

MICROSTRUCTURAL CHARACTERIZATION OF THERMAL BARRIER COATING ON INCONEL 617 AFTER HIGH TEMPERATURE OXIDATION

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Abstract

A turbine blade was protected against high temperature corrosion and oxidation by thermal barrier coatings (TBCs) using atmospheric plasma spraying technique (APS) on a Ni-based superalloy (Inconel 617). The coatings (NiCr6AlY/YSZ and NiCr10AlY/YSZ) consist of laminar structure with substantial interconnected porosity transferred oxygen from Yttria stabilized Zirconia (YSZ) layer toward the bond coat (NiCrAlY). Hence, a thermally grown oxide layer (TGO) was formed on the metallic bond coat and internal oxidation of the bond coat occurred during oxidation. The TBC systems were oxidized in a normal electrically heated furnace at 1150 °C for 18, 22, 26, 32 and 40h. Microstructural characterization of coatings demonstrated that the growth of the TGO layer on the nickel alloy with 6wt. % Al is more rapid than TGO with 10wt. % Al. In addition, many micro-cracks were observed at the interface of NiCr6AlY/YSZ. X-ray diffraction analysis (XRD) showed the existence of detrimental oxides such as NiCr₂O₄, NiCrO₃ and NiCrO₄ in the bond coat containing 6wt. % Al, accompanied by rapid volume expansion causing the destruction of TBC. In contrast, in the bond coat with 10wt. % Al, NiO, Al₂O₃ and Cr₂O₃ oxides were formed while very low volume expansion occurred. The oxygen could not penetrate into the TGO layer of bond coat with 10 wt. % Al during high temperature oxidation and the detrimental oxides were not

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extensively formed within the bond coat as more oxygen was needed. The YSZ with higher Al content showed higher oxidation resistance.

Keywords: Oxidation; Atmospheric plasma spray; NiCrAlY; TGO and YSZ.

Introduction

Thermal barrier coatings (TBCs) have been extensively applied on nickel based superalloys to improve the efficiency and durability of hot section components of gas turbines. A typical TBC system consists of a thermally insulating ceramic top-coat (yttria stabilized Zirconia (YSZ) layer) and an oxidation-resistant metallic bond coat on the nickel-based superalloy substrates. (Ni, Co) CrAlY is usually utilized as a bond coat to provide a suitable thermal expansion match between the topcoat and the substrate and to protect the substrate from rapid oxidation and hot corrosion [1]. Applying MCrAlY bond coating at high temperature causes the transfer of oxygen from the topcoat to the bond coat; so an oxide scale can be formed on the bond coat designated as thermally grown oxide (TGO). Although this scale protects the substrate against further oxidation, the growth of TGO during thermal cycling can lead to failure of the yttria stabilized Zirconia (YSZ) layer [2, 3].

Two mechanisms have been proposed for transferring oxygen from the plasma sprayed Zirconia coatings. Ionic diffusion from the crystalline structure of ZrO_2 and gas penetration through some porosity and micro cracks are the main mechanisms [4]. The thickness of TGO layer can be increased during the oxidation process. This can produce stress at the interface of the bond coat and the ceramic layer. This stress is higher than the strain tolerance of MCrAlY bond coating, causing delamination of the coating at the interface of bond coat and YSZ layer [5]. There are some studies about the bond coatings applying different percentages of aluminum [6,7]. It was found that a bond coating with low aluminum content cannot be utilized as a protective coating at high temperature, while the coatings prepared with a higher percentage of Al showed better oxidation behavior. This favorable oxidation performance can be mainly attributed to the microstructure of coating [6]. It can be said that a homogeneous adhesive TGO layer on the bond coat is the main cause of this behavior. In addition, the TGO layer protects the coating from rapid oxidation and avoids the formation of detrimental oxides [7-10]. However, the ever-increasing requirement of a higher operating temperature for better efficiency of the turbine blades gives a strong support to investigate new compositions. It is generally considered that the YSZ is transparent to oxygen due to lattice diffusion and the multitude of connected cracks. Therefore, it would be considered that the YSZ does not hinder oxygen attacking the bond coat.

