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Effects of Ar/O_2 ratio on preparation and properties of multilayer Cr_2O_3/α-Al_2O_3 tritium permeation barrier

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ABSTRACT

A multilayered Cr_2O_3/α-Al_2O_3 tritium permeation barrier coating containing a total of 10 nanoscale layers was prepared by radiofrequency magnetron sputtering without intentional heating. X-ray diffraction, Auger electron spectroscopy, and spherical aberration corrected transmission electron microscopy studies showed a multilayer structure and a Cr_2O_3 (104)/α-Al_2O_3 (104) coherent epitaxial growth. The effect of the Ar/O_2 gas flow ratio (Λ) on the structure and properties of the Cr_2O_3/Al_2O_3 multilayer coating were investigated. The results show that the crystallinity of the α-Al_2O_3 phase increased with decreasing Λ. The mechanical properties, He^+ ion irradiation tolerance, and corrosion resistance of the coating began to improve greatly when Λ was decreased to 1:1. The coating with Λ = 1:2 gave α-Al_2O_3 with the best properties, i.e., high nano-hardness (19.6 GPa), good corrosion resistance (i_{corr} = 10 nA/cm^2), and excellent irradiation resistance. The deuterium permeability of the Cr_2O_3/α-Al_2O_3 multilayer coating was also investigated.

1. Introduction

Thermonuclear fusion energy has attracted much attention as a potential clean energy source because of its advantages in terms of safety, fuel reserves, and minimum damage to the environment [1]. Fusion involves the fusing of hydrogen and its isotopes, i.e., deuterium and tritium. Because they are small, hydrogen and its isotopes can easily permeate metallic construction materials, resulting in material embrittlement, fuel loss, and radioactive contamination [2–6]. A promising solution to this problem is to apply a tritium permeation barrier (TPB) to the surface of construction materials.

Several types of TPBs, including oxides (Al_2O_3, Cr_2O_3, Y_2O_3, ZrO_2, and Er_2O_3), nitrides (Fe_2N, TiN, Al/TiN, and Si_3N_4), carbides (TiC and SiC), and their composites, help to minimize hydrogen isotope permeation. Al_2O_3 has the greatest potential as a coating because of its high permeation reduction factor (PRF), good irradiation resistance, compatibility with Pb-Li, and good corrosion resistance, mechanical properties, and wear resistance [2,7–9]. Several studies of composites such as Er_2O_3/Al_2O_3 [10], Cr_2O_3/Al_2O_3 [11–13], and $FeAl/Al_2O_3$ [14–16] have been performed to develop Al_2O_3 coatings with improved hydrogen permeation resistance. Coatings based on such composites are better than their single-layer counterparts because they have much higher PRF values. Multilayer Cr_2O_3/Al_2O_3 coatings [17], in particular, have attracted much attention. This is because in addition to its intrinsic good resistance to hydrogen isotope permeation [18,19], Cr_2O_3 can be used as a buffer layer to enhance the interfacial strength between an Al_2O_3 ceramic coating and a steel substrate [20]. The Cr_2O_3 sublayer can also act as a structural template [21–23], which can promote the formation of α-Al_2O_3, which has advantageous properties.

Several deposition parameters such as substrate temperature, substrate bias, modulation period, and sputtering power have important effects on the preparation, structure, and properties of Al_2O_3-based multilayer coatings [24–27]. For example, Cr_2O_3/α-Al_2O_3 multilayer coatings prepared using different modulation periods have distinct irradiation resistances [26]. $TiAlN/Al_2O_3$ multilayer coatings with different preferred orientations and mechanical properties were obtained by using different modulation periods and modulation ratios [28]. Studies have also shown that the ratio of non-reactive/reactive gas species significantly affects the structures and properties of many sputtered oxide coatings [29–31]. Coatings with various oxygen-

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to-aluminum concentrations (Al_xO_y) can be prepared by changing the Ar/O_2 sputtering ratio. It can change the stoichiometry and phase formation of Al_xO_y, and this affects the chemical and physical properties of the coating. However, the effects of the sputtering ratio on the structures and properties of Al_2O_3-based multilayer coatings have not yet been studied.

