Surface & Coatings Technology 309 (2017) 516–522

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Comparison of *in-situ* oxide formation and post-deposition high temperature oxidation of Ni-aluminides synthesized by cathodic arc evaporation

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ARTICLE INFO

Article history:
Received 7 October 2016
Revised 18 November 2016
Accepted in revised form 3 December 2016
Available online 07 December 2016

Keywords:
Cathodic arc
Aluminium nickel oxide
Aluminium nickel intermetallics
In-situ high temperature XRD

ABSTRACT

Thin coatings were synthesized by cathodic arc evaporation of powder metallurgically fabricated Al-Ni targets with the chemical compositions of $Al_{75}Ni_{25}$, $Al_{67}Ni_{33}$ and $Al_{52}Ni_{48}$ atomic percent. The coatings were produced both either from pure metallic vapour or in reactive oxygen atmosphere. Phase transformations and chemical composition at the target surface were investigated by X-ray diffraction (XRD) and by energy-dispersive X-ray spectroscopy (EDS) techniques and compared with the phases composition obtained in the coating. The deposition in non-reactive mode produces intermetallic coatings containing different Ni aluminides. The formation of the aluminides can be controlled by the target composition and is by trend predictable from the Al-Ni phase diagram. The coatings produced in reactive mode are composed of both Al_3Ni and Al_3Ni_2 with the additional formation of AlNi and Al_2NiO_4 in all the coatings. The coatings composed of intermetallics show high indentation hardness in the range of 10 GPA while the coatings composed of both oxides and intermetallics demonstrate exceptional high hardness of about 30 GPa. All coatings have been annealed in ambient air up to 1200 °C and were investigated by *in-situ* XRD analysis in order to follow in detail their oxidation process. For all coatings, the formation of α-Al_2O_3 and Al_2NiO_4 could be observed after annealing forming a thin high temperature stable protective layer for remaining AlNi. The coatings deposited in reactive atmosphere contain additional NiO, independently of their original composition.

1. Introduction

Due to their high strength at high temperatures and their low density, intermetallics have been investigated intensively during the last seven decades for the utilization as high-temperature structural materials. The use of these materials in gas turbines motivated research on oxidation-related wear resulting in intensive studies of the oxidation mechanism of aluminides. Among them, the formation of oxide scales has been of particular interest [1,2]. The further increase of the operation temperature in gas turbines initiated the concept of surface-engineered components by thermal barrier coatings (TBC) [3–5]. In this coating architecture, the bond coat is the most delicate part of the TBC because it has to match the surface of a metallic component with the porous oxide (PO), usually partially Y-stabilized zirconia (YSZ), for a wide temperature range and for severe mechanical requirements. Due to its low thermal conductivity, the PO can reduce the surface temperature of the component up to 150 °C, therefore allowing a higher operating temperature of the turbine air blades. However, yttria is not an oxygen barrier and the bond coat material would be destabilized by oxygen diffusion under high temperature conditions. This is the reason why the interface between the bond coat and the porous oxide needs an additional protection against oxygen diffusion. It is realized by a thermally grown oxide at the surface of the bond coat before the deposition of the PO. In addition, the bond coat material must form an excellent interface to the component material. It should allow limited diffusion to improve the adhesion to the component, but should suppress unwanted phase formations in the interface. To control the diffusion processes from the interface to the component surface, the bond coat material should be similar in composition, but should also allow the addition of dopants. Therefore, the function of the bond coat dictates an architecture incorporating the transition from metallic to oxidic character, whereby the oxide should be preferentially an alumina-based one. Although this bond coat architecture seems rather

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http://dx.doi.org/10.1016/j.surfcoat.2016.12.013
0257-8972/

simple, it is difficult to achieve in one single process step. In this work, we investigate cathodic arc evaporation for its ability to produce the metallic and the oxidic interface of the bond coat. This coating technology is based on the evaporation of materials from targets which are used as the cathode in a vacuum arc discharge. These targets can be produced as composite material from powders and allow therefore a rather free choice of material compositions and consequently the adjustment to the chemical composition of the component. Moreover, the coating method allows the evaporation in the pure metallic vapour as well as in pure oxygen gas. As a remarkable consequence, this technology could be a method to synthesize the metallic interface to the component as well as the oxide barrier to the PO *in-situ* in one single process. Reactive cathodic arc evaporation has been a production technology since 40 years, dedicated especially to tool coating with a variety of nitrides. The production of oxide coatings for this market segment started about 10 years ago with the utilization of Al-Cr-O to reduce the oxidation wear of cutting tools. Since that time, the material was also investigated as oxygen and hydrogen barrier [6–7]. Recently, the phase transformations initiated by the cathodic arc at the target surface have been investigated and it was found that they can be predicted to some extent for binary material systems by the comparison with the phase diagram [8–12]. Additional investigation showed that the phase composition at the target surface can support a more purposeful coating synthesis for the pure metallic as well as for the oxide coating synthesis. In the past already a number of aluminium-based materials have been investigated, namely Al-Cr [10–12], Al-Cr-Fe [13–15], Al-Cr-Si [16], Al-Si [17], Al-Hf [8–9]. MCrAlY and Al-Ni coatings deposited by cathodic arc evaporation were also already investigated in terms of composition and oxidation resistance [18–20]. This work presents a more specific study on the relation between the target and the coating compositions. The Al-Ni oxide formation *in-situ*, *i.e.* during cathodic arc evaporation in reactive oxygen atmosphere, is compared with the oxidation behavior of the coatings by post-deposition annealing in ambient atmosphere to 1200 °C. The indentation hardness and the Young's modulus are measured.

