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Microstructure and mechanical properties of alumina coatings prepared by double glow plasma technique

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ABSTRACT

Low-temperature growth (600 °C) of α-Al_2O_3 coatings on the stainless steel substrate by double glow plasma technique was achieved. The compositions and microstructures of the coatings prepared at different oxygen flow rates were characterized, respectively, by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectrometry. A phenomenological mechanism for the formation of the Al_2O_3 ceramic coatings during the oxidation process was proposed on the basis of the experimental results. It was obvious that the oxygen flow rates had a great effect on the surface structure of the prepared Al_2O_3 coatings. The dense and smooth Al_2O_3 coatings were prepared at the oxygen flow rate of 15 sccm. In addition, the correlations between the mechanical properties of Al_2O_3 coating and oxygen flow rates were also discussed. The coating prepared at 15 sccm oxygen flow rate exhibited the best mechanical properties with a maximum hardness of 31 GPa and elastic modulus of 321 GPa. The corresponding critical load of scratch adherence for this sample was 47 N.

1. Introduction

Alumina coatings are widely used as wear resistant, corrosion resistant and diffusion barrier coatings. Especially, alpha-phase aluminum oxide coatings have been the subject of great interest. It is chemically and mechanically stable at temperatures upward 1000 °C and has a melting point of 2053 °C [1]. In addition, the alpha-phase exhibits great hardness and wear resistance [2]. It is widely considered to be the best coating for preventing substrate oxidation at high working temperatures [3]. However, synthesis of this phase is not straightforward. The existence of several metastable phases complicates the growth of α-Al_2O_3, especially low-temperature growth is required (to limit the thermal load of the substrate). Consequently, many low-temperature growth studies, aimed at forming α-phase alumina, have been done during the last decade.

Alpha-Al_2O_3 coatings are successfully made by the thermal CVD process in commercial scale [4]. However, due to a high substrate temperature of over 1000 °C in the CVD process, the thermal expansion mismatch leads to the buildup of residual stress upon cooling that adversely affects adhesion through crack generation. Therefore, PVD techniques, which successively resulted in a significant decrease in α-phase formation temperatures [5,6], have been paid much attentions. Basing on the former researches, it is known that there are mainly four factors that may be of importance for the formation of α-Al_2O_3.

One approach to reduce the crystalline growth temperature of α-Al_2O_3 is to enhance the mobility of surface species through energetic ion bombardment. As examples in Refs. [7–9], these works have proven that it is possible to promote crystalline phase formation and the deposition temperature of α-Al_2O_3 can be decreased from 800–900 °C to 600–700 °C by applying a high substrate bias (<−100 V).

Another interesting approach to synthesize and stabilize the α-Al_2O_3 at lower temperatures is based on the utilization of additives elements such as Cr, Y, Ce, etc. [10,11]. It was reported by Brumm and Grabke [12] that, during the oxidation of NiA1–Cr alloys, chromium accelerates the θ to α-phase transformation and leads to higher values for the oxidation parabolic rate constant. A larger chromium concentration promotes the presence of α-Al_2O_3 nuclei. Consequently, the transformation from θ-$A1_2O_3$ to α-Al_2O_3 is accelerated. This rule was also testified by Levchuk' s research [13], in which a co-existence of alpha-chromia and alumina solid solution was obtained with an addition of 30 at.% Cr in the aluminum alloy target. The low deposition temperature for the synthesis of this corundum-type solid solution was only 550 °C.

In addition, the grain refinement of aluminum alloys for the formation of α-Al_2O_3 is another field of investigation [14]. At low temperature, by providing more nucleation centers, the grain size of the aluminum alloy affects the amount of metastable Al_2O_3 formed during the initial stages of oxidation and the subsequent transformation to the stable α-Al_2O_3. According to the work of

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Chen and Gao [15,16], nanocrystalline alloys or coatings exhibited excellent isothermal and cyclical oxidation resistance which were attributed to the formation of dense and continuous α-Al_2O_3.

The fourth approach for low-temperature deposition of α-Al_2O_3 is using α-Cr_2O_3 as a template. Following this methodology, Jin et al. [17], Morikawa et al. [18] and Andersson et al. [19] have reported that α-Al_2O_3 could be deposited upon a chromium oxide template layer and the lowest temperature for the deposition of α-Al_2O_3 using α-Cr_2O_3 template in the literature was 280 °C.

In summary, there have done many efforts to produce α-Al_2O_3 coatings at low temperatures. Although it was proved that α-Al_2O_3 could be synthesized by PVD method at low temperatures, the thickness and adhesion strength of the prepared films cannot meet practical demand. In this work, the viability of using the newly developed double glow plasma technique for producing Al_2O_3 coatings at low temperatures has been explored.

The double glow plasmas technique is a modern technology, which is the evolution of the plasma nitriding and the sputtering technique. This technology employs low-temperature plasma produced by a glow discharge to drive source material atoms of one or more elements to be sputtered, and then diffuse into the substrate surface. Solid metallic elements of Ni, Cr, Mo, W, Ta, Al, Ti, etc. and non-metallic elements of N, C, O, etc. have been studied [20,21]. In the plasma oxidation process of this technique, in contrast to conventional oxidation, the target material is continuously subjected to a flux of ions and neutrals present within a glow discharge. This oxidation technique has several advantages over other oxidation techniques, e.g., fast oxidation rate, the independent control of beam energy and current density of ion beam, and ease of forming uniform and dense oxide layer.

