	0.58 ±0.04 μm	1.01 ±0.31 μm
Skewness, S_{sk}	-2.32 ±0.18	-0.31 ±0.03
Kurtosis, S_{ku}	9.66 ±1.19	3.01 ±0.21

These metallic glass foil samples show small peaks with intense heights based on the Kurtosis value. The skewness value is negative in all cases, indicating that metallic glass foils possess some sharp surface peaks and valleys. Generally, for the cases examined, the wheel-side presented a greater depth of air pockets on its surface than the air-side, with a greater potential to act as stress concentrations that can affect fatigue life. As the number of cyclic loadings increases, leading to local stress concentrations that result in shear bands which can lead to crack formation on the surface due to the formation of micro-shear bands in a direction towards the outside of the specimen.

Stress concentrations can combine with surface effects, leading to the initiation and growth of fatigue cracks. These cracks can then propagate through the material, eventually leading to failure. The stress concentration factor (K_t) is directly related to the magnitude of stress at the concentration point and, thus, the crack growth rate. Therefore, the effective stress concentration factor and defects on the foil surface are primary determinants of the fatigue limit. The theoretical stress concentration factor is used to measure the localisation of high stresses σ_{max} . K_t is used to relate the actual maximum stress at the discontinuity to the nominal stress (tension or compression), and can be defined as follows [176][177]:

$$K_t = \frac{\sigma_{max}}{\sigma_{nom}} \quad 7-1)$$

Where K_t represents normal stress.

However, the geometry of the hole configuration determines the stress concentration factor. Figure 7-22 shows the nominal stress distribution for the foil loaded in bending mode. The presence of surface defects distorts the simple stress distribution. This results in localised high stresses or stress concentration.

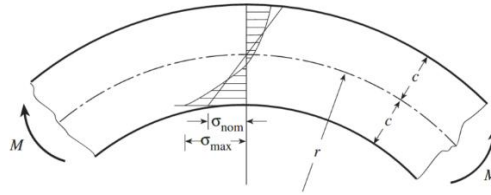


Figure 7-22. Stress concentration in a beam with two grooves loaded in bending.

Stress concentrations near defects exhibit maximum stress, while the areas away from the defects should experience smaller stress. The surface defects which possess an elliptical shape cause high stresses around themselves which can significantly impact the fatigue life of metallic glass foils, especially in situations involving cyclic loading.

However, examining stress concentration mechanics in depth is not within the scope of this work. Stress concentration in beam tension with notch defects, as shown in Figure 7-23. In our case, we applied stress concentration as found for beam bending, as no such investigation has been reported for the much more complicated situation of a foil shape.

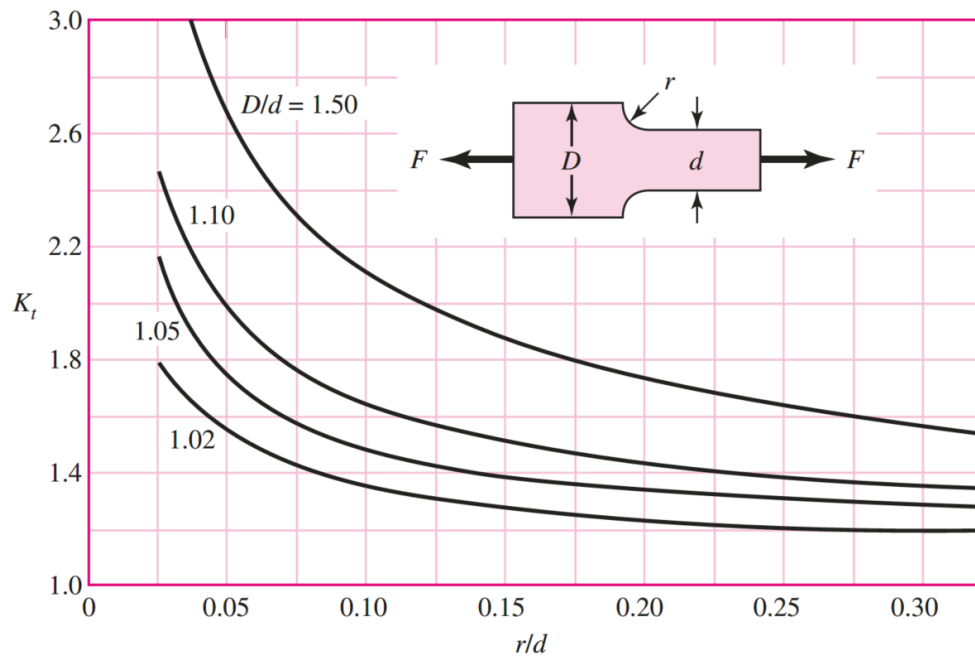


Figure 7-23. Stress concentration factor K_t for a notched beam in tension [176].

Analysis of stress concentration geometry is based on defects found on the surface, and the respective r/t ratios for each defect. Where r is the radius of a defect and t is the depth. The value of this ratio is selected from between 0.2 and 0.5, as shown in Figure 7-24. Based on the r/t values, the K_t value is in order of 1.6 to 2.6, therefore the actual stress is higher than corresponding expected stress. As seen in Figure 7-24, the stress concentration factor, K_t increases as the ratio r/t decreases. For the metallic glass foils studied the results of stress concentration factors are listed in Table 7-10. These results suggest that stress concentration averages a value of 2 for different MG foils, which will result in earlier than expected failure during cyclic loading. Localised high stress near surface defects, produce a stress concentration which impacts on the fatigue life of metallic glass foils. Local strain can double in magnitude during cyclic loading, unlike the calculated local strain at steps of distorted shape. The higher stress concentration induced by the surface defects promote local strain accumulation ahead of crack initiation, thereby helping cause fatigue failure of the metallic glass foils.

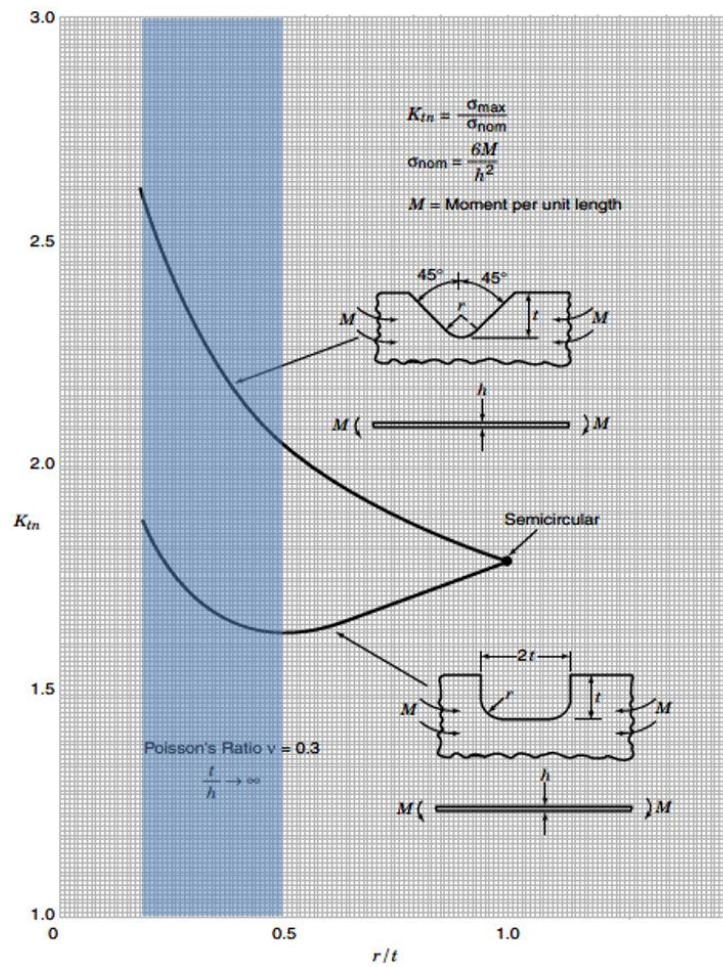


Figure 7-24. Stress concentration factor k_t for a notched plate in transverse bending [177].

Table 7-10. The parameters used to calculate stress concentration of metallic glass foils with different surface defects.

MG foil	Defect depth, t (μm)	Thickness, d (μm)	Ratio, t/d	Ratio, r/t	Stress concentration factor, K_t
Fe-based	7 to 8	19	0.36 to 0.42	1.9 to 2.6	~(1.9 to 2.6)
NiFe-based	6.5 to 10	25	0.40 to 0.26	0.27 to 0.41	~(1.7 to 2.4)
Ni-based	5 to 6	25	0.20 to 0.24	1.7 to 2.4	~(1.7 to 2.35)
Ni-based	5 to 6	40	0.12 to 0.15	1.7 to 2.4	~(1.7 to 2.35)

7.2.6 Suggestions to improve the fatigue property of metallic glass foils

Previous work [2] suggested, and this research has confirmed, that the fatigue cracking mechanism in MG foils is mediated by shear bands. Fatigue resistance of metallic glass foils can be enhanced, and cycle lifetime increased by controlling shear band behaviour and improving surface finishing. The fatigue life of many metallic glasses is presently unsatisfactory.

