

Full length article

A core-shell thermal barrier coating with strong resistance to molten silicate attack and fracture

Zichen Li^{a,b}, Gyaneshwara Brewster^c, Luis Isern^d, Christine Chalk^d, John Nicholls^d,
Ping Xiao^{a,b}, Xun Zhang^{b,e}, Ying Chen^{a,b,*}

^a Department of Materials, The University of Manchester, Manchester, M13 9PL, UK

^b Henry Royce Institute, The University of Manchester, Manchester, M13 9PL, UK

^c Rolls-Royce plc, P.O. Box 31, Derby DE24 8BJ, UK

^d Surface Engineering and Nanotechnology Institute (SENTI), Cranfield University, College Rd., Wharley End, Bedford MK43 0AL, UK

^e Department of Mechanical, Aerospace & Civil Engineering, The University of Manchester, Manchester, M13 9PL, UK

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ABSTRACT

We report a new thermal barrier coating (TBC) with strong resistance to calcia–magnesia–alumina–silicate (CMAS) attack and fracture. The design is based on a core-shell microstructure where each building block of the TBC comprises a tough yttria stabilised zirconia (YSZ) core and a CMAS-resistant shell. To demonstrate the feasibility of the design, we select alumina, an established CMAS-resistant ceramic, as the shell material and manufacture core-shell TBCs by first synthesising “YSZ core-alumina shell” powder using the sol-gel method and then thermally spraying the powder to form core-shell TBCs. Microstructural characterisations confirm that a core-shell coating structure is successfully manufactured. However, the melting and mixing of alumina and YSZ in thermal spray result in the formation of a microstructure composed of alumina-alloyed zirconia grains and intergranular alumina, with the overall alumina concentration increasing from the core to the shell. The CMAS penetration depth through the core-shell TBC is over an order of magnitude lower than that through the benchmark YSZ TBC, which is attributed to the multiscale protection of the core-shell microstructure against CMAS infiltration through cracks and grain boundaries. The core-shell TBC has a similar stiffness to the YSZ TBC but exhibits a lower erosion rate and higher fracture toughness, indicating enhanced fracture resistance without compromising strain tolerance. The improved fracture resistance of the core-shell TBC is attributed to its less defective intersplat structure and greater ferroelastic toughening strain. Compared to the YSZ TBC, the core-shell TBC shows lower stiffness and nearly identical fracture toughness after annealing.

1. Introduction

Yttria-stabilised zirconia (YSZ) thermal barrier coatings (TBCs) have been widely used in aircraft engines to insulate the superalloy components from the hot gases and enable the engines to run at higher temperatures for better efficiency [1–3]. However, one of the major issues for YSZ TBCs is that they are vulnerable to attack of environmental deposits when the engines are exposed to airborne dust, sand, or volcano ash. The deposits are primarily composed of amorphous calcia–magnesia–alumina–silicate (CMAS) and can melt on the TBC surface when they are ingested into the hot engine through the intake air. The vitreous CMAS can physically infiltrate into the porous TBC and chemically destabilise the tough coating composition. During cooling,

the infiltrated CMAS melt freezes within the TBC microstructure, resulting in a reduction of TBC strain tolerance and premature coating failure [4–6].

Many CMAS mitigation approaches have been proposed but one of the most effective strategies is to develop TBCs capable of reacting with the CMAS melt to promote the fast crystallisation of solid phases from the CMAS and seal the open pores in TBCs [5,7]. The primary material of choice for CMAS-resistant TBCs is rare-earth zirconates ($\text{RE}_2\text{Zr}_2\text{O}_7$) or their derivatives, such as $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2(\text{Zr}_{0.7}\text{Ce}_{0.3})\text{O}_7$ [8,9]. These materials can rapidly react with CMAS at high temperatures and precipitate fluorite and apatite crystals to fill up the CMAS infiltration pathways [5]. However, one major concern for the $\text{RE}_2\text{Zr}_2\text{O}_7$ ceramics is their low toughness [10,11], which makes $\text{RE}_2\text{Zr}_2\text{O}_7$ TBCs susceptible to

* Corresponding author at: Henry Royce Institute, The University of Manchester, Manchester, M13 9PL, UK.

E-mail address: ying.chen-2@manchester.ac.uk (Y. Chen).

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delamination in thermomechanical cycling and material loss in erosion. For instance, the erosion rates of $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramics and TBCs are nearly an order of magnitude higher than their YSZ counterparts [12,13]. Another well-studied CMAS reactive material is alumina, which can shift the primary phase field of CMAS from vitreous glass to solid anorthite and spinel phases, thereby blocking CMAS infiltration [5,14]. To introduce alumina to TBCs, one approach is to deposit an overlay alumina protective coating on top of a YSZ TBC [14,15] and the other is through alloying a high concentration of alumina (20 %) into YSZ to form an oversaturated metastable YSZ-alumina solid solution [16–18]. While both approaches improve the CMAS resistance, other important TBC-related properties, particularly the fracture resistance, of either the overlay alumina coating or the alumina alloyed metastable YSZ TBC remain to be studied for a more complete assessment of their suitability for TBC application.

2. New TBC design

This work reports a new TBC design for strong resistance to both CMAS attack and fracture. The design is based on a “core-shell” microstructural concept (Fig. 1) and is applicable to TBCs deposited by atmospheric plasma spray (APS). Each microstructural unit (splat) of the core-shell TBC comprises a tough YSZ core and a thin CMAS-resistant shell. The design fully capitalises the well-established CMAS attack mechanism (infiltration through the inter/intra-splat crack networks) by deploying the CMAS-resistant material exclusively to the edge of each splat, thereby mitigating CMAS attack on the TBC by promoting crystallisation of CMAS in its infiltration pathway (Fig. 1). The use of the YSZ core, which accounts for the main body of each splat, is expected to retain all the desirable properties of YSZ for TBC application, particularly its high fracture resistance from the ferroelastic toughening mechanism.

While the choice of the shell materials is open to many potential CMAS-resistant ceramics, alumina is selected as the shell material in this work to demonstrate the feasibility of the core-shell coating design.

Firstly, alumina has proven CMAS resistance [17,18]. Secondly, it has high melting point (2072 °C) [19]. Thirdly, it has high sintering resistance, and it is thermodynamically compatible with zirconia, which ensures the core-shell structure is stable in long term thermal exposure [20,21]. Fourthly, the coefficient of thermal expansion (CTE) of alumina (8 to $9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [22] is close to that of YSZ (10 to $11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) [23], which is helpful to maintaining a relatively low level of thermal stress between the core and the shell. In addition, the presence of the thin alumina shell has a minimal impact (<2 %) on the overall CTE of the coating, as demonstrated in Section 1 of the Supplementary Materials. Fifthly, the fracture toughness of alumina is $2.3 \text{ MPa}\cdot\text{m}^{1/2}$ [24], which is significantly higher than that of $\text{RE}_2\text{Zr}_2\text{O}_7$ (about $1 \text{ MPa}\cdot\text{m}^{1/2}$) [10,11], but only slightly lower than 8YSZ (about $3 \text{ MPa}\cdot\text{m}^{1/2}$) [25], thereby providing strong resistance against crack propagation along the splat boundaries. Sixthly, the thin alumina shell has a negligible impact (<4 %) on the overall low thermal conductivity of YSZ, as demonstrated by the finite element analysis (FEA) calculations (Section 2 in Supplementary Materials). Finally, alumina is cost-effective.

The core-shell TBC offers a design advantage over the conventional double-layer TBC that consists of an inner YSZ layer and an outer alumina layer. For the double-layer YSZ/alumina TBC, its CMAS resistance relies entirely on the durability of the outer alumina coating. If spallation occurs at the YSZ/alumina interface due to thermal mismatch, CMAS attack, erosion or poor interface bonding, the CMAS resistance of the double-layer TBC will be lost completely. In contrast, the core-shell design eliminates this risk by engineering a thin layer of alumina shell precisely along the CMAS infiltration pathways (inter/intrasplat boundaries) throughout the entire TBC. As a result, the core-shell TBC has robust CMAS resistance from top to bottom while mitigating the macroscale thermal mismatch stress that could otherwise lead to catastrophic failure of the outer alumina coating in conventional double-layer TBC design. Even in the event of partial delamination of the core-shell TBC, the remaining coating will continue to protect against CMAS attack.

To manufacture the core-shell TBCs, we first synthesised “YSZ core-

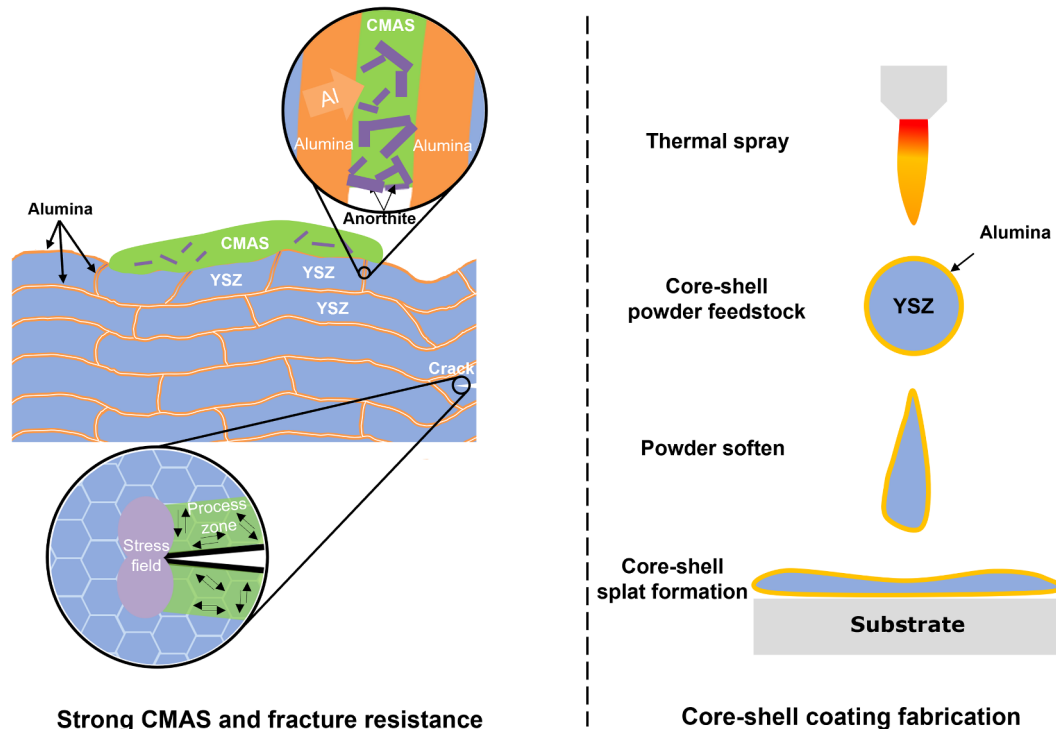


Fig. 1. Schematic illustration of the core-shell TBC: (left) Cross-section of the TBC. Each microstructural unit (splat) of the TBC comprises a tough YSZ core and a thin CMAS-resistant alumina shell. The shell provides effective CMAS mitigation, and the core provides high fracture resistance. (right) Production of the core-shell TBC, which involves synthesis of core-shell powder and thermal spray.

alumina shell" powder by the sol-gel method and then translated the core-shell structure from the powder to the coating using APS. During deposition the core-shell powder was expected to soften and deform into core-shell splats (Fig. 1), which then built up to form the core-shell APS TBCs. The microstructure of the core-shell TBCs was examined and their CMAS resistance, flexural modulus, and fracture resistance were evaluated to verify our design hypotheses.

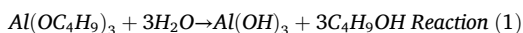
3. Materials and methods

3.1. Core-shell powder synthesis

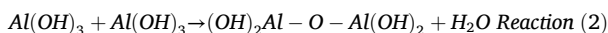
Core-shell powder was prepared by encapsulating the 8wt% YSZ (8YSZ) powder with a thin alumina shell. Spherical 8YSZ powder (METCO-233B) was purchased from Oerlikon as the core for encapsulation. The normal particle size ranges from 20 to 49 μm , which provides high flowability for thermal spray. To coat a thin alumina shell on the 8YSZ powder, the sol-gel method was selected because it is a non-line-of-sight process and allows production of thin ceramic films on irregular shaped surface from micro to macroscale. The chemicals used for sol-gel synthesis are aluminium tri-sec butoxide (ASB, 97 %, Sigma-Aldrich) and nitric acid.

The synthesis process of the core-shell powder involves the following steps. Firstly, 1 M nitric acid was mixed with de-ionized (DI) water in a volume ratio of 1/13.5 and heated to 80 °C. Next, the ASB precursor was added to the mixture (with water-to-precursor molar ratio of 150/1), which was then stirred at 80 °C for 20 mins to promote hydrolysis and gelation, as described in *Reactions (1) and (2), respectively*.

