journal

J. Am. Ceram. Soc., **80** [7] 1723–26 (1997)

Formation Kinetics of $MoSi_2$ and Mo_5Si_3 by the Reactive Diffusive Siliciding of Molybdenum

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The formation kinetics of products formed by the reaction between dense molybdenum and vapor-supplied silicon at an activity approximating that of solid silicon under open flowing gas conditions was studied at 1200°C. An outer $MoSi_2$ layer overlaid the much thinner Mo_5Si_3 that formed on the molybdenum. Both phases obeyed parabolic growth laws over a 22 h period, having parabolic rate constants of 6.8×10^{-10} cm^2/s for the $MoSi_2$ and 1.3×10^{-13} cm^2/s for the Mo_5Si_3 phases. These results were }2 orders of magnitude less than prior results, mostly obtained by another processing route. Possible explanations include enhanced growth rates from chemical contamination. Gross distortion and abnormal layer thicknesses at specimen edges and the 159% volume increase during siliciding suggest that the kinetics also are strain dependent.

I. Introduction

The siliciding of molybdenum via silicon-vapor transport has been used in the past to produce the disilicide in bulk form as well as to impart an oxidation-resistant coating on the metal. In the usual, older, “pack process,” the siliciding of molybdenum has been done in a closed container. The metal is embedded in a mixture of inert particulates and silicon granules and a halide or halogen to produce a volatile silicon-containing species for shuttling silicon to the metal. Alternatively, as in this study, a flowing homogeneous mixture of gaseous $SiCl_4$ or $SiHCl_3$ and hydrogen gas is used to supply silicon vapor to the metal. By controlling the gas composition, the mixture can be made sufficiently reducing to deposit solid silicon. Under such a condition, the thermodynamic activity of the silicon should closely approximate that in the closed pack process. The kinetics for growth of the silicide layer has been studied by various investigators, mostly under closed pack process conditions. The outer layer that grows in contact with the vapor-supplied silicon is $MoSi_2$. In all the studies but one,[1] a relatively thin layer of Mo_5Si_3 has been observed to separate the disilicide from the unreacted metal, but the least silicon-rich $MoSi_3$ phase has not been detected to occur under growth conditions. Prior studies have concluded that the kinetics for the formation of $MoSi_2$ obey a parabolic growth law. However, kinetic behavior for Mo_5Si_3 is less certain,[2] especially during early stages of growth. It has been established[1,3] that silicon transport dominates the growth processes.

Its oxidation resistance, refractoriness, and attractive high-temperature thermomechanical properties have initiated interest in $MoSi_2$ for high-temperature structural applications.[4–7] In a prior study in our laboratory, siliciding of *porous* compacts of molybdenum under open flowing conditions at 1200°C has been investigated as a route for producing oxide-free $MoSi_2$[8–10] by exposure to a controlled reducing mixture of dry $SiCl_4$ and hydrogen gases.

The present paper reports on a parallel study at 1200°C for the siliciding of *dense* molybdenum metal under identical open flowing gas conditions that includes determination of the kinetics for the growth of $MoSi_2$ and Mo_5Si_3 layers. As given in detail below, we find that, under these conditions, the kinetics for the formation of $MoSi_2$ differ markedly both from those previously reported for the siliciding of dense molybdenum[1,11] via closed pack processing and those found with porous compacts[10,12] via open flowing gas conditions. The growth kinetics found at short times for the very thin Mo_5Si_3 layer also are at variance with those previously reported.[2,14]

When the flux of the reactant species is limited by transport across chemical reaction barriers, the reaction product thickness grows linearly with time; if the flux is diffusion-controlled, the thickness increases proportionally to the square root of the reaction time. The growth data can be analyzed to elucidate which mechanism(s) is operating. The kinetics of the process in which several reaction products grow in tandem have been modeled both analytically[15] and by a finite-element computer code[16] that shows the geometric progress of the advancing layers for various-shaped porous compacts.

II. Experimental Procedure

Solid molybdenum metal was available as 2.5 mm thick “archival” material of unknown initial source. Analysis by SEM and X-ray fluorescence found only an extremely faint suggestion of iron. The metal was cut into 6 mm × 6 mm coupons weighing ~0.9 g each. In addition, for purposes of verifying that present processing conditions were unchanged from those of our previous study, a few compacts were made by compressing molybdenum powder following the procedure used in that study.[9]

The siliciding was done in a cylindrical, graphite-lined furnace at 1200° ± 5°C such as used in our previous study. A flowing mixture of $SiCl_4$ and hydrogen gases was supplied at a pressure ratio of 1:13 at a total pressure of 2 torr (270 Pa). The samples were held in a molybdenum-wire basket suspended in the furnace. The procedure has been given in detail elsewhere.[9] Silicon-metal deposited on the walls of the furnace, showing that the effective vapor pressure of silicon in the gas mixture exceeded that over pure, solid silicon.

