Article ID: 1003-6326(2005)01-0018-05

Morphology and structure of high temperature $MoSi_2$ coating on niobium①

XIAO Lai-rong(肖来荣), YI Dan-qing(易丹青),
YIN Lei(殷 磊), CAI Zhi-gang(蔡志刚)
(College of Materials Science and Engineering, Central South University,
Changsha 410083, China)

Abstract: The high-temperature oxidation-resistant $MoSi_2$ coating on the Nb substrate was prepared by slurry firing. The structure, compositions and phase distribution of the coating and the relationship between these features and the oxidation resistance of the coating were investigated by SEM, EDS and XRD. The results indicate that the interface between the coating and the substrate has metallurgic combination, and a transitional layer is formed by diffusion. The multi-layer structure improves the oxidation resistance of the coating. The method of slurry firing to prepare the high-temperature $MoSi_2$ coating on Nb is feasible. The SiO_2 scale, which is formed on the surface of the coating by the self-oxidation of $MoSi_2$, prevents the further diffusion of oxygen.

Key words: Nb; high temperature oxidation resistance; $MoSi_2$; coating
CLC number: TG 174.44 **Document code:** A

1 INTRODUCTION

Nb and Nb-based alloys are important high temperature structural materials due to their high melting point, good corrosion resistance and high temperature strength. But the applications are limited by their poor oxidation resistance[1-5]. A great deal of work has been done by many researchers. The alloying method can improve the oxidation resistance properties of the Nb-based alloys greatly. But the modified alloys still can't be used above 1 200 ℃. On the other hand, the mechanical properties would be decreased with a great deal of modified elements. The protective coating is an effective method to insure the high temperature application of the Nb-based alloys[6, 7].

Compared with other coating systems, the protective effect of the silicide coating is better. The R512A (Si-20Cr-5Ti) and R512E (Si-20Cr-20Fe) silicide systems have been successfully applied to the orbital attitude control engine of the spaceship and the satellite[8-11]. With the requirement for the improvement of high speed and stability on the advanced aerospace, the further investigations of the corresponding coating materials and technologies should be put on the plan as soon as possible. $MoSi_2$, which has been widely used as a heating component, is a promising candidate for oxidation resistant coating materials. With the protective SiO_2 scale formed, $MoSi_2$ can work above 1 600 ℃. Tiwari and Herman[12] study the $MoSi_2$ coating prepared by plasma spraying. Although the coating showed good high-temperature oxidation resistance, the problems of destructive pest oxidation and poor mechanical properties are of critical concern. Andrew et al[13] sputtered a Mo-W layer on the surface of Nb substrate, then embedded the sample in the Ge and Si composite powder to prepare a modified $MoSi_2$ coating. Brian et al[14, 15] studied B-modified and Ge-doped silicide coatings by pack cementation method. Among the different surface technologies, each process has its own characteristics. Powder packed cementation method needs the sample to anneal at high temperature for a long time, so the mechanical performance of the substrate is easily damaged during longer production cycle. The change of the composites is limited for the coating prepared by chemical vapor deposition. As novel surface technologies, plasma spraying and laser melting overlay are not easy to get close coating. Another shortage of these methods is that they are very difficult to treat the parts with complex shapes, especially with an inner chamber. Compared with those methods above, the slurry firing is more suitable to prepare the silicide system coating. This technology can solve the problem of complex shapes, changeable compositions and high melting point of the silicide[16]. In our work we selected $MoSi_2$ as a coating system, used the slurry firing to produce a high temperature oxidation resistant coating on the Nb substrate. The morphology, structure and compo-

① **Foundation item:** Project(20010533003) supported by the Special Research Foundation of PhD Study
Received date: 2004-08-27; **Accepted date:** 2004-10-26
Correspondence: XIAO Lai-rong, Associate Professor; Tel: +86-731-8830263; E-mail: xiaolr368@sina.com

sitions of the coating are studied, and the effect of these characteristics on the properties of the sample is also studied.

2 EXPERIMENTAL

The particle size of the initial $MoSi_2$ powders is about 50 μm, and the purity is above 99.9%. The powders added by some contents of addition agents are mixed to form slurry by ball milling. A sheet of pure niobium (99.9% in mass fraction) was rolled to 2 mm in thickness, and cut into pieces of 8 mm × 10 mm. The sample surface was pretreated, and then was dropped into the slurry to cover an uniform thin layer. After drying, the sample was put into a vacuum furnace above 1 700 ℃ to form a $MoSi_2$ coating on Nb substrate.

