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Synthesis and Characterization of Superalloy Coatings by Cathodic Arc Evaporation

J. Ast^a, M. Döbeli^b, A. Dommann^c, M. Gindrat^d, X. Maeder^a, A. Neels^c, P. Polcik^e, M.N. Polyakov^a, H. Rudigier^f, K.D. von Allmen^c, B. Widrig^f, J. Ramm^f

^aLaboratory for Mechanics of Materials and Nanostructures, Empa, Feuerwerkerstrasse 39, 3602 Thun, Switzerland

^bIon Beam Physics, ETH Zurich, Otto-Stern-Weg 5, CH-8093 Zürich, Switzerland ^cCenter for X-ray Analytics, Empa, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland ^dOerlikon Metco AG, 5610 Wohlen, Switzerland

^ePlansee Composite Materials GmbH, Siebenbürgerstraße 23, D-86983 Lechbruck am See, Germany

^fOerlikon Surface Solutions AG, Iramali 18, LI-9496 Balzers, Liechtenstein

juergen.ramm@oerlikon.com

Abstract

Superalloy targets were produced from Ni-(Al-C-Co-Cr-Mo-Ta-Ti-W) powders by spark plasma sintering technology. The crystalline structure of the as-produced targets was investigated by XRD analysis and compared with the evolution of phases resulting from the operation of the cathodic arc at the target (cathode) surface. Coatings were synthesized at superalloy substrates utilizing these superalloy targets in non-reactive and reactive evaporation processes. Synthesized coatings and target surfaces were compared with respect to chemical composition and crystal structure. The interface between coating and superalloy substrates was investigated by TEM. As an example, a complete layer stack was synthesized by cathodic arc evaporation starting from the superalloy

substrate - superalloy coating interface to a fully oxidized superalloy coating showing epitaxial growth in the interface to the superalloy substrate.

Scheric Minutes

Introduction

The research for materials utilized at high temperature and in oxidizing and corroding environments has been an ongoing effort for applications in aircraft, gas turbine and combustion engines [1-10]. Despite the different final utilization and the difference in design and dimensions, the trend in these industries is going towards the same goal, which is a continuous improvement of engine efficiency to reduce fuel consumption but also to comply with more strict regulations concerning CO₂ emission. This implies running the engine at higher temperatures, thus increasing consequently the need for more robust, stable and resistant base materials operated in harsh environment at different sections of a turbine engine. Even with the use of the most advanced materials such as superalloys or composites, coating technologies cannot be by-passed when it comes to improving the lifetime of the components by increasing the resistance to oxidation, wear, erosion and corrosion at high operating temperatures [11-13]. Despite the fact that the coating technologies introduced many decades ago are well established and continuously being improved utilizing new processes and new coating materials, the coating systems produced on engine components require increased complexity. Therefore, the interactions e.g. between layers, the methods for surface preparation, heat treatments and diffusion issues become increasingly important [14]. Moreover, the requirements of the next generation engines are quite challenging for these existing technologies due to their limitations and the inability to provide the required bulk material properties. Typical coating systems in gas turbines are made of several layers, generally consisting of a bond coat, a thermally grown oxide and a top ceramic layer. Bond coats, which are used to protect the turbine against oxidation, are typically produced either by diffusion processes for PtAl, electron beam physical vapor deposition (EB-PVD) or low pressure plasma spraying for MCrAlY [15,16]. There have been also attempts to utilize Physical Vapour Deposition (PVD) by cathodic arc for the bond coat [17,18]. The bond coat and the top ceramic layer form the so-called thermal barrier coating

(TBC). The top ceramic coating is produced by atmospheric plasma spraying as a porous coating or EB-PVD as a columnar structured coating [19-22]. The design of the bond coat is challenging because it has to realize two sophisticated interfaces: the one to the superalloy substrate to guarantee mechanical stability for a wide temperature range, and the other one to the porous oxide providing an excellent oxygen barrier. This implies not only an intelligent design of the bond coat, but it also requires high reproducibility in the fabrication of the coating system (layer stack).

