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# Microstructural analysis of Ta-containing NiCoCrAlY bond coats deposited by HVOF on different Ni-based superalloys

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ABSTRACT

The microstructural and chemical evolution after different processing steps of Ta-containing NiCoCrAlY bond coats (BC) sprayed by high velocity oxy-fuel on Ni-base superalloy (SA) substrates, top-coated with 7YSZ and furnace cycled at 1100 °C focusing along the BC/SA interfaces is presented. Three superalloys were selected considering their Ta content relative to that within the BC: a) no Ta in the superalloy composition (IN100) and either b) similar or c) higher Ta content with respect to the BC (M247LC SX and CMSX-4, respectively). The processing conditions were as-sprayed, as-annealed, after EB-PVD deposition of a 7YSZ top coat, and after furnace cyclic tests (1100 °C/120 h). The evolution of chemical composition after the different process steps are presented that include a normalization criteria to a Ni-Al-Cr system, elemental profiles as well as Weibull distribution plots of minor containing elements such as Ti, Ta, Mo, or W at the BC/SA interface. The effect of Ta was activated in some coated substrates by the presence of Ti and C in the superalloy consisting of inward Ta-diffusion, trapping of outward diffusing Ti and the subsequent formation of (Ta, Ti)-rich carbides in the BC avoiding possible segregation effects as titanium oxide in the oxide scale.

## 1. Introduction

Advanced coatings are a necessity to protect metallic components exposed to harsh environments, e.g., for components used in the aeronautical or stationary gas turbines for power generation. For instance, thermal barrier coatings systems (TBC) have proven effectiveness in protecting metallic parts against extreme operating conditions, which are characterized by structural loads, oxidizing and corrosive atmospheres as well as thermal cycles at high temperatures [1–7]. TBC systems consist of a low thermal conductivity top coat (TC), typically yttria-stabilized zirconia (YSZ) protecting a nickel-based superalloy substrate (SA). The TC is bonded to the SA by an aluminum-containing bond coat (BC), which can form a thermally grown oxide (TGO), preferably α-$Al_2O_3$. Depending on the BC fabrication process, they are classified as diffusion- or overlay-types. A typical overlay BC is a MCrAlX alloy, where M stands for nickel, cobalt or both and X is usually yttrium and is commonly deposited by either sputtering or thermal spray processes. The latter are typically air plasma spraying (APS), low pressure plasma spraying (LPPS) or vacuum plasma spraying (VPS) and more recently high velocity oxy-fuel (HVOF), which has been used in order to yield high density coatings [8,9]. The selected composition depends on the BC application and operating conditions. NiCoCrAlY-type alloys are widely employed because they exhibit a higher oxidation resistance than NiCrAlYs and better corrosion resistance (e.g., sulfidation) than CoCrAlYs [10]. The microstructure of NiCoCrAlY coatings consists mainly of γ-Ni and β-NiAl phases, with their relative volume fractions dependent on the chemical composition. The γ-Ni phase is a face-centered cubic solid solution of Ni, Cr, and Co, whereas the β-phase is an ordered NiAl intermetallic that crystallizes in a primitive cubic CsCl (B2) structure [1,11,12]. γ′-$Ni_3Al$ may also be

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observed as a result of Al depletion of the β-NiAl phase [1]. However, novel NiCoCrAlY-type coatings modified with either reactive (Hf, Y, Zr) or refractory elements (Re, Ta), among others have been widely studied because of their higher oxidation resistance. For instance, Hf, Re, Pt, or Ta have been included in the chemical composition of bond coats to promote the formation of a slow growing α-$Al_2O_3$ scale and to improve the thermo-mechanical stability of the BC [13–15]. Moreover, it has been reported that additions of Ta to NiCoCrAlY coatings modify the microstructure compared with a non-Ta-containing NiCoCrAlY coating [14] and reduce the oxidation kinetics, irrespective of the coating fabrication technique (e.g. HVOF vs VPS) [14]. However, even when improvements in oxidation resistance are reported in that work, they are not directly associated to microstructure changes in the coating. The only reported effect about the advantages of Ta-additions in NiCoCrAlY-bond coats is to reduce the chemical activity and thus the diffusion rate of Ti from specific superalloys by trapping Ti to form stable (Ta,Ti)-carbides [16–19]. Overlay bond coats also have strong chemical interaction with the superalloy substrate under cyclic conditions at high temperature and thus diffusion processes strongly depend on the composition of the superalloy [20]. For instance, it is well known that, the presence of elements such as Ti in SA's is beneficial because, in the case of Ti, it promotes the formation of the ordered γ′ phase, which in fact confers strength to the superalloy [21]. However, it has been claimed that in the bond coat, the presence of Ti is detrimental due to the formation of oxides ($TiO_2$) and thus less protective scale than in the case of pure α-$Al_2O_3$ [16–19]. $TiO_2$ inclusions are formed as particles within the α-$Al_2O_3$ scale causing microcracks which induce the scale spallation. Moreover, the fast diffusion of Ti causes the incorporation of $Ti^{4+}$ ions into the scale increasing the concentration of aluminum vacancies or oxygen interstitials which in fact increases the formation kinetics of α-$Al_2O_3$ [20]. Thus, the addition of refractory elements, such as Ta to NiCoCrAlY coatings has potential for future development on TBC systems. However, diffusion processes of Ta from NiCoCrAlYTa commercial bond coats and its interaction with other elements from different superalloys have been barely reported. Previous reports have been focused on oxidation effects (e.g., weight gain, lifetime under furnace cycling tests) as well as oxide scales and bond coat characteristics [14,22–24]. Moreover, few investigations have been conducted to understand the interplay of Ta with Ti, Hf, Re, among other elements from the used superalloys, and the way it affects the microstructure and diffusion phenomena between the bond coat and the substrate, especially at their interface [25–27]. In this contribution, the effect of the chemical composition of IN100, CMSX-4 and M247LC SX superalloys on the microstructural and chemical evolution of a NiCoCrAlYTa BC through different processing stages and thermal cycling tests is presented and discussed. These superalloys were selected to study three cases relative to Ta-content with respect to the BC: a) no Ta in the superalloy composition (IN100) and either b) similar or c) higher Ta content with respect to the BC (M247LC-SX and CMSX-4, respectively).

