



Characterisation of APS TBC system during isothermal oxidation at 1100°C

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ABSTRACT

Purpose: The purpose of presented investigations was metallographical characterization of failure modes of air plasma sprayed thermal barrier coatings system in isothermal oxidation test conditions at 1100°C.

Design/methodology/approach: The research allowed the characterization of microstructural changes during oxidation test of zirconia coating in area of ceramic top-layer, bond coat and superalloy substrate. The examinations were conducted on TBC's specimens after 50, 120, 500, 1000, 1500 and 2000h of exposition and encompassed a microstructural analysis with the use of macro and micro investigation - LM, SEM microscopy.

Findings: It was found that the durability of commercially quality TBC system is related to progress of degradation modes of bond coat and top layer. During isothermal oxidation test, the bond coat was oxidized to form of a dens alumina and a porous mixed oxide layer between the top coat of YSZ and bond coat of NiCoCrAlY alloy. At the moment of oxidation acceleration, the process of cracks initiation and propagation was observed mainly in the mixed oxide layer near the YSZ. The observed crack propagation induced the delamination and spallation of top coat after 1000h oxidation.

Research limitations/implications: The discussed research showed that main reason of degradation in TBC system is related to development of cracks at the interface between thermally grown oxide and bond coat, within the top coat or at its interface with TGO.

Practical implications: The results allow the determination of the degree of durability lost of the thermal barrier coating system and specification of the time of safety operation.

Originality/value: The obtained results are valuable contribution to characterization of TBC systems. They enable the identification of the degradation mechanisms, which enhances the durability and safety of high temperature operation.

Keywords: Thin&thick coatings; TBC; Degradation; Oxidation

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

In the last ten years, the development and manufacturing of ceramic TBCs on turbine parts have been the focus of the research on account of the traditional turbine materials being insufficiently thermally strong for further technological development. To improve the heat resistance, thermal barrier coatings (TBCs) are employed on the surface of high temperature superalloy

substrates. TBCs have been extensively employed in hot-section metal components of gas turbines for two purposes: the increase of the inlet temperature (which, consequently, improves the efficiency) or the reduction of the demand for the cooling air [1–10]. Generally, the TBC applied in gas turbines is made up of two components: a bond coat created by the vacuum or low pressure plasma-sprayed MCrAlY (M = Ni, Co) and a top coat of yttria and partially stabilized zirconia produced by the atmospheric plasma spraying or electron beam-physical vapour deposition

(EB-PVD) [11,12]. A typical superalloy/TBC system consists of plasma-sprayed zirconia-yttria ceramic layer with a nickel-chromium-aluminum-yttrium bond coat on a substrate made of nickel-based superalloy. These superalloy/TBC systems can be applied in both aerospace and land-based gas turbine engines. In automotive use, the piston head for diesel engine is coated to enhance lifetime and performance as far as fuel demand reduction and power improvement are concerned.

These coatings, nevertheless, exhibit relatively short lifetime, which is the result of the applied material and thermal contrast between the coating and the base metal. Thermal residual stresses occur in TBC/metallic substrate during cooling from the temperature of processing. Environmental effects, specifically oxidation, create additional residual stresses as the oxide layer grows, resulting in additional material mismatch between the oxide surface and the TBC. These residual stresses could originate micro-cracks including debonding and radial cracks, deeply affect the response of the TBC and cause interfacial damage accumulation and failure. Their understanding is fundamental for the prediction of the functioning of the coatings and their performance [13].

The bond coat seems to be the key element of the TBC system [14]. Its chemistry and microstructure modify the durability of the system via both the structure and the morphology of TGO created during the oxidation. What is more, the performance also appears to be connected to its creep and yield features. There are two categories of barrier coatings: NiCoCrAlY-system-based coatings and Pt-modified diffusion aluminide coatings. The link between BC and TGO, whose morphology is altered in service, is another essential factor: typically, the interfacial zone is subject to a great amount of stress, which results from oxide condensation, thermal expansion mismatch and applied loads. Consequently, a crack can be generated and propagated, which results in the ceramic layer spalling off, inducing the degradation of the system [15].

2. Description of experiments, methodology and materials.

In the present study, Ni-base superalloy In 738 was employed as a substrate material for the TBC system. Amdry 365-2 powder was first applied by plasma spraying to form the bond coat, which was to serve as an adhesive plus bonding factor and as a corrosion resistance enhancer for the TBC. Finally, Metco 204B-NS zirconia powder (stabilized with 8 wt.% yttria) was plasma-sprayed on the bond coat as ceramic top-coat. APS method with regular plasma-spray parameters was employed for the preparation of the samples (3 cm-long rolls, measuring 1,5 cm in diameter). The nominal thickness of all bond coatings was 120 μ m and the thickness of the ceramic top layer was identical as well: circa 500 μ m. [16]

Amdry 365-2 bond coat powder was composed of Ni23%Co17%Cr12.5%Al0.45%Y (wt.%). The isothermal oxidation test of the samples, which was done in air at 1150°C, lasted for 50, 120, 500, 1000, 1500 and 2000h.