Hydrolysis:



Condensation:



Then, the mixture was transferred to a crystallising dish and heated to 250 °C to evaporate the excessive water. After that, 0.5–1.8g 8YSZ powder per mmol precursor (for obtaining different shell thicknesses) was mixed with the gel with the assistance of magnetic stirring to avoid agglomeration. The mixture was dried at 80 °C overnight to produce the gel-encapsulated powder, which was then ground, sieved with 200-mesh screen, and calcined in a Carbolite furnace at 1200 °C for 2 h. Due to gel shrinkage during drying, the process was repeated for another two cycles to improve the shell coverage and integrity. After powder encapsulation, a focused ion beam (FIB, Helios NanoLab 660, FEI) was used to cross-section the core-shell powder to measure the shell thickness and study the shell morphology.

3.2. Proof-of-concept study

To test our hypothesis on the resistance of the core-shell structure to CMAS attack, porous bulk ceramics were sintered from the core-shell powder for CMAS tests. Although porous ceramics do not fully replicate the microstructural features of APS TBCs, they offer a simple, rapid way for a proof-of-concept study. Benchmark ceramics with similar porosity were also sintered from uncoated 8YSZ powder and then tested for CMAS resistance as a reference. Another purpose of the proof-of-concept study is to determine an optimal alumina shell thickness for coating deposition. While the alumina shell is required to be as thin as possible to retain the desirable properties of YSZ, the shell at the same time must reach a critical thickness and so it can supply sufficient alumina to mitigate CMAS infiltration. The critical shell thickness can be estimated by comparing the CMAS infiltration depths between the bulk ceramics sintered from core-shell powder with different thicknesses in the proof-of-concept study.

Raw 8YSZ powder and core-shell powder with five different shell

thicknesses (with average thicknesses ranging from 168 nm to 862 nm) synthesised via the sol-gel method were cold pressed into pellets with a 10 mm diameter, which were then sintered to porous ceramics at 1500 °C in a Carbolite box furnace for 10h. Next, a layer of CMAS with a dose of 20mg/cm² was applied on the surface of each type of ceramics. The chemical composition of the CMAS used in the work was 35CaO–10MgO–7AlO_{1.5}–48SiO₂ (in mole percent), and its liquidus temperature was about 1235 °C [26]. The CMAS was prepared by pre-melting the mixed oxides at 1500 °C for 4 h in a platinum crucible in a CM rapid cycle furnace, followed by air-quenching to room temperature to form homogeneous glass. The CMAS glass was then crushed into fine powder for CMAS tests. The CMAS-coated ceramics were heat treated at 1250 °C for 30 mins to evaluate their resistance against CMAS infiltration. After the CMAS test, the ceramics were cross-sectioned, mounted, ground, and polished for microstructural examination and CMAS infiltration depth measurements. To account for the potential influence of difference in porosity between the ceramics on the CMAS infiltration depth, the open porosities of all samples were quantified following the ASTM C20–00 standard [27].

3.3. Core-shell TBC deposition

Manufacturing of TBCs was carried out at Rolls-Royce (Annesley, United Kingdom) using Diamond Jet 2600 and 3 MB thermal spray guns (Oerlikon Metco). One kilogram core-shell powder with the critical shell thickness determined in Section 3.2 was first synthesised by the sold-gel method and then deposited onto the CoNiCrAlY-coated Nimonic 263 superalloy buttons (Φ 25.4 mm $\times$ 5 mm) via APS to form the core-shell TBCs with a thickness about 400 μm . For comparison, standard 8YSZ TBCs were also manufactured from the untreated powder by APS using the same processing parameters as those for core-shell TBCs.

3.4. CMAS resistance

Core-shell and 8YSZ TBC buttons were cut into 5 mm $\times$ 5 mm blocks using a diamond-coated abrasive cutting blade in a precision cut-off machine. CMAS was applied on the TBC surfaces of the blocks, which were then annealed at high temperature to evaluate the CMAS resistance. In addition to the model CMAS used in the proof-of-concept study, a second CMAS composition (27.8CaO–4MgO–5AlO_{1.5}–61.6SiO₂–0.6FeO–1KO_{0.5}, in mole percent) simulating desert sand was also used to evaluate the CMAS resistance of the core-shell TBC in a broader range of environments. The CMAS has a lower melting temperature of 1122 °C [28]. The CMAS dose and heat treatment parameters were the same as those used in the proof-of-concept study. After the CMAS test, the samples were impregnated with an epoxy resin and cut in half to expose the TBC cross-sections after the resin was fully cured. The resin impregnation eliminated potential artificial damages introduced during sample preparation. The TBC cross-sections were then ground and polished for microstructural examination.

3.5. Mechanical properties

Apart from the strong CMAS resistance, the other key hypothesis of the core-shell TBC design is its strong resistance to fracture. The implication of this hypothesis is that the stiffness (which governs the global strain energy for failure) and the fracture resistance of the core-shell TBC should be comparable to those of standard 8YSZ TBCs. To test the hypothesis, three-point bending test, erosion test and microcantilever beam bending test were carried out to measure the stiffness and fracture resistance of the core-shell and 8YSZ TBCs.

3.5.1. Three-point bending test

The three-point bending test was performed on freestanding TBC beams using a bend fixture (10mm span) mounted on an Instron 3344 L machine with a loading rate of 0.05mm/min. To prepare the

freestanding TBC beams, the coated superalloy buttons were cut into 15 mm long beams with an average width of 2 mm using a precision cut-off machine. Next, the beams were soaked into the aqua regia to remove the bond coats and substrates. After that, the free-standing TBC beams were washed with the DI water. Some of the beams were isothermally treated at 1300 °C in a Carbolite box furnace for 100 hours to evaluate the effect of long-term thermal exposure on the flexural modulus. The thickness and width of each beam were measured by a digital calliper before the bending test.

The flexural modulus E_f is determined by [29]:

$$E_f = \frac{L^3}{48I} \frac{dP}{d\delta} \quad (1)$$

Where L is the span; P is the applied load; δ is the displacement at the centre of the beam; $\frac{dP}{d\delta}$ is the gradient of the elastic section of the load-displacement curve and I is the area moment of inertia of the cross section. For a rectangular beam cross section with a width of b and a thickness of h , I is given by:

$$I = \frac{bh^3}{12} \quad (2)$$

Three beams were prepared for each type of the coating and the average flexural modulus was taken as the measure of strain tolerance.

3.5.2. Erosion test

Erosion testing of TBCs was performed in the high-velocity erosion rig at Cranfield University [30]. This test has the advantage of evaluating the fracture resistance of the material as a whole with both material properties and microstructure effects included, as the area affected by the test is roughly ~20 mm in diameter and covers all microstructural features from the microscale to the macroscale. The experimental setup is described in detail by Nicholls et al in [31]. Button samples with thermally-sprayed 8YSZ and core-shell TBCs were mounted in the sample holders for sequential exposure to a high-velocity stream of particles at an angle of attack of 90°. Angular alumina erodent with a particle size ranging from 90 to 125 µm was fed at a rate of 0.460 ± 0.005 g/min into the pressurised air flow and accelerated to a speed of about 140 m/s. Samples were weighed and photographed at regular intervals (starting at 30 s, then 60 s and progressively longer times while maintaining a constant 0.46 g/min feed rate) to determine mass loss, erosion rate and point of failure. TBC failure is defined as the first inspection at which any amount of bond coat is exposed.

3.5.3. Microcantilever beam bending test

The fracture toughness of the TBCs was measured by the microcantilever beam bending test. Unlike the erosion test, which assesses the fracture resistance of both the material and microstructure at the macroscale, the microcantilever beam bending test provides the site-specific testing capability at the microscale. This allows it to probe the intrinsic fracture toughness of the coating material by fracturing a small volume of defect-free material. For sample preparation, microcantilever beams with a symmetric pentagonal cross-section were machined on the polished cross-sections of the TBCs using a focused ion beam (FIB, Nova FEI) following the steps described in our previous work [32]. The beams were milled with their long axis parallel to the coating thickness direction. The size of the beams is about 30 µm in length, 4 µm in width and 6 µm in height (Figure S 3 a and b in Supplementary Materials). Pre-cracks were introduced near the fixing end of each beam by a small beam current (80 pA) to guide the crack propagation. The microcantilever beam bending test was carried out *in-situ* in a Zeiss Sigma SEM using a Hysitron PicoIndenter fitted with a sapphire conical indenter with a tip radius of 2 µm. The load was applied to the free end of the beam at a constant loading rate (3 µN/s) until beam fractures. Microcantilever beams were prepared from TBCs in both the as-deposited condition and after annealing at 1300 °C for 100 h. Three beams were

prepared and tested for each type of the TBCs in each condition.

The fracture toughness is given by [32]:

$$K_{IC} = \sigma_c \sqrt{\pi a} F\left(\frac{a}{h}\right) \quad (3)$$

Where σ_c is the fracture stress; a is the depth of the pre-crack; h is the height of the beam; and $F\left(\frac{a}{h}\right)$ is the dimensionless shape factor. σ_c is given by:

$$\sigma_c = \frac{P_f L_c y}{I} \quad (4)$$

Where P_f is the load when beam fractured; L_c is the horizontal distance between loading point and crack; y is the vertical distance between the upper surface of the beam and neutral plane; and I is area moment of inertia. For a symmetric pentagonal cross-section, y and I are given by:

$$y = \frac{6h_1^2 + 3h_1h_2 + h_2^2}{12h_1 + 3h_2} \quad (5)$$

$$I = \frac{wh_1^3}{12} + \left(y - \frac{h_1}{2}\right)^2 h_1 w + \frac{wh_2^3}{36} + \left(\frac{h_2}{3} + h_1 - y\right)^2 \frac{wh_2}{2} \quad (6)$$

The meanings of w , h_1 and h_2 are illustrated in Figure S 3 (b) in Supplementary Materials. The shape factor $F\left(\frac{a}{h}\right)$ was determined by finite element analysis (FEA) and the methodology was described in detail in our previous work [32].

3.6. Characterisations

All the scanning electron microscope (SEM) images were taken using a Tescan Mira3 SEM. The crystallographic information of the TBCs was examined by X-ray diffraction (XRD, Pert Pro, Malvern Panalytical) using Cu Kα radiation ($K\alpha_1 = 1.540598$ Å). A Talos F200A transmission electron microscope (TEM) fitted with an energy-dispersive X-ray spectroscopy (EDS) system was used for compositional and microstructural analysis from the nanoscale to atomic scale. The TEM samples were in the form of thin lamellae prepared by FIB milling and *in-situ* lift-out from the areas of interest. Software ImageJ and OriginPro was used for quantitative image analysis and XRD peak fitting, respectively.

