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ARTICLE

Micro-morphology and Performance of Cr-TiAlSiN Composite Coatings Deposited on Zirconium Tube

Zhou Jun[1], Fan Xiangfang[1], Qiu Changjun[1], Feng Bin[1], Liu Yanhong[2], Li Huanlin[2]

[1] University of South China, Hengyang 421001, China; [2] National Electricity Investment Group Central Research Institute, Beijing 102209, China

Abstract: Cr-TiAlSiN composite coatings were deposited on the substrate of zirconium alloy tubes by multi-arc ion plating and intermediate frequency unbalanced magnetron sputtering, separately. The micro-morphology of surface and cross-section of the composite coatings was observed by a scanning electron microscopy; the porosity and the quantity of large particles on the surface were analyzed by Image J software; the adhesion strength between the coatings and substrate was measured by a pull pressed spring testing machine; the samples were subjected to high temperature oxidation test at 800 ºC and high temperature quenching test at 1200 ºC using a high temperature furnace. The results show that there are more large particles on the surface of the coating deposited by multi-arc ion plating, but the porosity of that is relatively low, so that its high temperature oxidation resistance behavior is better. The interface of the composite coatings is relatively clear and uniform, and the adhesion strength between the coatings and substrate is relatively strong, both of which are higher than 22.68 MPa. According to the high temperature quenching test at 1200 ºC, it also turns out that the adhesion strength is better with the process of multi-arc ion plating.

Key words: zirconium tube; multi-arc ion plating; intermediate frequency unbalanced magnetron sputtering; adhesion strength; oxidation resistance performance

Zirconium alloys perform well and are widely used in nuclear cladding[1-2]. Existing in the position of nuclear reactor where nuclear fission reacts and heat energy turned from nuclear energy releases, the nuclear cladding tube is the first barrier to prevent the radioactive fission products from escaping of the reactor, withstanding high temperature, oxidation, corrosion, erosion and radiation. At a certain stage when pressurized water reactor loses cooling water, nuclear fuel cladding tube may be brittle resulted from hydrogen absorption, which will seriously affect the safety of heart of the reactor[3-5]. Therefore, it has practical significance and good application prospects to study the high temperature oxidation resistance coating on the surface of zirconium alloys cladding tubes. TiAlSiN coating, the second generation based on the TiAlN coating, has excellent performance of high hardness, strong adhesion, small friction coefficient and so on[6,7]. Previous experiments show that TiAlSiN coating, which is directly coated on the surface of the zirconium tubes, performs poorly in high temperature oxidation resistance, whose average oxidation rate is 9.1 g/cm^2 per hour, and the coating with high temperature oxidation at 800 ºC is spalled partially after 1 h. Moreover, due to the residual stress in the coating, the adhesion strength between the coating and substrate is relatively low, which is about 15.24 MPa. The coating of pure Cr performs strongly in corrosion resistance, low friction coefficient and moderate hardness, and the Cr_2O_3 phase produced from oxidation performs well in high temperature oxidation resistance[8]. In this study, the gradient Cr-TiAlSiN composite coatings are deposited on the surface of zirconium tubes by the techniques of multi-arc ion plating and intermediate frequency unbalanced magnetron sputtering, separately, to improve the adhesion strength between the coatings and

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Corresponding author: Fan Xiangfang, Ph. D., School of Mechanical Engineering, University of South China, Hengyang 421001, P. R. China, E-mail: hefanyibang@163.com

substrate and high temperature oxidation resistance performance, so as to acquire better coating, in this way, the experimental basis of improving the performance of the zirconium tube are provided.

1 Experiment

Zirconium alloy cladding tubes used as the substrates were about □10 mm in diameter, 200 mm in length, 0.6 mm in wall thickness. The surface of zirconium tubes was preprocessed with sandpaper through coarse grinding and exact grinding to 1200#, and then was processed with the gold phase sandpaper through W10, W7, W4.5 of fine grinding in turn, and finally was polished mechanically up to no visible scratches. The zirconium tubes were immersed in the alcohol solution to be cleaned ultrasonically for 20 min. In the end, the tubes were blown dry with a blower and then were placed on the central stand of the deposition chamber.