3. Description of achieved results of own researches

3.1. Characterization of Amdry 365-2 and Metco 204B-NS powder

Results of XRD investigations of bond coat powder's showed that NiAl phase modified by Co - Al(Ni,Co) and phase on the base Ni - Ni(Cr,Y) type were predominant in initial condition (Fig.1). The quantitative analysis proves that contribution of aluminide phase is ca. 60%. SEM microphotographs of NiCoCrAlY powder (Fig.2) and microprobe analysis of chemical composition showed that powder shape is generally nearing to sphere with small effect of conglomeration. Analysis of chemical composition in micro-areas do not showed in principle the presence of contaminations (Tab.1).

X-ray diffraction of ceramic powder in initial conditions as well proved the presents of zirconia in three crystallographic form: monoclinic, tetragonal and cubic. The quantitative investigations give the possibility of estimation of capacity of monoclinic zirconia and other phases (Fig.3).

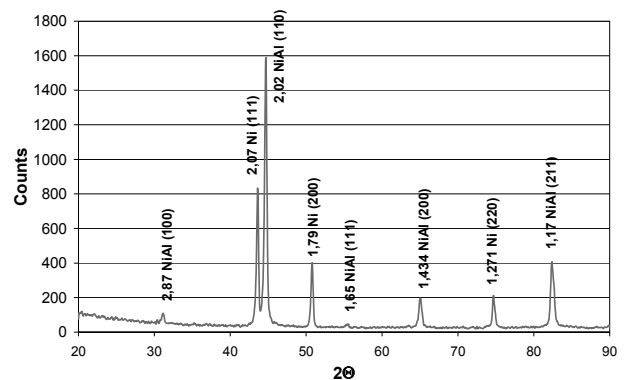


Fig. 1. X-ray diffraction analysis of powder Amdry 365-2 in initial conditions

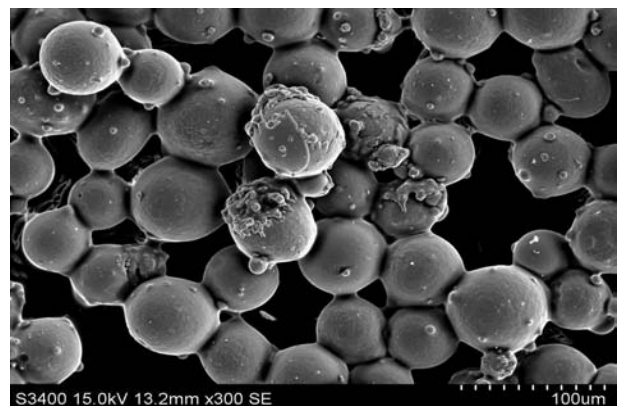


Fig. 2. Morphology of Amdry 365-2 powder

Table 1. Results of chemical composition in marked micro-area from Amdry 365-2 powder

	Al	Cr	Co	Ni	Y
% at.	18.83	20.60	21.50	38.78	0.29
% wt.	9.87	20.80	24.61	44.22	0.50

In the case of Metco 204B-NS powder the contribution of monoclinic ZrO₂ was 7,5%, cubic – 37% and tetragonal 55%.

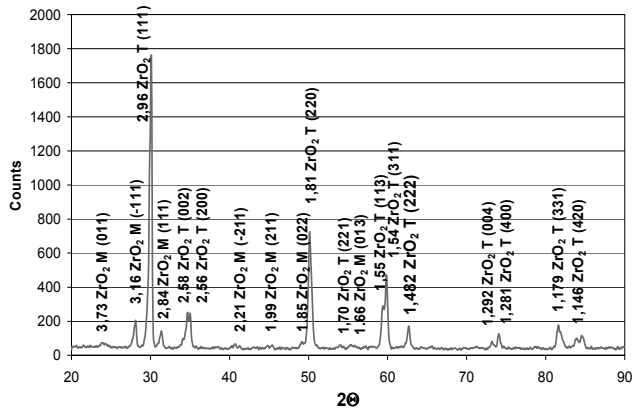


Fig. 3. X-ray diffraction analysis of powder Metco 204NS in initial conditions

SEM microphotography of Metco 204B-NS ceramic powder (Fig.4) exhibit in generally nearing to sphere shape of powder with small effect of conglomeration.

