High-Temperature Oxidation Resistance of Silicide Coating on Nb/NbCr2 Alloy Surface (Postprint)

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Abstract

Silicide coatings were prepared on Nb/NbCr2 alloy surfaces by diffusion siliconizing, and the oxidation behavior of the substrate alloy and coatings at 1250°C was investigated. The results indicate that the silicide coating obtained by Si diffusion on the Nb/NbCr2 alloy surface is composed of two phases, (Nb, Cr)Si2 and (Cr, Nb)Si2, with a transition layer of (Nb, Cr)5Si3, and the coating growth kinetics obey a parabolic law. The oxide film formed on the substrate alloy during oxidation at 1250°C exhibits a porous structure with alternating Nb2O5 and CrNbO4, showing delamination from the substrate. The oxide film formed on the Si-diffused coating during oxidation at 1250°C is relatively dense and intact, well-bonded to the remaining coating, consisting of a mixed oxide film of SiO2 and CrNbO4, which improves the high-temperature oxidation resistance of the alloy.

Full Text

Preamble

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High Temperature Oxidation Resistance of Silicide Coatings on Nb/NbCr2 Alloy

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Abstract

Silicide coatings on Nb/NbCr2 alloy were prepared by pack cementation method. The oxidation behavior of the bare- and coated-alloy was examined by isothermal test at 1250 °C in static air. The results show that the silicide coatings are composed of (Nb, Cr)Si2 and (Cr, Nb)Si2 phases. There exists a transitional layer of (Nb, Cr)5Si3 between the main coating and substrate. The coating growth kinetics at 1250°C follows a parabolic law. The oxidation of Nb/NbCr2 alloy resulted in alternate layers of Nb2O5 and CrNbO4 with porous structure, which was wrinkling and even spalling off after oxidation. The scale formed on the silicide coating after oxidation at 1250°C was mainly composed of SiO2 and CrNbO4. The scale was relatively dense and had a good bond with the residual coating, thus showing excellent oxidation resistance.

KEY WORDS materials failure and protection, Laves phase NbCr2, pack cementation process, silicide coating, oxidation resistance

Introduction

With the rapid development of aerospace technology, Laves phase NbCr2 has attracted considerable attention due to its appropriate density (7.7 g/cm^3), high melting point (1770°C), excellent mechanical properties at elevated temperatures, and potential oxidation resistance [1,2]. However, the ordered lattice structure and coexistence of metallic and covalent bonds in this phase result in severe room-temperature brittleness, which significantly hinders its practical application [3,4]. Consequently, numerous reported studies have focused on the toughening of this alloy through alloying, grain refinement, and second-phase toughening. For instance, Chan et al. [1] improved the fracture toughness to 20.1 $\mathrm{MPa}\cdot\mathrm{m}^1/^2$ by adding Ti. Lu et al. [5,6] achieved good results by toughening Laves phase NbCr2 with soft second-phase solid solutions and Al additions. However, another obstacle limiting the practical application of Laves phase NbCr2 alloys is their poor oxidation resistance above 1149°C [7]. Therefore, improving high-temperature oxidation resistance is crucial for service above 1200°C.

Brady et al. [8,9] investigated the oxidation behavior of Laves phase NbCr2 alloys in dry air, humid air, and sulfur-containing atmospheres, finding that the formed oxide scales were prone to spallation. Ohta et al. [10] prepared NbCr2 by powder metallurgy and examined its oxidation resistance at 950°C, observing linear oxidation kinetics with time. Lu et al. improved oxidation resistance through alloying and process optimization, finding that Al had minimal effect while Si significantly enhanced oxidation resistance, and that combined additions of Al, Si, and Y performed better than single-element additions [11-13]. Grain refinement improved oxide scale adhesion and thus oxidation resistance [14,15], and optimization of mechanical alloying and hot pressing parameters could also enhance oxidation resistance by controlling grain size [16,17]. However, despite these improvements, the alloy still readily exhibited "pesting" oxidation. Surface coating technology offers an effective approach to balance oxidation resistance and mechanical properties. This study prepared silicide coatings on Nb/NbCr2 alloy by high-temperature solid-state Si pack cementation, analyzed the coating phase structure, and investigated the static oxidation behavior of the substrate and Si-coated specimens at 1250°C.

1 Experimental Methods

Master alloy ingots with a nominal composition of Nb-35Cr (at.%) were prepared by vacuum arc melting. Block samples measuring 7 mm × 7 mm × 7 mm were cut from the ingots by wire electrical discharge machining. The surfaces were ground sequentially to 1200-grit SiC paper, ultrasonically cleaned in alcohol, and dried. The pack mixture consisted of 10Si-5NaF-85Al2O3 (wt.%). The constituent powders were weighed according to the target ratio and ball-milled for 3.5 h to ensure thorough mixing and refinement. The samples were embedded in the pack mixture contained in an Al2O3 crucible, which was sealed with a high-temperature adhesive. Silicide coatings were prepared by holding at 1250°C for various durations. Static oxidation tests of the substrate and Si-coated samples were conducted in a tube furnace at 1250°C for 10 h.

