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Effect of siliconizing temperature on microstructure and phase constitution of Mo–$MoSi_2$ functionally graded materials

Yingyi Zhang[a,b,*], Wenjie Ni[c], Yungang Li[d]

[a] School of Metallurgical Engineering, Anhui University of Technology, Maanshan 243002, Anhui Province, PR China
[b] College of Material Science and Engineering, Chongqing University, Chongqing 400030, PR China
[c] School of Metallurgy, Northeastern University, Shengyang 110819, Liaoning Province, PR China
[d] College of Metallurgy and Energy, North China University of Science and Technology, Tangshan 063009, PR China

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ABSTRACT

Mo–$MoSi_2$ functionally graded materials were prepared by a liquid phase siliconizing method. The microstructure, phase constitution, cross-section elemental distribution, grains size, and coating thickness of these materials were investigated with scanning electron microscopy (SEM), back scattered electron (BSE), energy dispersive spectroscope (EDS), glow discharge spectrum (GDS) and X–ray diffraction (XRD). The results indicate that the Mo–$MoSi_2$ functionally graded materials have a dense multi-layer structure, mainly composed of surface layer (Si–$MoSi_2$ layer, 1–10 μm), intermediate layer ($MoSi_2$ layer, 22–40 μm), transitional layer (Mo_5Si_3 and Mo_3Si layer, 2–3 μm) and Mo substrate. Moreover, the silicon concentration, grains size, and coating thickness increase gradually with the increasing temperature. The surfaces silicon concentrations are about 68–75 wt%, the average grains sizes of $MoSi_2$ columnar crystals are about 7.1–9.4 μm, and the coating thicknesses are about 28–35 μm.

1. Introduction

Molybdenum (Mo) with a high melting point of 2617 °C, excellent electrical and thermal conductivity and mechanical properties, is widely used in electronics, metallurgy, nuclear industry, and aerospace, etc. [1,2]. However, a poor oxidation resistance of these alloys seriously restricts their application at high temperatures [3–6]. Many studies have focused on silicide as the coating material for Mo and Mo-based alloys. Among a variety of silicide material systems, molybdenum disilicide ($MoSi_2$) material has long been known as an attractive coating material for protecting Mo and Mo-based alloys in an oxidative atmosphere at high temperatures [7–9]. It has a high melting point (2020 °C), low density (6.24 g/cm^3) and excellent high-temperature oxidation resistance [10]. The excellent oxidation resistance of $MoSi_2$ coating is due to the formation of an adherent and continuous SiO_2 film on the surface at high temperatures, which protects the coating material from further oxidation [11,12].

At present, the $MoSi_2$ coating on Mo substrate is produced by various processes such as electrochemical deposition [13], chemical vapor deposition (CVD) [14,15], fused salt electrolysis deposition [16], pack siliconizing [17], and vacuum sintering [18] at high temperatures. When above methods are used to prepare the $MoSi_2$ coating, the pore and crack defects are hardly inhibited, and the surface and cross section qualities of $MoSi_2$ coating are relatively poor [19–21]. However, little research has been reported on preparing $MoSi_2$ coatings on Mo substrates by the liquid phase siliconizing technology. Zhang et al. [22,23] prepared the Mo–$MoSi_2$ functionally graded materials by the liquid phase siliconizing technology, and found that the surface of Mo-$MoSi_2$ functionally graded materials are very dense and smooth without pore and crack defects, and good metallurgy bond is achieved between $MoSi_2$ coating and Mo substrates. Moreover, a large amount of researches have been focused on siliconizing or aluminizing coatings on titanium alloys substrates. These researches found that the liquid-phase siliconizing method C remarkably improve the high oxidation resistance of the TiAl-based alloy [24–26], high silicon concentration had a marked effect on the growth rate of coating, using the melt with a higher silicon concentration resulted in formation of the coating with almost a double thickness of traditional coating [27].

The liquid phase siliconizing method has been demonstrated to be an effective method to prepare Mo-$MoSi_2$ functionally graded materials [28]. Its advantages include short siliconizing time, low cost and near net shape [29]. During the liquid phase siliconizing process, liquid silicon or silicon-based alloys melts were infiltrated into the Mo or Mo-based alloys under the driving force of diffusion. The molten silicon

* Corresponding author at: School of Metallurgical Engineering, Anhui University of Technology, Maanshan 243002, Anhui Province, PR China.
E-mail address: zhangyingyi@cqu.edu.cn (Y. Zhang).

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melts reacted with the Mo or Mo-based alloys, ultimately resulted in the formation of a dense and smooth silicide coating. It should be mentioned that siliconizing temperature was a very important parameter in the liquid phase siliconizing process [30]. The Mo or Mo-based alloys substrate cannot be completely infiltrated by the molten silicon melt if the siliconizing temperature is too low, while over high siliconizing temperature may lead to the excessive reaction of Mo with the silicon melt, which may cause a negative effect on silicon melt and the mechanical properties of the Mo–$MoSi_2$ functionally graded materials.

In the present work, Mo–$MoSi_2$ functionally graded materials were prepared by a liquid phase siliconizing method. The effect of siliconizing temperature on microstructure, phase constitution, cross-section elements distribution, grains size, and coating thickness was investigated.

2. Material and methods

2.1. Liquid phase siliconizing

The Mo substrates were cut into 50 mm × 20 mm × 2 mm from a block of pure molybdenum substrate (99.95 wt%). These samples were hand-polished up to 2 mm by using 2000 grit SiC paper, then ultrasonically cleaned in alcohol and dried at 373 K for 20 min.