For instance, Yousfi, et al., [2] conducted compression-decompression fatigue experiments on $\text{Fe}_{90.65}\text{B}_{3.9}\text{Cr}_{2.75}\text{Si}_{2.7}$ glassy foil with 3 sinusoidal arcs and found that the fatigue endurance limit was only around 7×10^3 cycles. They suggested that improving the surface quality of metallic glass foils may significantly increase the cycling lifespan which is in agreement with the results reported in this study. According to the present results, the low fatigue endurance limit of these metallic glass foils may be attributed to the surface defects, which cannot effectively block the shear band propagation and fatigue crack initiation. Therefore, elimination of defects in the surface of metallic glass foils could be a key to improving the fatigue property of metallic glasses. This might be achieved by avoiding casting defects during fabrication by using moulds with better surface finish.

7.2.7 Suggestions force ranges and fatigue life requirements in spring applications

As a result of the applied load, each of the glassy alloys tested displayed good fatigue endurance. The majority of the specimens tested reached up to 27×10^3 cycles, for specific conditions $L=20$ mm and depending on arc formation. At the force range of 1N Fe-based glassy foil exhibited comparable fatigue endurance to the commercial alloys reached 2.3×10^5 cycles. Based on these preliminary results, the Fe-based alloy exhibits potential for fatigue applications, e.g., micro-flat spring mechanisms. However, fatigue performance was not as good as that of conventional crystalline alloys but may be sufficient if force /or strain levels are relatively kept low. Due to this, fatigue life requirements for spring applications can vary depending on factors such as their type, intended use, material, and

design. Fatigue life is a critical consideration for springs because they often undergo cyclic loading (compression and expansion) during their operational life.

Figure 7-4 (in section 7.2.2) suggests that the fatigue life and force ranges expected in metallic glass foils for applications such as springs such as MEMS, shock absorbers and micro-flat springs to estimate their lifespan based on the applied load. Consequently, the load versus number of cycles under loading conditions can be used to understand fatigue behaviour of springs as a function of load. It is essential to control the loading conditions to prevent spring fatigue. Fatigue resistance of springs can be determined by considering the expected load levels, whether in high-cycle or low-cycle applications. Table 7-11 provides load ranges of fatigue life requirements expected for metallic glass foils tested in this work to be used as spring applications.

Table 7-11. Force ranges and fatigue limit requirements in MG foils for spring applications.

Metallic glass foil	Boundary lengths L	Cycles to failure (N_f)	Max-strain (%)	Max-Working load (N)	Sinusoidal arcs formation
Fe-based	20	2.3×10^5 to 10^3	0.2 to 1.9	120	2 to 6
Ni-based- 25 μm	20	19×10^3 to 546	0.42 to 1.8	186	2 to 5
NiFe-based- 25 μm	20	25×10^3 to 840	0.42 to 1.8	170	2 to 5

Certain spring applications such as the helical compression springs, are made of Si-Cu alloyed valve spring wire with a diameter between 2mm to 5 mm. The fatigue cycle to failure for these springs falls within the range of 10^7 to 10^9 cycles, with an ultimate strength of 2216 MPa [178].

Additionally, for leaf spring type SAE, the predicted fatigue life is based on Figure 7-25, which indicates a maximum stress of 885 MPa and an initial stress value of

200 MPa. The intersection of 885 MPa and 200 MPa lies in the zone of 5×10^4 to 7.5×10^4 cycles. According to the vehicle manufacturer, the maximum stress of 896 MPa corresponds to the maximum load of 2 g, while the minimum stress of 269 MPa corresponds to the maximum load of 0.6 g. Based on these estimates, the leaf spring is expected to sustain around 6.8×10^4 cycles [179].

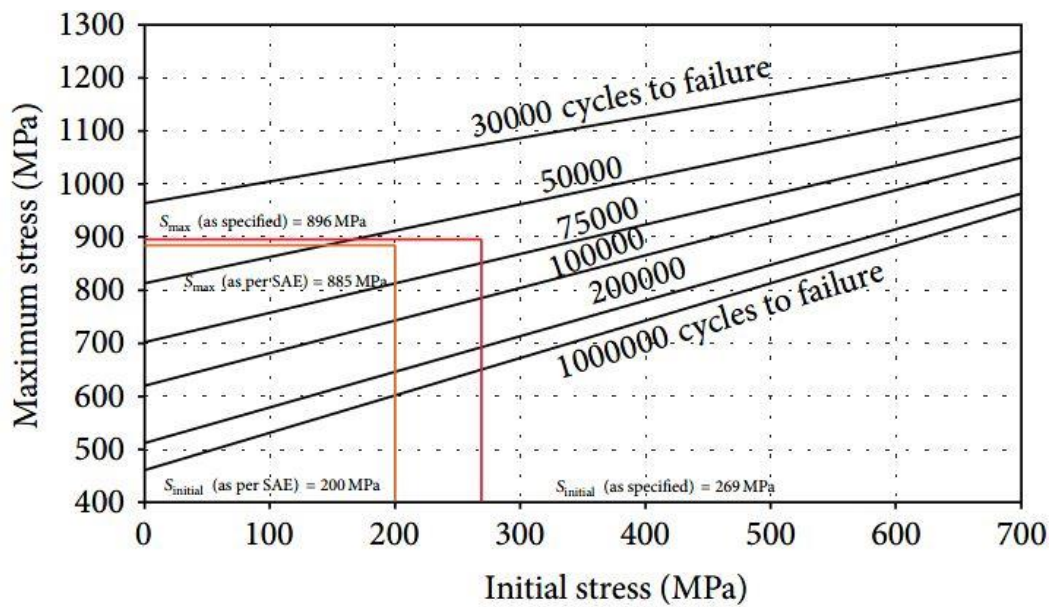


Figure 7-25. Maximum applied load versus initial load /or stress for leaf spring [179].

Another type of spring applications used in shock absorbers in automobile suspension systems as triangular wave with a frequency of 4 HZ and SAE standard suspension loading. The fatigue cycle to failure around 4×10^5 cycles. Overall, these springs must sustain millions of cycles of operation without failure [180]. Table 7-12 summarises the fatigue life of spring-type applications and their force range.

Table 7-12. Fatigue life requirements of spring applications.

Spring applications	Material	Cycles to failure (Nf)	Max-Working stress (MPa)
Helical spring	Si-Cu alloyed	10^7 to 10^9	2216
Leaf spring	SAE 65Si7	6.8×10^4	896
Shock absorber	SAE 9254	4×10^5	2950

7.3 Conclusions

The cyclic lifetime of metallic glass foils of Fe-Cr-Si-B, Fe-Ni-Si-B-Mo and Ni-B-Si containing the crystalline phase has been studied. Due to their being thinner, the metallic glass foils of Fe-Cr-Si-B alloy showed higher cyclic loading than the two other glassy foils. The cycles to failure for low strain, which is run from initial arc-shaped to 2 sinusoidal arcs just before a new arc formation (n_i+1), was found to be higher than 225×10^3 cycles compared to 27×10^3 with cyclic loading form (1 to 2) entirely perfect sinusoidal arcs. Tension-compression during cyclic loading is upturned within undulatory behaviour, further degrading the lifespan of metallic glass foils. When the fatigue results were plotted in terms of applied load and strain range, the Fe-based foil had higher fatigue life in terms of cycles to the failure than the other glassy foils. The present results show that crack sites in the different glassy foils are located in much the same positions, in the middle or near the edges of foils. It was observed that crack initiation occurred when the maximum strain was present at the crack site.

Surface analysis showed that the surface state significantly affected the fatigue life and led to crack initiation due to stress concentration which often occurred near casting defects on the wheel-side. The bottom of valleys tins the casting defects are sites for nucleation and crack initiation, indicating that the highest stress occurred around these defects.

The fatigue performance of the glassy foils could be improved in two ways: (1) reducing surface defects and enhancing surface finish during foil manufacture to reduce the number and magnitude of consequential stress concentrations, and (2) avoiding foil misalignment as much as possible during set-up.

Increasing stress, reduces fatigue resistance against strain at specific sites, primarily due to surface defects. The fatigue performance of glassy foils under an applied undulatory loading is limited due to stress acting along the foils. It was found that Fe-based foils had a superior fatigue life compared to the other glassy foils tested due to a difference in Young's modulus and thickness, resulting in a higher resistance to strain.

8 Conclusions and future work

8.1 General conclusions

The thesis investigates the undulatory behaviour of metallic glass foils that can potentially be exploited for engineering purposes. The undulatory behaviour of metallic glasses of different compositions and thicknesses was studied. Moreover, partially crystalline structures also were examined. The fatigue life of metallic glass foils was determined. Different parameters (boundary lengths L , amplitude h and thickness d) were tested.

In depth critical literature review has been carried out to meet **objective 1**. Based on this literature it has been unidentified that:

The main research findings related to the undulatory behaviour and mechanism of undulatory behaviour that causes these transitions. The fatigue life of metallic glass foils considered in this work suggests that the other metallic glass foils selected for in-depth testing would be feasible due to the presumed ability of the fatigue lives for those metallic glass foils. The main findings from this investigation are:

Firstly, the undulatory behaviour has been shown for various metallic glass foils of a fully amorphous and partially crystalline nature. Extensive experimental work on investigates the effect of geometrical characteristic, impact loading rate and impact of foil thickness has been carried out to meet **objectives 2, 3 and 4**. The effect of the geometry initial sinusoidal arc set-up on the boundary length L was investigated. It was found that higher L values lead to a lower load for the same number of arcs. However, the initial arc set-ups with higher L values can allow the formation of a higher number of arcs while remaining in the elastic deformation region of the metallic glass foils, thus being able to reach higher loads before (local) plastic deformation occurs. For a set-up of the same geometry (initial length L and arc's amplitude h) the new arc formation ($n+1$) occurs at the same displacement independently of the type of alloy or the thickness of the ribbon. It was shown that the undulatory behaviour is repeatable after cycling loading and unloading, returning to the initial shape and position,

similar to a non-linear spring-type behaviour. However, undulatory behaviour showed a hysteresis during unloading compared to the loading path.