Ten runs were made with exposure times ranging from 0.5 h, which is the shortest practicable time, to 22 h. The reaction layer thicknesses were determined gravimetrically, and by direct optical microscope and SEM image measurements. The weight increase of the exposed coupons was measured to a nominal accuracy of 0.01 mg. Special care was used in the polishing and etching of the coupons to avoid producing artifacts that might introduce ambiguities in the optical and SEM images used to determine the thicknesses of the $MoSi_2$ and Mo_5Si_3 layers. The identity of the silicide phases was verified by elemental analysis in the SEM.

The layer thicknesses for $MoSi_2$ were determined by three independent means: (a) calculation using the known density of $MoSi_2$, weight gain, and measured surface area of the coupon;

N. Jacobson—contributing editor

Manuscript No. 191778. Received April 1, 1996; approved December 19, 1996.
Supported by the National Science Foundation under Grant No. DMR-9417499.

*Member, American Ceramic Society.

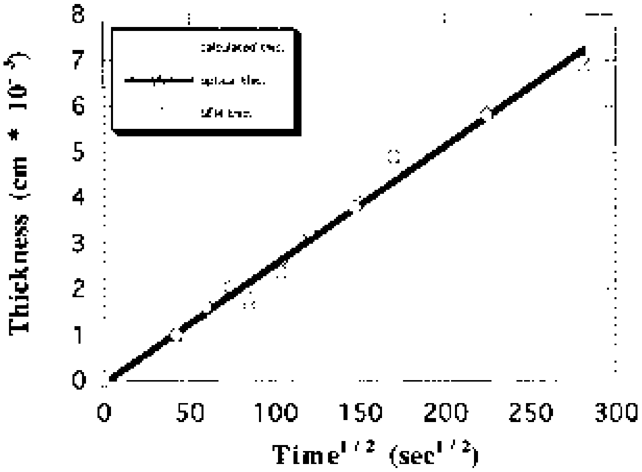

Fig. 1. Plot of $MoSi_2$ layer thickness as determined by three independent methods versus the square root of time.

(b) optical microscopy at 500× using a micrometer eyepiece; and (c) measurements on micrographs from SEM at ~1000×. The values from (b) and (c) are averages of measurements taken at five or more different locations. Determination of the Mo_5Si_3 layer thickness required procedure (c) at 20 000×.

III. Experimental Results

(1) Dense Molybdenum Coupons

The thickness measurements from the above three methods for $MoSi_2$ are given as a function of time in Fig. 1. The good agreement between the thickness values calculated from the weight gains and the direct measurements made by optical microscopy and SEM indicates freedom from spalling. Figure 2(A) is a representative micrograph of the silicide layers, in this case after 14 h of exposure to the silicon vapor. Silicon-metal did not deposit on the siliciding coupons for exposure times shorter than 22 h. This failure of elemental silicon to deposit indicates that, at these shorter times, the silicon-gas supersaturation is insufficient to nucleate the silicon on the $MoSi_2$ surface. A very thin layer of Mo_5Si_3 is shown in Fig. 2(A) to separate the metal from the $MoSi_2$ phase. Figure 2(B) is a magnified view showing more clearly the Mo_5Si_3 layer that has formed after 3 h of exposure to the vapor. Table I shows that, at all exposure times, the Mo_5Si_3 layer remains <2% of the thickness of the $MoSi_2$ layer.

