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

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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% Y2O3 partially stabilized ZrO2 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.

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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 σY, failure stress, etc.) of the TC 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 photoluminescence 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 Tₐ = 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 aluminate [15] or MCrAlY (where M refers to one or more of the elements Co, Ni and Fe). Zhang and Heuer [16] observed in 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 ≥ 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 strips 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 1/4 Eulerian cradle using Cu Kα radiation (45 kV, 40 mA, Ni Kα 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. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | 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              | 23.3 ± 0.8     | 22.4 ± 0.4      | 11.8 ± 0.4  | 10.7 ± 0.3      |
| Cr              | 27.2 ± 0.3     | 26.5 ± 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            |               |                 |
collected using a point focus, X-ray lense and cross-slit assembly in the primary beam, X’accelerator position sensitive detector and 800 s/frame accumulation time. Textures were measured with a step size of 5° for both $\phi$ rotations (0–360°) and $\psi$ tilts (0–85°) using 20 step size of 0.02° and 10–30 s/step accumulation time. Lorentz-polarization, K$_c$2 stripping as well as background corrections of the diffraction profiles were performed. Peak positions for residual stress analysis were determined as the centres of gravity. Specimen height adjustment was accomplished using a special PanAnalytical micrometer device with a $\pm$ 2 $\mu$m accuracy. If necessary, the data for the YSZ samples were corrected for $\Psi$ misalignment using the (331) reflection of stress-free powder Si standard and the X’Pert Stress software.

2.3. Raman spectroscopy

Raman spectra from the TC were collected at RT using a WITec® confocal Raman spectrometer equipped with a 1800 l/mm grating, a 50 $\mu$m optic fibre and an objective with a >20 magnification. Spectra from the surface of all TC samples were measured using a 532 nm wavelength. The nominal resolution of the spectrometer was <0.9 cm$^{-1}$. Spectra taken from different locations on the surface were very similar. In all cases, 60 accumulations and 1 s integration time were applied. Care was taken to place the outermost polished surface of the TC on the focusing point of the incident laser beam. The location of the incident laser beam was always selected to avoid pores, cracks or defects on the surface visible under the optical microscope of the spectrometer. The spectra were corrected for instrumental spikes and the auxiliary fluorescent background was subtracted, if necessary. The Raman bands at 620 and 640 cm$^{-1}$ were split into $\psi$/0 $\mu$m and $\psi$ splitting of the cubic reflections $\Psi$2. No significant sharpening of the diffraction peaks is observed after annealing, like in YSZ TC prepared by electrostatic spray-assisted vapour deposition (ESADV) [25]. This indicates the absence of significant grain growth of the investigated TC during annealing at $T_a = 1000 ^\circ$C on the scale of 10–100 nm, where XRD analysis is sensitive. Variation in the integral intensities of some reflections suggests changes in the texture with annealing time.

2.4. Scanning electron microscopy and image analysis

The microstructure of the specimens was investigated using a ZEISS ULTRA 55 scanning electron microscope equipped with a field emission gun. After standard grinding and polishing of the cross-sections, the polished surfaces were ion-beam etched. The ion beam etching was performed with a Gatan High Resolution Ion beam Coater Model 683, including auxiliary equipment for etching. The EDX analyses device of the SEM (Oxford Instruments, High Wycombe, United Kingdom) was used for quantitative element analyses, operating at 20 kV.

For image analysis of SEM micrographs of the TC and the BC, the ImageJ Version 1.41 software [21] was used. For the determination of the widths of the TC columns, line profiles (typically 300 $\mu$m length) were taken in SEM micrographs with relatively small magnifications between 500$\times$ and 1000$\times$. For the determination of the intracolumnar pore size distributions in the upper part of the TC, the contrast of the SEM micrographs (magnification between 10000$\times$ and 30000$\times$) was first adjusted, then the image contrast was improved using the image sharpening function of the image analysis software, and finally, the micrographs were converted into binary black-and-white images. At least 3 columns having typically between 50 and 445 intracolumnar pores were analyzed for each sample. The pore-size lower resolution limit was 0.0004 $\mu$m$^2$ in all cases. Prior to the determination of the areas of the $\gamma$-grains in the BC, the perimeters of the grains were manually drawn to ensure that grain boundaries with weak contrast are also taken into account. On average, 40 grains per sample were considered.

2.5. Nanoindentation

Nanoindentation measurements were performed at room temperature both on polished cross-sections and on the polished surface of the TCs with a XP™ Nanoindenter (MTS Systems Corporation) using a Berkovich diamond tip and different maximum peak loads ($F_{\text{max}}$). The nanoindentation data were corrected for thermal drift and machine compliance using the MTS software TestWorks™. Peak load hold periods (typically 10 s) were used, as recommended by Oliver and Pharr [22], in order to diminish possible non-elastic effects in the loading sequence. In all cases the loading rate was 1 mN/s. Each measurement was repeated at least three times. The E and H values were determined using the Oliver and Pharr method [22], as implemented in the TestWorks™ software. The Poisson’s ratios of the TC and the BC, necessary for the calculation of the Young’s moduli, were taken equal to 0.25 [23] and 0.32, respectively.

3. Experimental results

3.1. Phase composition

Fig. 1 shows the diffraction patterns of the as-deposited TC and samples annealed for 100 and 200 h, respectively. They indicate that the TC consists only of tetragonal YSZ with strong (110) and (211) texture components. The reflections in Fig. 1 and in the text are given correspondingly in tetragonal setting. The tetragonal lattice parameters $a_0$ and $c_0$, determined from the positions of the (110), (220), (002) and (004) reflections, are almost identical ($a_0 = 3.816 \pm 0.002 \AA; c_0 = 5.173 \pm 0.003 \AA$) for all samples and are in good agreement with literature data [24]. The tetragonal lattice distortion of YSZ is small. That is why some authors use a cubic setting for indexing of the diffraction peaks. The diffraction patterns (Fig. 1) clearly show the presence of weak tetragonal peaks [like the (102) reflexion at about 42.45° 2$\theta$] and the tetragonal splitting of the cubic reflections [(200)$_c$ splits into (110)$_t$, (002)$_c$; (400)$_c$ splits into (220)$_t$ + (004)$_c$]. No significant sharpening of the diffraction peaks is observed after annealing, like in YSZ TC prepared by electrostatic spray-assisted vapour deposition (ESADV) [25]. This indicates the absence of significant grain growth of the investigated TC during annealing at $T_a = 1000 ^\circ$C on the scale of 10–100 nm, where XRD analysis is sensitive. Variation in the integral intensities of some reflections suggests changes in the texture with annealing time.