The foil reaches maximum local strain at those steps (waveforms) with a maximum distorted shape that exhibit the highest bending or the smallest radius of curvature. The local strain on the foils at the distorted shape is significantly higher compared to the local strain at the perfect sinusoidal arcs; thus, the limitation for the maximum number of arcs must be measured at the steps of maximum distortion of the foils. Therefore, the strain must be primarily considered immediately at steps of maximum distortion, before forming a new (n_i+1) arc.

With increasing the foil's thickness, the required load cause bending and buckling to increase; however, plastic deformation would be reached earlier (in terms of number of arcs) compared to thinner foil.

Based on the experimental work and analysis carried out, the ability of processing the mechanism mentioned in **objective 5** through the studied underlying mechanism led to undulatory behaviour and the pathway to arc multiplication. The following is the conclusion made; the main phenomena occurring include bending, buckling and post-buckling in a repeatable manner. The Euler equation was used to analyse the buckling critical load during the undulatory behaviour.

A modified expression of the standing wave equation was found to describe well the waveforms where the foil exhibits only perfect sinusoidal arcs. In contrast, it cannot describe waveforms with distorted shapes. Even though this Equation does not give information on the applied load within undulatory behaviour, it can still be a valuable tool in designing any type of spring set-ups. Furthermore, it can generate unlimited waveforms of sinusoidal arcs as it does not restrict to metallic glass foils limitation of 2% strain.

Extensive experimental work on fatigue and analysis crack initiation and surface finishing has been carried out to meet **objective 6**. Based on the experimental work key operational parameters and materials analysis work gave in-depth understanding of the fatigue life of various of metallic glass foils. This work has led to the following conclusions; the main tests of the cyclic loading/unloading

behaviour was characterised under various applied load or/strain range conditions. The cycle fatigue life of glassy alloy foils was found to be greater than partially crystalline. The fatigue lifespan of metallic glass foils undergoing cyclic loading decreased as the maximum local strain increased, and the thickness of the foil influences fatigue life during cyclic loading due to different stress and strain values involved in different foil thicknesses. Cracking was found to initiate from surface defects of MG foil acting as stress concentration points and leading to localised plastic deformation and crack formation. Similarly, the side edges of the foils can also act as stress concentration points due to their sharp geometry, leading to crack initiation under cyclic loading conditions. For further improvement, post-surface treatment is expected to increase the lifespan of glassy foils by eliminating surface casting defects.

8.2 Future work recommendations

This section focuses on proposing the possible aspects that can be considered to further extend or improve this research work in the future:

The undulatory behaviour of arc-shaped metallic glass foils studied in this work could be modelled using programming to read data of undulation that needs to be analysed. For example, Abaqus can be used to simulate the undulatory behaviour of metallic glass foils by creating a finite element model. However, it needs to define an appropriate constitutive model that captures the non-linear behaviour of MG foils. It is worth noting that modelling the behaviour of metallic glass foils in Abaqus can be challenging due to the complex nature of their deformation behaviour. The simulation results' accuracy depends on the material model's accuracy and the assumptions made during the modelling process. It is recommended to validate the model against experimental data and adjust the material parameters if needed.

Surface defects were found to be a primary reason for generating cracks at these sites; further work would be of interest if capturing initial crack defects applied using impact sound were seen to cause early stages of crack initiation. Also, from the results of this work, it is found that the limited fatigue life is due to the maximum local strain around crack sites. These multiple mechanisms would be

available to cause fatigue failure. Further work would be interesting to identify mechanisms that relieve strain along metallic glass foils within undulatory behaviour to extend fatigue life during cyclic loading. Carefully optimising the loading conditions can help minimise strain along the ribbon; it is possible to reduce strain accumulation and mitigate fatigue damage.

The undulatory behaviour of metallic glass foils can be used to develop sensors and actuators that can detect and respond to environment changes, such as sensing and actuation. Future work could focus on optimising the design and fabrication of these devices to improve their sensitivity and response time.

In addition, the undulatory behaviour of metallic glass foils can also be used to generate electricity from vibrations and other types of mechanical energy. It would be an exciting future project to develop new materials and designs for energy harvesting devices to take advantage of this behaviour and improve their efficiency and durability. Furthermore, the undulatory behaviour of these foils can be used to improve their ability to absorb shock and resist deformation under extreme conditions. Future work could focus on developing new materials and designs for structural applications that can take advantage of this behaviour and improve their performance and reliability.

REFERENCES

- [1] Panagiotopoulos, N. T., Yousfi, M. A., Georgarakis, K. and Yavari, A. R. (2016) 'Mechanically induced waves in metallic glass foils', *Materials and Design*, 90, pp. 1110–1114. doi: 10.1016/j.matdes.2015.10.149.
- [2] Yousfi, M. A., Panagiotopoulos, N. T., Jorge Junior, A. M., Georgarakis, K. and Yavari, A. R. (2017) 'Novel micro-flat springs using the superior elastic properties of metallic glass foils', *Scripta Materialia*, 131, pp. 84–88. doi: 10.1016/j.scriptamat.2017.01.012.
- [3] Son, K., Soejima, H., Nishiyama, N., Wang, X. M. and Inoue, A. (2007) 'Process development of metallic glass wires by a groove quenching technique for production of coil springs', *Materials Science and Engineering A*, 448–451, pp. 248–252. doi: 10.1016/j.msea.2006.02.309.
- [4] Schuh, C. A., Hufnagel, T. C. and Ramamurty, U. (2007) 'Mechanical behavior of amorphous alloys', *Acta Materialia*, 55(12), pp. 4067–4109. doi: 10.1016/j.actamat.2007.01.052.
- [5] Chan, K. C. and Sort, J. (2015) 'Metallic glasses', *Metals*, 5(4), pp. 2397–2400. doi: 10.3390/met5042397.
- [6] Qiao, J., Jia, H. and Liaw, P. K. (2016) 'Metallic glass matrix composites', *Materials Science and Engineering R: Reports*, 100, pp. 1–69. doi: 10.1016/j.mser.2015.12.001.
- [7] Ye, J. C., Lu, J., Liu, C. T., Wang, Q. and Yang, Y. (2010) 'Atomistic free-volume zones and inelastic deformation of metallic glasses', *Nature Materials*, 9(8), pp. 619–623. doi: 10.1038/nmat2802.
- [8] Kruzic, J. J. (2016) 'Bulk metallic glasses as structural materials: a review', *Advanced Engineering Materials*, 18(8), pp. 1308–1331. doi: 10.1002/adem.201600066.
- [9] Inoue, A. (1998) 'Amorphous, nanoquasicrystalline and nanocrystalline alloys in Al-based systems', *Progress in Materials Science*, 43(5), pp. 365–520. doi:

10.1016/S0079-6425(98)00005-X.

[10] Chen, H. S. (1974) 'Thermodynamic considerations on the formation and stability of metallic glasses', *Acta Metallurgica*, 22(12), pp. 1505–1511. doi: 10.1016/0001-6160(74)90112-6.

[11] Inoue, A., Yamaguchi, H., Zhang, T. and Masumoto, T. (1990) 'Al-La-Cu amorphous alloys with a wide supercooled liquid region', *Materials Transactions, JIM*, 31(2), pp. 104–109. doi: 10.2320/matertrans1989.31.104.

[12] Inoue, A. and Zhang, T. (1995) 'Fabrication of bulky Zr-based glassy alloys by suction casting into copper mold', *Materials Transactions, JIM*, 36(9), pp. 1184–1187. doi: 10.2320/matertrans1989.36.1184.

[13] Inoue, A., Nishiyama, N. and Kimura, H. (1997) 'Preparation and thermal stability of bulk amorphous Pd₄₀Cu₃₀Ni₁₀P₂₀ alloy cylinder of 72 mm in diameter', *Materials Transactions-JIM*, 38, pp. 179–183. doi: 10.1016/S0022-3093(03)00006-1.

[14] Telford, M. (2004) 'The case for bulk metallic glass', *Materials Today*, 7(3), pp. 36–43. doi: 10.1016/S1369-7021(04)00124-5.

[15] Ritchie, R. O. (2011) 'The conflicts between strength and toughness', *Nature Materials*. Nature Publishing Group, 10(11), pp. 817–822. doi: 10.1038/nmat3115.

[16] Greer, A. L. (2009) 'Metallic glasses...on the threshold', *Materials Today*, 12(1–2), pp. 14–22. doi: 10.1016/S1369-7021(09)70037-9.

[17] Egami, T., Iwashita, T. and Dmowski, W. (2013) 'Mechanical properties of metallic glasses', *Metals*, 3(1), pp. 77–113. doi: 10.3390/met3010077.

[18] Ashby, M. F. and Greer, A. L. (2006) 'Metallic glasses as structural materials', *Scripta Materialia*, 54(3), pp. 321–326. doi: 10.1016/j.scriptamat.2005.09.051.