In the present study, a Cr_2O_3/α-Al_2O_3 multilayer coating was deposited by magnetron sputtering with different Ar/O_2 sputtering gas ratios (Λ). Comprehensive characterization using X-ray diffraction (XRD), spherical aberration corrected transmission electron microscopy (ACTEM), and Auger electron spectroscopy (AES) showed the formation of a multilayer structure and an α-Al_2O_3 phase. The effects of Λ on the microstructure, nanomechanical properties, corrosion resistance, and irradiation resistance of the multilayer coating were investigated systematically. The deuterium permeation behavior of the Cr_2O_3/α-Al_2O_3 multilayer coating was discussed.

2. Materials and methods

2.1. Preparation

Using a radiofrequency (RF) magnetron sputtering system (base pressure $< 2 \times 10^{-4}$ Pa), Cr_2O_3/Al_2O_3 multilayer coatings were deposited on Si (100), CLF-1 reduced- activation ferritic/martensitic steel and 316 L stainless steel (used for deuterium permeation test). The substrates were first polished to mirror surface and cleaned in acetone and ethanol by ultrasonic bath. Then the substrates were electrochemical polished in 10% perchloric acid solution for 10 s, followed by distilled water cleaning using ultrasonic bath and drying in air.

A two-step deposition method was used to obtain a multilayer structure. No intentional heating was employed and the temperature of the samples was controlled below 326 K by the loop cooling water system during the two-step depositing process. In the first step, a Cr_2O_3 template sublayer was deposited by sputtering a Cr target (99.99% purity) at a RF power of 60 W for 20–30 min using Ar (99.99% purity) and O_2 (99.99% purity) as sputtering gas, the total gas pressure was kept at 1.2 Pa. The flux ratio of Ar to O_2, which was defined as Λ, was fixed to be 96 sccm: 32 sccm. The second step involved deposition of an Al_2O_3 sublayer by sputtering an Al target (99.999% purity) at a RF power of 80 W for 30 min, without breaking the vacuum. In this step, we applied a high substrate self-bias of −200 V and optimized the conditions for Al_2O_3 formation by changing the Λ. The employed Λ values were 3:1 (42 sccm: 14 sccm), 2:1 (38 sccm: 19 sccm), 1:1 (31 sccm: 31 sccm) and 1:2 (24 sccm: 48 sccm), respectively. The total gas pressure was kept at 0.6 Pa. Finally, a multilayer Cr_2O_3/Al_2O_3 coating was produced by repeating the above steps five times.

2.2. Characterization

Crystal structures were studied using X-ray diffraction (XRD, RigakuD/max–2500), with Cu Kα radiation, at 40 kV and 30 mA. XRD pole figures were acquired in the title-angle (α) range 0–75° and the azimuth-angle (β) range 0–360° with α and β steps of 5° by using Panalytical Xpert Pro MRD diffractometer equipped with a PW3050/60 goniometer. Orientation distribution function (ODF) was calculated using the MTex software [32]. Microstructures and elements distributions were examined using field emission scanning electron microscope (FESEM, JEOL JSM-6700F), spherical aberration corrected transmission electron microscopy (ACTEM, FEI Image Corrected Titan G2 60-300) coupled with energy dispersive X-ray spectrometry (EDX) and auger electron spectroscopy (AES, PHI 680 SAM). The cross-sectional TEM specimens were prepared by milling in a focused ion beam (FIB, FEI HELIOS NanoLab 600i) system. The nano-hardness was determined from typical load-displacement curves according to the Oliver formula [33], using a nanoindentation tester (NHT2, Anton Paar). The indentation depth was chosen to be not > 1/10 of the coating thickness to eliminate substrate effects. The composite corrosion resistance was tested at room temperature (298 K) in 3.5% NaCl solution, using a three-electrode electrochemical system (Solartron 1287, Solartron Metrology).

