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ARTICLE

Preparation of Alumina Coatings as Tritium Permeation Barrier by a Composite Treatment of Low Temperature Plasma

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Abstract: The alumina coatings as a tritium permeation barrier were prepared on stainless steel bulk by a composite low temperature plasma method of magnetron sputtering, heat treatment and O ion implantation. The phases, surface morphologies, chemical composition and O element distribution of the coatings were characterized by XRD, SEM, EDS and AES individually, and scratch adhesion test, thermal shock resistance and tritium permeability test were also performed. The results show that the Al coatings deposited by magnetron sputtering are well, and Fe-Al alloys interlayer is formed after heat treatment. In O ion implantation process, the oxygen depth is deepened and the oxygen density gradient decreases with higher accelerating voltage at definite doses; meanwhile it can be seen that 8×10^{17} ions/cm^2 is the crucial dose, above which the oxygen density is more homogeneous. After a series of tests, the obtained coatings have the good performance of film-substrate cohesion, thermal shock resistance and the tritium permeation resistance, and the coatings, which were treated by superposition at 8×10^{17} ions/cm^2 doses, have the best tritium permeability resistance, and the trillium permeability decreases 3 orders of magnitude compared with that of the stainless steel bulk at 600 ℃.

Key words: alumina coatings; tritium permeation barrier; magnetron sputtering; O ion implantation; heat treatment

Tritium is the important nuclear material and it is widely used in the nuclear field. Because tritium has high permeability and toxicity, the tritium permeation not only causes nuclear pollution, but also wastes large sums of raw material. Tritium permeation resistance is always an important issue in the nuclear field [1]. The preparation of coatings of ceramic material on structure material 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. Preparation of alumina coatings as tritium permeation barrier on stainless steel is one of the research focus. During the working process, the thermal stresses were set up in film-substrate interfaces by the mismatch of thermal expansion coefficients and cause the alumina coatings shed. In order to handle this situation, the FeAl/Al_2O_3 coatings is a good way since formed FeAl alloy can decrease the thermal stresses after the Al coatings on stainless steel was heated. There are many preparation methods of FeAl/Al_2O_3 coatings, VPS-heat treatment, HAD- high temperature oxidation, PC-CVD, etc[2]. The coatings which were obtained by VPS-heat treatment crack easily, the coatings which were obtained by HAD- high temperature oxidation has bad film-substrate cohesion, while the coatings which were obtained by PC-CVD cause stress corrosion due to chloride exits in PC process[3,4]. However, the coatings, which were obtained through the way of low temperature plasma, have no disadvantages mentioned above. Meanwhile the low temperature plasma is

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harmless to substrate. It is worthy studying that $FeAl/Al_2O_3$ is obtained through the low temperature plasma on stainless steel.

In the present paper, Al thin films were deposited with magnetron sputtering process on stainless steel first and then the FeAl alloy was produced after heat treating, and finally Al_2O_3 coatings were obtained after oxygen implantation. The parameters of magnetron sputtering and oxygen implantation were investigated. After a series performance tests (such as thermal shock resistance and the tritium permeation resistance), better coatings were obtained.

1 Experiment

The 316L stainless steel samples of Φ10 mm×1 mm were polished with abrasive papers, degreased in the acetone medium and thoroughly dried. The Al coating was deposited with magnetron sputtering on stainless steel under the condition of base vacuum 2×10^{-3} Pa, temperature 100 ℃, Ar pressure 0.30 Pa. And then it was put into a vacuum firing furnace in base vacuum 6×10^{-4} Pa at 600 ℃ for 180 min. In the oxygen ion implantation experimental process, base vacuum, O pressure and accelerating current were 3.0×10^{-4} Pa, 2×10^{-2} Pa and 4 mA, respectively, accelerating voltage was in the range from 30 kV to 70 kV, and implantation dose was in the range from 4×10^{17} to 1×10^{18} ions/cm^2. The phases were characterized by X-ray diffraction, which was made on the surface of the treated samples, by X'PertProMPD powder diffract metric with Ni filtered Cu Kα radiation (λ=0.15418 nm) and scintillation detector within 2θ in the range 25°~100°. The microstructure was observed by scanning electron microscopy (SEM). The chemical composition was characterized by EDS, which was own equipment of SEM. The film-substrate cohesion test was performed with scratch tester under different loads (50, 60, 70, 80, 90, and 100 N). The thermal shock resistance was tested in the muffle furnace repeatedly, the sample was heated to a fixed temperature (550 ℃)[5], which was the sensitizing temperature of 316L stainless steel, and then was immersed in room temperature water until the sample was cooled down completely. The Al coating thickness was measured by an eddy current method. As the oxygen implantation coatings thickness is difficult to test by conventional methods, it was analyzed by auger electron spectroscopy (AES). The coatings tritium permeability was tested by deuterium permeation measurement equipment.