3.2. Texture

Texture can strongly influence the mechanical properties of materials and provides valuable information about the evolution of the
microstructure with annealing time. That is why the texture of the investigated TCs was studied by measuring pole figures for the (101) and (110) reflexions. Due to the small penetration depth of the X-rays, the pole figures provide information about the preferred orientation of the grains only in a thin surface layer of the TC of approximately 10–12 μm thickness for Cu Kα radiation. The pole figures for the as-

![Pole figures of the TCs](image)

Fig. 2. Pole figures of the TCs: (a) as-deposited; (b) annealed for 50 h; (c) annealed for 100 h; (d) annealed for 200 h.
deposited TC are given in Fig. 2(a). Both pole figures show single-crystal type textures (all grains have approximately the same crystallographic orientation). The (110) pole figure demonstrates that in the majority of grains the (110) lattice planes are oriented parallel to the coating surface [the TC grains (columns) grow perpendicular to the coating surface along the <110> direction]. The misorientations of the (110) grains are distributed anisotropically with an inclination of approximately 12±4° with respect to the surface normal. The (101) pole figure of the as-deposited sample shows a four-fold symmetry. Similar (101) and (110) pole figures [in cubic setting (111) and (100) pole figures] have been reported for other as-deposited EB-PVD TCs [26–29].

According to the literature, the orientation of the TC columns depends on the deposition conditions such as rotation speed and vapour inclination angle (angle between the coating vapour flux and the substrate surface normal) during the coating process. Schulz et al. [27] investigated the influence of the vapour incidence angle during deposition and found that for angles below 25° the columns are aligned parallel to the <100> direction in cubic setting, which corresponds to the <110> direction in tetragonal setting. Zhao et al. [29] found that in coatings, which were deposited without rotation of the specimen, the columns are aligned mainly parallel to the <111>, direction, while for coatings deposited with substrate rotation speeds from 1 to 30 rpm the columns are aligned parallel to the <100> direction, corresponding to the <110> direction. Since the specimens investigated in the present study were coated with a rotation speed of 12 rpm and a vapour incidence angle below 25°, the results are in good agreement with the data reported in [27,29].

The pole figures of the TCs annealed for 50 h (Fig. 2b), 100 h (Fig. 2c) and 200 h (Fig. 2d) show an increase of the misorientation of the grains with increasing \( t_A \). As a quantitative measure of the misorientations, we consider the relative pole intensity \( \rho_{\text{rel}} = I_{\text{hat}} / I_{\text{max}} \) of the (110) pole figure at \( \psi \sim 30° \) and \( \phi \sim 90° \), where \( I_{\text{hat}} \) is the pole intensity at the point with polar coordinates \((\psi, \phi)\), and \( I_{\text{max}} \) is the maximum intensity. \( \rho_{\text{30,50}} \) increases from 1.4±0.5% in the as-deposited state to 7.8±0.5% after 50 h, to 8.2±0.2% after 100 h annealing and to 12.1±0.2% after 200 h annealing. Evidently, there is an increasing number of grains with (110) lattice planes at angles of 30° to the surface of the coating with increasing \( t_A \). In addition we observe in Fig. 2c–d the development of a weak (110) fibre texture at \( \psi \sim 50° \) after annealing. As a measure of the (110) fibre texture we have taken the relative intensity \( \rho_{\text{rel}} \) at \( \psi \sim 50° \) and \( \phi \sim 135° \), Fig. 3(a), as well as the degree of fibre texture, Fig. 3(b). The degree of fibre texture is defined as \( \Delta \rho_{\text{f}} / \rho_{\text{360°}} \), where \( \Delta \rho_{\text{f}} \) is the total angular range covered by the ring-like intensity distributions at \( \psi \sim 50° \). There is an increase for \( t_A \geq 100 \) h in the number of grains with (110) lattice planes at ~50° with respect to the coating surface, which have no preferred orientation in the coating plane.

3.3. Residual stresses

The residual stresses in the surface layer of the investigated TCs were estimated using both XRD and Raman spectroscopy and will be compared with previous XRD [30–32] and Raman [30,33–36] studies.

3.3.1. X-ray diffraction results

The XRD technique is a well developed tool for estimation of residual stresses. It is based on the assessment of the lattice strain normal to the surface:

\[
\varepsilon_{hkl}^{\phi \psi} = \left( d_{hkl}^{\phi \psi} - d_{hkl} \right) / d_{hkl}
\]

(1)

where \( d_{hkl} \) is a stress-free spacing and \( d_{hkl}^{\phi \psi} \) is the lattice spacing of a given \((hkl)\) diffraction peak, measured in a direction defined by the polar angle \( \phi \) and tilting angle \( \psi \). For strongly textured materials, like the investigated TC, the determination of residual stresses using XRD is rather complicated due to the anisotropy (orientation dependence)

of the X-ray elastic constants. Relationships between \( \varepsilon_{hkl}^{\phi \psi} \) and the components of the residual stress tensor have been derived for textured materials by Dölle and Hauk [37]. However, for \((h00)\) and \((hhh)\) reflections of cubic materials the X-ray elastic constants of textured materials do not depend on \( \phi \psi \) [37,38]. In this case the relationship between \( \varepsilon_{hkl}^{\phi \psi} \) and the residual stresses is reduced to the solution for isotropic (non-textured) materials [37,38], assuming zero diffractometer alignment errors:

\[
\varepsilon_{hkl}^{\phi \psi} = \frac{1}{2} \left[ \sigma_1 \left( 1 + \frac{1}{\tau_{\phi}} \right) - \sigma_3 \right] + \frac{1}{2} \left[ \sigma_2 \left( 1 + \frac{1}{\tau_{\psi}} \right) - \sigma_3 \right] + \frac{1}{2} \left[ \sigma_3 \right] + \frac{1}{2} \left[ \sigma_3 \right] + \frac{1}{2} \left[ \sigma_3 \right]
\]

