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ARTICLE

Preparation and Properties of Alumina Coatings as Tritium Permeation Barrier by Plasma Electrolytic Oxidation

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Abstract: The alumina coatings as tritium permeation barrier were deposited on 316L stainless steel substrates by plasma electrolytic oxidation. The effects of plasma electrolytic oxidation on the coatings were investigated, and phase, surface morphology and thickness were characterized by XRD, SEM and eddy current method, respectively. After scratch adhesion test, thermal shock resistance test and tritium permeability test, the optimized coatings were obtained. The results show that the phase, the surface morphology and the thickness are affected by current density, voltage and PEO (plasma electrolytic oxidation) duration time. The current density and voltage can change the phase structure of coatings, higher current density propels the transformation of $Al \rightarrow Al_2O_3$ and higher voltage propels the transformation of γ-$Al_2O_3 \rightarrow \alpha$-$Al_2O_3$. With increasing voltage and duration time, the pore size becomes bigger and the quantity is less so that the surface morphology is worse. With current density increasing to appropriate value (9 A/dm^2), surface morphology becomes good. After a series of tests, the coatings, which are obtained at 6 A/dm^2, 300 V, 30 min, exhibit good performances with good film-substrate cohesion, thermal shock resistance, and the tritium permeation resistance of coated sample is improved by 3 orders of magnitude higher than that of the 316L stainless steel bulk.

Key words: alumina coatings; tritium permeation barrier; plasma electrolytic oxidation (PEO)

Tritium is the important nuclear material and widely used in the nuclear field. Because tritium has high permeability and toxicity, its permeation not only causes nuclear pollution, but also wastes large sums of raw materials. Tritium permeation resistance always is an important issue in the nuclear field[1]. The preparation of ceramic coatings on structure materials with low diffusivity (so-called penetration barriers) seems to be a better practical method to reduce or hinder the permeation of tritium through the substrates. The preparation of alumina coatings as tritium permeation barrier on stainless steel substrate is one of the research focuses, because alumina coatings have the following characteristics: the permeation reduction factor (PRF) is high where PRF is ratio of deuterium permeability of uncoated sample to deuterium permeability of coated sample; meanwhile alumina coatings have the ability of self-repairing as the active Al atom can capture O atom and then the coatings coexisting with their cracks, are repaired[2,3].

There are many preparation methods of alumina coatings as tritium permeation barrier, including magnetron sputtering, chemical vapor deposition, ionic liquid electroplating-high temperature oxidation, double glow plasma surface alloying technique, etc[4-7]. Through the methods presented above, the PRF of alumina coatings as

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tritium permeation barrier is usual low, and the reasons are as follows: 1) the worse film-substrate cohesion causes alumina coatings failure; 2) the coating thickness is thin (below 1 μm); 3) the low tritium permeability α-Al_2O_3 is not the dominant phase in the alumina coatings. As shown above, it is very crucial to obtain good film-substrate cohesion, thick and high α phase alumina containing coatings for the high tritium resistivity.

On the basis of recent developments, the alumina coatings obtained by plasma electrolytic oxidation, are thick and have good film-substrate cohesion with high α phase content, and 316L stainless steel is an important structural material in nuclear fusion. It is worthy studying the alumina coatings obtained through plasma electrolytic oxidation on 316L stainless steel substrate[8].

The aim of the present investigation is to prepare a stainless steel substrate sample tightly coated with alumina by the plasma electrolytic oxidation technique. For this purpose, some important parameters of PEO (current density, voltage, duration time. etc.) influencing the properties of coated samples such as film-substrate cohesion, thermal shock resistance etc. were studies in detail.

