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Effects of annealing on the microstructure and the mechanical properties of EB-PVD thermal barrier coatings

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ABSTRACT

The effects of thermal annealing at 1000 °C in air on the microstructure and the mechanical properties (Young's modulus and hardness) of thermal barrier coatings consisting of a 4 mol% Y_2O_3 partially stabilized ZrO_2 top coat and a NiCoCrAlY bond coat, deposited by electron beam physical vapour deposition on nickel-based superalloy IN 625, have been investigated using X-ray diffraction, Raman spectroscopy, scanning electron microscopy (SEM), image analysis and nanoindentation. During annealing, the ceramic top coat undergoes sintering and recrystallization. These processes lead to stress relaxation, an increase of the intra-columnar porosity and the number of large pores as measured by image analysis of SEM micrographs. An increase of the grain size of the γ-phase in the bond coat, accompanied by changes in the morphology of γ-grains with annealing time, is also observed. Correlations between these microstructural changes in the top coat and the bond coat and their mechanical properties are established and discussed.

1. Introduction

Thermal barrier coatings (TBC), manufactured by electron beam physical vapour deposition (EB-PVD), air plasma spraying (APS) or high velocity oxygen fuel spraying (HVOFS) are currently employed to protect turbine blades, made of Ni-based superalloys, which are located in the hot section of aero engines and stationary gas turbines. A TBC-system consists of a ceramic top coat (TC) deposited onto a metallic substrate or intermediate bond coat (BC). Between the TC and the BC a thermally grown oxide layer (TGO) forms during deposition and further thermal exposure in service. In order to simulate service life, data for the mechanical properties (Young's modulus E, hardness H, yield stress σ_Y, failure stress, etc.) of the TBC system after extended thermal annealing (representing the time at high temperature in service) or more complex thermo-mechanical treatments are needed. The performance and lifetime of TBCs are strongly affected by the state and the amount of residual stresses in the TBC system, because these stresses lead to cracking, shape change and finally failure of the coating layer during service. The failure is usually in the TGO or in the YSZ TC close to the TGO, as revealed by measurements of the residual stresses in the TGO using photo-luminescence piezo-spectroscopy [1,2]. The failure typically occurs by spallation of the TC at ambient temperature after cooling down from high temperature in service due to the thermal mismatch of the TBC components (TC, TGO, and BC). That is why we have focused in the present study on the mechanical properties and residual stresses of TBC samples measured at ambient temperature after prolonged annealing at high temperature.

The mechanical properties of the TBCs depend strongly on their microstructure, which exhibits severe changes in service. Furthermore, the measured mechanical properties depend on the length scale probed by the different test methods. This especially holds for coatings deposited by EB-PVD having a complex columnar microstructure, which gradually changes from the TC/BC interface towards the TC surface. For understanding of the mechanisms controlling the evolution of the global properties of the coatings during long term thermal exposure it is necessary to investigate the microstructural changes, which occur during thermal annealing and their influence on the local mechanical properties. In the short review of previous works on the subject given below we intentionally discuss mainly research results on EB-PVD TCs, because TBCs prepared by other methods like APS have quite different morphology, microstructure (porosity) and, consequently, quite different mechanical and thermal properties.

The available data on the change of the mechanical properties of EB-PVD TCs with annealing time, measured at RT, show an increase of the apparent Young's modulus of the TC, which was qualitatively attributed to the formation of sintering contacts between the columns [3,4]. Recently, Zotov et al. [5] described a more complex behaviour of the mechanical properties of an EB-PVD TBC-system, measured by nanoindentation in cross-sections, as function of annealing time at $T_A = 1000$ °C. An initial increase of E and H of the TC and the BC was

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followed by a decrease for longer annealing times exceeding 100 h. An increase of the micro- and nano-hardness of EB-PVD TCs after annealing for 100 h at $T_A = 1100$ °C and for 24 h at $T_A = 1500$ °C, respectively, has been reported by Wellman et al. [6] for indentation experiments performed on polished TC surfaces. Using nanoindentation, Vecchione et al. [7] found both on polished surfaces and on cross sections of an EB-PVD TC an increase of H and E after 80 h annealing at $T_A = 1100$ °C. Guo and Kagawa [8] reported ultra-micro-indentation results for an EB-PVD TC, which indicate an increase of H with annealing time and temperature measured both on cross sections and polished surfaces. For E measured on the surface, they observed that an initial increase of E with annealing time (at $T_A = 1400$ °C) was followed by a subsequent decrease, while the Young's modulus measured on cross-sections increases both with T_A and with annealing time. The increase of H and E with annealing time and temperature for EB-PVD TCs has been attributed to microstructural changes due to sintering processes [5,8], while the decrease of E was not explained. Flores Renteria et al. [9,10] concluded by measurements of the surface area of open and closed pores that in the temperature range 900–1100 °C the main sintering mechanism for EB-PVD TCs is surface reduction via surface diffusion. Since the global dimensions of a TC deposited on a substrate cannot change significantly, the local material redistribution due to surface diffusion should result in a change in the pore size distribution, as observed for example in [11]. Residual stresses develop in the TCs during deposition and could have a large impact on the apparent Young's modulus as measured by both macroscopic [12] and nanoindentation [13] methods. It can be expected that during extended annealing the diffusion-controlled material redistribution could lead to changes in the residual stress state and thus affect the apparent Young's modulus. There are very limited data for in-situ measurements of the mechanical properties of the TC at high temperatures. Kim and Heuer [14] reported a decrease of both E and H of EB-PVD TCs with increasing temperature up to 900 °C using a special high-temperature vacuum displacement-sensitive microindenter.