[19] Klement, W., Willens, R. H. and Duwez, P. (1960) 'Non-crystalline structure in solidified gold–silicon alloys', *Nature*, 187(4740), pp. 869–870. doi: 10.1038/187869b0.

- [20] Cheng, Y. Q. and Ma, E. (2011) 'Atomic-level structure and structure-property relationship in metallic glasses', *Progress in Materials Science*, 56(4), pp. 379–473. doi: 10.1016/j.pmatsci.2010.12.002.
- [21] Debenedetti, P. G. and Stillinger, F. H. (2001) 'Review article Supercooled liquids and the glass transition', *Nature*, 410(March), p. 259.
- [22] Löffler, J. F. (2003) 'Bulk metallic glasses', *Intermetallics*, 11(6), pp. 529–540. doi: 10.1016/S0966-9795(03)00046-3.
- [23] Ediger, M. D., Angell, C. A. and Nagel, S. R. (1996) 'Supercooled liquids and glasses', *Journal of Physical Chemistry*, 100(31), pp. 13200–13212. doi: 10.1021/jp953538d.
- [24] Suryanarayana, C. and Inoue, A. (2012) 'Metallic Glasses', in *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, pp. 413–454. doi: 10.1002/14356007.a16_335.pub2.
- [25] Suryanarayana, C. and Inoue, A. (2017) *Bulk metallic glasses*. 2nd edn. Boca Raton: CRC Press.
- [26] Suryanarayana, C. and Inoue, A. (2010) 'Synthesis of Bulk Metallic Glasses', *Bulk Metallic Glasses*, (May), pp. 145–186. doi: 10.1201/9781420085976-5.
- [27] Greer, A. L. (2001) 'Metallic glasses', in *Encyclopedia of Materials: Science and Technology*. 2nd edn. Elsevier, Amsterdam, pp. 5529–5537. doi: 10.1016/B0-08-043152-6/00967-0.
- [28] Greer, A. L. (1995) 'Metallic glasses', *Science*, 267(5206), pp. 1947–1953. doi: 10.1126/science.267.5206.1947.
- [29] Suryanarayana, C. and Inoue, A. (2010) *Bulk metallic glasses*. 1st edn. CRC Press. doi: 10.1201/9781420085976.
- [30] Shyh-Chin, H. and Fiedler, H. C. (1981) 'Effects of wheel surface conditions on the casting of amorphous metal ribbons.', *Metallurgical transactions. A, Physical metallurgy and materials science*, 12 A(6), pp. 1107–1112. doi: 10.1007/BF02643492.

- [31] Lin, C. J. and Spaepen, F. (1986) 'Nickel-niobium alloys obtained by picosecond pulsed laser quenching', *Acta Metallurgica*, 34(7), pp. 1367–1375. doi: 10.1016/0001-6160(86)90024-6.
- [32] Schwarz, R. B. and Johnson, W. L. (1983) 'Formation of an amorphous alloy by solid-state reaction of the pure polycrystalline metals', *Physical Review Letters*, 51(5), pp. 415–418. doi: 10.1103/PhysRevLett.51.415.
- [33] Trexler, M. M. and Thadhani, N. N. (2010) 'Mechanical properties of bulk metallic glasses', *Progress in Materials Science*, 55(8), pp. 759–839. doi: 10.1016/j.pmatsci.2010.04.002.
- [34] Inoue, A. and Takeuchi, A. (2011) 'Recent development and application products of bulk glassy alloys', *Acta Materialia*, 59(6), pp. 2243–2267. doi: 10.1016/j.actamat.2010.11.027.
- [35] Carmo, M., Sekol, R. C., Ding, S., Kumar, G., Schroers, J. and Taylor, A. D. (2011) 'Bulk metallic glass nanowire architecture for electrochemical applications', *ACS Nano*, 5(4), pp. 2979–2983. doi: 10.1021/nn200033c.
- [36] Wang, W. H. (2012) 'The elastic properties, elastic models and elastic perspectives of metallic glasses', *Progress in Materials Science*, 57(3), pp. 487–656. doi: 10.1016/j.pmatsci.2011.07.001.
- [37] Sun, B. A. and Wang, W. H. (2015) 'The fracture of bulk metallic glasses', *Progress in Materials Science*, 74, pp. 211–307. doi: 10.1016/j.pmatsci.2015.05.002.
- [38] Tian, L., Cheng, Y. Q., Shan, Z. W., Li, J., Wang, C. C., Han, X. D., Sun, J. and Ma, E. (2012) 'Approaching the ideal elastic limit of metallic glasses', *Nature Communications*, 3, pp. 1–6. doi: 10.1038/ncomms1619.
- [39] Cheng, Y. Q. and Ma, E. (2011) 'Intrinsic shear strength of metallic glass', *Acta Materialia*, 59(4), pp. 1800–1807. doi: 10.1016/j.actamat.2010.11.046.
- [40] Wang, W. H. (2006) 'Correlations between elastic moduli and properties in bulk metallic glasses', *Journal of Applied Physics*, 99(9). doi: 10.1063/1.2193060.

- [41] Wang, W. H. (2012) 'Metallic glasses: Family traits', *Nature Materials*, 11(4), pp. 275–276. doi: 10.1038/nmat3277.
- [42] Greaves, G. N., Greer, A. L., Lakes, R. S. and Rouxel, T. (2011) 'Poisson's ratio and modern materials', *Nature Materials*, 10(11), pp. 823–837. doi: 10.1038/nmat3134.
- [43] Qiao, J. C., Wang, Q., Pelletier, J. M., Kato, H., Casalini, R., Crespo, D., Pineda, E., Yao, Y. and Yang, Y. (2019) 'Structural heterogeneities and mechanical behavior of amorphous alloys', *Progress in Materials Science*, 104, pp. 250–329. doi: 10.1016/j.pmatsci.2019.04.005.
- [44] Song, K. K., Pauly, S., Sun, B. A., Tan, J., Stoica, M., Kühn, U. and Eckert, J. (2013) 'Correlation between the microstructures and the deformation mechanisms of CuZr-based bulk metallic glass composites', *AIP Advances*, 3(1). doi: 10.1063/1.4789516.
- [45] Pauly, S., Gorantla, S., Wang, G., Kühn, U. and Eckert, J. (2010) 'Transformation-mediated ductility in CuZr-based bulk metallic glasses', *Nature Materials*, 9(6), pp. 473–477. doi: 10.1038/nmat2767.
- [46] Hufnagel, T. C., Schuh, C. A. and Falk, M. L. (2016) 'Deformation of metallic glasses: Recent developments in theory, simulations, and experiments', *Acta Materialia*, 109, pp. 375–393. doi: 10.1016/j.actamat.2016.01.049.
- [47] Klaumünzer, D., Maa, R., Torre, F. H. D. and Löffler, J. F. (2010) 'Temperature-dependent shear band dynamics in a Zr-based bulk metallic glass', *Applied Physics Letters*, 96(6). doi: 10.1063/1.3309686.
- [48] Chen, J. H., Jiang, M. Q., Chen, Y. and Dai, L. H. (2013) 'Strain rate dependent shear banding behavior of a Zr-based bulk metallic glass composite', *Materials Science and Engineering A*, 576, pp. 134–139. doi: 10.1016/j.msea.2013.03.082.
- [49] Han, Z., Wu, W. F., Li, Y., Wei, Y. J. and Gao, H. J. (2009) 'An instability index of shear band for plasticity in metallic glasses', *Acta Materialia*, 57(5), pp. 1367–1372. doi: 10.1016/j.actamat.2008.11.018.

- [50] Wu, F. F., Zhang, Z. F. and Mao, S. X. (2007) 'Compressive properties of bulk metallic glass with small aspect ratio', *Journal of Materials Research*, 22(2), pp. 501–507. doi: 10.1557/jmr.2007.0064.
- [51] Inoue, A. (1997) 'Bulk amorphous alloys with soft and hard magnetic properties', *Materials Science and Engineering A*, 226–228, pp. 357–363. doi: 10.1016/s0921-5093(97)80049-4.
- [52] Shen, J., Chen, Q., Sun, J., Fan, H. and Wang, G. (2005) 'Exceptionally high glass-forming ability of an FeCoCrMoCBY alloy', *Applied Physics Letters*, 86(15), pp. 1–3. doi: 10.1063/1.1897426.
- [53] HAN, J., WANG, C., KOU, S. and LIU, X. (2013) 'Comparison of fatigue behaviour of a bulk metallic glass and its composite', *Transactions of Nonferrous Metals Society of China*, 23(1), pp. 148–155. doi: 10.1016/S1003-6326(13)62441-3.
- [54] Inoue, A. (2000) 'Stabilization of metallic supercooled liquid and bulk amorphous alloys', *Acta Materialia*, 48(1), pp. 279–306. doi: 10.1016/S1359-6454(99)00300-6.
- [55] Inoue, A. and Shen, B. (2002) 'Soft magnetic bulk glassy Fe-B-Si-Nb alloys with high saturation magnetization above 1.5 T', *Materials Transactions*, 43(4), pp. 766–769. doi: 10.2320/matertrans.43.766.
- [56] Stoica, M., Eckert, J., Roth, S., Zhang, Z. F., Schultz, L. and Wang, W. H. (2005) 'Mechanical behavior of Fe_{65.5}Cr₄Mo₄Ga₄P₁₂C₅B_{5.5} bulk metallic glass', *Intermetallics*, 13(7), pp. 764–769. doi: 10.1016/j.intermet.2004.12.016.
- [57] Makino, A., Li, X., Yubuta, K., Chang, C., Kubota, T. and Inoue, A. (2009) 'The effect of Cu on the plasticity of Fe-Si-B-P-based bulk metallic glass', *Scripta Materialia*, 60(5), pp. 277–280. doi: 10.1016/j.scriptamat.2008.09.008.
- [58] Inoue, A., Shen, B. L., Yavari, A. R. and Greer, A. L. (2003) 'Mechanical properties of Fe-based bulk glassy alloys in Fe-B-Si-Nb and Fe-Ga-P-C-B-Si systems', *Journal of Materials Research*, 18(6), pp. 1487–1492. doi: 10.1557/JMR.2003.0205.

