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Reactivity of a glassy and a crystalline $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ alloy towards aluminum during sintering: A comparative study

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Reactivity of a glassy and a crystalline Fe₆₆Cr₁₀Nb₅B₁₉ alloy towards aluminum during sintering: a comparative study

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Abstract

A glassy Fe₆₆Cr₁₀Nb₅B₁₉ alloy and its crystalline counterpart consisting of the α -(Fe,Cr), FeNbB and Fe₂B phases were spark plasma sintered with aluminum at 570 °C to investigate the interfacial reactions in the systems. In the mixture containing the crystalline alloy, α -(Fe,Cr) and Fe₂B reacted with aluminum forming the Fe-Al intermetallic reaction products. The crystallites of FeNbB were distributed in the intermetallic matrix. The absence of α -(Fe,Cr) and Fe₂B in the composite sintered from the glassy alloy was confirmed by Mössbauer spectroscopy. Overall, under the short SPS processing, the crystalline alloy was found to be more reactive towards aluminum than the glassy alloy. An increased reactivity was due to the presence of α -(Fe,Cr), a Fe-rich phase, in the crystalline alloy.

Keywords: metallic glass, aluminum, intermetallic, reactivity.

1. Introduction

The dependence of chemical reactivity of a material on its crystalline structure is one of the principal questions for solid-state chemistry. For compositions with glass-forming ability, it is of fundamental interest to determine the influence of the alloy structure (amorphous versus crystalline) on its reactivity. The amorphous state is metastable, possessing additional free energy and featuring free volume. However, atomic diffusion in amorphous solids is generally slower than in their crystalline counterparts [1]. At room temperature, metallic glasses are less reactive towards the aggressive media than their crystalline counterparts [2, 3]. At $T_g < T < T_x$ (T_g – glass transition temperature, T_x – crystallization temperature), the glassy compositions become liquid-like. The chemical properties of supercooled liquids have been studied much less than those of metallic glasses at room temperature.

Combining metallic glasses with crystalline metals is a promising approach to the development of composite materials [4]. The interaction between metallic glasses and crystalline metals can occur during high-temperature consolidation of the mixtures. If the metal diffusing into the glassy alloy reduces its glass forming ability, a change in the elemental composition will be accompanied by devitrification of the glass.

To the best of our knowledge, no direct comparison between the reactivity of an amorphous alloy and a crystalline alloy of the same composition towards aluminum has been reported. Upon crystallization, an alloy decomposes into different phases, which may differ in reactivity. In the present work, a glassy Fe₆₆Cr₁₀Nb₅B₁₉ alloy and its crystalline counterpart consisting of α -(Fe,Cr), Fe₂B and FeNbB phases were spark plasma sintered with aluminum at 570 °C to study the interfacial interaction in the systems. A comparative study was conducted on single-phase and multi-phase materials of the same elemental composition.

2. Materials and Methods

Mixtures with a composition of 40 wt.% Fe₆₆Cr₁₀Nb₅B₁₉–Al were prepared using a glassy and a crystalline Fe₆₆Cr₁₀Nb₅B₁₉ alloy. The glassy powder was obtained by gas-atomization [5]; the fraction <30 μ m was used for the experiments. The crystalline powder was obtained by annealing of the as-atomized powder at 850 °C for 2 h in vacuum. An aluminum powder with an average particle size of 6 μ m (PAD-6 grade) was used. A mixture containing the glassy and the crystalline powder (10 wt.% each) was also prepared. The Al/Fe molar ratio in the mixtures was

4:1. The characteristic temperatures of the glassy $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ were reported in [5]: $T_g=521\text{ }^\circ\text{C}$; $T_x=573\text{ }^\circ\text{C}$ (determined at $10\text{ }^\circ\text{C min}^{-1}$).

Spark plasma sintering (SPS) of the mixtures was carried out using a SPS Labox 1575 apparatus (SINTER LAND Inc., Japan) in vacuum at a uniaxial pressure of 40 MPa and a temperature of 570 $^\circ\text{C}$ (heating rate 50 $^\circ\text{C min}^{-1}$, soaking time 1 min). The powder mixtures were placed in a graphite die 20 mm in diameter. The temperature during SPS was measured by a thermocouple inserted into a near-through hole in the die wall. The real temperature of the sintered sample was about 30 $^\circ\text{C}$ higher than the measured temperature.