In this work, a bond coat concept is investigated which is sketched in Fig. 1. The approach is based on the formation of a "substrate-identical" interface (IF-1) to the bulk superalloy substrate (SA-S) and a subsequent transition from IF-1 to a partially or fully oxidized coating ending in a second interface (IF-2). This IF-2 may be an oxygen diffusion barrier and/or a nucleation layer for a porous oxide as it is utilized in the design of a TBC [23]. It could also be an oxygen diffusion strengthened coating or a mixture of oxides which are formed during the oxidation of the superalloy vapour. The whole layer stack is synthesized in one process under vacuum conditions typical for PVD. Nonreactive and reactive arc evaporation is utilized to produce this coating design by *in-situ* processing. This work discusses the manufacturing of targets from powder more or less identical in chemical composition with the bulk superalloy, examines the influence on the chemical composition and phase evolution at target surface for the evaporation by arc under non-reactive and reactive (in oxygen) conditions, and characterizes the coatings obtained under these conditions. A layer stack was synthesized for which the transition from IF-1 to a fully oxidized superalloy coating is demonstrated. Main emphasis of this work was the investigation of IF-1 and the substrate-identical superalloy coating.

Experimental

The substrates as well as the targets were produced from powders with the chemical composition listed in Table 1 (2nd column). The composition of the powders was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). It corresponds to the elemental composition of the superalloy PWA1483 (proprietary alloy of Pratt & Whitney). For the experiments, the substrates as well as the targets were fabricated by spark plasma sintering (SPS) at approximately 1200 °C and 30 MPa (PLANSEE Composite Materials GmbH). This technology has been increasingly utilized during the last decade to synthesize difficult to fabricate materials with dedicated properties [24,25]. In our studies, it was required to achieve a mechanical stable and smooth target surface after arc operation under non-reactive and reactive conditions. Because of the method of manufacturing, it is likely that this material differs from the industrially utilized PWA1483 bulk material produced by melting and casting [26]. Considering this, we will further denominate this material as SA-S (if it is utilized as substrate) and SA-T (if it is used as target for the evaporation). Small discs (Ø 60 mm) were produced from this material and machined to the size of (30 mm x 10 mm x 5 mm) for the SA-S. In identical processes, the SA-T discs (Ø 150 mm) were fabricated.

Table 2 lists the main process parameters utilized in the cathodic arc evaporation using the SA-T as cathodes. Before deposition, the process chamber was evacuated below 0.2×10^{-3} mbar and standard heating and etching steps were performed to ensure a sufficient coating adhesion to the substrate. In process A, the total pressure drops during deposition slightly due to gettering of residual gases by the metallic vapour. The total pressure of process B starts with 0.3×10^{-3} mbar (shorter gettering) and reaches finally 25×10^{-3} mbar if stabilized in oxide synthesis. A net deposition time of 45 min was chosen for the non-reactive process (metallic vapour only) and was increased to 240 min for the reactive processes in oxygen. This is due to the reduced evaporation rate of the SA-T in pure oxygen reactive gas, resulting in coating thicknesses of 1.5 µm (non-reactive process A) and 2.2 µm

for whole layer stack of process B), respectively. The cathodes were operated with DC arc currents of 140 A, either in metallic vapour only, or with a gas flow of 800 sccm oxygen (reactive processes) using an INNOVA batch-type production system of Oerlikon Surface Solutions AG. SA-S together with sapphire substrates were coated at substrate temperatures of approximately 550 °C. Only one arc source was utilized for deposition. A symmetric bipolar bias voltage of -40 V with a frequency of 25 kHz and a negative pulse length of 36 μ s and 4 μ s positive pulse length was applied to the substrate during processing in oxygen.

The target surface was analyzed in a LEO 1530 scanning electron microscope (SEM). The chemical compositions of the SA-T and SA-S were measured by energy-dispersive X-ray spectroscopy (EDX) in the SEM. The errors in this standard-less EDX analysis is estimated to be 3 wt.%. The small amount of C in the target as well as in the coating, and the C contamination of the scanned area in the SEM, do not allow a quantitative EDX analysis of this element.

X-ray diffraction (XRD) measurements on polished slices of the polycrystalline target material were performed on a Bruker D8 Davinci diffractometer equipped with a Göbel mirror for the generation of a parallel beam and with a LynxEye 1D detector using Cu-K α radiation. The measurements were carried out in $\theta/2\theta$ mode between 5-140°. For phase analysis, the software Diffrac.Eva V4.1 from Bruker was used in combination with the crystal open database [27].

