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ARTICLE

Preparation of Al₂O₃ Coatings as Tritium-Resistance Coating by Ion Implantation on 316L Stainless Steel

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Abstract: The alumina coatings as a tritium-resistance coating were deposited on 316L stainless steel by ion implantation. The effects of different parameters of ion implantation process on the wear resistance, corrosion resistance, thermal shock resistance, and tritium permeation resistance of α -Al₂O₃ were investigated. Results show that the content of α -Al₂O₃ is affected by temperature, acceleration voltage, and ion implantation dose. With increasing the temperature, the content of α -Al₂O₃ is increased. With increasing the acceleration voltage or ion implantation dose, the content of α -Al₂O₃ is firstly increased and then decreased. The wear resistance and corrosion resistance are mainly affected by the ion implantation dose: with increasing the ion implantation dose, the wear and corrosion resistance becomes better. The Al₂O₃ coatings hardly changes after 200 times of thermal shock tests, indicating a good thermal shock resistance. The tritium permeability of the coated specimen is reduced by 3 orders of magnitude, compared with that of the 316L stainless steel bulk.

Key words: ion implantation; alumina coatings; tritium-resistance coating

Tritium is an important nuclear material, and it is widely used in the nuclear fusion^[1]. As tritium has high permeability and toxicity, preparation of tritium-resistance coating becomes one of the key scientific and technological problems in the field of tritium self-support and tritium safety protection in nuclear fusion^[2]. Because of its high tritium permeation reduction factor and self-repairing performance, Al₂O₃ coating attracts much attention^[3] and is regarded as the prior-development coating in the field of nuclear fusion^[4]. At present, the preparation of α -Al₂O₃ of high content at low temperature is a technical difficulty for the preparation of Al₂O₃ tritium-resistance coating. The results show that ion bombardment plays an important role in the formation of α -Al₂O₃ at low temperature and is closely related to the bombardment energy^[5]. The accumulated energy caused by defects in materials due to ion bombardment can be released at a certain temperature, thereby promoting the formation of α -Al₂O₃. Ion implantation can produce the high energy for plasma bombardment, and the cascade collision of ion implantation can also cause a lot of defects which are more

beneficial to the formation of α -Al₂O₃ in theory^[6]. In addition, ion implantation is widely used in the surface modification, which is conducive to the improvement of the actual service performances (wear resistance, corrosion resistance, thermal shock resistance, etc.) of tritium-resistance coatings^[7,8]. In this research, the tritium-resistance coating of Al₂O₃ prepared by O-ion implantation was studied. The influence of acceleration voltage, ion implantation dose, and the temperature on the phase structure of α -Al₂O₃ coatings was discussed; meanwhile the influence of ion implantation dose on the coating properties was discussed.

1 Experiment

The 316L stainless steel substrate was aluminized by magnetron sputtering, and then the O-ion implantation experiment was conducted. The 316L stainless steel specimens with dimension of $\Phi 20$ mm \times 3 mm were used and the thickness of Al coating is about 5 μ m. In the oxygen implantation experiment process, base vacuum, O pressure, and acceleration current were 2.0×10^{-4} Pa, 2×10^{-2} Pa, and 3

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mA, respectively; acceleration voltage ranged from 10 kV to 70 kV; ion implantation dose ranged from 4×10^{17} ion/cm² to 1.0×10^{18} ion/cm².

The phases of coatings were characterized by X-ray diffraction (XRD). The observation surface of specimens was treated by X'PertProMPD powder diffractometer with Ni filtered Cu K α radiation ($\lambda = 0.15418$ nm) and scintillation detector with $2\theta = 25^\circ \sim 90^\circ$.

The wear resistance of tritium-resistance coatings was tested by ball and disk friction. The dual ball was WC ball, the sliding speed was 5 mm/s, and the load was 1.96, 4.9, and 9.8 N. The corrosion resistance was tested by the electrochemical test system composed of electrochemical analyzer and analysis software. The corrosion current density and corrosion potential were analyzed. The thermal shock resistance of the specimen was tested by muffle furnace. The specimen was heated to a fixed temperature of 600 °C which is the working temperature of tritium-resistance coatings, and then immersed in water at room temperature until it was cooled completely. The surface of the coatings was observed. Due to the strict control of tritium use, the deuterium gas phase permeation method was used to measure the tritium permeability of the coatings.

