Environmental protection of Nb/Nb₅Si₃-based alloys by E/TBC systems

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ABSTRACT:

Environmental/thermal barrier coatings (E/TBCs) were applied on an Nb/Nb₅Si₃-based alloy. The substrate material with the nominal composition Nb-23Ti-4Hf-3Cr-6Al-20Si (at.%) was manufactured by plasma melting. Rectangular platelets of this alloy were coated with chromia-silica forming M₇Si₆-based (M = Ti, Nb, Cr, X with X = Ni, Co, Fe) bond coats produced by pack cementation. The Co- and Fe-modified M₇Si₆-based layers also contained boron. On these grit blasted bond coats, ceramic topcoats of 7 wt.% yttria partially stabilised zirconia (YSZ) and gadolinium zirconate (GZO) were deposited using electron-beam physical vapour deposition. The E/TBC systems were thermally cycled at 1100°C and 1200°C in laboratory air (1 h at high temperature, 10 minutes at ambient temperature). Cross-sectional examinations of the samples after cyclic testing were carried out using scanning electron microscopy to study the protection capability of the E/TBC systems and failure mechanisms.

The lifetimes of the E/TBC systems exceeded the maximum exposure period of 1000 cycles at 1100°C. When cyclically tested at 1200°C, the samples with Ni-modified and boron containing Co-modified M₇Si₆-based bond coats failed within 700 cycles. Failure was caused by spallation of thick oxides scales thermally grown on the substrate after degradation of the bond coats. The E/TBC systems with boron containing Fe-modified M₇Si₆-based bond coats exhibited lifetimes approaching 1000 cycles at 1200°C. For both YSZ and GZO topcoats, chemical reactions with the TGOs were observed.

Introduction

Efficiency and performance of jet engines improve with higher gas inlet temperatures [1]. This increase in operating temperature is now approaching a limit imposed by the temperature capability of the currently used Ni-based superalloys. With melting points above 1750°C, Nb-silicide-based composites are promising candidates for high-temperature applications at temperatures exceeding 1150°C, the upper limit for Ni-based superalloys [1-5]. They possess good fatigue and creep behaviour, good fracture toughness and an approximately 20% lower density compared to that of Ni-based superalloys. These composites exhibit a multiphase microstructure consisting of a metallic Nb solid solution and Nb₃Si and/or Nb₅Si₃ silicides [6]. The volume fraction of the silicides varies between 0.35 and 0.6. A typical composition of such a composite referred to as metal and silicide composite (MASC) is Nb-25Ti-8Hf-2Cr-2Al-16Si [2]. Studying Nb/Nb₅Si₃-based alloys with different chemical compositions, the oxidation resistance was claimed to be enhanced by increasing the silicon and aluminium content and decreasing the Hf and Ti content compared to the MASC composition [7]. An optimised composition of Nb-23Ti-4Hf-2Cr-6Al-20Si (at.%) was proposed. Furthermore, an increase in silicon content is expected to increase the amount of silicide phase concomitant with a reduction in density and an increase in high-temperature strength [8]. For a multi-component Nb-silicide composite manufactured by powder metallurgy, reasonable high-temperature strength and high strength at room temperature were determined [9].

However, the oxidation resistance of Nb/Nb₅Si₃-based alloys is still considered to be inadequate for long-term high temperature exposure due to the formation of the non-protective oxides Nb₂O₅ and TiNb₂O₇ [5]. To improve the oxidation behaviour protective coatings are probably necessary to exploit the potential temperature capability of Nb-silicide-based composites [3,10]. For niobium alloys, coatings of complex (TiNbXCr)₇Si₆ (X = Ni, Co, Fe) silicide phases have been developed, forming duplex scales constituted of chromia and silica [11,12]. These silicide phases, hereinafter referred as M₇Si₆, exhibited high oxidation resistance at temperatures between 1100°C and 1300°C, being effective oxidation protective coatings for Nb-based composites.

The service temperature and/or the lifetime of gas turbine components can also be raised by application of thermal barrier coatings (TBCs) [13,14]. These TBC systems widely applied on Ni-based superalloys consist of a ceramic topcoat, a bond coat and the high temperature substrate material. The bond coat, forming a thin thermally grown oxide (TGO) on top, ensures oxidation protection of the substrate material and adhesion of the TBC. Bond coats used for Ni-based superalloys, MCrAlY (M = Ni and/or Co) and Pt aluminides, are alumina formers [15]. The industrial standard ceramic topcoat is 7 wt.% yttria partially stabilised zirconia (YSZ), exhibiting good adhesion and chemical compatibility with the alumina based TGO [14,15]. The YSZ topcoat can be applied for long-term exposure up to 1200°C [16]. Beyond this temperature YSZ degrades due to phase transformation and sintering. Because Nb/Nb₅Si₃-based alloys are designed to outperform the operating temperatures of Ni-based superalloys (a temperature benefit of ~200°C is expected [3]), TBCs with improved thermal stability are required. Gadolinium zirconate (Gd₂Zr₂O₇, GZO), which exhibits a pyrochlore structure with a thermal stability at temperatures exceeding 1500°C, is a promising candidate with higher temperature capability [14,17]. Because oxidation protective coatings for Nb-silicide-based alloys rely on the

formation of silica and silica/chromia scales, the application of GZO as well as YSZ topcoats leads to novel TBC systems with TGOs possibly not compatible with the ceramic topcoats.