Conventional electron backscatter diffraction (EBSD) analyses was performed on the SA-T surfaces in a dual FIB FEG-SEM Lyra3 from Tescan, using a Digiview IV EDAX camera. An acceleration voltage of 20 kV and an emission current of 5 nA were used. Furthermore, Transmission-EBSD or Transmission Kikuchi Diffraction (TKD) [28] was done on lift-out specimens of about 100 nm thickness, mounted on a holder with a pre-tilt angle of 20° to the pole piece with 3 mm working distance. Beam conditions were 30 kV and 5 nA. The chemical segregation was analysed by means of ion channeling contrast imaging which was performed using 30 kV and 1.5 pA Ga ions. The lift-

out lamellae were finally analyzed by transmission electron microscopy (TEM) in a JEOL JEM 2200fs equipped with an EDAX EDS system.

Results and Discussion

Virgin Target (Cathode)

The chemical composition of the SA-T manufactured by spark plasma sintering was investigated by EDX. Due to the large number of elements to be analyzed and their different sensitivity for this method, a quantitative analysis is difficult. However, the similarity in the materials allow (apart from C) a qualitative comparison. Table I (3^{rd} column) shows the results for the as manufactured virgin surface of the manufactured target. Except for tungsten and tantalum, there is a fair agreement in composition with the original powder. The crystal structure of the virgin target surface obtained by XRD analysis was compared with the target surface after arc operation in non-reactive processes. The $\theta/2\theta$ scans are shown in Fig. 2.

The XRD diffractogram of a virgin target (blue line) shows several main peaks which all can be indexed as fcc cubic (Fm-3m) with a = 3.59 Å. Due to the elemental composition of the target, the diffractogram is likely composed of a multitude of different compounds with very similar cubic lattice parameters. Consequently, their individual peaks superpose and resolve in one broadened diffraction peak profile. Pure and intermetallic phases (according to the powder composition in Table 1) such as Cr₂Ni₃, Al_{2.6}Ni_{10.7}Ta_{0.7}, Ni_{0.9}Ta_{0.1}, Ni₁₇W₃, Co_{0.87}W_{0.13}, Ni_{3.28}Ti_{0.72}, Ni_{0.85}W_{0.15} or CrNi can be indexed and may be considered as potential candidates for the observed fcc phase. Peaks with intensities below 1 % are also visible in the XRD diffractogram of the virgin target surface. They may belong to the XRD peaks of tantalum oxide phases which form as a result of surface oxidation in the fabrication process. Peaks of the XRD diffractogram revealed for the operated target show a similar fcc cubic (Fm-3m) phase as observed for the virgin target surface.

The peaks of the operated target are slightly shifted towards higher angles indicating a decrease of the unit cell parameter a from 3.59 Å for the virgin target to 3.58 Å for the operated target. At the same time the peaks of the operated target become narrower than those of the virgin target which may be due to recrystallization processes on the target surface and consequently the formation of larger crystallites. The slight difference in the unit cell parameters between virgin and operated target surface can be attributed to the difference in the fabrication process of the target and the melting/quenching process in the region of the arc spot during arc operation, especially with respect to the difference in temperatures during these processes. Arc operation may contribute to stress relaxation in the surface region of the target manufactured by SPS. It is surprising that arc evaporation does not create phases with very different unit cell parameters. To verify the supposition of the presence of different intermetallic compounds from the X-ray diffraction analysis, TEM investigations were performed (see below).