A TSU-650 type multi-function coating machine was used as the coating deposition equipment. The Cr-transition coating was prepared with a circular Cr target of arc evaporation, the size of which is 100 mm×18 mm and the purity of which is 99.99%, by the method of double multi-arc ion plating. The sputtering gas was argon and nitrogen and the chamber was evacuated to 4.0×10^{-3} Pa. Before depositing, the glow cleaning was carried out by applying negative bias of 1000 V and the duty ratio of 70% to the substrate. The process parameters of the deposition are shown in Table 1.

TiAlSiN functional coatings were prepared on the surface of zirconium tubes with Cr transition coating, separately by multi-arc ion plating and intermediate frequency unbalanced magnetron sputtering with a rectangular TiAlSi (Ti:Al:Si=30:60:10) alloys target, the size of which was 508 mm×88 mm×8 mm, and a round arc evaporating TiAlSi (Ti:Al:Si=30:60:10) alloy target, the size of which was □100 mm×18 mm. The process parameters of TiAlSiN coating are shown in Table 2.

The morphology of Cr-TiAlSiN composite coatings was observed by the JSM-6490LA scanning electron microscopy; the quantity of porosity and large particles on the surface of coating was statistically analyzed by the Image J software; the adhesion strength between the coatings and substrate was measured by a pull pressed spring testing machine; and the high temperature oxidation resistance performance of coated samples was tested by an electric resistance high temperature oxidation furnace at 800 ºC. The samples were weighed every 30 min and were processed with quenching test at 1200 ºC to examine the adhesion strength between the coatings and substrate.

2 Results and Analysis

2.1 Analysis on micro-morphology of the coatings

The surface micro-morphology of multi-arc ion plated Cr-TiAlSiN composite coatings is shown in Fig.1a, and that of intermediate frequency unbalanced magnetron sputtered Cr-TiAlSiN composite coatings is shown in Fig.1b. Fig.1a shows that there are a large number of large particles on the surface of the coatings, which are stacked with many grains of different sizes, resulting in the rough and uneven coatings. It can be found from Fig.1b that there are less large particles on the surface, and also, there are some micro-holes, but the surface is relatively flat. The sectional micro-morphology of multi-arc ion plated Cr-TiAlSiN composite coating is shown in Fig.2a, and that of intermediate frequency unbalanced magnetron sputtered Cr-TiAlSiN composite coatings is shown in Fig.2b. From Fig.2, it can be observed that the composite coatings have a thickness of about 10 to 12 μm, which is relatively uniform and dense. Moreover, the coatings are well combined and the interface is clear. It can be found from Fig.2a that the coating thickness is about 1.7 μm. Combining the coating time, which is 120 min, the deposition rate can be seen as 0.85 μm/h. And it can be found from Fig.2b that the coating thickness is about 2 μm, with 180 min of coating time, so the deposition rate is 0.66 μm/h. By comparing the two sets of data, it can be found that the deposition rate of the multi-arc ion plating process is relatively fast, which is mainly due to the higher ionization rate of the target of the multi-arc ion plating process, which increases the moving rate of ions[9,10]. The deposition rate of magnetron sputtering process is mainly affected by the size of sputtering power, which is mainly related to the two parameters of substrate bias and current. In this experiment, low sputtering power is likely to ionize less particles from the target surface per unit area, which will result in low deposition rate in the corresponding coatings[11].

