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Document status and date:
Published: 01/01/1982

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Link to publication

Download date: 08. Feb. 2024

Phase relations and diffusion paths in the Mo-Si-C system at 1200 °C

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Presented at the 10th Plansee Seminar, 1-5 June 1981, Reutte, Austria

Abstract. The 1200 °C cross section through the Mo-Si-C phase diagram has been established by analyzing equilibrated ternary alloys and diffusion couples by means of optical, microprobe, and x-ray techniques. The diffusion kinetics in couples of the type Mo/SiC has been investigated. Three phases are formed in the diffusion zone, each exhibiting a clearly distinguishable texture. The total layer thickness is found to grow parabolically with time.

Introduction

The investigation of diffusion couples in binary multiphase systems is a well-known technique for acquiring data for the phase diagrams. The same technique can be used for the determination of isothermal cross sections of the phase diagrams in ternary systems.

Figure 1 shows hypothetical phase diagrams for the A-B-C ternary system. If the phases C and X are in contact at the (high) temperature for which these isothermal cross sections are given, interdiffusion will occur. The phases which can be formed and the morphology of the reaction layers cannot be predicted in this case, unlike the case of binary systems. Several situations are possible, some of which are shown in figures 1a-1e.

By determining all the compositions that occur in the region between the pure phase X and the pure phase C and plotting these values in the composition triangle, the so-called diffusion path can be found (Kirkaldy and Brown 1963). In figure 1 this path is drawn as a full line if the compositions are actually present in the couple, whereas a dashed line denotes a 'concentration gap' in the couple. The latter situation occurs if the diffusion path runs parallel to a tie line as, for example, in the two-phase region X-T in figure 1a. Here, the particular concentration components in X and T are in equilibrium along the whole interface; thus the interface is planar, as found in normal binary diffusion couples.

There are, however, other possibilities. The phases T and Z might develop, for instance, as shown in figure 1b. Here the diffusion path again runs parallel to the tie lines; hence planar interfaces are found in the couple. In figure 1c a diffusion path is shown which again reveals the phases T and Z, but now the path crosses the tie lines in the two-phase fields. This means that at various points at the interface different concentrations are in equilibrium, and that nonstraight (waved or serrated) phase boundaries are found. In figure 1d the diffusion path represents the existence of a zone of precipitates of X in a matrix of T. In figure 1e a diffusion path is shown which crosses the three-phase triangle T-Z-C. In this case the T phase at the boundary is in equilibrium with both Z and C.

It is clear that by determining the boundary concentrations in a number of diffusion couples with different terminal compositions an isothermal cross section may be constructed. This method has been used to investigate diffusion paths and phase relations in a number of metal and oxide systems (Laheij et al 1980a, 1980b;

Loo et al 1978, 1980, 1981). In these investigations the resulting phase diagrams
always agreed with the compositions found in equilibrated alloys. This proves the
measured interface concentrations in these diffusion couples to be real equilibrium
values. Once the phase diagram is established, our aim is to find out why nature
chooses only one particular path out of so many possible diffusion paths. To find an
answer to this fundamental question it seems appropriate to investigate these diffusion
paths in relatively simple ternary systems for which many diffusion and thermo-
dynamic data are already known.

The system Mo-Si-C meets these requirements, and this system is of great
technological interest. In particular the interactions between pyrolytic silicon carbide
coatings and molybdenum substrates are of interest in view of their potential
importance in, for example, fusion reactor technology (see Fukutomi et al 1979) and
the insulation of electrochemical machining (ECM) electrodes (see Verspui 1977,
1979). In the latter case a strong adhesion between coating and substrate is
necessary because of the mechanical straining of the coatings in the final shaping of
the electrodes. The correlation between adhesion and the presence of interaction
layers is quite clear (Verspui 1979): from Auger and x-ray diffraction analyses of
SiC-coated molybdenum it was shown that in well-adhering coatings the phases Mo_5Si_3
and Mo_2C were formed at the interface. We decided therefore to investigate phase
relations and diffusion paths in this system at the deposition temperature of 1200 °C.

