

Production of Molybdenum Disilicide using a Silicon-Containing Molten Bath via the Hot Dipping Method

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ABSTRACT

Molybdenum disilicide (MoSi_2) is a promising material for thermal applications due to its excellent heat and oxidation resistance. It can operate at temperatures of up to 1800°C as furnace heating elements and protect refractory metals such as molybdenum from rapidly reacting with air to form volatile molybdenum oxides at elevated temperature. In this work, the feasibility of forming MoSi_2 on a molybdenum substrate by hot dipping in a silicon-saturated molten metal bath was investigated. This method is simple, predictable, and can be used to coat large components and complex parts.

It was found that tetragonal MoSi_2 can be successfully synthesized on the surface of the substrate after dipping for 15 minutes at 1000°C using molten tin (Sn), bismuth (Bi), and copper (Cu) baths. The growth of the MoSi_2 layer was fast within the first 15 minutes, and then gradually slowed down with time. After dipping for 60 minutes at 1000°C , the thickness of the MoSi_2 layer were measured as 441.5, 19.5, and 13.1 μm for the copper, tin, and bismuth baths, respectively. The MoSi_2 coating synthesized in this study provided oxidation resistance at 1150°C by forming a protective SiO_2 layer on the surface. The SiO_2 layer prevented the sample from rapidly oxidizing by inhibiting direct contact between the molybdenum substrate and oxygen in the atmosphere.

Compared to conventional methods, the proposed hot dipping method produces a MoSi_2 layer more rapidly and at much lower operating temperatures. This makes it a more attractive option for coating large and complex components, with the potential to enable the use of MoSi_2 in a wider range of applications.

INTRODUCTION

High-temperature applications in oxidizing environments, including power generation, metal processing and aerospace industries, require materials with exceptional resistance against heat and oxidation. Molybdenum disilicide (MoSi_2) is a candidate material for these purposes due to its low density (6.31 g/cm^3), high melting point (2030°C), excellent oxidation resistance, satisfactory electrical and thermal conductivities, chemical inertness, and relatively low coefficient of thermal expansion (Shah, 1992; Vasudévan and Petrovic, 1992; Jeng and Lavernia, 1994). However, despite these outstanding physical and chemical properties, limitations associated with conventional manufacturing methods for MoSi_2 components and MoSi_2 -coatings restrict its application to simple shapes and small components.

Molybdenum and its alloys, on the other hand, are considered the next-generation materials to replace nickel super alloys (Kamata et al., 2018). However, the poor heat and oxidation resistance of molybdenum seriously limits its applications. At elevated temperatures, molybdenum readily reacts with oxygen in air to form volatile molybdenum oxide species, such as MoO_3 and MoO_2 , leading to material loss and failure (Brewer and Lamoreaux, 1980).

To address the limitations of both MoSi_2 and molybdenum alloys, surface modification of molybdenum alloys to produce an oxidation resistant MoSi_2 layer on the surface emerges as a promising solution. The MoSi_2 is expected to provide a uniform protective layer that prevents direct contact between molybdenum and oxygen, significantly enhancing material performance. Among various siliconizing techniques such as the halide-activated pack cementation (Ito et al., 2003; Sakidja et al., 2005; Majumdar, 2012; Sun et al., 2016), slurry sintering (Suzuki et al., 2000; Cai et al., 2017; Li et al., 2018), spark plasma sintering (Reisel et al., 2001; Nomura et al., 2003; Zhu et al.,

2019; Sun et al., 2019), and chemical vapor deposition (Cox and Brown, 1964, Rice and Sarma, 1981, Govindarajan et al., 2002, Yoon et al., 2002), the hot dipping method emerges as the most practical way to produce MoSi₂ due to its short treatment time, simple and straightforward procedure, and applicability to large and complex shapes (Gamutan and Miki, 2022).

Table 1 shows the various molten bath compositions used to siliconize molybdenum and its alloys using the hot dipping method. Zhang et al. (2021) used pure molten silicon at elevated temperatures (1480°C to 1560°C) to create a multi-layered surface of Si, MoSi₂, Mo₅Si₃, and Mo₃Si. Meanwhile, Christian and Narita (1998) employed molten In-Si bath under vacuum at 1000-1200°C to achieve an MoSi₂ layer with a thin Mo₅Si₃ interlayer. Due to its lower melting temperature, silicon-containing molten aluminium baths were also used at dipping temperatures of 700°C to 1000°C to form Mo(Si,Al)₂ layers (Sharifitabar et al., 2021; Nanko et al., 2001; Yanagihara et al., 1994). However, the use of these molten metal baths is limited due to the high dipping temperatures required and the cost of silicon and aluminium. Additionally, In-Si melts involve the use of indium, a very rare and highly volatile element. Therefore, for practical applications, a readily available, inexpensive, and low-melting silicon-containing bath is desired.

Table 1. Molten bath composition and the growth rate of different hot dipping methods to siliconize molybdenum and its alloys.