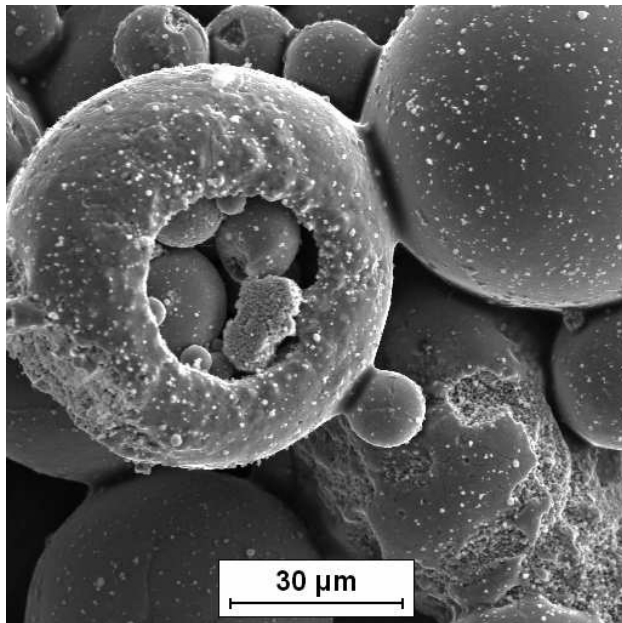


Fig. 4. Morphology of Metco 204B-NS powder

3.2. Characterization of as-sprayed TBC system

X-ray diffraction of as-sprayed ceramic top layer detected the presents of primarily of a tetragonal ZrO₂ phase, with minor amounts of cubic and monoclinic phases (Fig.5).

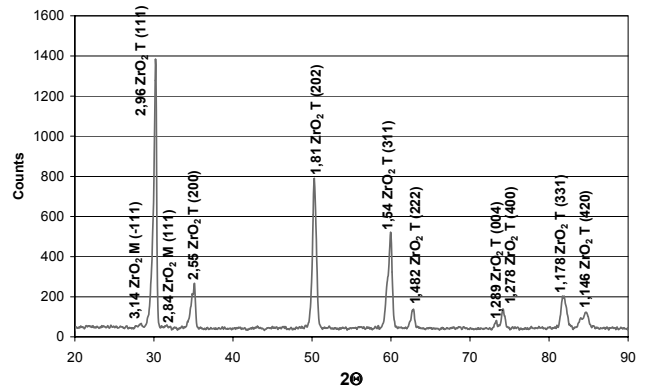


Fig. 5. X-ray diffraction analysis of powder Metco 204B-NS as-spray condition

The TBC system in as-spray condition are shown in (Fig. 6 and 7). Figure 6 presents an air plasma sprayed coating with layered structure of ceramic top coat and inner bond coat. The thickness of ceramic layer was ca. 550 μm and was very similar on the all surface of the specimen. The thickness of bond coat was ca. 130 μm. The typical microstructure of the plasma sprayed YSZ could be seen with pores, lamellae boundaries and micro-cracks. The metallography of the as-sprayed NiCoCrAlY bond revealed a dense, non-homogeneous coating structure containing visible splat boundaries and very small interlamellar porosity, isolated spherical internal porosity, and non-uniform dispersion of Y₂O₃ and Al₂O₃ (Fig.7). Total porosity of the ceramic top layer and bond coat were evaluated by image analysis from the polished cross section.

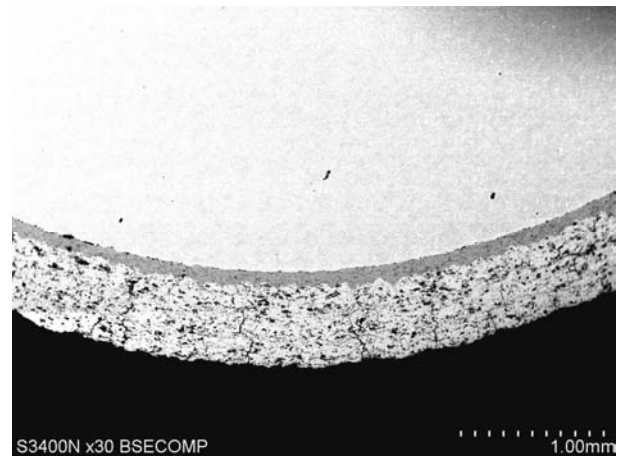


Fig. 6. General view of the TBC system in before the oxidation

In initial condition of TBC's total porosity was ca. 0,9%. The details of ceramic top coat showed pores and probably vertical segmentation crack are present on Fig. 8.