Before the oxidation resistant testing, the Al_2O_3 crucible which contained the coating sample should be calcined to 1 200 ℃ for several hours. The coating samples were pushed into the furnace at 1 500 ℃ in air condition until the yellow powders appeared on the surface of the sample. Both the original coating and the samples after oxidation testing were examined by KYKY-2800 scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer. The phases on samples surface were identified by SIMENS-500X X-ray diffractometry (XRD) with Cu K_α radiation (λ= 1.540 6 Å).

3 RESULTS AND DISSCUISON

3.1 Morphology and structure of original coating

The morphology of the original coating is shown in Fig. 1. The surface of the coating is very coarse, most of the parts consist of the incoherent fusing island, and many globular particles can be seen at the edge of the island (Fig. 1(a)). Some microholes can be seen in Fig. 1(b). The analyses by XRD and EDS show that the incoherent islands are $MoSi_2$, and those globular particles are impurity Fe. The morphology and the compositions of the original coating surface have close relations with the coating system and the technology. Due to the ball milling in the slurry, the impurity Fe has been added during impact and friction happens between the ball and the tin. Compared with the high melting point of phase $MoSi_2$ (2 047 ℃), the melting point of Fe is too low to affect the profiles of the coating. The coating prepared by slurry firing is formed by diffusion reaction between the solid and the liquid phases. In other words, the silicide coating is formed by the diffusion reaction between the silicide fused mass and Nb substrate when the treatment temperature is high enough. During the cooling process, the high melting point $MoSi_2$ phases contract. Great thermal stress concentration comes into being, and the interfaces among the particles are broken. As the result, the coarse inherent island and many microholes can be seen on the surface of the coating. On the other hand, the relative low-melting-point Fe is difficult to infiltrate with $MoSi_2$, and is discharged to the surface with liquid phase to form globular particles.

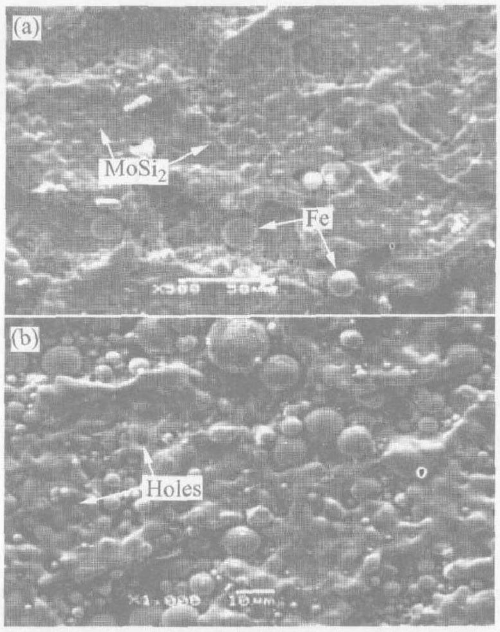

Fig. 1 Original surface morphologies of $MoSi_2$ coating on Nb substrate
(a) —Morphology and distribution of $MoSi_2$ and impurity Fe caused by ball milling;
(b) —Micro-holes in surface of coating

The structure of the original $MoSi_2$ coating on Nb substrate is shown in Fig. 2. It can be seen from the SEM photograph of the cross-section (Fig. 2(a)) that the coating has typical double-layer structures, and its thickness is about 85 μm. The dark outer layer which is the body of the coating consists of $MoSi_2$ with an average thickness of 70 μm. Between the $MoSi_2$ layer and the substrate was the transitional layer which consists of $(Mo, Nb)_5Si_3$. This layer is about 15 μm thick, and combines very tightly with the substrate. Some bright prominence parts are the flaws produced during the fabrication of the SEM sample. The sketch of the structure is also given (Fig. 2 (b)). But no Fe is found in coating. The reason is that the impurity Fe is nonwettable with $MoSi_2$. During the slurry-firing processing, nearly all Fe elements are discharged to the surface of the coating.