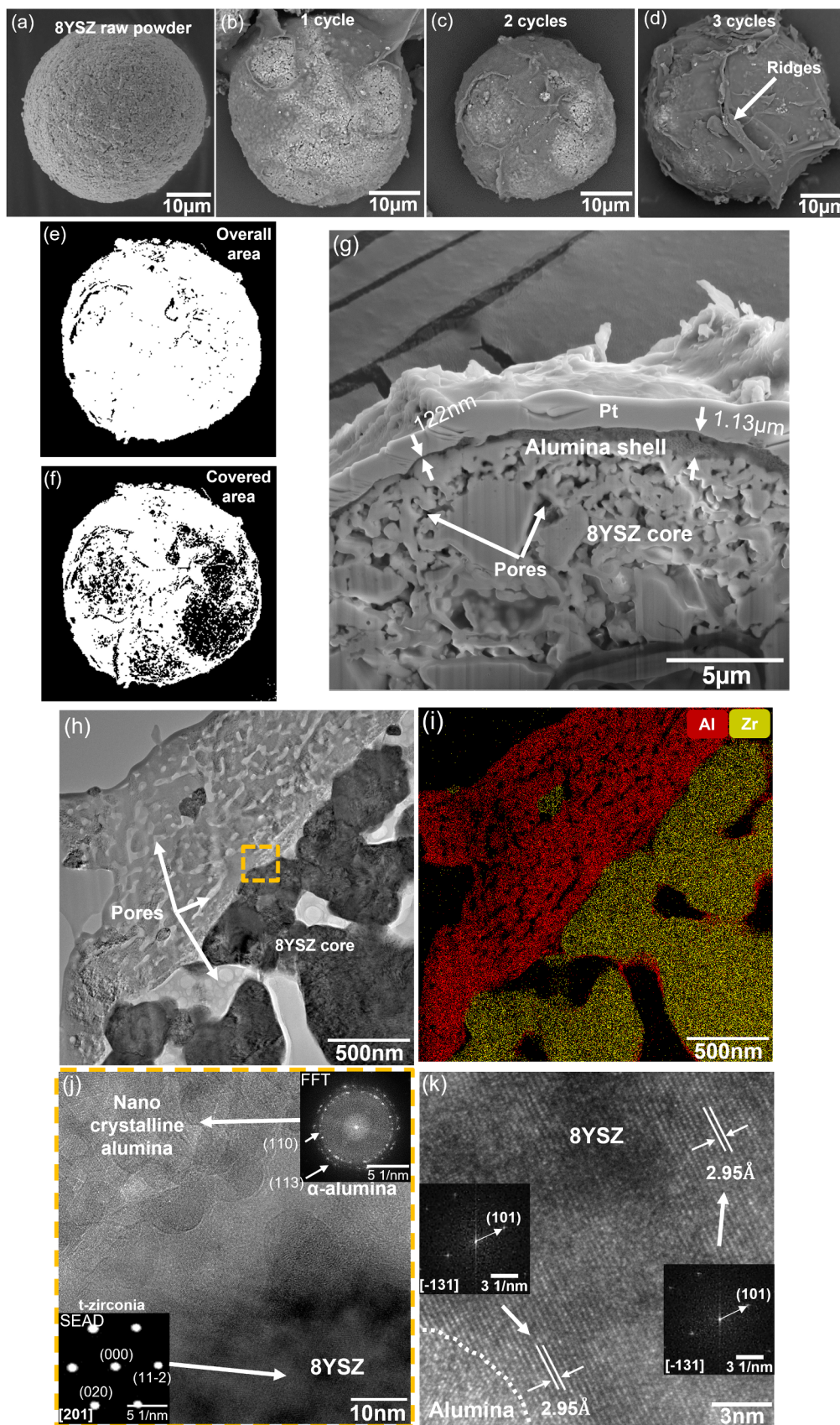
4. Results and discussion

4.1. Powder encapsulation via sol-gel process

The raw 8YSZ powder for encapsulation is granulated spherical powder with porosity between the primary particles, as indicated by the surface and cross-sectional SEM images in Fig. 2(a) and (g). During the sol-gel process, the 8YSZ powder was encapsulated with the Al(OOH) wet gel, which was then transformed to α -alumina after drying and heat treatment at 1200 °C, as indicated by the high-resolution TEM (HR-TEM) analysis and the STEM-EDS mapping of the shell cross-section in Fig. 2(j) and (i), respectively. Based on the EDS mapping, there is a small amount of alumina inside the 8YSZ core powder, which is attributed to the porous nature of the raw powder where the wet gel can infiltrate through during the encapsulation process.

The 8YSZ core region mainly consists of tetragonal crystals with a grain size of a few hundred nanometres. However, the grain size of the alumina shell is much smaller, as suggested by the rings in its FFT pattern in Fig. 2(j). There is high porosity in the alumina shell, which is indicated by the bright contrast inside the shell in the bright-field TEM image in Fig. 2(h). The formation of the pores is likely due to the wet gel shrinkage during the drying stage where water is lost [33].

After the first processing cycle, only about half of the powder surface was encapsulated, as shown in Fig. 2(b), and so more cycles were repeated to ensure the powder surface was fully covered by an alumina shell. To evaluate the encapsulation efficiency and find the number of



(caption on next page)

Fig. 2. Processing and characterisations of the core-shell powder: Backscattered electron (BSE) image of (a) the raw 8YSZ powder; (b-d) alumina encapsulated powder after 1, 2 and 3 process cycles, respectively. The 2D projections of the core-shell powder and areas covered by the alumina shells are highlighted in (e) and (f), respectively; (g) Cross-sectional SEM image of the core-shell powder; (h, i) TEM bright-field image and EDS analysis across the interface between the 8YSZ core and the alumina shell; (j) TEM bright-field image showing the area highlighted by the yellow dash rectangle in (h). The insets in (j) show the fast Fourier transformation (FFT) patterns of shell and selected area electron diffraction (SAED) patterns of the core. (k) High-resolution TEM (HR-TEM) image of the core-shell interface, showing the d-spacing of the (101) plane for t-zirconia next to and away from the shell calculated from inset FFT images.

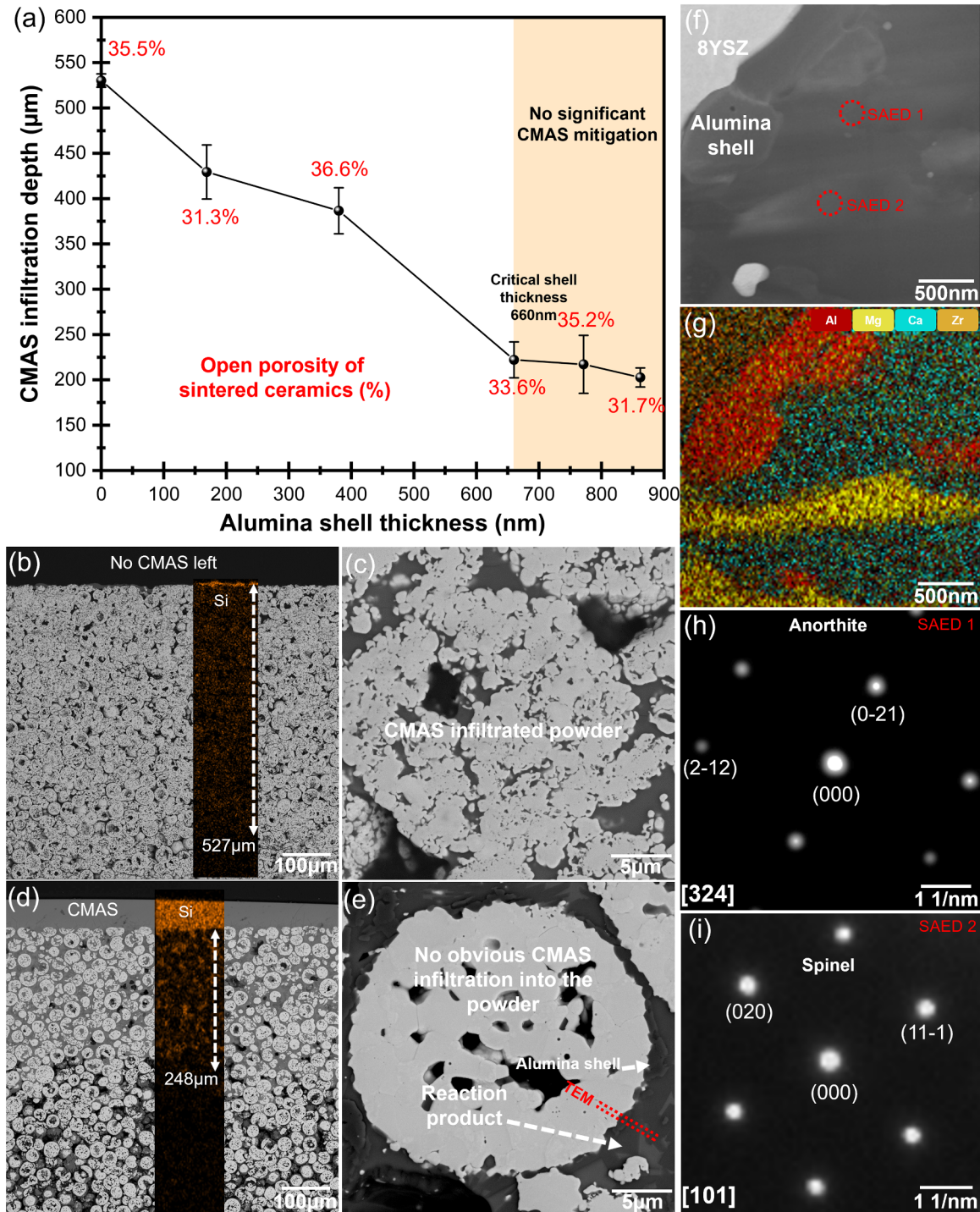


Fig. 3. CMAS resistance of the sintered core-shell ceramics: (a) CMAS infiltration depth as a function of the alumina shell thickness. The data point with zero shell thickness represents the 8YSZ ceramic and apparent porosities of these sintered ceramics are labelled next to each data point. (b, d) Cross-sectional BSE Images of the CMAS infiltrated 8YSZ and core-shell ceramics, respectively. The EDS Si maps were superimposed on the images for illustration of the CMAS infiltration depths. (c, e) Locally magnified BSE images of the CMAS infiltrated zones in the 8YSZ and core-shell ceramics, respectively, showing the absence of CMAS infiltration into the grain boundaries and the porosity inside the spherical particles of the core-shell ceramic. (f, g) High-angular dark field (HAADF) image and EDS analysis, respectively, of an area across the CMAS-alumina shell interface (the red dash rectangle in e). (h, i) SAED patterns of the CMAS-alumina reaction products marked in (f).

cycles needed, the encapsulation rate, which is defined as the ratio of the projected area covered by alumina to the projected area of the core-shell powder, was calculated as a function of the cycle number via the ImageJ software, as illustrated in Fig. 2(e) and (f). The encapsulation rate after the first cycle was 47 % and reached 95 % in the third cycle (Fig. 2b-d), suggesting that the 8YSZ powder was almost fully encapsulated by the alumina shell.

After three processing cycles, the powder was cross sectioned through its great circle plane by FIB milling (Fig. 2g) for shell thickness measurements. It is found that the shell thickness varies from place to place, ranging from 122 nm to 1.13 µm. The large variation in thickness is due to the presence of the alumina ridges on the surface, as shown in Fig. 2(d). The formation of the ridges is attributed to the bridging of the Al(OOH) wet gel between adjacent powders, which was subsequently dried and fractured when the powder agglomeration was broken apart.

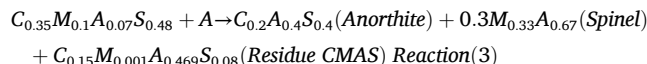
The bonding between the alumina shell and 8YSZ powder surface is likely to be mechanical interlocking because the encapsulation process relies predominantly on physical deposition once the alumina shell is formed via the sol-gel method. STEM-EDS mapping across the core-shell interface (Fig. 2i) shows no overlap between the Al-rich and Zr-rich regions, confirming the lack of interdiffusion or chemical bonding between the YSZ core and the alumina shell. Additionally, HR-TEM and corresponding FFT analysis (Fig. 2k) reveals that the d-spacing of the (101) plane in tetragonal YSZ is identical in regions both near and away from the core-shell interface, indicating no mutual dissolution between the alumina and YSZ.

4.2. Proof of concept: CMAS resistance of the core-shell ceramics

Fig. 3(a) plots the CMAS infiltration depth through the bulk core-shell ceramic as a function of the alumina shell thickness (the first data point with the shell thickness equal to 0 stands for the 8YSZ ceramic without an alumina shell). The porosities of all these ceramics were measured to be between 31 %–37 % and so the effect of porosity difference on the CMAS infiltration was ignored in this study. The high porosity is likely due to the limited green packing density and the poor sintering ability associated with the large, spherical powder (Fig. 2a d). Such high porosities enable CMAS to easily flow through the ceramics, thereby setting a model condition for evaluating the CMAS mitigation mechanism of core-shell structure. The CMAS infiltration depth reaches to 527 µm in the 8YSZ ceramic but is reduced significantly with the introduction of the alumina shell and the increase of the shell thickness, suggesting that the core-shell structure is very effective in mitigating CMAS penetration. However, when the shell thickness exceeds 660 nm, the CMAS infiltration depth levels off at approximately 215 µm and there is only minor reduction in CMAS infiltration depth with a further increase in the shell thickness. The levelling-off suggests that shell thickness above 660 nm would offer little extra benefit in mitigating CMAS infiltration, which might be due to the saturation of alumina in the CMAS melt. As a result, the critical shell thickness was taken as 660 nm (translated to an alumina content of about 6.12wt%/8.57vol%), and the core-shell powder with a shell thickness of about 660 nm was synthesised for deposition of the core-shell TBCs (see Section 4.3).

To investigate the CMAS mitigation mechanism, the microstructures of the CMAS infiltrated 8YSZ and core-shell ceramics (with a shell thickness of 660 nm) were examined by SEM, as shown in Fig. 3(b-e). The infiltration depth in the 8YSZ ceramic is more than twice the depth in the core-shell ceramic. All the CMAS applied on the surface of the 8YSZ ceramic before the CMAS test infiltrated into its pores and grain boundaries. However, for the core-shell ceramic, there is a remaining thick CMAS layer left on the top surface, and the inter-particle gaps in the CMAS affected regions are filled with CMAS and CMAS-alumina reaction product (darker contrast as shown in Fig. 3e). To investigate the reaction product in detail, a thin lamella sample across the reaction interface highlighted by the red rectangle in Fig. 3(e) was prepared by FIB and then analysed by TEM. The HAADF-EDS analysis and SAED

patterns suggest that the reaction products in Ca-rich and Mg-rich regions are anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and spinel (MgAl_2O_4), respectively, as shown in Fig. 3(f-i). The formation of these reaction products follows the Reaction (3),



Where C, M, A, and S represent CaO, MgO, $\text{AlO}_{1.5}$, and SiO_2 respectively.