A micrograph of the SA-T surface obtained from SEM with backscattered electrons using 20 kV beam voltage is displayed in Fig. 3a. The contrast in the backscattered image is mainly due to grain orientation. This was verified by the corresponding EBSD crystal orientation map (Fig. 3b) of the investigated surface by inverse pole figure (IPF) coloring. The EBSD analysis indicates 88% high angle and 12% low angle grain boundaries and 7% Σ 3 twin boundaries with an average grain size of (5.9±3.1) µm. The shown EBSD map is a cross-section through the volume of the spark plasma-sintered material (target as well as substrate). The grain size distribution is supposed to be homogeneous in the volume. If the smallest grains in an EBSD scan are close to average grain size, which was the case in our measurement, the grain size distributions from 2D and 3D measurements overlap and show similar results as discussed by Mingard et al. [29]. However, in the case of many very small grains with respect to the average grain size, the average grain size may be underestimated from 2D measurements. The white spots in the observed backscattered image of

Fig. 3a were identified in the TEM as precipitates rich in titanium and tantalum (not shown here). An enlarged section with different grains is shown in the bright-field and dark-field scanning transmission electron microscopy images in Fig. 4a and b, respectively. An EDX mapping of this detail is given in Fig. 5. The mapping indicates that Cr, Co and Mo are segregating together, also within the grains. The same holds for Ni, Al, Ti and Ta. In addition, the mapping suggests that the precipitates consist mainly of Ta and Ti.

As mentioned earlier, the XRD diffractogram obtained from the surface of as manufactured and operated targets can be indexed with fcc phases for which different intermetallic compounds may be potential candidates (Fig. 2). This assumption is supported by scanning transmission electron microscopy (STEM) investigations, where chemical segregation was observed within and between the grains (not shown here). Fig. 6 shows as examples bright-field (Fig. 6a) and dark-field (Fig. 6b) micrographs for the transitions across two grain boundaries. The arrow in Fig. 6a indicates the position for which the EDX line scan shown in Fig. 6c was performed. The qualitative distribution of only the predominant elements is plotted and it changes significantly between the two investigated grains. Segregation of Ni/Al and Co/Cr is observable, which is in good agreement with the mapping shown in Fig. 5. This was the case for many similar line scans, which indicate the presence of more than one fcc phase with very similar lattice constants.

The analysis of the target indicates that the spark plasma sintering process produces a target material with polycrystalline structure of nearly random grain orientation. In addition, the analysis proves the presence of different intermetallic phases with similar lattice constants and the existence of precipitates in the produced material.

Operated targets

In a next step, the as manufactured targets were utilized as cathodes and evaporated by arc. The evaporation was performed under the conditions mentioned in Table 2. In the non-reactive process, no additional gases were utilized during evaporation. This approach relinquishes of the possible reduced incorporation of droplets in the deposited coatings due to multiple scattering with gas atoms, however, it allows to maintain the higher degree of ionization and the higher kinetic energy of the metallic vapour supporting coating condensation at higher energy [30]. The reactive process was performed in oxygen only. The value of oxygen flow was chosen to ensure an oxygen to evaporated metal atom ratio of about 4 to 5 which should result in a nearly full oxidation of the coating. The chemical compositions of the targets after processing were measured by EDX and are given in Table 1 (4th and 5th column). Interestingly, there is no oxygen detectable at the target surface after arc evaporation in oxygen. This indicates that the cathodic arc evaporates thin oxides formed at the target surface during arc evaporation in oxygen reactive gas preferentially. Visually this can be observed by an extensive splitting of the arc spots over the target surface if oxygen gas is added to the arc discharge. Compared with powder composition, the analysis of the target surface indicates a slight reduction in Mo and Ti for Process A and Al and Ti for process B, but no drastic change in the composition for the other target elements. Previous work on operated Al-Hf and Al-Ni targets shows similar trends for Al depletion of the target surface [31,32]. The XRD diffractogram of the target surface after arc operation in non-reactive mode is given in Fig. 2 (red line). Compared with the virgin target, peaks of the operated target are narrower and shifted towards higher angles. They can as well be assigned to fcc cubic phase (Fm-3m). The average unit cell of the operated target is slightly smaller and the lattice parameter decreases from 3.584 Å (before operation) to 3.568 Å (after operation) and the reduced full width at half maximum indicates recrystallization processes on the target surface.

Coating synthesis

Coatings were synthesized with the parameters of process A given in Table 2 by non-reactive processing to investigate if the chemical composition of the target can also be maintained in the coating. The composition obtained by EDX is displayed in Table 3. The analysis indicates for the Al and Ti concentration a reduction in the coating while Ta shows an increase. Initially, XRD analysis of the coatings was performed on the SA-S substrate. As coating and SA-S have very similar lattice constants, the observed Bragg reflections could not be assigned unambiguously to the coating. Therefore, the measurements have been repeated for coatings on sapphire substrates (Fig.7).