3.2 Transformation of morphology and structure of coating during oxidation

The surface morphology of the $MoSi_2$ coating on Nb substrate after exposure at 1 500 ℃ is shown in Fig. 3. The morphology and structure of the

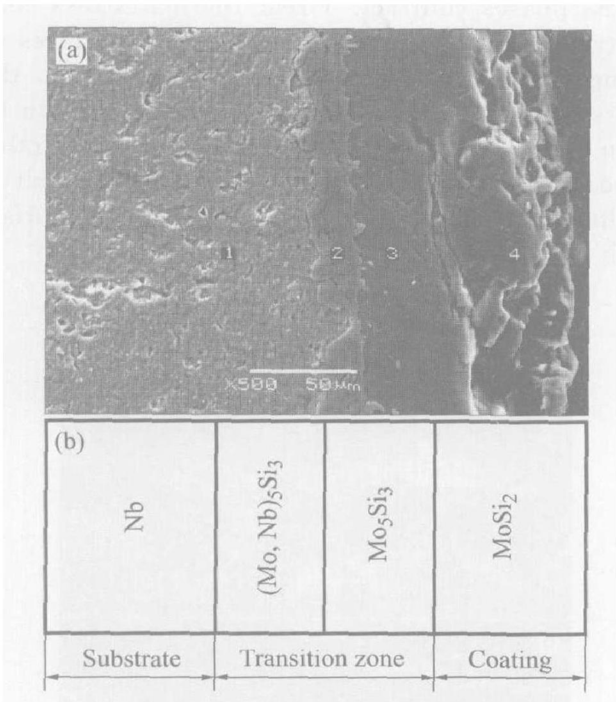

Fig. 2 Structure of original $MoSi_2$ coating on Nb substrate
(a) —SEM photograph of cross-section;
(b) —Sketch of structure

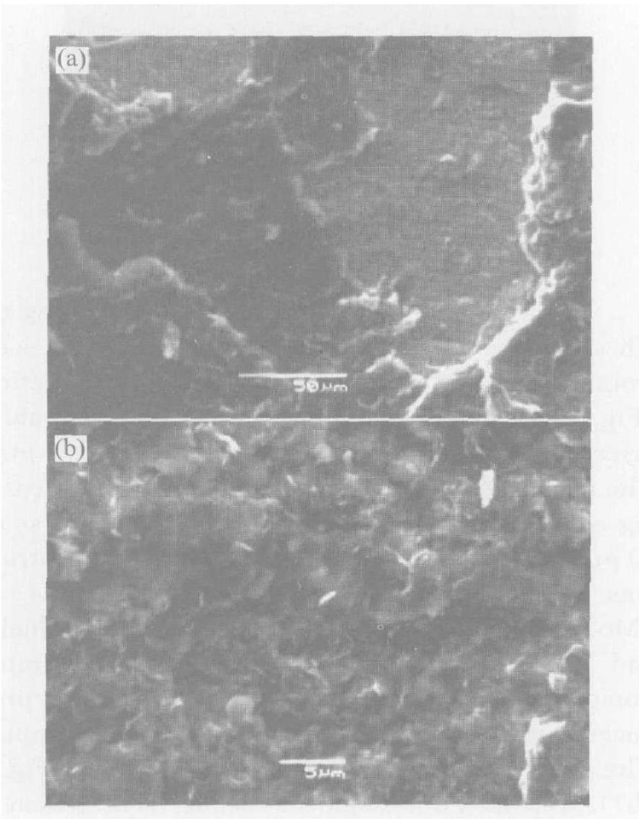

Fig. 3 Surface morphologies of $MoSi_2$ coating on Nb substrate after exposure at 1 500 ℃
(a) —Surface morphology of $MoSi_2$ coating during early course of oxidation in air at 1 500 ℃;
(b) —Surface morphology of coating covered with glass layer

coating change greatly after the oxidation testing. The surface of the coating is smoother compared to Fig. 2, but some part of the coating flake off (Fig. 3(a)). The high magnification SEM image shows not too much holes exist on the surface. The further analyses by XRD show that a thin glass SiO_2 layer covers on the coating. During the high temperature oxidation atmosphere, the following reactions happen in the coating:

