Slurry-based protective coatings for Oxide/Oxide ceramic matrix composites

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In a pilot study zirconia/zircon, and zirconia/yttrium-mono-silicate composite coatings for oxide ceramic matrix composites (Ox-CMC) with highly porous matrices were fabricated by deposition of powder dispersions (‘ slurries’) and subsequent firing. During firing, thermal degradation of Ox-CMC as well as constrained sintering of powder compacts deposited on the rigid CMC substrate are key challenges. The oxidation-related volume expansion of zirconium-disilicide starting powders and reactivity of oxidation products zirconia and silica were used to compensate shrinkage and provide consolidation of powder compacts at process temperatures of 1300°C. Similar processes are commonly referred to as ‘reaction-bonding’. Well-adherent, crack-free reaction-bonded coatings could be fabricated on Whipox-type Ox-CMC. Resulting microstructures are strongly depending on the composition, morphology, and reactivity of constituents, in particular of transient oxide phases. Zirconia/zircon reaction-bonding systems yield composite coatings with relative low porosity whereas as much lower densification capability of the zirconia/yttrium-mono-silicate system was observed.

Key-words : Oxide CMC, Coatings, Reaction-bonding, YSZ, Y2SiO5

1. Introduction

Oxide/Oxide ceramic matrix composites (Ox-CMC) are promising materials for high-temperature applications where substantial mechanical strength, toughness, and damage tolerance are mandatory. The German Aerospace Center (DLR) has introduced an Ox-CMC material on the basis of filament winding which is known under the name WHIPOX (wound highly porous oxide CMC).1,2) Ox-CMC combustor liners for turbine engines have been developed and assessed in a variety of R&D programs3)-6). Ox-CMCs are also used for special components of hypersonic vehicles or spacecraft: Ox-CMC are transparent for electromagnetic waves which makes them ideal for protection for antennas, e.g. used for data transmission. In DLR’s hypersonic/re-entry SHEFEX missions (sharp edge flight experiment), Ox-CMC shingles and antenna covers were successfully employed as part of the vehicle’s thermal protection system.7) Other applications of Ox-CMC in aeronautics are exhaust cones or mixers of turbine engines. State-of-the-art Ox-CMCs consist of thin, polycrystalline Al2O3 or mullite fibers embedded in porous Al2O3 or mullite-matrices. This concept is commonly referred to as ‘weak matrix composites’ where the significant difference between fiber and matrix modulus is considered a key for the favorable, non-brittle fracture behavior. Despite of their favorable properties, porous matrices are intrinsically prone to degradation in harsh environments. On the one hand, temperature-induced sintering and shrinkage will transform the weak porous into a strong, dense matrix. Additional fiber/matrix sintering and fiber grain growth result in brittle CMC fracture behavior. On the other hand, porous weak matrices are evidently prone to micromechanical degradation such as high-velocity particle impact. Both mechanisms substantially affect stability of Ox-CMC and may impede their application in harsh environments. Consequently, effective protective ceramic coatings for Ox-CMC are prerequisite for many target applications.

Dip-coating or painting are considered attractive and cost-effective methods to fabricate protective ceramic coatings for CMCs. In a relative straightforward manner powder dispersions (‘ slurries’) of coating materials are prepared, applied to the CMC surfaces, dried, and finally consolidated by thermal treatment. The final microstructure of the coating evidently is highly depending on the final consolidation step, i.e. on the ultimate process temperature. Depending on the sintering activity of the respective ceramic coating material, fully dense coatings may require very high process temperatures which may exceed the actual stability limit of the CMC. In the case of highly stable on non-oxide CMC materials relative high coating process temperatures can be tolerated. For example,
mullite/Gd$_2$SiO$_5$ composite coatings could be deposited on $\alpha$-SiC by dip-coating and sintering at 1430 °C.\textsuperscript{8)}