Table I. Comparison of the Thicknesses of the Mo_5Si_3 and the $MoSi_2$ Layers as a Function of Siliciding Time at 1200°C

Time (h)	Thickness (μm)	
	$MoSi_2$	Mo_5Si_3
0.5	11	0.22
1	16	0.31
1.5	19	0.40
2	20	0.38
3	26	0.34
4	32	0.44
6	40	0.58
8	50	0.85
14	59	0.86
22	69	1.00

(2) Direct Comparison of Porous Molybdenum against Dense Molybdenum

A porous compact made from molybdenum powder and a coupon of dense molybdenum were placed side-by-side and exposed to the same siliciding procedure for 8 h as in the above experiments. The thickness of the layer in the dense molybdenum was 49.0 ± 0.7 μm, whereas it was 254.8 ± 1.5 μm in the porous molybdenum. This result was in excellent agreement with 251 μm, the value found in this laboratory in the prior systematic study[9] of the siliciding of porous molybdenum. Thus, this experiment demonstrated unambiguously that dense molybdenum silicided a factor of 5 more slowly than porous molybdenum and that the conditions for siliciding of dense molybdenum were unchanged from our previous study using porous molybdenum.

IV. Analysis of the Growth Kinetics

Transport of the reacting species silicon from the gas phase through the reaction products to the unreacted molybdenum base material is expected to control the growth kinetics of the solid reaction product(s). The relevant factors are the activity gradient[17] in the reaction product that drives the diffusion flux and the activity differences needed to transport silicon across the interphase boundaries. The growth laws that derive from these factors for the case where several phases are growing in tandem, such as Mo_5Si_3 phase preceding $MoSi_2$, have been presented elsewhere.[15,18] For each growing phase, a law of the form

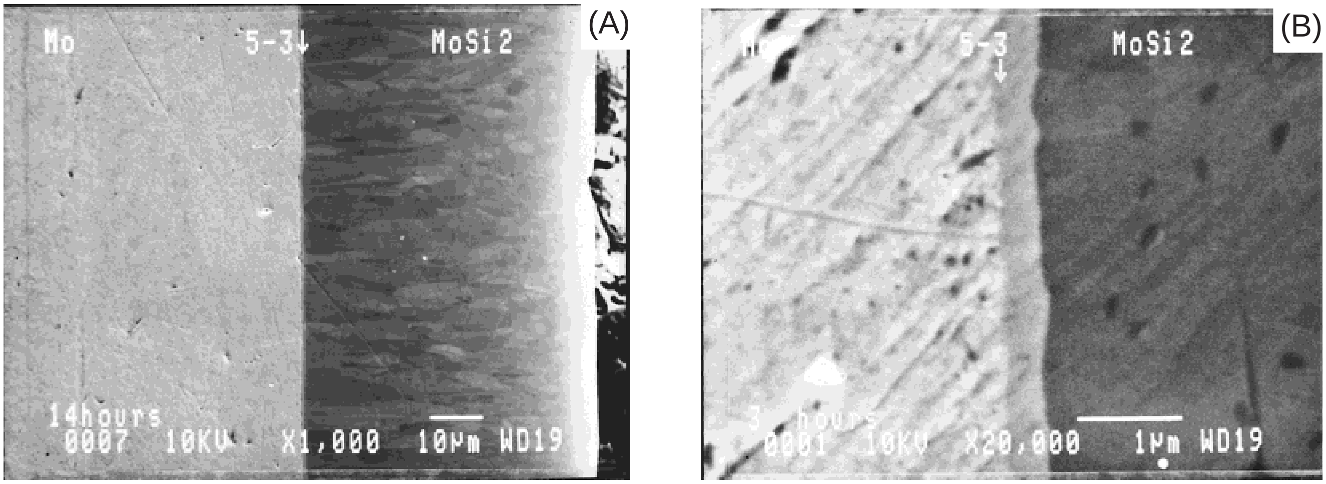

Fig. 2. (A) SEM image of the silicide layers formed upon 14 h exposure to silicon vapor. Note that the very thin layer of Mo_5Si_3 separates the metal (left) from the $MoSi_2$ phase (right). (B) SEM image similar to (A) of silicide layers formed upon 3 h of exposure. The thinner Mo_5Si_3 layer separates the molybdenum metal from the $MoSi_2$.

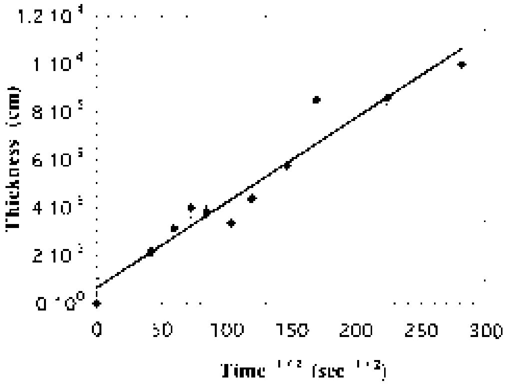

Fig. 3. Plot of Mo_5Si_3 layer thickness versus the square root of time.

$$t = \frac{x}{k_1} + \frac{x^2}{k_2} \tag{1}$$

is expected, where t is the reaction time, x the layer thickness at time t, and k_1 and k_2 the rate constants specific to those phases that reflect the reaction barrier and the diffusive terms, respectively. In the present work, the number of time intervals and the range of times, 0.5–22 h, over which the reaction was measured, were much more extensive than reported in prior studies.