Molten Bath Composition	Temperature (°C)	Growth Rate (µm/h)	Reference
Si bath	1480-1560	120	(Fu et al., 2024; Zhang et al., 2021)
In-Si bath	1000, 1200	2.8, 7.2	(Christian and Narita, 1998)
Al-12%Si bath	950	33.3	(Sharifitabar et al., 2021)
Al-26%Si bath	700	0.9	(Nanko et al., 2001)
Al-50%Si bath	1000	35.0	(Yanagihara et al., 1994)

This work explores the feasibility of using molten tin (Sn), bismuth (Bi), and copper (Cu) baths with silicon to form oxidation resistant MoSi₂ layers on pure molybdenum substrates. Commonly used in food packaging and soldering applications, molten tin and bismuth baths are excellent candidates due to their low melting points ($T_{m,Sn} = 232^{\circ}\text{C}$ and $T_{m,Bi} = 271^{\circ}\text{C}$) and relatively low cost and abundance. Moreover, according to the Sn-Si (Olesinski and Abbaschian, 1984) and Bi-Si (Olesinski and Abbaschian, 1985) binary phase diagrams, the solubilities of silicon in tin and bismuth are almost negligible, suggesting that when molybdenum is immersed into silicon-containing molten tin or bismuth bath, molybdenum should readily react with silicon to form MoSi₂. While copper has a relatively high melting point ($T_{m,Cu} = 1085^{\circ}\text{C}$), its thermodynamic relationship with silicon (Okamoto, 2012) and molybdenum (Subramanian and Laughlin, 1990) is similar to that of tin and bismuth, making it another potential candidate for this application.

The key aspect of this work involves investigating the composition, growth, and oxidation resistance of the MoSi₂ layers formed on pure molybdenum substrates using silicon-containing tin, bismuth, and copper baths. This technique has the potential to overcome the challenges of existing siliconizing methods and develop more efficient and cost-effective MoSi₂ coatings.

EXPERIMENTAL METHOD

Sample Preparation and Hot Dipping

Figure 1 shows a schematic diagram of the experimental set-up employed in this work. Molybdenum sheets (99.95% Mo) cut into 1×10×50 mm plates were used as the substrates for hot dipping in silicon-containing tin (98.8% Sn – 1.2% Si), bismuth (98.0% Bi – 2.0% Si), and copper (73.5% Cu – 26.5% Si) baths. The bath compositions were selected such that it fell within the two-phase region of the Sn-Si, Bi-Si, and Cu-Si systems, where the thermodynamic activity of silicon remains close to unity.

Prior to dipping, the Mo-plates were polished with silicon carbide paper and ultrasonically cleaned in ethanol. Then, the samples were positioned in the top-most portion of the furnace using a molybdenum wire (\varnothing 2mm). The same wire was used to push the samples down into the bath once the target temperature of 1000°C was achieved and stabilized. Immersion times were varied at 15, 30, and 60 minutes while the atmosphere was kept inert in argon (400 ml/min). After dipping, the Mo-substrates were pulled back to the top-most portion of the furnace and allowed to cool down to room temperature.

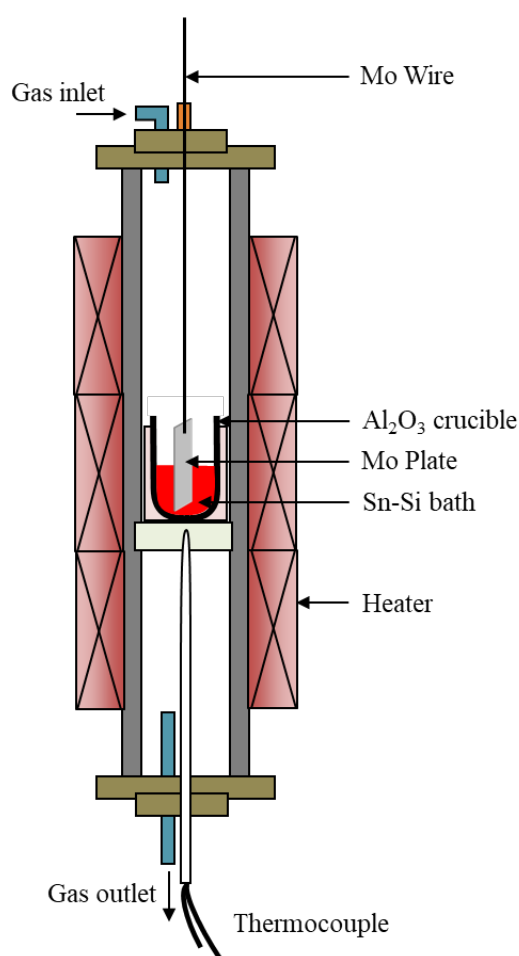


Figure 1. Schematic diagram of the experimental set-up.

Characterization of Samples

To characterize phase composition of the hot dipped samples, X-ray diffraction (XRD) technique with Cu-K α radiation at a 5° min⁻¹ scanning speed from 20° to 80° was employed. The raw XRD data were then analysed and indexed using Rigaku PDXL software. Meanwhile, Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) was used to investigate the morphology and composition of the sample cross-sections. Samples for SEM-EDS were prepared by mounting in a resin, polishing using silicon carbide paper, and a final ultrasonic cleaning step in ethanol.

Finally, to assess the oxidation resistance of the formed MoSi₂-layer, isothermal oxidation tests of fully coated and uncoated samples at 1150°C for 2 hours in air were conducted. Prior to testing, sample edges were protected with a SiO₂ ceramic paste. The change in weight of the samples before and after the oxidation tests were also measured to estimate the extent of oxidation reactions.