The multilayer coatings were irradiated with 30 keV He^+ ions at a fluence of 5×10^{17} ion/cm^2, using an anion implantation system. Samples were mounted on a water-cooled holder, and the temperature rise during irradiation was < 300 K during irradiation. The displacement per atom (DPA) and He concentration as a function of depth for the coatings were simulated using the Stopping Range of Ions in Matter (SRIM) code in Monolayer Collision Steps model [17,34,35]. DPA were calculated with the formula: $DPA = N_d N_i / N_a$ (N_d is the primary displacements unit length, N_a is atomic density of the target and N_i is the implanted ion fluence) [36,37]. The deuterium permeation properties were investigated using the method specified by the General Research Institute for Nonferrous Metals. Details of the apparatus and the measurement procedure are available in previous reports [12,38]. The coated side of the sample was mounted facing the upstream side. Deuterium was introduced into the upstream chamber at pressures ranging from 40 to 100 kPa. Quadrupole mass spectrometry (Hiden HPR30) was used to measure the deuterium permeation flux through the sample to the downstream chamber; the measurement temperature was 823–973 K.

3. Results and discussion

3.1. Effects of Λ on structure of Cr_2O_3/Al_2O_3 multilayer coatings

Fig. 1 shows the XRD patterns of Cr_2O_3/Al_2O_3 multilayer coatings prepared using various values of Λ. All the coatings gave two clear diffraction peaks, indicating formation of polycrystalline structure in all cases. A diffract peak centered at about 35.6° occurred at all Cr_2O_3/Al_2O_3 multilayers with different Λ, which can be indexed to Cr_2O_3 (104), α-Al_2O_3 (104) or Cr_2O_3 (110) due to their similar peak position [22,39,40] and the presence of satellite peaks, demonstrating a texture developed by the alignment of Cr_2O_3 (104), α-Al_2O_3 (104) or Cr_2O_3 (110) parallel to the substrate surface. It is expected that Cr_2O_3 (104)/α-Al_2O_3 (104) coherent epitaxial growths occur at Cr_2O_3/Al_2O_3 multilayer (further demonstrated by following HRTEM results), since crystal growth of epitaxial lattices usually promotes the development of a strong out-of-plane crystallographic texture improving their mutual coherence. Another broad peak at 63.8° performed similar behavior for the reported α-$(Cr, Al)_2O_3$ phase [40,41], also indicating a well coherent epitaxial growth at Cr_2O_3/Al_2O_3 multilayers. However, it is noteworthy that all peaks were narrowed and shifted systematically to lower 2θ angles with the decrease of Λ, towards the positions for α-Al_2O_3 (red lines shown in Fig. 1, reference PDF No. 46-1212 of the ICDD data base). When the flux ratio was decreased to Λ = 1:2, the peak position (35.2°) was very close to that of pure α-Al_2O_3, suggesting higher crystallinity of the epitaxial α-Al_2O_3 phase. The corresponding pole figure plot of the α-Al_2O_3 (104) peak (shown in Fig. 1(e)) demonstrates the α-Al_2O_3 layer (Λ = 1:2) had a pure fiber texture with the [104] out-of-plane orientation, consistent with the reported [104]-textured α-Al_2O_3 layer [42]. Similar results have proved in co-sputtered α-$(Cr, Al)_2O_3$ film that the diffraction peak positions become closer to that of pure α-Al_2O_3 by changing Al content [43]. We suppose that Λ = 1:2 endnoted the coating with optimal ratio of aluminum atoms to oxygen atoms, which accelerated some of them solutioned into Cr_2O_3 and decreased lattice mismatches at Cr_2O_3/Al_2O_3 interfaces effectively.

The structure, composition and formation of the α-Al_2O_3 phase were further confirmed on the basis of detailed ACTEM observations and AES analysis of the coating prepared with Λ = 1:2 (for higher crystallinity of α-Al_2O_3). Fig. 2 shows the cross-sectional bright-field TEM image with its corresponding EDX mapping image (Fig. 2(a)) and the AES depth profiles (Fig. 2(b)) of the coating. A total of 10 layers can be clearly seen in Fig. 2(a). Combing with the EDX and AES data, it concludes that the