Effect of Copper Addition on the Niobium Disilicide Coatings by Pack Cementation

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NbSi₂ coatings were deposited on pure niobium by halide-activated pack cementation method. The effect of copper addition in pack mixture on the siliconizing process was investigated. After siliconizing on niobium at 1050°C for 2 h using a pack mixture composed of Si, NaF and SiC, a single phase of hexagonal NbSi₂ coating was formed. The addition of copper in pack mixture not only increased the growth rate of the coatings, but also led to form a very thin interlayer between the NbSi₂ coating and the niobium substrate.

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1. Introduction

Niobium and niobium alloys are promising material for high temperature structural applications due to the attractive combination of high melting point, relatively low density and good mechanical properties at high temperatures. However, the inherently poor oxidation resistance at high temperatures greatly limits its applications.1–3) To restrain the catastrophic oxidation of niobium and niobium alloys at high temperatures, silicide and aluminide coatings have been developed by different techniques.4–12)

Pack cementation process is an in situ chemical vapor deposition technique carried out at high temperatures by embedding the substrate in a pack mixture consisting of fine powders of the depositing material (e.g. Al, Si, etc.), a halide activator (e.g. NaF, NH₄Cl, etc.) and an inert filler (e.g. Al₂O₃, SiC, etc.). The coating is formed through vapor transport and diffusion. Owing to low cost, simplicity and practicability, pack cementation process has been extensively studied and widely used to form different diffusion coatings.5–9,13–18)

In the present paper NbSi₂ coatings were formed on pure niobium by halide-activated pack cementation process. Emphasis was placed on the effect of copper addition in pack mixture on the growth rate, morphology, microstructure and phase composition of the coating.

2. Experimental Procedure

Sheets of pure niobium measuring 10 x 10 x 1.2 in mm were ground to a 600 grit finish, pickled in a solution of HF, HNO₃ and distilled water in a volume ratio of 1:1:1 for 1 min, ultrasonically cleaned in ethanol and acetone, then dried and weighed.

The siliconizing process was conducted at 1050°C for 2 h in a vacuum furnace with a pressure of 5 Pa. The niobium samples were embedded into the pack mixture placed in alumina crucibles. The pack mixture consists of 10 mass% pure Si powder (325 mesh), 3 mass% NaF (reagent grade), 0–5 mass% pure Cu powder (325 mesh) and 82–87 mass% SiC powder (325 mesh). After cooling in the furnace, the coated samples were ultrasonically cleaned in distilled water, dried and weighed again to examine the mass gain.

The surface morphologies were observed with a JEOL JSM-6700F field emission scanning electron microscopy (FESEM). X-ray diffractometry (XRD) was used to identify the phases in the coatings with a Rigaku D/MAX-2550V diffractometer using Cu Ka radiation (40 kV and 100 mA). The cross-sectional morphology and element distribution of the coatings were characterized by electron probe microanalysis (EPMA 8705QH², Shimadzu) using backscattered electron (BSE) micrograph and energy dispersive spectroscopy (EDS).

3. Results and Discussion

Figure 1 shows the mass gain of the niobium samples after siliconizing as a function of the content of copper in pack mixture. Obviously, the mass gain increases with the contents of copper. Figure 2 shows the FESEM micrographs of the surfaces of the as-formed coatings: (a) without copper and (b) with 3 mass% copper addition. The grain size of the coatings increased with copper addition. It can be concluded from Figs. 1 and 2 that copper addition accelerated the siliconizing process and enhanced the deposition rate.
The surface phases in both the siliconized niobium samples with and without copper addition were hexagonal NbSi$_2$ identified by XRD. However, there is a considerable difference in the observation of cross-sections of the two coatings. Figure 3 shows the BSE micrograph of the cross-section (a) and EDS composition profile (b) of the siliconized niobium sample without copper. With a thickness of about 25 $\mu$m, the coating is dense and has a distinct boundary with the niobium substrate. The concentrations of silicon and niobium in the coating are 66.6 mol% and 33.4 mol%, respectively, which agrees exactly with the NbSi$_2$ stoichiometry. Figure 3(b) indicates that the distribution of silicon and niobium is uniform throughout the whole coating and there is no interlayer between NbSi$_2$ coating and niobium substrate. It can be concluded from the EDS analysis and the XRD pattern that the coating consists of single phase of NbSi$_2$.