2 Results and Discussion

2.1 Magnetron sputtering coatings

After magnetron sputtering, the obtained coating thickness is about 5 um with the smooth surface. As can be seen from Fig.1, the diffraction peaks corresponding to the angles 38.5°, 44.8°, 65.1°,78.2°,82.5° show the presence of Al phase in coatings. The pronounced diffraction peaks illustrate the crystalline is well, which is about 94% by the Jade analysis. As can be seen from Fig.2, the grain size is uniform with no obvious defects. From the above, it can be seen that the Al coatings quality is well.

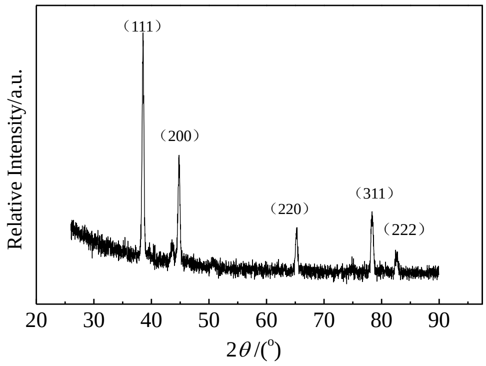

Fig.1 XRD pattern of coatings obtained by magnetron sputtering

2.2 Heat treatment coatings

After heat treatment, grazing incidence X-ray diffraction was performed, the XRD pattern of coatings is shown in Fig.3. The diffraction peaks corresponding to the angles 43.97°, 63.94°, 80.84° show the presence of FeAl phase in heat treated coatings. Under high temperature heat treatment, the Al atoms of the coating diffused into Fe bulk, meanwhile the Fe atoms diffused into Al coating, and the Fe-Al alloys (FeAl, Fe_2Al_5 phase) formed after holding a certain amount of time[6].

2.3 Oxygen ion implantation coatings

2.3.1 XRD analysis

XRD pattern of oxygen ion implantation coatings is given in Fig.4. The diffraction peaks corresponding to the angles 38.5°, 44.8°, 65.2°, 78.2°, 82.5° show the presence of Al phase and the diffraction peaks corresponding to the angles 66.7°, 45.7°, 37.5° show the presence of γ-Al_2O_3 phase.