The aim of this study is to reduce the thickness of TGO layer and decrease the detrimental oxides using NiCr(x)AlY layer. Two TBC systems (NiCr6AlY/YSZ and NiCr10AlY/YSZ) were oxidized in a normal electrical furnace at 1150°C for 22 and 40h. This study is also focused on the development of a new coating combination while plasma spray technique is applied as the coating process. Microstructural changes in TBC surfaces were examined using scanning electron microscopy (SEM), X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-Ray analysis (EDS).

Experimental procedure

Materials

A nickel-based superalloy (Inconel 617) disc of 30×5mm, grit blasted with alumina particles was used as substrate. Two powders were used as bond coatings and had the composition of Ni-22 (wt. %) Cr-10 (wt. %) Al-1 (wt. %) Y (with an average grain size of 57 μm) and Ni-25 (wt. %) Cr-6 (wt. %) Al-0.4 (wt. %) Y (with an average grain size of 55 μm). For the thermal barrier coating ZrO₂-8%Y₂O₃ (with an average grain size of 33 μm) was utilized.

Coating preparation

NiCr6AlY/YSZ and NiCr10AlY/YSZ coatings were generated applying atmospheric plasma spray (APS) method. Tables 1 and 2 show the characteristics of the coatings and the parameters of atmospheric plasma spraying process, respectively.

Table 1. Details of two different YSZ thermal barrier coating compositions on Inconel 617.

TBC	Layer thickness (μm)	
	NiCrAlY	Yittria stabilized Zirconia
NiCr10AlY/YSZ	110	260
NiCr6AlY/YSZ	120	250

Table 2. Parameters of air plasma spraying.

Parameter	Unit	NiCr(x)AlY	YSZ
Current	A	450	550
Voltage	V	50	70
Primary gas, Ar	l/min	85	38
Secondary gas, H ₂	l/min	15	17
Powder feed rate	g/min	15	35
Spray distance	cm	15	7.5

High temperature oxidation test and microstructural characterization

The coatings were inserted in an electric furnace with air atmosphere at 1150°C for 18, 22, 26, 32 and 40 h. Microstructural characterization of the coatings was performed before and after oxidation by field emission electron microscope (Hitachi S-4160), scanning electron microscope (Japan, JSM-7100F) equipped with energy dispersive spectrometer (EDS). The surface of bond coatings, without YSZ layer, after oxidation was investigated using X-ray diffraction (XRD) for determining the crystalline structure of the oxide scales.

Results and discussion

Fig.1 shows cross section of two TBC systems of metallic bond coat (NiCrAlY) and the ceramic top layer (YSZ) on the surface of Inconel 617 before oxidation. All of

the coatings exhibit a layered structure as a main characteristic of the plasma sprayed coating.

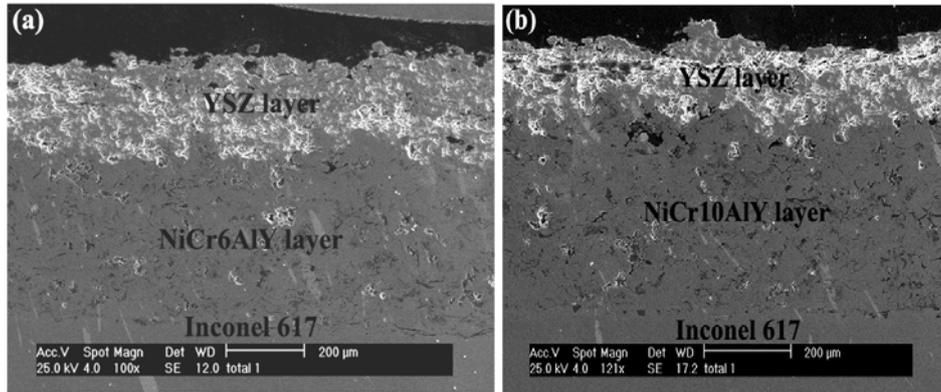


Fig.1. SEM images of TBC surfaces prepared by APS; (a) NiCr6AlY/YSZ and (b) NiCr10AlY/YSZ.