Coating and oxide scale thicknesses were measured using an optical microscope (4XB-TV). The microstructures of coatings and oxide scales were examined by scanning electron microscopy (SEM, TESCAN MIRA 3). Phase constituents and microzone compositions were identified by X-ray diffraction (XRD, Panalytical X' Pert PRO) and energy-dispersive spectroscopy (EDS).

2 Results and Discussion

2.1 Microstructure of Substrate Alloy

Figure 1 shows backscattered electron (BSE) images of the as-cast Nb/NbCr2 alloy. The microstructure is uniform and primarily consists of two phases (Fig. 1a [Figure 1: see original paper]). EDS analysis revealed that the bright region in Fig. 1b contains 80.97Nb-19.03Cr (at.%), corresponding to the Nb solid solution. The gray-white alternating region contains 49.56Nb-50.44Cr, representing the NbCr2+(Nb) eutectic, consistent with the results of Bewlay et al. [18,19]. Therefore, the as-cast alloy comprises massive Nb solid solution and NbCr2+(Nb) eutectic.

2.2 Formation of Coating Microstructure

Figures 2 [Figure 2: see original paper] and 3 [Figure 3: see original paper] present the surface XRD patterns and cross-sectional BSE images of Si coatings prepared at 1250°C for various holding times (0.5, 2, 5, and 8 h). The XRD results show that coatings prepared at different times consist of (Nb, Cr)Si2 and (Cr, Nb)Si2 phases. The cross-sectional BSE images reveal that coatings held for 0.5-8 h are uniform in thickness, primarily single-layered, relatively dense, with an indistinct transition layer (Fig. 3). However, due to the intrinsic brittleness of silicides, numerous cracks are present in the coating, some penetrating through the entire thickness. The coating thickness is approximately 80 m after 0.5 h and increases with holding time, reaching about 237 m at 8 h, while the structure and phase composition remain unchanged.

Figure 4 shows magnified BSE images of the coating prepared at 1250°C for 8 h. EDS analysis of the bright region in the coating yields a composition of 27.42Nb-6.70Cr-65.88Si (at.%), with a molar ratio n(Nb+Cr):n(Si) 1:2, indicating (Nb, Cr)Si2. The gray region contains 28.32Cr-3.23Nb-68.45Si, with n(Cr+Nb):n(Si) 1:2, corresponding to (Cr, Nb)Si2, consistent with XRD analysis (Fig. 2). A discontinuous transition layer 2-5 m thick exists at the coating-substrate interface, with a composition of 56.40Nb-7.53Cr-36.07Si and molar ratio n(Nb+Cr):n(Si) 5:3. According to the Nb-Cr-Si ternary phase diagram, this transition layer is (Nb, Cr)5Si3 [20]. Additionally, the substrate microstructure exhibits minimal change during coating preparation.

During Si pack cementation, coating growth is controlled by the inward diffusion rate of Si atoms into the alloy and the outward diffusion rate of substrate atoms. Initially, Si reacts with the activator NaF to form gaseous fluorides SiFx (x=1, 2, 3, 4), which diffuse to the substrate surface driven by activity gradients of NbSi2 and CrSix+Si. Decomposition, displacement, or disproportionation reactions at the interface generate active Si atoms [21,22]. SiF2 has the highest partial pressure among these fluorides, thus dominating Si transport and deposition. After active Si atoms are generated, they diffuse inward under concentration gradients to form silicide coatings.

In the Nb/NbCr2 system, Si diffusion initially forms low-silicide phases NbSix and CrSix (x<2). With continued Si influx, these transform to high-silicide phases NbSi2 and CrSi2 via reactions: NbCrSi2 + Si → NbSi2 + CrSi2. According to literature [23], Nb solid solution first reacts with Si to form Nb5Si3, which subsequently transforms to NbSi2 via Nb5Si3 + Si → 5NbSi2. In the Ti-Si system, progressive Si infiltration leads to Ti3Si → Ti5Si3 → Ti5Si4 → TiSi2, ultimately forming TiSi2 coatings [24]. The Cr-Si system follows a similar transformation sequence [24,25], potentially undergoing Cr5Si3 → Cr3Si → CrSi2 to form CrSi2 coatings. Therefore, in the NbCr2+(Nb) eutectic, (Nb) directly transforms to (Nb, Cr)Si2. Based on compositional analysis, NbCr2 transforms to (Cr, Nb)Si2 with n(Nb):n(Cr) 1:2 (Cr and Nb contents of 28.32 and 3.23 at.%, respectively). Since the (Nb, Cr)Si2 transformed from eutectic (Nb) is slightly larger than in the substrate, most Nb from NbCr2 reacts with Si to form (Nb, Cr)Si2. Consequently, the coating microstructure essentially retains the original alloy morphology after Si pack cementation. This is similar to the findings of Guo et al. [26,27], who reported that after Si-Al-Y or Si-Zr-Y co-deposition on Nb-Ti-Si based ultrahigh-temperature alloys, the granular (Nb,X)Si2 (X=Ti, Cr, Hf) and blocky (Ti,Nb)5Si4 retained the morphology of original (Nb,X)5Si3.

