Siliconizing of Molybdenum Metal in Indium-Silicon Melts

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Siliconizing of Mo to form a silicide layer was investigated in the In-Si melt alloy with a two phase mixture of a solid Si and an In-Si melt at temperatures between 1273 and 1473 K for up to 90 ks in a vacuum ampoule. The MoSi₂ layer was grown in thick because an activity of silicon in the melt alloy is close to unity, accompanied by a formation of a thin Mo₅Si₃ layer between the MoSi₂ layer and Mo substrate. These two layers grew in accordance with a parabolic rate law.

Chemical diffusion coefficients in both the MoSi₂ and Mo₅Si₃ layers were obtained using Wagner analysis for the diffusion couple of a Mo/Mo₅Si₃/MoSi₂/Si (in the melt). Activation energies for the growth rate constants are 157 kJ/mol for the MoSi₂ and 350 kJ/mol for the Mo₅Si₃, respectively, and they are the same as those for chemical diffusion coefficients due to the fact that terminal compositions of 37.5 and 39.1 at%Si for both sides of the Mo₅Si₃ layers are almost independent of temperature. Composition of 39.1 at%Si was coincided with the measured one for the two MoSi₂+Mo₅Si₃ phase alloy, which was smaller than 40 at%Si cited in the phase diagram. Duplex layer structure and its growth kinetics in the present In-Si melt method were consistent with those obtained in the CVD method.

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I. Introduction

Molybdenum disilicide⁽¹⁾ is one of the candidate materials for high temperature applications, because of its excellent anti-oxidation property at high temperatures. Up to present a number of investigations⁽²⁾ have been carried out for fabrication of Mo-disilicide using hot pressing, hot isostatic pressing, and the recently developed spark plasma sintering process.

Coating techniques have been developed in order to form a MoSi₂ film on the Mo metal substrate, including a CVD siliconizing method⁽³⁻⁶⁾, deposition of a MoSi₂ film by a magnetron dc-reactive sputtering⁽⁷⁾ using Mo target in an containing silane gas atmosphere, and a CVD coating in a mixture of 90% Si powder and 10% reagent grade NaF to form MoSi₂ on Mo substrate⁽⁸⁾. Seybolt *et al.*⁽⁹⁾ obtained a MoSi₂ coating film on a Mo substrate in the fused salt electrolysis process, in which pure Si stick and strip of Mo were used as anode and cathode materials, respectively, in an equi-molar KF-NaF with 1% Na₂SiF₆ at plating temperatures of 973–1023 K. Sampath *et al.*⁽¹⁰⁾ has reported the use of a vacuum plasma spray (VPS) process to form MoSi₂ coating.

Figure 1 shows phase diagrams of both In-Mo and In-Si systems⁽¹¹⁾. In these phase diagrams solubilities of In into Mo or Si seem to be negligible, although they are not determined precisely yet. Therefore, it could be expected that when a Mo metal is dipped into the In-Si melt, Mo can react with Si in the melt to form silicides on the Mo substrate, where the activity of Si in the melt could be assumed close to unity, while an In-diffusion can be disregarded.

Fig. 1 Binary phase diagrams of In-Si, and In-Mo alloy systems.

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In this report a siliconizing behavior of Mo in the In-Si melt was investigated in the temperature range of 1273–1473 K, which seems to provide a simple and useful development strategy for coating of intermetallic disilicides on a Mo metal substrate. Particular attentions have been paid to measure compositions and film-structures of the reaction diffusion layers as well as their growth rate constants, in comparison with those of the CVD process⁽¹²⁾ reported previously.

II. Experimental Procedures

Molybdenum metal sheet (commercial pure grade 99.9%, supplied by NILACO Co.) was cut into coupons (0.5 mm × 7 mm × 15 mm) and then polished successively using SiC papers and 1 micron-diamond paste. The polished coupons were ultrasonically cleaned in a benzene-methyl alcohol mixture, and then dried. Mass and surface area were measured for the specimen in prior to the coating.

An In-Si alloy used for the Si-diffusion source was prepared using pure silicon (99.99 at% Si) and 5N purity In metal. The alloy composition, as indicated by an arrow in the In-Si phase diagram in Fig. 1, exists within the two phases region consisted of a solid-Si and In-Si melt, in order to maintain a constant activity of Si in the melt during a coating process. Because of negligible dissolution of In into the solid-Si phase, an activity of Si in the melt could be assumed to be unity, and then the highest silicide as the Mo-disilicide could be formed on a surface of the Mo-substrate.