Fig.2 shows cross section of TBC systems after high temperature oxidation test at 1150 °C for 40h. It can be inferred that the oxygen was easily penetrated through the YSZ layer through pores and micro-cracks of YSZ towards the bond coat causing the formation of oxide scale on the surface of bond coat. The internal oxidation was occurred in NiCrAlY layer during oxidation. The oxygen diffused into the bond coat because of the existence of micro-cracks in the TGO and interconnected porosity in the NiCrAlY layers.

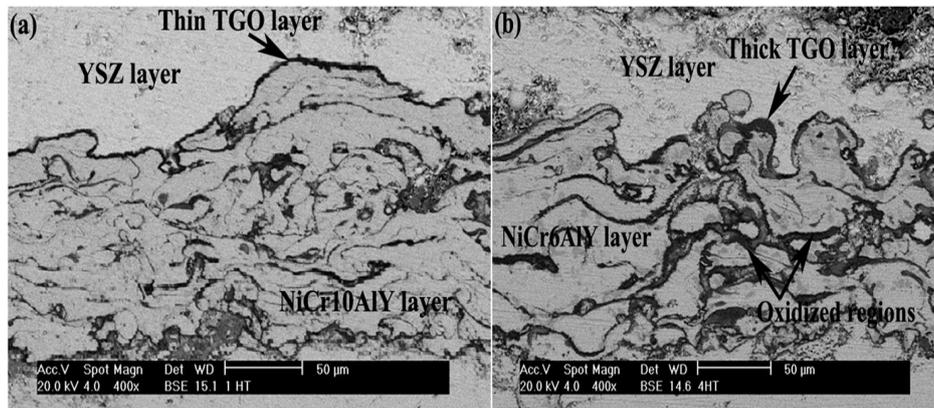


Fig.2. SEM images of TBC surfaces prepared by APS; (a) NiCr10AlY/YSZ and (b) NiCr6AlY/YSZ after high temperature oxidation test at 1150 °C for 40h.

A comparison between Fig.2a and Fig.2b illustrates that the amount of oxidized regions in the NiCrAlY layer with 10 wt. % Al is lower than at the NiCrAlY layer with 6wt. % Al. The percentage of oxidized regions (dark zone) was estimated using image analysis, as shown in Fig.3. As it can be seen the percentage of internal oxidation of the NiCr6AlY layer with 6 wt. % is higher than of the NiCrAlY with 10 wt.% Al.

As aluminum has a high affinity for reaction with oxygen, the formation of Al_2O_3 or TGO layer was facilitated at the bond coat/ceramic interface (see Fig.2). The EDS analysis of the TGO layer of NiCr6AlY coating showed higher percentage of oxygen and aluminum and lower percentage of Ni and Cr, as shown in Fig.4, meaning that the TGO layer is mostly consisted of Al_2O_3 .

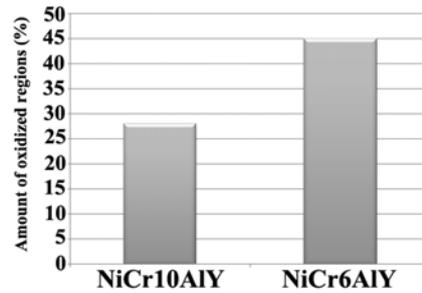


Fig.3. Amount of oxidized regions (dark zones) in NiCrAlY layer after high temperature oxidation test.