## 2. Material and methods

Commercial NiCoCrAlYTa powder (Amdry 997, Oerlikon Metco) was utilized to deposit thermally-sprayed bond coats on three different Ni-based superalloys. Rectangular flat plates of 18 × 12 × 2 mm were used as substrates, consisting either of a commercial polycrystalline IN100 and CMSX-4 single crystal superalloys as well as M247LC SX, processed from its commercial condition to a single crystal in the metals and alloys department, University of Bayreuth (LMW-UBayreuth). Before deposition, the substrates were cleaned by abrasive grit blasting using alumina particles ANSI G-24. Subsequently, bond coats were manufactured by high velocity oxy-fuel (HVOF) thermal spray process using a Diamond Jet 2700 spraying gun from Oerlikon Metco, which is manipulated with a 6-axis robot arm (KRC2, Kuka) from the thermal spray facilities of CENAPROT national laboratory. The parameters for BC deposition were chosen from a study reported elsewhere based on a design of experiments methodology as well as statistical analysis of variance [28]. The used parameters for HVOF Ta-containing NiCoCrAlY bond coats deposition are given in Table I. The surface of the as-sprayed bond coats was smoothed in two steps to reach an adequate roughness for future application of the ceramic top coat. The first step consisted of a coarse grinding by using an oscillating machine with silicon carbide powder 400 [P800] reaching a roughness $R_a$ from ~7 μm to ~1 μm. As a second step, a shot peening process with yttria balls is carried out to densify the bond coat surface and to promote the formation of an alumina scale during the subsequent ceramic top coat deposition. Thereafter, in order to activate the elemental diffusion between SA substrates and BC, the specimens were annealed at 1080 °C for 4 h in vacuum ($p_{O_2} < 10^{-5}$ mbar). After this treatment, the specimens were coated with 7 wt% yttria-stabilized zirconia by electron beam physical vapor deposition (EB-PVD) technique at DLR under well-established parameters in a semi-industrial 150 kW (40 kV) dual-source jumping beam (Ardenne Anlagentechnik) EB-PVD coater. After this experimental step the samples are considered “as-coated”.

**Table I**
HVOF spraying parameters used to produce bond coats.

| Parameter | Value |
|---|---|
| Stand-off distance (mm) | 335 |
| $C_3H_8$ fuel flow (scfh) | 115 |
| $O_2$ flow (scfh) | 303 |
| Air flow (scfh) | 434 |
| $N_2$ flow (scfh) | 355 |
| Fuel/oxygen ratio | 0.3 |
| Powder feed rate (g/min) | 40 |
| Raster speed (m/min) | 60 |
| Number of passes | 10 |

As-coated TBC samples were exposed to cyclic oxidation in air at 1100 °C in the DLR furnace for cycling testing (FCT). The oxidation treatment was performed for 120 h in a bottom-drop thermal cycle furnace. One cycle includes 45 min of heating at 1100 °C followed by 15 min of forced air-cooling. The microstructure of powder particles, superalloys, and BC + SA systems was analyzed at LMW-UBayreuth by scanning electron microscopy (1540EsB Cross Beam, Zeiss) adapted with an energy dispersive X-ray detector (Noran System Six EDX-System, Thermo) to evaluate the chemical composition. The chemical composition of the SA/BC systems was obtained from EDS measurements of areas (approx. 12 $\mu m^2$) from several zones along the cross sections, covering the matrix and in some cases multiphase zones, excluding the carbides, pores and internal oxides. The data was normalized to a Ni-Al-Cr System following the site preference criteria of transition metals, reported by Jiang [29].

Size distribution of the spray powder was measured in a laser diffraction sensor for particles in the range of 0.1 to 875 μm (HELOS/BR-OM, Sympatec). The crystalline structure of the powder and bond coats was characterized by X-ray diffraction using a Bragg-Brentano geometry with Cu-$K_{\alpha I}$ radiation separated from $K_{\alpha II}$ with a monochromator, a step size of 0.02°, and step time of 0.5 s (D8 Discover, Bruker AXS). Additionally, EBSD analysis was carried out to confirm the presence of carbides and topologically close-packed phases, which were observed after annealing treatment and thermal cyclic oxidation. Cross-sectional micrographs, recorded by scanning electron microscopy were processed by image analysis (ImageJ software) to determine porosity level in the bond coats.

## 3. Results and discussion

### 3.1. Raw materials

The microstructural characteristics of the powder for HVOF deposition and of the substrates are essential to understand the diffusion