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High vacuum arc ion plating NiCrAlY coatings: Bias effect and approach to preparation of functional gradient coatings

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The substrate bias effects on high vacuum arc ion plating (HV-AIP) of NiCrAlY coatings on superalloy were investigated at the vacuum level of 10^{-3}–10^{-4} Pa, which are 2–3 orders in magnitude better than that of conventional low vacuum arc ion plating (LV-AIP). The negative bias applied to the substrate was in the range of −50 V to −450 V. Microstructures, deposition rates, and chemical compositions of the coatings are significantly influenced by the negative bias. Except for commonly observed bias induced densification in microstructure and decrease in deposition rate, strong preferential sputtering effect at high bias was observed. The sputtering yield for Cr was estimated to be ranged from ~0.1 to ~0.2 at bias from −50 V to −450 V, while those for Ni and Al were from ~0.1 to 1.5. As a result, the major phase constitution of the coatings changed from γ-Ni/γ′-Ni_3Al phases at bias of −50 V to α-Cr phase at bias of −450 V. Such stronger preferential sputtering effect in HV-AIP fosters a strategy for preparing compositionally gradient NiCrAlY coatings just by control of the substrate bias without the need of further treatments or multi-targets. Based on this concept, preparation of several types of gradient NiCrAlY coatings with great flexibilities by one target and one process was demonstrated.

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1. Introduction

Protecting hot-section components of new generation aero and land based gas turbines, which have to withstand increasingly harsher environments, issues demand for more advanced processing techniques that can produce coatings with artificially delicate microstructures [1–4]. MCrAlY (M = Ni, Co or NiCo) coatings, are the most widely used protective coatings either as standalone coating or bond coat in thermal barrier coating system (TBCs), because they possess better balance, as compared with β-NiAl and NiPtAl coatings, among good thermo-mechanical properties to withstand mechanical load, superior resistance against high temperature oxidation and hot corrosion, and affordable prices. Many researches have been done in efforts to modify the MCrAlY coatings via microstructural or compositional optimization. Various methods have been explored to deposit MCrAlY coatings including hot spray techniques e.g. high-velocity oxy-fuel technique (HVOF) [5], air or low vacuum plasma spray (APS, LVPS) [6], and physical vapor deposition (PVD) techniques e.g. electron beam physical vapor deposition (EB-PVD) [7], magnetron sputtering (MS) [8,9], and arc ion plating (AIP) (or vacuum cathodic arc deposition) [10–12]. MCrAlY coatings prepared by PVD techniques usually have better oxidation resistance than those of sprayed ones [5,6,8–12], because there are more voids and contaminant in the latter [13,14]. What makes AIP special among other PVD methods is its capability of generating high proportion of ionized species from target materials. This characteristic enables AIP method to deposit dense and well-bonded MCrAlY coatings and to a large extent to overcome the "line-of-sight" effect which yields insufficient coverage of the coatings on substrate. However, conventional AIP methods were usually operated under a relatively lower vacuum (LV) level of about 10^{-1} Pa, which can introduce gas inclusions in the coating [15–17].To deal with this problem, Russo and co-authors developed an ultrahigh vacuum cathodic arc (UHVAC) method by evacuating the vacuum chamber to 10^{-8} Pa for depositing high quality Nb film with dense microstructure and free of gas inclusions [18], which lighted a prospective field and strategy of depositing high quality coatings in high vacuum condition instead of the conventional one [17–20]. Recently, we have successively explored high vacuum arc ion plating NiCrAlY coatings at a higher vacuum level of 10^{-3}–10^{-4} Pa [17]. It showed that the HV NiCrAlY coatings possessed a much denser microstructure and better oxidation resistance than that of conventional LV ones. Moreover, the HV-AIP can eliminate coating blistering phenomenon that was encountered in the gas-containing LV-AIP coatings during high temperature oxidation. Thus, more systematic and deeper exploration of HV-AIP NiCrAlY coatings should be of concern to us. Substrate bias voltage is one of the most significant parameters which affect much on the chemical compositions of coatings deposited by conventional LV-AIP using multi-component alloy targets [21–23]. For instance, the Ti/Al ratio of the coatings deviated from that of the initial target when a much stronger bias was applied in deposition of TiAlN coatings with TiAl target at vacuum of 2 Pa [21]. It is considered as the major cause that ions released from the target yield strong sputtering

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effect on the growing coating when accelerated by strong substrate bias. In the HV condition, metal ions can have much higher kinetic energy when they arrive to substrate due to their greater mean free path (MPF) as compared with the LV one [17]. Hence, it is believed that a stronger compositional deviation as well as changes in phase constitution between coating and target might be expected in HV-AIP [24]. Furthermore, appropriate control of the compositional deviation might lead us to a flexible and simple deposition technique that is able to prepare functional gradient NiCrAlY coatings using one target just by controlling the substrate bias during HV-AIP processing, whereas the state of the art deposition methods for gradient NiCrAlY coatings are based on multi processes and multi targets [10–12,25].

This study focuses on the substrate bias effect on the microstructure, deposition rate, composition and phase constitution of HV-AIP NiCrAlY coatings. Moreover, based on the coating composition-bias relation, flexible design of compositionally gradient NiCrAlY coatings is presented.

2. Experiments procedures

Nickel-base superalloy K438G was used as the substrate material for the deposition of NiCrAlY coatings, the nominal chemical compositions of the K438G alloy and NiCrAlY target are shown in Table 1. A spark discharge machine was used to cut the alloy into samples with dimensions of 15 × 10 × 2.5 mm. The samples were ground with SiC paper down to 800-grit followed by sand blasting with air pressure of about 0.4 MPa and then were ultrasonically cleaned within ethanol and acetone for 5 min.

