

Oxidation Behavior and Pack Siliconized Oxidation-resistant Coatings of an Nb-based Ultrahigh Temperature Alloy

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Abstract. The halide-activated pack cementation method was utilized to deposit silicide coatings on a multicomponent Nb-Ti-Si based alloy. The siliconized temperature was 1150 °C and the holding time was 10h. Both the specimens with siliconized coatings and without coatings were oxidized at 1250°C for 5, 10, 20, 50 and 100h respectively. The coating possessed a double layer structure with the composition of (Nb,X)Si₂ (X represents Ti, Cr and Hf), and the outer layer was denser. The major structure in the outer layer was composed of columnar crystals perpendicular to the interface between the coating and the substrate, and that in the inner layer was mainly composed of equiaxed crystals. A transitional layer about 5µm thick was found between the coating and the substrate. After oxidation at 1250°C, the major constituents in the scale were SiO₂ and TiO₂ and the mole ratio of these two phases was about 2:1. The thickness of the (Nb,X)Si₂ layer decreased and that of transitional layer increased as the oxidation time prolonged. The siliconized coating exhibited excellent oxidation-resistance at 1250°C within 50 hours.

Introduction

Nb-Ti-Si based alloy is expected to be one of the candidate materials employed in the temperature range of 1200~1450°C due to its advantages such as high melting point, low density and relatively excellent mechanical properties at elevated temperatures[1,2]. However, its high temperature oxidation resistance is obviously poor. In general, there are two methods to protect Nb-Ti-Si based alloy from oxidation [3,4]. One is adding alloying elements such as Ti, Cr, Hf and Al to the base alloy so that protective oxide film forms on the surface of the base alloy, and another is surface treatment, which can be applied to prevent or restrict the access of oxygen to the base metal. The pack cementation process is an effective and inexpensive method. Recently, proper silicide protective coatings for niobium or niobium based solution strengthened alloys have been developed [5,6]. However, the structure, phase constituents and formation process of the pack siliconized coatings on Nb-Ti-Si based alloys have still not been reported in detail up to now. In this paper, an oxidation-resistant siliconized coating on an advanced Nb-Ti-Si based multicomponent alloy was prepared, and furthermore, the oxidation behavior of the siliconized coating was revealed.

Experimental Procedures

The multicomponent Nb-Ti-Si based alloy ingot with the nominal composition of Nb- 24Ti- 16Si- 6Cr- 4Hf- 3Al- 1B- 0.05Y(at.%) was prepared by vacuum consumable arc-melting method. Substrate specimens were prepared by cutting the ingots into coupons with dimensions about 9×9×9 mm³. Pack powder mixtures comprising a master alloy powder (Si, 20wt.%), halide activator powder (NaF, 5wt.%) and inert filler powder (SiC, 75wt.%) were prepared by 4 hours' ball milling. The coupon was embedded in the pack powder mixtures in an Al₂O₃ crucible which was then sealed with an alumina

lid using silica sol binder. Once the sealed Al_2O_3 crucible was loaded in the pack cementation furnace, a vacuum about 2.6×10^{-2} Pa was pumped in the furnace chamber by a vacuum-pump system. The pack cementation temperature was 1150°C and the holding time was 10h. Both the arc-melted and coated samples were oxidized at 1250°C for 5, 10, 20, 50 and 100h respectively. The thicknesses of the scales of the specimens oxidized at 1250°C for different time were measured in an optical microscope with a microscale. XRD, SEM and EDS were used to characterize the microstructures and compositions of both the coated and oxidized specimens.

Results and Discussion

Structure and Phase Constituents of the Siliconized Coatings. As Fig. 1(a) shown, coarse and island-like microstructure existed in the surface of the coatings. Fig. 1(b) presents an SEM image of the coating after being stripped of several microns. It can be seen that equiaxed crystals existed and the grain size was approximately less than $1\mu\text{m}$. The result of X-ray diffraction analysis of the coating surface, which is shown in Fig. 2, revealed that the coating was composed of $(\text{Nb},\text{X})\text{Si}_2$ (X represents Ti, Cr and Hf), which is further confirmed by the results of EDS.