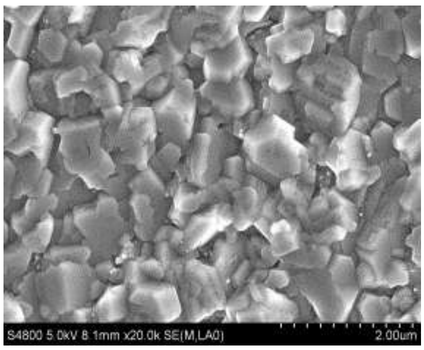

Fig.2 SEM image of coatings obtained by magnetron sputtering

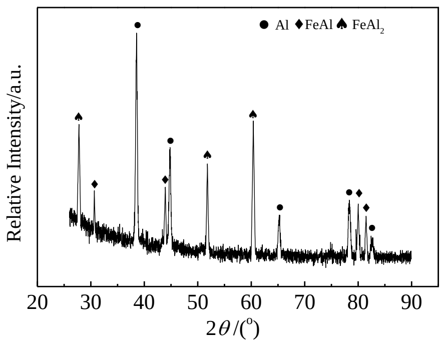

Fig.3 XRD pattern of coatings after heat treatment

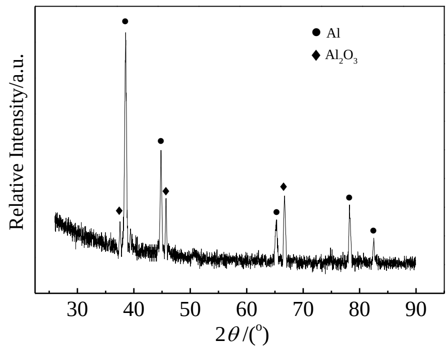

Fig.4 XRD pattern of coatings after oxygen ion implantation

2.3.2 AES analysis

As can be seen from Fig.5, at definite 4×10^{17} ions/cm^2 doses, oxygen element distribution is inconformity with Gauss law and it becomes worse with the lower accelerating voltage. The implantation projected range, in which the oxygen relative density is the highest, measured as 50, 140, 240, and 340 nm with the accelerating voltage are 10, 30, 50, and 70 kV. The implantation projected range increases with higher accelerating voltage, because the higher energy O ion is more capable to overcome nuclear and electronic stopping, thus implanting deeper in the Al material[7]. Because O ion is lighter than Al (it was implanted), large-angle scattering appears easily in near surface, that is to say the O ion cannot reach implantation projected range, which lead to O ion accumulation between surface and implantation projected range[8]. If the large-angle scattering ion number is definite, the O ion accumulation become worse as the implantation projected range is less with lower accelerating voltage. In theory, the oxygen relative density integral sum is equal to the implantation doses without considering loss[9]. Therefore, at definite doses, the oxygen depth deepened and the oxygen density gradient decreased with higher accelerating voltage, meanwhile the oxygen distribution is closer to Gauss law.

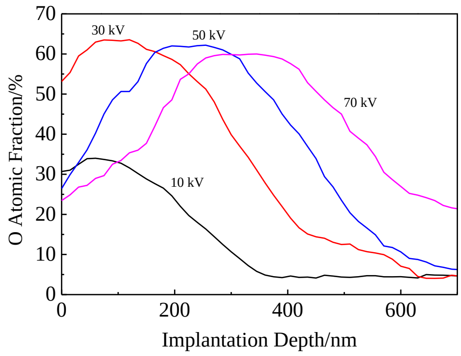

Fig.5 AES result of oxygen element distribution at different acceleration voltages

As can be seen from Fig.6, at definite 50 kV accelerating voltage, the implantation projected range has little change. With the doses increasing from 4×10^{17} ions/cm^2 to 8×10^{17} ions/cm^2, oxygen distribution gradient decreases greatly. But the doses increase from 8×10^{17} ions/cm^2 to 1×10^{18} ions/cm^2, oxygen distribution change little.

2.3.3 Oxygen distribution

In theory, tritium permeability resistance was better with the more thickening and more homogeneous O distribution of aluminum coatings[10]. And on the basis of above results, it shows that the higher accelerating voltage and doses can improve tritium permeability resistance of coatings. With the higher accelerating voltage and doses, the more O ions with higher energy implanted the Al material, it brings more defects of displacement damage in the coatings. As tritium is easy to pass through defects of coatings, it affects the coatings tritium permeability resistance. In order to obtain suitable thickness and homogeneous aluminum coatings, it is crucial to choose parameters of accelerating voltage and doses.

As oxygen distribution gradient is high at the single acceleration voltage, the presented used superposition voltage, which were 30, 50, 70 kV, respectively. Meanwhile considering 8×10^{17} ions/cm^2 doses can refine the grains to nanometer-size, the total doses was 8×10^{17} ions/cm^2, as shown in Table 2. As the 50 kV implanted region was the middle position, it was superimposed by three acceleration voltage and the doses of 50 kV are the least for homogeneous coatings. After the superposition, the AES results of coatings are shown in Fig.7 The O density is higher level with little change in the range from about 50 nm to 480 nm, and thus the coatings is more homogeneous than before superposition.