(2a)

where \( s_1 = -\tau_{\phi} / \tau_{\phi} \) and \( s_2 = (1 + \tau_{\phi} / \tau_{\phi}) \) are the X-ray compliances for the selected \((hkl)\) reflection, \( \tau_{\phi} \) is the Poisson’s ratio, \( \sigma_1 = \sigma_1 \cos^2(\phi) + \sigma_2 \sin^2(\phi) \) and \( \sigma_3 \) are the normal stress and \( \tau_{\phi} = \sigma_1 \cos(\phi) + \sigma_2 \sin(\phi) \) stands for the shear stress along the \( \phi \) direction. If the shear stresses \( \sigma_1 \) and/or \( \sigma_2 \) are non-zero, a plot of \( \varepsilon_{hkl}^{\phi \psi} \) versus \( \sin^2(\psi) \) splits into 2 branches with elliptical curvature. Thus, the presence of \( \sin^2(\psi) \)-splitting indicates non-zero shear stresses. Eq. (2a) is often further simplified assuming a bi-axial in-plane stress state with \( \sigma_3 = 0 \):}

\[
\varepsilon_{hkl}^{\phi \psi} = \frac{1}{2} \left[ \sigma_1 \left( 1 + \frac{1}{\tau_{\phi}} \right) - \sigma_3 \right] + \frac{1}{2} \left[ \sigma_2 \left( 1 + \frac{1}{\tau_{\psi}} \right) - \sigma_3 \right] + \frac{1}{2} \left[ \sigma_3 \right]
\]

(2b)

Eq. (2b) predicts a linear relationship between \( \varepsilon_{hkl}^{\phi \psi} \) and \( \sin^2(\psi) \). Generally, the residual stresses calculated from lattice strains represent

![Fig. 3. Variation with \( t_A \) of: (a) the (110) relative pole intensity at \( \phi \sim 135°, \psi \sim 50° \) and (b) the degree of fibre texture.](image-url)
values averaged over the X-ray beam spot area and over the penetration depth of the X-rays (~12 μm for YSZ TC and Cu Kα radiation). Therefore, it cannot be assumed a priori that the averaged stress components \( \sigma_{13} \), \( \sigma_{22} \) and \( \sigma_{33} \) are zero, especially when direction-dependent grain interactions and/or stress gradients are present. That is why we have used Eq. (2a) for the analysis of the residual stresses from XRD.

Measurements were performed using the (220) reflection at about 74.2° 2θ. For YSZ, the degree of tetragonal distortion of the lattice is relatively small and the tetragonal (220) reflection corresponds to the (400) reflection in cubic setting. This justifies the use of Eq. (2a) for the analysis of the residual stresses in the TC. Measurements were done at polar angles \( \phi = 0^\circ \) and 90°. In the first case \( \sigma_{11} - \sigma_{33} = \sigma_{13} \) and \( \tau_{16} = \sigma_{13} \). In the second case \( \sigma_{16} - \sigma_{33} = \sigma_{22} - \sigma_{33} \) and \( \tau_{16} = \sigma_{23} \). The determination of all 6 components of the stress tensor, however, is tedious, requiring measurements for at least 3 different polar angles and is beyond the goals of the present study. Fig. 4 shows a typical \( \sin^2(\psi) \) plot for the sample annealed for 100 h with \( \phi = 0^\circ \). Similar \( \sin^2(\psi) \) plots are obtained for the other samples using both point focus and line focus. These plots exhibit \( \sin^2(\psi) \)-splitting, indicating the presence of shear stresses and justifying the use of Eq. (2a) rather than the linear Eq. (2b). Closer inspection of the \( d_{220}^{\phi = \phi_0} - \sin^2(\psi) \) plot in [34] shows some slight \( \sin^2(\psi) \)-splitting, suggesting the presence of some shear stresses also in these APS TBCs. In addition, some small oscillations of the data points are observed in our \( d_{220}^{\phi = \phi_0} - \sin^2(\psi) \) plots. They may suggest an inhomogeneous distribution of the stresses (presence of stress gradients) in the surface layer of the TBCs [38]. But they could also be due to the strong texture of the EB-PVD TBCs [31]. This additionally complicates the accurate determination of the components of the residual stress tensor.

The normal and shear stresses, calculated from Eq. (2a) using least-squares fit and the X’Pert Stress software (Ver. 1.0) are given in Table 2. A good agreement, within error limits, is observed between the values obtained with point focus and line focus, indicating that the effect of geometrical aberrations is small. The normal stresses are plotted as a function of \( \phi_{\psi} \) in Fig. 5. The reported uncertainties in the stresses were calculated from the least-squares fit by the X’Pert software. The XRD method for estimation of residual stresses is based on changes in the lattice spacing of the individual YSZ grains (Eq. (11)). Since each single-crystalline grain scatters coherently, the appropriate stiffness modulus should reflect bulk properties. Richter et al. [31] also considered the use of bulk Young’s modulus for EB-PVD TBCs plausible due to the fact that the EB-PVD TBCs consist of single crystal-like columns. That is why the compliances \( s_1 \) and \( s_2 \) were calculated in the present study for all samples using \( v = 0.25 \) [23] and the average Young’s modulus for dense YSZ, \( E = 220 \) GPa [39]. As can be seen in Fig. 5, both the normal stresses \( \sigma_{11} - \sigma_{33} \) and \( \sigma_{22} - \sigma_{33} \) are compressive (except \( \sigma_{22} - \sigma_{33} \) for the sample annealed for 50 h) and show a decrease with increasing annealing time (stress relaxation). The in-plane residual stresses in APS TBC, measured by the hole drill method, also decrease after annealing at 1050 °C [40]. Both shear stresses are relatively small. The shear stresses \( \tau_{13} \) are negative, while the shear stresses \( \tau_{23} \) are positive. They arise most probably due to the inhomogeneous microstructure of the TC (see Section 3.5.1). The absolute values of \( \sigma_{11} \) and \( \tau_{16} \) could be affected by the presence of small residual errors \( \Delta \psi \) in the zero of the \( \psi \) tilt [41]. However, for comparing samples measured under identical diffractometer conditions, this effect can be neglected. Some variation in the absolute values of the residual stresses due to the different positions of the samples with respect to the rotation axis during deposition could not be ruled out as well. The main factor affecting the statistical errors in \( \sigma_{11} - \sigma_{33} \) and \( \tau_{16} \) given in Table 2, is the strong texture. For some directions \( \phi_{\psi} \), the (220) peak is almost completely absent, for other \( \phi_{\psi} \) directions the (220) peak is rather weak and broad. As a result the accuracy in the determination of \( d_{220}^{\phi = \phi_0} \) decreases and the standard deviations in \( \sigma_{11} - \sigma_{33} \) as well as in \( \tau_{16} \) increase. Similar difficulties in the evaluation of \( \sin^2(\psi) \) plots from strongly textured EB-PVD TBCs were encountered also by Richter et al. [31].