$$3Fe + 2O_2 = Fe_3O_4 \quad (1)$$

$$5/7MoSi_2 + O_2 = 1/7Mo_5Si_3 + SiO_2 \quad (2)$$

$$MoSi_2 + 7/2O_2 = 2SiO_2 + MoO_3 \quad (3)$$

When the $MoSi_2$ coating is exposed to high temperature oxidation atmosphere, a SiO_2 scale is formed on the surface. This scale with liquidity can seal a part of the micro-holes on the outer layer. But the impurity Fe is oxidized rapidly, and the coarse surface of the coating provides the path for the oxygen to penetrate into the inner coating. Some part of $MoSi_2$ can not supply enough SiO_2 to form a glass layer on the outer layer. As a result, some area scale off after exposed to high temperature air in a short time, and the anti-oxidation property of the coating is descended.

The structure of the $MoSi_2$ coating on Nb substrate after exposure in air at 1 500 ℃ is shown in Fig. 4. It can be seen from the SEM photograph of the cross-section that a porous structure appears in the layer of the coating after exposure to high temperature air. The thickness increases to about 30 μm, and many cavities appear in the interface between the substrate and the transitional layer. The porous structures can effectively reduce the elastic modulus of the layer, and improve the thermal shook property of the coating. The formation of the loosen structure in the coating is relative to the diffusion of Si element. The diffusion of Si atoms through the silicide needs the reverse flow of the vacancy in the sublattices or the movement along the grain boundary. The cavities are formed by the gradual aggregation of vacancies in a gross. The formation of the continuous low silicides in coating is due to the short-distance diffusion of Si atoms. There is one thing to be noticed that the double-phase zone can not exist in the diffusion zone of binary system. In other words, each layer is single-phase zone. From the view of the thermodynamics, the driving force of the diffusion is chemical potential gradients. The diffusion is induced by the difference of the chemical potential gradients, and the atoms of the variant components always diffuse from high chemical potential zone to low chemical potential zone. According to the phase rule, if a double phase mixture zone which is composed of the two phases with same chemical potential exists at a certain temperature, the chemical potential gradients should be zero, i. e. $d\mu/dx = 0$. There is no driving force of the diffusion, and the diffusive flux is zero, so the diffusion can be interrupted in this zone. But the assumption does not agree with the fact. So the double phase mixture zone can not appear in the variant layer of the $MoSi_2$ coating. The double phase zone only exists in the system with two or more components. The quarter-phase structure can provide the rapid path for the diffusion of Si element in the interfaces of the coating, promote the formation of the Nb_5Si_3 transitional layer, and also accelerate the formation of the cavities and the consumption of Si element near the interface between the coating and the substrate.