In summary, coating formation is primarily controlled by inward Si diffusion. Figure 5 [Figure 5: see original paper] shows the relationship between coating thickness and holding time. The coating thickness is proportional to the square root of holding time, following the fitted equation:

$$y = 19.91 + 73.31\sqrt{t} \quad (0.5 \leq t \leq 8)$$

where y is coating thickness in m and t is holding time in h. This parabolic relationship indicates diffusion-controlled coating growth.

2.3 Oxidation Behavior at 1250°C

Figure 6 [Figure 6: see original paper] shows XRD patterns of oxide scales formed on the substrate alloy and Si-coated specimen (8 h) after oxidation at 1250°C for 10 h. The uncoated substrate formed an oxide scale primarily consisting of CrNbO4 and Nb2O5. Figure 7 [Figure 7: see original paper] presents cross-sectional BSE images of the substrate alloy after oxidation at 1250°C for 10 h. The oxide scale is porous and cracked, approximately 2-2.2 mm thick, with delamination from the substrate, indicating non-protective oxidation at 1250°C. Figures 7b-d show magnified BSE images of the scale, which consists mainly of light-gray and dark-gray phases. EDS analysis gives compositions of 24.18Nb-1.17Cr-74.65O and 20.17Nb-17.47Cr-62.36O for the light and dark phases, respectively. Combined with XRD results, the light-gray phase is Nb2O5 and the dark-gray phase is CrNbO4. The scale exhibits an alternating two-phase distribution. This occurs because Nb2O5 formation causes significant volume expansion and scale spallation, enriching the scale front in Cr, which subsequently oxidizes to CrNbO4. This alternating process creates the layered Nb2O5 and CrNbO4 structure [28]. Figure 7e shows the interface between the oxide scale and substrate. Compositions at points "A" and "B" are 77.61Nb-7.19Cr-15.20O and 53.73Nb-32.26Cr-14.01O, respectively, with Cr contents significantly lower than those in the substrate' s Nb solid solution (19.03 at.%) and NbCr2+(Nb) eutectic (50.44 at.%). This indicates significant Cr outward diffusion during oxidation.

Figures 8a and 8b [Figure 8: see original paper] show cross-sectional BSE images of the Si-coated specimen (8 h) after oxidation at 1250°C for 10 h. A relatively dense and intact oxide scale formed above the coating, bonding well with the residual coating, with a thickness of 80-92 m. Meanwhile, cracks in the original coating were sealed by glassy SiO2 at high temperature. Thus, the silicide coating significantly improved the oxidation resistance of Nb/NbCr2 alloy at 1250°C. Combined XRD (Fig. 6a) and EDS analysis identify the gray structure in Fig. 8b as CrNbO4 phase (13.76Cr-16.65Nb-69.59O) and the black structure as SiO2 phase (28.21Si-0.65Cr-0.92Nb-70.22O). In the residual coating, the original eutectic-transformed silicides partially oxidized to SiO2 (21.99Si-3.89Cr-4.56Nb-69.56O), becoming Si-depleted and forming (Nb, Cr)5Si3 (39.83Si-19.77Cr-40.40Nb). Figure 8c shows the interface between the residual coating and substrate after oxidation. The (Nb, Cr)5Si3 transition layer thickened to 6-9 m (composition: 35.80Si-6.22Cr-57.97Nb). An interdiffusion layer (layer C) formed at the transition layer-substrate interface with composition 17.28Si-48.76Cr-33.96Nb, corresponding to high-Si content Nb(Cr, Si)2 according to the Nb-Cr-Si ternary phase diagram [20]. In summary, the mixed SiO2 and CrNbO4 oxide scale formed on the Si-coated specimen effectively prevents further oxygen diffusion into the coating, providing excellent oxidation protection for Nb/NbCr2 alloy at 1250°C.

Conclusions

1. The silicide coating formed on Nb/NbCr2 alloy consists primarily of (Nb, Cr)Si2 and (Cr, Nb)Si2 phases, with a thin (Nb, Cr)5Si3 transition layer. The coating growth kinetics follow a parabolic law.
2. The oxide scale formed on Nb/NbCr2 alloy at 1250°C is a porous, alternating structure of Nb2O5 and CrNbO4. The Si-coated specimen forms a dense, intact mixed SiO2 and CrNbO4 oxide scale that bonds well with the residual coating, demonstrating superior high-temperature oxidation resistance.

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