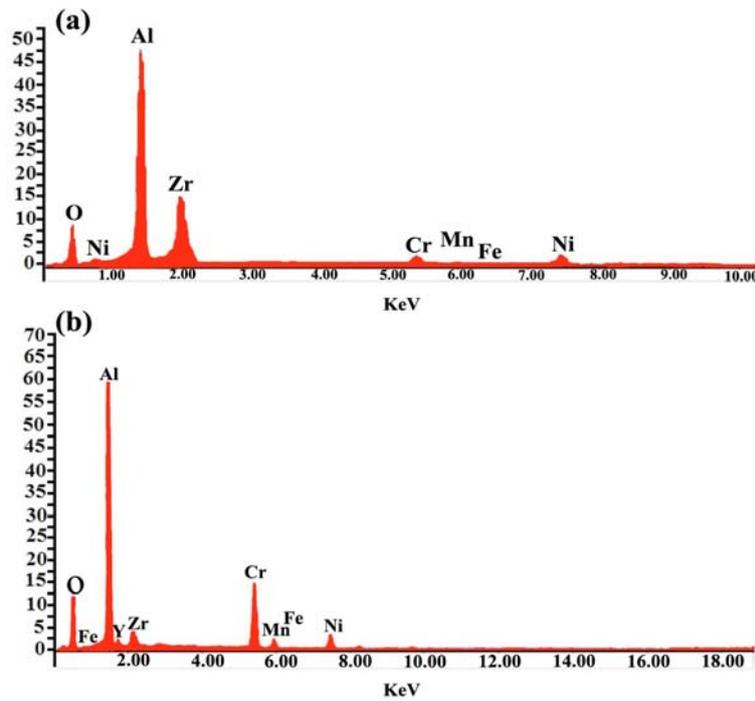


Fig.4. The EDS analysis of TGO layer at interface of NiCrAlY/YSZ after 40 h of oxidation, (a) TGO layer of NiCr10AlY coating, and (b) TGO layer of NiCr6AlY coating.

The thickness of the TGO layer at NiCrAl10Y/YSZ interface was measured after oxidation for 22 and 40h at 1150°C . The TGO thickness was measured to determine the

rate of TGO growth. TGO thickness was measured on each SEM micrograph at more than 20 locations and the average value was used to determine the rate of TGO growth. Fig.5 shows the TGO thickness against the time of oxidation for the two thermal barrier coatings. The TGO thickness of NiCr10AlY bond coating is lower in comparison with NiCr6AlY bond coating after 40 h of oxidation. It may be also seen that the growth of TGO layer approximately followed a parabolic relationship. After approximately 22h the oxide on the 6%Al bondcoat was thicker than that on the 10%Al coating, however the rate of TGO growth was not different. In addition, the rate of TGO growth of the NiCr10AlY bond coating is lower than NiCr6AlY bond coating after 22 h of oxidation. This case is mainly attributed to the formation of a uniform, dense and continuous Al_2O_3 layer on the NiCr10AlY coating (as shown in Fig. 2a). In addition, the TGO layer on NiCr6AlY was about $2.7\mu\text{m}$ in 40 h of oxidation.

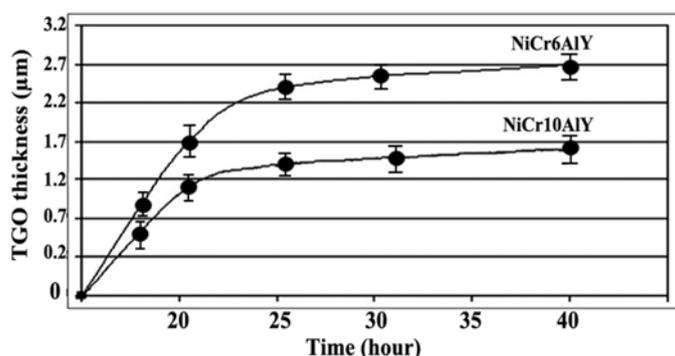


Fig.5. TGO thickness vs. time of oxidation for two prepared TBCs.

As shown in Fig.5, the rate of TGO growth was fast after 22 h due to the inward penetration of oxygen and outward diffusion of Al. The accelerated TGO growth during the initial exposure of NiCr10AlY bond coating to high temperature (after 22h) may be attributed to the increased Al transport through the higher levels of grain boundaries in comparison with a NiCr6AlY bond coating with lower levels of grain boundaries and less aluminum. The Al_2O_3 layer was formed at the bond coat/YSZ interface and reduced the permeation of oxygen towards the bond coat causing a decrease in the rate of TGO growth in longer holding time. It is well known that MCrAlY coatings as used in the present study form initially transient oxides (including oxides of the main elements Ni and Cr) before later the more protective alumina scale forms. This results in an initial scale rapid TGO growth rate which then later substantially slows down. The transient oxidation stage is more pronounced in a 6%Al coating than in a 10%Al coating (as clearly seen in Fig.5). The Figure also confirms that after this initial stage the rate of oxidation is (as expected) is very similar for both coatings. The process is certainly affected by the fact that part of the aluminum is depleted during the APS process. The thicker TGO layer was shown to have high stress at the TGO/YSZ interface [11, 12] leading to the growth of the cracks at the interface of TGO/YSZ layer (see Fig.6).