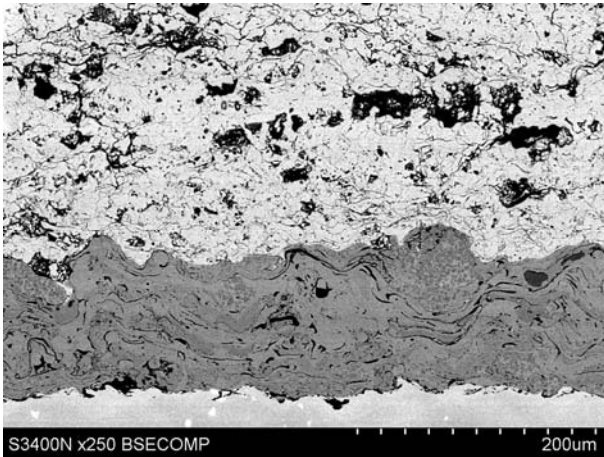


Fig. 7. Optical microstructure of the investigated TBCs

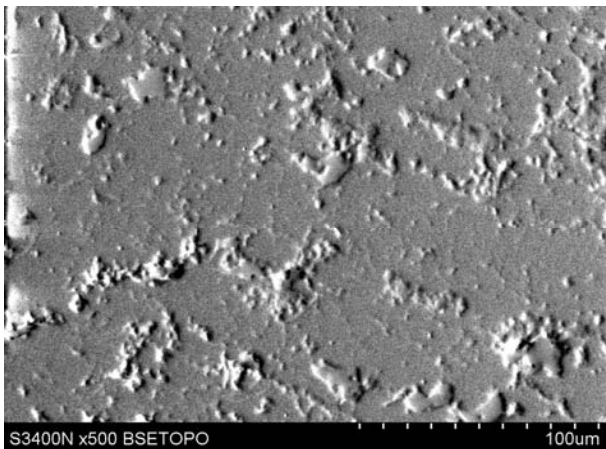
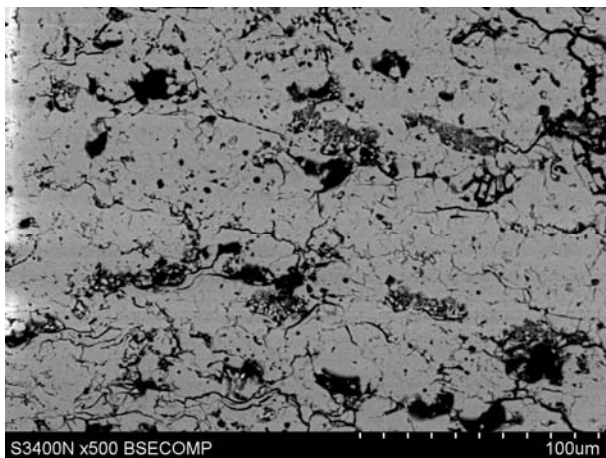


Fig. 8. Details of microstructure if TBCs in initial conditions – porosity and micro cracks

The use of BSETOPO method permitted on clear distinction porosity as well as cracks. Comparing both pictures, some of cracks seem to be inequivalence.

Figure 9 shows the failure progress of TBC's during isothermal conditions. The failure nature is different in different time of test. There is not observed macro-degradation effect after first 500h of exposure.

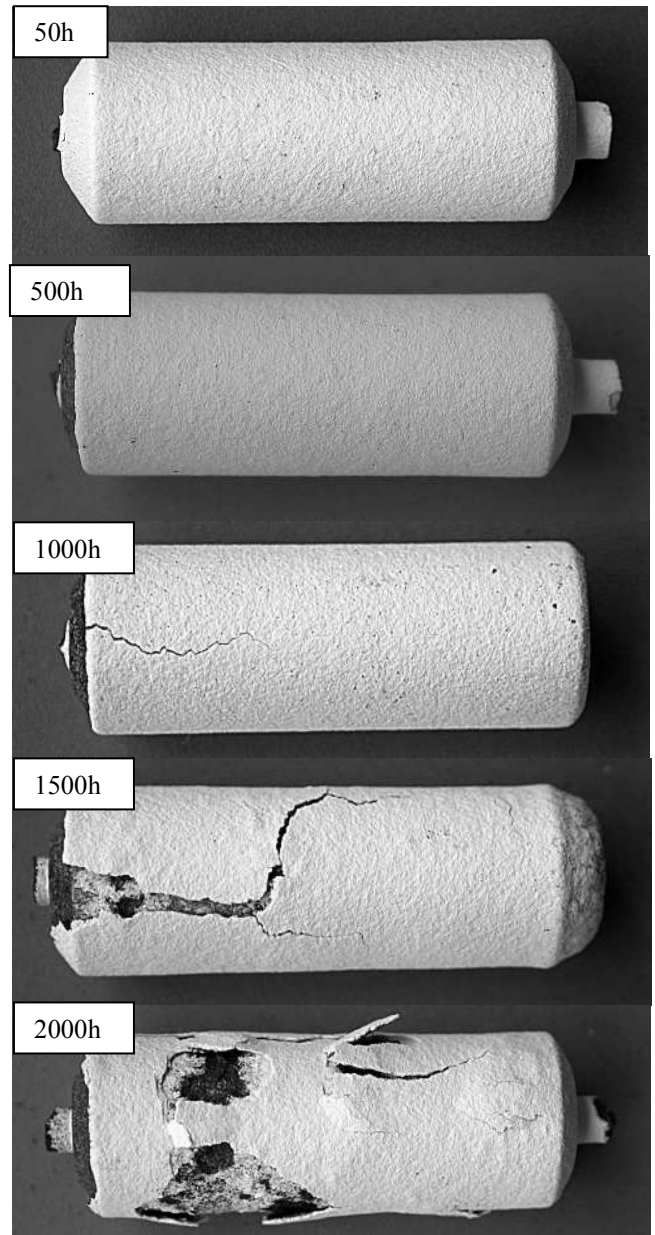


Fig. 9. General view of specimens with TBCs after each stage of isothermal oxidation at 1100°C

The most remarkable differences is observed from 1000 to 2000h of oxidation test. After 1000h the final failure appears by macro- cracking starting from edge of the ceramic top coat but

still larger areas of the TBC system are adherent. This type of crack formation is more typical for cyclic oxidation test than oxidation in isothermal conditions. After longer time of exposure during in this conditions the failure occurred is related to partially (1500h) and nearing totally delamination and in consequence spallation of the top-coat.