### 3.3.2. Raman spectroscopy results

The advantage of micro-Raman spectroscopy for the determination of residual stresses is that it could provide information for the local residual stresses on the scale of few μm, which is less than the typical width of the TC columns. Fig. 6 shows the Raman spectrum measured on the surface of the as-deposited TC. The inset shows the profile decomposition of the 620 and 640 cm\(^{-1}\) bands. The Raman
spectra for all samples are similar to those for ESAVD YSZ TC [25], APS YSZ TC [30,34,35], bulk tetragonal YSZ [33,36,42,43] and undoped ZrO₂ [43,44]. As one would expect from the XRD results, no characteristic Raman bands of monoclinic ZrO₂ [43–45] are observed.

Determination of the residual stresses by Raman spectroscopy is based on peak shifts of specific Raman bands due to stresses and conversion of these shifts into stress values by the use of tensor coefficients known as phonon deformation potentials or piezo-spectroscopic coefficients [33,36]. In polycrystalline materials the average stress tensor $<\sigma>$ is related to the shift $\Delta\Omega$ of a given Raman line by

$$<\sigma> = b\Delta\Omega$$

(3)

where $\Delta\Omega = \Omega - \Omega_0$ and $\Omega_0$ is the position of the selected Raman line for a stress-free sample. In other words, a linear relationship between the applied average stress and the peak shift $\Delta\Omega$ is expected. In the present study we have used the strong Raman line with $\Omega_0 = 642$ cm$^{-1}$ for the determination of the residual stresses. The spectral shift $\Delta\Omega$ in the as-deposited TC is $-3.2$ cm$^{-1}$ and decreases gradually to about $-1.8$ cm$^{-1}$ after 200 h annealing. This suggests a decrease of the compressive residual stresses with increasing annealing time.

The constant $b$ can be, in principle, calculated from the elastic constants and the phonon deformation potentials of the material. In practice, the application of Raman spectroscopy for the determination of residual stresses in a series of similar samples requires calibration of $b$ by measuring $\Delta\Omega$ for samples, subjected to a series of reference stresses. Limarga and Clarke [36] have recently reviewed the literature data for the calibration coefficients $b$ of dense undoped, yttria- and ceria-stabilized ZrO₂ and compared with their own new calibration measurements on dense YSZ with 7 wt.% Y₂O₃. Their precise data [36] cannot be directly used for EB-PVD TCs because of the high porosity of the EB-PVD TCs, which influences the apparent piezo-spectroscopic coefficients. However, Tanaka et al. [35] suggested that the calibration coefficient $b$ for the 642 cm$^{-1}$ line is proportional to $(E_{TC}/E_0)$, where $E_{TC}$ is the apparent Young’s modulus of the TC and $E_0$ is the bulk Young’s modulus. Using this idea and data for several TCs with different microstructure and Young’s moduli taken from [33–36], we have derived an empirical equation:

$$b = 0.95 \pm 0.06(E_{TC}/E_0)$$

(4)

Eq. (4) provides a simple way to calculate the calibration coefficient $b$ from the apparent Young’s modulus. It indirectly accounts for the dependence of the piezo-spectroscopic coefficient $b$ on the TC microstructure via the dependence of the Young’s modulus on the microstructure (porosity). The average $E_{TC}$ for our as-deposited TC, determined from nanoindentation experiments [5] on cross-sections, is equal to $126 \pm 25$ GPa. In this case Eq. (4) gives $b = 0.54 \pm 0.14$ GPa cm. Assuming, on the other hand, that $E_{TC}$ is equal to $46 \pm 5$ GPa, as determined by mixed numerical–experimental technique [46] on macroscopic EB-PVD samples, Eq. (4) yields $b = 0.20 \pm 0.03$ GPa cm. These differences in the piezo-spectroscopic coefficients reflect the range of Young’s moduli values measured on local and global length scales.

In order to estimate the residual stresses on the surface of the TCs by Raman spectroscopy, we have first calculated for each annealing time the corresponding $b$ coefficient using the Young’s modulus values measured on the surface (see Fig. 7) and Eq. (4). The piezo-spectroscopic coefficient $b$ is equal to $0.67 \pm 0.19$ GPa cm in the as-deposited state and decreases to $0.47 \pm 0.09$ GPa cm after 200 h annealing. Then the residual stresses were calculated from Eq. (3) using these $b$ values and the corresponding spectral shifts. The resulting $<\sigma>$ values are plotted in Fig. 8. The uncertainties in Fig. 8 were estimated from the uncertainties in the $b$ coefficients and the $E_{TC}$ values using standard error propagation analysis.

Comparison of the XRD and Raman spectroscopy results show a similar behaviour of the residual stresses and clearly demonstrates that stress relaxation takes place in the surface layer of the TC with

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**Fig. 6.** Raman spectrum taken at the surface of the as-deposited TC. The inset shows the profile decomposition of the 620 and the 640 cm$^{-1}$ Raman bands.

**Fig. 7.** Variation with $t_A$ of the Young’s modulus of the TCs, measured on the TC surface.

**Fig. 8.** Variation with $t_A$ of the residual stresses, measured by Raman spectroscopy on the TC surface.
increasing annealing time. The differences in the absolute values of the residual stresses determined by XRD and Raman spectroscopy are due to two main reasons. The first one is the dependence of the piezospectroscopic coefficient on \( E_{TC} \). This would require, in principle, calibration of \( b \) for each annealed EB-PVD TC sample and will be the subject of a future more precise study. On the second place, Raman spectroscopy and XRD probe different components of the stress tensor. The XRD method gives the normal stresses \( \sigma_{ij} \), while the Raman method yields an average stress tensor \( \langle \sigma \rangle \).