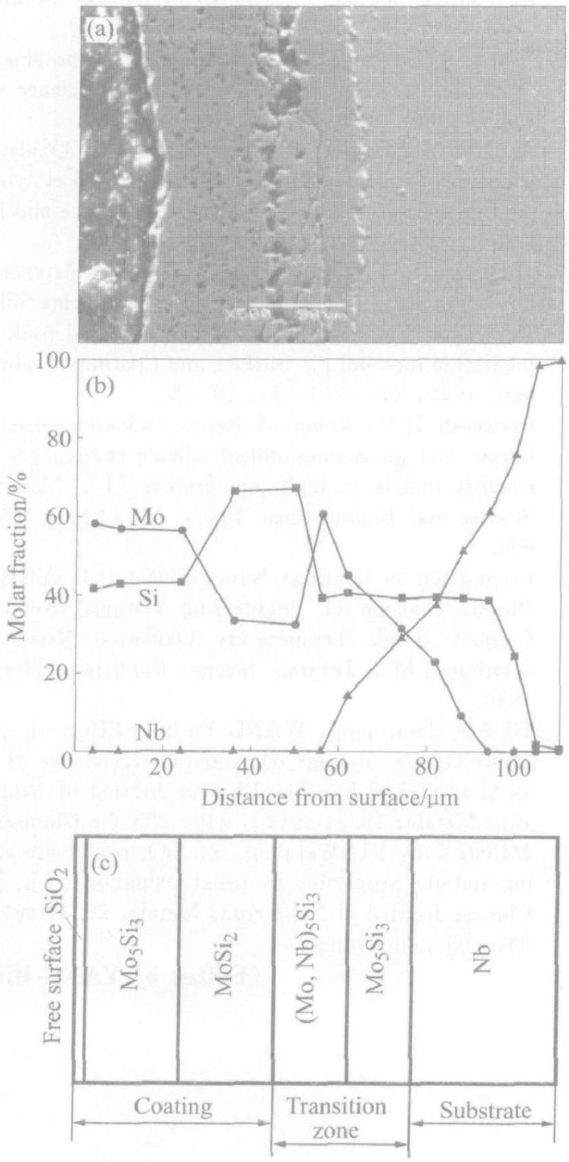

Fig. 4 Structure of $MoSi_2$ coating on Nb substrate after exposure in air at 1 500 ℃
(a) —SEM photograph of cross-section of coating;
(b) —Composition profiles of cross-section;
(c) —Sketch of structure of $MoSi_2$ coating

After exposed to the high temperature air for several hours, some massive areas scale off. But the coating can still withstand the oxidation for a short time. The structure of the $MoSi_2$ coating breaks through the interface between the coating and the transitional layer as shown in Fig. 5. It can be seen that a Nb_5Si_3 transitional layer still exists at the outer zone of the substrate. The coating is broken at the interface between the outer layer and the transitional layer. The Si element of the coating diffuses to Nb substrate continuously, and the low silicide transitional layer is formed due to the reaction of the Si and Nb. Great deal of continuous and dense cavities are formed in the interface between the outer layer and the transitional layer. As the time expands, these cavities perforate transversely, so the coating breaks through the interface and scales off. As the oxidation time prolongs further, the yellow powder appears on the surface of the sample, and the coating is invalidated. The analyses of EDS and XRD show that the yellow powder is Nb_2O_5. The morphology of the oxide on the surface of Nb substrate after the invalidation of the $MoSi_2$ protective coating is shown in Fig. 5(b). It can be seen that a great deal of disorderly coarse arborescent crystals grow to the outer surface. Because of the characteristic of the Nb_2O_5, the oxygen can penetrate into the inner zone, and the substrate "pest" oxidation rapidly.

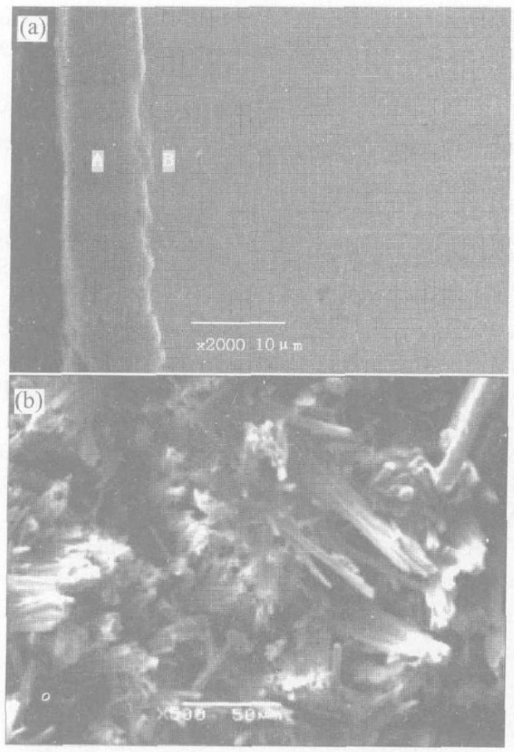

Fig. 5 Structure of $MoSi_2$ coating after coating breaks interface between coating and transitional layer(a); and morphology of oxide on surface of Nb substructure after invalidation of $MoSi_2$ protective coating(b)

4 CONCLUSIONS

The interface between the coating and the substrate has metallurgic combination, and a transitional layer is formed by diffusion. The multi-layer structure improves the oxidation resistance of the coating. The method of slurry firing to prepare the high temperature $MoSi_2$ coating on Nb is feasible. The SiO_2 scale, which is formed on the surface of the coating by the self-oxidation of $MoSi_2$, prevents the further diffusion of oxygen. After a long time exposure in high temperature oxidizing environment, the porous microstructure is formed as a result of the diffusion of silicon in the coating. As further inter-diffusion of the element between the coating and the substrate, a large number of cavities are formed and perforated transversely. The coating breaks through the interface between the outer coating and the transitional layer.

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(Edited by YANG Bing)