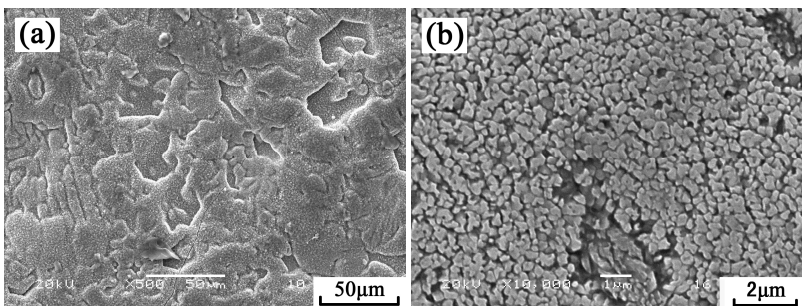


Fig. 1 SEM images of the siliconized coating surface.
(a) original and (b) stripped of several microns

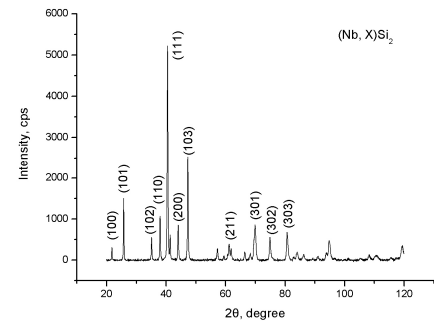


Fig. 2 XRD spectrum of the siliconized coating surface

Fig. 3(a) shows the cross-sectional optical micrograph of the siliconized coatings on Nb-Ti-Si based alloy at 1150°C for 10h. The coating was about $80\mu\text{m}$ thick. It is evident that the coating possessed two layers, and the outer layer was denser. Few cracks were observed in the coating. As Table 1 presented, the compositions of the two layers are similar. The content of Si in the coating tallies well with that of NbSi_2 , and the content of Nb + Ti + Hf + Cr is about 33at.%, so it can be concluded that the phase of the coating was $(\text{Nb},\text{X})\text{Si}_2$ (X represents Ti, Cr and Hf). Figs. 3(b) and (c) show respectively the cross-sectional SEM image of the outer layer and that of inner layer in the coating. It can be seen that the major structure in the outer layer was columnar crystals, whose growth direction was vertical to the interface between the coating and the substrate. The length and width of the columnar crystals were about $1\sim 5\mu\text{m}$ and $0.5\sim 1\mu\text{m}$ respectively. In the inner layer, shown in Fig. 3 (c), some equiaxed crystals existed, which was about 60% in area percentage. In addition, there were a lot of micropores in the inner layer. A transitional layer about $5\mu\text{m}$ thick can be observed between

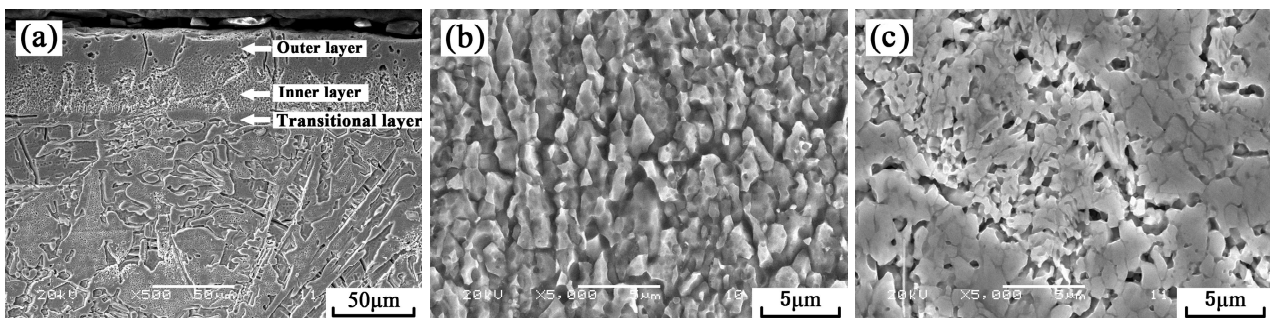


Fig. 3. Cross-sectional micrographs of the siliconized coating. (a) overall image of the coating, (b) SEM image of the outer layer and (c) SEM image of the inner layer