For the liquid phase siliconizing process, the polysilicon with a purity of 7 N was used as a siliconizing melt in this work. First, the polysilicon was placed in an alumina crucible, then smelted inside a vertical alumina tube furnace. Second, the treated samples were vertically immersed into the molten silicon bath for 15 min at a constant temperature in Ar atmosphere, and the temperatures are 1430 °C, 1460 °C, 1490 °C, 1520 °C, respectively. Finally, the Mo–$MoSi_2$ functionally graded materials were obtained at different temperatures. The experiment instrument is shown in Fig. 1.

2.2. Characterization

The surfaces of the Mo–$MoSi_2$ functionally graded materials were examined by using scanning electron microscopy (SEM, S3400–N). Some of the samples were mounted in the cold-setting epoxy resin to examine the cross-section in the SEM under back scattered electron image (BSE), the distributions of elements in the various cross-sections were analyzed by glow discharge spectrum (GDS), and the phase constitutions were analyzed by using X–ray diffraction (XRD) and energy dispersive spectroscope (EDS).

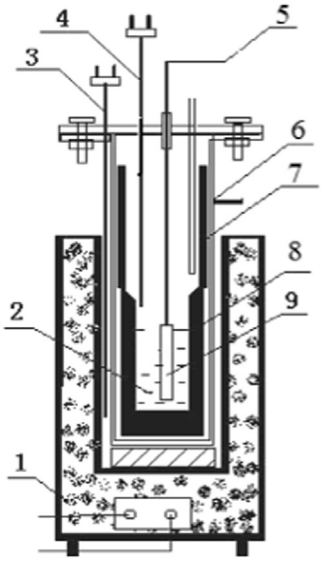

Fig. 1. Experimental installation drawing. 1. Electrical furnace; 2. Polysilicon melt; 3–4. Thermocouple; 5. Molybdenum wire; 6. Alumina ceramic tube; 7. Graphite sleeve; 8. Corundum crucible; 9. Mo substrate.

Table 1
The surface chemical compositions of Mo–$MoSi_2$ functionally graded materials.

Testing areas	Weight (%)		Atom (%)		Phase constitution	Average grain size (μm)
	Si	Mo	Si	Mo		
Fig. 3(a)-Area 3	75.33	24.67	91.28	8.72	$MoSi_2$-60.94 wt%Si	13.0
Fig. 3(b)-Area 3	41.67	58.33	71.00	29.00	$MoSi_2$-7.64 wt%Si	7.1
Fig. 3(c)-Area 3	52.35	48.65	78.66	21.34	$MoSi_2$-23.69 wt%Si	9.0
Fig. 3(d)-Area 3	56.42	43.58	81.60	19.40	$MoSi_2$-28.90 wt%Si	9.4

3. Results and discussion

3.1. Effect of temperature on phase constitution

The surface phase constitutions of the Mo–$MoSi_2$ functionally graded materials obtained at various temperatures were analyzed by energy dispersive X-ray spectroscope (EDS) and X–ray diffraction (XRD). The surface chemical compositions and XRD patterns of Mo–$MoSi_2$ functionally graded materials are shown in Table 1 and Fig. 2, respectively. It can be seen that the temperature has an important effect on the phase constitutions and grain orientations of the Mo–$MoSi_2$ functionally graded materials. Fig. 2(a) shows that when the temperature is 1430 °C, the coating surface is composed of Si and $MoSi_2$, and the $MoSi_2$ crystalloid has strong preferred orientation on the (101), (110) and (200) crystal faces. Fig. 2(b) shows that when the temperature is 1460 °C, the coating surface is only composed of $MoSi_2$ phase, and the $MoSi_2$ crystalloid has strong preferred orientation on the (103), (211) and (004) crystal faces. From Table 1 we found that the surface silicon concentration is the lowest when the temperature is 1460 °C, the Si concentration is only 7.6 wt%, which may be the main reason for the failure to detect Si (111) in XRD analysis. Fig. 2(c) shows that when the temperature is 1490 °C, the peak intensity of $MoSi_2$ (110) becomes the strongest and the peak intensity of Si (111) becomes weaker, the coating surface is mainly composed of $MoSi_2$ and a small amount of silicon. Fig. 2(d) shows that when the temperature is 1520 °C, the peak intensities of $MoSi_2$ (211) and Si (111) become weaker, $MoSi_2$ crystalloid has strong preferred orientation on the (110), (200) and (211) crystal faces, the coating surface is mainly composed of $MoSi_2$ and a small amount of silicon.

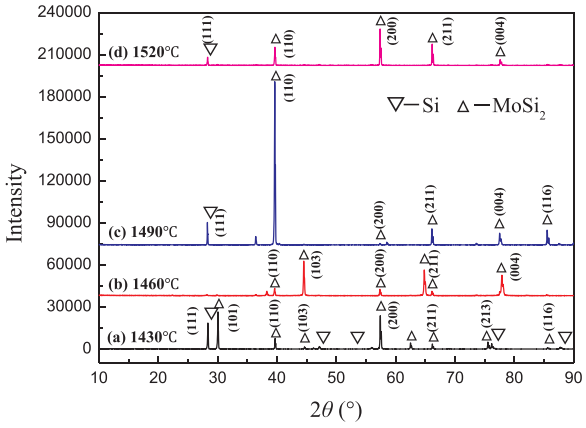

Fig. 2. Surface XRD patterns of Mo–$MoSi_2$ functionally graded materials obtained at different temperatures.