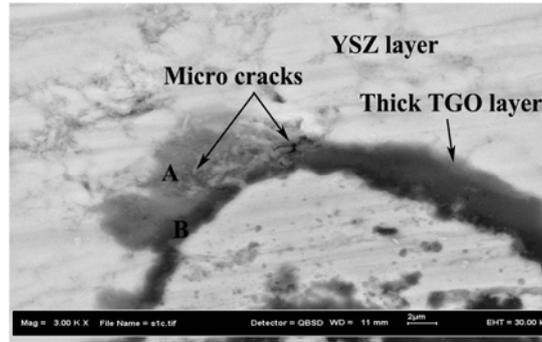


Fig.6. Formation of micro-cracks at the interface of TGO/YSZ layer in TBC prepared by NiCr6AlY at 1150 °C after 40 h (Field emission electron microscope (Hitachi S-4160) was used to recognize the microcracks.).

However, crack formation in the spinel is because of the lower fracture toughness of this oxide compared to that of alumina. Consequently, as the amount of stresses in the gray region of TGO (point A) is much higher than the dark region of TGO (point B), the cracks were more expanded at the gray region of TGO (spinel). The chemical composition of spinel (point A) was examined by EDS, as shown in Fig.7.

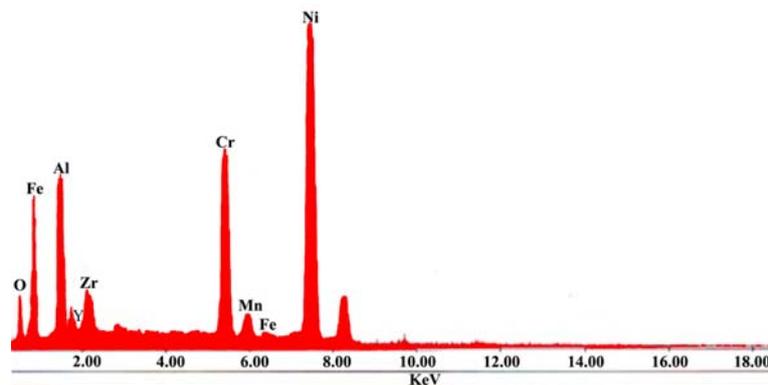


Fig.7. EDS analysis of spinel (point A shown in Fig.6).

The TGO usually comprises large residual compressive stresses when it cools to ambient temperature because of its thermal expansion misfit with the substrate [13]. During the thermal cycle, stress relieving was occurred at the TGO/ceramic layer interface, leading to crack and spallation at the interface [14]. It is obvious that the thicker TGO layer incorporates higher stresses [4]. Hence, the crack formation at the interface of TGO/YSZ can be easily observed in Fig.6. It can be said that the oxygen can penetrate into the micro-cracks and some porosity of the TGO layer towards the NiCrAlY layer during the thermal cycling and then the internal oxidation of NiCrAlY layer can occur [15]. As shown in Fig.2, the internal oxidation of the NiCr6AlY layer with thicker TGO is much higher than NiCr10AlY layer with thinner TGO. Internal oxidation of bond coat is mainly related to the plasma spray deposition leading to the formation of lamellar structure with interconnected porosity and micro-cracks [16]. The

interconnected porosity provides strain tolerance during thermal cycling and decreases the thermal conductivity of TBCs. The microcracks and porosity allow oxygen transfer to the bond coat at elevated temperature. However, the TGO usually prevents the penetration of oxygen into the bond coat [17]. The oxidation behavior of the NiCrAlY's is governed by the typical porosity of the APS coatings. This has as result that "particles and splashes" are isolated areas with a limited Al reservoir. These areas become more rapidly depleted in Al during the coating process. The result is that in a low-Al coating the Al content locally (external as well as internal) decreases down to levels in which substantial amounts of Ni- and/or Cr-rich oxides (e.g. spinels) are being formed instead of alumina [18].