Table 1 Process parameters of the Cr-transition coating

Substrate bias voltage/V	Duty ratio/%	Multi-arc current/A	Rate of argon flow/ $mL\cdot min^{-1}$	Rate of nitrogen flow/$mL\cdot min^{-1}$	Deposition time/min
-200	50	65	110	0	240

Table 2 Process parameters of the functional coating

Coating process	Substrate bias voltage/V	Multi-arc current/A	Medium frequency current/A	Substrate temperature/℃	Rate of nitrogen flow/$mL\cdot min^{-1}$	Rate of argon flow/$mL\cdot min^{-1}$
Multi-arc ion plating	-200	60	0	300	75	160
Intermediate frequency unbalanced magnetron sputtering	-100	0	6	180	75	160

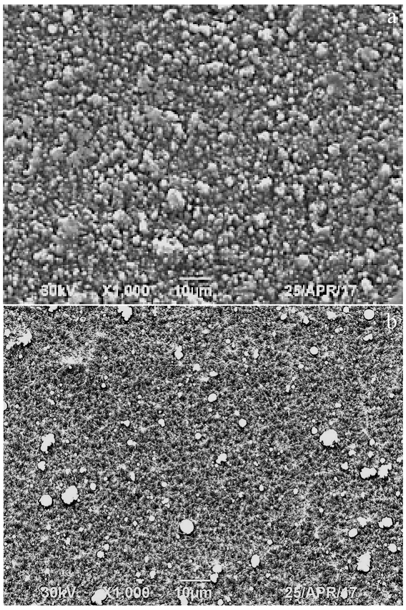

Fig.1 Surface micro-morphologies of Cr-TiAlSiN composite coatings deposited by multi-arc ion plating (a) and intermediate frequency unbalanced magnetron sputtering (b)

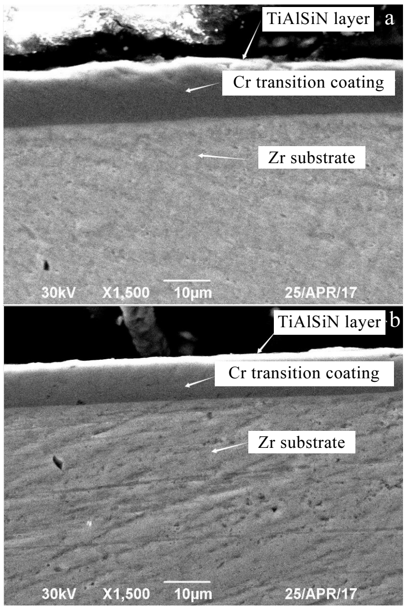

Fig.2 Section micro-morphologies of Cr-TiAlSiN composite coatings deposited by multi-arc ion plating (a) and intermediate frequency unbalanced magnetron sputtering (b)

2.2 Statistical analysis on porosity and large particles of the coatings

Fig.3 and Fig.4 show the micro-morphology processed by Image J software, which has a good correspondence with the original morphology, providing a guarantee for the porosity analysis and the statistics of the quantity of large particles on the coatings. Analysis results are shown in Table 3, and it can be learned that the quantity of large particles on the surface of the coatings obtained by multi-arc ion plating process is larger, but the surface porosity is lower. The larger number of large particles on the surface is probably resulted from the low flow of nitrogen and the large multi-arc current, which makes evaporation rate of the target too fast, resulting in a lot of metal droplets without ful ionization, and thus causing a large number of droplets to deposit on the substrate; in this way, large particles are formed[10]. Low surface porosity may be due to the high incident energy of particles sputtered by multi-arc ion plating, making the density of coating better[12]. The high ionization rate of the target makes other plasmas have the advantage to react with each other, making the coating more uniform. There are a small number of large particles on the surface of the coatings prepared with intermediate frequency unbalanced magnetron sputtering process, which is likely to be affected by the sputtering current. The smaller the sputtering current, the smaller the kinetic energy of the particles' migration. The small kinetic energy of the particles deposited on the substrate reduces the probability of the formation of large particles[13]. In addition, by the effect of the magnetic field of the chamber, it is more difficult for the ionized particles to deposit on the surface of the substrate with the magnetic field weakening, so that the deposition rate is low and the obtained coating is thin, resulting in a coating surface of high porosity[14].