Cross-sectional metallurgical investigations after 50h of oxidation (Fig.10) showed any important effect of cracks nucleation and delamination processes. The dark layer of TGO between ceramic layer and bond coat is dense with small amount of gray areas of oxides attached to the YSZ. After 50h of exposition the thickness of oxides in TGO is ca. 6µm.

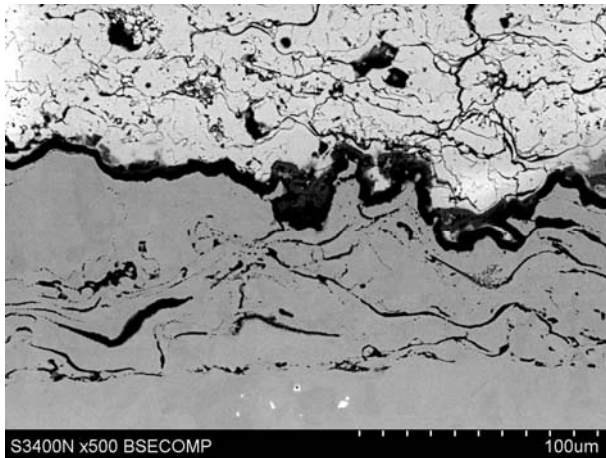


Fig. 10. Cross section of sample oxidized at 1100°C for 50h

After 120h of exposition dark layer of oxides in TGO became bigger then after 50h (Fig.11). The microanalysis of chemical composition of oxides areas in TGO showed that dense dark areas are rich in Al (the main component is Al_2O_3 , but in the gray oxides EDS showed presents of Al, Cr, Co and Ni. In this area exist probably mixed oxides such as Al_2O_3 , Cr_2O_3 and probably spinel $(Ni,Co)(Cr,Al)_2O_4$. Results of EDS analysis of oxide layer are presented in Tab.2.

Table 2. Results of EDS analysis from TGO oxides after 120h of exposition (wt.%).

	Al-K	Cr-K	Co-K	Ni-K	Zr-L
Gray oxides	19.62	26.99	16.46	25.61	11.32
Dark oxides	71.37	4.08	3.33	9.36	11.86

Prior the final failure, damages in the form of micro-cracks were observed in the area of TGO. All this cracks are oriented parallel to the interfaces BC-TGO-YSZ. The presents of micro-cracks and cracks in TGO led to oxygen penetration through the TGO and in consequence internal oxidation of in the bond coat were some areas of oxides were detected (Fig.11).

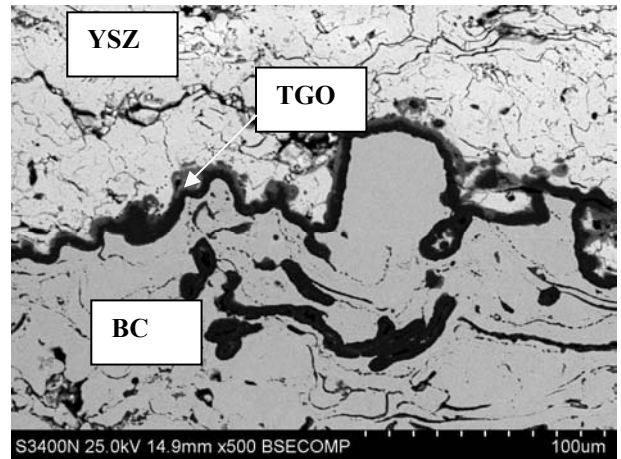


Fig. 11. Cross section of sample oxidized at 1100°C for 120h

The investigations of TBC system after 500h of oxidations in air showed initial stages of partially delamination effects in area of TGO and YSZ (Fig.12). In additions, the horizontal cracks are observed from top surface of ceramic to bond coat.