Selected sintered samples were annealed in a vacuum furnace at 700 $^\circ\text{C}$ for 2 h.

The equilibrium phase composition of the system at 600 $^\circ\text{C}$ was determined using thermodynamic calculations in PandatTM 2022 software (CompuTherm LLC) using PanAl2022 database.

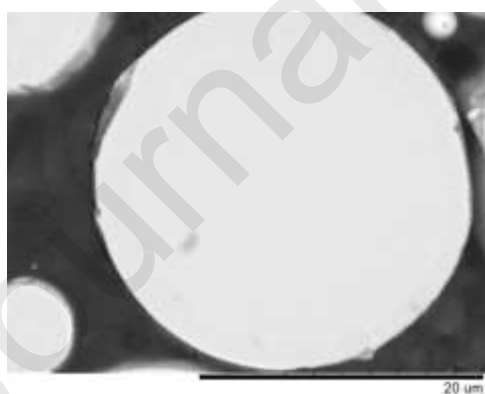
X-ray diffraction (XRD) patterns of the samples were recorded by a D8 ADVANCE diffractometer (Bruker AXS, Germany) with Cu $K\alpha$ radiation (step size $\Delta 2\theta = 0.0195^\circ$, counting time 35.4 s per step). Mössbauer spectroscopy was carried out on a NP 255/610 spectrometer (Budapest, Hungary) with a $^{57}\text{Co(Rh)}$ source. The microstructure of the samples was studied by scanning electron microscopy using a TM-1000 Tabletop microscope (Hitachi, Japan) and a S-3400N (Hitachi, Japan) microscope. Elemental maps were obtained using a NORAN Spectral System 7 (Thermo Fisher Scientific Inc., USA).

3. Results and Discussion

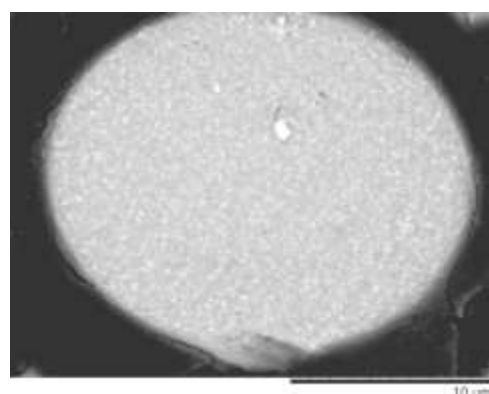
As seen in Figure 1a, the microstructure of the as-atomized alloy is featureless, which is expected for an alloy of amorphous nature. The crystalline alloy shows a submicrometer-grained structure (Figure 1b). In the XRD pattern of the glassy alloy, only a halo is present, confirming the absence of crystalline phases (Figure 1c). The crystalline alloy consists of the α -(Fe,Cr), FeNbB and Fe₂B phases (Figure 1d). The shape of the Mössbauer spectrum of the glassy alloy (Figure 1e) is consistent with that reported in [6] for an alloy with a close composition and can be represented by two doublets (blue and green lines). After annealing, the spectrum of the powder changes dramatically (Figure 1f) and can be decomposed into three sextets (green, red and purple lines) and a doublet (blue line). The sextets are due to the presence of submicron grains of α -(Fe,Cr) differing in composition and possibly Fe₂B [7].

By comparing the microstructure of composites formed from the glassy and crystalline powders (Figure 2a,b), it can be concluded that the crystalline alloy was almost fully transformed in a reaction with aluminum, while the glassy alloy particles reacted with aluminum to form thin shells. A higher reactivity of the crystalline alloy towards aluminum was also confirmed by the experiment with a composite containing both glassy and crystalline powders (Figure 2c). The products of interaction of both alloys with aluminum are FeAl₃ and Fe₂Al₅ intermetallics (Figure 3a,b). The XRD analysis confirms a higher concentration of intermetallics in the case of the crystalline alloy. Although the temperature of the sample during SPS was slightly higher than the crystallization temperature of the glass, no evidence of the presence of magnetically ordered phases (α -(Fe, Cr) or Fe₂B) is seen in the Mössbauer spectrum of the composite obtained from the glassy alloy (Figure 3c). The spectrum can be decomposed into a doublet (blue line) corresponding to Fe-Al phases [8] and a singlet (green line). In the case of the crystalline alloy, the reaction layers around the cores possess a complex “matrix-inclusions” structure (Figure 2d). The elemental maps (Figure 2d) confirm that this layer has a uniform distribution of Al, Fe and Cr. By analyzing the microstructure together with the XRD pattern (Figure 3b), it is possible to conclude that the gray matrix is the FeAl₃ phase. The submicron particles on a gray background are FeNbB and Fe₂Al₅. Chromium can also be contained in the Fe-Al intermetallic phases and FeNbB, partially substituting iron.