As shown in Fig.8, there are some Al-depleted regions (grey zones) within the NiCrAlY layer caused by reaction of oxygen with Al and altering the Al-rich phases (dark zones) to (Ni/Cr)-O rich phases (spinels). In this paper, the surface of bond coatings was examined using XRD after 40 h of oxidation at 1150 °C. For this purpose, NiCr6AlY and NiCr10AlY powders sprayed on Inconel 617 and oxidized at 1150 °C for 40 h, separately without MCrAlY bond coating or YSZ were examined using XRD analysis. The results showed that some oxide compounds like NiCr₂O₄, NiCrO₃ and NiCrO₄ were formed (see Fig.9a) on the NiCr6AlY layer and some oxide phases such as NiO, Al₂O₃ and Cr₂O₃ appeared in the NiCr10AlY layer (Fig.9b).

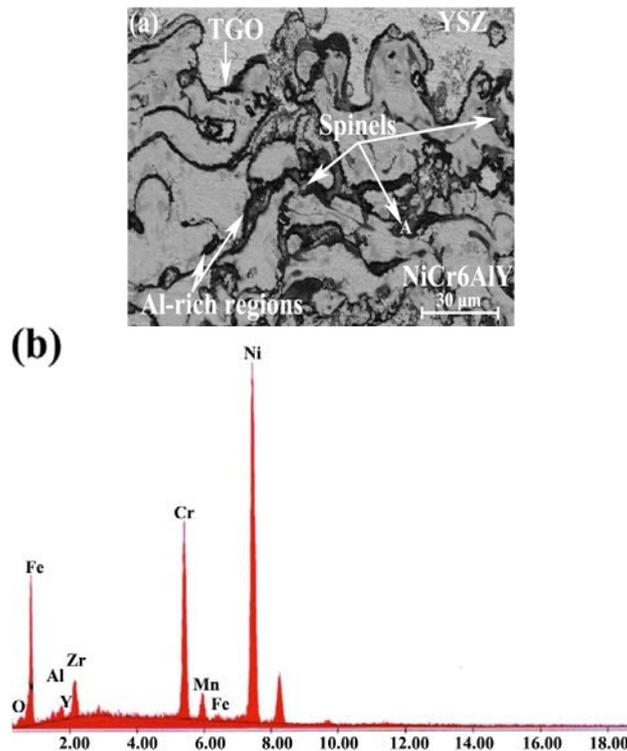


Fig.8. SEM micrograph of NiCr6AlY layer after 40 h of oxidation at 1150 °C; (a) there are some undulations, full of Al-poor regions (grey zones), within the NiCr6AlY layer; and (b) EDS analysis of point A.

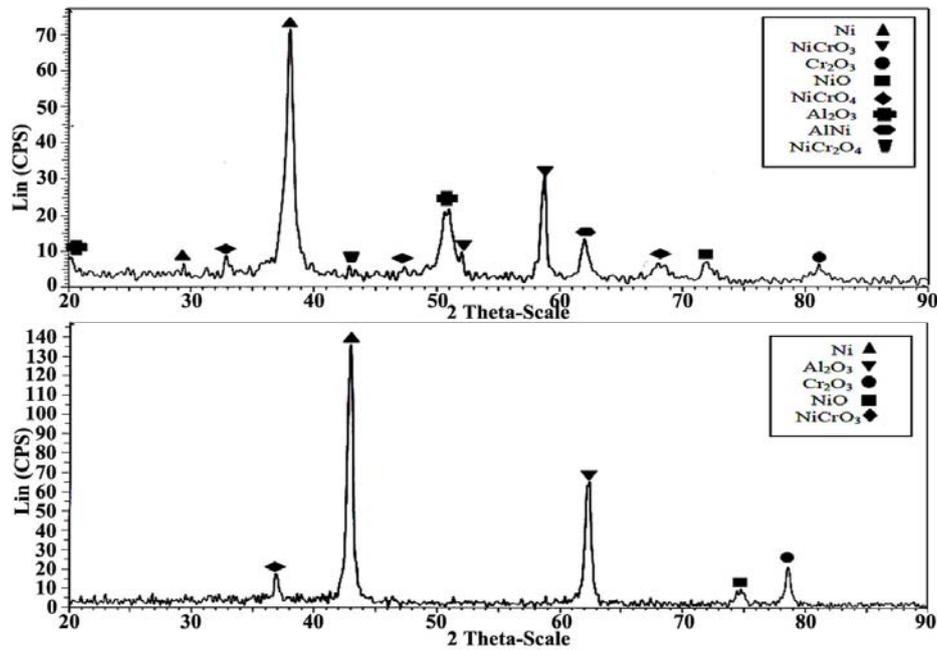
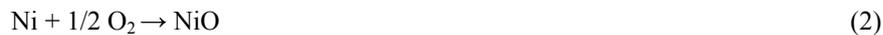