- [59] Gu, X. J., Poon, S. J. and Shiflet, G. J. (2007) 'Mechanical properties of iron-based bulk metallic glasses', *Journal of Materials Research*, 22(2), pp. 344–351. doi: 10.1557/jmr.2007.0036.
- [60] Amiya, K., Urata, A., Nishiyama, N. and Inoue, A. (2004) 'Fe-B-Si-Nb bulk metallic glasses with high strength above 4000 MPa and distinct plastic elongation', *Materials Transactions*, 45(4), pp. 1214–1218. doi: 10.2320/matertrans.45.1214.
- [61] Ponnambalam, V., Poon, S. J., Shiflet, G. J., Keppens, V. M., Taylor, R. and Petculescu, G. (2003) 'Synthesis of iron-based bulk metallic glasses as nonferromagnetic amorphous steel alloys', *Applied Physics Letters*, 83(6), pp. 1131–1133. doi: 10.1063/1.1599636.
- [62] Ponnambalam, V., Poon, J. S. and Shiflet, G. J. (2004) 'Fe-based bulk metallic glasses with diameter thickness larger than one centimeter', *Journal of Materials Research*, 19(5), pp. 1320–1323. doi: 10.1557/JMR.2004.0176.
- [63] Gu, X. J., McDermott, A. G., Poon, S. J. and Shiflet, G. J. (2006) 'Critical Poisson's ratio for plasticity in Fe-Mo-C-B-Ln bulk amorphous steel', *Applied Physics Letters*, 88(21), pp. 86–89. doi: 10.1063/1.2206149.
- [64] Ponnambalam, V., Poon, S. J. and Shiflet, G. J. (2004) 'Fe-Mn-Cr-Mo-(Y,Ln)-C-B (Ln = Lanthanides) bulk metallic glasses as formable amorphous steel alloys', *Journal of Materials Research*, 19(10), pp. 3046–3052. doi: 10.1557/JMR.2004.0374.
- [65] McHenry, M. E., Willard, M. A. and Laughlin, D. E. (1999) 'Amorphous and nanocrystalline materials for applications as soft magnets', *Progress in Materials Science*, 44(4), pp. 291–433. doi: 10.1016/S0079-6425(99)00002-X.
- [66] Inoue, A., Shinohara, Y. and Gook, J. S. (1995) 'Thermal and magnetic properties of bulk Fe-based glassy alloys prepared by copper mold casting', *Materials Transactions, JIM*, 36(12), pp. 1427–1433. doi: 10.2320/matertrans1989.36.1427.
- [67] Thorsson, L., Unosson, M., Teresa Pérez-Prado, M., Jin, X., Tiberto, P.,

Barrera, G., Adam, B., Neuber, N., Ghavimi, A., Frey, M., Busch, R. and Gallino, I. (2022) 'Selective laser melting of a Fe-Si-Cr-B-C-based complex-shaped amorphous soft-magnetic electric motor rotor with record dimensions', *Materials & Design*, 215, p. 110483. doi: 10.1016/j.matdes.2022.110483.

[68] Li, H. X., Lu, Z. C., Wang, S. L., Wu, Y. and Lu, Z. P. (2019) 'Fe-based bulk metallic glasses: glass formation, fabrication, properties and applications', *Progress in Materials Science*, 103, pp. 235–318. doi: 10.1016/j.pmatsci.2019.01.003.

[69] Inoue, A. and Gook, J. S. (1996) 'Effect of additional elements (m) on the thermal stability of supercooled liquid in fe₇₂-xal₅ga₂p₁₁c₆b₄mx glassy alloys', *Materials Transactions, JIM*, pp. 32–38. doi: 10.2320/matertrans1989.37.32.

[70] Inoue, A., Zhang, T. and Takeuchi, A. (1997) 'Bulk amorphous alloys with high mechanical strength and good soft magnetic properties in Fe-TM-B (TM=IV-VIII group transition metal) system', *Applied Physics Letters*, 71(4), pp. 464–466. doi: 10.1063/1.119580.

[71] Zhang, W. and Inoue, A. (2000) 'Formation and magnetic properties of bulk glassy Fe-Co-Nd-Dy-B alloys with high boron concentrations', *Materials Transactions, JIM*, 41(12), pp. 1679–1682. doi: 10.2320/matertrans1989.41.1679.

[72] Shen, B., Kimura, H., Inoue, A. and Mizushima, T. (2000) 'Bulk glassy Fe-Co-Ga-P-C-B alloys with high glass-forming ability, high saturation magnetization and good soft magnetic properties', *Materials Transactions, JIM*, 41(12), pp. 1675–1678. doi: 10.2320/matertrans1989.41.1675.

[73] Shen, B. L., Koshiba, H., Mizushima, T. and Inoue, A. (2000) 'Bulk amorphous Fe-Ga-P-B-C alloys with a large supercooled liquid region', *Materials Transactions, JIM*, 41(7), pp. 873–876. doi: 10.2320/matertrans1989.41.873.

[74] Shen, T. D. and Schwarz, R. B. (2001) 'Bulk ferromagnetic glasses in the Fe-Ni-P-B system', *Acta Materialia*, 49(5), pp. 837–847. doi: 10.1016/S1359-6454(00)00365-7.

- [75] Chen, Q., Zhang, D., Shen, J., Fan, H. and Sun, J. (2007) 'Effect of yttrium on the glass-forming ability of Fe-Cr-Mo-C-B bulk amorphous alloys', *Journal of Alloys and Compounds*, 427(1–2), pp. 190–193. doi: 10.1016/j.jallcom.2006.03.013.
- [76] Inoue, A., Kong, F. L., Man, Q. K., Shen, B. L., Li, R. W. and Al-Marzouki, F. (2015) 'Development and applications of Fe- and Co-based bulk glassy alloys and their prospects', *Journal of Alloys and Compounds*, 615(S1), pp. S2–S8. doi: 10.1016/j.jallcom.2013.11.122.
- [77] Savva, G., Waseda, Y. and Aust, K. T. (1987) 'Corrosion of Fe-Cr-Si-B metallic glass wires', *Materials Science and Engineering*, 85, pp. 157–164. doi: 10.1016/0025-5416(87)90477-0.
- [78] Inoue, A. and Wang, X. M. (2000) 'Bulk amorphous FC20 (Fe-C-Si) alloys with small amounts of B and their crystallized structure and mechanical properties', *Acta Materialia*, 48(6), pp. 1383–1395. doi: 10.1016/S1359-6454(99)00394-8.
- [79] Amiya, K., Urata, A., Nishiyama, N. and Inoue, A. (2007) 'Thermal stability and magnetic properties of (Fe, Co)-Ga-(P, C, B, Si) bulk glassy alloys', *Materials Science and Engineering A*, 448–451, pp. 356–359. doi: 10.1016/j.msea.2006.02.397.
- [80] Liu, F. J., Zhang, T., Pang, S. J. and Yao, K. F. (2010) 'Ductile Fe-based amorphous alloys with high iron content', *International Journal of Minerals, Metallurgy and Materials*, 17(2), pp. 199–203. doi: 10.1007/s12613-010-0213-z.
- [81] Inoue, A., Shen, B. L. and Chang, C. T. (2004) 'Super-high strength of over 4000 MPa for Fe-based bulk glassy alloys in [(Fe_{1-x}Co_x)_{0.75}B_{0.2}Si_{0.05}]₉₆Nb₄ system', *Acta Materialia*, 52(14), pp. 4093–4099. doi: 10.1016/j.actamat.2004.05.022.
- [82] Verduzco, J. A., Hand, R. J. and Davies, H. A. (2002) 'Fatigue behaviour of Fe-Cr-Si-B metallic glass wires', *International Journal of Fatigue*, 24(10), pp. 1089–1094. doi: 10.1016/S0142-1123(02)00014-2.