In the crystalline alloy, the α -(Fe,Cr) phase should possess the highest reactivity towards aluminum, as this phase has the lowest concentration of alloying elements (Fe-rich phase). Therefore, it is the α -(Fe,Cr) that reacted with aluminum forming Fe-Al intermetallics. The Fe₂B phase was no longer present in the sintered material and must have also reacted with aluminum.



a



b

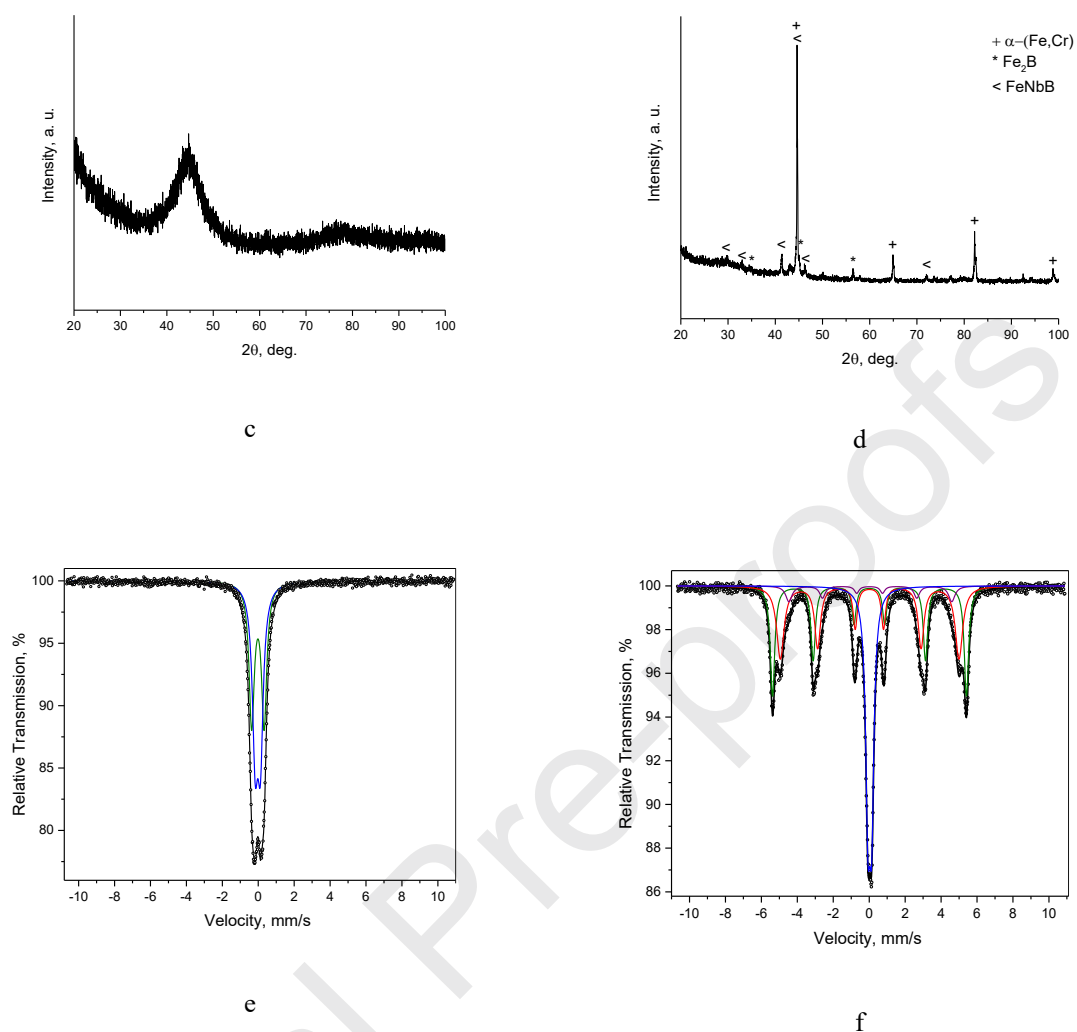
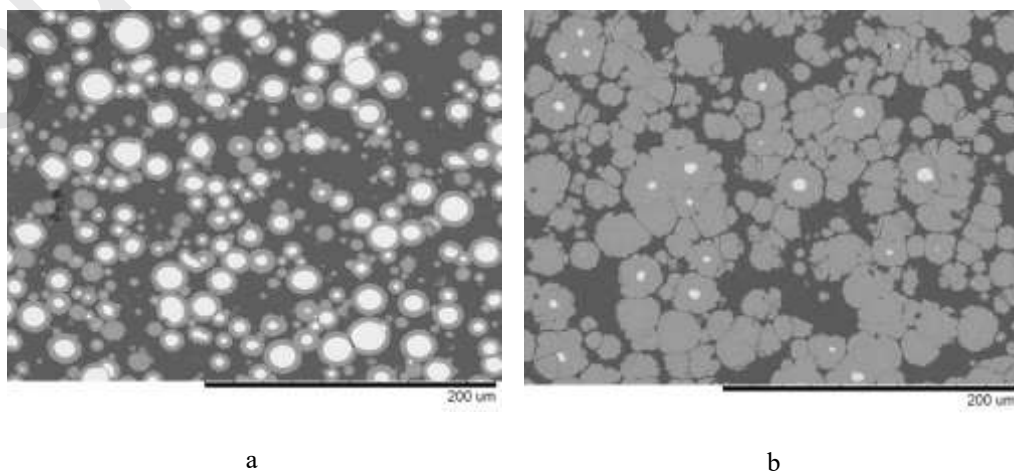