Much less attention has been paid also in the literature to the changes in the microstructure and the mechanical properties of the BC after prolonged annealing. Currently two types of BCs are used — either a Pt-modified nickel aluminide [15] or MCrAlY (where M refers to one or more of the elements Co, Ni and Fe). Zhang and Heuer [16] observed the appearance of a martensitic product phase in a Pt-modified BC after annealing for 1 h at $T_A = 1200$ °C. Similarly, Mendis et al. [17] observed by transmission electron microscopy (TEM) that Ni-rich β-NiAl grains in the as-deposited NiCoCrAlY BC partially transform to $L1_0$ martensite after isothermal annealing for 100 h at $T_A = 1100$ °C. Baufeld et al. [18] have studied NiCoCrAlY EB-PVD BCs isothermally treated for 24 h at temperatures between 840° and 1100 °C and quenched to ambient temperature in water. For temperatures between 840 and 970 °C spherical γ′ precipitates (Ni_3Al phase with $L1_2$ structure) were observed both in the γ phase of the BC and in the diffusion zone (DZ) between the BC and the substrate. These precipitates disappear for $T_A > 970$ °C.

As can be seen from this brief overview of previous papers on EB-PVD TBC systems, there is a shortage of quantitative measures of the interrelations between the mechanical properties and the microstructure of EB-PVD TBC systems. In order to contribute for the better understanding of these correlations, the present study combines X-ray diffraction (XRD), scanning electron microscopy (SEM) image analysis and nanoindentation of *both* the TC and the BC of EB-PVD TBC after annealing for different times at $T_A = 1000$ °C. Since the Young's modulus of the TC may well depend on the residual stresses present [12,13,19], special emphasis was paid on the residual stresses in the surface layer of the TC using XRD and Raman spectroscopy. Several authors have already reported data for the Young's modulus and/or hardness of TCs annealed at relatively high temperatures ($T_A \geq 1200$ °C). In the present study, we focus on a lower annealing temperature, which is characteristic for the long-term service conditions of coatings in gas turbines for aero engines.

2. Experimental details

2.1. Sample preparation

The samples consisted of 4 mm thick Inconel 625 (IN625) Ni-based superalloy substrates with 100 ± 22 μm thick NiCoCrAlY BC and ~275 μm thick YSZ TC containing ~4 mol% Y_2O_3. Both BC and TC were prepared by EB-PVD. The BC was deposited by means of a Leyboldt ESC 60 (60 kW) coating facility from Leyboldt–Haereus. All TCs were produced in one single EB-PVD coating run using a 150 kW coater manufactured by von Ardenne Anlagentechnik. The substrate temperature during the deposition of the TC and the BC was 1000 °C, and the substrate rotated during deposition (12 rpm). Before deposition of the TC, the BC was densified by shot peening and annealed for 4 h at 1080 °C in vacuum (typically between 1×10^{-4} and 1×10^{-3} Pa). The initial TC specimen was a plate, which was later cut into stripes with dimensions of approximately 100 mm × 10 mm. Some stripes were annealed at $T_A = 1000$ °C in air at ambient pressure and used for macro-indentation tests. The furnace was preheated at 1000 °C and the samples were inserted within 3 s in the hot zone. The annealing times were 50, 100 and 200 h, respectively. For cooling, the specimens were taken out of the furnace and cooled in calm air to room temperature (RT). The cooling rate could affect the microstructure and the mechanical properties but investigation of this effect is beyond the scope of the present paper. Due to the low cooling rate used in the present study it can be expected that the phase composition of the BC is close to equilibrium [18].

Cross-sections were prepared from as-coated and annealed stripes for nanoindentation. All cross-sections were cut in the same orientation with respect to the rotation axis of the sample holder during coating. In order to avoid TC delamination or damage during the cross-section cutting, the coatings were impregnated with epoxy. For texture and residual-stress measurements by XRD as well as by Raman spectroscopy smaller samples (~15 × 10 mm) were cut from the annealed stripes and their surfaces were polished down to a 1 μm diamond paste finish.

The chemical composition of the IN625 Ni-based superalloy substrate, determined by SEM energy-dispersive X-ray (EDX) analysis, in the as-deposited state is (in at.%): 63.8Ni–23.8Cr–5.6Mo–2.2Nb–0.7Al–0.2Ti–3.4Fe–0.3C, similar to the IN625 composition reported in the literature [20]. The as-deposited BC contains two phases, β-NiAl and γ-(Ni,Cr,Co) [18]. The overall chemical composition of the BC is (in at%): 43.2Ni–17.6Co–16.5Cr–22.2Al–0.5Y. The average compositions of the γ- and the β-phases in the as-deposited state and after 200 h annealing at 1000 °C in air are given in Table 1. During the deposition, a thin TGO layer (thickness ~0.3 μm) consisting mainly of Al_2O_3 is formed between the BC and the TC.

2.2. X-ray diffraction

XRD measurements were performed at RT on a Philips X'Pert diffractometer equipped with a ¼ Eulerian cradle using Cu K_α radiation (45 kV, 40 mA, Ni K_β filter). The positioning accuracy was 0.001° 2θ, where 2θ is the scattering angle. Diffraction patterns were

Table 1
Chemical compositions (in at.%) of the γ and β phases present in the BCs, as determined by EDX.

	γ phase		β phase	
	As-deposited	After 200 h annealing	As-deposited	After 200 h annealing
Ni	37.4 ± 0.8	41.4 ± 0.6	47.6 ± 0.4	49.3 ± 0.4
Co	25.3 ± 0.8	22.4 ± 0.4	11.8 ± 0.4	10.7 ± 0.3
Cr	27.2 ± 0.3	26.6 ± 0.5	8.4 ± 0.6	8.2 ± 0.5
Al	9.1 ± 0.3	9.5 ± 0.5	32.1 ± 0.6	31.7 ± 0.5
Y	≤1.0	≤1.0		