Another example was the dip-coating of C/C composites with Y2SiO5 and sintering in Ar at 1560 °C.\textsuperscript{9)} The situation is much more difficult for porous Ox-CMCs which are typically much more susceptible to thermal overload, resulting not only in matrix densification but also in fiber grain growth and fiber/matrix reactions. In Fig. 1, temperature – time conditions are plotted schematically. A plausible estimate is that serious CMC-damage can be expected from thermal treatment parameters inside the cross-hatched area, while no serious damage is likely to happen in the plain area. Therefore, there is only a limited processing window allowing acceptable consolidation of particle deposits as well as tolerable thermal load of Ox-CMC. A plausible window is inserted in Fig. 1; covering process temperatures between 1200 and 1300 °C for 10 to 1 h, respectively. Since tolerable peak temperatures are relatively low, the use of conventional sintering processes is challenging. Consolidation of ceramic powder compacts normally requires much higher temperatures for sintering and suitable bonding. Very fine ceramic powders, however, frequently exhibit much higher sintering activity and can be consolidated at the envisaged process temperatures, but also produce substantial sintering shrinkage. In the case of particle deposits on a CMC substrate, this shrinkage will inevitably lead to the formation of ‘mud cracks’ after consolidation. This effect becomes even more relevant since the CMC substrate is rigid and sintering of the particle deposit especially at the interface is constrained. Consequently, there is demand for powder deposits which can be consolidated sufficiently under minimal volume change between 1200 and 1300 °C. A potential way to achieve low-temperature processing of oxide ceramics is the so-called ‘reaction-bonding’ process, where non-oxide powders are added to the green powders. During thermal processing in air the oxidation of these particles produces a significant volume expansion which can (partly) compensate the sintering shrinkage in situ [Fig. 2(c)]. Additionally, newly formed, ‘transient’ oxide phases promise ‘pristine’, frequently non-crystalline interfaces with enhanced reactivity and thus improved bonding of particles. The reaction-bonding process was initially developed for the near-net shape processing of ceramic bodies. In the field of oxide ceramics, prominent example is the reaction-bonding of Al$_2$O$_3$ (‘RBAO’).\textsuperscript{10)} The RBAO process involves the use of Al$_2$O$_3$ powders which are blended with Al-metal powders as volume expanding component. Depending on the thermal treatment, intermediate Al-melts also contribute to good bonding of particles. The RBAO process could be adapted successfully for coating of Al$_2$O$_3$-based Ox-CMC with Al$_2$O$_3$.\textsuperscript{11)} Although the process temperature was limited to 1300 °C, a good particle/particle as well as coating/substrate bonding was achieved. Although RBAO has been considered a versatile coating material for Ox-CMC, it is plausible that specific target applications will require alternative coating concepts. For instance, the use of Ox-CMC in highly aggressive combustion environments calls for coatings providing protection against corrosive combustion products as well as excessive temperatures. Such coatings are commonly referred to as environmental barrier coatings (EBC). In previous studies a variety of oxide materials have been screened as potential EBC for CMC. It turned out that several compounds of ZrO$_2$, Y$_2$O$_3$, and SiO$_2$ exhibit promising stability against hydroxylation and subsequent volatilization in H$_2$O-rich combustion atmosphere. Among them, Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) and Yttrium-monosilicate (Y$_2$SiO$_5$) showed good corrosion resistance.\textsuperscript{12)–14)} Therefore, such coatings are considered...
attractive EBC for Ox-CMC. For particle loaded environments high toughness YSZ coatings with good erosion resistance are considered highly attractive. Preliminary work, however, revealed that slurry-based fabrication of such coatings on Ox-CMC is challenging if only oxide powders are employed as starting materials. State-of-the-art YSZ powders could be deposited on Ox-CMC and consolidated at 1300 °C, but high sintering-related shrinkage led to crack formation and spallation. Consolidation of Y₂SiO₅ powder deposits turned out to be impossible due to very low diffusivity and related sintering activity. These observations led to the assumption that only reactive processes such as reaction-bonding using non-oxide starting materials will enable processing of slurry-based coatings in the ZrO₂–YO₁.₅–SiO₂ system at viable process conditions.

A model reaction-bonding process was demonstrated by the German Research Center Karlsruhe (now KIT) in order to fabricate net-shape Zircon ceramics (ZrSiO₄). This process takes advantage of the oxidation of zirconium-disilicide ZrSi₂, providing both significant volume expansion and transient ZrO₂ and SiO₂ as reactive components. Further adding of ZrO₂ yields a stoichiometric, near-net shape transformation to ZrSiO₄ ceramics. These results were the motivation to explore ZrSi₂ as non-oxide starting material for the fabrication of slurry-based, reaction-bonded coatings for Ox-CMCs. In this pilot study two types of materials in the system ZrO₂–YO₁.₅–SiO₂ were evaluated as protective coatings for Al₂O₃-based Ox-CMC.

