INFLUENCE OF ISOTHERMAL EXPOSURE ON MICROSTRUCTURAL CHANGES RESULTING IN DELAMINATION OF EUTECTIC $Al_2O_3+ZrO_2+SiO_2$ THERMAL BARRIER COATINGS

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Abstract

Eutectic ceramic Al_2O_3-ZrO_2-SiO_2 also termed Eucor (as a top coat) and CoNiCrAlY (as a bond coat) coatings were sprayed onto the surface of recently developed fine-grained cast polycrystalline nickel-based superalloy Inconel 713 LC by means of water stabilized plasma (WSP) and atmospheric plasma spraying (APS) techniques, respectively. Specimens were subjected to isothermal oxidation at 1050 °C for 10, 50, 100, 200 and 500 hours in ambient atmosphere, prior to which a half of the as-sprayed specimens was annealed at the temperature of 950 °C for 10 hours. Influence of short-time and long-time isothermal exposure on interactions at the bond-coat/top-coat interface was studied. The uniform and continuous oxide layer, also termed the thermally grown oxide (TGO), was formed and grew at the bond-coat/top-coat interface in all samples, both with and without the heat pre-treatment. Relationship between the dwell time, heat treatment and TGO growth kinetics was quantified. Microstructural changes at top-coat/bond-coat interface were investigated by means of a scanning electron microscope equipped with an energy dispersive microanalyzer and by means of image analysis techniques. Delamination of the ceramic top coat in the region near to the top-coat/TGO interface was evocated by stresses initiated in the Eucor top coat due to its shrinkage during cooling.

Keywords: Thermal Barrier Coatings, Thermal Plasma Spraying, Heat Treatment, Electron Microscopy - Scanning, Image Analysis

1. INTRODUCTION

Thermal barrier coatings (TBCs) represent advanced multilayer material systems essential in the aerospace, automotive and power generation industries, where they are used for protecting key engine components against high-temperature degradation (oxidation, hot-corrosion) and the heat flux [1-3]. Conventional TBCs utilize zirconia partially stabilized with yttria (YSZ) for the top coat as it has a convenient mixture of the high melting point, low thermal conductivity and relatively high coefficient of thermal expansion and fracture toughness, all of which are the crucial properties in designated applications [3-5]. Ever increasing demands for higher engine efficiency and lower operational costs, i.e. the higher inlet temperatures and increased coatings' durability, however, motivates a currently seen extensive search for efficient alternatives. One of the promising TBCs is the nanoscrystalline ceramic coatings based on $Al_2O_3+SiO_2+ZrO_2$ with a near-eutectic composition (Eucor) [6]. The processes affecting its high-temperature structural integrity include mainly the inter-diffusion of species between the substrate and the coatings, the formation of the thermally grown oxide (TGO) layer at the bond-coat/top-coat interface and a solid-state phase transformation and growth of nanoparticles in the top coat [3-7]. Furthermore, the actual degradation of the system is strongly influenced by

TBC microstructure and its prior thermal history. The role of the these factors is assessed in the present work that focuses on a microstructural stability of as-coated and pre-annealed CoNiCrAlY+Eucor TBCs during isothermal high-temperature oxidation at 1050 °C for various dwell times.

2. MATERIAL AND METHODS

Sheet of fine-grained polycrystalline nickel-based superalloy Inconel 713LC was used as the substrate. The sheet surface was grit blasted with angular alumina particles and washed with acetone cleaning bath before thermal barrier coating system deposition. The CoNiCrAlY (32 wt% Ni, 21 wt% Cr, 8 wt% Al, 0.5 wt% Y, bal. Co) bond coat in thickness of approx. 200 μm was produced by means of atmospheric plasma spraying. The near eutectic ceramic Al_2O_3-SiO_2-ZrO_2 top coat was deposited in thickness of 200 μm onto the bond coat by means of water-stabilized plasma spraying. After the spraying, the sheet was sectioned into samples of 10 × 10 × 3 mm in size. Specimens were subjected to isothermal oxidation at 1050 °C for 10, 50, 100, 200 and 500 hours in ambient atmosphere. Prior to isothermal oxidation, a half of the as-sprayed specimens was annealed at the temperature of 950 °C for 10 hours, in order to induce crystallization of nanoparticles in the Eucor top coat. After experiments, the specimens were grounded using increasingly finer abrasive papers (up to #4000) and subsequently polished with diamond pastes (down to 1 μm) and with the OP-U colloidal silica final suspension (Co. Struers GmbH). Microscopical investigations were accomplished by means of the scanning electron microscope (SEM) MIRA 3 Tescan equipped with the energy dispersive X-ray (EDX) spectroscopy microanalyser. The average thickness of the thermally grown oxide layer formed during the heat treatment, was evaluated by using the image analysis (IA) software StreamMotion.