The Mo-Si-C system at 1600 °C has previously been investigated thoroughly by
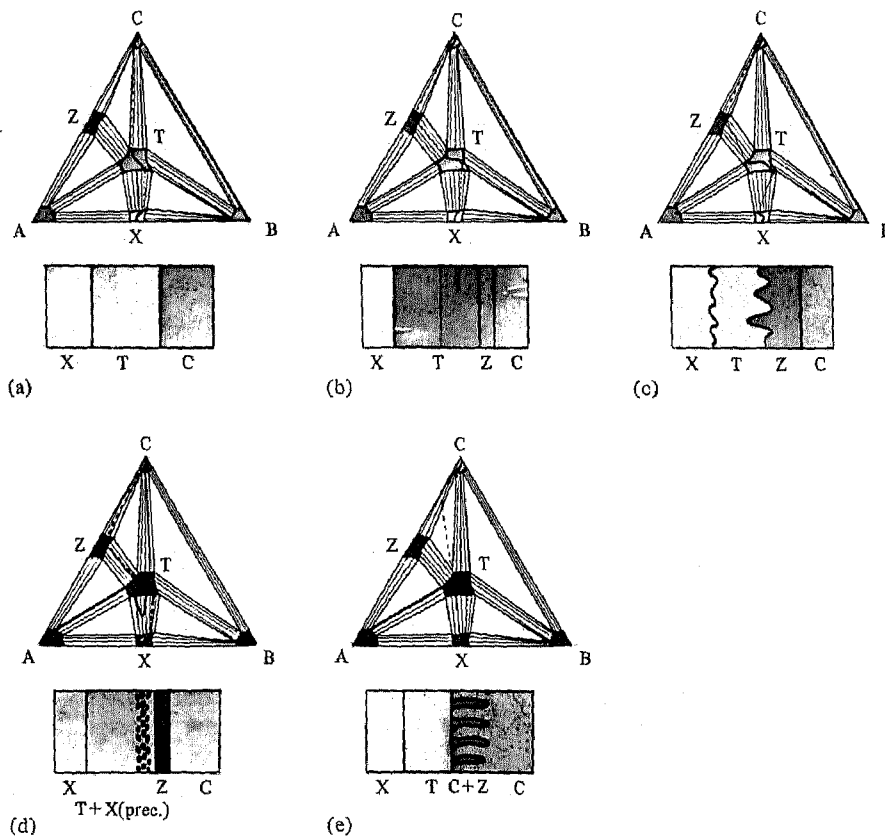Nowotny et al (1954), who published an isothermal cross section through the phase

Figure 1. (a)-(e) Some possible diffusion paths in a C/X couple in a hypothetical A-B-C phase
diagram.

diagram and revealed the existence of a ternary phase Mo_4Si_3C. Steinmetz and Roques (1976) have investigated the siliciding of superficially carburized molybdenum and the diffusion in a coating resulting from such a treatment.

2 Experimental procedure

The starting materials used were molybdenum sheet (99·9 wt%, Halewood), silicon bar (Hoboken), Mo_2C powder (99·8 wt%, MRC), and pyrolytic SiC. Alloys were prepared by repeated argon-arc melting. For the binary Mo-Si alloys, molybdenum and silicon were melted in the appropriate weight ratio; for the ternary compositions binary Mo-Si alloys were melted together with the appropriate amounts of Mo_2C. The alloys were homogenized at 1200 °C for at least 64 h in sealed evacuated silica capsules.

Diffusion couples were made in two ways. First, by resistance welding of mechanically polished slices of the terminal materials in a modified arc furnace. During this process generally a diffusion layer of ~1 μm thickness was formed. For couples of the type Mo/SiC we also have made use of a chemical vapour deposition (CVD) process. β-SiC Coatings up to 30 μm in thickness were applied to molybdenum ribbons in a manner described by Verspui (1977, 1979). During this process a diffusion layer thinner than 1 μm was formed (see figure 2). Before coating the cold-rolled ribbons were recrystallized. They were clearly textured with a strong {100}⟨011⟩ component, while the SiC was grown with a ⟨111⟩ fibre texture perpendicular to the substrate.

After diffusion annealing in evacuated silica capsules, the couples were embedded, ground and polished parallel to the diffusion direction, and etched with an aqueous solution containing 100 g $K_3Fe(CN)_6$ and 100 g KOH per litre. The etched surface was examined microscopically and the couple was subjected to microprobe analysis (Jeol Superprobe). Concentrations were determined by use of the Colby Magic 3B program. Since carbon was determined indirectly as the remaining element after counting $MoL\alpha$ and $SiK\alpha$ pulses, the measurements had to be performed very precisely because of the low weight fraction of carbon in most phases.