RESULTS AND DISCUSSION

Phase Composition and Growth

Sn-Si Bath (98.8% Sn – 1.2% Si)

The x-ray diffraction patterns of the bulk Mo-substrate samples before and after siliconizing in a molten Sn-Si bath for 15 and 60 minutes at 1000°C are shown in **Figure 2**. While the peaks of molybdenum remain, the formation of new MoSi₂ peaks with a strong preferred orientation on the (103) crystal face was observed after dipping for 15 and 60 minutes. It was found that with longer immersion times, the intensity of MoSi₂ relative to molybdenum increased. These results suggest the successful formation and growth of the formed MoSi₂ layer on the surface of the Mo-substrate by hot dipping at 1000°C in a silicon-containing tin bath. Peaks of tin were also detected in samples after hot dipping, suggesting incomplete removal of the residual material during cleaning, or penetration of the MoSi₂ layer by molten tin (Gamutan and Miki, 2022).

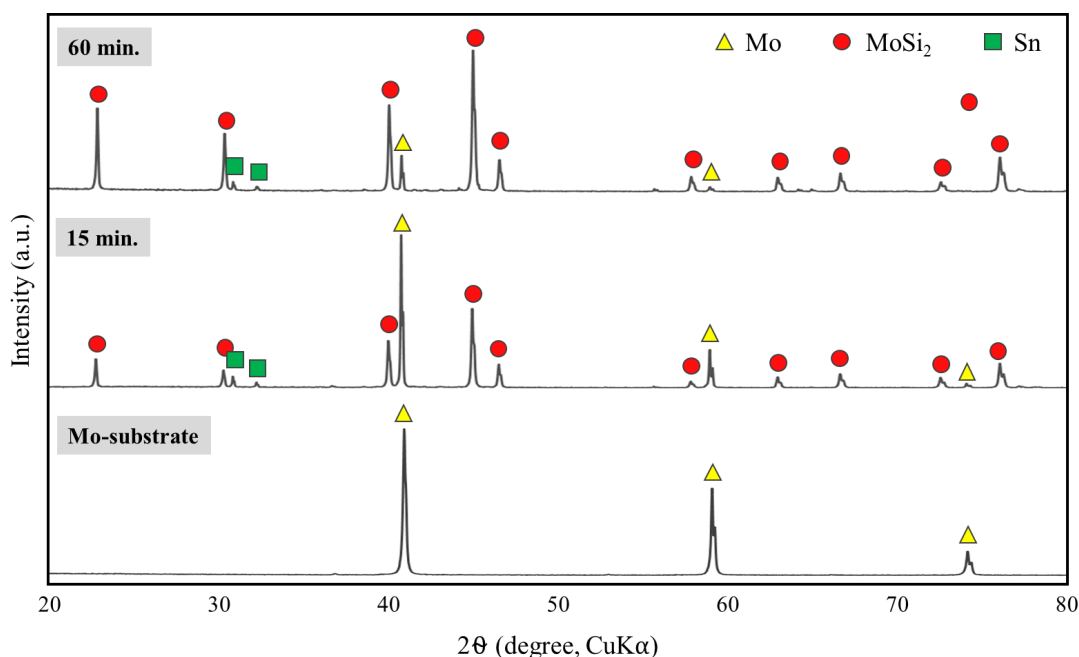


Figure 2. XRD patterns of the bulk Mo-substrate before after hot dipping in a Sn-Si bath for 15 and 60 minutes at 1000°C.

SEM micrograph and EDS investigation of the sample cross-sections after dipping for 15 and 60 minutes are shown in **Figure 3**. The black-coloured area in the micrographs corresponds to the carbon resin used to mount the samples, while the grey-coloured area corresponds to the sample cross section. EDS mapping of the sample cross section suggests the formation of a dense layer containing molybdenum and silicon approximately 10-20 μm thick on the surface of the Mo-substrate. Point analysis indicate that the Mo:Si atomic ratio of the formed layer is approximately 1:2, confirming the formation of MoSi₂. EDS results also reveal about 0.5% Sn in the formed MoSi₂ layer, confirming that appearance of the peaks of tin observed via XRD was due to the uptake of molten tin by the MoSi₂ layer.