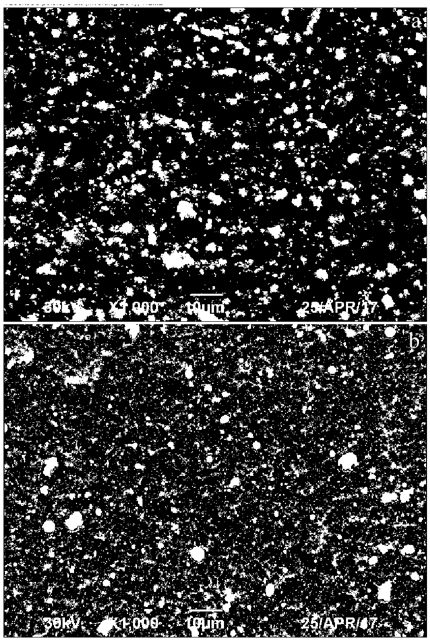

Fig.3 Analysis on the quantity of large particles on the surface of Cr-TiAlSiN composite coatings deposited by multi-arc ion plating (a) and intermediate frequency unbalanced magnetron sputtering (b)

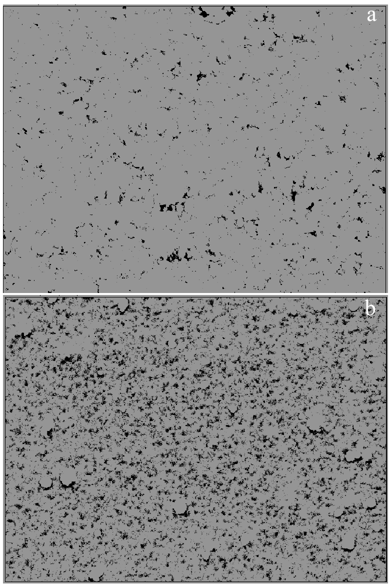

Fig.4 Analysis on the porosity on the surface of Cr-TiAlSiN composite coatings deposited by multi-arc ion plating (a) and intermediate frequency unbalanced magnetron sputtering (b)

Table 3 Number and distribution of large particles on the surface of the coatings prepared with different techniques

Techniques	Density/μm^{-2}	Average size/μm	Number of large particles（≥5 μm）	Porosity/%
Intermediate frequency unbalanced magnetron sputtering	0.12	1.585	8973	6.52
Multi-arc ion plating	0.14	3.683	13659	1.23

2.3 Analysis on the adhesion strength between the coatings and substrate

Given that the distortion of adhesion strength easily occurs when it is tested with the tube substrate by scratch equipment, the substrate slice stripping method was used to detect the adhesion strength between the coatings and substrate in order to accurately test the adhesion strength. The pull pressed spring testing machine was used as the experimental instrument. The critical adhesion strength of coating was determined by the contact area between substrate slice and coating and the shear stress. The substrate slice was closely bonded to the coating with the cementing agent. The macro- morphology of the cemented sample is shown in Fig.5a and Fig.6a. The cemented sample is placed in a holding furnace for at least 3 h and the holding temperature is between 90 and 110 ºC. Then, the dried sample was placed on the pull pressed spring testing machine. During the experiment, the shear stress was applied evenly and slowly up to the stripping of the substrate slice and the coating. The value of the shear force was recorded at the very moment. The micro-morphology of samples after stripping is shown in Fig.5b and Fig.6b. With regard to the coating prepared by intermediate frequency unbalanced magnetron sputtering process, the shear area is about 21.6 mm^2 and the load is 490 N when the stripping occurs, and the coating is partially stripped from the zirconium tube. The adhesion strength of the coating and the zirconium tube is about 22.68 MPa, which is derived from the following formula for calculating shear adhesion strength.