Fig.9. XRD patterns of NiCrAlY layers without YSZ as top layer after oxidation at 1150 °C for 40 h; (a) NiCr6AlY layer and (b) NiCr10AlY layer.

The difference of the crack formation in the TGO in the low- and high-Al coating is related to the difference in surface oxide composition. The formation of NiCr₂O₄, NiCrO₃ and NiCrO₄ oxides was accompanied by volume expansion producing localized stress and consequently leading to the formation of cracks or spallation of the ceramic layer [19, 20-22]. The localized stresses and the growth of the TGO layer caused the formation of cracks at the YSZ/NiCrAlY interface. The Al₂O₃, NiO, and Cr₂O₃ oxides can be simultaneously formed at the interface of NiCrAlY/YSZ during oxidation. It can be declared that only Al₂O₃ can continue to grow after a continuous TGO is developed because the Al₂O₃ is one of the most thermodynamically stable oxides. The formation of NiO and Cr₂O₃ oxides is due to the depletion of Al at NiCrAlY/TGO interface and reaction of Ni, Cr with oxygen (reactions 1 and 2). Therefore, Ni (Al,Cr)₂O₄ spinels will be formed in the TGO layer which are mainly produced by the reaction of NiO with Al₂O₃ and Cr₂O₃ (see reaction 3).



However, in this research, the formation of spinels on the TGO layer of NiCr10AlY bond coating was much lower compared to that of NiCr6AlY bond coating after 40 h of oxidation, as shown in Fig.9. This case is mainly due to the amount of Al in the two of NiCrAlY bond coatings. However, one of the reasons for the differences in

the behavior of the two coatings might be related to the difference of the powder sizes (57 and 55 μm) and the density of the coatings. The formation of micro-cracks at the interface of TGO/YSZ in NiCr10AlY/YSZ coating was not seen after oxidation at 1150 $^{\circ}\text{C}$ for 40 h (Fig.10). This is because of the lower thickness of the TGO and lack of detrimental oxides such as NiCr_2O_4 , NiCrO_3 and NiCrO_4 . The amount of the oxidized regions (dark zone) in the NiCr10AlY layer was decreased to a quarter of the one treated at 1150 $^{\circ}\text{C}$ for 22 h. Therefore, it can be considered that the internal oxidation of NiCr10AlY layer is much lower than NiCr6AlY layer.

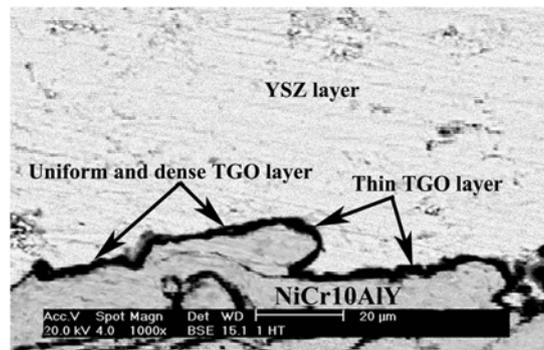


Fig.10. SEM image showing the absence of micro-cracks at the interface of TGO/YSZ in case of the NiCr10AlY/YSZ coating after 40 h of oxidation at 1150 $^{\circ}\text{C}$.