In the high-temperature atmosphere of turbine engines with high gas velocities, protective oxide scales and ceramic topcoats can be vulnerable to environmental attack. Water vapour contained in the combustion environment causes volatilisation of chromia and silica by hydroxide formation [18]. Furthermore, the protective coatings can be subjected to chemical attack by calcium-magnesium-alumino-silicate (CMAS) associated with the ingestion of sand, dust and volcanic ashes [19]. Therefore, environmental barrier coatings (EBCs) have to be applied to hamper water vapour corrosion and CMAS attack. The ceramic topcoats deposited on Nb/Nb₅Si₃-based alloys with chromia-silica forming bond coats should provide simultaneously environmental and thermal protection, and, thus, are referred as E/TBCs. Standard YSZ topcoats possess durability in water vapour containing atmospheres as proven by its successfully application on gas turbine components [18,20]. But the resistance of YSZ against CMAS attack is rather poor; higher CMAS resistance was reported for GZO [19,21].

In previous studies, we investigated the performance of YSZ and GZO topcoats deposited on MASC coupons with various M₇Si₆-based bond coats [22]. The promising results obtained encouraged further optimisation of the bond coat manufacturing process, in particular that of boron containing Fe-modified M₇Si₆-based coating. With this bond coat, enhanced lifetimes of E/TBC systems with YSZ, GZO and combined Y₂SiO₅ + GZO topcoats were determined [23]. However, substantial material recession was observed with prolonged furnace cycling testing. Local degradation of the protective coatings caused severe oxidation of the MASC substrate, whereas no significant spallation of the ceramic topcoats was observed. Therefore, the potential capability of the E/TBC systems deposited on Nb-based composites was not finally demonstrated because testing was terminated due to poor oxidation resistance of the substrate material used. In the present work, the performance of E/TBC systems applied on an Nb/Nb₅Si₃-based alloy with adjusted chemical composition was investigated, assuming improved oxidation behaviour. The YSZ and GZO topcoats were produced using electron-beam physical vapour deposition (EB-PVD). The ceramic topcoats were deposited on coupons coated with M₇Si₆-based bond coats with and without boron addition manufactured by pack cementation. The lifetime of the E/TBC systems was determined performing thermal cycling tests in a temperature range that allows comparison with existing systems, i.e. at 1100°C and 1200°C in air. After high temperature exposure of the coated samples, thorough cross-sectional examinations were carried out to study the compatibility of the ceramic topcoats with the thermally grown oxides. Microstructural analyses of the E/TBC system with a combined Y₂SiO₅ + GZO topcoat applied on MASC samples indicated interfacial reactions [23]. Therefore, in the present work, microstructural investigations focused on chemical reactions between TGO and the ceramic topcoats.

EXPERIMENTAL

A button weighing about 1 kg of an Nb/Nb₅Si₃-based alloy with the nominal composition of Nb-23Ti-4Hf-3Cr-6Al-20Si (at.%) was produced by plasma melting.

The microstructure of the as-cast alloy was composed of niobium solid solution (Nb,Ti)_{ss} and the silicides γ -Nb₅Si₃ (D8₈ structure) and β -Nb₅Si₃ (D8_m structure), the latter changing to α -Nb₅Si₃ (stable D8_i structure) after the heat treatments performed for the bond coat deposition, as well as HfO₂ [7-9]. From these buttons 2.5 mm thick rectangular platelets with 15 mm × 10 mm in size were machined. The specimens were all-side coated with Ni-modified and boron containing Co- and Fe-modified M₇Si₆-based oxidation protective layers using halide activated pack cementation. The thickness of the coatings was about 100 μ m. Details of the manufacturing process are given elsewhere [11,24]. With the boron containing Co- and Fe-modified M₇Si₆-based coatings, boron was introduced into the subsurface of the silicide layers in a second pack cementation step. Microstructural characterisations of the as-deposited coatings have been reported in [24]. According to their nickel, cobalt or iron modification and the addition of boron the protective layers are noted hereafter Ni-M₇Si₆-, B+Co-M₇Si₆-, and B+Fe-M₇Si₆-based bond coats.

E/TBCs of YSZ and GZO were deposited on the rectangular platelets with the different bond coats using EB-PVD. Their thickness ranged from 150 to 180 μ m. The ceramic topcoats were deposited only on about 80-90% of the front side of the specimens because of the sample holder geometry. No E/TBC was on the rear side. Prior to E/TBC deposition the bond coats were grit blasted to reduce the surface roughness using white aluminium oxide with a particle size of 63 – 90 μ m. The arithmetical mean roughness R_a of the smoothed surfaces was 3.28 μ m. After deposition the ceramic topcoats were tightly-adherent to the bond coats (Figure 1). Despite previous grit blasting, appreciable surface roughness of the bond coat remained, visible in Figure 1 due to replication of the surface morphology by the EB-PVD process.

The lifetime of the E/TBC systems was determined performing furnace cycling tests at 1100°C and 1200°C in laboratory air. Using automated rigs, the specimens were placed in a hot furnace for one hour and then subjected to forced air cooling outside the furnace at ambient temperature for 10 minutes. Spallation of more than 20% of the ceramic topcoat was considered as failure criterion. Post-oxidation cross-sectional analyses were carried out using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

RESULTS

Thermal cycling at 1100°C

Results of thermal cycling testing at 1100°C are illustrated in Figure 2 (it has to be noted that the data mostly present results from single sample testing; due to shortage in the substrate material, only for a few E/TBC systems duplicate specimens were tested). The samples with YSZ topcoat exhibited lifetimes exceeding 1000 cycles, the maximum testing period, independent upon the bond coat applied. No spallation of the E/TBC was observed. However, mass loss occurred at areas without ceramic topcoat, particularly at the corners (Figure 3a). The samples with GZO topcoat were also tested for up to 1000 cycles. One of the samples with Ni-M₇Si₆-based bond coat failed after the maximum exposure period. Furthermore, substantial material recession was observed with the sample with B+Fe-M₇Si₆-based bond coat (Figure 3b). This damage was initiated at corners and edges of the sample probably by