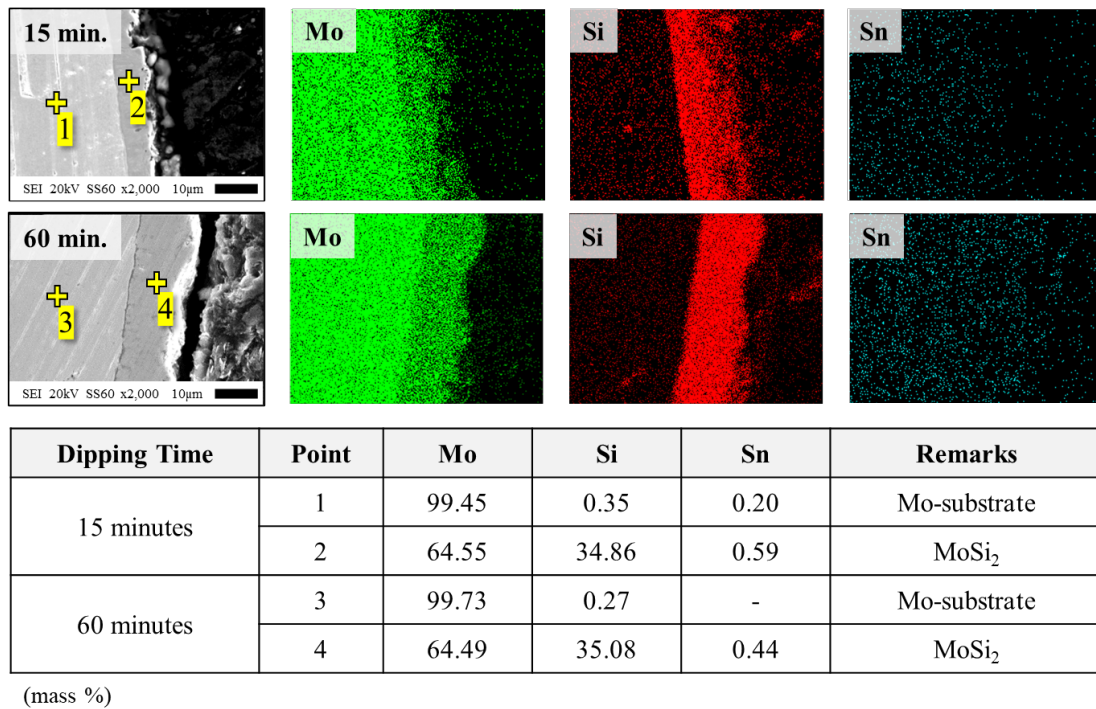


Figure 3. Cross-section micrographs and EDS analysis of the siliconized molybdenum samples after hot dipping in Sn-Si bath at 1000°C for 15 and 60 minutes.

Bi-Si Bath (98.0% Bi – 2.0% Si)

Figure 4 shows the XRD patterns of the samples before and after dipping in a silicon-containing molten bismuth bath at 1000°C for 15 and 60 minutes. While the peaks of molybdenum remain, new peaks of Mo₅Si₃ and MoSi₂ were observed after hot dipping for 15 and 60 minutes. As dipping time increased, the intensities of Mo₅Si₃ and MoSi₂ peaks relative to the molybdenum peak increased, confirming the successful formation and growth of Mo₅Si₃ and MoSi₂ layers on the molybdenum surface through hot dipping at 1000°C in a molten Bi-Si bath.

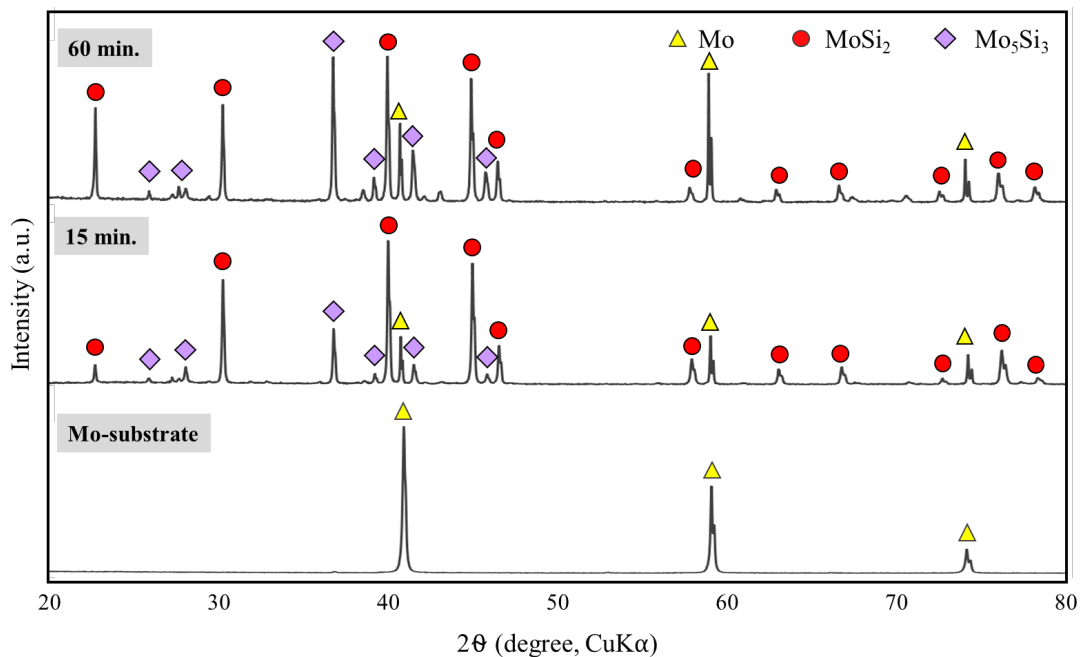


Figure 4. XRD patterns of the bulk Mo-substrate before after hot dipping in a Bi-Si bath for 15 and 60 minutes at 1000°C.

Figure 5 shows the cross-section micrographs and EDS analysis results of the siliconized molybdenum samples after hot dipping in Bi-Si bath at 1000°C for 15 and 60 minutes. Similar with the results when using a Sn-Si bath, SEM-EDS results suggest the formation of about 12- μm thick layer, which contains both molybdenum and silicon, on the surface of the Mo-substrate. Point analysis of the layer reveals a Mo:Si atomic ratio of 1:2, confirming the formation of MoSi_2 . However, the presence of other silicide compounds of molybdenum, such as Mo_5Si_3 which were determined via XRD, was not detected using SEM-EDS. In contrast, the presence of 0.39% and 3.52% Bi in the formed MoSi_2 layer was measured using EDS point analysis, but peaks of bismuth were not detected via XRD analysis.