As a result of applying more Al in the coating, a uniform, dense and thin TGO layer can be obtained because of the structure of the NiCrAlY layer. This can be a reason for the lower diffusion of oxygen into the TGO layer at high oxidation temperature as the detrimental oxides cannot be extensively formed within the bond coat. The bond coat with higher percentage of Al exhibited better oxidation behavior. It was found that the oxidation rate at the NiCr(x)AlY/YSZ interface increases with holding time as shown in Fig.11. This behavior can be shown by the following relationship [23].

$$C_{\text{oxidation}} = \sqrt{h_p t} \quad (4)$$

where $C_{\text{oxidation}}$ is the concentration of oxides in the holding time (t) and h_p as a constant for NiCr6AlY is $7.1 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ and for NiCr10AlY is $3.1 \times 10^{-13} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ at 1150 $^{\circ}\text{C}$. In general, the absolute values (e.g. the time period of the transient oxidation) are affected by (e.g. Al oxidation during) the spraying process but the differences between the two coatings are related to differences in the formation of the transient oxides. This results in a higher amount of spinel phase (resulting from the early stages of oxidation) on the 6% Al coating before more protective alumina scale forms. This spinel phase is more prone to crack formation than the alpha-alumina. Thus, the TGO on the 6% Al coating will be more prone to cracking than that on the 10%Al coating, as experimentally observed. The fact that the oxide after 40 h of oxidation is thicker on the 6% Al coating than on the 10% Al coating (Fig. 5) is really logic (in spite of the fact that the growth rates between approximately 25-40 hours are virtually identical). The difference in internal oxidation of the two bondcoats can easily be

related to the difference in transient oxidation states resulting in difference of protectiveness of the transient oxides. Even if equal amounts of oxygen would be taken up into the coating interior, different types and amounts of internal oxide would be expected to form, i.e. more voluminous spinel type oxides in the 6% Al coating than in the 10% Al coating.

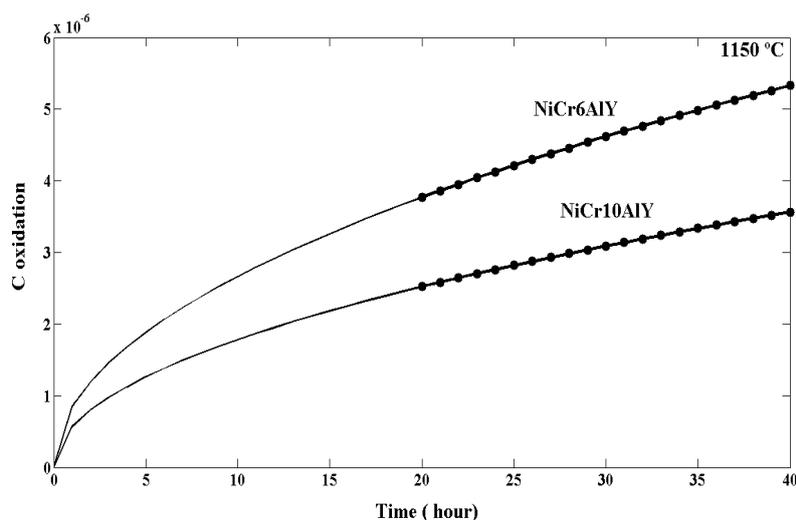


Fig.11. Concentration of oxides ($C_{oxidation}$) of the bond coat as a function of time.

Conclusion

Thermal barrier coating was applied to Inconel 617 using a NiCr6AlY/YSZ and NiCr10AlY/YSZ bond coat. The specimens (with and without a YSZ-TBC) subjected to high temperature oxidation were studied after short time oxidation at 1150 °C by SEM and XRD and the following results were achieved:

1) The TGO layer at the NiCr(x)AlY/YSZ interface was mainly consisting of Al_2O_3 . The TGO layer on NiCr6AlY was thicker than that on NiCr10AlY after 40h of oxidation, reaching to 2.7 μ m.

2) The formation of spinles on the TGO layer of NiCr10AlY coating was much lower compared to that of NiCr6AlY coating after 40 h of oxidation. This case is mainly due to the amount of Al in the NiCr(x)AlY coatings.

3) The internal oxidation of the NiCr10AlY bond coat was lower in comparison with NiCr6AlY and detrimental oxides such as $NiCr_2O_4$, $NiCrO_3$ and $NiCrO_4$ were not observed in the NiCr10AlY layer after oxidation.

4) A uniform, dense and thin TGO layer was formed on the NiCr10AlY bond coat as a result of a decrease in the amount of oxygen in the TGO layer. Furthermore, the bond coat with higher Al showed better oxidation behavior.

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