The present data were subjected to linear regression analyses to find the best fits for k_1 and k_2 as well as to test the validity of the assumed transport model discussed above. Equation (1) can be linearized with respect to x by dividing through by x. The data also were analyzed in terms of an empirical power law of the form $x = kt^n$, or alternatively,

$$\log x = \log k + n \log t \tag{2}$$

Diffusion-controlled growth without interface barriers was expected to yield $n = 1/2$, providing that the diffusion coefficient remained substantially constant.

Figure 1 shows an apparent linear relation between the thickness of the $MoSi_2$ layer and $t^{1/2}$. This suggests a simple diffusion-controlled growth behavior. A linear-regression analysis based on Eq. (1) gives $1/k_1 = (1.5 \pm 3.5) \times 10^5$ s/cm^2 and $1/k_2 = (1.4 \pm 0.1) \times 10^9$ s/cm^2 or $k_2 = (6.8 \pm 0.5) \times 10^{-10}$ cm^2/s. The indicated uncertainties represent the root-mean-square error. Thus, the $1/k_1$ term is statistically indistinguishable from zero, so that, within the given uncertainty, there is no evidence for a kinetic growth barrier. When the $MoSi_2$ data are modeled by Eq. (2), a linear-regression analysis gives $n = 0.529 \pm 0.016$.

When the experimental thicknesses of the Mo_5Si_3 layer are plotted against $t^{1/2}$, as shown in Fig. 3, the curve again appears to be linear, but, because of the greater scatter, the data have been modeled by $x = c_0 + c_1 t^{1/2}$ for use in a linear-regression analysis to obtain the best fits to c_0 and c_1. A nonzero value for c_0 indicates a nonparabolic contribution to the kinetics. The analysis gives $c_0 = 0.06 \pm 0.05$ μm, which is nearly indistinguishable from zero, and $c_1 = (3.6 \pm 0.3) \times 10^{-7}$ cm/s$^{1/2}$, which translates to $k_2 = (1.3 \pm 0.2) \times 10^{-13}$ cm^2/s. When the data are analyzed in the form of Eq. (2), the linear-regression analysis yields $n = 0.405 \pm 0.044$ as the best fit for the exponent.

The above analyses of the data for $MoSi_2$ indicate diffusion-controlled, parabolic growth without a chemical kinetic barrier. The growth kinetics for the Mo_5Si_3 layer appear probably to be diffusion controlled. Our confidence in this conclusion is tempered by the facts that the value of c_0 hinted at a deviation from pure parabolic behavior, as did the deviation of n by more than 2 standard errors from the theoretical value of 1/2.

V. Comparison of Present and Prior Results for $MoSi_2$ and Mo_5Si_3 Growth

The processes and conditions used by prior investigators are compared with those used in the present study in Tables II and III. Both pack and CVD methods of siliciding have been used. The siliciding studies on porous molybdenum by Ramakrishnan[9] and the present ones on dense molybdenum used CVD processes under identical conditions, as verified experimentally. The rate constant in the present work for the conversion of dense molybdenum to $MoSi_2$ at 1200°C is only 0.023 of that found for porous molybdenum. Furthermore, the side-by-side processing of porous and dense molybdenum clearly demonstrates that the latter converts much more slowly under flowing-gas conditions. Whereas the rate constants found by Gage and Bartlett[1] on dense molybdenum differ substantially from ours, they are in good agreement with the result obtained using porous molybdenum.

The prior kinetic data on the growth of the Mo_5Si_3 phase are compared with the present data in Table III. The present results give a growth-rate constant that is substantially smaller than those reported in previous investigations. This discrepancy lies well outside of the uncertainty in the present measurements.