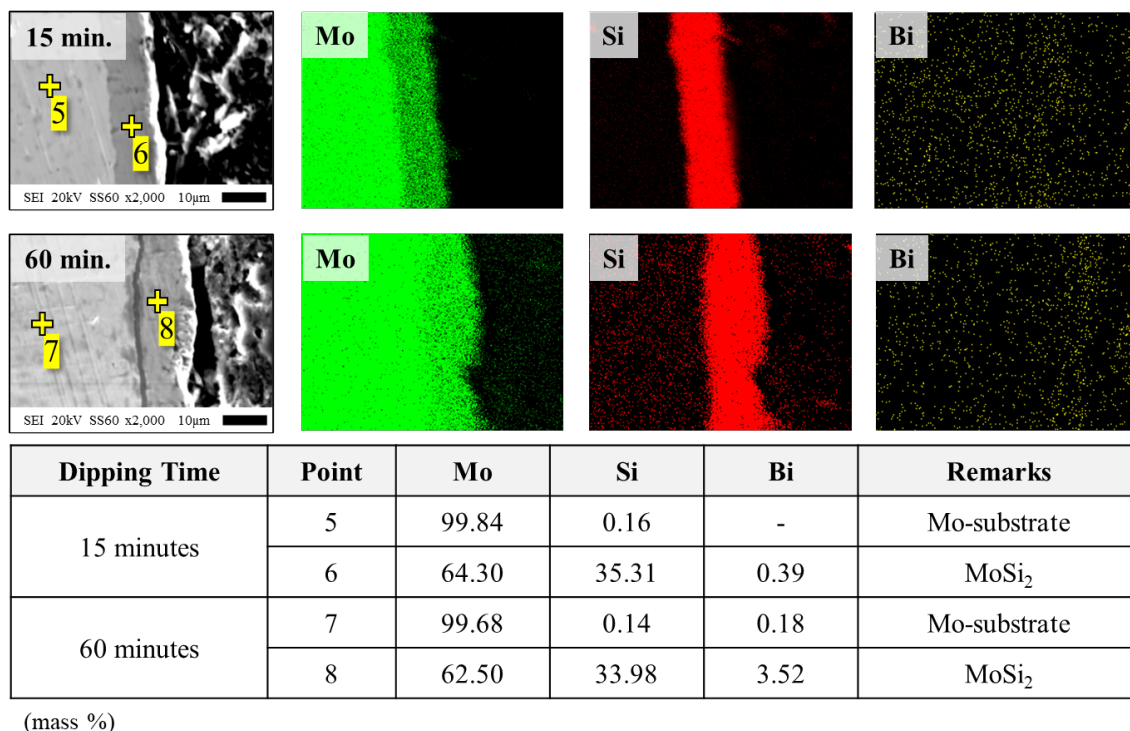


Figure 5. Cross-section micrographs and EDS analysis of the siliconized molybdenum samples after hot dipping in Bi-Si bath at 1000°C for 15 and 60 minutes.

Cu-Si Bath (73.5% Cu – 26.5% Si)

Due to the irregularity in shape and the difficulty in obtaining good measurement results, only the XRD patterns of the sample immersed in molten Cu-Si bath for 15 minutes at 1000°C were obtained in this work, as shown in **Figure 6**. After dipping for 15 minutes, formation of the characteristic peaks of MoSi_2 were found, while the formation of new Cu_3Si peaks were also observed. However, continuous dipping for 60 minutes resulted in the formation of thick, dendrite-like protrusions along the sample edges, impeding true and representative sampling for XRD analysis without breaking off or damaging the surface.

Figure 7 shows the cross-section micrographs and EDS analysis results of the samples after dipping for 15 and 60 minutes. These results confirm the formation of MoSi_2 on the surface of the Mo-substrate, and a new layer composed primarily of copper and silicon. Point analysis of this layer revealed a Cu:Si atomic ratio of approximately 3, confirming the formation of Cu_3Si , which was also identified via XRD analysis. The Cu_3Si layer was found primarily located on the outermost surface of the sample, but it also appeared in between the Mo-substrate and formed MoSi_2 layers, particularly in the sample immersed for 60 minutes.

The formation of other molybdenum silicide compounds was not detected using either XRD or SEM-EDS analysis, but the presence of about 4-5% Cu in the formed MoSi_2 layer was identified using EDS point analysis. While we cannot draw definitive conclusions without XRD data for longer dipping

times, the extremely rapid growth of the MoSi₂ layer when using molten Cu-Si bath and the substantial concentration of copper within the layer suggest that penetration of copper caused significant expansion of the MoSi₂ lattice, facilitating the faster diffusion of silicon towards the unreacted Mo-substrate (Gamutan and Miki, 2022).

The thickness of the formed MoSi₂ layers after dipping for 15 and 60 minutes, measured at 268 μm and 441 μm, respectively, showed a tenfold increase in growth rate when using molten Cu-Si bath compared to samples immersed in molten Sn-Si and Bi-Si baths.