2 Results and Discussion

2.1 Microstructure and composition of coating

Fig. 1 shows the scanning electron microscope (SEM) images of Al coating and Al₂O₃ coating. After the oxygen ion implantation, the surface of coatings is uniform without obvious defects. The grain size of Al₂O₃ coating after O-ion implantation is smaller than that of Al coating after magnetron sputtering, suggesting that ion implantation has the grain

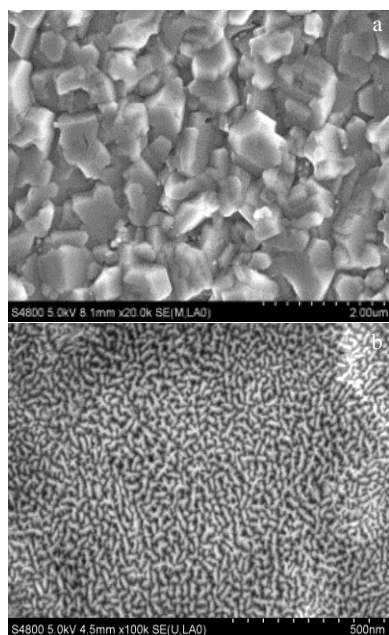


Fig.1 SEM images of Al coating after magnetron sputtering (a) and Al₂O₃ coating after O-ion implantation (b)

refinement effect.

As shown in Fig.2, after oxygen ions are injected into the Al coating, there is no obvious interface between the injection layer and the Al coating. Table 1 shows the energy disperse spectroscopy (EDS) analysis results of area 1 and area 2 in Fig.2. After oxygen ion implantation, the oxygen content in the middle part (area 1) of Al₂O₃ coating is very low, while that in the superficial part (area 2) of the Al₂O₃ coating is high, reaching 25.31at%. The atomic ratio of aluminum to oxygen is similar to that of alumina, indicating that alumina may form in the coating.

Fig.3 shows the auger electron spectroscopy (AES) result of Al₂O₃ coating after O-ion implantation. The distribution of

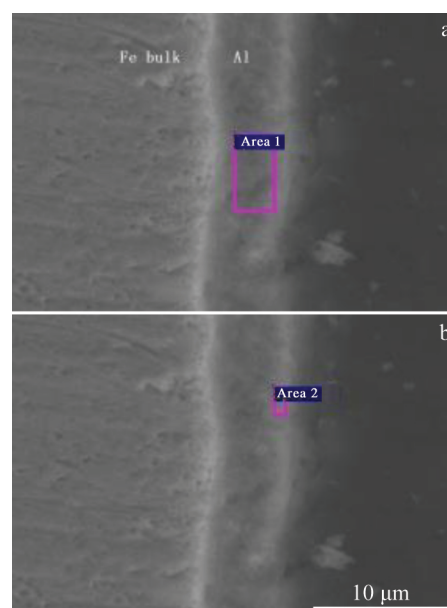


Fig.2 EDS images of Al₂O₃ coating after O-ion implantation

Table 1 EDS analysis results of area 1 in Fig.2a and area 2 in Fig.2b (at%)

Area	Fe	Al	O
1	4.35	95.65	-
2	-	74.69	25.31

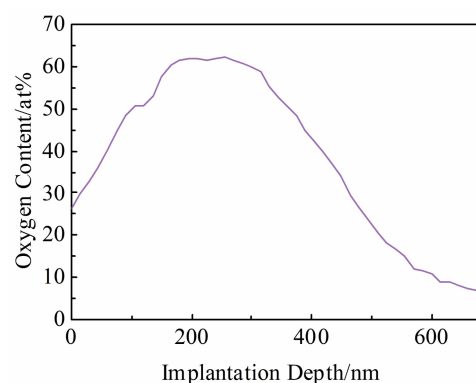


Fig.3 AES result of Al₂O₃ coatings obtained by O-ion implantation

oxygen along depth conforms to the quasi-Gaussian law. The depth of oxygen ion implantation is less than 0.6 μm , i.e., the thickness of the coatings is less than 0.6 μm .