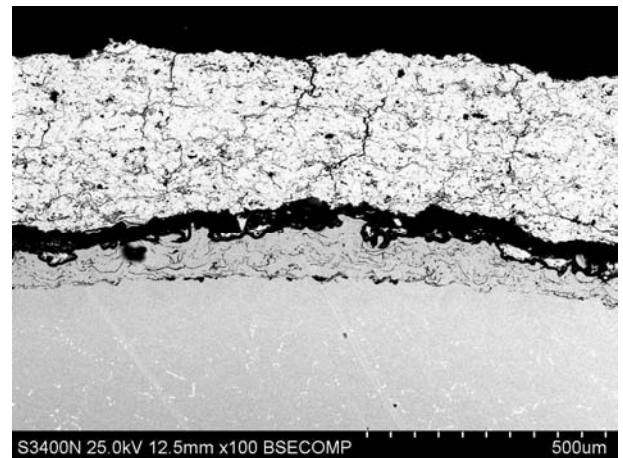


Fig. 12. Cross section of sample oxidized at 1100°C for 500h

The micro-cracks were either located within TGO or start in the TGO and subsequently penetrate into the zirconia top-coat (Fig.13). The main crack is formed in the TGO in the area of porous gray mixed oxides. This type of oxides dominated after 500h of exposition.

For longer exposure time of $t > 1000h$ the longer cracks in TGO area were observed. Cracks were parallel to the BC-TGO interface and analogical for earlier observations, their penetrate into zirconia top-coat (Fig.14 - 16). Metallographic examinations of cross section showed presents not only horizontal cracks but also long vertical macro-cracks especially in area of ceramic top-coat. Process of delamination was located generally in zirconia near TGO interfaces (Fig.17-19).