Figure 2 shows a schematic diagram adopted for siliconizing of Mo substrate in the In-Si melt. The polished Mo specimen and the pre-prepared In-Si alloy lumps were put into an alumina crucible with 99.5 mass% purity, and then they were sealed under vacuum 1.3×10^{-3} Pa in a quartz ampoule. Siliconizing of the Mo substrate in the In-Si melt was carried out at temperatures of 1273, 1373, and 1473 K for up to 90 ks. After siliconizing, the quartz ampoule was overturned quickly in order to

scavenge the In-Si melt. In order to remove the melt residues on the surface, the as-coated sample was cleaned in a reagent grade nitric acid, followed by rinsing and ultrasonic cleaning in a benzene-methyl alcohol mixture.

The siliconized samples were first analyzed using X-ray diffraction to identify phases of the silicides, and then they were mounted in an electrically conducting resin. The cross-section of the samples was analysed by an electron probe micro-analyser (EPMA) to determine concentration profiles of each constituent element.

III. Results and Discussion

Figure 3 shows X-ray diffraction patterns taken from the surface of the as-coated molybdenum substrate. In this figure a X-ray diffraction result obtained in our previous investigation⁽¹²⁾ for the surface of as-coated CVD sample was also given for comparison purpose. These two diffraction patterns are similar to each other, suggesting a formation of MoSi₂ surface coatings. This MoSi₂ formation could be explained reasonably from both a phase diagram of the Mo-Si system⁽¹¹⁾ as shown in Fig. 4 and a silicon activity in the In-Si melt was close to unity, as mentioned previously from the In-Si phase diagram.

Figure 5 shows the cross-sectional microstructure of the sample, immersed at a temperature of 1473 K for 90 ks, and a duplex layer structure was observed, consisting of both the MoSi₂ and Mo₅Si₃ layers. Other silicide such

Fig. 2 Schematic diagram adopted for siliconizing Mo in the In-Si melt.

Fig. 3 X-ray diffraction charts of surface of the as-siliconized molybdenum substrate in (a) the In-Si melt and (b) the CVD. ● MoSi₂, ◇ Si.

Fig. 4 A phase diagram of a Mo-Si alloy system.

Fig. 5 SEM micrograph of a cross-section of the Mo substrate after siliconizing it in the In-Si melt at 1473 K for 90 ks. (A: MoSi₂, B: Mo₅Si₃, C: Mo substrate)

as Mo₃Si and a dissolution of Si into Mo substrate in Fig. 4 were not observed.

Thicknesses of both the MoSi₂ and Mo₅Si₃ layers were measured as functions of temperature and time, and they were given in Fig. 6, where the thickness squared was plotted against time. It was found that both the MoSi₂ and Mo₅Si₃ layers grew parabolically.

The parabolic rate constants were obtained from the slopes in Fig. 6, and they were plotted against a reciprocal of an absolute temperature in Fig. 7. Activation energies for growth of MoSi₂ and Mo₅Si₃ layers were 158 and 349 kJ/mol, respectively.

Figure 8 shows changes in thickness of the MoSi₂ and Mo₅Si₃ layers obtained by both the In-Si melt method and the CVD method in our previous investigation⁽¹²⁾. It could be considered within their error limits that the Mo₅Si₃ layer grows from an initial stage of the reaction in both methods, resulting in the parabolic rate constant of $1.1 \times 10^{-15} \text{ m}^2/\text{s}$. The MoSi₂ layer formed in the In-Si melt grows from the initial reaction stage, while in case of the CVD method there is an incubation period for

Fig. 6 Plots of thickness squared against time for (a) MoSi₂ and (b) Mo₅Si₃. Fig. 7 Arrhenius plots of parabolic rate constants, K_p and chemical diffusion coefficients, D for MoSi₂ and Mo₅Si₃ layer growths. K_p for $\odot$ MoSi₂, and $\bullet$ Mo₅Si₃, D for $\oplus$ MoSi₂, and $\square$ Mo₅Si₃

several ks before on-set of the parabolic growth. This incubation period seems to be due to the fact that MoSi₂

Fig. 8 Changes in thickness of (a) MoSi_2 and (b) Mo_5Si_3 layers with time for both the In-Si melt and CVD siliconizing methods at 1473 K. ● is for the (In-Si) method and ○ is for the CVD method.

reacted with Mo to form Mo_5Si_3 , leaving a very thin layer of MoSi_2 , because a supply of Si from the gas phase is probably insufficient at an initial stage of the coatings. For longer periods it tended to be controlled by the diffusion process in both the MoSi_2 and Mo_5Si_3 layers. A parabolic rate constant for the MoSi_2 obtained in the In-Si melt method is close to that of the CVD method, giving $3.5 \times 10^{-13} \text{ m}^2/\text{s}$.

From the parabolic growth of each layer, the siliconization of Mo in the In-Si melt could be concluded to be a diffusion-controlled process, and it is regarded as a diffusion couple composed of the $\text{Mo}/\text{Mo}_5\text{Si}_3/\text{MoSi}_2/\text{Si}$ (in the melt). Figure 9 shows an example of concentration-penetration profiles of the sample siliconized in the In-Si melt at a temperature of 1473 K for 90 ks.