2.2 Influences of process parameters on coating

2.2.1 Temperature

Under the fixed conditions of acceleration voltage of 50 kV and ion implantation dose of 6×10^{17} ion/cm², the phases of coatings treated at different temperatures are shown in Fig. 4. The diffraction peaks corresponding to 2θ of 38.5°, 44.8°, 65.2°, 78.2°, and 82.5° indicate the presence of Al phase; the diffraction peaks corresponding to 2θ of 43.5°, 35.1°, 57.5°, and 68.3° indicate the presence of α -Al₂O₃ phase; the diffraction peaks corresponding to 2θ of 66.7°, 45.7°, 37.5°, and 39.4° indicate the presence of γ -Al₂O₃ phase. At the lowest temperature of 280 °C, α -Al₂O₃ phase with good crystallinity can be obtained by ion implantation. With increasing the temperature from 280 °C to 450 °C, the content of α -Al₂O₃ is increased obviously. Through software analysis, the content of α -Al₂O₃ is about 33.2% at 450 °C. With further increasing the temperature, the content of α -Al₂O₃ is slightly increased. At 650 °C, the content of α -Al₂O₃ is about 37.6%. The increase in temperature can promote the orderly arrangement of atoms and facilitate the generation of crystalline α -Al₂O₃ coating. Considering the influence of high temperature on 316L stainless steel substrate (sensitization temperature of 650 °C) and the fact that ion implantation may cause a certain temperature rise (normally lower than 100 °C) of the substrate surface, the ion implantation temperature was set at 450 °C for the subsequent experiments.

2.2.2 Acceleration voltage

Under the fixed condition of temperature of 450 °C and ion implantation dose of 6×10^{17} ion/cm², the phases of coatings treated under different acceleration voltages are shown in Fig. 5. When the acceleration voltage is 10 kV, there is no α -Al₂O₃, but a small amount of γ -Al₂O₃. At acceleration voltage of 30 kV, α -Al₂O₃ appears. With increasing the acceleration voltage to 50 kV, the content of α -Al₂O₃ is increased to some extent; with increasing the acceleration voltage to 70 kV, α -Al₂O₃ is decreased slightly. In brief, the content of α -Al₂O₃ becomes higher with increasing the acceleration voltage from 10 kV to 50 kV, while it becomes lower as the acceleration

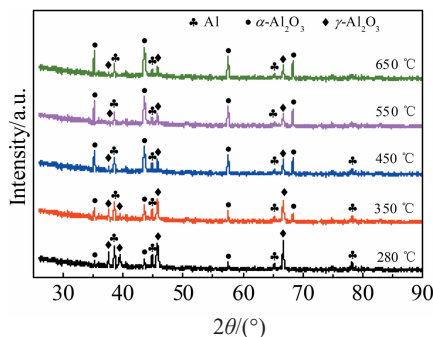


Fig.4 XRD patterns of Al₂O₃ coatings after ion implantation at different temperatures

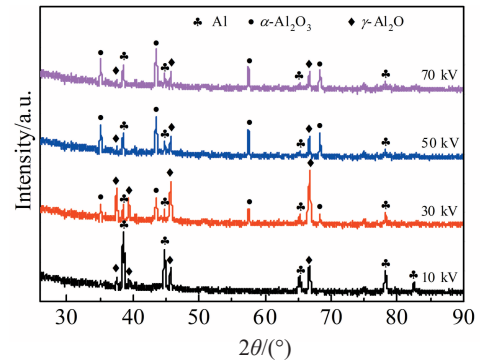


Fig.5 XRD patterns of Al₂O₃ coatings after ion implantation at different acceleration voltages

voltage increases from 50 kV to 70 kV. The increasing voltage indicates the enhanced effect of injection and bombardment caused by higher injection energy^[9], and α -Al₂O₃ can be formed at low temperature, resulting in a certain increase of α -Al₂O₃ content in the early stage. When the voltage exceeds a certain value, the high atomic injection energy may cause more violent collision among the internal atoms, which easily leads to the formation of voids, thereby making the material more defective and affecting the crystal structure of the coating.

2.2.3 Ion implantation dose

Under the fixed condition of temperature of 450 °C and acceleration voltage of 50 kV, the phases of coatings treated under different ion implantation doses are shown in Fig. 6. When the ion implantation dose is 6×10^{17} ion/cm², α -Al₂O₃ appears. As the ion implantation dose increases to 8×10^{17} ion/cm², the content of α -Al₂O₃ increases significantly. When the ion implantation dose increases to 1.0×10^{18} ion/cm², α -Al₂O₃ content decreases, and amorphous characteristics appear. The quantity of defects is increased with increasing the ion implantation dose, and an appropriate number of defects can promote the formation of α -Al₂O₃. In brief, the content of α -Al₂O₃ becomes higher with increasing the ion implantation dose from 4×10^{17} ion/cm² to 8×10^{17} ion/cm², while it becomes lower as the ion implantation dose increases

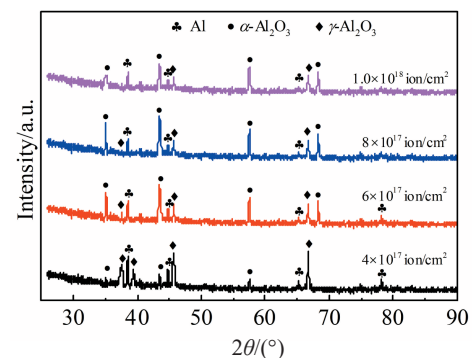


Fig.6 XRD patterns of Al₂O₃ coatings after ion implantation with different ion implantation doses

from 8×10^{17} ion/cm² to 1.0×10^{18} ion/cm².