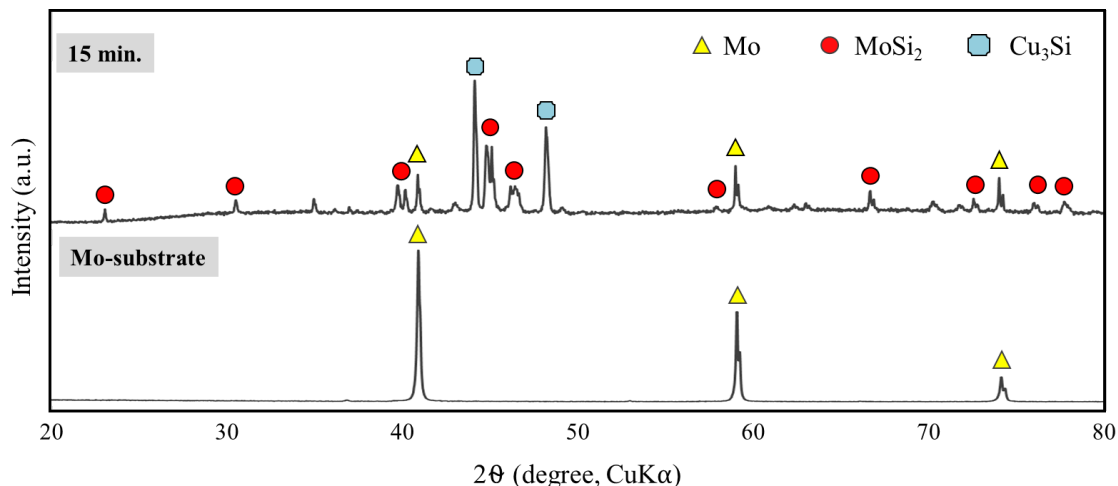
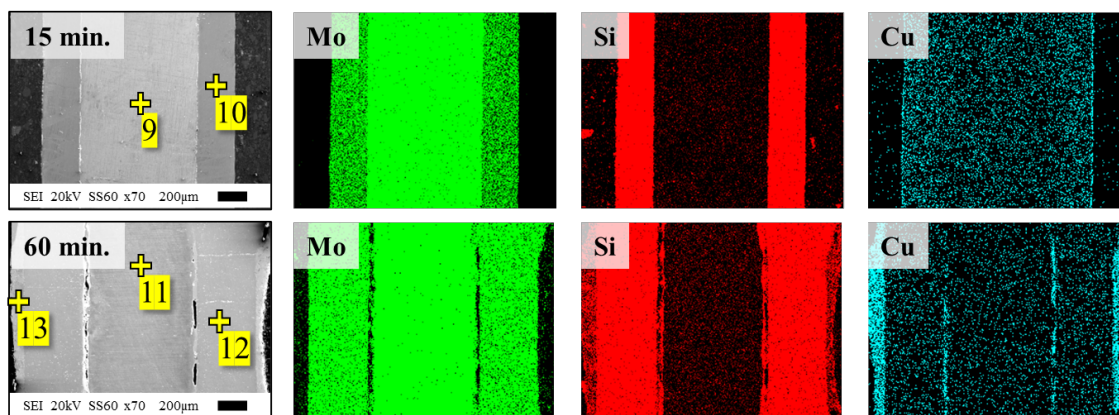


Figure 6. XRD patterns of the bulk Mo-substrate before after hot dipping in a Cu-Si bath for 15 minutes at 1000°C.



Dipping Time	Point	Mo	Si	Cu	Remarks
15 minutes	9	99.42	0.57	0.02	Mo-substrate
	10	60.28	34.47	5.25	MoSi ₂
60 minutes	11	99.40	0.28	0.32	Mo-substrate
	12	61.15	34.74	4.11	MoSi ₂
	13	0.25	12.78	86.97	Cu ₃ Si

(mass %)

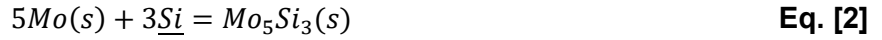
Figure 7. Cross-section micrographs and EDS analysis of the siliconized molybdenum samples after hot dipping in Cu-Si bath at 1000°C for 15 and 60 minutes.

Mechanism and Kinetics of MoSi₂ Formation

The above-mentioned findings indicate that the formation of MoSi₂ at the surface of the Mo-substrate was possible by dipping molybdenum in various silicon-containing tin (98.8% Sn – 1.2% Si), bismuth (98.0% Bi – 2.0% Si), and copper (73.5% Cu – 26.5% Si) baths. The concentration of silicon in these baths were designed such that the thermodynamic activity of silicon in this melt was close to unity, and molybdenum reacts with silicon in the bath according to the following reaction:



Meanwhile, the formation of intermediate compounds of molybdenum and silicon, such as Mo₅Si₃, also suggest the occurrence of following reaction:



The measured thickness of the MoSi₂ layer formed by hot dipping in various silicon-containing molten baths is shown in **Figure 8(a)**. The thickness was an average of six measurements made at different positions in the sample. It was found that the MoSi₂ layers grew with dipping time and growth was fastest when using molten Cu-Si bath, followed by molten Sn-Si and Bi-Si baths.

