Oxidation Resistance of Mo Coated with Mo(Si,Al)\textsubscript{2} Layer Prepared by Dipping into Liquid of Al-25 mass%Si alloy

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A homogeneous layer of molybdenum aluminosilicide Mo(Si,Al)\textsubscript{2} with C(40) structure was made on the sample surface of molybdenum by dip-coating technique using Al-25 mass%Si liquid at 1123 K. Adherent Al-Si was removed by soaking the dipped samples in the NaOH saturated hydraulic solution. The Mo samples coated with the Mo(Si,Al)\textsubscript{2} layer were found to have excellent oxidation resistance in air even at 1473 K due to formation of a dense alumina film on the sample surface during oxidation. The formation of Mo(Si,Al)\textsubscript{2} layer was also observed at the interface between the Mo substrate and the Mo(Si,Al)\textsubscript{2} layer.

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1. Introduction

Mo-based alloys are well-known as a material with great potential in use at elevated temperatures because of its high melting point of 2900 K. However, practical utilization of Mo-based alloys at high temperatures is limited in inert atmospheres. Disadvantages of Mo in practical use in air are easy oxidation above 700 K and evaporation above 1150 K. Therefore, oxidation-resistance coating on Mo-based alloys is necessary for using Mo-based alloys in oxidizing atmospheres. Molybdenum silicide MoSi\textsubscript{2} and molybdenum aluminosilicide Mo(Si,Al)\textsubscript{2} are candidates for oxidation-resistance coating materials. MoSi\textsubscript{2} is known to exhibit high oxidation resistance at high temperatures from 973 to 1973 K, because of formation of a SiO\textsubscript{2} scale.\textsuperscript{1} However, MoSi\textsubscript{2} has a serious problem of low toughness at temperatures around 780 K, which is called pesting.\textsuperscript{2,3} Yanagihara et al.\textsuperscript{5,6} reported that Mo(Si,Al)\textsubscript{2} with hexagonal C40-type structure has good oxidation resistance in air at temperatures up to 1673 K due to formation of a protective alumina scale. The pesting of Mo(Si,Al)\textsubscript{2} was also found to be suppressed.\textsuperscript{7,8} Although the oxidation rate of Mo(Si,Al)\textsubscript{2} is higher than that of MoSi\textsubscript{2}, the scales developed on Mo(Si,Al)\textsubscript{2} have good adherence to the substrate.\textsuperscript{7} Recently it was reported that Mo(Si\textsubscript{1-x}Al\textsubscript{x})\textsubscript{2} with C40-type structure was formed in a composition range of x = 0.130 to 0.456.\textsuperscript{9}

Yanagihara et al.\textsuperscript{10} reported that a dense Mo(Si,Al)\textsubscript{2} layer developed on Mo by dipping into Al liquid saturated with Si at temperatures between 1000 and 1200 K. The compositions of the melt were changed in the range from 27 to 55 at%Si. Nanko et al.\textsuperscript{11} studied the growth mechanism of the Mo(Si,Al)\textsubscript{2} layer formed by dipping Mo into Al liquid saturated with Si. The use of Al liquid saturated with Si for formation of Mo(Si,Al)\textsubscript{2} was determined in a view point of the phase reaction.\textsuperscript{10,11}

Unfortunately, there is no investigation in which the oxidation resistance of Mo samples coated with Mo(Si,Al)\textsubscript{2} experimentally was evaluated although Mo(Si,Al)\textsubscript{2} would be expected to exhibit excellent oxidation resistance. Nobody could completely remove the adhesive Al-Si solid on the sample surface formed by dipping Mo sample into the melt. The Al-Si solid reacts intricately with the coatings during oxidation experiments, so that the oxidation resistance of the Mo(Si,Al)\textsubscript{2} layer on Mo samples could not be observed.

The purpose of this work is first to make clear chemical composition and microstructure of the Mo(Si,Al)\textsubscript{2} layer formed on the sample surface by dip-coating technique using an unsaturated Al-25 mass% Si liquid at 1123 K. The second purpose is to develop a new technique of removing the adhesive Al-Si solid layer in order to evaluate the exact oxidation resistance of the Mo(Si,Al)\textsubscript{2} layer. Furthermore, some features of oxidation resistance of Mo samples covered with the Mo(Si,Al)\textsubscript{2} layer without Al-Si solid layer are studied.

2. Experimental

Mo disc samples ($\phi$10 mm $\times$ 15 mm) of 99.95% purity were used as sample for dip-coating experiments. The surfaces of Mo disc samples were polished using the emery paper of 8800, 1000, 1500 and 2000. Corners of the samples were cut off in order to avoid occurrence of the radial cracks at the substrate corners during the coating process. Dipping experiments of Mo samples were carried out in Al-Si liquid in a graphite crucible at 1123 K in a muffle furnace. The chemical composition of the liquid was Al-25 mass%Si. After dip-coating for approximately 43.2 ks, the samples were picked up from the crucible and cooled in air. The samples were soaked in the saturated solution of NaOH in order to remove the adherent Al-Si solid. The samples were

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heated in air at 1473 K from 3.6 to 360 ks. The oxidation resistance of dip-coated samples was evaluated by measuring the mass gain of the samples. The products formed on the samples subjected to dip-coating and subsequent oxidation were examined on the sample surface by X-Ray diffractmeter (XRD, RINT-2500, Rigaku). Microstructure and chemical composition of the dipped samples were studied with a scanning electron microscope with electron probe microanalyzer (EPMA, JXA-8100, JEOL).