2.4 Coatings property tests

2.4.1 Scratch adhesion test

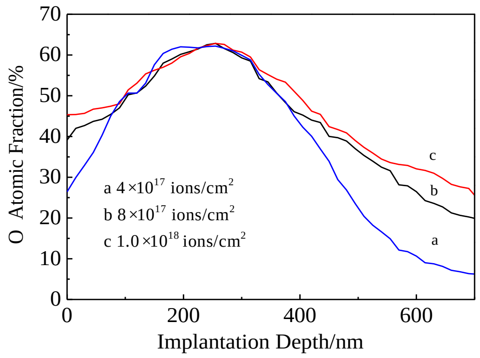

Fig.6 AES result of oxygen distribution at different doses

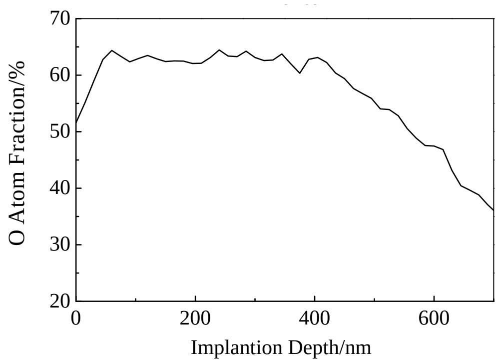

Fig.7 AES result of oxygen distribution at optimized parameter ion implantation

Table 2 Parameter of optimized ion implantation

Voltage/kV	30	50	70
Dose/$\times 10^{17}$ ions cm^{-2}	3.0	1.5	3.5

The load, in which the sample presented film peeling, is considered as the critical load of coatings. Five samples were tested. The critical load results measured by the adhesion test are the average value for five samples. At a lower load of 70 N, there is smoothing continuous scratches in the surface of all samples without any transverse crack. When the load is 80 N, there is transverse crack in the surface of some samples, and few samples present film peeling. Increasing the load to 100 N, all samples present film peeling. After calculating, the bonding strength of coating is about 86.4 N, which is good enough for tritium permeation barrier.

2.4.2 Thermal shock resistance test

In the test, the sample was heated up to 550 °C in the muffle furnace and then cooled to room temperature. It leads to thermal stress, which influences the surface quality of sample. As can be seen from Fig 8, the sample surface is good with the color being changed only, and then it shows that the thermal shock resistance is good.

2.4.3 Tritium permeability test

The PRF (PRF =the deuterium permeability of uncoated sample/the deuterium permeability of coated sample) was yardstick of tritium permeability of coatings[11].

As can be seen from Table 3, the obtained coatings has the good the tritium permeation resistance (above 350), and the coatings, which were treated by superposition, have better tritium permeability resistance than others, and it was improved 3 orders of magnitude high than the stainless steel bulk. Meanwhile it shows that homogeneity affects tritium permeability of coatings.

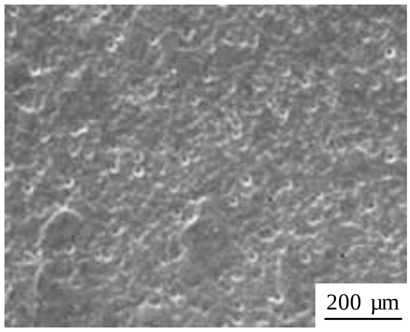

Fig.8 SEM image of surface morphology of the specimen after thermal shock test

Table 3 PRF of the samples at different parameters of ion implantation at 600 °C

Sample number	1	2	3	4
Voltage/kV	50	70	70	30, 50, 70
Dose/$\times 10^{17}$ ions cm^{-2}	4	4	8	8
PRF	363	476	665	1009

3 Conclusions

1) In O ion implantation process, the oxygen depth is deepened and the oxygen density gradient decreases with higher accelerating voltage at definite doses; meanwhile it can be seen that 8×10^{17} ions/cm^2 is the crucial dose, above which the oxygen density is more homogeneous.

2) The obtained coatings have the good performance such as film-substrate cohesion, thermal shock resistance and the tritium permeation resistance, and the coatings treated by superposition, have the best tritium permeability resistance, and trillium permeability decreases 3 orders of magnitude than that of the stainless steel bulk at 600 °C.

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低温等离子复合技术制备氧化铝阻氚涂层

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摘 要：采用低温等离子复合技术，先后经过磁控溅射镀铝，热处理及氧离子注入，在不锈钢基体上制备了氧化铝阻氚涂层。利用 XRD、SEM、EDS、AES 对涂层进行了相结构、表面形貌、成分、氧元素分布等分析，并进行了划痕试验、抗热震及阻氚性能测试。结果表明：磁控溅射获得了高质量的铝涂层，热处理后形成了 FeAl 合金过渡层。在氧离子注入中，当注入剂量不变电压增加时，离子注入深度增加，而氧元素分布梯度降低；当注入剂量达到 8×10^{17} ions/cm^2 以上时，氧元素分布变得均匀。所获得的氧化铝涂层具有较好膜/基结合力、抗热震性能及阻氚性能。经过叠加电压注入且剂量达到 8×10^{17} ions/cm^2 的膜层具有最好的阻氚性能，在 600 ℃能使不锈钢的氚渗透率降低 3 个数量级。

关键词：氧化铝涂层；阻氚；磁控溅射；离子注入；热处理

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