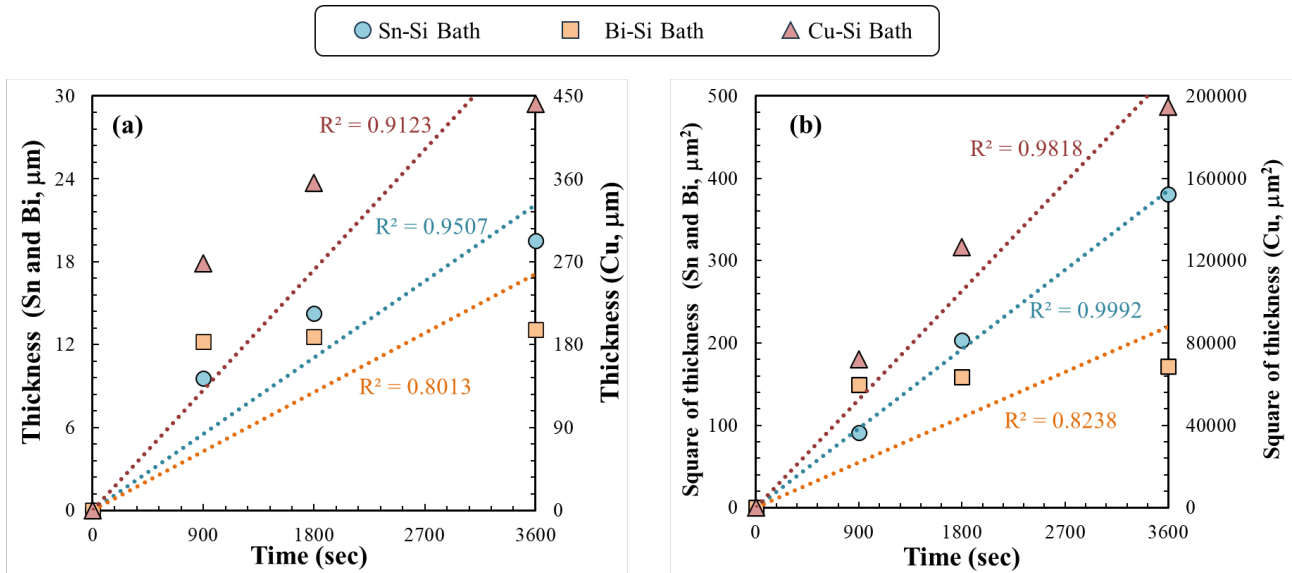


Figure 8. Growth of MoSi₂ layer thickness as a function of time according to (a) reaction-controlled growth mechanism and (b) diffusion-controlled growth mechanism.

To determine whether the growth of the MoSi₂ layer was controlled either by the reaction at the Mo-substrate interface or by diffusion through the formed MoSi₂ product layer, variation in thickness versus time was plotted as follows. For a reaction-controlled growth, it is known that MoSi₂ layer thickness should increase linearly with time according to the following equation:

$$y = kt \quad \text{Eq. [3]}$$

where y is the MoSi₂ layer thickness (μm) at a certain dipping time t (sec). For a diffusion-controlled growth, the thickness should increase parabolically with time according to the following equation:

$$y^2 = kt \quad \text{Eq. [4]}$$

Plotting the measured MoSi₂ layer thickness from this study revealed through linear regression that R² values were closer to unity for the parabolic growth rate model, as shown in **Figure 8(b)**. This suggests that siliconization of the Mo-substrate via the hot dipping method was primarily a diffusion-controlled process. This is particularly true for samples immersed in molten Sn-Si and Cu-Si bath, with very high R² values of 0.9992 and 0.9818, respectively. Consequently, promoting diffusion of silicon through the formed MoSi₂ layer could potentially improve growth, which aligns with the findings above, particularly in the case of silicon-containing copper bath.

However, attempts to apply both reaction and diffusion-controlled growth models to samples dipped in a molten Bi-Si bath did not achieve very strong linear relationships. In fact, the thickness of the formed MoSi_2 layer barely increased. These results imply that another factor influenced the growth kinetics of the MoSi_2 layer. Based on our observations, the formation and presence of the intermediate phase, Mo_5Si_3 , might be the rate-limiting step. Further investigation is required to solidify this conclusion.

To summarize, the mechanism of growth of the MoSi_2 layer on the surface of Mo-substrate can be schematically described as shown in **Figure 9**. When pure molybdenum is dipped into the silicon-containing bath, silicon initially diffuses through the molten bath, as shown in **Figure 9(a)**, until it comes into contact with the molybdenum surface. Due to the elevated temperature conditions employed in the hot dipping experiment, diffusion of silicon through the molten bath is assumed to be fast enough such that its influence on the kinetics of growth could be neglected.