- [83] Olofinjana, A. O. and Davies, H. A. (1994) 'Determination of the static and dynamic mechanical properties of FeCrSiB metallic glass wire', *Materials Science and Engineering A*, 186(1–2), pp. 143–149. doi: 10.1016/0921-5093(94)90313-1.
- [84] Hasegawa, R. (2001) 'Applications of amorphous magnetic alloys in electronic devices', *Journal of Non-Crystalline Solids*, 287(1–3), pp. 405–412. doi: 10.1016/S0022-3093(01)00633-0.
- [85] Yodoshi, N., Yamada, R., Kawasaki, A. and Makino, A. (2014) 'Micro viscous flow processing of Fe-based metallic glassy particles', *Journal of Alloys and Compounds*, 615(S1), pp. S61–S66. doi: 10.1016/j.jallcom.2013.12.256.
- [86] Vodă, M., Codrean, C., Chicot, D., Șerban, V. A., Uțu, D., Linul, E. and Buzdugan, D. (2019) 'Characterization of brazed joints by electrical resistance spot brazing with Ni-based amorphous self-flux alloys', *Journal of Manufacturing Processes*, 37, pp. 617–627. doi: 10.1016/j.jmapro.2018.10.029.
- [87] Inoue, A., Furukawa, S., Hagiwara, M. and Masumoto, T. (1987) 'Preparation, mechanical strengths, and thermal Stability of Ni-Si-B and Ni-P-B Amorphous Wires', *Metallurgical and Materials Transactions A*, 18(4), pp. 621–628. doi: 10.1007/BF02649477.
- [88] Zhang, T. and Inoue, A. (2002) 'New bulk glassy Ni-based alloys with high strength of 3000 MPa', *Materials Transactions*, 43(4), pp. 708–711. doi: 10.2320/matertrans.43.708.
- [89] Choi-Yim, H., Xu, D. and Johnson, W. L. (2003) 'Ni-based bulk metallic glass formation in the Ni-Nb-Sn and Ni-Nb-Sn-X (X = B, Fe, Cu) alloy systems', *Applied Physics Letters*, 82(7), pp. 1030–1032. doi: 10.1063/1.1544434.
- [90] Wang, Y., Sun, X., Lei, X., Yang, J., Huang, J., Chen, S. and Zhao, Y. (2020) 'Preparation of Ni–Si–B nano-crystalline film and mechanism analysis using first-principle calculations', *Journal of Alloys and Compounds*, 828, p. 154407. doi: 10.1016/j.jallcom.2020.154407.
- [91] Ipatov, M., Zhukova, V., Dominguez, L., Alvarez, K. L., Chizhik, A., Zhukov,

- A. and Gonzalez, J. (2021) 'Structural and low-temperature magnetic properties of as-quenched and annealed Ni–Si–B alloys produced by rapid solidification', *Intermetallics*. Elsevier Ltd, 132, p. 107140. doi: 10.1016/j.intermet.2021.107140.
- [92] Donald, I. W. and Davies, H. A. (1980) 'The influence of composition on the formation and stability of Ni-Si-B metallic glasses', *Journal of Materials Science*, 15(11), pp. 2754–2760. doi: 10.1007/BF00550543.
- [93] Saiseng, S., Winotai, P., Nilpairuch, S., Limsuwan, P. and Tang, I. M. (2004) 'Nanocrystallization in amorphous Fe₄₀Ni₄₀(Si+B) 19Mo₁₋₂ ribbons', *Journal of Magnetism and Magnetic Materials*, 278(1–2), pp. 172–178. doi: 10.1016/j.jmmm.2003.11.404.
- [94] He, K. Y., Zhao, Y. H., Li, G. G., Cheng, L. Z., Wu, B., Sui, M. L. and Chen, W. Z. (2007) 'Studies of crystallization and soft magnetic properties of FeNiMoB(Si) alloys', *Journal of Magnetism and Magnetic Materials*, 316(1), pp. 34–39. doi: 10.1016/j.jmmm.2007.03.193.
- [95] Chen, H. S. and Polk, D. E. (1974) 'Mechanical properties of Ni-Fe based alloy glasses', *Journal of Non-Crystalline Solids*, 15(2), pp. 174–178. doi: 10.1016/0022-3093(74)90046-5.
- [96] Polk, D. E. and Chen, H. S. (1974) 'Formation and thermal properties of glassy NiFe based alloys', *Journal of Non-Crystalline Solids*, 15(2), pp. 165–173. doi: 10.1016/0022-3093(74)90045-3.
- [97] Shen, B., Chang, C. and Inoue, A. (2006) 'Ni-based bulk glassy alloys with superhigh strength of 3800 MPa in Ni-Fe-B-Si-Nb system', *Applied Physics Letters*, 88(20), pp. 1–4. doi: 10.1063/1.2204440.
- [98] Zhang, L., Ma, X., Li, Q., Zhang, J., Dong, Y. and Chang, C. (2014) 'Preparation and properties of Fe_{80-x}Ni_xP₁₄B₆ bulk metallic glasses', *Journal of Alloys and Compounds*, 608, pp. 79–84. doi: 10.1016/j.jallcom.2014.04.114.
- [99] Timoshenko, S. P. and Gere, J. M. (2012) *Theory of elastic stability*. London: Dover publications.

- [100] Li, B., Cao, Y. P., Feng, X. Q. and Gao, H. (2012) 'Mechanics of morphological instabilities and surface wrinkling in soft materials: A review', *Soft Matter*, 8(21), pp. 5728–5745. doi: 10.1039/c2sm00011c.
- [101] Shima, H. (2011) 'Buckling of carbon nanotubes: a state of the art review', *Materials*, 5(12), pp. 47–84. doi: 10.3390/ma5010047.
- [102] Sato, M. and Patel, M. H. (2007) 'Exact and simplified estimations for elastic buckling pressures of structural pipe-in-pipe cross sections under external hydrostatic pressure', *Journal of Marine Science and Technology*, 12(4), pp. 251–262. doi: 10.1007/s00773-007-0244-y.
- [103] Zhang, Y. Y., Wang, C. M. and Tan, V. B. C. (2008) 'Examining the effects of wall numbers on buckling behavior and mechanical properties of multiwalled carbon nanotubes via molecular dynamics simulations', *Journal of Applied Physics*, 103(5). doi: 10.1063/1.2890146.
- [104] Jeong, B. W., Lim, J. K. and Sinnott, S. B. (2008) 'Tuning the torsional properties of carbon nanotube systems with axial prestress', *Applied Physics Letters*, 92(25), pp. 1–4. doi: 10.1063/1.2945665.
- [105] Wang, X., Sun, B. and Yang, H. K. (2006) 'Stability of multi-walled carbon nanotubes under combined bending and axial compression loading', *Nanotechnology*, 17(3), pp. 815–823. doi: 10.1088/0957-4484/17/3/034.
- [106] Zhang, R., Wen, Q., Qian, W., Su, D. S., Zhang, Q. and Wei, F. (2011) 'Superstrong ultralong carbon nanotubes for mechanical energy storage', *Advanced Materials*, 23(30), pp. 3387–3391. doi: 10.1002/adma.201100344.
- [107] Yap, H. W., Lakes, R. S. and Carpick, R. W. (2007) 'Mechanical instabilities of individual multiwalled carbon nanotubes under cyclic axial compression', *Nano Letters*, 7(5), pp. 1149–1154. doi: 10.1021/nl062763b.
- [108] Kuzumaki, T. and Mitsuda, Y. (2006) 'Nanoscale mechanics of carbon nanotube evaluated by nanoprobe manipulation in transmission electron microscope', *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers*, 45(1 A), pp. 364–368. doi:

10.1143/JJAP.45.364.

[109] Ajori, S., Parsapour, H., Ansari, R. and Ameri, A. (2019) 'Buckling behavior of various metallic glass nanocomposites reinforced by carbon nanotube and Cu nanowire: A molecular dynamics simulation study', *Materials Research Express*, 6(9), p. 095070. doi: 10.1088/2053-1591/ab2cfd.

[110] Sun, F. W., Li, H. and Liew, K. M. (2010) 'Compressive mechanical properties of carbon nanotubes encapsulating helical copper nanowires', *Carbon*, 48(5), pp. 1586–1591. doi: 10.1016/j.carbon.2009.12.056.

[111] Wachter, J., Gutiérrez, G., Zúñiga, A. and Palma, R. (2014) 'Buckling of Cu-Zr-based metallic glasses nanowires: Molecular dynamics study of surface effects', *Journal of Materials Science*, 49(23), pp. 8051–8056. doi: 10.1007/s10853-014-8512-9.

[112] Demetriou, M. D., Hanan, J. C., Veazey, C., Michiel, M. Di, Lenoir, N., Üstündag, E. and Johnson, W. L. (2007) 'Yielding of metallic glass foam by percolation of an elastic buckling instability', *Advanced Materials*, 19(15), pp. 1957–1962. doi: 10.1002/adma.200602136.

[113] Wang, J. G., Chan, K. C., Fan, J. C., Xia, L., Wang, G. and Wang, W. H. (2014) 'Buckling of metallic glass bars', *Journal of Non-Crystalline Solids*, 387, pp. 1–5. doi: 10.1016/j.jnoncrysol.2013.12.008.

[114] Meduri, C. S., Hu, Z., Blawdziewicz, J. and Kumar, G. (2019) 'Buckling of metallic glass supercooled liquid layer during embossing', *Applied Physics Letters*, 114(11), pp. 0–4. doi: 10.1063/1.5091721.

[115] Chen, T. H. and Tsai, C. K. (2015) 'The microstructural evolution and mechanical properties of Zr-based metallic glass under different strain rate compressions', *Materials*, 8(4), pp. 1831–1840. doi: 10.3390/ma8041831.

[116] Li, J. F., Soldatov, I. V., Tang, X. C., Sun, B. Y., Schafer, R., Liu, S. L., Yan, Y. Q., Ke, H. B., Sun, Y. H., Orava, J. and Bai, H. Y. (2022) 'Metallic Mimosa pudica: A 3D biomimetic buckling structure made of metallic glasses', *Science Advances*, 8(31), pp. 1–9. doi: 10.1126/sciadv.abm7658.