### 3. Result and Discussion

Figures 1(a) and (b) show the appearance of the samples before and after dipping, respectively. The dipped sample is covered with Al-Si solid which was formed during the cooling process. An image and cross-sectional microstructure of a sample subjected to the NaOH treatment are shown in Fig. 1(c) and Fig. 2(a), respectively. One can see that the Al-Si solid is not adherent to the sample surface. This result suggests that the NaOH treatment is very effective for removing the Al-Si solid from the sample surface without any damage. Such a clean surface is expected to provide an exact evaluation of oxidation behavior of samples covered with a Mo(Si,Al)$_2$ layer at elevated temperatures.

The compound layer on Mo substrate was clearly observed to be uniformly formed in Fig. 2(a). The thickness of the compound layer was 80 µm in the sample dipped into Al-25 mass%Si liquid for 43.2 ks at 1123 K. Similar formation of the compound layer was reported in the case of dipping using Al liquid saturated with Si.$^{10,11}$

Figure 2(b) shows concentration profiles of Mo, Si and Al which were determined by the EPMA quantification analysis in the dipped sample. The compositional changes of the elements are shown as a function of the distance from the interface between the compound layer and the Mo substrate. A chemical composition of (Mo:Si:Al) = (31:59:10) in atomic percent remains constant throughout the compound layer. Figure 3(a) shows a XRD pattern of the same sample as shown in Fig. 2, suggesting that the compound layer is Mo(Si,Al)$_2$ with a hexagonal C40-type structure. The compound layer was therefore found to be Mo(Si$_{0.85}$Al$_{0.15}$)$_2$ which corresponds to (Mo:Si:Al) = (31:59:10) in atomic percent. It is noteworthy that the composition of Mo(Si$_{0.85}$Al$_{0.15}$)$_2$ in this study is similar to the sample dipped into Al liquid saturated with Si.$^{11}$

Fig. 1(d) shows that the appearance of the sample after oxidation in air at 1473 K for 360 ks (d). It has no trace of ablating Mo
substrate. Therefore, the Mo sample coated with Mo(Si,Al)₂ layer has excellent oxidation resistance in air even at 1473 K for 360 ks. The growth of the compound layer in Al-25 mass%Si liquid will be reported on a subsequent report.

Figure 4 shows EPMA maps of the cross-sectional part of the Mo(Si,Al)₂ layer oxidized at 1473 K for 360 ks of the same sample as that shown in Fig. 1(d). Four different layers are clearly observed. The aluminum and oxygen maps indicate that the layer I is a continuous alumina scale. As shown in Fig. 3(b), the XRD pattern also indicates the formation of alumina. The scale was dense and adherent. Any formation of cracks was not observed. The layer II beneath the alumina layer I consisted of Mo₅(Si,Al)₃, Mo(Si,Al)₂ and Al₂O₃ which were determined by EPMA quantification analysis. In the layer III Mo(Si,Al)₂ and Mo₅(Si,Al)₃ were detected. The layer IV of Mo₅(Si,Al)₃ was formed between the layer III and Mo substrate. Many voids are observed in the layer II. It is suggested that the formation of the voids is caused by outer-diffusion of Al from the compound layer.

Figure 5 shows mass change of Mo samples coated with a Mo(Si,Al)₂ layer as a function of heating time in air at 1473 K from 3.6 to 360 ks. Mass gain per unit surface area \( (\Delta W/A) \) obeys a parabolic rate law with a rate constant \( (k_p) \).

\[
(\Delta W/A)^2 = k_p \cdot t
\]

The parabolic rate constant at 1473 K is \( 2.1 \times 10^{-4} \) g²m⁻⁴s⁻¹. The value of \( k_p \) in the present study is a little higher than that of bulk Mo(Si₀.₉₉₉,Al₀.₁₂₂)².1² Ramberg and Worrell¹² reported that the value of \( k_p \) for bulk Mo(Si₀.₉₉₉,Al₀.₁₂₂)² was \( 1.8 \times 10^{-4} \) g²m⁻⁴s⁻¹. These results indicate that the Mo(Si₀.₈₅,Al₀.₁₅)₂.₂₅ layer formed on Mo by dipping in this study has excellent oxidation resistance similar to bulk Mo(Si,Al)₂ sample.

Figure 6 shows growth of the layer IV of Mo₅(Si,Al)₃, yielding a parabolic rate law. The growth of this layer may be controlled by inward diffusion of Si in Mo₅(Si,Al)₃.
4. Conclusion

A uniform layer of molybdenum aluminosilicide Mo(Si,Al)$_2$ on molybdenum was developed by dip-coating technique using Al-25 mass%Si liquid at 1123 K. The compound layer with a hexagonal C40-type structure was homogeneous in composition of Mo(Si$_{0.85}$,Al$_{0.15}$)$_2$. Oxidation resistance can be evaluated through a novel technique of removing the adherent Al-Si solid by soaking the dipped sample in the saturated solution of NaOH. The sample has high oxidation resistance at 1473 K for 360 ks. The mass gain per unit surface area obeys a parabolic rate law with a rate constant ($k_p$). The value of $k_p$ at 1473 K was $2.1 \times 10^{-4}$ g$^2$m$^{-4}$s$^{-1}$. Four different layers were formed on the oxidized samples. The excellent oxidation resistance came from the formation of a dense alumina layer on the sample surface. Mo$_3$(Si,Al)$_3$ was formed at the interface between the Mo substrate and the Mo(Si,Al)$_2$ layer.

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