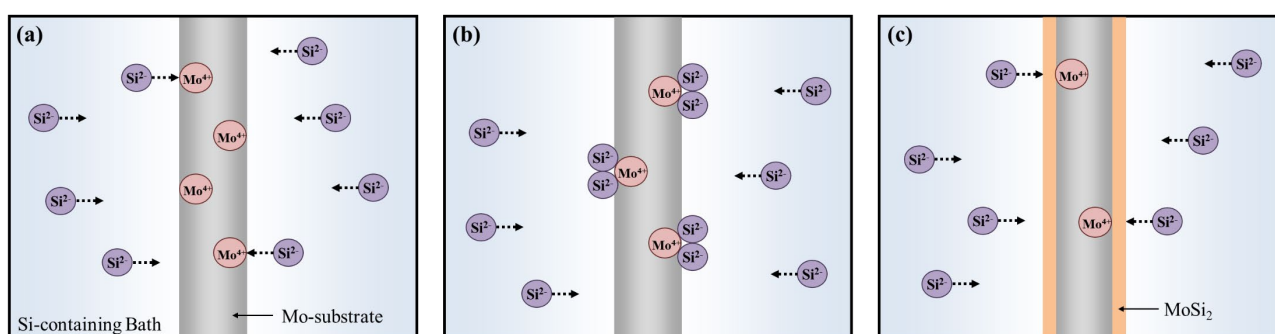


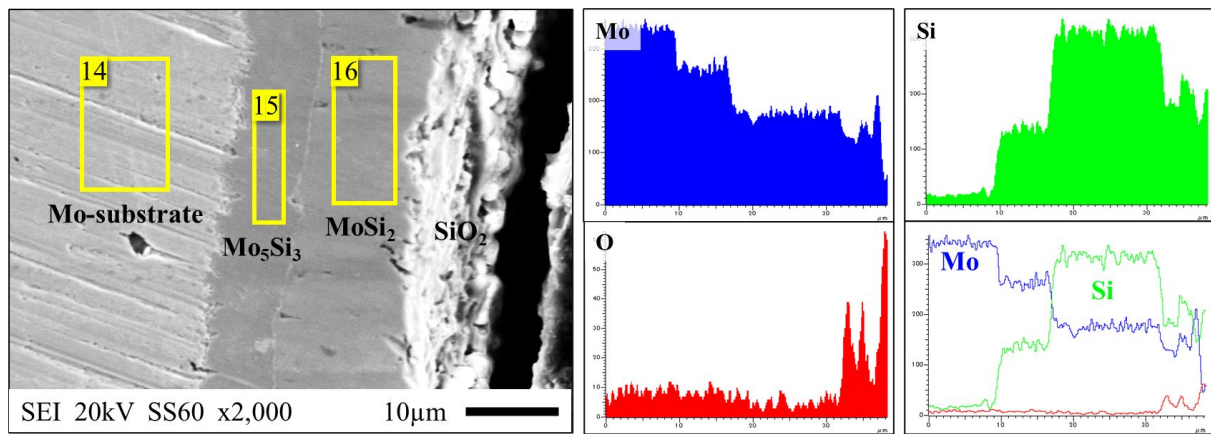
Figure 9. Proposed mechanism of MoSi_2 formation via the hot dipping method.

Next, once the silicon, with thermodynamic activity close to unity, comes into contact with molybdenum, both elements react together according to **Equation [1]** to produce MoSi_2 as shown in **Figure 9(b)**. Potentially, **Equation [2]** also occurs to form Mo_5Si_3 , particularly when using molten Bi-Si bath, due to low silicon concentrations within the interface. Eventually, the MoSi_2 layer grows and thickens, forming a product layer, which substantially slows down the rate at which silicon reaches the unreacted molybdenum surface, as shown in **Figure 9(c)**.

Oxidation Resistance Behaviour

Fully coated samples produced via hot dipping in molten Sn-Si bath at 1000°C for 60 minutes were subjected to oxidation test carried out at 1150°C for 2 hours in air. While the bare uncoated molybdenum sample was completely oxidized and lost in the form of gaseous molybdenum oxides, the fully coated samples suffered a mass loss of about 4% only. These results suggest that formation of a MoSi_2 layer on the surface of molybdenum imparts oxidation resistance at elevated temperatures, a promising solution to address the challenges to both MoSi_2 and molybdenum alloys.

Figure 11 shows the cross-section micrograph and EDS analysis results of the siliconized molybdenum samples after the oxidation test. As evident from the micrograph, the density of the MoSi_2 layer did not change significantly, and the oxidized surface consisted of three layers – an outer SiO_2 layer followed by the MoSi_2 layer and a thin intermediate layer on top of the Mo-substrate. Area analysis of this intermediate layer showed a Mo:Si atomic ratio of about 5:3, indicating that the main phase composition of this layer is Mo_5Si_3 . Line scan also supports the formation of these three layers, revealing a clear change in molybdenum and silicon concentrations. To determine the exact oxidation resistance mechanism of the MoSi_2 layer, further tests with higher temperatures, longer holding times, and enhanced sensitivity is necessary.



Area Analysis	Si	Mo	Sn	Remarks
14	-	99.78	0.22	Mo-substrate
15	14.30	85.69	0.01	Mo ₅ Si ₃
16	35.41	64.59	-	MoSi ₂

(mass %)

Figure 10. Cross-section micrograph and EDS analysis of the siliconized molybdenum samples after the oxidation test at 1150°C for 2 hours in air.

CONCLUSIONS

The present work demonstrates the feasibility of a novel hot dipping method to produce a protective MoSi₂ layers on pure Mo-substrate using silicon-containing tin (98.8% Sn – 1.2% Si), bismuth (98.0% Bi – 2.0% Si), and copper (73.5% Cu – 26.5% Si) baths. This simple and straightforward method enabled the formation of a dense MoSi₂ layer after hot dipping at 1000°C for 15-60 minutes with thickness of about 10-20 μm, 12-μm, and 268-441 μm, respectively. The silicon-containing molten copper bath allowed MoSi₂ to be synthesized most rapidly, followed by tin and bismuth.

Siliconization of the Mo-substrate using Sn-Si and Cu-Si baths was found to be mainly a diffusion-controlled process. Meanwhile, other factors, such as the formation of an intermediate Mo₅Si₃ layer, were found to be potentially rate-limiting when using a Bi-Si bath. Finally, oxidation test of the fully coated samples confirms the potential of MoSi₂ to protect molybdenum and its alloys from rapid oxidation loss at elevated temperatures.

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