2. Experimental procedure

Staring materials for reaction-bonding were fully stabilized YSZ powders (TZ 8Y, Tosoh, Japan, grain size 0.2 μm), Y₂O₃ powders (99.9 %, H.C. Starck, Germany, grain size 0.2 μm) and ZrSi₂ powders. (ABCR, Germany, grain size approximately 100 μm) Whereas YSZ and Y₂O₃ powders were used in the as received form, ZrSi₂ powders were pre-treated in isopropanol in a ball mill (Pulverisette 7 premium line, Fritsch, Germany) using Si₃N₄ jars and ZrO₂ milling media (YTZ, Tosoh, Japan). Ball-milled ZrSi₂ exhibited grain sizes of approximalety 1–3 μm. Reaction-bonding powder slurries with a solid content of 30 wt % were also homogenized by high-energy ball milling using isopropanol as dispersant and of 2 wt % polyethylene-glycol (PEG 1500, Aldrich, Germany) as processing aid. Whispox-type Al₂O₃/Al₂O₃ CMC fabricated at DLR were employed as substrate materials. Before coating the surfaces were ground and polished by means of 320 grit SiC paper. Green powder deposits were fabricated by means of ‘painting’ the CMC surface with the slurries with a conventional hairbrush, dried, and fired in a box furnace (Nabertherm, Germany). The oxidation behavior of ZrSi₂-containing mixtures was analyzed by thermogravimetry (STA 409 F3 Jupiter, Netzsch, Germany). Phase formation during oxidation and reaction-bonding was monitored in situ by X-ray powder diffraction (XRD; D8 Advance Bruker AXS, Germany) using a high-temperature stage with Pt-strip heating (HTK 1600 N, Anton Paar, Austria). Volumetric effects were analyzed on powder compacts in an optical dilatometer (L74/HS/1600, Linseis, Germany). Analyses were performed under similar conditions (air atmosphere, heating rate 10 K/min, Tₘᵡᵦ = 1300 °C, dwell time 60 min). Microstructural analyses were performed by scanning electron microscopy (Ultra 55, Zeiss, Germany) combined with energy-dispersive spectroscopy (EDS; Aztec, Oxford Instruments, United Kingdom).

3. Results and discussion

3.1 Oxidation behavior of ZrSi₂ powders

The envisaged reaction-bonding process on the basis of ZrSi₂ is controlled by oxidation kinetics and morphology of primary oxidation products ZrO₂ and SiO₂. By means of thermogravimetric analysis (TGA) the oxidation of pre-milled ZrO₂ mixed with starting YSZ powders (10/90 wt %) was studied (Fig. 3). The TGA plot indicates a significant weight gain starting at approximately 550 °C (mark #1), a region of strong weight gain between about 600 and 800 °C where the major part of oxidation is occurring. The TGA curve, in particular the relative sharp discontinuity above 850 °C, does apparently not display the typical linear-parabolic behavior of many materials which develop an oxide scale acting as ‘protective’ diffusion barrier for oxygen. Moreover, the TGA curve shows no evidence for stepwise, i.e. decoupled oxidation of components Zr and Si. It can thus be concluded, that the oxidation of ZrSi₂ produces a significantly different morphology e.g. compared to pure Si. The SEM analysis of a similar ZrSi₂/ ZrO₂ powder compact quenched from 1100 °C revealed the characteristic morphology of fully oxidized ZrSi₂ particles (Fig. 4). In contrast to most single-component materials, ZrSi₂ is forming some kind of ‘nanocomposite’ upon oxidation. Large, former ZrSi₂ particles now have transformed into particles consisting of light-contrasted nano-scaled, globular grains which are fully embedded in a gray-contrasted matrix. Qualitative EDS analyses suggest that the ‘matrix’ consists of pure SiO₂ whereas nanoparticles are
pure ZrO2. The morphology of the nanocomposites gives no evidence for growing oxide scales impeding oxygen transport, which explains the observed high oxidation rate at relative low temperatures. In this intermediate stage of reaction no substantial formation of ZrSiO4 has occurred, therefore SiO2 is still available as reactive constituent.