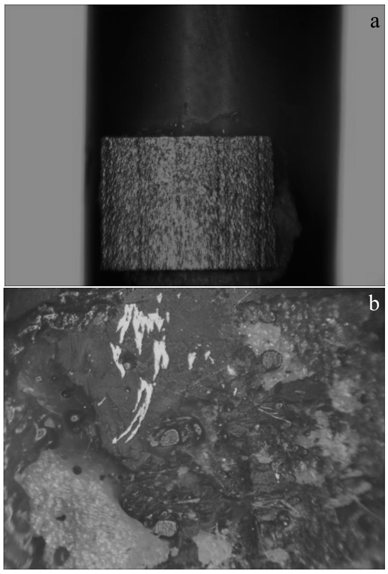

Fig.5 Images of the samples processed by intermediate frequency unbalanced magnetron sputtering

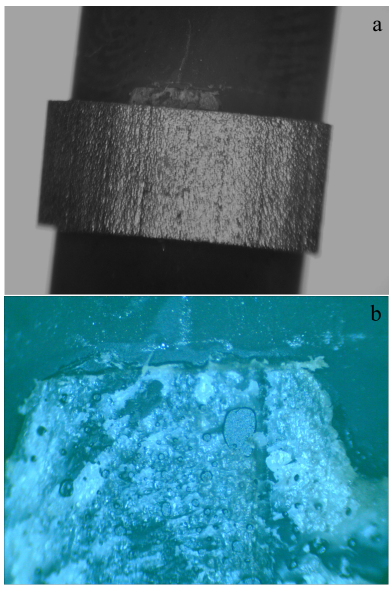

Fig.6 Images of the samples processed by multi-arc ion plating

$\tau = F/S$

where, τ is adhesion strength; F is shear stress; S is shear area

With the same test method for the coatings prepared by multi-arc ion plating process, it can be found that the substrate slice strips from the coatings but the coatings and the substrate remain to be together when the shear stress is 546 N. In the same way, combining the shear area of 22.3 mm^2 and the formula for calculating shear adhesion strength, the adhesion strength between the coatings and substrate can reach more than 24.48 MPa. The adhesion strength obtained by the intermediate frequency unbalanced magnetron sputtering process is relatively low, which may be due to low sputtering power in the process of coating deposition, resulting in the ionized particles carrying less energy and the substrate with low temperature, so that it weakens the ability of the substrate to absorb particles. In this way, it cannot produce a good sputtering effect when the particles reach the surface of the substrate, leading to coatings with poor adhesion strength between the coatings and substrate, a lower coating density and a higher porosity [15,16].

2.4 Performance analysis on high temperature oxidation resistance of the coatings

The coated zirconium tube was cut into tubular samples by wire cutting process, the length of which was 20 mm. After being placed in the ethanol solution of high purity, they were washed with ultrasonic for 20 min and then placed in the high temperature furnace at 800 ºC, and were weighed every 30 min. The tubular samples were taken into the high temperature furnace at 1200 ºC for 5 min, and then were removed quickly into the cold water to examine the adhesion strength between the coatings and substrate. According to the oxidation mass gain of the sample, the oxidation kinetic curve came out. The oxidation rate curve of the sample at 800 ºC is shown in Fig.7, and the macro-morphology after quenching at 1200 ºC is shown in Fig.8. By observing the oxidation kinetic curve, it can be seen that the composite coatings deposited on zirconium tube can improve the performance of high temperature oxidation resistance of the substrate. The main reason is likely be that it will produce Al_2O_3 barrier layer on the surface during the oxidation process, while Cr transition coating can not only make up the holes produced by a single coating, but also promote the selective oxidation of Al elements to improve self-repair capacity of the coatings; moreover, Cr_2O_3 phase produced by oxidation can also resist oxidation[17]. By further observation of Fig.7, it can be learned that the coating prepared with the technique of multi-arc ion plating shows better high temperature oxidation resistance behavior, which is mainly due to the low porosity of the coating surface. Low porosity can effectively inhibit the diffusion of oxygen element to the substrate surface through the holes. From macro- morphology of the coating after quenching, it can be found that the coating prepared with the intermediate frequency unbalanced magnetron sputtering process are spalled partially, which shows that the adhesion strength between the coating and substrate with the multi-arc ion plating process is better.