Figure 1. Microstructure of $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ particles (a, b); XRD patterns (c, d) and Mössbauer spectra of the alloys (e, f). Glassy (a, c, e), crystalline (b, d, f).



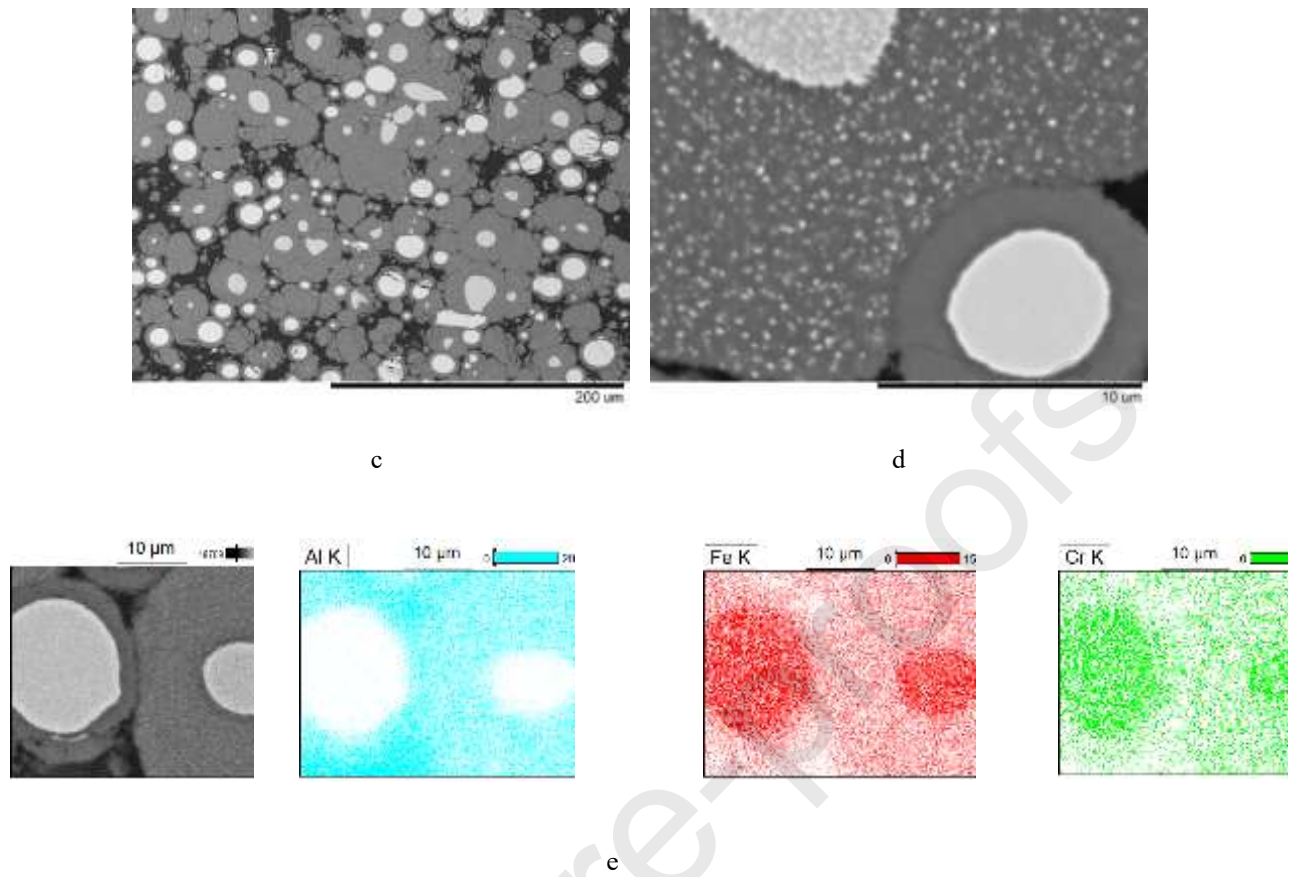
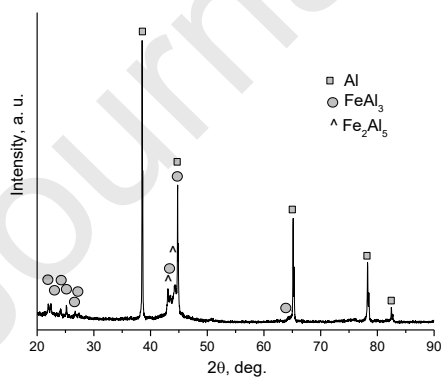
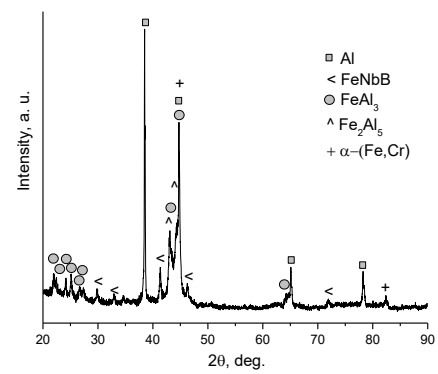