the coating and the substrate, which combined the coating tightly with the substrate, as shown by the arrow in Fig. 3(a). EDS analysis indicated that the composition of the transitional layer accorded with the molecular formula of $(\text{Nb},\text{X})_5\text{Si}_3$ (X represents Ti, Cr and Hf).

Table 1 Compositions (at.%) of different layers in the coating

Elements	Al	Si	Ti	Cr	Nb	Hf
Outer layer	0.30	67.21	10.87	1.43	18.97	1.23
Inner layer	0.46	66.05	10.86	1.21	20.15	1.28

Morphologies of Both Scale and Siliconized Coatings Oxidized at 1250°C. Fig. 4 (a) presents the cross-sectional micrograph of coated Nb-Ti-Si based alloy oxidized at 1250°C in air for 50h. Compared with Fig. 3(a), it can be seen obviously that the thickness of the coating decreased and that of the transitional layer increased after oxidation. Furthermore, the total thickness of the coating plus

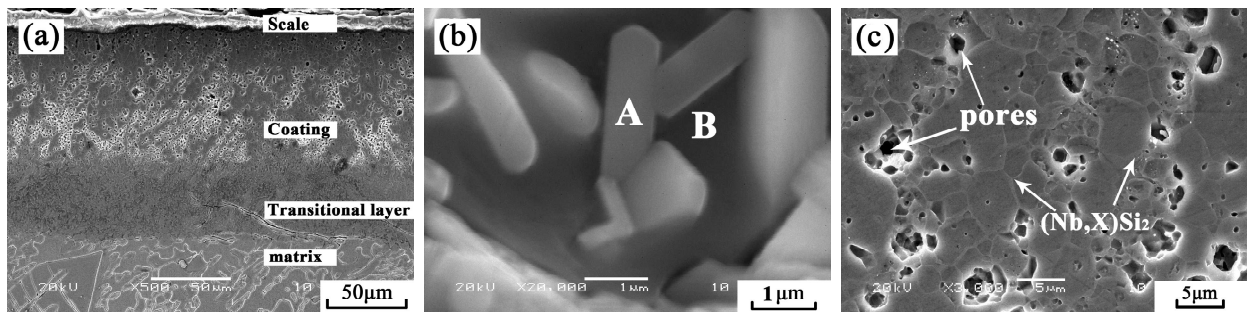


Fig. 4. SEM images of the coated specimen after oxidation at 1250°C for 50 hours. (a) four layers in the specimen, (b) morphology of the scale and (c) morphology of the coating

the transitional layer increased after oxidation. X ray diffraction and EDS analyses confirmed that the major phases in the coatings and transitional layers after oxidation were still $(\text{Nb},\text{X})\text{Si}_2$ and $(\text{Nb},\text{X})_5\text{Si}_3$ respectively. There existed four layers in the cross-section, which were respectively scale, coating, transitional layer and substrate from the surface to the base metal. The coating still possessed two layers, and the outer layer was denser and finer. XRD and EDS analyses determined that the major phases in the scales were SiO_2 and TiO_2 , and the mole ratio of the two phases was 2:1, as presented in Tables 2 and 3. The scale was less than 5 μm thick after oxidation for 5h, and just 11 μm thick when the oxidation time was 50h. However, the scale got loosened as the oxidation time prolonged, and had peeled off from the substrate substantially when the oxidation time was 100 hours. Fig. 4 (b) shows that some white clavated plate structure (A) existed on the dark base (B), which were TiO_2 and SiO_2 respectively as determined by EDS analysis. Fig. 4 (c) shows the SEM image of the $(\text{Nb},\text{X})\text{Si}_2$ layer in the coating after being oxidized at 1250°C for 50 hours. It can be seen apparently that the previous columnar crystals as shown in Fig.3(b) in the coating have transformed into compact equiaxed crystals after oxidation. Moreover, some micropores can be observed.