### 3.4. Nanoindentation results

#### 3.4.1. Measurements on cross-sections

According to [5], the average Young’s modulus of the TC, measured on cross-sections, increases from \( E_{TC} = 126 \pm 25 \) GPa in the as-deposited state up to \( 156 \pm 27 \) GPa after 100 h annealing. Then it decreases to \( 103 \pm 26 \) GPa after 200 h annealing. The standard deviations of \( E_{TC} \) are relatively large because of the inhomogeneous nature of the TC (local variations of the TC microstructure). The average Young’s modulus of the BC (\( E_{BC} \)) increases from \( 166 \pm 7 \) GPa in the as-deposited state up to \( 193 \pm 10 \) GPa after 100 h annealing and then decreases to \( 168 \pm 9 \) GPa after 200 h annealing [5]. Similar trends were observed for the hardness evolution, because there is generally one-to-one correspondence between \( H \) and \( E/(1−v^2) \) [5].

Generally, the Young’s modulus and the hardness measured by nanoindentation methods can depend on the deformed volume under the indenter, which is commonly referred to as the indentation size effect (ISE). In the as-deposited state we observed no ISE for the Young’s modulus of the BC and the Ni-superalloy substrate, while an inverse ISE (increase of \( E \)) was reported in [47] for bulk YSZ ceramics with 4 mol% \( Y_2O_3 \), sintered at \( T_s = 1500 \) °C for 2 h. In order to cross-check the effect of \( E_{max} \) on our annealed samples, new measurements were performed with different \( E_{max} \). The Young’s modulus of the BC is independent of \( E_{max} \) for all annealing temperatures. A weak inverse ISE is observed for the Young’s modulus of the TC in all annealed samples. The variations of \( E_{TC} \) and \( E_{BC} \) as a function of \( t_A \) are shown in Fig. 9 for \( E_{max} = 50 \) and 200 mN. These data together with the data for \( E_{max} = 100 \) mN [5] show that the Young’s moduli of the TC and the BC are strongly correlated and decrease for \( t_A > 100 \) h, regardless of the deformed volume under the indenter.

To investigate the effect of the TC on the BC, a series of samples consisting of only a Ni-based superalloy substrate IN 625 plus a BC were annealed under identical conditions. The mechanical properties (\( E_{BC} \) and \( H_{BC} \)) were determined using nanoindentation measurements under identical conditions and compared with the data for the TBC samples with TC. In the as-deposited state \( E_{BC} \) of the sample without TC is independent of \( E_{max} \) and equal to \( 152 \pm 2 \) GPa. This value is slightly lower than that for the BC + TC sample (175 ± 2 GPa). Fig. 10 shows that both \( E_{BC} \) and \( H_{BC} \) of the samples without TC increase slightly with \( t_A \) (6% increase in \( E_{BC} \)) and 15% increase in \( H_{BC} \) after 200 h annealing), opposite to what is observed for the TBC samples with TC.

#### 3.4.2. Measurements on the surface of the top coat

The microstructure of the investigated TCs is strongly textured (see Section 3.3). It may be expected that differences exist in the mechanical properties measured by nanoindentation on cross-sections (parallel to the TC/BC interface) and on the surface of the TC (perpendicular to the TC surface). Indeed, it has been already reported [48] that the Young’s modulus of EB-PVD TCs measured on the surface have a nearly constant value of 230–250 GPa regardless of the substrate rotation speed (porosity), while the Young’s modulus measured on cross-sections decreases with increasing substrate rotation speed (porosity). Vecchione et al. [7] also reported that \( E_{TC} \) of as-deposited EB-PVD YSZ TCs measured on the surface (152 GPa) is larger than that measured on cross-section (81 GPa).

In order to probe the mechanical anisotropy of the investigated TCs, nanoindentation measurements were performed on the polished surface of the TCs (the corresponding Young’s modulus and hardness will be denoted \( E_{TC}^S \) and \( H_{TC}^S \) hereafter). The nanoindentation curves

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**Fig. 9.** Variation with \( t_A \) of \( E_{TC} \) (squares) and \( E_{BC} \) (circles) measured on cross-sections: full symbols — \( E_{max} = 50 \) mN; empty symbols — \( E_{max} = 200 \) mN.

**Fig. 10.** Variation with \( t_A \) of: (a) \( E_{BC} \) and (b) \( H_{BC} \) for samples with and without TC.
of our samples measured on the surface show often pop-in and non-indentational elastic recovery effects, which impede the accurate determination of $E_{TC}$ and $H_{TC}$. The pop-in effects are most probably due to crushing of pores beneath the indenter. The non-indentational elastic recovery events are usually attributed to lateral displacement of the columns [5,7]. In the as-deposited state $E_{TC}$, averaged over randomly selected indentation sites, is independent of $F_{max}$ and equal to $155 \pm 35$ GPa. It is slightly higher than the Young's modulus measured on cross-sections ($126 \pm 25$ GPa [5]) in qualitative agreement with [7,48]. The degree of plasticity $\delta_p = h_i/h_{max}$ also exhibits slight anisotropy in the as-deposited state, where $h_{max}$ is the maximum penetration length and $h_i$ is the residual indentation depth after the removal of the indenter. $\delta_p$ is equal to $0.62 \pm 0.10$, when measured on cross-sections [5]. $\delta_p$ is equal to $0.50 \pm 0.10$, when measured on the surface of the TC.

With increasing annealing time $E_{TC}$ starts to decrease (Fig. 7). After 200 h annealing time the $E$ values measured on cross-sections [5] and on the surface of the TC are similar ($103 \pm 26$ GPa and $109 \pm 15$ GPa, respectively). These results suggest that the anisotropy in the mechanical properties of the TCs decreases with annealing time, most probably due to changes in the spatial distribution of the pores and increase of the fraction of polycrystalline fiber texture (Fig. 3).

3.5. Microstructure

3.5.1. Top coat

A significant number of papers describe the microstructure of the YSZ EB-PVD TCs and the effects of deposition parameters (see reviews [10,49]). Generally, EB-PVD YSZ TCs have a columnar structure with inter-columnar gaps between the columns and lateral feather-like micro-columns due to shadowing effects during deposition. Each column contains also globular and elongated intra-columnar pores (type III nano-pores according to the nomenclature of Zhao et al. [29]). The intra-columnar pores are arranged in layers inward from the edge to the centre of the columns due to the rotation of the substrate during deposition [49]. Correspondingly, the total porosity of the TC can be approximately separated into intra-columnar porosity ($P_{intra}$) and inter-columnar porosity ($P_{inter}$).