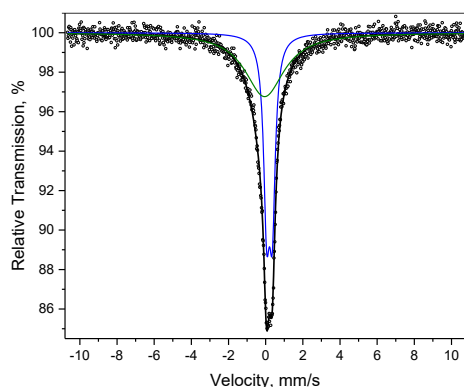
Figure 2. Microstructure of composites obtained by SPS: (a) glassy, (b) crystalline alloy, (c, d) mixture of the glassy and crystalline alloys. (e) An area of the composite shown in (c, d) and maps of Al, Fe and Cr.



a



b

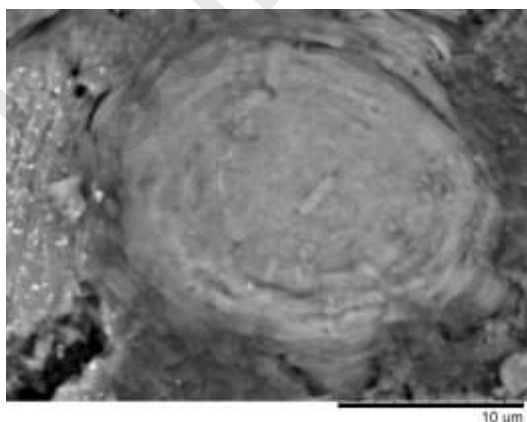


c

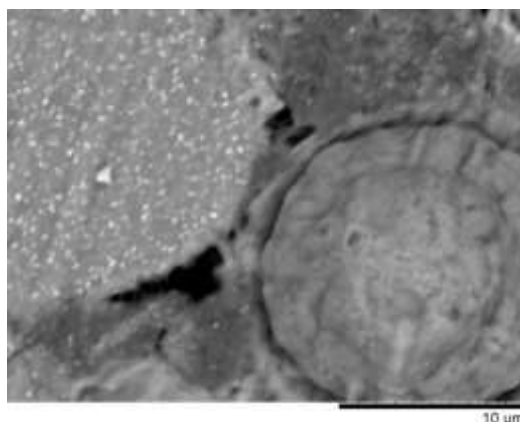
Figure 3. XRD patterns of composites obtained from the glassy (a) and crystalline alloy (b); Mössbauer spectrum of the composite obtained from the glassy alloy (c).