thermal stresses causing localised degradation of the bond coat. Large oxide nodules formed there. After their spallation subsequent break-away oxidation of the substrate resulted in material recession and chipping of the E/TBC at the rims [23]. Nevertheless, the E/TBC system was intact, except edge chipping caused by disintegration of the subjacent substrate material. The deterioration by oxidation is also evidenced by the mass change curves plotted in Figure 4. Whereas an almost parabolic oxide growth rate was observed for the specimens with B+Co-M₇Si₆-based bond coat, oxide spallation caused a decrease in the mass change curves of the other samples, indicating the beginning of material recession (because zirconia exhibits high oxygen permeability [15,17], the YSZ topcoat was not expected to significantly affect the oxidation kinetics of the bond coats applied, what was also assumed for GZO). For the sample with B+Fe-M₇Si₆-based bond coat and GZO topcoat, this mass loss started already after 80 cycles, resulting in substantial material recession after 1000 cycles (Figure 3b).

The results of thermal cycling testing were confirmed by SEM cross-sectional examination of the coated samples. The ceramic topcoats were tightly-adherent to the oxide scales grown on the bond coats after 1000 cycles of exposure to air at 1100°C, as shown in Figure 5 for samples with Ni- and B+Co-M₇Si₆-based bond coats and YSZ topcoat. The oxide scales consisted of a mixture of Ti-, Cr-, and Nb-oxides interspersed with silica. In the oxides grown on the Co-modified bond coat, cobalt was also detected, but no nickel in the oxides on the Ni-modified bond coat. The thickness of the TGO formed on the former bond coat was higher (~30 µm) compared to that on the latter (10-15 µm), as also evidenced by the higher mass gain of the former coating (Figure 4a). Between the TGO and the YSZ topcoat, a thin reaction zone was observed, consisting primarily of titania with about 2 at.% zirconium (Table 1). The latter oxides also filled the fissures and pores in the root area of the YSZ topcoat. On the scales grown on the Ni-M₇Si₆-based bond coat, a thin outermost layer rich in titania formed containing also chromium and niobium up to about 3 at.% each (Figure 5a, Table 1). On the B+Co-M₇Si₆-based bond coat, a mixed Co-, Cr- and Al-rich oxide was also observed in the reaction zone. In addition, oxide particles rich in zirconium and silicon as well as zirconium and yttrium were detected by EDS point analyses (Figure 5b, Table 1). Because the ratios of concentrations (in at.%) of Zr/Si and Zr/Y were approximately 1, the EDS measurements suggested the formation of zircon (ZrSiO₄) and yttrium zirconate (Y₂Zr₂O₇), respectively. Zircon was prevalently found in the fissures of the YSZ root area filled with oxides. The remaining bond coats below the TGOs still protected the substrate material against oxidation. Similar results were found for the sample with the B+Fe-M₇Si₆-based bond coat and YSZ topcoat (Figure 6). The E/TBCs exhibited good adherence to the TGO which was comprised of a mixture of Fe-, Ti-, Cr- and Nb-oxides embedded in silica. The outermost oxides contained high amounts of iron; between TGO and ceramic topcoat a slight reaction occurred resulting in mixed Fe-, Cr-, and Ti-oxides with about 2 at.% Zr (Figure 6b, Table 1). In the reaction zone, yttrium-rich particles were sometimes observed again, possibly yttrium zirconate, as suggested by EDS point analyses.

The GZO topcoats also revealed good adhesion to the oxide scales grown on the Ni-M₇Si₆-based (two samples) and B+Co-M₇Si₆-based (one sample) bond coats after 1000 cycles of exposure at 1100°C (Figure 7). A thin reaction zone was observed between the GZO topcoat and the TGO formed on the B+Co-M₇Si₆-based bond coat (Figure 7b). Besides oxygen, zirconium and gadolinium (from the Gd₂Zr₂O₇ topcoat),

titanium, chromium and cobalt were detected by EDS point analysis of this zone, indicating diffusion of the latter elements into the ceramic topcoat (Table 1). However, the Ni-modified bond coat on the second sample with GZO topcoat was severely degraded and a thick oxide scale formed, causing failure of the E/TBC system after 1000 cycles of exposure at 1100°C by spallation of the oxide layer (Figure 8). SEM examinations revealed also complete oxidation of the bond coat at the rear side without GZO topcoat (not shown); however, the rear side of the second sample with Ni-modified bond coat did not fail after 1000 cycles: only isolated large oxide nodules were found due to localised degradation of the bond coat. The difference in the performance of the oxidation protective layer indicates a variation in the coating quality produced by the applied pack cementation process.

Figure 9a shows the cross-section of an Nb/Nb₅Si₃-based alloy sample with B+Fe-M₇Si₆-based bond coat and GZO topcoat after 1000 cycles of exposure at 1100°C. The gap between the GZO topcoat and the TGO was probably caused by cross-section preparation, which was not optimised for this E/TBC system. These fissures between the ceramic topcoat and the TGO can also be attributed to the lower toughness of the GZO coating compared to the YSZ coating, as reported in the literature [25], reducing the resistance against delamination [26]. However, the E/TBC did not spall off during the maximum exposure period. The thickness of the remaining bond coat was sufficient to protect the substrate material during continued thermal cycling. EDS profiling across the bond coat showed a remaining thickness of about 50 µm (Figure 9b).

Thermal cycling at 1200°C

Figure 10 shows the lifetimes of Nb/Nb₅Si₃-based alloy samples with Ni-, B+Co-, and B+Fe-M₇Si₆-based bond coats as well as YSZ and GZO topcoats which were thermally cycled at 1200°C. The samples with Ni- and boron containing Co-modified bond coats failed after exposure periods ranging from 20 to 700 cycles. The lifetimes of the E/TBC systems with GZO topcoat were shorter than those with YSZ topcoat. For the samples with B+Fe-M₇Si₆-based bond coat, substantial material recession was observed, leading to test termination, although the E/TBC did not spall off at the front side. However, thermal cycling was stopped to perform SEM examinations. One sample with GZO topcoat was tested up to the maximum exposure period of 1000 cycles.