VI. Discussion and Conclusions

It is unclear as to why $MoSi_2$ forms at such a greater rate in porous molybdenum than we find using dense molybdenum, or why our results using dense molybdenum differ so much from the prior ones. We also find a large difference between the prior and the present kinetic constants for the growth of the Mo_5Si_3 layer. We find no evidence for a reaction barrier. This argues against a chemical growth poisoning that could slow down the growth rate. Except for the work by Fitzer and Matthias,[3] who used a nonflowing mixture of hydrogen and $SiHCl_3$ gases to silicide dense molybdenum, all other reported siliciding studies

Table II. Experimental Results for $MoSi_2$ at 1200°C

Investigator	Process	Form	Growth constant (cm^2/s)
Gage and Bartlett[1]	Pack	Dense	$3.5 \times 10^{-8\dagger}$
Fitzer and Matthias[3]	Gas/closed	Dense	$4.5 \times 10^{-8\dagger}$
Maas and Rieck[11]	Pack	Dense	3.7×10^{-9}
Ramakrishnan[9]	Gas/open	Porous	2.9×10^{-8}
Present work	Gas/open	Dense	6.8×10^{-10}

†Signifies a value calculated from a reported temperature dependence.

Table III. Experimental Results for Mo_5Si_3 at 1200°C

Investigator	Process	Form	Growth constant (cm^2/s)
Perkins[14]		Dense (?)	1.7×10^{-11}
Bartlett *et al.*[13]	Pack	Dense	2.2×10^{-11}
Fitzer and Matthias[3]	Gas/closed	Dense	5.9×10^{-11}
Present work	Gas/open	Dense	$(1.3 \pm 0.2) \times 10^{-13}$

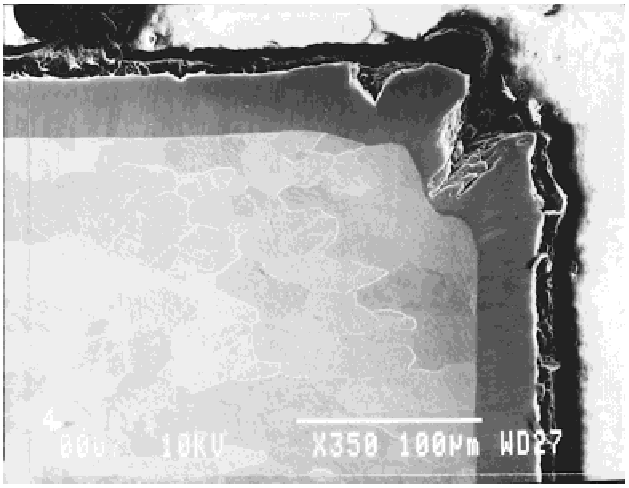

Fig. 4. SEM image of end region of a specimen silicided for 4 h.

use the closed pack process. Fitzer and Matthias provide no details of their experiments, but they report the greatest rate constants for the growth of both the $MoSi_2$ and Mo_5Si_3 layers. Their values are in the range of those reported by others using the pack process.

The most obvious differences between the pack process and those used in the present work are in the gas conditions. Our study used flowing, dry, tank gases; $SiCl_4$ vapor; and samples having a small surface area. Nominally, this system is oxygen- and water-free. By way of a possible explanation, we offer the following conjecture.

In the pack process, there is opportunity for adsorbed water or other contaminant species to remain confined in the closed gas environment. The use of powdered molybdenum as the starting material also may increase the likelihood for contamination. Thus, during siliciding, contaminant species may be introduced that affect the density or structure of grain boundaries or the lattice defect structure in the silicide phases which, in turn, could enhance grain boundary or lattice transport of silicon.

There has been a study[11] that shows that substrate orientation has some effect on the crystallographic texture and a modest effect on the growth kinetics of $MoSi_2$. We have found no indication of a preferred orientation texture in the dense molybdenum. However, a columnar texture, directed normal to the growing layer, is evident in the $MoSi_2$ phase with grain-boundary spacings of the order of 2–7 μm, as shown in Fig. 2(A).

Finally, we note the occurrence of distortion of the $MoSi_2$ layer near the corners of the molybdenum coupons, as shown in Fig. 4. This appears to be plastic deformation needed to accommodate the large volumetric increase that accompanies the siliciding of molybdenum. In this region, the Mo_5Si_3 layer is appreciably thinner than elsewhere. Anomalous layer geometry and relative thicknesses of $MoSi_2$ and Mo_5Si_3 phases suggestive of large plastic deformation also have been observed in the corner regions of porous molybdenum coupons.

Investigation of this phenomenon is in progress and will be reported separately. Clearly, more experimental studies are needed to resolve which are the dominant factors that control the growth kinetics in this system.

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