The densely distributed anorthite and spinel crystals between the inter-particle gaps seal the CMAS infiltration path, leading to the reduction of the CMAS infiltration depth. There is no obvious CMAS hotspot in the 8YSZ core as shown in the HAADF-EDS mapping, suggesting that the CMAS has not infiltrated into the internal porosity or grain boundaries due to the shielding of the alumina shell.

4.3. Microstructure of core-shell TBCs

The core-shell powder with an average shell thickness of about 660 nm was deposited by APS to form the core-shell TBC. The coating cross-section shows regular variation of contrast between grey and bright through the thickness, suggesting the presence of a core-shell microstructure (Fig. 4a). The core-shell coating microstructure is further confirmed by the high-magnification BSE image (Fig. 4b) which shows strips with alternating contrasts of grey and bright. EDS analysis (Fig. 4c and d) shows that the strips with grey contrast are rich in Al but the ones with bright contrast are rich in Zr. Quantitative EDS point analysis of the core-shell splats, however, shows that both the core and shell regions contain Al and Zr (Table 1). On average, the Al and Zr concentrations in the shell region are 11.3 at% and 21.3 at%, respectively, whereas in the core region, the Al and Zr concentrations are 6.9 at% and 26.4 at%, respectively. The co-existence of substantial Al and Zr in both the core and shell regions suggests that there is mixing between the alumina shell and the 8YSZ core during coating deposition.

The XRD patterns of core-shell and 8YSZ TBCs are shown in the Fig. 5. For comparison, the XRD patterns of the core-shell and 8YSZ powders are also included. Both core-shell and 8YSZ powders predominantly consist of tetragonal YSZ, with minor monoclinic and cubic phases. Compared to the 8YSZ powder, α -alumina peaks are observed in the XRD pattern of the core-shell powder, corresponding to the synthesised α -alumina shell. For the APS core-shell TBC, no peak for alumina is observed; instead, it shows similar diffraction patterns to the 8YSZ TBC. The finding, together with the EDS analysis in Table 1, suggests that the mixing of the shell and core during APS has diluted the shell to an extent that the original crystalline alumina is replaced by an alumina-alloyed zirconia phase. Phase identification confirms that both type of the coatings are composed of tetragonal (t) and metastable (t') zirconia phases. The formation of t' is due to the diffusionless transformation of zirconia induced by the rapid cooling during APS deposition, where zirconia ceramic melt crystallizes to cubic-zirconia followed by a displacive transition to t'-zirconia [34]. However, compared to the 8YSZ coating, the core-shell coating has slightly larger diffraction angles for all the crystal planes sampled by XRD. For example, the 2 θ angle of the (101) plane in the core-shell coating shows a 0.18° shift to a higher angle compared to that in the 8YSZ coating, indicating a decrease in d-spacing in the core-shell coating. This is likely due to the substitution of the larger Zr^{4+} ions (ionic radius 0.8 Å) by the smaller Al^{3+} ions (ionic radius 0.5 Å) in the crystalline lattice.

The results presented in Figs. 4 and 5 indicate that while the core-shell TBC has been successfully manufactured by APS, its building block (splat) comprises an alumina-rich zirconia shell and an alumina-poor zirconia core rather than a pure alumina shell and a 8YSZ core due to the mixing of alumina and 8YSZ during coating deposition. The mixing is expected to occur when the core-shell particles are melted by the high temperature plasma jet during the APS process. Although

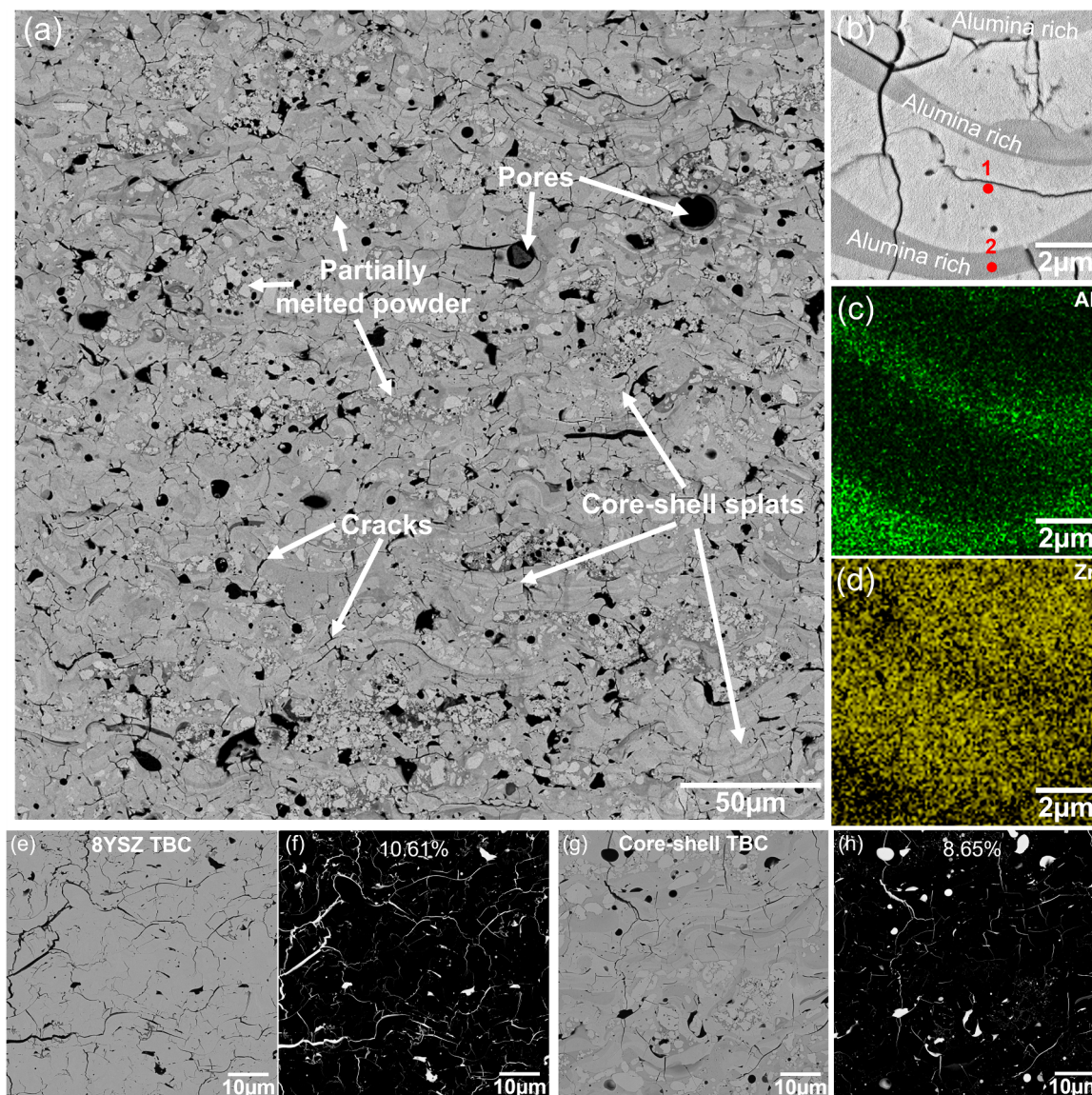


Fig. 4. Microstructural and compositional analysis of the core-shell TBC: (a and b) Cross-sectional BSE images at low and high magnifications; (c and d) EDS maps of Al and Zr in the area shown in (b); (e, g) Cross-sectional SEM images of 8YSZ and core-shell TBCs at the same magnification and (f, h) Segmented images of (e, g) highlighting the microstructural defects and porosities.

Table 1

Quantitative EDS point analysis of the locations highlighted by the red dots in Fig. 4(b).

Location	Elemental concentration (at%)			
	Zr	Al	Y	O
1 (core)	26.4	6.9	2.2	64.5
2 (shell)	21.3	11.3	2.3	65.2

alumina has very limited solubility zirconia in solid form, they are fully miscible in liquid phases, as indicated by the liquid phase field in the binary phase diagram in Figure S 4 in Supplementary Materials [35]. It is expected that the mixing is much more significant near the surface of the core-shell powder (where the temperature is higher, and the core and shell are in direct contact) compared with that in the centre of the core far away from the shell. Due to the rapid cooling in the APS process, the composition of the mixture and its gradient, resulting from the varying degrees of liquid mixing, is largely retained after coating deposition, which leads to the formation of the zirconia-based splats with

alumina-poor cores and alumina-rich shells (Fig. 4b). It is worth noting that while previous studies [36,37] have reported the formation of amorphous zirconia-alumina phases during thermal spray of zirconia-alumina composite powders, our subsequent TEM analysis (Fig. 6) did not detect such a phase in the as-deposited core-shell TBC. This is likely due to the significantly lower alumina content (6.12 wt%) in our core-shell powder compared to that in the composite powders (~60 wt%) used in those studies. Another difference in the XRD patterns between 8YSZ and core-shell TBCs is that the latter shows larger peak widths. For example, the full width at half maximum (FWHM) of the (101) peak of the core-shell coating is over three times greater than that of the 8YSZ coating. There are two possible reasons for the difference. One is that the core-shell coating has smaller grain size due to the addition of alumina, which hinders the grain growth. The other is the variation in the concentration of alumina solid solution throughout the coating, which results in differences in the lattice parameters and d-spacing.

Compared to the conventional 8YSZ TBC, the core-shell TBC shows slightly different microstructural features (Fig. 4e-h). The 8YSZ coating mainly comprises horizontally aligned intersplat cracks and vertically

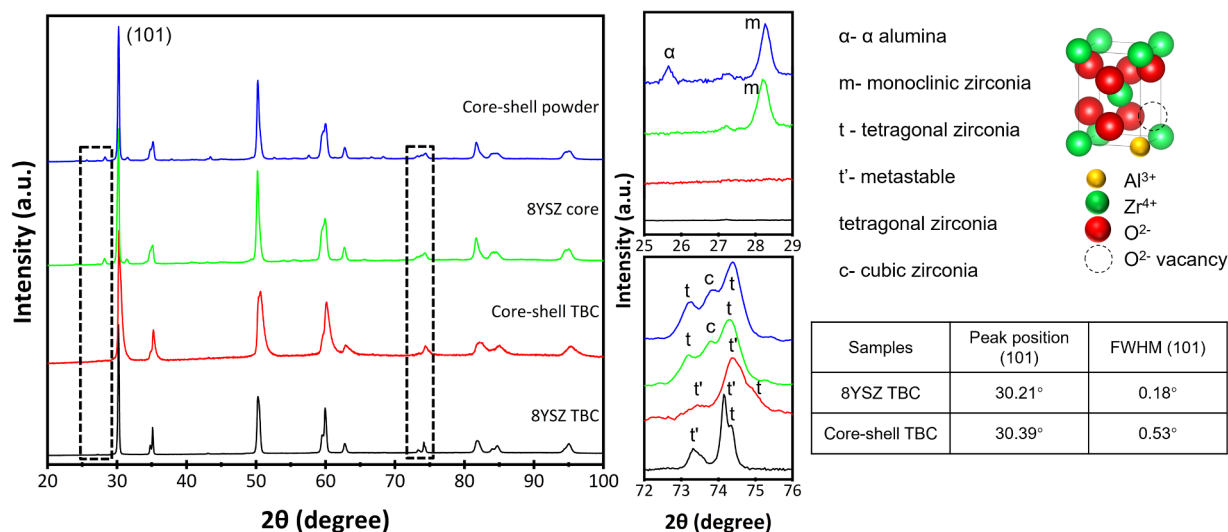


Fig. 5. XRD patterns of the core-shell and 8YSZ powders and TBCs, with patterns from 25° to 29° and 72° to 76° highlighted. The schematic illustration describes the unit cell of zirconia with alumina in solid solution formation during the APS process due to liquid mixing and subsequent rapid cooling. The table lists the peak position and full width at half maximum (FWHM) of the (101) plane in each type of the coating.

aligned fine intra-splats cracks. However, the intersplat cracks in the core-shell coating appear to be finer and less pronounced than those in the 8YSZ coating. Quantitative image analysis shows that the porosity of the core-shell coating is about 2 % less than that of the 8YSZ coating. The difference between the 8YSZ and the core-shell TBCs in the microstructural features is likely due to the addition of alumina which lowers the melting points of the ceramic. Based on the binary phase diagram of the zirconia and alumina system (Figure S 4 in Supplementary Materials), 6.12 wt% alumina addition lowers the melting point of the system from 2710 °C to approximately 2540 °C. As a result, the core-shell powder melts to a greater extent, with lower viscosity, better wetting and stronger intersplat bonding. More research will be carried out in future work to understand the relationship between the processing and microstructure of the core-shell TBC.