The XRD pole figures for our as-deposited sample (Fig. 2) show that the columns grow predominantly along the $\langle 110 \rangle$ direction, perpendicular to the coating surface. The inclination of the TC columns of the investigated samples with respect to the coating surface vary slightly due to the different locations within the initial stripes, from which the cross-sections were cut. The inclination angles, determined by XRD texture analysis, are between $0$ and $17^\circ$, in qualitative agreement with the value $12 \pm 4^\circ$ obtained from image analysis of SEM micrographs.

The average width of the columns at about $30 \mu m$ below the surface of the TC is about $11 \pm 4 \mu m$ for the as-deposited sample, in good agreement with the value of $10 \mu m$ reported earlier [10] for similar EB-PVD TCs. Annealing at $T_a = 1000$ °C leads to changes in the microstructure of the TC. The width of the individual columns at about $30 \mu m$ below the coating surface decreases to $9.0 \pm 5 \mu m$ after 100 h and further to $7 \pm 4 \mu m$ after 200 h annealing. The annealing leads also to changes in the intra-columnar porosity. Fig. 11 shows typical SEM micrographs of individual TC columns (magnification $30000 \times$) from the upper parts of the TCs near the surface. The pores in the as-deposited state (Fig. 11a) are rather small and arranged in layers at angles of $32–42^\circ$ to the surface of the TC. Image analysis of SEM micrographs of similar EB-PVD TCs [10] show that the intra-columnar pores form layers at $31–33^\circ$ to the surface also in these TCs. In the sample annealed for 200 h (Fig. 11b), a significant increase of the gap widths between the columns in the upper part of the TC, an increase of the number of large pores as well as a change of their shape and orientation are observed. However, no delamination of the TC is observed after 200 h annealing.

Figs. 12 and 13 show the variation with $T_a$ of the average intra-columnar pore area $<A_{pore}>$ and the average intra-columnar porosity $<P_{intra}>$ of columns from the upper part of the TC. The standard deviations of $<A_{pore}>$ and $<P_{intra}>$ in Figs. 12 and 13 are relatively large, despite the large number of pores analyzed, because the pore-size distributions are rather broad. The inset in Fig. 13 shows an example of such a distribution for the sample annealed for 200 h. Initially, a small decrease of $<A_{pore}>$ with $T_a$ is observed. Some sintering of the YSZ ceramic evidently appears to take place initially. After 100 h annealing time the average pore size starts to increase again. It should be noted also that the pore sizes, determined from analysis of two-dimensional images, could be larger than the actual average pore size, if the variance of the pore size distribution is large [50]. Therefore, the performed image analysis of the SEM micrographs probably tends to overestimate the porosity to some extent.

The pore size distributions in the upper part of the TCs are similar for all samples and are dominated by the number of small pores ($A_{pore} < 0.01 \mu m^2$). However, a continuous increase of the number of large pores ($A_{pore} > 0.015 \mu m^2$) is observed with $T_a$. The number of large pores is close to zero in the as-deposited state, it increases to $0.4%$ after 50 h, to $1.1%$ after 100 h and to $6.1%$ after 200 h annealing. Large pores can be formed either through coalescence of initially isolated smaller pores or by nucleation and growth during the recrystallization of the TC. Schulz et al. [3] suggested that larger globular pores in annealed samples are formed via sintering of secondary micro-columns (feather-like arms). The intra-columnar porosity increases continuously with $T_a$ (Fig. 13).

3.5.2. Bond coat

The SEM micrographs show that in the as-deposited state, the microstructure of the investigated BC consists of finely intermixed $\gamma$ and $\beta$ grains (Fig. 14), similar to [17,18]. The compositions of the $\gamma$ and the $\beta$ phases in the as-deposited state (Table 1) are in good agreement.
with previous reports for NiCoCrAlY BC prepared by EB-PVD [18]. After annealing for 200 h the data in Table 1 show a small decrease of the Co concentration and a simultaneous small increase of the Ni concentration in both phases. These changes are probably due to interdiffusion between the BC and the superalloy substrate as well as due to the formation of the TGO. We cannot exclude the presence of some γ precipitates (Ni3Al with L12 structure) in the γ grains, as reported before using TEM [17,18]. However, TEM studies of the investigated BCS is beyond the goals of the present paper. A narrow layer (~4–5 μm), enriched in the γ phase (Al depletion), is observed for all samples close to the TGO/BC interface due to the formation of the TGO. The width of the DZ between the BC and the substrate increases from 4.9±0.6 μm in the as-deposited state to 6.6±0.6 μm after 50 h annealing and to 10.9±1.3 μm after 200 h annealing.

The fraction of the γ phase, determined from the image analysis, remains practically constant for all samples and is equal to 43.0±0.8%. The fraction of the β phase is correspondingly 57%, in good agreement with the results of Hasegawa and Kagawa [51] for their as-deposited APS BC.

Significant changes are observed in the microstructure of the investigated BC by SEM with increasing \( t_A \) (Fig. 14). An increasing number of needle-like γ grains, oriented approximately perpendicular to the TC/BC interface, are formed. The average grain size \( D_{\gamma} > A_{\gamma} \) of the γ phase increases continuously with \( t_A \) (Fig. 15). The standard deviations in \( D_{\gamma} > A_{\gamma} \) are relatively large due to the broad distribution of γ grain sizes observed (see the insert in Fig. 15). The data in Fig. 15 indicate that \( D_{\gamma} > A_{\gamma} \) increases, within error limits, linearly with \( t_A \), thus suggesting a reaction-controlled rather than diffusion-controlled growth [52] of the γ phase.