An AIP machine (DH-15, Beiyu Vacuum Technology, Shenyang, China) was employed to deposit the NiCrAlY coatings on the K438G substrates. The sizes of the cylinder NiCrAlY target are 100 mm in diameter and 40 mm in height. The coatings were deposited with different substrate bias voltage varying in the range of −50 V to −450 V (−50 V, −100 V, −150 V, −200 V, −250 V, −350 V, −450 V). The samples were suspended on the same place of a sample holder with a rotation rate about 10 r/min during the coating preparation. Distance between the rotating center and the target is around 250 mm. It has been noticed that using metal ions of cathodic arc plasma to clean the samples surfaces has great advantages over the conventional argon ions cleaning for obtaining a cleaner sample surfaces for the coating deposition [26]. Hence, the ion etching or cleaning of the samples prior coating deposition was also conducted without using any Argon gas. After the base vacuum of the chamber was pumped down to 3×10^{-3} Pa by an oil diffusion pump backed by a rotary pump, the etching process was set at bias voltage of −900 V at 20% in duty cycle for 5 min. Due to the slightly longer distance between the samples and the target, a high arc current of 200 A DC was used to compensate the decrease of deposition rate induced by the increased distance from the target. The deposition time lasted for 3 h. During the deposition, the magnetic field at the surface of the target surface was adjusted in real time to keep the arc spot moved uniformly on the target surface.

In order to estimate the specific mass gains of the coatings deposited on the samples with different bias voltages, the dimensions of the substrates were measured before the deposition process. The masses of each specimen before and after the deposition process were also weighed by a precision electronic balance (0.01 mg precision, BP211D, Sartorius, Germany). The phases of the coatings were characterized by means of X-ray diffraction (XRD, X' Pert PRO, PANalytical Co., Almelo, The Netherlands, Cu Kα radiation at 40 kV). The compositions and the cross section morphology were measured by the scanning electron microscopy (SEM, InspectF 50, FEI Co., Hillsboro, OR) with energy dispersive spectroscopy (EDS, INCA, X-Max, Oxford instruments Co., Oxford, U.K.). The mean thickness was obtained by calculation of coating area divided by coating length in the cross-sectional image. The Adobe Photoshop software was used to calculate the area and length of the coating by extracting the pixel numbers of the scale bar in the image. At first, the image was cut into two parts along the interface of the substrate and the coating. Only the part with the coating side was left. Then, the pixel numbers of the coating area and coating length was obtained with assistance of the magic wand and line tools. Based on the pixel numbers, the mean thickness of the coating was obtained.

Table 1
The nominal composition of the substrate K438G alloy (in weight percent, wt.%).

Ta	Cr	Co	Ti	Al	Mo	C	W	Nb	B	Ni
1.75	16.34	8.38	3.81	4.0	1.77	0.16	2.66	0.76	0.01	Balance

3. Results and discussion

3.1. Deposition rate and microstructure

Fig. 1 shows the deposition rates of the NiCrAlY coatings for 3 h under different negative bias from −50 V to −450 V. Generally, the stronger the bias was applied, the lower the deposition rate was. This trend is in accordance with that of conventional LV-AIP coatings [22, 27], which can be attributed to the sputtering effect of ions from the arc plasma. However, the deposition rate seems to decrease much more sharply in HV than that in LV condition while increasing the negative bias, indicating a stronger sputtering effect in HV-AIP [17]. For instance, almost 70% decrease in coating thickness occurred when the bias was increased from −50 V to −450 V. In contrast, only 30% reduction in deposition rate was observed on CrAlN coatings when the bias was increased from −100 V to −500 V [27]. Also it can be noticed that the deposition rate dropped about 3 μm/h per 50 V from −50 V to −100 V while it dropped only about 1 μm/h per 50 V later from −100 V to −450 V, implicating the sputtering effects under substrate bias might be more complicated than expected.

Fig. 2 shows the back-scattered SEM images of cross sections of the HV-AIP NiCrAlY coatings deposited under different negative bias from −50 V to −450 V. Although a small amount of pores of 1–2 μm in size was observed in the coating prepared with the bias of −50 V, coating blistering, which happened in LV-AIP NiCrAlY coatings during high temperature oxidation, was not observed [17]. As expected, fewer voids were observed in the coatings prepared with more negative bias.

3.2. Composition and phase

Fig. 3 displays remarkable bias dependence of the chemical compositions of the coatings. We have measured the content of Y in the

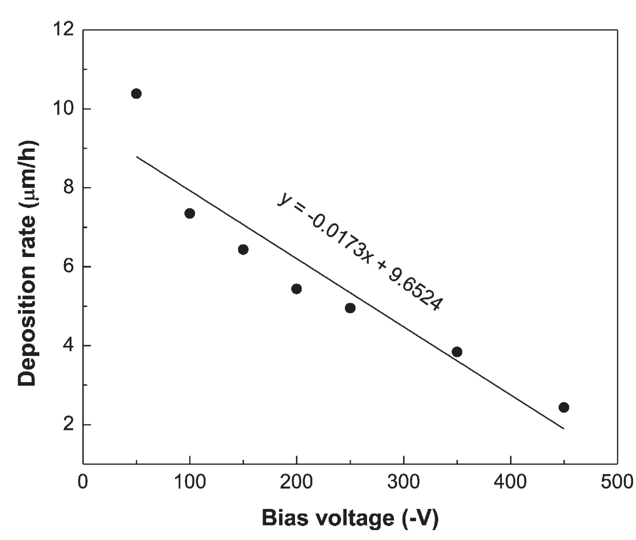

Fig. 1. Deposition rates of the NiCrAlY coatings deposited under different bias voltages from −50 V to −450 V.

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