In general, the acceleration voltage, ion implantation dose, and temperature have a positive effect on the phase structure of coatings. The content of coating phases can be increased by increasing the abovementioned parameters in a certain range. However, when the parameters are too high, the phase structure of coating will degrade.

2.3 Coating performance

2.3.1 Friction and wear resistance

It can be seen from Fig.7 and Fig.8 that with increasing the ion implantation dose, the coefficient of friction (COF) of the prepared specimen is reduced, the wear mass is also reduced, and therefore the friction and wear performance is greatly improved. The friction and wear performance strongly depends on the physical and chemical properties (hardness, strength, etc.) near the surface. If the physical and chemical properties are better, the friction and wear performance will be better. Because the increase in ion implantation dose causes the amorphous injection layer rather than crystal or crystalline structure of substance, the coating has better physical, chemical, and mechanical properties with high strength and high hardness. Generally, after ion implantation, the sub-surface structure of the implanted layer changes, forming a high hardness zone^[10,11]. The friction and wear performance of the coatings is improved after ion implantation. The larger the

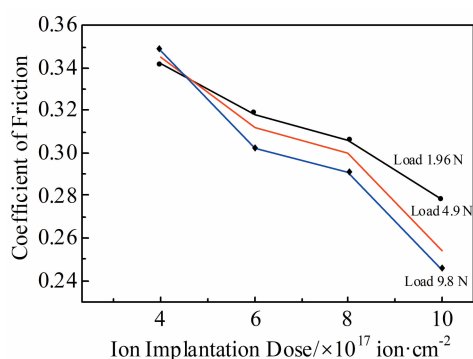


Fig.7 Coefficient of friction of Al₂O₃ coatings after ion implantation at different ion implantation doses

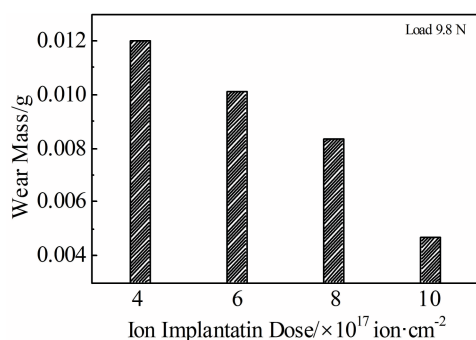


Fig.8 Wear mass of Al₂O₃ coating after ion implantation at different ion implantation doses

ion implantation dose, the better the performances are.

2.3.2 Corrosion resistance

Fig. 9 shows the corrosion resistance of Al₂O₃ coatings prepared on stainless steel substrate with different process parameters in 3.5wt% NaCl solution. Compared with the stainless steel matrix, all Al₂O₃ coating specimens have an obvious passivation phenomenon: the self-corrosion potential increases, and corrosion current density reduces. With increasing the ion implantation dose, the self-corrosion potential of the coatings is increased gradually. When the ion implantation dose is 1.0×10^{18} ion/cm², the self-corrosion potential of the coating reaches the maximum value of -0.085 V, while the corrosion current of coating reaches the minimum value of $0.003 \mu\text{A/cm}^2$. Therefore, the corrosion rate is the lowest. This is mainly because with increasing the ion implantation dose, the prepared coatings become thick, uniform, and amorphous. Thereby the coatings have better corrosion resistance. The larger the ion implantation dose, the better the corrosion resistance^[12].

2.3.3 Thermal shock resistance

In order to test the bonding strength of Al₂O₃ coatings, the thermal shock resistance of Al₂O₃ coatings was tested. The results show that all the Al₂O₃ coatings do not peel off and hardly change after 200 thermal cycling tests at 600 °C. Although the thermal shock resistance of the coatings prepared at different ion implantation doses is slightly different, all the Al₂O₃ coatings are well bonded with the stainless steel substrate and show good thermal shock resistance. Fig. 10 shows the surface morphology of Al₂O₃ coating treated with ion implantation dose of 8×10^{17} ion/cm² after 200 times of thermal shock at 600 °C. It can be found that there is no peeling or crack on the coating surface, so the Al₂O₃ structure has good thermal shock resistance.