4.4. TEM analysis of the core-shell splats

To examine the difference in microstructure and composition between the shell and the core in greater detail, a thin lamella was prepared by FIB across the core-shell interface for TEM characterisation. Fig. 6(a) shows a HAADF image of an area across the core-shell interface in a splat. The shell region has a darker contrast due to its higher Al content. Another difference between the core and the shell is their grain size and morphologies: the core comprises columnar grains (grain size 72 nm), but the shell is composed of finer equiaxed grains (grain size 30 nm), as shown in Fig. 6(b) and (e), respectively. The Al distribution maps show that there are Al hotspots at the grain boundaries in both the core and the shell (Fig. 6c and f). HR-TEM analysis suggests that the Al-rich phase at the grain boundaries is amorphous (Fig. 6d). The formation of the amorphous phase is likely attributed to the rapid quenching during coating deposition, which suppresses crystallisation [36,37]. In both the core and shell regions near the interface, the Al concentrations inside the grains have similar values, which are around 10 at% based on the quantitative EDS analysis (Table 2). Based on the previous characterisations in Section 4.3, the presence of alumina in the zirconia-based grains is due to the fast cooling of the mixed ceramic melt during coating deposition, which freezes some alumina solute in the crystallised zirconia grains. Due to the same cooling conditions, the concentration of the alumina solid solution is similar across the coating in both core and shell regions. Upon further cooling to solidus temperature, the remaining melt solidifies to alumina. However, the high cooling rate inhibits crystallisation [38], leading to the formation of amorphous alumina

between the alumina-alloyed zirconia grains [36]. Since the shell is composed of pure alumina prior to the APS process, more intergranular amorphous alumina forms in the shell regions of the core-shell TBC, along with smaller equiaxed zirconia grains, compared to the core regions.

After exposure to 1300 °C for 1 hour (Fig. 6g), the amorphous alumina in the as-deposited core-shell TBC crystallises into fine nano-sized α -alumina (the darker contrast in Fig. 6g) at the zirconia grain boundaries. The α -alumina crystals are much more densely populated in the shell than in the core due to the higher alumina content in the shell. The α -alumina phase is further confirmed by the SAED analysis after annealing at 1300 °C for 100 h (Fig. 6h). The long-term thermal exposure results in significant grain growth and formation of a composite shell with alumina grains embedded in a zirconia matrix. In the core, the alumina grains are no longer detectable due to diffusion and migration of alumina towards the shell, where grains coalesce.

4.5. CMAS resistance and mitigation mechanisms

CMAS infiltration tests were performed on the core-shell and 8YSZ TBCs to compare their CMAS resistance and investigate the potential CMAS mitigation mechanism in the core-shell TBCs. We will use the model CMAS (35CaO–10MgO–7AlO_{1.5}–48SiO₂) as an example to demonstrate the CMAS resistance because the attack of the second CMAS (artificial desert sand) on both types of TBCs is phenomenally similar to that of the model CMAS. Fig. 7(a, c, e and g) show the CMAS infiltration behaviours of the 8YSZ and core-shell TBCs for durations of 30 mins and 15 h. After 30 mins exposure to CMAS, the 8YSZ TBC suffers from severe CMAS attack, with the thickness of the CMAS-infiltrated layer reaching about 192 μ m based on the Ca map in Fig. 7(b). The CMAS infiltrated not only through the coating porosity (e.g., pores and inter/intra-splat space) but also along the YSZ grain boundaries within the splats (e.g., the inset in Fig. 7a). At the top of the CMAS infiltrated region, there is a layer (18–32 μ m) of globular zirconia particles, which is likely formed via the dissolution-precipitation mechanism [5]. After 15 h exposure, CMAS infiltrated through the entire TBC, resulting delamination near the surface (Fig. 7c and d).

For the core-shell TBC, after 30 mins CMAS exposure (Fig. 7e), there was only a thin, CMAS induced reprecipitation layer formed in the surface region, and the remaining part of the coating shows no sign of CMAS infiltration and has an identical microstructure with that prior to the CMAS test (the inset in Fig. 7e). The resulting CMAS infiltration

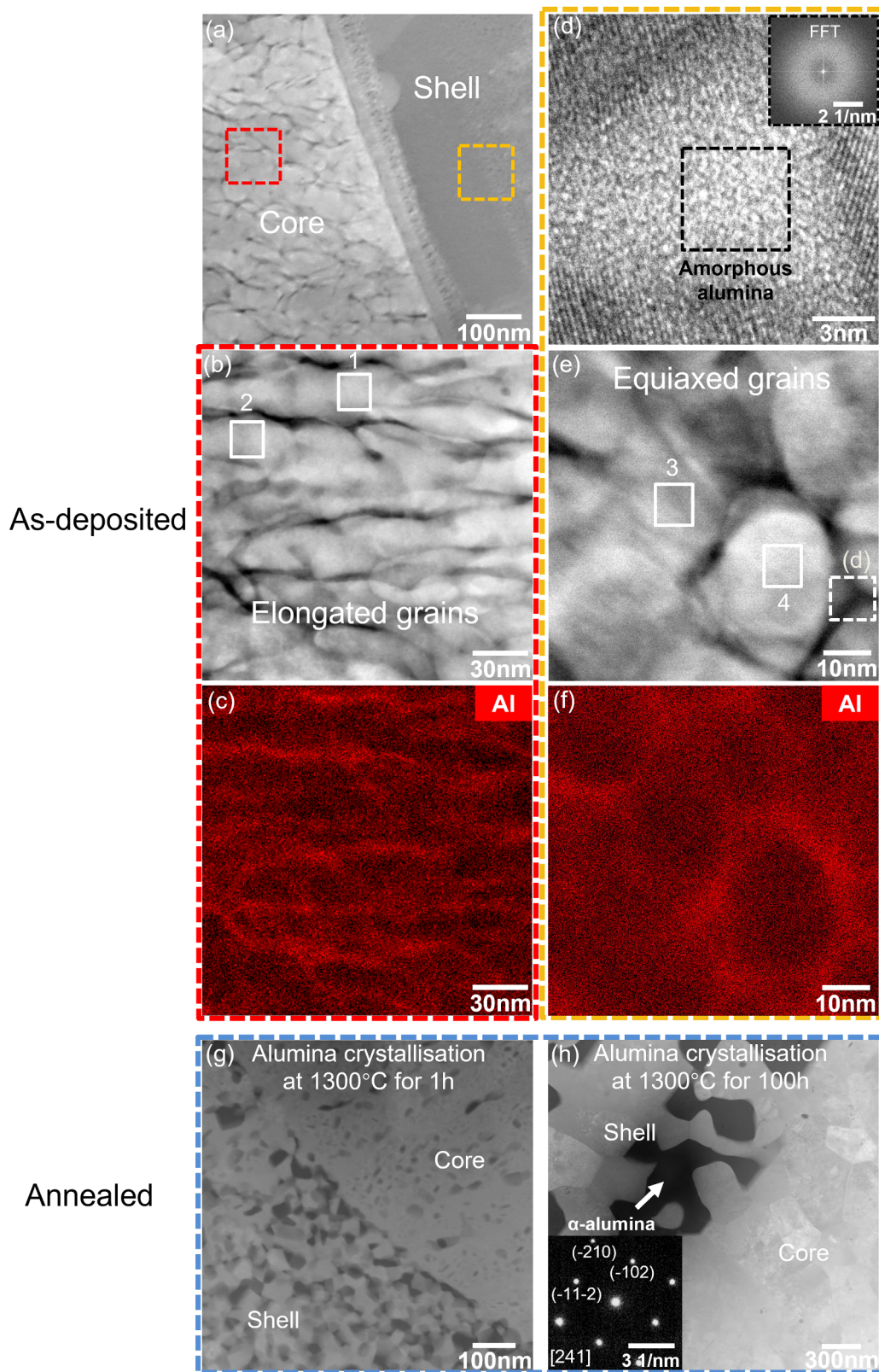


Fig. 6. TEM analysis of the core-shell splat: (a) HAADF image of an area across the core-shell interface of a splat; (b, c) high magnification HAADF image of the core and corresponding EDS map of Al, respectively; (e, f) high magnification HAADF image of the shell and corresponding EDS map of Al; (d) HRTEM analysis of the intergranular Al-rich phase in the shell highlighted by the white dash rectangle in (e). The phase has no lattice fringe, suggesting its amorphous nature. (g, h) HAADF images of the core-shell interfaces after isothermal exposure at 1300 °C for 1 h and 100 h, respectively, with inset SAED pattern in (h) showing the crystalline α -alumina.

Table 2

Al concentration in the areas in the core and shell regions highlighted by the white rectangles in Fig. 6(b, e).

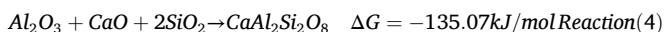
Locations	1	2	3	4
Al (at%)	10.08	10.86	9.61	9.52

depth (15 µm) is over an order of magnitude lower than that in the 8YSZ TBC, as shown in Fig. 7(f). Within the remaining CMAS on the top surface, there are needle-shape CMAS-alumina reaction products, which are likely to be anorthite induced by the reaction between the CMAS and the alumina from either the grain boundaries or the alumina-alloyed zirconia grains in the core-shell TBC. After long-term CMAS infiltration test (15h), a grain boundary infiltration region (Fig. 7g inset) developed beneath the surface reprecipitation layer, and this region is characterised by irregular grain shapes (original grain shape) as opposed to globular-shaped reprecipitation grains. However, the overall CMAS infiltration depth increased only to 50.3 µm, which is 87 % smaller compared to the whole thickness infiltration (386.9 µm) observed in of the 8YSZ TBC.

Fig. 7(i) highlights the reaction front (30mins) between the infiltrated CMAS and the Al-rich shell near the coating surface. Within the shell, there are two pre-existing cracks which are the major CMAS infiltration paths (highlighted in the red dash rectangle). However, CMAS infiltration stopped halfway through the cracks without reaching the coating beneath the shell, as indicated by the difference in contrast between CMAS (grey) and cracks (black). The EDS maps (Fig. 7k and l) of the same area suggest that there are Mg hotspots in the shell, but other CMAS elements, such as Si, were not found. Based on the previous characterizations in Section 3.2, the Mg-rich region is likely to be the reaction product (spinel) between magnesia and alumina. To confirm this argument and study the CMAS mitigation mechanism of the core-shell TBC, a thin lamella that includes a crack partially infiltrated by CMAS in the shell (as highlighted by the red dash rectangle in Fig. 7i) was prepared by FIB and analysed by TEM. Within the crack, there are two main phases labelled as P1 and P2, respectively (Fig. 8a). They are confirmed to be the CMAS and anorthite by the Al and Ca maps (Fig. 8b and c) and HR-TEM images (Fig. 8e and g) with their FFT patterns (Fig. 8f and h). Within the anorthite crystals, there are twin structures formed during crystallisation [39]. The formation of densely populated anorthite seals the crack against further CMAS infiltration. Within the shell, intergranular nanoparticles with a darker contrast and rich in both Al and Mg (Fig. 8b and d) were observed. HR-TEM images and their FFT patterns in the corresponding region suggest that this phase is spinel, a reaction product between alumina and magnesia (Fig. 8i and j).

When CMAS infiltrates the alumina-rich shell, two main reactions occur between CMAS and alumina, forming anorthite and spinel, respectively, as described by the following reactions:

Formation of Anorthite:



Formation of Spinel:



However, since the change in Gibbs free energy of the former reaction (−135.07 kJ/mol, Reaction (4)) is more negative compared to that of the later (−27.44 kJ/mol, Reaction (5)) at 1250 °C [40], CMAS will first crystallise to anorthite by consuming the alumina solute in the alumina-alloyed zirconia grains and the alumina at the grain boundaries, as indicated by the Al-depletion layer next to CMAS (Fig. 8a and b). Meanwhile, the CMAS composition at the reaction front becomes Mg-rich compared to its original composition. The Mg-rich CMAS melt then infiltrates the grain boundaries, reacts with the intergranular alumina, forming the spinel phase and blocking the grain boundary infiltration pathway. The sequential reactions are consistent across

core-shell TBC, even in the areas without pre-existing defects, as indicated by the Mg-rich layer (spinel) beneath the Si hotspots (CMAS and anorthite) (Fig. 7k and l).

The sequential Reactions (4) and (5) also occur in the attack of the second CMAS (artificial desert sand) on the core-shell TBC (see Figure S 5 in Supplementary Materials). However, the spinel crystals formed via Reaction (5) between the CAMS and the intergranular alumina are incorporate Fe due to the presence of FeO in the artificial desert sand, as confirmed by the TEM and EDS analysis in Figure S 5. Owing to the CMAS mitigation mechanisms enabled by Reactions (4) and (5), the CMAS infiltration depth in the core-shell TBC after 15 h is 64.5 µm, which is reduced by 83.6 % compared to the full through-thickness infiltration depth (393.8 µm) observed in the 8YSZ TBC (Figure S 5 a, b, d, and e).