The equilibrium phase composition of the material studied in this work at 600 °C is ~88 vol.% (Fe,Cr)Al₃, ~4 vol.% Al, ~4 vol.%NbB₂ and ~4 vol.% AlB₂. In the composite sintered from a mixture of the glassy and crystalline powders and annealed at 700 °C, the glassy cores were fully converted into the Fe-Al intermetallics (Figure 4a). The FeNbB phase remained after annealing (Figure 4b, c). Therefore, in order to convert FeNbB into FeAl₃, higher temperatures/longer annealing are required. Due to the short processing times, the composites did not reach the equilibrium state.

As long as α -(Fe, Cr) is present in the system, the crystalline alloy is more reactive towards aluminum than the glassy alloy. A lower reactivity of the glassy alloy can be explained by the slower diffusion processes in an amorphous solid [1] and the difficulties of nucleation/growth of reaction product phases, requiring redistribution of elements in the quaternary alloy. As fine-grained Fe₆₆Cr₁₀Nb₅B₁₉ alloys possess hardness close to that of the glassy material [2], both the glassy and crystalline alloys may be suitable as reinforcements for aluminum matrices. At the same time, as this work has shown, it is vital to take into account the differences in the reactivity of the alloys towards aluminum.



a



b

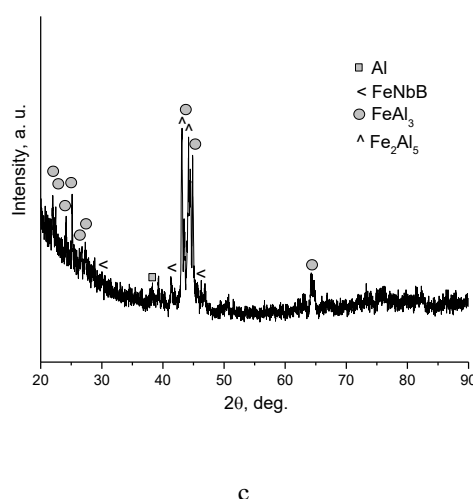


Figure 4. Fracture surface (a, b) and XRD pattern (c) of the composite sintered using the mixture of the glassy and crystalline alloys and annealed at 700 °C.

4. Summary

A glassy $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ alloy and its crystalline counterpart consisting of $\alpha\text{-(Fe,Cr)}$, FeNbB and Fe_2B were spark plasma sintered with aluminum at 570 °C to investigate the interfacial reactions in the systems. The transformation degree of the crystalline alloy into the reaction products was higher than that of the glassy alloy, which indicated a higher reactivity of the crystalline alloy towards aluminum under selected conditions. When the crystalline alloy reacted with aluminum, the $\alpha\text{-(Fe,Cr)}$ and Fe_2B phases transformed into the Fe-Al intermetallics. The FeNbB phase remained in the composite after SPS and after post-sintering annealing at 700 °C.

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Credit Author Statement

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Dina V. Dudina: Conceptualization, Writing – review & editing, Funding acquisition, Project administration.

Boris B. Bokhonov: Conceptualization, Investigation, Writing – review & editing.

Sergey A. Petrov: Methodology, Investigation.

Arina V. Ukhina: Investigation.

Konstantinos Georgarakis: Conceptualization, Methodology, Writing – review & editing.

Francisco Gil Coury: Methodology, Investigation.

Guilherme Yuuki Koga: Methodology, Investigation, Writing – review & editing.

Highlights

- Al was sintered with glassy and crystalline $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ alloys at 570 °C
- The crystalline alloy consists of α -(Fe,Cr), Fe_2B and FeNbB
- Crystalline $\text{Fe}_{66}\text{Cr}_{10}\text{Nb}_5\text{B}_{19}$ alloy interacts more actively with Al than glassy alloy
- The reaction layers contain Al_3Fe and Al_5Fe_2 intermetallics
- FeNbB does not react with Al during sintering



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