2.4 Tritium permeability

The coating treated under the condition of temperature of 450 °C, acceleration voltage of 50 kV, and ion implantation dose of 8×10^{17} ion/cm² was selected for the tritium permeability tests.

The value of steady-state permeation flux J , the specimen thickness, and basal area were measured after the tests, and

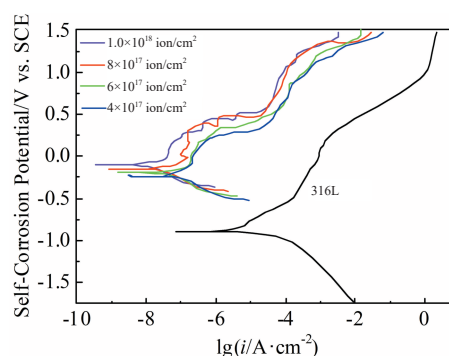


Fig.9 Corrosion resistance of 316L substrate and Al₂O₃ coatings after ion implantation at different ion implantation doses

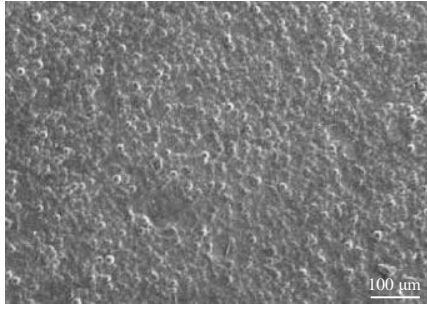


Fig.10 SEM image of surface morphology of Al_2O_3 coating treated with ion implantation dose of 8×10^{17} ion/cm² after 200 times of thermal shock at 600 °C

then the permeability (ϕ) could be calculated by Eq. (1), as follows^[13,14]:

$$\phi = \frac{JL}{SP} \quad (1)$$

where J is steady state permeation flux, L is specimen thickness, S is specimen basal area, and P is deuterium pressure.

The results show that the coatings have a good resistance to tritium penetration. At 600 °C, compared with that of 316L stainless steel substrate, the factor of resistance to deuterium penetration of Al_2O_3 coatings is 1442, so the tritium permeability of the coated specimen is reduced by 3 orders of magnitude^[15]. Therefore, the deuterium/tritium resistance performance of the coatings is good.

3 Conclusions

1) For the Al_2O_3 coatings prepared by ion implantation on 316L stainless steel, the temperature can increase the content of α - Al_2O_3 within a certain range (from 280 °C to 650 °C). The higher temperature can promote the α - Al_2O_3 growth.

2) The acceleration voltage can affect the content of α - Al_2O_3 in the coatings. The content of α - Al_2O_3 becomes higher with increasing the acceleration voltage from 10 kV to 50 kV, while it becomes lower as the acceleration voltage increases from 50 kV to 70 kV.

3) The ion implantation dose can also affect the content of α - Al_2O_3 in the coatings. The content of α - Al_2O_3 becomes

higher with increasing the ion implantation dose from 4×10^{17} ion/cm² to 8×10^{17} ion/cm², while it becomes lower as the ion implantation dose increases from 8×10^{17} ion/cm² to 1.0×10^{18} ion/cm².

4) The ion implantation dose can affect the wear resistance and corrosion resistance of the coatings. The resistance becomes better with increasing the ion implantation dose. The thermal shock resistance is good (the coatings hardly changes after 200 times of thermal shock), and the tritium permeability of coated specimen is reduced by 3 orders of magnitude, compared with that of the 316L stainless steel bulk.

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离子注入法在316L不锈钢基体上制备 Al_2O_3 阻氚涂层

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摘 要: 采用离子注入技术在316L不锈钢基体上制备了氧化铝阻氚涂层。对离子注入法的不同工艺参数对 α - Al_2O_3 涂层摩擦磨损、耐腐蚀、抗热震、阻氚性能的影响进行了研究。结果表明: 温度、加速电压及离子注入剂量对 α - Al_2O_3 的含量均有影响。温度升高时, α - Al_2O_3 的含量增加。增大加速电压及离子注入剂量时, α - Al_2O_3 含量均出现先升高后降低的规律。离子注入剂量对涂层的摩擦磨损、耐腐蚀性能影响比较大: 离子注入剂量越大, 涂层的耐磨、耐腐蚀性能越好。涂层经过200次热震测试后未发生变化, 抗热震性能较好。 Al_2O_3 膜层具有优异的阻氚性能, 在600 °C下能使316L不锈钢的氚渗透率降低3个数量级。

关键词: 离子注入技术; 氧化铝涂层; 阻氚涂层