1 Experiment

316L stainless steel samples with 30 mm×30 mm×5 mm dimension were polished with abrasive papers, degreased in acetone medium and thoroughly dried. The hot-dip aluminizing coatings with about 40 μm thickness were prepared by two bath flux method on 316L stainless steel substrates, and then the sample oxide films were cleaned in an aqueous solution of HF+ HNO_3. After washing with acetone and pure water, natural drying, the samples were treated by plasma electrolytic oxidation in an phosphate electrolytic solution. All chemical reagents were analytically pure and the solution temperature was controlled to below 40 ºC by adjusting the flowing velocity of the cooling water. In the experimental process, the pulse frequency and duration ratio was 366 Hz and 10%, respectively, and the current density, voltage and duration time were in the ranges from 3 A/dm^2 to 12 A/dm^2, 200 V to 500 V, and 10 min to 40 min, respectively.

The phase was characterized by X-ray diffraction meter with Ni filtered Cu Kα radiation (λ=0.15418 nm) and scintillation detector within 2θ in the range 25^o~85^o. The microstructures were observed by scanning electron microscopy (SEM). Coatings thicknesses were measured by an eddy current method. The film-substrate cohesion test was performed with scratch tester at different loads (50, 60, 70, 80, 90, 100 N). During the thermal shock resistance experiment, the sample was heated to a fixed temperature (550 ºC) in the muffle furnace, and then immersed in room temperature water until the sample was cooled down completely; after many times the surface was analyzed. As tritium is difficult to get by conventional means and it is highly toxic, the coatings tritium permeability was tested by deuterium permeation measurement equipment.

2 Results and Discussion

2.1 Effects of different parameters on coatings

2.1.1 Phase structure of coatings

The effects of different current densities and voltages on phase compositions are given in Fig.1 and Fig.2, respectively. The diffraction peaks corresponding to the angles 43.5°, 35.1°, 57.5°, and 68.3° show the presence of α-Al_2O_3 phase in both figures. meanwhile the diffraction peaks corresponding to the angles 66.7°，45.7°, 37.5°, and 39.4° show the presence of γ-Al_2O_3 phase, and the diffraction peaks corresponding to the angles 38.5°, 44.8°, 65.2°, 78.2°, and 82.5° show the presence of Al phase. α-Al_2O_3 is a high temperature phase in the alumina family, which can only be obtained above 1200 ºC[9]. During PEO process, the great heat releases because of instant discharging breakdown, it gets to high temperature(above 1200 ºC) and then stimulates the generation of α phase [10]. When the reaction is insufficient, the molten Al produced by local reaction high temperature is easily clad by Al_2O_3 coatings, and thus there is Al phase in XRD results [11].

As seen from Fig.1, Al_2O_3 phase diffraction peaks are more pronounced and the crystalline becomes well with current density changing from 3 A/dm^2 to 9 A/dm^2; meanwhile Al phase diffraction peaks are weaker. But when the current density increases from 9 A/dm^2 to 12 A/dm^2, there is no significant change in the diffraction peaks. With current density increasing in a certain range, the power increases greatly and PEO reaction becomes sufficient gradually, the less molten Al is clad by Al_2O_3 coatings. That is to say the driving force for the transformation of Al→Al_2O_3 is big in a certain range, so the relative content of Al phase decreases and Al_2O_3 phase increases obviously. With current density changing from 3 A/dm^2 to 12 A/dm^2, the value P (ratio of α-Al_2O_3/γ-Al_2O_3) increases slowly, which changes from 0.41 to 0.47 according to the Jade analysis. That is to say the driving force for the transformation of γ-Al_2O_3→α-Al_2O_3 is little.

As seen from Fig.2, the α-Al_2O_3 phase diffraction peaks are more pronounced, and γ-Al_2O_3 phase diffraction peaks are weaker with the voltage change from 200 V to 400 V; meanwhile Al phase diffraction peaks change less. But when the voltage increases from 400 V to 500 V, no significant change occurs in the diffraction peaks. With the voltage increasing in a certain range, the alumina coatings are generated in the strong electric and magnetic field on the sample surfaces. Then the instant discharging breakdown is stronger, great heat is released, and the temperature becomes higher within a short time and increases to above 1200 ºC. That is to say, the driving force