Based on the above characterisations and analysis, the strong CMAS mitigation effect of the core-shell TBC is realised by the intergranular alumina phase and the alumina solute in the zirconia grains which react with the CMAS melt to form anorthite and spinel crystals, thereby sealing the infiltration pathways (pre-existing defects and grain boundaries). This process, along with the reaction products and their spatial distribution relative to the splat and grain boundaries, is schematically illustrated in Fig. 8k. This has demonstrated that the unique core-shell microstructure produced by the APS process is very effective in mitigating CMAS attack.

4.6. Flexural modulus

The flexural modulus of the core-shell and 8YSZ TBCs in the as-deposited condition and after annealing at 1300 °C for 100 h were determined via the three-point bending test. Fig. 9 shows the typical load-displacement curves for both types of the coatings and their average flexural modulus determined from all the load-displacement curves.

For the as-deposited TBCs, the average modulus of the core-shell and 8YSZ TBCs is 13.87 and 12.21 GPa, respectively. The slightly higher modulus of the core-shell TBC is likely due to its lower porosity (2 % lower, as quantified in Fig. 4f and h) and the introduction of stiffer alumina into the coating. However, such a minor difference in the modulus (1.66 GPa) suggests that the core-shell structure has negligible impact on the coating stiffness. The load-displacement curves for the two types of the coatings show a similar slope in the initial bending stage (hence similar stiffness), but as the loading continues to increase the slope of the curve for the 8YSZ TBC gradually decreases and show pop-in near the end of the test, indicating early crack propagation. Compared with the 8YSZ TBC, the core-shell TBC shows a more linear load-displacement curve without any visible pop-in during the test. The different behaviour between the 8YSZ TBC and the core-shell TBC is likely attributed to the larger number of microstructural defects in the 8YSZ TBC (Fig. 4f and h), which is expected to cause more local stress concentrations and the gradual decrease in the slope of the load-displacement curve during bending. The higher porosity can also create a greater opportunity for defect coalescence and crack propagation in the 8YSZ TBC, thereby resulting in the pop-in events. Nevertheless, the flexural modulus obtained from the three-point bending test suggests that the core-shell TBC has similar strain tolerance as the 8YSZ TBC.

Annealing significantly stiffens both types of TBCs, as reflected by the much steeper load-displacement curves. The 8YSZ TBC shows a fivefold increase in modulus (from 12.21 to 59.22 GPa) after annealing at 1300 °C for 100 h, while the core-shell TBC exhibits a fourfold increase (from 13.87 to 53.94 GPa). The increase in modulus is primarily due to sintering. In the core-shell TBC, annealing promotes the crystallisation of the amorphous alumina phase, which provides an additional contribution to the increase in modulus, as the modulus of amorphous alumina is about 3.1–3.7 times lower than that of crystalline alumina [41]. However, the fact that the modulus of the core-shell TBC is 5.28 GPa lower than that of the 8YSZ TBC after annealing indicates that the

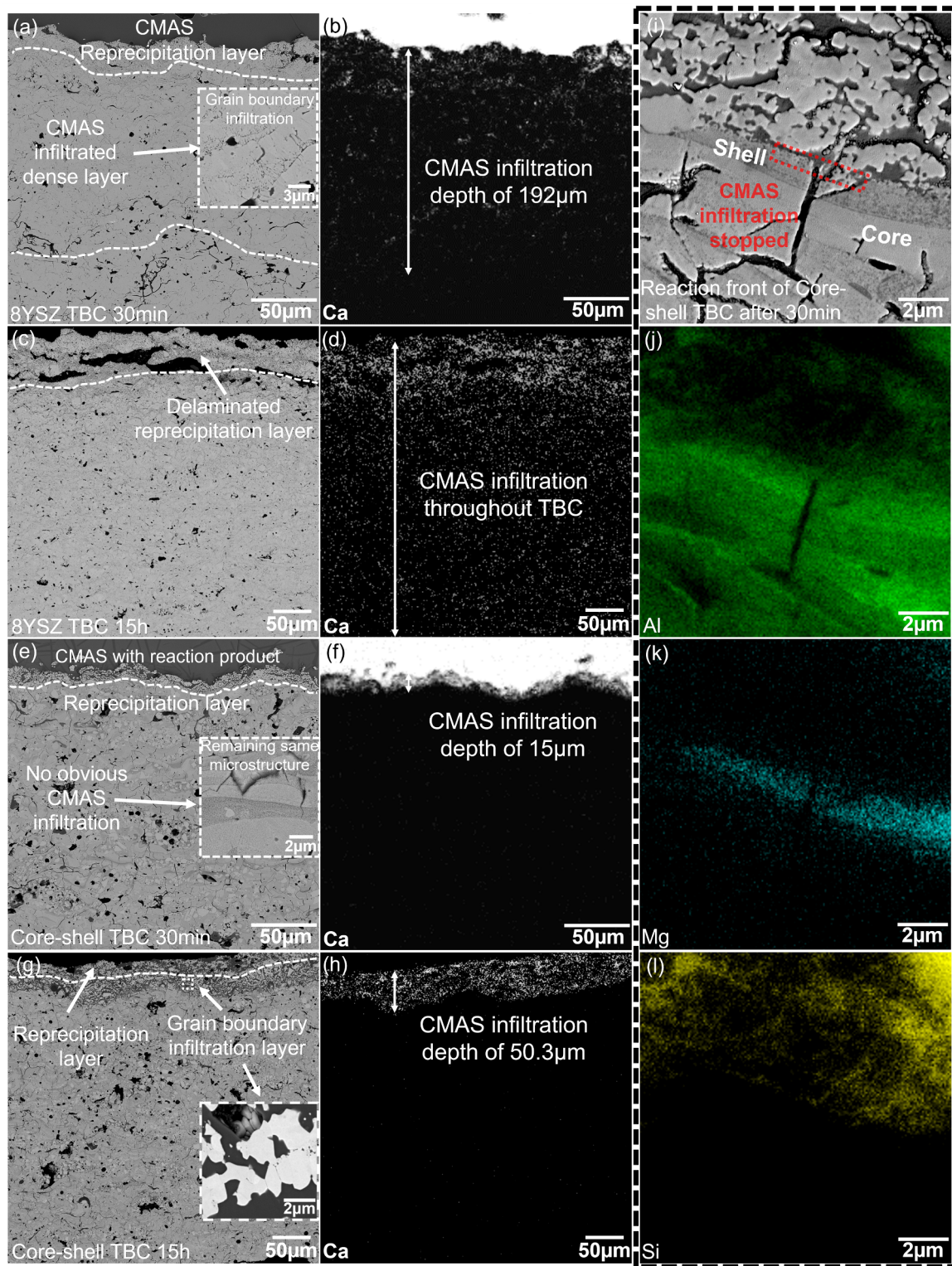


Fig. 7. Comparison of CMAS resistance between the 8YSZ and core-shell TBCs: Cross-sectional BSE images of the (a, c) 8YSZ and the (e, g) core-shell TBC after exposure to CMAS for different durations ($t = 30$ mins and 15 h). The high-magnification inset images in (a, e and g) show the microstructures below the CMAS-induced reprecipitation layers on the surface; (b, d, f and h) Ca maps in the same areas as those in (a, c, e and g) illustrating the CMAS infiltration depths; (i-l) high-magnification BSE image and corresponding Al, Mg, and Si maps at the reaction front (30mins reaction time) between the CMAS and the core-shell TBC.

core-shell TBC exhibits greater resistance to sintering compared to the 8YSZ TBC. The densification of ceramics mainly relies on material transport through grain boundary and lattice diffusion. Of these two mechanisms, grain boundary diffusion typically requires lower activation energy and acts as the dominant mechanism for densification. In the

core-shell TBC, annealing leads to the formation of α -alumina phase at the YSZ grain boundaries, as indicated by the inset TEM image in Fig. 9. YSZ and α -alumina are immiscible in solid form, and the intergranular second-phase α -alumina particles can inhibit grain boundary diffusion by reducing the grain boundary mobility through disrupting diffusion

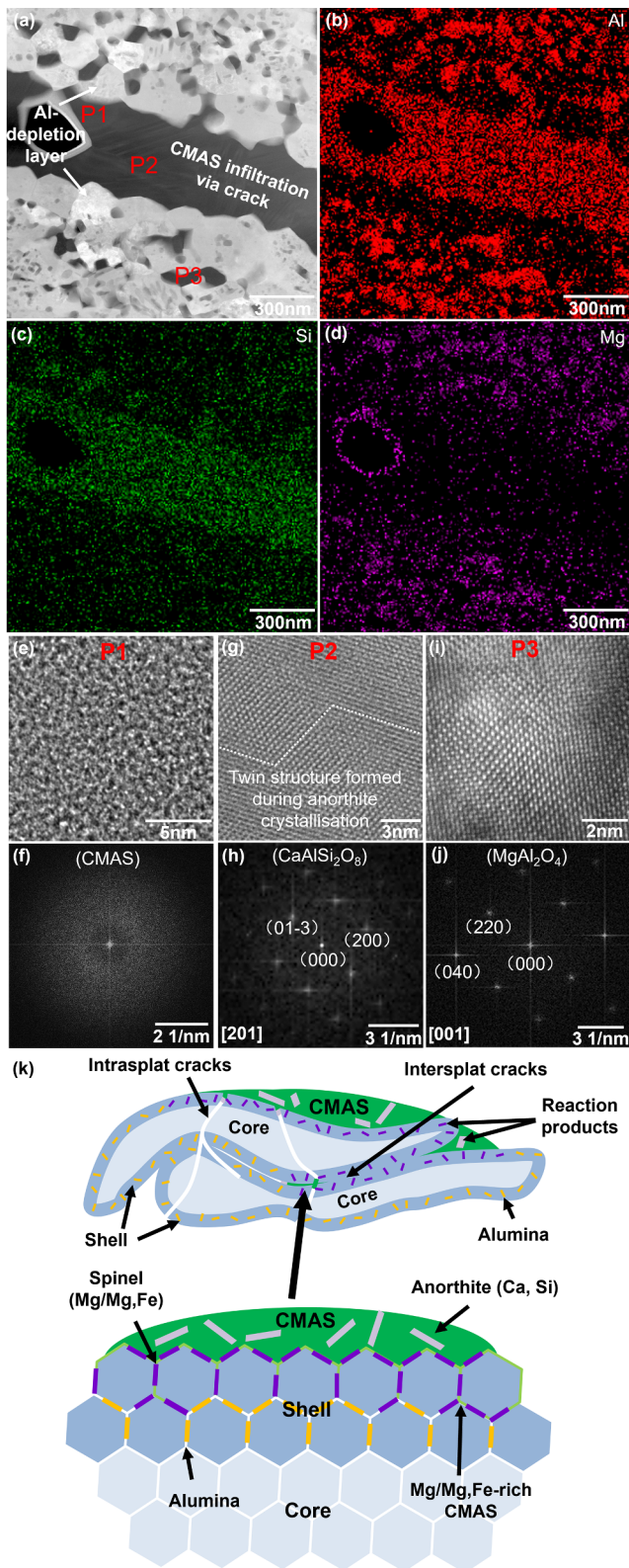


Fig. 8. TEM analysis of a splat shell that includes a crack partially filled by CMAS: (a) HAADF image showing a CMAS-shell interface region with three different phases labelled; (b-d) EDS maps of Al, Si, and Mg in the area in (a); (e, g, and i) HRTEM images of the three different phases labelled as P1, P2 and P3 in (a); (f, h, and j) FFT patterns of P1, P2 and P3. The TEM sample was taken from the area highlighted by the red dash line in Fig. 7(i); (k) Schematic diagrams illustrating the multiscale CMAS mitigation mechanism in the core-shell TBC.

pathways, thereby increasing the activation energy for diffusion [42, 43]. The superior sintering resistance of the core-shell TBC helps to lower the strain energy within the coating during long-term thermal exposure, thereby reducing the driving force for failure.

4.7. Erosion resistance

Erosion tests were performed on the core-shell and 8YSZ TBCs to evaluate and compare their resistance to fracture induced by particle impact. Fig. 10(a) and (b) shows an example of the surface of the two types of TBCs where the coatings are damaged by high-velocity erosion. For the 8YSZ TBC, the main damage mechanism is the propagation of cracks along the splat boundaries, but there is also evidence of intra-splat crack formation (e.g. delamination of the highlighted splat is helped by an intra-splat crack propagating and joining the pre-existing intersplat cracks). This corresponds to the common failure mechanism described in the literature for thermally-sprayed TBCs [44]. However, the erosion front of the core-shell TBC shows more diverse cracking patterns. Apart from the horizontal delamination between the splats, a higher density of intra-splat cracking is also identified in the coating. This is linked to the distinct microstructural features of the core-shell coating. Firstly, the vertical cracks are more pronounced than the horizontal intersplat cracks in the core-shell coating (Fig. 4g and h), thereby creating easy paths for crack propagation in the vertical direction. Secondly, the stronger intersplat bonding in the core-shell coating, which results from the lower melting points of alumina and is reflected by the finer and fewer intersplat cracks (Fig. 4g and h), provide greater resistance against cracking in the horizontal direction. As a result, vertical cracks are generated to release the impact energy induced in the erosion test.