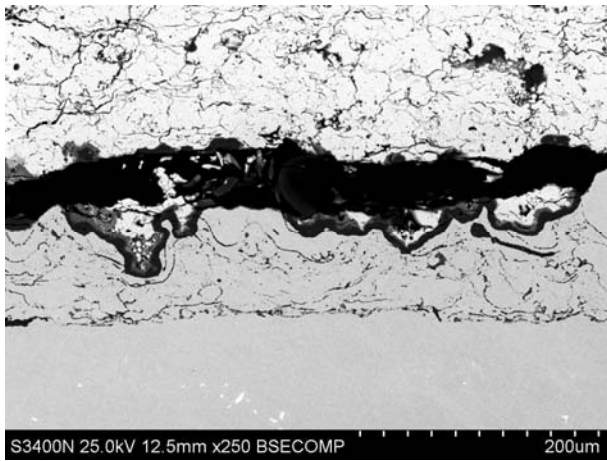


Fig. 13. Cross section of sample oxidized at 1100°C for 500h

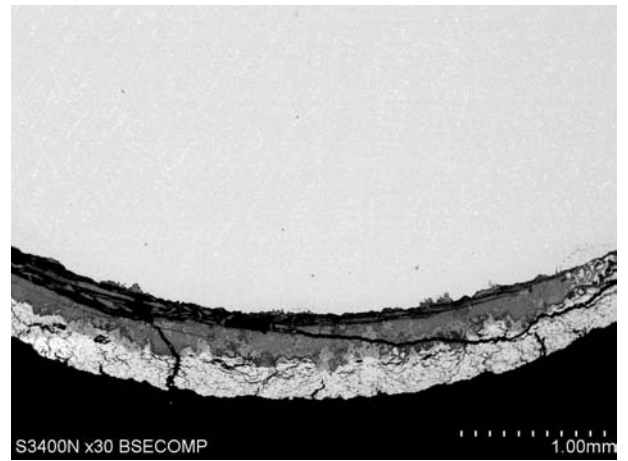


Fig. 16. Cross section of sample oxidized at 1100°C for 2000h

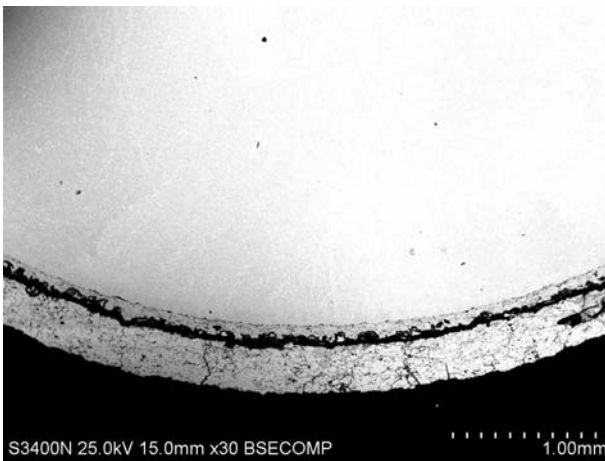


Fig. 14. Cross section of sample oxidized at 1100°C for 1000h

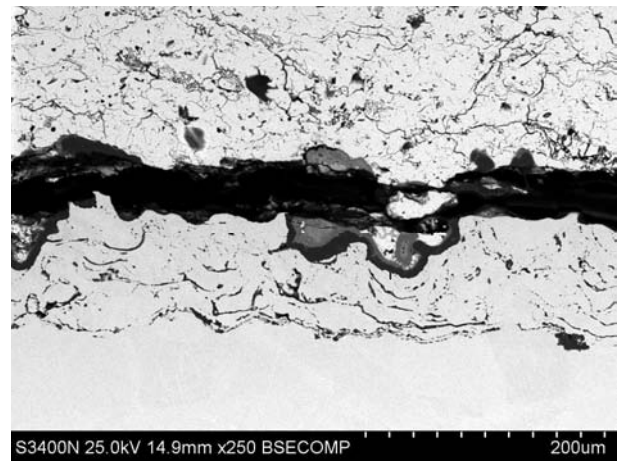


Fig. 17. Detail from Fig.14

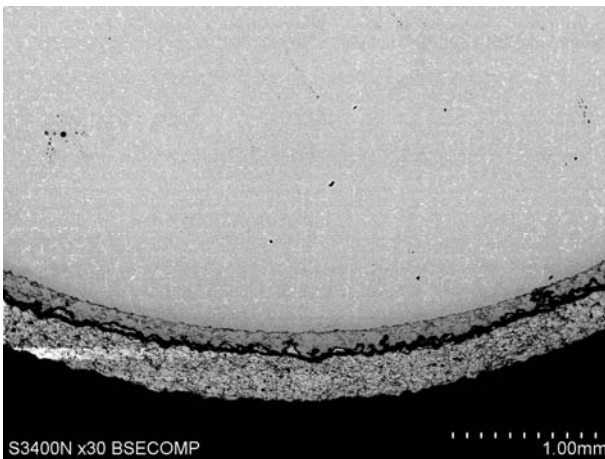


Fig. 15. Cross section of sample oxidized at 1100°C for 1500h

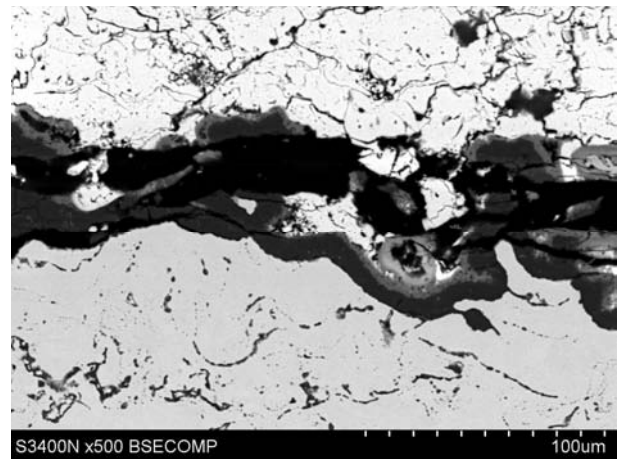


Fig. 18. Detail from Fig.15

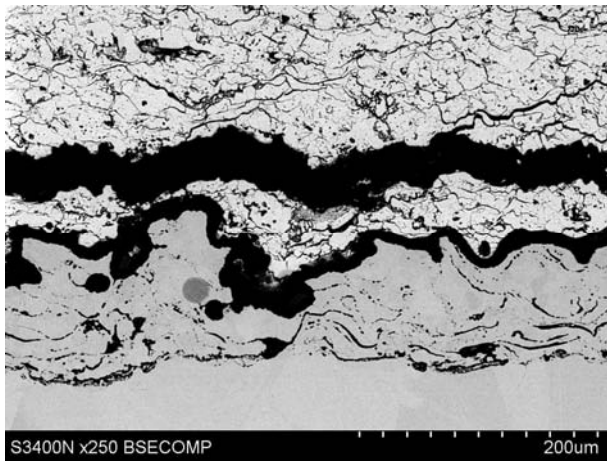


Fig. 19. Detail from Fig.16

EDS analysis of oxides in TGO after 2000h and others times of oxidations showed that in this area dominated two types of oxides: dark on the base of Al_2O_3 and gray probably on the base spinel $(Ni,Co)(Cr,Al)_2O_4$ (Fig.20).

The oxidation kinetics of TBC was determined by measuring the thickness of the TGO as a function of square root of oxidation time (Fig.21). The oxidation rate followed the parabolic law for up to 500h. This stable state of oxidation is due to protective influence of TGO, because its growth rate was quite low. At longer time of exposure oxidation led to a substantial increase in the TGO growth rate and in consequence in thickness, but it appeared that the oxidation rate still followed the parabolic law with high oxidation rate constant.

3.3. Summary

The degradation air plasma-sprayed thermal barrier coating resulting from high temperature (1100°C) was measured.

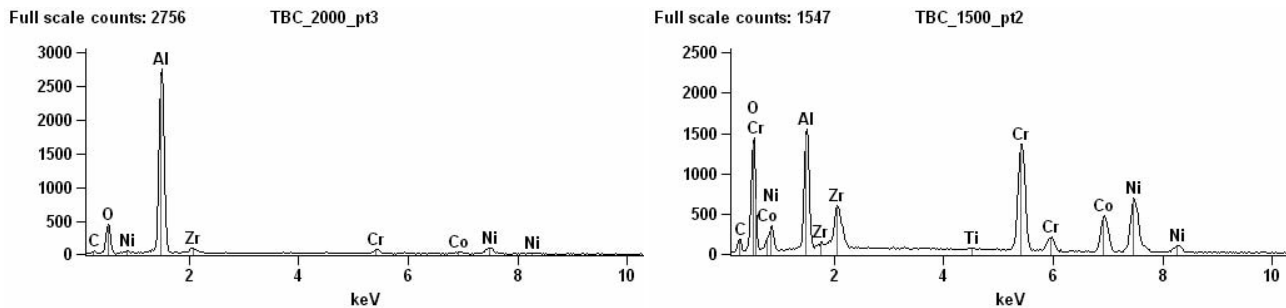


Fig. 20. EDS results from gray and dark oxides in TGO after 2000h of exposition at 1100°C