- [117] Yousfi, M. A., Ammari, C., Hajlaoui, K., Panagiotopoulos, N. T., Georgarakis, K. and Tourki, Z. (2017) 'On a new electromechanical switch using the reversible wavy elastic response of metallic glass ribbons', *Comptes Rendus - Mecanique*, 345(11), pp. 797–804. doi: 10.1016/j.crme.2017.07.005.
- [118] Panagiotopoulos, N. T., Georgarakis, K., Jorge, A. M., Aljerf, M., Botta, W. J., Greer, A. L. and Yavari, A. R. (2020) 'Advanced ultra-light multifunctional metallic-glass wave springs', *Materials and Design*, 192, p. 108770. doi: 10.1016/j.matdes.2020.108770.
- [119] Yousfi, M. A., Ammari, C., Hajlaoui, K., Loukil, H. and Tourki, Z. (2019) 'Constitutive modelling of wavy elastic response of metallic glass ribbon', *Philosophical Magazine Letters*, 99(11), pp. 414–423. doi: 10.1080/09500839.2019.1696482.
- [120] Peker, A. and Johnson, W. L. (1993) 'A highly processable metallic glass: Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}', *Applied Physics Letters*, 63(17), pp. 2342–2344. doi: 10.1063/1.110520.
- [121] Wang, W. H., Dong, C. and Shek, C. H. (2004) 'Bulk metallic glasses', *Materials Science and Engineering R: Reports*, 44(2–3), pp. 45–89. doi: 10.1016/j.mser.2004.03.001.
- [122] Nguyen, D. S., Halvorsen, E., Jensen, G. U. and Vogl, A. (2010) 'Fabrication and characterization of a wideband MEMS energy harvester utilizing nonlinear springs', *Journal of Micromechanics and Microengineering*, 20(12). doi: 10.1088/0960-1317/20/12/125009.
- [123] Grech, D., Kiang, K. S., Zekonyte, J., Stolz, M., Wood, R. J. K. and Chong, H. M. H. (2014) 'Highly linear and large spring deflection characteristics of a Quasi-Concertina MEMS device', *Microelectronic Engineering*. Elsevier B.V., 119, pp. 75–78. doi: 10.1016/j.mee.2014.02.016.
- [124] Yavari, A. R. (2006) 'A new order for metallic glasses', *Nature*, 439(7075), pp. 405–406. doi: 10.1038/439405a.
- [125] Pang, S. J., Zhang, T., Asami, K. and Inoue, A. (2002) 'Synthesis of Fe-Cr-

Mo-C-B-P bulk metallic glasses with high corrosion resistance', *Acta Materialia*, 50(3), pp. 489–497. doi: 10.1016/S1359-6454(01)00366-4.

[126] Georgarakis, K., Aljerf, M., Li, Y., Lemoulec, A., Charlot, F., Yavari, A. R., Chornokhvostenko, K., Tabachnikova, E., Evangelakis, G. A., Miracle, D. B., Greer, A. L. and Zhang, T. (2008) 'Shear band melting and serrated flow in metallic glasses', *Applied Physics Letters*, 93(3), pp. 2–5. doi: 10.1063/1.2956666.

[127] Aljerf, M., Georgarakis, K. and Yavari, A. R. (2011) 'Shaping of metallic glasses by stress-annealing without thermal embrittlement', *Acta Materialia*. Acta Materialia Inc., 59(10), pp. 3817–3824. doi: 10.1016/j.actamat.2011.02.039.

[128] Taub, A. I. and Spaepen, F. (1980) 'The kinetics of structural relaxation of a metallic glass', *Acta Metallurgica*, 28(12), pp. 1781–1788. doi: 10.2307/1513287.

[129] Taub, A. I. and Walter, J. L. (1984) 'Scaling the kinetics of flow and relaxation in amorphous alloys', *Materials Science and Engineering*, 62(2), pp. 249–260. doi: 10.1016/0025-5416(84)90228-3.

[130] Yousfi, M. A., Ammari, C., Hajlaoui, K. and Tourki, Z. (2020) 'Lecture notes in mechanical engineering', in Kharrat, M., Baccar, M., and Dammak, F. (eds) *Advances in IC engines and combustion technology*. Cham: Springer, pp. 320–326. doi: 10.1007/978-3-030-52071-7_44.

[131] Callister, W. D. and Rethwisch, D. G. (2011) *Materials Science and Engineering*. 8th edn. Hoboken: Wiley.

[132] Davis, L. A. (1976) 'Fatigue of metallic glasses', *Journal of Materials Science*, 11(4), pp. 711–717. doi: 10.1007/BF01209458.

[133] Gilbert, C. J., Schroeder, V. and Ritchie, R. O. (1999) 'Mechanisms for fracture and fatigue-crack propagation in a bulk metallic glass', *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 30(7), pp. 1739–1753. doi: 10.1007/s11661-999-0173-y.

- [134] Menzel, B. C. and Dauskardt, R. H. (2006) 'Stress-life fatigue behavior of a Zr-based bulk metallic glass', *Acta Materialia*, 54(4), pp. 935–943. doi: 10.1016/j.actamat.2005.10.021.
- [135] Peter, W. H., Liaw, P. K., Buchanan, R. A., Liu, C. T., Brooks, C. R., Horton, J. A., Carmichael, C. A. and Wright, J. L. (2002) 'Fatigue behavior of Zr_{52.5}Al₁₀Ti₅Cu_{17.9}Ni_{14.6} bulk metallic glass', *Intermetallics*, 10(11–12), pp. 1125–1129. doi: 10.1016/S0966-9795(02)00152-8.
- [136] Qiao, D. C., Fan, G. J., Liaw, P. K. and Choo, H. (2007) 'Fatigue behaviors of the Cu_{47.5}Zr_{47.5}Al₅ bulk-metallic glass (BMG) and Cu_{47.5}Zr₃₈Hf_{9.5}Al₅ BMG composite', *International Journal of Fatigue*, 29(12), pp. 2149–2154. doi: 10.1016/j.ijfatigue.2007.01.009.
- [137] Wang, G. Y., Liaw, P. K., Yokoyama, Y., Peker, A., Peter, W. H., Yang, B., Freels, M., Zhang, Z. Y., Keppens, V., Hermann, R., Buchanan, R. A., Liu, C. T. and Brooks, C. R. (2007) 'Studying fatigue behavior and Poisson's ratio of bulk-metallic glasses', *Intermetallics*, 15(5–6), pp. 663–667. doi: 10.1016/j.intermet.2006.10.034.
- [138] Wang, G. Y., Liaw, P. K. and Morrison, M. L. (2009) 'Progress in studying the fatigue behavior of Zr-based bulk-metallic glasses and their composites', *Intermetallics*, 17(8), pp. 579–590. doi: 10.1016/j.intermet.2009.01.017.
- [139] Wang, G. and Liaw, P. K. (2010) 'Bending-fatigue behavior of bulk metallic glasses and their composites', *JOM*, 62(4), pp. 25–33. doi: 10.1007/s11837-010-0055-1.
- [140] Agnew, S. R., Vinogradov, A. Y., Hashimoto, S. and Weertman, J. R. (1999) 'Overview of fatigue performance of Cu processed by severe plastic deformation', *Journal of Electronic Materials*, 28(9), pp. 1038–1044. doi: 10.1007/s11664-999-0181-0.
- [141] Alpas, A. T., Edwards, L. and Reid, C. N. (1989) 'Fracture and fatigue crack propagation in a nickel-base metallic glass', *Metallurgical Transactions A*, 20(8), pp. 1395–1409. doi: 10.1007/BF02665497.

- [142] Davis, L. A. (1975) 'Fracture of Ni-Fe base metallic glasses', *Journal of Materials Science*, 10(9), pp. 1557–1564. doi: 10.1007/BF01031856.
- [143] Gilbert, C. J., Ritchie, R. O. and Johnson, W. L. (1997) 'Fracture toughness and fatigue-crack propagation in a Zr-Ti-Ni-Cu-Be bulk metallic glass', *Applied Physics Letters*, 71(4), pp. 476–478. doi: 10.1063/1.119610.
- [144] Suresh, S. (1998) *Fatigue of Materials*. 2nd edn. Cambridge University Press. doi: 10.1017/CBO9780511806575.
- [145] Wang, G. Y., Liaw, P. K., Peker, A., Yang, B., Benson, M. L., Yuan, W., Peter, W. H., Huang, L., Freels, M., Buchanan, R. A., Liu, C. T. and Brooks, C. R. (2005) 'Fatigue behavior of Zr-Ti-Ni-Cu-Be bulk-metallic glasses', *Intermetallics*, 13(3–4), pp. 429–435. doi: 10.1016/j.intermet.2004.07.037.
- [146] Aydinler, C. C., Üstündag, E. and Hanan, J. C. (2001) 'Thermal-tempering analysis of bulk metallic glass plates using an instant-freezing model', *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 32(11), pp. 2709–2715. doi: 10.1007/s11661-001-1023-8.
- [147] Launey, M. E., Busch, R. and Kruzic, J. J. (2006) 'Influence of structural relaxation on the fatigue behavior of a Zr 41.25Ti13.75Ni10Cu12.5Be 22.5 bulk amorphous alloy', *Scripta Materialia*, 54(3), pp. 483–487. doi: 10.1016/j.scriptamat.2005.09.048.
- [148] Wang, G. Y., Liaw, P. K., Peker, A., Freels, M., Peter, W. H., Buchanan, R. A. and Brooks, C. R. (2006) 'Comparison of fatigue behavior of a bulk metallic glass and its composite', *Intermetallics*, 14(8–9), pp. 1091–1097. doi: 10.1016/j.intermet.2006.01.045.
- [149] Zhang, Y., Wang, W. H. and Greer, A. L. (2006) 'Making metallic glasses plastic by control of residual stress', *Nature Materials*, 5(11), pp. 857–860. doi: 10.1038/nmat1758.
- [150] Wang, G. Y., Liaw, P. K., Peter, W. H., Yang, B., Yokoyama, Y., Benson, M. L., Green, B. A., Kirkham, M. J., White, S. A., Saleh, T. A., McDaniels, R. L., Steward, R. V., Buchanan, R. A., Liu, C. T. and Brooks, C. R. (2004) 'Fatigue

behavior of bulk-metallic glasses', *Intermetallics*, 12(7–9), pp. 885–892. doi: 10.1016/j.intermet.2004.02.043.