SEM examinations of the failed E/TBC systems with Ni- and B+Co-M₇Si₆-based bond coats revealed severe degradation of the bond coats and partial oxidation of the substrate (Figures 11-13). Between ceramic topcoat and substrate, oxide scales with thickness exceeding 100 µm formed. These oxide layers spalled off, causing failure of the E/TBC system. On the rear side without E/TBC, the bond coats were also severely degraded and oxidation of the substrate occurred. For both bond coats, longer lifetimes were determined for the E/TBC systems with YSZ topcoat in comparison to those with GZO topcoat, particularly evident for the samples with the B+Co-M₇Si₆-based bond coat. In this system, failure might be also associated with spallation of the GZO topcoat due to poor adhesion of the GZO to the TGO (Figure 13). On the samples with the B+Co-M₇Si₆-based bond coat, both ceramic topcoats reacted with the TGOs. After 300 cycles of exposure, ZrSiO₄ formed at the TGO/YSZ interface, as supported by EDS analysis (Figure 12b, Table 2). Zircon also formed in

the inter-columnar gaps in the bottom area of the YSZ topcoat. In the outer layer of the TGO, titanium was predominantly detected, but also chromium, niobium and cobalt. At some areas, EDS analysis suggested the formation of hafnium silicate (HfSiO_4) probably by a reaction between hafnia and silica (Table 2). At the TGO/GZO interface, gadolinium niobate (GdNbO_4) formed even after a short exposure of 33 cycles (Figure 13, Table 2), embedded in a mixture of Cr- and Co-oxides (outermost oxides) as well as Ti- and Nb-oxides (oxides below). Zircon was also found occasionally. In the root area of the GZO topcoat, Ti (8-9 at.%), Cr (~2 at.%), Co (~3 at.%), and Al (~1.5 at.%) were detected.

SEM cross-sectional analyses of the Nb/Nb₅Si₃-based alloy sample with B+Fe-M₇Si₆-based bond coat and YSZ topcoat revealed excellent adhesion of the ceramic topcoat to the TGO after 860 cycles of exposure to air at 1200°C (Figure 14). An about 50 µm thick oxide layer formed which was composed of oxides of titanium, iron, chromium and niobium as well as silica. Chemical reactions occurred at the TGO/YSZ interface. Adjacent to the YSZ topcoat, a thin layer with similar concentrations of yttrium and zirconium formed (Figure 14b, Table 2). According to the chemical composition determined by EDS it might be yttrium zirconate ($\text{Y}_2\text{Zr}_2\text{O}_7$). In addition, Ti, Fe, Cr and Al were detected in this layer. That compound also filled the inter-columnar gaps and pores of the root area of the ceramic topcoat. Beneath the yttrium zirconate layer, particles of ZrSiO_4 were observed, as corroborated by EDS analysis, embedded in outermost Fe- and Ti-rich oxides followed by the outer scale of mixed oxides of Fe, Ti, Cr and Al, the latter in small amounts (Table 2). Approximately half of the bond coat was consumed. Its remaining part protected the substrate against oxidation. At 1200°C, the interdiffusion/reaction zone between ceramic topcoat and TGO was more pronounced in comparison to the samples exposed at 1100°C. Similar results were found for the two samples with GZO topcoat and B+Fe-M₇Si₆-based bond coat (Figure 15). After 1000 cycles of exposure at 1200°C, the bond coat, whose remaining thickness was a little less than half of the as-produced coating, still provided oxidation protection to the substrate (Figure 15b). A thin pore-free dense zone was observed in the lower root area of the GZO topcoat. In this zone, titanium and iron up to ~9 at.% were found by EDS analysis, as well as chromium and aluminium, the latter elements in lower amounts (1-2 at.%, see Table 2). In the outer oxide scale below, Fe, Ti and Cr (each with 10-15 at.%) as well as Al (~1.5 at.%) were detected again.

DISCUSSION

Results obtained in the present work are in agreement with our previous studies of similar E/TBC systems applied on MASC specimens [22,23]. For the latter substrate material, lifetimes determined for E/TBCs of YSZ and GZO also exceeded 1000 cycles at 1100°C. However, severe material recession was observed too, starting from edges and corners of the coupons. At 1200°C, the lifetimes approached 850 cycles for MASC samples with B+Fe-M₇Si₆-based bond coat, whereas specimens with Ni- and Co-modified bond coats failed during 400 cycles of exposure associated with entire degradation of the bond coats. Hence, the performance of E/TBC systems on MASC substrate material was similar to that found in this work for the Nb/Nb₅Si₃-based alloy with increased Si and Al content. At areas with damaged bond coats, severe oxidation of the latter alloy occurred during long-term exposure, indicating poor oxidation resistance similar to that of the MASC substrate material. The expected improved oxidation behaviour of the Nb/Nb₅Si₃-based alloy with adjusted

chemical composition was not confirmed; and, therefore, due to substantial material recession, thermal cycling tests of the E/TBC systems with B+Fe-M₇Si₆-based bond coat were terminated at 1200°C before significant spallation of the ceramic topcoats occurred. Focusing on the failure of the ceramic topcoats on the front side of the samples far from the edges, the lifetimes of the E/TBC systems applied on Nb/Nb₅Si₃-based alloys with B+Fe-M₇Si₆-based bond coats were similar to those for YSZ TBCs on Ni-based superalloys with alumina forming bond coats, as discussed in our previous paper [23]. Due to shortage in substrate material, only single specimen was mainly tested for the different E/TBC systems in the previous as well as present investigations. Thus, the overall results obtained from these thermal cycling tests enhance the significance of the lifetime data determined.