3.2 Reaction-bonding of ZrO2/ZrSiO4 composite coatings

In a first case study the potential of reaction-bonded ZrO2/ZrSiO4 (RBZ/ZS) was evaluated with respect to fundamental aspects such as phase formation, volume effects and microstructural evolution of coated Ox-CMC. Owing to the high molar volume expansion of about 157% which is expected during the oxidation of ZrSi2 [theoretical balance after stoichiometric reaction: ZrSi2 (ρ=4.9; ≈30 cm3/mol) → ZrO2 (ρ=6.0; ≈20 cm3/mol) + 2 SiO2 (ρ=2.2; ≈27 cm3/mol)], the composition of powder mixtures was set to 10 wt% ZrSi2 and 90 wt% YSZ. With respect to an expected thermal expansion mismatch between CMC and coating, a beneficial effect of the composite coating material was considered as well: combining the higher CTE of cubic YSZ (≈11 ppm/K) and the lower bulk CTE of ZrSiO4 (≈5 ppm/K), the theoretical bulk CTE of the final phase mixture (≈77/33 wt% or ≈70/30 vol% YSZ/ZrSiO4) is calculated to be ≈9 ppm/K, matching well the CTE of Al2O3-CMC. According to the estimated thermal stability of CMC (see above), all experiments were performed at 1300 °C and dwell times of one hour. Taking into account the rapid oxidation of ZrSi2 (see Fig. 3), the phase formation was analyzed in situ by means of high-temperature XRD. A helpful representation for phase transformations or reactions is obtained if XRD data is plotted as ‘plane’ or ‘Z-view’ where heating ramp and dwell time can be displayed simultaneously (Fig. 5). In this style of representation XRD peaks now appear as streaks, while their brightness is correlated to peak height, i.e. diffraction intensities. The HT-XRD clearly shows that the streaks related to ZrSi2 fade out above 600 °C and eventually disappear above 850 °C. On the other hand, new streaks are clearly observed after 15 min at 1300 °C (arrows). Considering the peak shift due to thermal expansion, the XRD reflections can be attributed to newly formed ZrSiO4. In the region between 850 and 1300 °C neither ZrSi2 nor ZrSiO4 is observed. Although oxidation-derived SiO2 is present as amorphous phase unless there is no crystallization of ZrSiO4. Since all volumetric effects play a crucial role for successful processing of envisaged reaction-bonded CMC coatings, the same powder mixture was used to prepare a 5 mm cylindrical powder compact by uniaxial pressing. This sample was analyzed in a heating microscope/optical dilatometer (Fig. 6). Note that data reflect reaction-related volume effects as well as thermal expansion of constituents. A significant, reaction-related volume expansion is starting at about 550 °C (1). The major part of the volume expansion is observed between 650 and 850 °C (2) where the sample expands by about 30 vol%. Above 850 °C the dilatometer curve flattens out significantly. The onset of a second major volume effect is at about 1100 °C (3) where the sample starts to shrink rapidly. Shrinkage slows down after reaching the 1300 °C dwell temperature and comes to an end abruptly after a few minutes at 1300 °C (4). All observed volume effects must evidently be reflected and supported by results from the other experimental methods. The initial expansion phase starting at 550 °C is undoubtedly reflecting the weight gain of oxidizing ZrSi2. At first glance, the 30% volume expansion is much higher than expected: 10 wt% ZrSi2 present in the starting powder theoretically yield an expansion of only about 5%. A plausible explanation is the packing of powders: a significant proportion of small ZrO2 grains are filling small voids between larger ZrSi2...
grains. This leads to a continuous ‘skeleton’ of ZrSi₂ grains which can contribute to the expansion disproportionately, resulting in a veritable ‘inflation’ of the sample. The region with relative low expansion between 850 and 1100 °C can be explained by some residual oxidation and thermal expansion of constituents. The strong shrinkage above 1100 °C is explained by the very high sintering activity of employed 8-mol% Y₂O₃ stabilized YSZ particles which normally can be fully densified at temperatures as low as 1300 °C. A second effect contributing to the strong shrinkage is the decreasing viscosity of newly formed non-crystalline SiO₂ which can promote sintering efficiently. There is an obvious correlation between the formation of ZrSiO₄ detected by XRD and the quasi arrested sample shrinkage after a few minutes at 1300 °C: the crystallization of ZrSiO₄ is consuming amorphous SiO₂ which is consequently less available for viscous phase sintering. With respect to the total volume balance the about 15% volume loss during reaction of amorphous SiO₂ and ZrO₂ to ZrSiO₄ [theoretical balance ZrO₂ (ρ≈6.0; ≈20 cm³/mol) + SiO₂ (ρ≈2.2; ≈27 cm³/mol) → ZrSiO₄ (ρ≈4.7; ≈40 cm³/mol)] is considered less relevant.