During the erosion test, the coated button samples were eroded until the TBCs were completely removed and the metallic bond coats were exposed (the darker contrast in the centre of the red circle in the inset of Fig. 10c). To quantify the erosion behaviour, the coating mass loss was plotted against the amount of erodent used (Fig. 10c). The plots exclude the last data point in the erosion test, when TBC failure has occurred, to avoid the contribution from the bond coat material loss and because runaway TBC delamination is common after the bond coat is exposed. The erosion curves for both types of the TBCs show similar profiles, with the initial 4–6 datapoints belonging to the transient regime followed by the steady state, where material loss is linearly proportional to the amount of erodent used. This suggests that both types of the TBCs have a similar failure mechanism that involves crack initiation, propagation, and coalescence with the pre-existing defects, eventually leading to material removal. To compare the fracture resistance between the core-shell and 8YSZ TBCs, their erosion rates (g of material loss per kg of erodent), were calculated from the curve slopes for three samples per coating system: 23.4, 24.0 and 23.4 g/kg for core-shell and 24.6, 25.4 and 25.3 g/kg for the 8YSZ. This highlights the coating homogeneity across samples of the same type and shows the average erosion rate (as listed in Fig. 10c) of the core-shell TBCs is 5.98 % lower than that of the 8YSZ TBCs, suggesting that the core-shell TBCs have higher resistance to fracture induced by particle erosion. To account for the difference in density between the 8YSZ and the core-shell TBCs, the weight loss was converted to the volumetric loss using the theoretical densities estimated from the compositions of the TBCs, and the results are listed Fig. 10(d). Even when the density is taken into consideration, the erosion rate of the core-shell TBC remains 2.47 % lower than that of the 8YSZ TBC. In sum, the core-shell TBC shows stronger resistance to erosion than the 8YSZ TBC, regardless of the unit used to measure the erosion rate.

The higher erosion resistance of the core-shell TBC can be explained by two reasons. The first one is that there are fewer pre-existing microstructural defects in the core-shell TBCs, which mitigates crack propagation and coating delamination. The second one is the contribution from ferroelastic toughening of the t' -phase in the core-shell TBC.

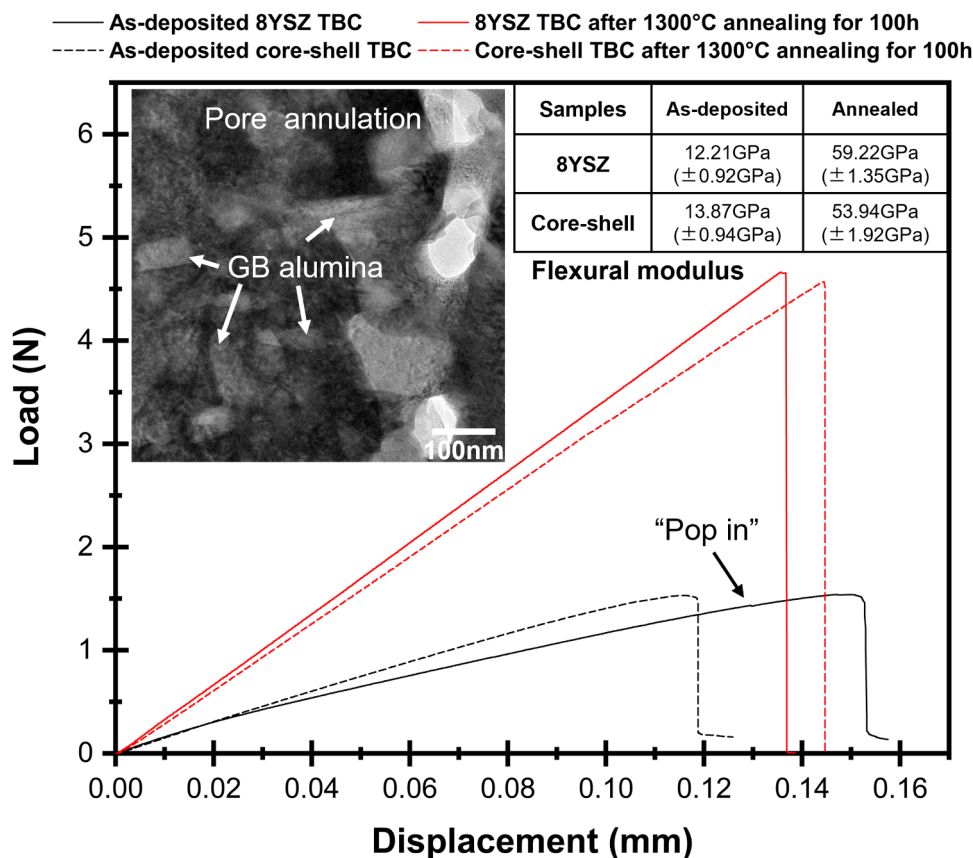


Fig. 9. Load-displacement curve of 8YSZ and core-shell TBCs in the as-deposited condition and after annealing at 1300 °C for 100 h in three-point bending tests. The average flexural modulus determined from all the load-displacement curves is listed at the top right. The inset TEM image at the top left shows the nanoscale at the grain boundaries (GB) of YSZ in the core-shell TBC after annealing at 1300 °C for 5h.

To prove the existence of the ferroelastic toughening mechanism in the core-shell TBC, a thin lamella that contains erosion-induced cracks was prepared from the surface area of the remaining coating (Fig. 11a) and then analysed by TEM. For the coating material away from cracks, straight lattice fringes are observed (Fig. 11b). However, in the region close to the cracks, a high density of Moiré patterns was observed (Fig. 11c) and FFT analysis of this region shows two sets of lattices with same patterns with a slight rotation angle around the $[3\ 1\ 1]$ zone axis (FFT2 in Fig. 11f), which is a characteristic feature of ferroelastic domain switching [25]. In the regions without Moiré pattern, however, FFT analysis shows that there is only one set of lattice, suggesting no lattice rotation. The observation further suggests that the Moiré patterns are caused by the lattice rotation associated with ferroelastic domain switching illustrated by the schematic drawing in Fig. 11. Similar lattice features, such as Moiré patterns, are also observed in the t' -8YSZ TBC next to an erosion induced crack (Fig. 11g and h), confirming the presence of ferroelastic domain switching during crack propagation in the 8YSZ TBC. These TEM observations are consistent with the atomic-scale features associated with domain switching in t' -YSZ coatings [45]. Therefore, on the material aspect, the core-shell TBC shows ferroelastic toughening mechanism similar to that of the 8YSZ TBC, which contributes to its high erosion resistance.

4.8. Microcantilever beam bending tests

Microcantilever beam bending tests were performed to evaluate the fracture toughness of the core-shell TBC in the as-deposited state and after annealing at 1300 °C for 100 h from the material perspective and compare it to that of the 8YSZ TBC. To reveal the intrinsic material fracture resistance, beams were prepared in areas without visible

microstructural defects. Due to the wavy morphologies of the splats, the resulting fracture surface from the microcantilever beam bending test typically contains both the core and the shell regions. Therefore, the fracture toughness determined from the test reflects the average fracture resistance of the core and the shell.

For the as-deposited TBCs, the load-displacement curves in Fig. 12(a) show that both types of the coatings failed in a brittle manner with several pop-in observed during the loading. The core-shell TBC, however, shows a more linear load-displacement than 8YSZ TBC, which is similar to the observations in the three-point bending test. The fracture toughness of the core-shell TBC is determined to be $1.72\text{ MPa}\sqrt{\text{m}}$, which is 31.3 % higher compared to that of the 8YSZ TBC ($1.31\text{ MPa}\sqrt{\text{m}}$). The fracture surfaces of the microcantilever beams show no obvious microstructural defects, which suggests that fracture toughness measured by the microcantilever beam bending test reflects the intrinsic fracture resistance of both the core and shell materials. The higher fracture toughness, together with the lower erosion rate shown in Section 4.7, indicates that the core-shell TBC has stronger resistance to fracture at both the micro and macroscale than the 8YSZ TBC.

The fracture surfaces also shows that the as-deposited 8YSZ coating undergoes a mixed mode of intergranular and transgranular fracture, but the fracture model of the as-deposited core-shell coating is exclusive transgranular (Fig. 12b and c). One possible reason for the transgranular cracking in the core-shell TBC is that the intergranular alumina is in residual compression due to its lower coefficient of thermal expansion than zirconia and this compressive stress prevents cracking from going through the intergranular alumina. The observations suggest that the fracture toughness of the core-shell TBC originates from the fracture resistance of the alumina-alloyed zirconia grains. Since it has been confirmed that the core-shell TBC exhibits a ferroelastic toughening

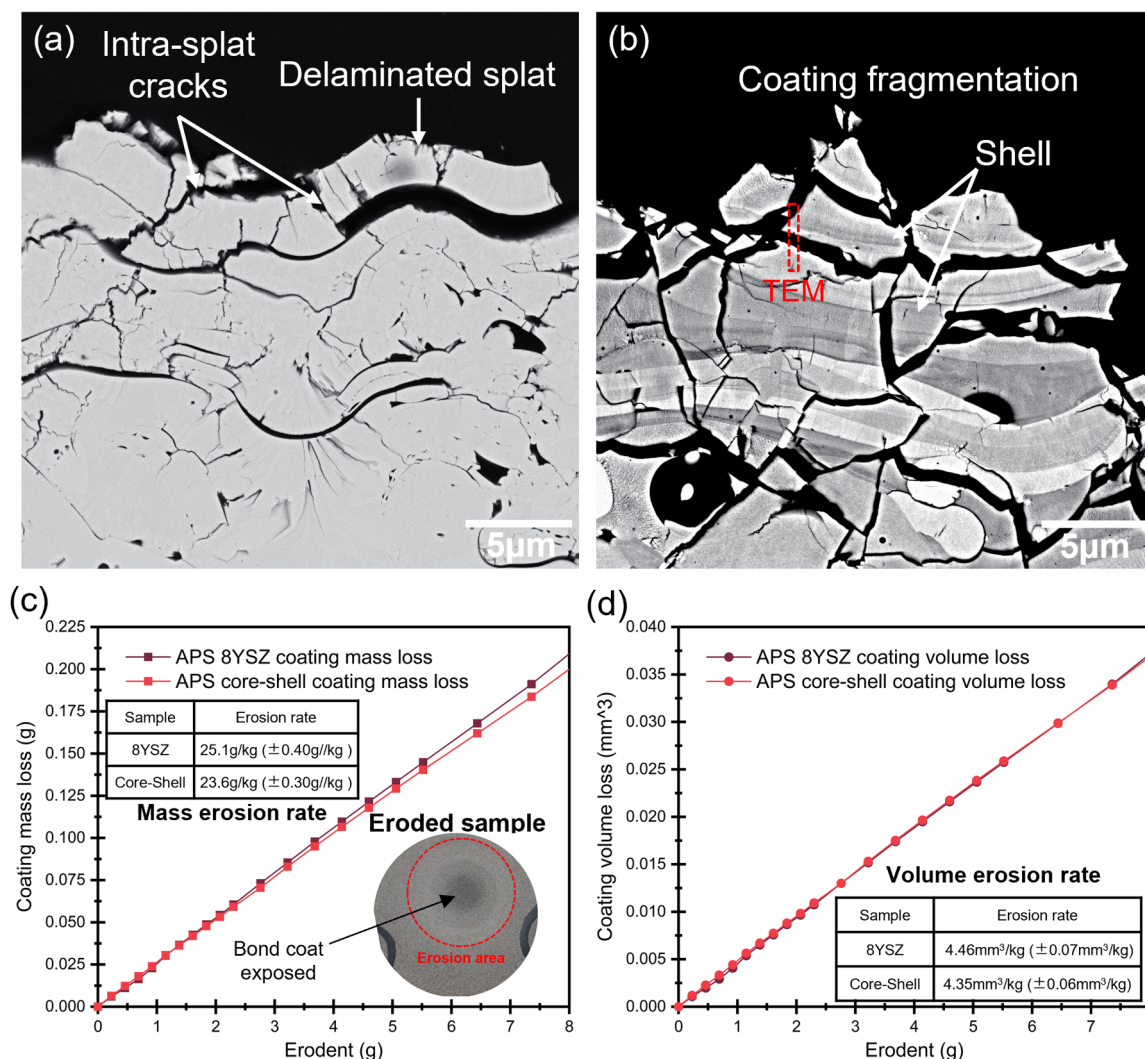


Fig. 10. Analysis of a 8YSZ and core-shell TBCs after the erosion test: (a, b) Cross-sectional BSE images of the erosion front for 8YSZ and core-shell TBCs with cracks and delaminated coating splats caused by erodent; (c, d) Mass and volume based erosion curve for 8YSZ and core-shell TBCs, with inset image showing top view of an eroded button sample and tables listing the erosion rates (ratio of coating material loss and the mass of erodent used).

mechanism in fracture induced by erosion, we hypothesise that the t' -zirconia in the core-shell TBC has a higher tetragonality (c/a ratio) than the t' -phase in the 8YSZ TBC due to the alloying of alumina as solid solution. A higher c/a ratio is capable of accommodating a larger stain and, therefore, results in a higher fracture toughness promoted by domain switching [25,46]. To validate our hypothesis, the c/a ratios of the 8YSZ and core-shell TBCs were determined based on XRD analysis (Figure S 6 in Supplementary Materials). It is found that the c/a ratio of the core-shell coating is 0.3 % larger than that of the 8YSZ TBC, as listed in Figure S 6. The finding confirms our hypothesis and suggests that the increase in the c/a ratio is one of the contributing factors to the higher fracture toughness of the core-shell TBC.