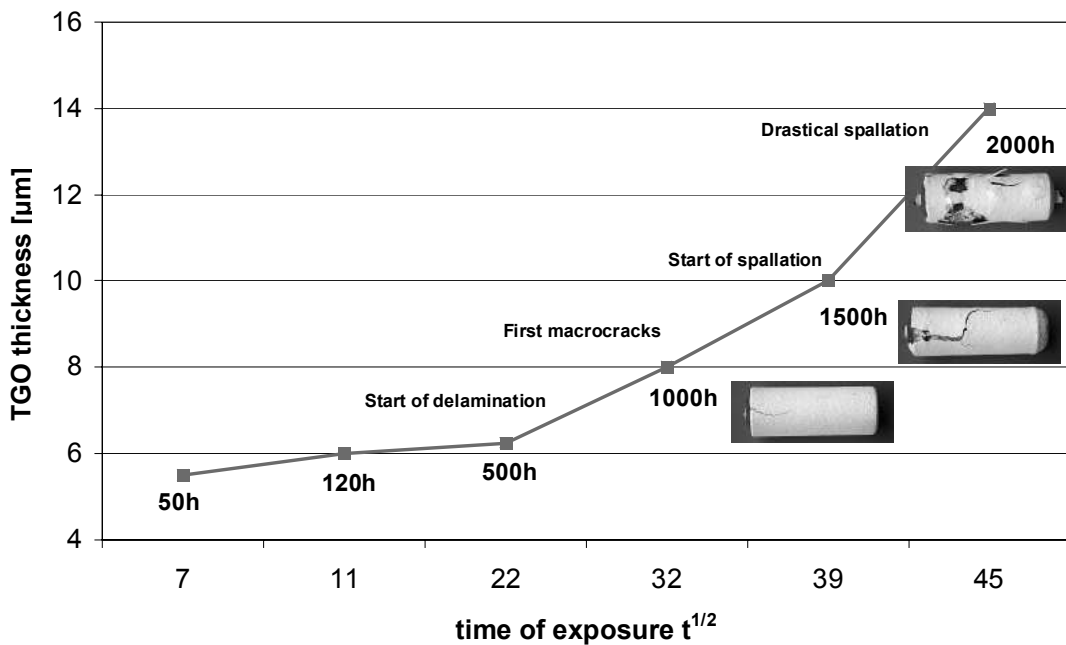


Fig. 21. Scale thickness vs. oxidation time for TBC system oxidized in air at 1100°C

During 2000h of isothermal oxidation testing in air, the first notable degradation effects of TBC were detected after 500h of exposure. This degradation seems to be connected to micro-cracking in TGO area and, consequently, with local delamination on interface between TGO and ceramic top-layer. At this stage alumina was formed, originally netted to the NiCoCrAlY sublayer. A mixed grey oxides layer, presumably consisting of chromia and (Ni,Co)(Cr,Al)₂O₄ spinel was created nearby zirconia at the time of subsequent oxidation. The thickness of the oxide sublayer grew proportionally to the time of oxidation progress.

The examination after 1000h of exposure revealed a noticeable effect of macro-cracks and, following that, a local and full effect of spallation of the ceramic top-coat. This effect is resulted from the increasing oxidation ratio, primarily restrained by the diffusion through the alumina, then limited by the diffusion through the mixed oxide. The significant growth in the oxidation speed caused the creation of micro-cracks in the TGO area, followed by their development into vertical and horizontal cracks and, consequently, their conversion into macro-cracks, delamination and finally spallation of top-layer.

4. Conclusions

- A top coat Metco 204B-NS together with Amdry 365-2 can be effectively coated on the surface of basic superalloy compound by APS method.
- The quality of ceramic sub-layer, bond coat and interfaces between them and substrate are satisfactory. Mechanical bonding strength between coating and matrix is quite good.
- Oxidation test showed that oxidation resistance of basic alloy was improved.
- The main mode of air plasma spraying TBC's degradation appears to result from thermal expansion misfit strains and interfacial oxide scale development, which are the dominant mechanisms leading to the failure of TBC system by spallation of the YSZ top coat.
- Crack initiation and propagation in the TGO layer were also discovered to cause the failure of thermal barrier coating system.
- A substantial degree of degradation was observed after 500h of exposition, following the pattern: the initiation of delamination; 1000h- macrocracks in the top-surface layer; 1500h – partial spallation of zirconia, 2000h – total spallation of the top-coat.

Acknowledgements

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