3. RESULTS AND DISCUSSION

The microstructure of the APS CoNiCrAlY bond coat, which was deposited onto a substrate made of a recently developed fine-grained cast polycrystalline nickel-based superalloy Inconel 713 LC, exhibits patterns typical for plasma spraying and consist of the flattened splats, partially unmolten particles and of oxides formed at splat interfaces due to interaction with an ambient atmosphere during spraying. The metallic bond coat is usually composed of two-phases (β-NiAl and either γ-Ni solid solution or γ´-Ni3Al) and, in some cases, a small amount of Ni-Y intermetallic may be also present [7]. The top coat near-eutectic composition enabled formation of Eucor amorphous structure during rapid solidification. The nanocrystallization of the eutectic from the amorphous phase occurred during annealing (950 °C for 10 hours) and the nanoparticles with the average size of 10 nm were formed within the ceramic top coat. After isothermal exposure at 1050 °C, the uniform and continuous thermally grown oxide layer was formed in all samples (both with and without the heat pre-treatment) along the entire bond-coat/top-coat interface even for the shortest dwell-time of 10 hours, see **Fig. 1**. The TGO was composed of a single layer of predominantly Al_2O_3, in contrast to the results obtained earlier for conventional thermal barrier coating system (YSZ+CoNiCrAlY), where the double TGO layer was formed as a continuous Al_2O_3 layer and irregular layer of complex oxide based on $(Cr,Al)_2O_3$+$(Co,Ni)(Cr,Al)_2O_4$ [8]. The short-time isothermal exposure (50, 100 hrs) results in no significant changes in microstructures of the bond coat when compared to microstructure after 10 hrs of isothermal exposure, except the increasing thickness of the TGO layer. The **Figs. 1, 2** distinctly demonstrate the influence of isothermal exposure dwell on the TGO growth kinetics.