Oxidation protection by the bond coats

The rather poor oxidation behaviour of Nb/Nb-silicide based alloys forming oxides with low spallation resistance is a challenge for a successful application of these ultra-high temperature materials. This most likely requires effective protective coatings of high quality avoiding localised degradation. However, edges and corners of components often turned out to be weak points for brittle coatings leading to their rapid degradation. MoSi₂ coatings deposited on Mo-9Si-18B alloys by pack cementation were found to be always cracked at corners and edges of the specimens with cracks reaching the substrate [27]. Similar results were observed for a MoSi₂ coating produced by pack siliconizing of rectangular pure Mo specimens, revealing discontinuity at the sample's edges which caused severe oxidation of the substrate [28]. This degradation of MoSi₂ was attributed to micro-cracks nucleating at corners and edges because of locally high thermal stresses [29]. A similar mechanism is probably operating in the M₇Si₆-based coatings applied on Nb/Nb₅Si₃-based alloys. A coefficient of thermal expansion (CTE) of $10.5 \times 10^{-6} \text{ K}^{-1}$ was measured for MASC substrate material [2], and CTE values of $(12-15) \times 10^{-6} \text{ K}^{-1}$ were determined for M₇Si₆ compounds [30,31]. At corners and edges of the Nb/Nb₅Si₃-based alloy samples, this CTE mismatch, concomitant with high brittleness of the coatings [30], might cause initiation of cracks propagating to the substrate.

The three M₇Si₆-based bond coats used provided effective oxidation protection to the Nb/Nb₅Si₃-based alloy at 1100°C. During exposure to air at 1100°C and 1200°C, these coatings developed protective scales mainly composed of chromia and silica, but containing small amounts of other oxides [11]. At 1200°C, the Ni- and Co-modified bond coats entirely degraded within 700 cycles of exposure, whereas the B+Fe-M₇Si₆-based bond coat revealed a considerable remaining thickness after 1000 cycles (Figures 14 and 15). In the latter coating, (Cr_x,Fe_{1-x})₂O₃ formed, reducing the volatilisation of CrO₃ above 1000°C [12]. Boron introduced into the coating formed borides in the subsurface, providing self-healing capacity with regard to cracks initiated in the oxide scale [24]. Therefore, the B+Fe-M₇Si₆-based bond coat exhibits great potential to be applied in E/TBC systems on Nb/Nb₅Si₃-based alloys.

Ceramic topcoats on silica/chromia forming bond coats

To our knowledge, only one further study of thermal barrier coatings deposited on Nb/Nb₅Si₃-based alloys has been published in the literature [3,32]. In the latter work, a TBC of yttria stabilised zirconia was deposited on Nb silicide composites by air

plasma spraying. The bond coat used was a silicide layer with a thickness of approximately 100 μm . This TBC system was tested at 870, 1200 and 1370°C in air under cyclic conditions (1h at high temperature, 10 min forced air cooling) up to 100 cycles. Neither internal oxidation of the substrate nor peeling were observed at the different temperatures. The TBC was adherent to the bond up to 100 cycles at 1370°C.

Most of the TBC systems reported in the literature contain an alumina forming bond coat. There are only few papers dealing with chromia forming bond coats. These TBC systems consisted of plasma sprayed YSZ on Ni-based superalloys with multilayer bond coats comprising an aluminized NiCrAlY layer and an outer NiCr layer containing also low amounts of silicon [33-35]. At the bond coat/topcoat interface, an adherent protective oxide scale formed composed of a thick outer chromia layer and a thin inner silica layer. The YSZ topcoat did not spall off during exposure to laboratory air at 800°C for up to 3000 h [35]. Promising results were also obtained for YSZ topcoats on a chromia forming NiCr substrate. No failure was observed at 1000°C during 1000 1-h cycles in dry flowing oxygen [36]. These chromia forming bond coats have been considered to provide protection against hot corrosion and oxidation at intermediate temperatures. The present study shows that chromia-silica forming bond coats can also be applied at temperatures up to 1200°C.

Chemical reactions between TGO and E/TBC

Microstructural SEM examinations of the cross-sections of thermally cycled Nb/Nb₅Si₃-based alloy specimens revealed that both YSZ and GZO topcoats reacted at high temperatures with the TGOs formed on the bond coats used. The occurrence of zircon found in the transition region between ceramic topcoat and TGO suggests a reaction between YSZ and silica. Zircon was reported to form from amorphous silica and tetragonal zirconia at temperatures down to 1200°C [37]. During sintering of ZrO₂-SiO₂ powder blends, a probably diffusion controlled reaction led to formation of ZrSiO₄ after 4 h annealing at 1200°C [38]. Furthermore, zircon formation was also observed in YSZ TBCs with deposits of artificial volcanic ash containing substantial amount of SiO₂ during exposure at 1200°C [39]. Similarly, solid ZrSiO₄ was observed in YSZ TBCs with embedded boron containing MoSi₂ particles which were exposed to air at 1100°C for 20 h [40]. After oxidation induced decomposition of MoSi₂ into volatile MoO₃ and amorphous silica, ZrSiO₄ formed due to chemical reaction between SiO₂ and YSZ, exhibiting tight adhesion to the TBC and healing cracks. Therefore, for the E/TBC systems studied in the present work, a chemical reaction between the ceramic topcoats and the silica containing TGOs is highly expected and corroborated by SEM cross-sectional analysis.