Table 2 Compositions (at.%) of different layers of coated specimens after being oxidized at 1250°C for 50h, corresponding to Fig. 4 (a).

Elements	O	Al	Si	Ti	Cr	Nb	Hf
Coating	1.68	0.50	64.37	12.06	1.59	18.96	0.85
Transitional layer	—	—	38.81	18.37	1.12	35.47	4.23
Scale	60.00	3.92	20.41	10.43	4.89	0.35	—

Table 3 Compositions (at.%) of the different phases in the scale corresponding to Fig. 4 (b).

Elements	O	Al	Si	Ti	Cr	Nb	Hf
A	61.53	0.96	4.69	29.28	0.94	1.41	1.19
B	58.02	4.49	33.62	3.86	—	—	—

Oxidation Kinetics. The isothermal oxidation kinetics of the silicide coated specimens at 1250°C is presented in Fig. 5. For comparison, the kinetics curve of bare Nb-Ti-Si based alloy at 1250°C was also drawn in the figure. It can be found that both the scale thicknesses of bare Nb-Ti-Si based alloy and that of coated specimens were nearly linear to the square root of oxidation time, which means that both the oxidation behavior of bare Nb-Ti-Si based alloy and that of coated samples followed parabolic laws. Given that the format of the parabolic equation was $y^2=kt$ (where y is the thickness of the scale, t is the oxidation time and k is the parabolic rate constant), the parabolic rate constant of bare Nb-Ti-Si based alloy was $1.37 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$, and that of coated samples was $8.01 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$. The silicized coating can improve the oxidation-resistance of Nb-Ti-Si based alloy significantly, by 4~5 orders of magnitude.

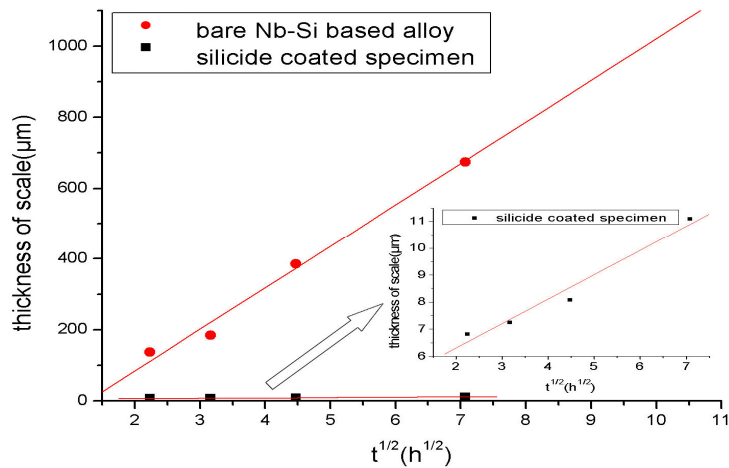


Fig. 5. Comparison of isothermal oxidation kinetics for silicide coated Nb-Ti-Si based alloy with that of bare Nb-Ti-Si based alloy at 1250°C

Conclusions

1. The siliconized coating had a double layer structure, the phase constituent in both layer was $(\text{Nb},\text{X})\text{Si}_2$ (X represented Ti, Cr and Hf), and the outer layer was denser. A transitional layer existed between the coating and the substrate, and its phase constituent was $(\text{Nb},\text{X})_5\text{Si}_3$.
2. After being oxidized at 1250°C for different time, the thickness of the coating decreased and that of the transitional layer increased with the prolonging oxidation time. The major phase in the coating remained $(\text{Nb},\text{X})\text{Si}_2$ after oxidation. The major phases in the scales were SiO_2 and TiO_2 .
3. Both the oxidation behavior of bare Nb-Ti-Si based alloy and that of coated samples followed parabolic laws at 1250°C, and the siliconized coating improved the oxidation-resistance of Nb-Ti-Si based alloy by 4~5 orders of magnitude

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