After annealing at 1300 °C for 100 h, the fracture toughness of the 8YSZ and core-shell TBCs increases to 2.07 and 2.03 MPa $\sqrt{m}$, respectively (Fig. 12a). The increase in fracture toughness is primarily attributed to the stiffening of the TBCs, as evidenced by their flexural modulus after annealing (Fig. 9). Nevertheless, the nearly identical fracture toughness of the two TBCs (differing by <2 %) indicates that the core-shell TBC offers the same fracture resistance to the 8YSZ TBC after long-term heat treatment. The fracture surfaces of core-shell TBC microcantilever beams reveal both intergranular and transgranular fracture patterns in the alumina and zirconia grain regions (Fig. 12d), indicating the absence of weak zones that could preferentially guide

crack propagation after the crystallisation of the amorphous alumina.

5. Conclusion

This paper introduces a new core-shell TBC and studies its processing, CMAS and fracture resistance. The core-shell TBC microstructure was successfully manufactured by plasma spraying “YSZ core-alumina shell” powder synthesised through a sol-gel process. However, due to the complete mutual miscibility between alumina and zirconia in the liquid form, there is intermixing between the YSZ core and the alumina shell when they are melted during the APS process. The mixing results in the formation of a gradient microstructure that comprises alumina-alloyed zirconia grains and intergranular alumina, with the overall alumina concentration increasing from the core to the shell. During CMAS attack on the core-shell TBC, both the intergranular alumina and the alumina solute within the zirconia grains reacted with CMAS to form crystallisation products (anorthite and spinel), which sealed the CMAS infiltration pathways (cracks and grain boundaries) and provided strong CMAS resistance for the core-shell TBC. The stiffer, lower-melting alumina reduced the porosity of the core-shell TBC by about 2 %, but causes only a slight increase (1.66 GPa) in elastic modulus compared to the industry benchmark 8YSZ TBC. The alumina in the core-shell TBC also leads to a less-defective intersplat structure and enhances the

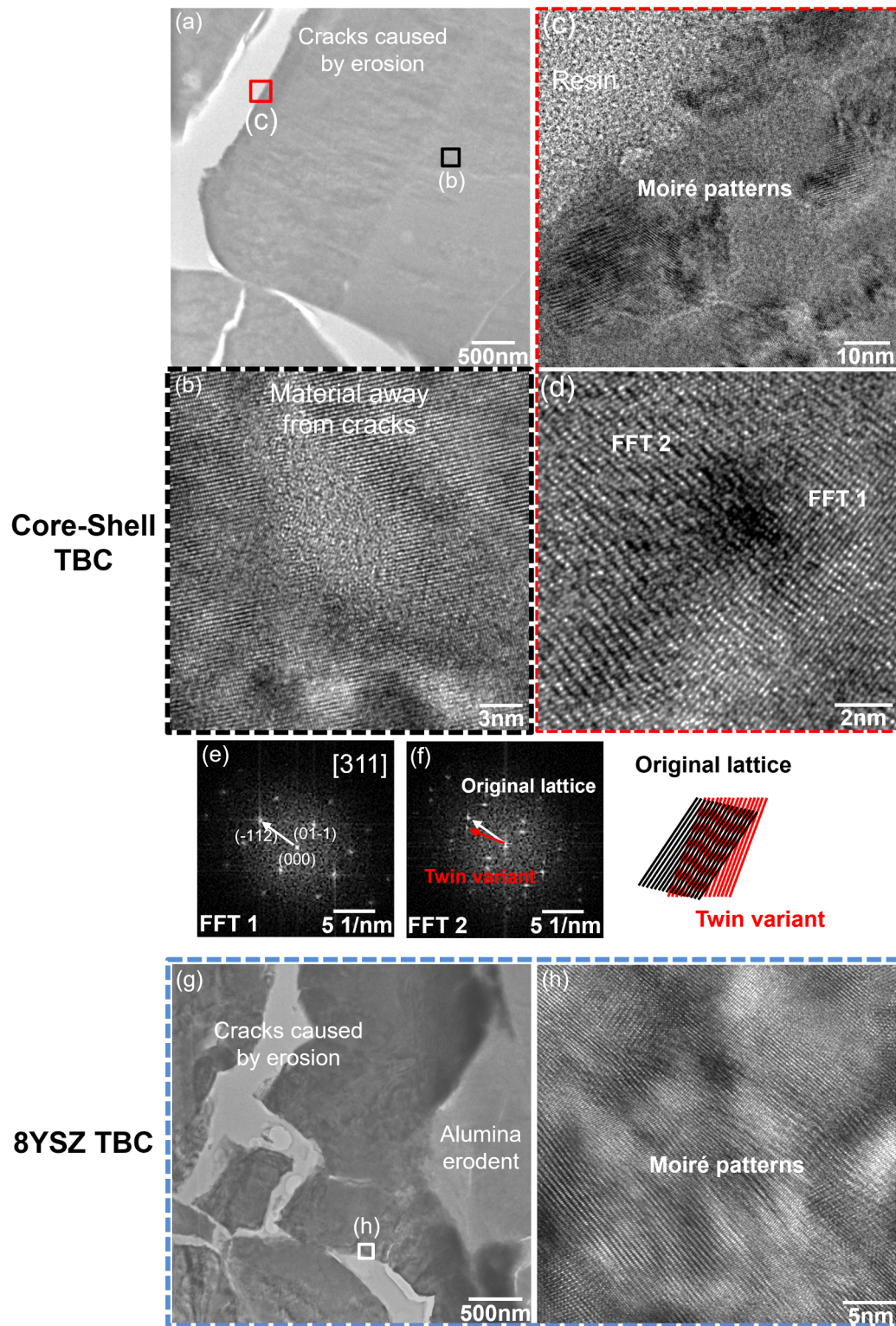


Fig. 11. TEM analysis of the material close to and away from the erosion-induced cracks in a (a-f) core-shell and (g, h) 8YSZ TBC: (a) Overview of the TEM sample containing erosion-induced cracks in the core-shell TBC. The sample was prepared from the area highlighted by red dash rectangle in Fig. 10(b); (b) Bright-field image away from cracks; (c-f) Bright-field images and FFT analysis next to a crack. FFT1 and FFT2 were taken from two typical areas without and with Moiré patterns, respectively. A schematic drawing was also presented to show the lattice rotation associated with the Moiré patterns. (g) Overview of the TEM sample from the erosion front of the 8YSZ TBC, containing embedded alumina erodent and erosion-induced cracks. (h) Bright field image of a region next to the crack.

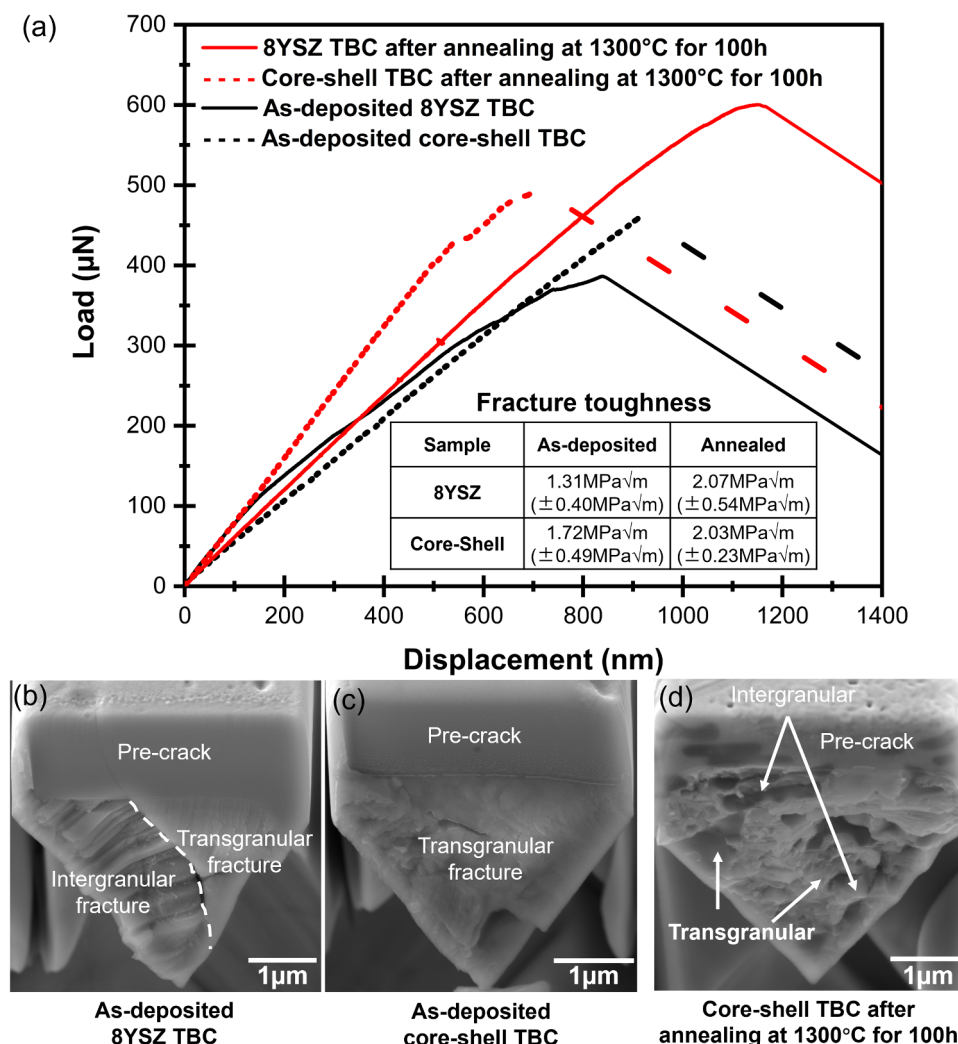


Fig. 12. Microcantilever beam bending test: (a) Load-displacement curves of microcantilever beams prepared from the 8YSZ and core-shell TBCs in the as-deposited condition and after annealing at 1300 °C for 100h. The inset table lists the average fracture toughness of the as-deposited and annealed 8YSZ and core-shell TBCs; (b, c, d) Fracture surfaces of the 8YSZ and core-shell microcantilever beams in the as-deposited condition and after annealing at 1300 °C for 100 h prepared from as-deposited coatings.

ferroelastic toughening strain due to the larger tetragonality in the alumina-alloyed zirconia. This results in improved fracture toughness and greater resistance to particle erosion compared to the 8YSZ TBC. During high temperature exposure, the amorphous alumina at the zirconia grain boundaries in the core-shell TBC crystallised into α -alumina, enhancing the sintering resistance of the coating by slowing grain boundary diffusion. As a result, the core-shell TBC exhibits lower stiffness compared to the 8YSZ TBC after annealing at 1300 °C for 100 h. Meanwhile, the core-shell TBC shows nearly identical fracture toughness to the 8YSZ TBC after annealing. The evidence collectively demonstrates the high potential of the core-shell TBC in mitigating CMAS attack while maintaining its high strain tolerance and fracture resistance during long term thermal exposure.

CRediT authorship contribution statement

Zichen Li: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Gyaneshwara Brewster:** Resources, Methodology. **Luis Isern:** Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Christine Chalk:** Methodology, Investigation, Data curation. **John Nicholls:** Methodology. **Ping Xiao:**

Resources, Project administration. **Xun Zhang:** Methodology, Investigation, Formal analysis. **Ying Chen:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2025.120870](https://doi.org/10.1016/j.actamat.2025.120870).

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A core-shell thermal barrier coating with strong resistance to molten silicate attack and fracture

Li, Zichen; Brewster, Gyaneshwara; Isern, Luis; Chalk, Christine; Nicholls, John R. ...

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