Furthermore, yttrium zirconate was found below the YSZ topcoat on Nb/Nb₅Si₃-based alloy sample with B+Fe-M₇Si₆-based bond coat after 860 cycles of exposure at 1200°C. The formation of Y₂Zr₂O₇ was probably promoted by consumption of zirconia due to a reaction with silica forming zircon. In crystalline solid solutions of ZrO₂ with various Y₂O₃ concentrations, the formation of the cubic pyrochlore Y₂Zr₂O₇ phase was observed at Y₂O₃ contents ≥ 9.2 mol% [41]. X-ray investigations of mixtures of ZrO₂ + Y₂O₃ revealed that formation of Y₂Zr₂O₇ started at a sintering temperature of 1100°C with 4 h annealing [42]. Therefore, partial transformation of ZrO₂ depleted YSZ into yttrium zirconate appears to be possible in the reaction zone below the ceramic topcoat. In the present work, the compounds formed by reactions between

TGOs and E/TBC were identified only by EDS analysis. Their formation, however, has to be confirmed by thorough transmission electron microscopy studies of the TGO/ceramic topcoat interfaces.

Whereas YSZ has been established as standard TBC on Ni-based superalloys with alumina forming bond coats [14,15], the novel TBC materials $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Sm}_2\text{Zr}_2\text{O}_7$ were found to be incompatible with Al_2O_3 at very high temperatures ($\geq 1100^\circ\text{C}$) [43,44]. During high temperature exposure, aluminate phases such as GdAlO_3 and SmAlO_3 formed at the TGO/topcoat interfaces. In the present work, Ti, Cr, Al and Fe or Co were found in the root area of GZO topcoat, indicating diffusion of these elements into the E/TBC and slight solubility of their oxides in GZO. At the TGO/GZO interface of the sample with B+Co- M_7Si_6 -based bond coat thermally cycled at 1200°C , GdNbO_7 and ZrSiO_4 were found, suggesting a chemical reaction of $\text{Gd}_2\text{Zr}_2\text{O}_7$ with niobium oxides and silica. Formation of zircon was also observed in GZO TBCs covered with silica-rich artificial volcanic ash [45]. During exposure to air at 1200°C , Gd_2O_3 was continuously leached out from GZO, and zircon was finally formed. Due to the chemical incompatibility of GZO with alumina as well as its low fracture toughness, an YSZ interlayer was deposited between bond coat and GZO topcoats for long-term exposure on Ni-based superalloys with alumina forming bond coats [46,47]. However, YSZ interlayers seem to be inappropriate with bond coats forming silica containing TGOs, because of its poor compatibility with silica, as revealed by SEM cross-sectional analysis in the present work. For silica forming bond coats, rare earth silicates might be more appropriate, as shown by preliminary studies of an E/TBC system with a combined Y_2SiO_5 + GZO topcoat applied on MASC samples [23]. Whereas yttrium silicates, in particular $\text{Y}_2\text{Si}_2\text{O}_7$ appear chemically compatible with silica (see the Y_2O_3 - SiO_2 phase diagram [48]), their compatibility with other oxides formed in the TGOs (Ti-, Cr-, Fe-oxides) as well as with the GZO topcoat needs further examinations.

E/TBC failure

Failure of TBC systems with YSZ topcoat and alumina forming bond coats applied on Ni-based superalloys occurs at the bond coat/TGO interface or between TGO and ceramic topcoat [49,50]. The durability of these TBC systems is considered to be mainly affected by TGO growth rate and thermal expansion mismatch [51,52]. The elastic strain energy stored in the scale causes finally failure occurring at a critical TGO thickness. Critical thickness values ranging from 4 to 7 μm were determined for MCrAlY and Pt aluminide bond coats on Ni-based superalloys [51,53,54]. But the simple concept of a critical TGO thickness at failure cannot generally be employed. For TBC systems composed of NiCoCrAlY and YSZ deposited by EB-PVD on different Ni-base superalloys, the substrate alloy was also found to play a crucial role in the TBC lifetime [55].

For E/TBC systems on Nb/Nb₅Si₃-based alloys, the thickness of the thermally grown oxide scales below the ceramic topcoat approached 35 μm at 1100°C ; at 1200°C , it increased to approximately 50 μm on the B+Fe- M_7Si_6 -based bond coat (Figures 14 and 15). Up to these thicknesses no failure of the E/TBC system by spallation was observed. The YSZ topcoat was well-adherent to the TGO. In the cross-sections of the samples with GZO topcoats, gaps were often observed between TGO and ceramic topcoat, probably associated with cross-section preparation. However, failures of E/TBC systems were observed for specimens with Ni- and B+Co- M_7Si_6 -

based bond coats which were thermally cycled at 1200°C (Figure 10). SEM cross-sectional examinations revealed that both bond coats exposed at 1200°C were entirely degraded and oxidation of the substrate occurred (Figures 11 and 12). Thick oxide scales formed between substrate and ceramic topcoat which spalled off causing failure of the E/TBC system. For Nb/Nb₅Si₃-based specimens with remaining bond coat, a critical TGO thickness at which the E/TBC system failed could not be determined during the maximum exposure periods of thermal cycling testing. The 150-180 µm thick YSZ and GZO topcoats seem to withstand quite thick oxide layers (up to 50 µm) smoothly grown on the bond coats. However, both the YSZ and GZO topcoats were found to be incompatible with the TGOs. Interdiffusion and/or chemical reactions may have strengthened the bonding/adhesion between TGO and ceramic topcoat. A similar behaviour was observed for TBC systems deposited on γ-TiAl based alloys. The lifetime of the TBC systems with YSZ topcoat applied on the latter alloys predominantly depended on the oxidation protection capability of the intermetallic and ceramic bond coats used [56,57]. The failure observed was associated with entire degradation of the oxidation protective coatings and formation of thick oxide layers. Again, an excellent adhesion of the YSZ TBC was observed to the outer oxide scale consisting of alumina particles embedded in TiO₂ formed after degradation of the oxidation protective coatings. Therefore, detailed studies have to be conducted to assess the influence of chemical incompatibility of the ceramic topcoat with the TGO on the lifetime of E/TBC system. Interdiffusion and chemical reactions at the TGO/ceramic topcoat interface, which seem to enhance the adhesion, might be too sluggish to deteriorate significantly the lifetime of E/TBC systems.