For the fabrication of RBZ/ZS coatings on Ox-CMC, an isopropanole-based slurry with a solid content of 30 wt% was prepared and applied to the substrate by a hairbrush. It turned out that slurry deposition on the highly porous ‘filter’-like CMC substrate requires relative low solid content in order to avoid excessive drying and subsequent cracking of freshly formed green powder deposits.

**Figure 7** shows the microstructure of RBZ/ZS coated Ox-CMC after one hour processing at 1300 °C. The SEM overview (a) shows the conformal deposition of a crack-free and well-adherent reaction-bonded ZrO₂/ZrSiO₄ composite coating. Higher magnification (b) reveals the overall higher coating density as compared to the highly porous Al₂O₃-CMC matrix. Nonetheless, there exists still significant coating porosity. The resulting lower stiffness may explain the absence of vertical ‘mud’-type cracks although the bulk coating material exhibits significant shrinkage. Some large particulate features (arrows) represent incompletely transformed ZrSi₂ particles, i.e. still co-existing ZrO₂/SiO₂ ‘nanocomposites’. It can be concluded from the results that the RBZ/ZS process can be performed successfully in a temperature/time window not exceeding the stability limits for Ox-CMC. Optimization is...
clearly possible with respect to employed ZrSi2 starting powders where smaller grains and a narrow size distribution promise enhanced reactivity as well as more homogeneous microstructures. The currently selected starting materials produce a net volume loss, but also a high volume change over the course of the entire process. Overall volume effects can be balanced and adjusted to a certain extent by adapted starting compositions; however, significant de-coupling of expansion and shrinkage is system intrinsic. Nonetheless, the basically crack-free microstructures indicate sufficient tolerance of this coating process against volume effects.