2. Experimental

Table 1 lists the main process parameters of the cathodic arc evaporation using three different Al-Ni cathode compositions, $Al_{75}Ni_{25}$, $Al_{67}Ni_{33}$ and $Al_{52}Ni_{48}$. The cathodes were operated with a DC arc current of 140 A, either in metallic vapour only (non-reactive processes 1–3, Table 1), or with a gas flow of 400 sccm oxygen, resulting in an oxygen pressure of 1.1 Pa in the chamber (reactive processes 4–6, Table 1), using an INNOVA batch-type production system of Oerlikon Surface Solutions AG. The cathodes were powder metallurgically fabricated targets of 150 mm diameter (PLANSEE Composite Materials GmbH). Polished single crystal sapphire has been used as substrates in the depositions. Sapphire substrates rather than a nickel aluminide or nickel-based superalloys were selected to avoid any influence of the substrate surface on the nucleation process for a specific chemical composition and to reduce possible diffusion processes induced from the substrate. Before deposition, the process chamber was evacuated below 10^{-3} Pa and standard heating and etching steps were performed to ensure a sufficient coating adhesion to the substrate. The substrate temperature was kept at 550 °C during deposition. The deposition time was 100 and 120 min for the non-reactive process and was increased to 140 min for the reactive processes in oxygen due to the reduced evaporation rate of the Al-Ni target in oxygen, resulting in a coating thickness between 4 and 5 μm. The operation time ensures stable conditions for the oxygen pressure and ensures a conditioned cathode surface. Only one arc source was utilized during deposition. A symmetric bipolar bias voltage of 40 V was applied to the substrate with a frequency of 25 kHz and a negative pulse length of 36 μs and 4 μs positive pulse length.

Table 1
Process conditions for the different cathodic arc operations and the associated coating synthesis.

Process	Target	Oxygen flow [sccm]	Arc current [A]	Deposition time [min]	Substrate bias [V]
1	$Al_{52}Ni_{48}$	0	140	100	−40
2	$Al_{67}Ni_{33}$	0	140	120	−40
3	$Al_{75}Ni_{25}$	0	140	120	−40
4	$Al_{52}Ni_{48}$	400	140	180	−40
5	$Al_{67}Ni_{33}$	400	140	180	−40
6	$Al_{75}Ni_{25}$	400	140	180	−40

The analysis of the target surfaces was performed in a LEO 1530 scanning electron microscope (SEM). The morphology and thickness of the deposited layers was obtained from fracture cross-sections (X-SEM) of the substrate. Depth profiles of the layer composition have been made by energy-dispersive X-ray spectroscopy (EDS).

Additional composition analysis was performed by Rutherford Backscattering Spectrometry (RBS) [21] at the EN tandem accelerator of the Federal Institute of Technology in Zurich. The measurements were performed using a 2 MeV, ^4He beam and a silicon PIN diode detector under 168°. The collected data were evaluated using the RUMP program [22].

The hardness and the Young's modulus of the coating have been measured by nanoindentation following to the ISO 14577 norm and using a fischerscope indenter. The indentation depth (h_{max}) for the measurements was in the range between 150 nm to 250 nm and 20 to 30 indentations were performed to determine the values for indentation hardness and Young's modulus.

In-situ high temperature XRD measurements were performed on the layers deposited on sapphire substrates produced by the reactive and non-reactive processes in order to study their oxidation behavior. The measurements were carried out in a $2\Theta/\omega$ mode with 1° offset in order to avoid the (024) peak of the single crystal sapphire substrate on a PANalytical X'Pert MPD instrument using Cu-Kα radiation. The coatings have been heated in an Anton Paar HTK16 chamber in air on a platinum strip up to a nominal temperature of 1400 °C, with a heating rate of 5 °C/min. XRD $2\Theta/\omega$ scans were performed every nominal 100 °C starting from 25 °C (platinum strip temperatures controlled by a welded thermocouple). At each step, the temperature has been maintained for 5 min before starting the $2\Theta/\omega$ scan, which is lasting 10 min. Therefore, the sample was maintained in total 15 min at each temperature steps. In total, the ramping up to 1400 °C is lasting 6 h. Cooling down to room temperature has been done with a rate of −5 °C/min, meaning that the Pt strip stay in total 3.5 h above 1000 °C. The temperature of the layer at the sapphire substrate is lower than the temperature of the platinum heating strip due to some heat loss. The calibration of the temperature has been done using the sapphire (024) peak shift of the substrates prior to the experiments. The change in the lattice parameter due to the thermal expansion of sapphire has been measured for the temperature range between 200 and 1400 °C. The temperature of the sapphire substrate has been determined by using a mean coefficient of thermal expansion of $9.33 * 10^{-6}$/K calculated from Watchman et al. [23]. The results give a temperature of the substrate of about 1200 ± 20 °C at the maximum platinum strip temperature of 1400 °C. Additional XRD measurements were performed on the layers at room temperature before and after annealing on the PANalytical X'Pert PRO MRD instrument using Cu-Kα radiation in a 2Θ mode with 1° grazing incidence angle. The small grazing incidence angle has been used to get maximum information of the surface of the film and to avoid the signal from the substrate. The ICSD-data base was used to identify the crystallographic phases.

3. Results and discussion

3.1. Target surfaces vs deposited coatings

3.1.1. Non-reactive processes

Fig. 1 shows the $2\Theta/\omega$ diffractograms of the cathode surface after arc operation for the non-reactive processes 1–3 (Table 1) and the 2Θ diffractograms with 1° grazing incident angle of the respective