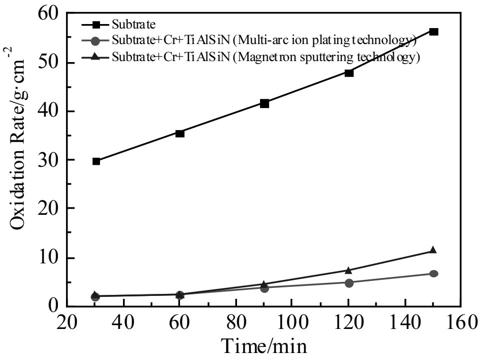

Fig.7 Oxidation rate curves of the Cr-TiAlSiN coatings at 800 ºC

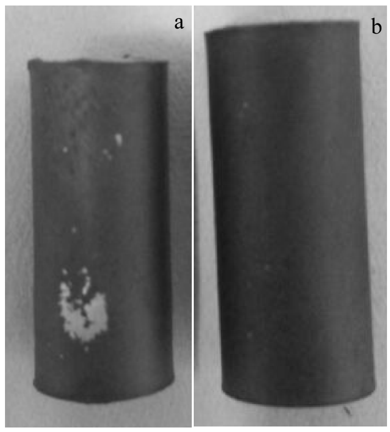

Fig.8 Macro-morphologies of the Cr-TiAlSiN coatings after quenching at 1200 ºC: deposited by intermediate frequency unbalanced magnetron sputtering process (a) and deposited by multi-arc ion plating process (b)

3 Conclusions

1) By observing the micro-morphology of coatings separately prepared by multi-arc ion plating and intermediate frequency unbalanced magnetron sputtering, it can be found that the interface of the coatings and substrate is relatively clear and the coatings are uniform. Comparatively, on surface of the coating prepared with intermediate frequency unbalanced magnetron sputtering process, there are less large particles, but large porosity because the coating is thin.

2) The adhesion strength of the coatings prepared by multi-arc ion plating process is stronger. The main reason is that the energy carried by the particles evaporated by the arc is higher and the deposition rate of that is faster, so that the coating is more compact and the adhesion strength is

stronger (24.48 MPa).

3) In high temperature oxidation resistance, the coatings prepared by multi-arc ion plating process are better, which is mainly because of the low porosity on the surface of the coatings and the formation of dense Al_2O_3 coating. Furthermore, Cr transition coating can compensate for the defects produced by a single coating and effectively prevent the diffusion of oxygen element to improve its high temperature oxidation resistance performance. The adhesion strength between the coating and substrate by multi-arc ion plating process is stronger.

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锆管表面沉积 Cr-TiAlSiN 复合涂层的表面形貌与性能研究

周　军[1]，樊湘芳[1]，邱长军，冯　彬[1]，刘艳红[2]，李怀林[2]

(1. 南华大学，湖南 衡阳 421001)

(2. 国家电投集团中央研究院，北京 102209)

摘　要：分别采用多弧离子镀和中频非平衡磁控溅射工艺，在锆合金管材基体上制备 Cr-TiAlSiN 复合涂层。利用扫描电镜对复合涂层的表面及截面微观形貌进行观察；利用 Image J 软件对复合涂层进行孔隙率和表面大颗粒数目统计分析；利用弹簧拉压试验机对涂层的膜基结合强度进行测量；利用高温热处理炉对试样进行 800 ℃高温抗氧化试验和 1200 ℃高温淬火实验。结果表明：采用多弧离子镀工艺所获得的涂层表面大颗粒物质比较多，但是孔隙率比较低，致使其高温抗氧化性能较好。复合涂层膜基界面比较明显且比较均匀，膜基结合强度较高，大于 22.68 MPa，1200 ℃高温淬火实验侧面表明采用多弧离子镀工艺的涂层其膜基结合强度较好。

关键词：锆管；多弧离子镀；中频非平衡磁控溅射；膜基结合强度；抗氧化性

作者简介：周　军，男，1990年生，硕士，南华大学机械工程学院 湖南 衡阳 421001，E-mail: 1298227966@qq.com