4. Discussion

4.1. Top coat

Different behaviour of \( E_{TC} \) and \( H_{TC} \) with annealing time was reported in the literature, as summarized in Section 1. The origin of these differences in the behaviour of \( E_{TC} \) is not well understood. One possible reason could be the different annealing temperatures \( T_A \) used, because surface and bulk diffusion increase rapidly with \( T_A \), thus enhancing the sintering of the individual columns at higher temperatures [53]. Indeed, \( T_A \) was chosen equal to 950° and 1050° C in [54], 1000° C in the present study, while \( T_A \geq 1100° C \) was selected in [6–8]. Previous studies on YSZ TCs show clearly that sintering via diffusion processes is enhanced at higher temperatures. SEM micrographs were taken in [8] on the polished top surface of EB-PVD TCs annealed for 100 h at \( T_A = 1200° C \) and at \( T_A = 1400° C \). At \( T_A = 1200° C \) the gaps between the columns are still clearly observed, while at \( T_A = 1400° C \) they disappear almost completely [8]. For our TCs, inter-columnar gaps on the polished top surface are clearly seen under optical microscope even after 200 h annealing. Both some intra-columnar pore closure (decrease of \( P_{\text{intra}} \)) and an intensive feather-arm broadening (increase of \( P_{\text{inter}} \)) was observed in [11] after 1 h annealing at \( T_A = 1000° C \). However, after annealing for 1 h at \( T_A = 1100° C \) severe closure of the feather-like micro-columns takes place [11]. High-temperature dilatometry measurements on APS zirconia-based TCs [55] also show that the shrinkage strain rates, arising from sintering effects, are very low at \( T_A = 1000° C \), but rapidly increase for \( T_A \geq 1100° C \). The results of Thompson et al. [56] show that \( E_{TC} \) of APS TCs is almost independent of \( t_A \) for \( T_A = 1000° C \), but it rapidly increases with \( t_A \) at \( T_A = 1300° C \) and 1400° C. These limited data from the literature demonstrate that enhanced sintering effects both in EB-PVD and APS TCs take place for \( T_A \geq 1100° C \). At \( T_A \geq 1100° C \) sintering is probably the dominant effect, which influences \( E_{TC} \). At lower temperatures of about 1000° C diffusion processes are slower, but changes in the pore size distribution and stress relaxation can also affect the apparent Young’s modulus.

Most generally, the Young’s modulus of EB-PVD TCs deposited on substrates will depend on both the residual stresses \( \sigma \) and the porosity \( P \). Experimentally, different behaviour of \( E_{TC} \) with \( \sigma \) or \( P \) has been reported. The global in-plane elastic modulus increases linearly with increasing compressive in-plane residual stresses [12]. On the other hand, Zhao and Xiao [13] reported a non-linear increase of the local Young’s modulus, measured by nanoindentation, with increasing compressive residual stresses. A non-linear decrease of \( E_{TC} \) for EB-PVD TCs with increasing total porosity was experimentally established in [57]. Theoretically, the Young’s modulus for an ideal elastic–plastic von Mises solid can be written as \( E = \sigma_Y / \varepsilon (\varepsilon / \varepsilon_Y)^{n} \), where \( n=0.5 \) is the strain-hardening exponent and \( \varepsilon_Y \) is the yield stress [58]. The functional dependence of \( E \) on \( \sigma \) for EB-PVD TCs, however, is to the best of our knowledge, not known.

Several phenomenological models for the relation between \( E \) and porosity (\( P \)) exist. The simplest theoretical relation is the so-called Spriggs equation [59]:

\[
E = E_0 \exp(-cP)
\]  

where \( E_0 \) is the Young’s modulus for the bulk material with zero porosity and \( c \) is a phenomenological material constant. Eq. (5) was extended to include quadratic terms in porosity [60]. \( E_0 \), for polycrystalline YSZ with zero porosity is ~220 ± 20 GPa [39]. The total porosity of the as-deposited TC, determined from density measurements, is about 20% [5]. Using Eq. (5), this gives a value \( c = 2.8 \) for the investigated TC in the as-
deposited state, consistent with values of \( c \) between 1.7 and 5.0, reported in [60]. Density measurements of annealed EB-PVD samples [61] show that the total porosity \( P_{\text{tot}} \) remains constant within error limits. This means that Eq. (5) with \( P = P_{\text{tot}} \) cannot rationalize the observed variation of \( E_{\text{TC}} \) with \( t_a \) (Fig. 9).

The SEM micrographs show that the nanoindentation impressions for \( F_{\text{max}} \leq 100 \text{ mN} \) are smaller than the average width of the YSZ columns (11 ± 4 \( \mu \text{m} \)). In many cases such indents lay within a single YSZ column (see Fig. 16). It seems reasonable to assume that the intra-columnar porosity rather than the total porosity, should be used in Eq. (5). However, Eq. (5) with \( P = <P_{\text{intra}}> \) also cannot explain the observed variation of \( E_{\text{TC}} \) with \( t_a \) (Fig. 13), while \( E_{\text{TC}} \) shows a maximum at about 100 h independent of the maximum indentation load (Fig. 9).

The SEM micrographs of nanoindentation impressions on cross-sections show also different number of pores and micro cracks beneath the indenter. Comparing the corresponding Young’s moduli, the following new empirical equation is proposed:

\[
E = E^*(\sigma)\left[1 - \eta <A_{\text{pore}}>\right]
\]

where the Young’s modulus \( E^* \) is generally stress-dependent and the coefficient \( \eta \) depends on the density of pores beneath the indenter.

**Fig. 14.** SEM micrographs of the BCs in cross-sections.

**Fig. 15.** Variation with \( t_a \) of the average grain size of the \( \gamma \) phase \(<D_\gamma>\). The inset shows the area distribution of the \( \gamma \)-grains for the as-deposited sample.

**Fig. 16.** SEM micrograph of a nanoindentation impression on the TC for which \( E = 166 \text{ GPa} \).
The Young’s modulus data for the investigated TCs, measured on cross sections with \( F_{\text{max}} \leq 100 \text{ mN} \), are plotted as a function of \(<A_{\text{pore}}>\) in Fig. 17. A linear fit with Eq. (6) gives \( E' = 250 \pm 10 \text{ GPa} \) and \( \eta = 150 \pm 5 \mu \text{m}^{-2} \). The derived \( E' \) value is slightly bigger than \( E_o \) for bulk YSZ with zero porosity \( (220 \pm 20 \text{ GPa}) \), probably due to the presence of residual stresses, in the investigated TCs, which could lead to an increase of the apparent Young’s modulus [12,13,19].

4.2. Bond coat

The variations of \( E_{\text{BC}} \) and \( E_{\text{TC}} \) with annealing time are very similar (Fig. 9). The results obtained in Section 3.4 indicate that the presence of residual stresses in the TC + BC layer system is probably one of the main reasons for this correlation. Indeed, the XRD and Raman spectroscopy measurements given in Figs. 5 and 8 both show that stress relaxation takes place in the surface layer of the TC. It may be expected that some reduction of the residual stresses in the TC near the TC/BC interface and in the BC takes place as well. This might contribute to the observed decrease of \( E_{\text{BC}} \) and \( H_{\text{BC}} \) for \( t_A \geq 50\text{–}100 \text{ h} \). However, direct measurements of the residual stresses in the BC for annealed TBCs would be rather difficult even using neutron diffraction, which is a well-established method for determination of residual stresses deep inside the material [62], due to the relatively small thickness of the BC compared to the TC.