The first of the two observed phases, denoted as M-1 (a = 3.60 Å), is nearly identical with the phase of the uncoated SA-S (a = 3.59 Å) (Fig. 7). Reflections of the second phase (M-2) are shifted towards higher 20 angles (a = 3.56 Å). This indicates that the nucleation behaviour on the sapphire substrate is slightly different from SA-S. The lattice constant of the phase M-2 has been determined to be approximately 3.56 Å. The TEM investigations of the target (and substrate) material already indicated more than one intermetallic phase and EDX mapping showed that there are at least two groups of elements in addition to precipitates which are segregating together. It is likely that these two groups condensate at different temperatures resulting in a phase separation. It also indicates a correlation between melting/quenching of the target surface and the condensation of high energetic vapour at substrate surface.

In additional experiments, a complete stack of layers was investigated according to process B. After initial pre-treatment of the SA-S as described above, the IF-1 was formed by arc evaporation in non-reactive mode and without additional interfaces at the SA-S with a thickness of about 0.5 μ m. In subsequent steps, 800 sccm oxygen was fed to the arc evaporation process and a short transition (0.2 μ m) from the non-reactive to the reactive mode was performed. Together with the double

rotation of the substrate, this results in a multilayer structure and finally in the nucleation of an oxide coating of about 1.5 µm. A STEM bright-field image of the complete layer stack is shown in Fig. 8a. IF-1 (indicated by a arrows in Fig. 8a) is investigated in greater detail by TKD (Fig. 8b) and the corresponding image quality map (Fig. 8c). Orientation mapping indicates epitaxial growth at grains in the region of IF-1 followed by the nucleation of many and very small grains with arbitrary orientation which can't be indexed by TKD, and finally the growth of larger grains nucleating at the finer grains of this transition region and forming the oxidized region of the layer stack. A high resolution TEM micrograph of an enlarged region of the interface between IF-1 and SA-S is given in Fig. 9. The finite thickness of the lamella (approx. 100 nm) and a slight misalignment of the interface with the viewing direction results in the interface not be atomically sharp. However, the micrograph shows that the lattice planes of the SA-S and the coating IF-1 are parallel with the same distance between the planes confirming the epitaxial growth of the coating on the substrate.

Conclusion

The work discusses the possibility to create a complete layer stack for a bond coat by cathodic arc evaporation in an *in-situ* process sequence, i.e. without interruption of vacuum. It was demonstrated that targets from powders nearly identical in chemical composition with a superalloy substrate can be fabricated and utilized as cathodes in arc evaporation. The targets can be operated in non-reactive and reactive deposition processes. The investigation of the target surface after processing with and without oxygen reactive gas, revealed only little influence on chemical composition and crystal structure. Coatings synthesized in non-reactive deposition mode are also similar in chemical compositions and crystal structure with respect to the targets. The approach to create a complete layer stack for the bond coat in one process, allows a design principle of grading profiles either by the controlled addition of the reactive oxygen gas or by the operation of additional targets with the

same or different elemental compositions. In addition, epitaxial growth could be observed at the grains of the polycrystalline substrate at the substrate interface. The addition of oxygen to the running arc evaporation process results in a fine grained transition region and finally a nucleation of larger crystallites in the fully oxidized region of the layer stack. The presented approach has the potential to realize epitaxial growth at arbitrary superalloy materials and to perform gradients to coatings with different chemical composition and functionality. Future work will be devoted to investigate the thermal and mechanical stability of IF-1 and the development of a thin oxygen diffusion barrier for IF-2.

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Table captions

Table 1:

Elemental composition (measured on the target surface) of the as produced target and the targets after utilization in evaporation processes A and B in comparison with the original powder composition utilized for target manufacturing.

Table 2:

Process parameters utilized in arc evaporation and coating thickness for the non-reactive process A and reactive process B. Coating B consists of 0.5 μ m IF-1 (non-reactive process), 0.2 μ m transition layer in which the oxygen flow is ramped from 0 to 800 sccm, and 1.5 μ m layer which deposited in 800 sccm oxygen flow. The STEM bright-field image of the cross section of this layer stack obtained in process B is shown in Fig. 8a.