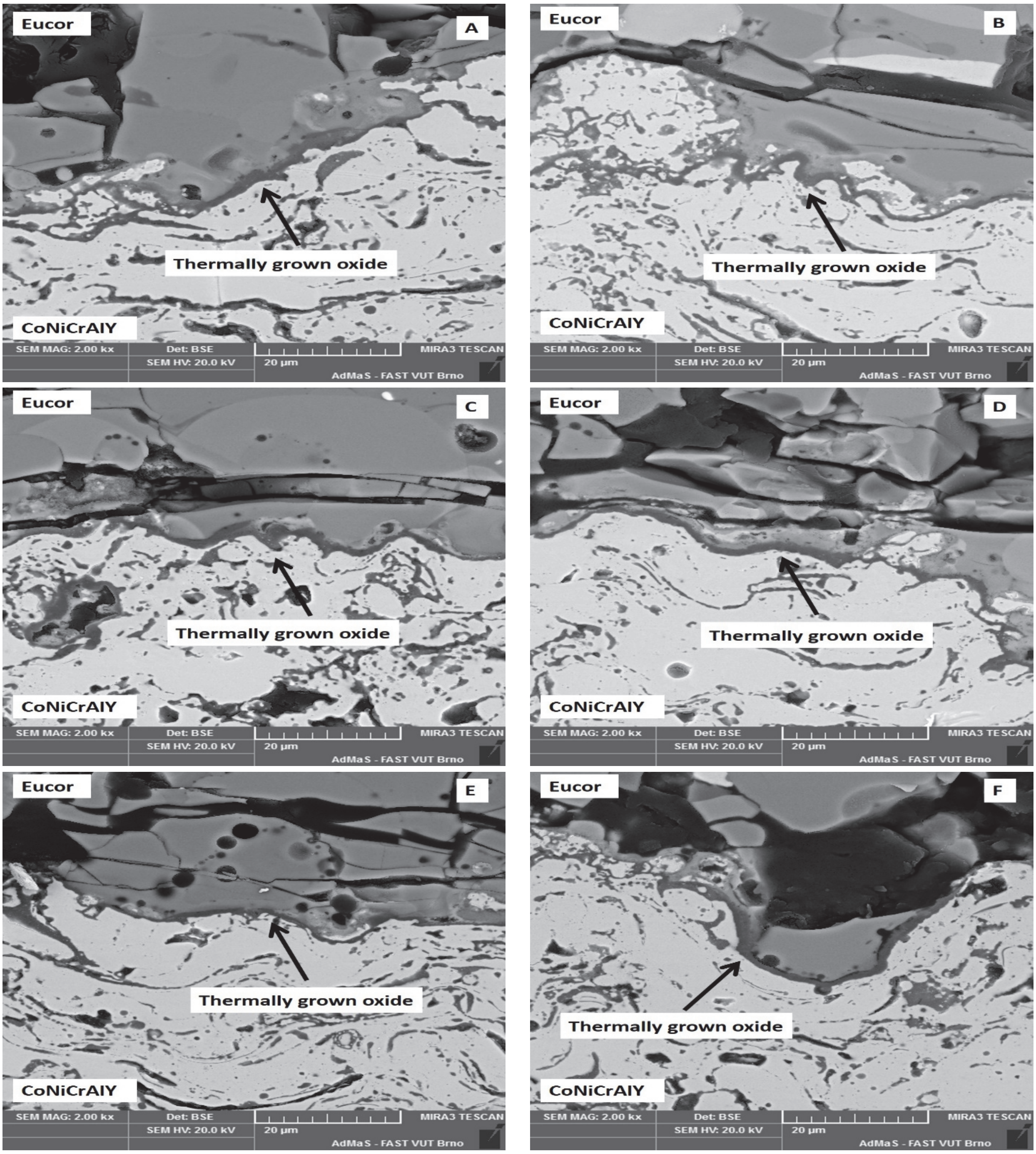

Fig. 1 detail SEM micrograph of Eucor-CoNiCrAlY interface after short-time isothermal exposure (A, C, E - heat treated samples after 10, 50, 100 hrs; B, D, F - samples without heat treatment after 10, 50, 100 hrs of isothermal exposure)

Similarly, the long-time isothermal exposure (200, 500 hrs) led to no substantial changes in the bond coat and the top coat microstructure except the continuous growing of the TGO layer, see **Fig. 2**.

The ceramic top coat of all samples without the heat pre-treatment was delaminated during slow cooling in ambient atmosphere after both short-time and long-time isothermal oxidation. This phenomenon probably occurred due to a shrinkage of the eutectic top coat after cooling. However, the delamination of the top coat in the specimens subjected to heat pre-treatment was less extensive and the top coat stayed attached to the bond coat in several cases, indicating that the heat pre-treatment reduced the internal stresses generated in both layers during the cooling phase after plasma spraying. Based on the previous experiments, it was expected that the delamination would occur at the critical top-coat/TGO interface in thermal barrier coating system [9], nevertheless the crack propagated mostly within the top layer near to this interface, similarly to thermal cycling mode [10].