SUMMARY AND CONCLUSIONS

Environmental/thermal barrier coating systems were applied on specimens of an Nb/Nb₅Si₃-based alloy and thermally cycled in air at 1100°C and 1200°C. Ni-modified as well as boron containing Co- and Fe-modified M₇Si₆-based bond coats were used, deposited by pack cementation. The 7 wt.% yttria partially stabilised zirconia and gadolinium zirconate topcoats were produced by electron-beam physical vapour deposition. The following results were obtained:

1. Lifetimes exceeding 1000 cycles were determined for the E/TBC systems with both YSZ and GZO topcoats at 1100°C. The ceramic topcoats were tightly-adherent to the thermally grown oxide scales. However, break-away oxidation occurred at corners and edges of the samples without E/TBC resulting in substantial material recession.
2. When thermally cycled at 1200°C, the E/TBC systems with Ni- and B+Co-M₇Si₆-based bond coats failed in the range between 20 to 700 cycles. Failure was caused by spallation of thick oxide scales grown on the substrate after complete degradation of the bond coats.
3. The lifetime of the samples with B+Fe-M₇Si₆-based bond coat and both YSZ and GZO topcoats approached 1000 cycles at 1200°C. The latter bond coat has great potential for application in E/TBC systems on Nb/Nb₅Si₃-based alloys.
4. For both YSZ and GZO E/TBCs, chemical reactions occurred at the TGO/ceramic topcoat interface. YSZ and GZO appeared sparsely compatible with scales

containing silica and oxides of alloying elements. Therefore, additional barrier layers are probably required for long-term exposure of these E/TBC systems at increased temperatures ($\geq 1200^{\circ}\text{C}$).

ACKNOWLEDGEMENTS

The work described in this paper and the research leading to these results received funding from the European Community's Seventh Framework Programme FP7/2007-2013 under grant agreement n°266214 of the HYSOP project. The authors would like to thank Mr. M. Wickins for the supply of the Nb/Nb₅Si₃-based alloy button, Mr. D. Peters and Mr. J. Brien for manufacture of the ceramic topcoats.

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Table 1: Chemical composition (in at.%) of phases and areas in the transition region between ceramic topcoat and bond coat of Nb/Nb₅Si₃-based alloy specimens with different E/TBC systems which were exposed to air at 1100°C for 1000 cycles. Average values of at least four EDS point analyses are given. The regions refer to the SEM micrographs of the specified figures.

Transition region between YSZ and Ni-M ₇ Si ₆ -based bond coat, Figure 5a										
<i>Phase / region</i>	<i>Zr</i>	<i>Y</i>	<i>Ti</i>	<i>Cr</i>	<i>Ni</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Thin reaction zone	2.3		19.9	2.7		1.5	2.3			71.4
Outermost oxide			20.8	3.1		1.1	2.9			72.1
Transition region between YSZ and B+Co-M ₇ Si ₆ -based bond coat, Figure 5b										
<i>Phase / region</i>	<i>Zr</i>	<i>Y</i>	<i>Ti</i>	<i>Cr</i>	<i>Co</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Reaction zone	2.0		26.3	0.9		0.1	0.5			70.3
Outermost oxide			0.7	12.4	13.1			11.3		62.4
Zircon	14.7		2.6	0.2	0.3	13.2		0.1	0.1	68.8
Yttrium zirconate	8.3	7.2	11.3	1.1	3.3	0.5		1.4	0.1	66.9
Transition region between YSZ and B+Fe-M ₇ Si ₆ -based bond coat, Figure 6b										
<i>Phase / region</i>	<i>Zr</i>	<i>Y</i>	<i>Ti</i>	<i>Cr</i>	<i>Fe</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Reaction zone	1.7		6.8	9.8	11.7	1.4		1.6		67.0
Outermost oxide	0.3		6.3	6.6	20.1			1.1		65.6
Yttrium zirconate	7.7	7.5	8.7	1.7	5.4	1.3		1.1		66.6
Transition region between GZO and B+Co-M ₇ Si ₆ -based bond coat, Figure 7b										
<i>Phase / region</i>	<i>Zr</i>	<i>Gd</i>	<i>Ti</i>	<i>Cr</i>	<i>Co</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Reaction zone	6.8	8.7	12.7	1.5	3.3			1.0	0.7	65.3

Table 2: Chemical composition (in at.%) of phases and areas in the transition region between ceramic topcoat and bond coat of Nb/Nb₅Si₃-based alloy specimens with different E/TBC systems thermally cycled at 1200°C in air. Average values of at least three EDS point analyses are given. The regions refer to the SEM micrographs of the specified figures.