Chemical diffusion coefficients of both the Mo_5Si_3 and MoSi_2 layers were calculated using Wagner's equation for the multi-layer diffusion couple⁽¹³⁾. The concentrations at the coexisting phase boundaries are given for the In-Si/ MoSi_2 : unit activity of Si in In-Si/67.1 at%Si; $\text{MoSi}_2/\text{Mo}_5\text{Si}_3$: 66.9/38.8 at%Si; and $\text{Mo}_5\text{Si}_3/\text{Mo}$:

Fig. 9 Concentration profiles of Si across the Mo_5Si_3 layers as-coated in the In-Si melt and the CVD method. Broken lines A and B represent terminal Si concentrations. ○ is for In-Si melt, and ● is for CVD method.

Table 1 Chemical diffusion coefficients in MoSi_2 and Mo_5Si_3 . Bracket denoted those obtained from the CVD method.

Temp. (K)	$D \text{ (m}^2 \text{ s}^{-1}\text{)}$	
	MoSi_2	Mo_5Si_3
1273	0.28×10^{-13}	3.4×10^{-16}
1373	1.1×10^{-13}	6.8×10^{-15}
1473	2.5×10^{-13}	2.9×10^{-14}
	(2.0×10^{-13})	(3.1×10^{-14})

37.7/0.1 at%Si at each temperature. The calculated values are given in Table 1, and semi-logarithmic plots between the chemical diffusion coefficient and a reciprocal of absolute temperature are shown in Fig. 7. Activation energies for chemical diffusivity are 350 and 157 kJ/mol for the Mo_5Si_3 and MoSi_2 layers, respectively. These are close to the activation energies obtained for the growth of the Mo_5Si_3 and MoSi_2 layers. This consistency in activation energies is coming from the fact that the composition ranges of both the Mo_5Si_3 and MoSi_2 phases are independent of temperatures. The chemical diffusion coefficient agreed with that of the CVD siliconizing at the corresponding temperature (1473 K), as given in brackets in Table 1. It was established in the CVD siliconizing process⁽¹²⁾ that growth of the silicide layers was solely controlled by Si diffusion, and then it is plausible that in the In-Si melt siliconizing process Si was the only diffusing species.

According to the Mo-Si phase diagram, the composition range of the Mo_5Si_3 phase is between 37.5 and 40 at%Si. However, as indicated in Fig. 9, the Mo_5Si_3 layer formed in the diffusion process ranged between 37.6 and 39.1 at%Si, and the same result has been obtained for the diffusion layer formed by the CVD method⁽¹²⁾. In order to elucidate these compositional differences, an alloy consisting of the $\text{Mo}_5\text{Si}_3 + \text{MoSi}_2$ phases was prepared us-

ing an argon arc-melting and then annealed for 1.44 Ms at 1273 K in the quartz ampoules, followed by a water-quenching. Both phases of the Mo_5Si_3 and MoSi_2 were identified by a X-ray diffraction analysis, and a Si concentration in the Mo_5Si_3 phase was 39.1 ± 0.1 at%Si. This composition is close to that observed in the diffusion layer formed by both the In-Si melt as shown in Fig. 9, and also to that obtained by the CVD method.

IV. Conclusions

The liquid In-Si alloy was successfully used for siliconizing of Mo to form the MoSi_2 coating layer. The results obtained are summarized as follows:

- (1) Siliconizing of Mo in the In-Si melt was carried out in the quartz ampoule at temperatures between 1273 and 1473 K for up to 90 ks, forming the MoSi_2 layer accompanied by a thin Mo_5Si_3 interlayer.
- (2) Both the MoSi_2 and Mo_5Si_3 layers grew parabolically at each temperature, and activation energies for the MoSi_2 and Mo_5Si_3 layer growth were 157 and 349 kJ/mol, respectively.
- (3) Chemical diffusion coefficients of the MoSi_2 and Mo_5Si_3 phases were calculated using Wagner analysis for the diffusion couple of Mo/ Mo_5Si_3 / MoSi_2 /Si (in the melt). Activation energies for chemical diffusion process were the same as those for growth kinetics of both layers.
- (4) Composition range of the Mo_5Si_3 layer was between 37.6 and 39.1 at%Si, and this is narrower than that cited in the phase diagram.

(5) From the equilibrium experiment with the $\text{MoSi}_2 + \text{Mo}_5\text{Si}_3$ composite alloy, a terminal composition of the Mo_5Si_3 was 39.1 ± 0.1 at%Si, which coincided with that in the diffusion layer.

(6) Duplex layer structure and their growth kinetics in the present In-Si melt method were consistent with those obtained in the CVD method.

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