BCs without TCs should be free of residual stresses arising from the mismatch in the thermal expansion coefficients between the TC and the BC. Correspondingly, their Young’s moduli should be generally lower than that of BCs with adherent TCs and should have different \( t_A \) dependence, as has been experimentally observed (Fig. 10).

Finite element modelling of nanoindentation experiments with sharp indenters, assuming ideal linear elastic, perfect plastic material behaviour, have shown that the ratio \( (h_{\text{max}} - h_i)/h_{\text{max}} \) is very sensitive to the presence of residual stresses [58,63]. According to these authors, the \( (h_{\text{max}} - h_i)/h_{\text{max}} \) ratio decreases with decreasing compressive residual stresses. A small decrease of this ratio for the BCs from 0.24 \pm 0.01 in the as-deposited state to 0.20 \pm 0.01 after 200 h annealing is observed in the BC + TC samples. At the same time the \( (h_{\text{max}} - h_i)/h_{\text{max}} \) ratio remains equal to 0.20 \pm 0.01, independent of the annealing time, for the BC samples without TCs. This comparison also suggests that some relaxation of the residual stresses in the BC + TC system takes place with annealing time.

The changes in the microstructure of the BC (Fig. 14) might also lead to changes in the BC mechanical properties. Fig. 18 shows several nanoindentation impressions (\( F_{\text{max}} = 50 \text{ mN} \)) on the BC annealed for 200 h. The average area of these impressions is about \( 12 \pm 2 \mu \text{m}^2 \) and encompasses 2–3 \( \beta \)- and \( \gamma \)-grains. Therefore, the \( E_{\text{BC}} \) and \( H_{\text{BC}} \) values derived from such nanoindentation measurements represent average \( \beta + \gamma \) values. The grain sizes of the \( \gamma \)- and the \( \beta \)-phases increase with increasing \( t_A \) (see Figs. 14 and 15). It may be expected that the probability of sampling individual \( \gamma \)- or \( \beta \)-grains increases. But the Young’s moduli of bulk \( \gamma \)-Ni and \( \beta \)-NiAl at RT are similar (\( E_{\gamma\text{-Ni}} = 220 \text{ GPa} \) [64]; \( E_{\beta\text{-NiAl}} = 199 \text{ GPa} \) [65]; \( E_{\gamma\text{-NiAl}} = 188 \text{ GPa} \) [66]; \( E_{\beta\text{-NiAl}} = 196 \pm 14 \text{ GPa} \) [67]). Therefore, the differences between the mechanical properties of the \( \beta \) and the \( \gamma \) phases alone cannot account for the observed changes in the mechanical properties of the BC with \( t_A \).

More important, however, is the general effect of grain sizes on the hardness of the BC. In conventional polycrystalline materials, \( \sigma_f \) is known to increase with decreasing grain size \( D \): \( \sigma_f = \sigma_{\text{YSW}} + k_D^\beta \) [68,69]. Since the hardness \( H \) is usually proportional to \( \sigma_f \) [70], it is expected that \( H \) will also increase with decreasing \( D \). In our samples, the grain size of the \( \gamma \)-phase increases with \( t_A \) (see Figs. 14 and 15).

According to the Hall–Petch relation, \( H_{\text{BC}} \) of the TC + BC samples should decrease with \( t_A \), as observed experimentally for \( t_A > 50 \text{ h} \) (Fig. 10b). Evidently, both the Hall–Petch effect and the stress relaxation contribute to the decrease of \( H_{\text{BC}} \) for \( t_A > 50 \text{ h} \) in the presence of TCs. Interestingly, the hardness of the BC samples without TC exhibits a slight increase with increasing annealing time. Correlations between the BC grain sizes in these samples and their mechanical properties will be the subject of a future study.

5. Summary and conclusions

Changes in the microstructure of EB-PVD deposited YSZ top coat and NiCrCoAlY bond coat specimens resulting from isothermal annealing at \( T_A = 1000 \text{ °C} \) in air have been studied and correlated with their mechanical properties (Young’s modulus and hardness), measured by nanoindentation at room temperature.

The nanoindentation experiments on cross-sections of the TC show interestingly an initial increase of the Young’s modulus and the hardness with annealing time followed by a decrease after 100 h annealing. The mechanical anisotropy of the TC decreases with increasing annealing time.

The heat treatment leads to changes in the intra-columnar porosity and the width of gaps between the single-crystal columns. The number of large intra-columnar pores (\( A_{\text{pore}} > 0.015 \mu \text{m}^2 \)) in the upper part of the TC increases continuously with \( t_A \), as determined by image analyses. Diffusion processes take place during thermal treatment, which result in a material redistribution with a reduction of the pore surface area [10]. This is accomplished by simultaneous healing of small pores, bridging of small cracks, growth of large pores and widening of the gaps between the columns, leading to a complex

![Fig. 17. Variation of \( E_{\text{TC}} \) with \(<A_{\text{pore}}>\). The dashed line is a linear fit with Eq. (6).](image-url)
dependence of the average intra-columnar pore size on the annealing time.

A new empirical equation, which relates the Young's modulus of the TC, measured on cross-sections, and the average intra-columnar pore area, is proposed. The evolution of the Young's modulus of the TC with annealing time is well rationalized by this model. However, the Young's modulus of the TC, extrapolated using this model down to zero intra-columnar-pore area, exceeds the value for the bulk material. This indicates that residual stresses in the TC have to be considered, which could lead to an increase of the apparent Young's modulus of the TC.

Residual stress measurements by both XRD and Raman spectroscopy revealed a stress relaxation with increasing annealing time and the presence of shear stresses in the surface layer of the TC. The relaxation of the residual stresses can be tentatively explained by widening of the gaps between the columns and reorientation of the grains near the TC surface, as observed by XRD texture measurements. This indicates that residual stresses in the TC have to be considered, which could lead to an increase of the apparent Young's modulus of the TC.

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