Transition region between YSZ and B+Co-M ₇ Si ₆ -based bond coat, Figure 12b										
<i>Phase / region</i>	<i>Zr</i>	<i>Y</i>	<i>Ti</i>	<i>Cr</i>	<i>Co</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Zircon	17.1					15.2				67.7
Outer oxide layer			17.1	5.9	2.3		4.4	0.8	0.5	68.9
Hafnium silicate						19.5		16.1		64.3
Transition region between GZO and B+Co-M ₇ Si ₆ -based bond coat, Figure 13										
<i>Phase / region</i>	<i>Zr</i>	<i>Gd</i>	<i>Ti</i>	<i>Cr</i>	<i>Co</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Root area of GZO	8.3	9.3	8.6	2.1	3.2			1.7	0.1	66.6
Gadolinium niobate		14.9	0.9	0.1		0.1	15.1			69.0
Outmost oxide			0.3	22.5	13.2	0.3		2.4		61.2
Outer oxide layer			16.7	1.5	1.9	1.0	8.0	0.1	0.8	69.9
Zircon	15.9	0.3		0.4		15.6			0.7	67.1
Transition region between YSZ and B+Fe-M ₇ Si ₆ -based bond coat, Figure 14b										
<i>Phase / region</i>	<i>Zr</i>	<i>Y</i>	<i>Ti</i>	<i>Cr</i>	<i>Fe</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Yttrium zirconate	8.0	8.5	8.5	2.1	5.0	0.6	0.2	1.2	0.2	65.8
Zircon	15.8		0.5	0.4	0.5	14.9	0.4	0.1	0.3	67.0
Outermost oxide	0.4		10.7	2.3	16.9	0.1	0.2	2.7		66.7
Outer oxide layer			10.8	9.1	12.3		0.1	1.5		66.2
Transition region between GZO and B+Fe-M ₇ Si ₆ -based bond coat, Figure 15b										
<i>Phase / region</i>	<i>Zr</i>	<i>Gd</i>	<i>Ti</i>	<i>Cr</i>	<i>Fe</i>	<i>Si</i>	<i>Nb</i>	<i>Al</i>	<i>Hf</i>	<i>O</i>
Reaction zone	8.8	10.8	9.4	1.2	6.9		0.8	1.4		60.8
Outer oxide layer			13.3	11.2	14.4			1.6		59.6

Figure 1: Nb/Nb₅Si₃-based alloy samples with B+Fe-M₇Si₆-based bond coat and (left) YSZ and (right) GZO topcoat after E/TBC deposition

Figure 2: Lifetime of E/TBC systems consisting of YSZ and GZO topcoats deposited on Nb/Nb₅Si₃-based alloy samples with Ni-, B+Co-, and B+Fe-M₇Si₆-based bond coats which were thermally cycled at 1100°C in air

Figure 3: Nb/Nb₅Si₃-based alloy samples with B+Fe-M₇Si₆-based bond coat and (a) YSZ and (b) GZO topcoats after 1000 cycles of exposure to air at 1100°C: front side with E/TBC; rear side without E/TBC

a

b

Figure 4: Mass change vs. number of cycle curves of Nb/Nb₅Si₃-based alloy samples with Ni, B+Co-, and B+Fe-M₇Si₆-based bond coats as well as (a) YSZ and (b) GZO topcoats which were thermally cycled at 1100°C

a

b

Figure 5: SEM images of Nb/Nb₅Si₃-based alloy samples with (a) Ni-, and (b) B+Co-M₇Si₆-based bond coats and YSZ topcoat which were exposed to air at 1100°C for 1000 cycles

a

b

Figure 6: SEM images of an Nb/Nb₅Si₃-based alloy sample with B+Fe-M₇Si₆-based bond coat and YSZ topcoat which was exposed to air at 1100°C for 1000 cycles, showing (a) the E/TBC system and (b) the TGO formed between bond coat and YSZ topcoat

a

b

Figure 7: SEM images of Nb/Nb₅Si₃-based alloy samples with (a) Ni-, and (b) B+Co-M₇Si₆-based bond coats and GZO topcoat which were exposed to air at 1100°C for 1000 cycles

a

b

Figure 8: SEM images of an Nb/Nb₅Si₃-based alloy sample with Ni-M₇Si₆-based bond coat and GZO topcoat which was exposed to air at 1100°C for 1000 cycles, showing (a) thick oxide scale grown after degradation of the bond coat and (b) failure of the E/TBC system by oxide spallation

a

b

Figure 9: (a) SEM image and (b) EDS analysis of an Nb/Nb₅Si₃-based alloy sample with B+Fe-M₇Si₆-based bond coat and GZO topcoat which was exposed to air at 1100°C for 1000 cycles (spectrum profiling across the TGO, coating and subsurface region of the substrate)

Figure 10: Lifetime of E/TBC systems consisting of YSZ and GZO topcoats deposited on Nb/Nb₅Si₃-based alloy samples with Ni-, B+Co-, and B+Fe-M₇Si₆-based bond coats which were thermally cycled at 1200°C in air

a

b

Figure 11: SEM images of Nb/Nb₅Si₃-based alloy samples with Ni-M₇Si₆-based bond coat and (a) YSZ and (b) GZO topcoats which were exposed to air at 1200°C for 700 and 233 cycles, respectively

a

b

Figure 12: SEM images of an Nb/Nb₅Si₃-based alloy sample with B+Co-M₇Si₆-based bond coat and YSZ topcoat after 300 cycles of exposure at 1200°C, showing (a) the thick oxide scale grown beneath the E/TBC and (b) the reaction zone between TGO and YSZ topcoat. The numbers 1 and 2 in (b) indicate positions where EDS point analyses corroborate the formation of ZrSiO₄ and HfSiO₄, respectively.

Figure 13: SEM image of an Nb/Nb₅Si₃-based alloy sample with B+Co-M₇Si₆-based bond coat and GZO topcoat which was exposed to air at 1200°C for 33 cycles

a

b

Figure 14: SEM images of an Nb/Nb₅Si₃-based alloy sample with B+Fe-M₇Si₆-based bond coat and YSZ topcoat after 860 cycles of exposure at 1200°C, showing (a) the E/TBC system and (b) the reaction zone between TGO and YSZ topcoat. The numbers 1 and 2 in (b) indicate positions where EDS point analyses corroborate the formation of Y₂Zr₂O₇ and ZrSiO₄, respectively.

a

b

Figure 15: SEM images of Nb/Nb₅Si₃-based alloy samples with B+Fe-M₇Si₆-based bond coat and GZO topcoat which was exposed to air at 1200°C for (a) 600 and (b) 1000 cycles