3.3 Reaction-bonding of ZrO2/Y2SiO5 (RBZ/YS) composite coatings

An analogous, second case study was performed in order to explore the potential of reaction-bonded ZrO2/Y2SiO5 (RBZ/YS) with respect to the identical fundamental properties such as phase formation, volume effects and microstructural evolution. In this concept, ZrSi2 oxidation derived SiO2 was envisaged to act as reactive constituent for the formation of Y2SiO5, finally resulting in a ZrO2–Y2SiO5 composite material. In order to obtain a fully crystalline, binary reaction-bonded system, the starting powder mixture was adjusted to a stochiometric consumption of Si by Y2SiO5 following the reaction ZrSi2 + 3O2 + 2 Y2O3 → ZrO2 + 2Y2SiO5. Also the HT-XRD of the RBZ/YS system (Fig. 8) displays ZrSi2 streaks fading out above 600 °C and disappearing above 850 °C. In contrast to the RBZ/YS system, new streaks are clearly observed in the RBZ/YS system only at about 1200 °C (arrows). These XRD reflections are definitively indicative for the direct formation of Y2SiO5. An accelerated formation of Y2SiO5 is evident above 1250 °C. Similar to the observation in the RBZ/YS system, the RBZ/YS system also exhibits a region where neither ZrSi2 nor Y2SiO5 are detectable by XRD, i.e. a substantial amount of non-crystalline SiO2 is presumably present. However, the temperature interval from 850 to 1200 °C is significantly smaller. Again, oxidation-derived nano-scaled ZrO2 is expected to co-exist in this region (see above). Note that in the present powder mixture, ZrO2 XRD reflections are hardly detectable due to co-existing Y2O3 XRD reflections across all reaction stages. The volumetric effects during reaction-bonding of Y2O3/ZrSi2 powder compacts are displayed in Fig. 9. Again, significant volume expansion associated with ZrSi2 oxidation is starting at about 550 °C (Fig. 9; 1). Also in the RB/YS system the volume expansion is taking place predominantly between 650 and 850 °C (2) where the dilatometer curve starts to flatten out. The onset of sample shrinkage is at about 1200 °C (3), i.e. later than in the RBZ/YS system (see Fig. 6). The end point of sample shrinkage, however, is reached substantially faster in the present RBZYS system: after reaching about 1300 °C densification abruptly stops (4). With respect to oxidation-related volume effects, the RBZ/YS system obviously behaves similar to the RBZ/YS system. A significantly differing behavior is observed in the sintering/shrinkage region. Firstly, the total net shrinkage is evidently much lower, although the bulk starting composition (24.6 wt % ZrSi2/75.4 wt % Y2O3) a priori provides a much higher amount of oxidation-derived SiO2 acting as aid for viscous sintering. Therefore, a first plausible reason for the lower shrinkage is the well-known much lower sintering activity of the Y2O3 component; the lack of highly sintering-active YSZ is reflected by a higher onset temperature for shrinkage. Secondly, the end of shrinkage (4) is obviously correlated to the Y2SiO5 crystallization which starts above 1200 °C and strongly accelerates above 1250 °C (HT-XRD, Fig. 8). As discussed before, Y2SiO5 crystallization is consuming free SiO2, inevitably decreasing viscous phase sintering. Expected volume effects from the formation of Y2SiO3 from Y2O3 and amorphous SiO2.
result in only limited volume loss of about 10% (theoretical balance $Y_2O_3$ ($\rho \approx 5.0$; $\approx 44 \text{ cm}^3/\text{mol}$) + $SiO_2$ ($\rho \approx 2.2$; $\approx 27 \text{ cm}^3/\text{mol}$) $\rightarrow$ $Y_2SiO_5$ ($\rho \approx 4.4$; $\approx 65 \text{ cm}^3/\text{mol}$)). As a consequence, total sintering/densification remain much lower in the RBZ/YS system. RBZ/YS coatings were deposited on $Al_2O_3$-based Ox-CMC in the same procedure as described above. With respect to thermal expansion mismatch between CMC and coating, again a beneficial effect of the composite material comes into play: combining the higher CTE of cubic YSZ ($\approx 11 \text{ ppm/K}$) and the lower bulk CTE of monoclinic $Y_2SiO_5$ ($\approx 7 \text{ ppm/K}$), the theoretical bulk CTE of the final 1:2 phase mixture is calculated to $\approx 8.3 \text{ ppm/K}$, again matching the CTE of $Al_2O_3$-CMC reasonably well. Figure 10 shows the microstructure of RBZ/YS coated Ox-CMC after one hour processing at 1300 °C. The SEM overview (a) shows the same conformal, crack-free and well-adherent morphology of the reaction-bonded $ZrO_2/Y_2SiO_5$ composite coating. High-magnification (b) reveals the overall much higher coating porosity in combination with very small grain sizes and few distinct voids. Again, the presence of a few larger features may indicate residual $ZrO_2/ SiO_2$ ‘nano-composites’, however the progress of the reaction is seemingly higher. The resulting microstructure is well reflecting the specific properties of used starting powders and reaction products. Basically the RBZ/YS process can be performed successfully in the required temperature/time window not exceeding the stability limits for Ox-CMC. As discussed above, optimization is clearly possible by using $ZrSi_2$ starting powders with small grains and narrow size distribution. The low sintering activity of $Y_2O_3$ as well as the early formation of $Y_2SiO_5$ (with low sintering activity) inevitably lead to much less densification potential, as can easily be seen in Fig. 9 where currently employed starting materials exhibit a much smaller sintering window and thus produce a net volume gain. On the other hand, the low overall volume change is considered advantageous for the coating process in terms of less danger of mud-crack formation.

4. Conclusions

Reaction-bonding processes using YSZ, $Y_2O_3$, and $ZrSi_2$ as reactive component are promising for the fabrication of protective coatings for Ox-CMC. Slurries can easily be prepared and deposited on substrate surfaces by means of cost-effective painting methods such as hair- or airbrushing. The key advantage of reaction-bonding is processing at moderate temperatures not exceeding the typical 1300 °C stability limit of standard Ox-CMC. Thermal treatment of two model composition yielded crystalline composite coatings consisting of YSZ/$ZrSiO_4$ or YSZ/$Y_2SiO_5$, respectively. Coating morphologies are strongly influenced by starting powders and the target phase composition. Overall volume effects can be balanced and adjusted to a certain extent by stoichiometry, however, significant de-coupling of oxidation-related volume expansion and subsequent sintering shrinkage is system intrinsic. Nonetheless, crack-free coating microstructures indicate sufficient robustness of the process. The variability of the process offers many ways to adapt coating processing and resulting properties to specific CMC substrates as well as target applications. In particular the use of $ZrSi_2$ starting powders with specifically designed particles is considered a key for advanced processing.
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