The present work intended to deposit thick α-Al_2O_3 coatings utilizing double glow plasmas technique. Furthermore, the influence of the oxygen flow rates on the microstructure, surface morphology, chemical concentration and mechanical properties of the Al_2O_3 coatings were also studied.

2. Experiments

Pure aluminum plates were used as the target material for supplying the needed element. 316L stainless steel plates (60 mm × 30 mm × 5 mm) were used as the substrate material. The chemical composition of the AISI 316L stainless steel in wt.% was: Ni, 10.128; Cr, 16.39; Mo, 2.515; C, 0.027; Si, 0.229; Mn, 1.716; N, 0.046; P, 0.032; S, 0.001 and the balance, Fe.

The equipment and its working principles were introduced in our previous work [22]. The fabrication processes for the Al_2O_3 coatings are listed as follows: (1) a thin aluminum layers, about 10 μm thick, were deposited directly onto the 316L substrates by double glow plasma technology. The glow-discharge sputtering conditions were: working pressure, 35 Pa; source electrode with direct current, voltage 850 V, current 4.5 A; workpiece electrode with pulse–time ratio of 0.6, voltage 300 V, current 1.5 A; the parallel distance between the source electrode and the substrate 15 mm, and treatment time 3 h. (2) Co-deposition of Al and O was conducted on the aluminizing layer in a mixture of argon and oxygen at a total pressure of 35 Pa. The argon flow rate was kept at 100 standard cubic centimeters per minute (sccm), while the oxygen flow rates varied from 5 to 20 sccm to obtain various oxygen concentrations in the coatings. The working temperature was kept at 600 °C. During this co-deposition process, the glow-discharge sputtering conditions were: source electrode, voltage 500 V, current 3.5 A; workpiece electrode, voltage 250 V, current 0.8 A; and treatment time 3 h.

In order to study the oxidation mechanism of the aluminum–oxygen co-deposition, a comparative experiment of plasma oxidation (without aluminum sputtering) was also carried out on the aluminizing layer. In this process, the source electrode was turned off while the cathode was kept on with a workpiece electrode, voltage 600 V and current 4.0 A. The oxidation temperature and time were kept unchanged.

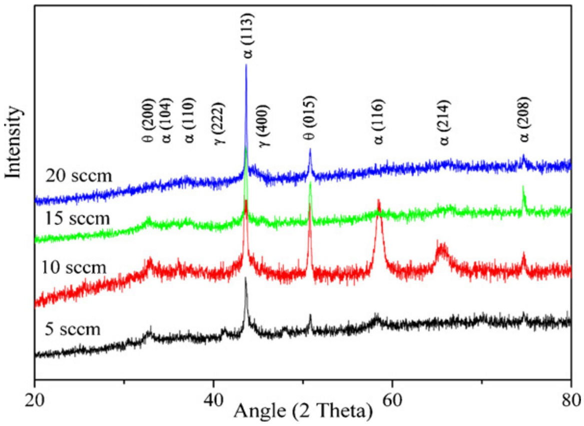

Fig. 1. XRD patterns of Al_2O_3 coatings deposited at different oxygen flow rates.

The phase, microstructure and chemical composition of the Al_2O_3 coatings were studied respectively by XRD (D8ADVANCE with Cu Kα radiation), SEM (Quanta200, FEI Company) and energy dispersive X-ray spectrometry coupled to the SEM instrument. Having a displacement and load resolution of 0.0002 nm and 1 nN, a Nanoindenter (SA2, MTS, USA) was used to determine the hardness and elastic modulus of the Al_2O_3 coatings. Before nanoindentation, all specimens were polished and ultrasonically cleaned in isopropanol. Finally, WS-2005 CSEM scratch test equipment was used to determine the adhesive properties of the Al_2O_3 coatings.

3. Experimental results

3.1. Microstructure and composition of oxide coatings

Al_2O_3 coatings formed at different oxygen flow rates were examined by XRD, as shown in Fig. 1. All the prepared samples contain three types of alumina, i.e. α-Al_2O_3, θ-Al_2O_3 and γ-Al_2O_3. Comparing to the peaks of θ and γ-phases, α-Al_2O_3 peaks are stronger, which means that the α-Al_2O_3 in the coatings is higher. It is also noticeable that, as the oxygen flow rate is increased, the intensity of (1 1 3) peak increases while (4 0 0) and (0 1 5) peak decrease. This implies that the increase of α-Al_2O_3 content in the coatings. From the XRD data it can be calculated that the maximum content of α-Al_2O_3 is 62% [23].

It is well known that, in the thermal oxidation process of alumina forming alloys and aluminides, Al_2O_3 occurs in different phases. At certain conditions, the metastable oxides γ, δ, and θ-Al_2O_3 will transform to the α-Al_2O_3 [24]. In our study, a high content of α-Al_2O_3 coatings form at lower temperatures and the phase content of α-Al_2O_3 increases as the oxygen flow rate is increased. It is reported previously that energetic ion bombardment can reduce the crystalline growth temperature of α-Al_2O_3. However, the key for achieving low-temperature α-alumina growth seems not to be just a highly energetic bombardment, but rather a bombardment within a suitable energy window and with a high enough ion (momentum) flux. Too high energy of the bombarding species results in the formation of amorphous films [25]. In the double glow-discharge process, the average energy of the ion is 20–50 eV [26]. It is in the range of energy that can form α-Al_2O_3 at 600 °C [8].