Figure 4 shows the BSE micrograph of the cross-section (a) and EDS composition profile (b) of the siliconized niobium with 3 mass% copper addition. As represented in Fig. 4(a), the coating consists of two layers with a total thickness of approximate 65 $\mu$m, which is about 2 times thicker than the coating without copper addition. This agrees with the results of the mass gain of siliconized niobium samples discussed above. The increase in the coating thickness indicates that copper addition in pack mixture increased greatly the growth rate of the coating.

Especially worthy of mention also is the duplex layer microstructure of the coating. The outer layer consisting of niobium and silicon with the corresponding concentration 33.1 mol% and 66.9 mol% can be identified as NbSi$_2$, which is also verified by the XRD pattern. Figure 4(b) shows that the niobium and silicon are uniformly distributed in the outer NbSi$_2$ layer. The thin inner layer at the NbSi$_2$/substrate interface consists of niobium (58.0 mol%), silicon (41.0 mol%) and very small amounts of copper (1.0 mol%), which does not agree with the stoichiometry of ternary Nb$_5$Cu$_3$Si$_4$ phase or Cu$_3$Nb$_5$Si$_4$ phase.$^{19,20}$ The Nb/Si atomic ratio is close to Nb$_3$Si$_2$, which was reported as a phase different from Nb$_5$Si$_3$.\textsuperscript{21,22} Nb$_3$Si$_2$ is considered to be one of metastable phases in the Nb-Si system formed usually due to impurity contamination.\textsuperscript{23} The interlayer may be composed of Nb$_3$Si$_2$ phase formed due to the presence of small amounts of copper. More detailed study is needed to identify the structure of the interlayer.

As can be seen from the experimental results, a single phase of hexagonal NbSi$_3$ coating was formed using a pack mixture without copper. There is not appreciable thermodynamically stable Nb$_5$Si$_3$ formed. Similar cases were observed.
when forming NbSi$_2$ coating on niobium and MoSi$_2$ coating on molybdenum using molten salt.$^{10,24}$ More recently, Milanese et al. reported that the growth rate of Nb$_5$Si$_3$ phase is very small in Nb/Si diffusion bulk couple annealed below 1200°C. When annealing a Nb-Si diffusion couple at 1350°C for 16 h, Nb$_5$Si$_3$ layer formed with a thickness of about 1 order of magnitude thinner than that of NbSi$_2$ layer.$^{25}$ The preferential formation of NbSi$_2$ might be related to the slower diffusion of silicon in the Nb$_5$Si$_3$ than that in the NbSi$_2$.$^{10}$

In the case of siliconizing on niobium using a pack mixture containing copper, copper deposited first or simultaneously with silicon on the niobium surface. It can be seen from the Cu-Si phase diagram that the eutectic point in the Cu-Si system is about 800°C,$^{26}$ which is much lower than the present siliconizing temperature. Therefore, it is likely that liquid phase containing copper and silicon formed on the niobium surface during siliconizing at 1050°C. The existence of liquid phase can accelerate the reaction rate of niobium and silicon, which resulted in larger grain size and greater growth rate of the as-formed coatings.

It should be noted, however, that the existence of copper has a great influence on the reaction between niobium and silicon even at temperatures below 800°C.$^{27}$ It is still unclear how the copper influences the reaction between niobium and silicon. The detailed effect mechanism of copper addition on the pack siliconizing on niobium should be studied further.

4. Conclusions

The effect of copper addition in pack mixture on the siliconizing process was investigated. The results are summarized as follows:

(1) The addition of copper in pack mixture increased the growth rate of NbSi$_2$ coatings and formed duplex layer microstructure.

(2) During siliconizing process at 1050°C using a pack mixture containing copper, Cu-Si liquid phase may be formed on the niobium substrate, which accelerated the reaction rate of niobium and silicon and resulted in larger grain size as well as greater growth rate of the as-formed coatings.

REFERENCES