Table 3:

Comparison of the chemical composition of the original powder with the chemical composition of the coating synthesized in process A (non-reactive) obtained by EDX.

Figure captions

- Figure 1: Schematics of the new bond coat concept (left) and an example (right) realized in this work by *in-situ* processing utilizing cathodic arc evaporation.
- Figure 2: $\theta/2\theta$ scans of the target surface of a virgin target (blue) and a target utilized in nonreactive processing (red). Both XRD diffractograms indicate the presence of an fcc phase.
- Figure 3: (a) SEM backscattered image of the target surface in the virgin (polished) state and (b) EBSD analysis indicating a polycrystalline and texture-free material.
- Figure 4: Bright-field (a) and dark-field (b) STEM micrograph of a virgin target section with different grains. (*) high angle boundaries; (**) dislocation arrays inside a grain; (***) twin boundary.
- Figure 5: EDX mapping of the elements Ni, Cr, Co, Ta, Ti, W, Mo and Al for the grains shown of Fig. 4.
- Figure 6: STEM bright-field (a) and dark-field (b) images with indication of an EDX line scan across two grain boundaries. (c) EDX line scan over the two grain boundaries.
- Figure 7: XRD diffractogram of a coating obtained by the non-reactive process A. Two phases can be distinguished: M-1 with a = 3.60 Å and M-2 with a = 3.56 Å.
- Figure 8: (a) STEM bright-field image of the layer stack which was synthsized by the combination of non-reactive and reactive deposition (process B) consisting of the IF-1 of about 0.5 μm thickness, the transition layer of about 0.2 μm and an oxide coating of about 1.5 μm. The transition between interface to the SA-S and IF-1 is indicated by arrows. For the indicated section in (a), a TKD measurement is shown in (b) and the corresponding image quality map is presented in (c). The dash line marks the interface between SA-S and superalloy coating (IF-1).

Figure 9: HR-TEM of the transition region between SA-S and IF-1 (named as interface in the

figure) demonstrating epitaxial growth.



Fig. 1















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Table 1

	Powder	Target Composition (EDX)			
	Composition				
Element	(ICP-OES and	as produced	Process A	Process B	
	ICP-MS)	[wt.%]	[wt.%]	[wt.%]	
	[wt.%]				
С	0.07	n.a.	n.a.	n.a.	
Al	3.6	3.8	3.2	1.6	
Та	5	8.3	5.5	4.6	
W	3.8	4.8	3.6	4.7	
Мо	1.9	2.0	1.3	1.6	
Ti	4.1	3.8	3.1	2.2	
Cr	12.2	11.1	14.3	11.8	
Со	9	8.7	9.1	9.6	
Ni	60.33	57.5	59.9	63.9	

Table 2

D	Arc	Deposition	Substrate	Oxygen	Total	Coating
Process	Current	Time	Bias	Flow	Pressure	Thickness
	[A]	[min]	[V]	[sccm]	[10 ⁻³ mbar]	[µm]
А	140	45	-40	0	0.1	1.5
				0	0.3	0.5
В	140	240	-40	$0 \rightarrow 800$	$0.3 \rightarrow 20$	0.2
				800	25	1.5

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Table 3

	Powder Composition	Composition Coating A
Element	(ICP-OES and ICP-MS) (EDX)	
	[wt.%]	[wt.%]
С	0.07	n.a.
Al	3.6	1.2
Та	5	6.4
W	3.8	4.3
Мо	1.9	1.5
Ti	4.1	2.8
Cr	12.2	14.1
Со	9	9.4
Ni	60.33	60.3

Highlights

- 1. Superalloy substrate-identical targets were fabricated and successfully utilized in nonreactive and reactive cathodic arc deposition
- 2. The chemical composition and structure of the targets were also found in the synthesized superalloy coating
- 3. An in-situ process sequence is demonstrated which allows a transition from the interface with the superalloy substrate to a second interface which could be the interface to the porous oxide of a thermal barrier coating
- 4. Epitaxial growth was achieved in the interface between superalloy coating and superalloy substrate