[151] Rivin, E. I. (2010) 'Modes of loading and stiffness of structural components', in *Handbook on stiffness and damping in mechanical design*. New York: ASME Press, pp. 53–112. doi: 10.1115/1.802939.ch2.

[152] Childs, P. (2014) 'Springs', in *Mechanical Design Engineering Handbook*. Amsterdam: Elsevier, pp. 625–675. doi: 10.1016/B978-0-08-097759-1.00015-0.

[153] *Types of springs and their applications* (2023) *Emlease Design*. Available at: <https://www.smlease.com/entries/mechanism/types-of-springs-and-their-applications/> (Accessed: 24 April 2023).

[154] Jutte, C. V. and Kota, S. (2008) 'Design of nonlinear springs for prescribed load-displacement functions', *Journal of Mechanical Design*, 130(8), pp. 0814031–08140310. doi: 10.1115/1.2936928.

[155] Rhoads, J. F., Shaw, S. W., Turner, K. L. and Baskaran, R. (2005) 'Tunable microelectromechanical filters that exploit parametric resonance', *Journal of Vibration and Acoustics*, 127(5), pp. 423–430. doi: 10.1115/1.2013301.

[156] Fukushige, T., Hata, S. and Shimokohbe, A. (2005) 'A MEMS conical spring actuator array', *Journal of Microelectromechanical Systems*, 14(2), pp. 243–253. doi: 10.1109/JMEMS.2004.839345.

[157] Wang, Yongliang, Feng, Q., Wang, Yan, Chen, W., Wang, Z., Ding, G. and Zhao, X. (2013) 'The design, simulation and fabrication of a novel horizontal sensitive inertial micro-switch with low g value based on MEMS micromachining technology', *Journal of Micromechanics and Microengineering*, 23(10). doi: 10.1088/0960-1317/23/10/105013.

[158] Lu, N. and Yang, S. (2015) 'Mechanics for stretchable sensors', *Current Opinion in Solid State and Materials Science*. Elsevier Ltd, 19(3), pp. 149–159. doi: 10.1016/j.cossms.2014.12.007.

[159] Migliore, S. A., Brown, E. A. and DeWeerth, S. P. (2007) 'Novel nonlinear

elastic actuators for passively controlling robotic joint compliance', *Journal of Mechanical Design*, 129(4), pp. 406–412. doi: 10.1115/1.2429699.

[160] Kumar, G., Desai, A. and Schroers, J. (2011) 'Bulk metallic glass: the smaller the better', *Advanced Materials*, 23(4), pp. 461–476. doi: 10.1002/adma.201002148.

[161] You, A., Be, M. and In, I. (2018) 'Creep and electrical resistivity of metallic glass', *American Institute of Physics*, 4880(July), pp. 4876–4880.

[162] Wesseling, P., Ko, B. C. and Lewandowski, J. J. (2003) 'Quantitative evaluation of α -Al nano-particles in amorphous Al₈₇Ni₇Gd₆ - Comparison of XRD, DSC, and TEM', *Scripta Materialia*, 48(11), pp. 1537–1541. doi: 10.1016/S1359-6462(03)00127-1.

[163] Gloriant, T., Gich, M., Suriñach, S., Baró, M. D. and Greer, A. L. (2000) 'Evaluation of the volume fraction crystallized during devitrification of Al-based amorphous alloys', *Materials Science Forum*, 343, pp. 365–370. doi: 10.4028/www.scientific.net/msf.343-346.365.

[164] Shahin Elzoubi, O., Panagiotopoulos, N. T., Stiehler, M., Salonitis, K. and Georgarakis, K. (2022) 'On the undulatory behaviour of metallic glass foils: A novel spring-type behaviour', in *11th International Conference on Through-life Engineering Services-TESConf2022, 8-9 November 2022, Paper number 7682*. Cranfield: Cranfield University. Available at: <https://dspace.lib.cranfield.ac.uk/handle/1826/18681>.

[165] Yoo, C. H. and Lee, S. C. (2011) 'Buckling of Columns', in *Stability of Structures: principles and applications*. Amsterdam: Elsevier, pp. 1–73. doi: 10.1016/B978-0-12-385122-2.10001-6.

[166] Halkyard, J. (2005) 'Floating offshore platform design', in Chakrabarti, S. K. (ed.) *Handbook of Offshore Engineering*. Amsterdam: Elsevier, pp. 419–661. doi: 10.1016/B978-008044381-2.50010-2.

[167] Gilbert, C. J., Lippmann, J. M. and Ritchie, R. O. (1998) 'Fatigue of a Zr-Ti-Cu-Ni-Be bulk amorphous metal: Stress/life and crack-growth behavior', *Scripta*

Materialia, 38(4), pp. 537–542. doi: 10.1016/S1359-6462(97)00522-8.

[168] Wang, X. D., Liu, P., Zhu, Z. W., Zhang, H. F. and Ren, X. C. (2020) ‘High fatigue endurance limit of a Ti-based metallic glass’, *Intermetallics*, 119, p. 106716. doi: 10.1016/j.intermet.2020.106716.

[169] Jia, H., Wang, G., Chen, S., Gao, Y., Li, W. and Liaw, P. K. (2018) ‘Fatigue and fracture behavior of bulk metallic glasses and their composites’, *Progress in Materials Science*, 98, pp. 168–248. doi: 10.1016/j.pmatsci.2018.07.002.

[170] Wang, G. Y., Liaw, P. K., Yokoyama, Y., Freels, M. and Inoue, A. (2010) ‘The influence of Pd on tension-tension fatigue behavior of Zr-based bulk-metallic glasses’, *International Journal of Fatigue*, 32(3), pp. 599–604. doi: 10.1016/j.ijfatigue.2009.04.009.

[171] Wang, X. D., Ren, X. C., Qu, R. T. and Zhang, Z. F. (2019) ‘Compression-compression fatigue behavior of a Zr-based metallic glass with different free volume contents’, *Journal of Alloys and Compounds*, 810, p. 151924. doi: 10.1016/j.jallcom.2019.151924.

[172] Wang, X. D., Qu, R. T., Wu, S. J., Zhu, Z. W., Zhang, H. F. and Zhang, Z. F. (2019) ‘Improving fatigue property of metallic glass by tailoring the microstructure to suppress shear band formation’, *Materialia*, 7, p. 100407. doi: 10.1016/j.mtla.2019.100407.

[173] Yue, Y., Wang, R., Ma, D. Q., Tian, J. F., Zhang, X. Y., Jing, Q., Ma, M. Z. and Liu, R. P. (2015) ‘Fatigue behavior of a Zr-based bulk metallic glass under uniaxial tension-tension and three-point bending loading mode’, *Intermetallics*, 60, pp. 86–91. doi: 10.1016/j.intermet.2015.02.005.

[174] Wang, X. D., Qu, R. T., Liu, Z. Q. and Zhang, Z. F. (2015) ‘Shear band-mediated fatigue cracking mechanism of metallic glass at high stress level’, *Materials Science and Engineering A*, 627, pp. 336–339. doi: 10.1016/j.msea.2015.01.008.

[175] Kamal, M. and Mohammad, U. S. (eds) (2012) *A Review: Chill-block melt spin technique, theories & applications*. Almansurah: Bentham Science.

- [176] Budynas, R. G. and Kieth Nisbett, J. (2011) *Shigley's mechanical engineering design*. 9th edn. The McGraw-Hill.
- [177] Pilkey, W. D. and Pilkey, D. F. (2007) *Peterson's Stress Concentration Factors*. 3rd edn. Hoboken, NJ, USA: John Wiley & Sons, Inc. doi: 10.1002/9780470211106.
- [178] BERGER, C. and KAISER, B. (2006) 'Results of very high cycle fatigue tests on helical compression springs', *International Journal of Fatigue*, 28(11), pp. 1658–1663. doi: 10.1016/j.ijfatigue.2006.02.046.
- [179] Arora, V. K., Bhushan, G. and Aggarwal, M. L. (2014) 'Fatigue Life Assessment of 65Si7 Leaf Springs: A Comparative Study', *International Scholarly Research Notices*, 2014, pp. 1–11. doi: 10.1155/2014/607272.
- [180] Kamal, M. and Rahman, M. M. (2014) 'Finite element-Based fatigue behaviour of spring in automobile suspension', *International Journal of Automotive and Mechanical Engineering*, 10(December), pp. 1910–1919. doi: 10.15282/ijame.10.2014.8.0159.