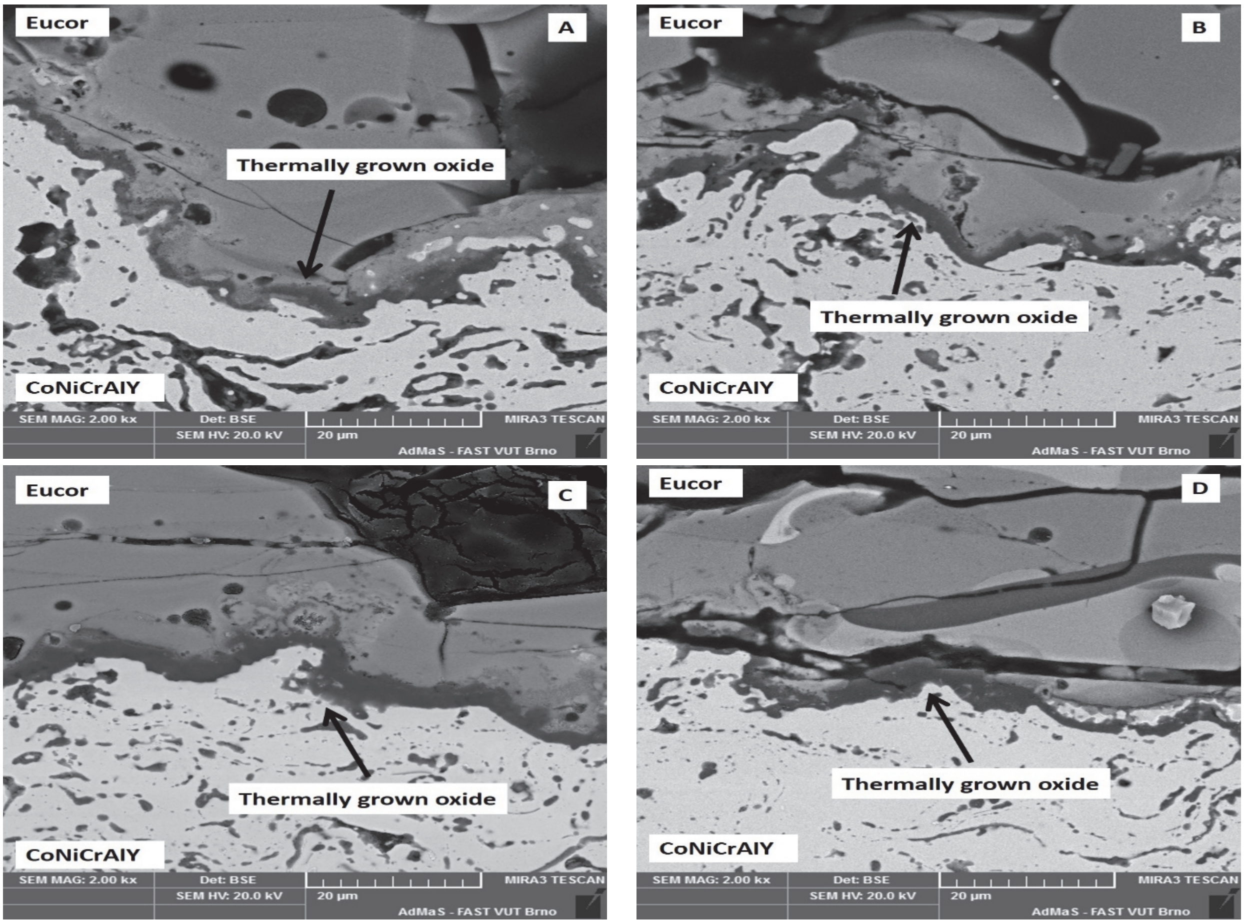

Fig. 2 detail SEM micrograph of Eucor-CoNiCrAlY interface after long-time isothermal exposure (A, C - heat treated samples after 200, 500 hrs; B, D - samples without heat treatment after 200, 500 hrs of isothermal exposure)

The TGO thickenings was quantified for all studied samples by using an image analysis software. The calculated average thickness is plotted in **Fig. 3** as a function of isothermal exposure dwell.

The influence of different heat treatments and increasing dwell times is apparent over the whole range of dwell times. The thickness of TGO is the lowest in the case of sample subjected to 10 hours of isothermal oxidation without previous annealing, t = 1.0±0.5 μm. In comparison,

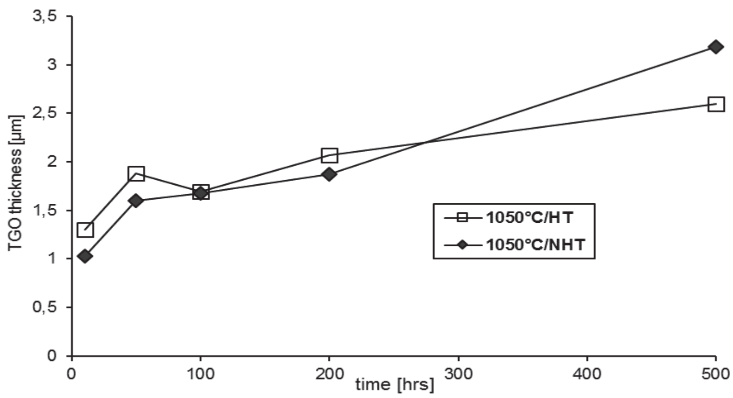

Fig. 3 The thickness of alumina TGO layer as a function of isothermal exposure dwell (HT - heat treatment at 950°C/10hrs; NHT - no heat treatment)

the thickness of t = 3.2±1.2 μm was obtained after 500 hours of isothermal exposure of sample without previous annealing.

CONCLUSIONS

A microstructural stability of as-coated and pre-annealed CoNiCrAlY+Eucor thermal barrier coatings was studied during isothermal high-temperature oxidation at 1050 °C for various dwell times in ambient atmosphere. The heat pre-treatment was found to improve the coatings' performance by partially reducing the quenching and thermal residual stresses induced in the TBC system during the coating deposition and subsequent cooling and, thus, to reduce the extent of the top coat delamination. In both as-coated and pre-annealed specimens, the delamination occurred in the ceramic top coat in the vicinity of the bond-coat/top-coat interface. The TGO growth kinetics was quantified based on the image analysis.

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