For x-ray diffraction analyses of the diffusion layers, the couples were ground and polished perpendicular to the diffusion direction. In a number of cases cylindrical camera photographs and texture goniometer analyses have been made.
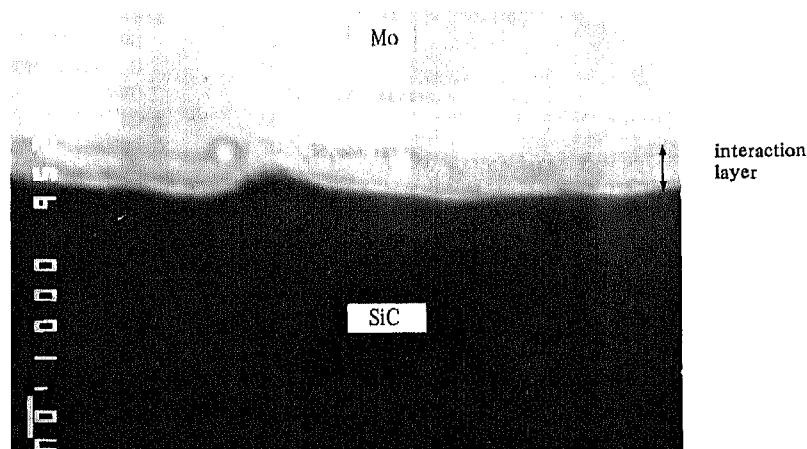

Figure 2. A backscattered electron image of a molybdenum substrate, coated with 28 μm SiC by CVD at 1200 °C. The length of the small vertical bar at bottom left denotes 1 μm.

3 Results

From the current investigation we will present here the results of the analyses of
three ternary alloys and of diffusion couples of the type Mo/SiC. Table 1 gives the
compositions of the phases present in the ternary alloys, together with some x-ray
diffraction data. Figure 3 is a microphotograph of the diffusion layer in an Mo/SiC
couple annealed for 96 h at 1200 °C. The total thickness of this reaction layer, d,
obeys the parabolic growth law, as shown in figure 4. The growth constant, $k = d^2/t$,
is $3 \cdot 7 \times 10^{-11}$ cm^2 s^{-1}. The layer morphology and thickness were the same for
couples made both by resistance welding and by CVD.

The reaction layer consists of a thin layer of a ternary compound of composition
Mo_5Si_3C and of a thick layer with two interwoven phases, Mo_5Si_3 and Mo_2C. A
clearly distinguishable texture develops in each layer. The Mo_5Si_3C layer was too
thin to provide very accurate x-ray results, but it is likely that a $\langle 001 \rangle$ fibre texture
oriented in the diffusion direction exists in this layer. In the Mo_5Si_3 layer the small
grains also revealed a strong $\langle 001 \rangle$ fibre texture. The Mo_2C layer was microscopically
fine-grained (see figure 3), but according to x-ray analysis it seemed to be coarse-
grained with an up to now unidentified non-rotationally symmetric texture, probably

Table 1. Phases present in some ternary alloys formed at 1200 °C. Compositions of the alloys are
given in at%.

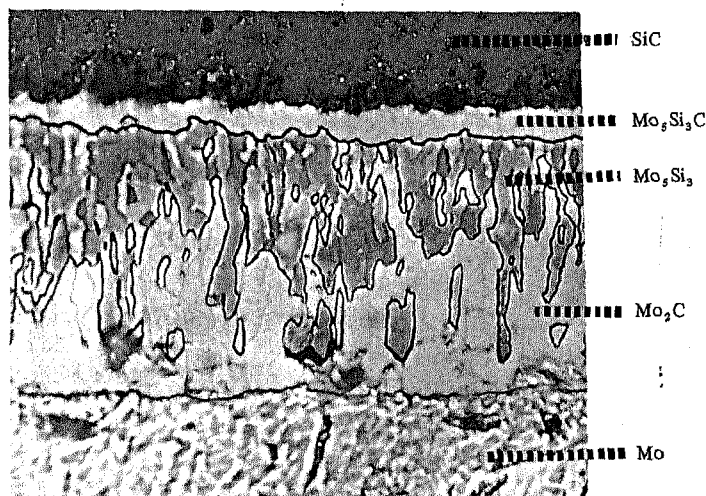| Ternary alloy	Phases	Crystal type	Lattice parameters/Å
$Mo_{46 \cdot 5}Si_{40}C_{13 \cdot 5}$	SiC		
	Mo_5Si_3	tetragonal	$a = 9 \cdot 645 \pm 0 \cdot 005$; $b = 4 \cdot 912 \pm 0 \cdot 005$
	Mo_5Si_3C	hexagonal	$a = 7 \cdot 295 \pm 0 \cdot 010$; $c = 5 \cdot 04 \pm 0 \cdot 01$
$Mo_{54}Si_{20}C_{26}$	C		
	Mo_5Si_3C	hexagonal	$a = 7 \cdot 282 \pm 0 \cdot 005$; $c = 5 \cdot 054 \pm 0 \cdot 005$
	Mo_2C	hexagonal	$a = 3 \cdot 008 \pm 0 \cdot 001$; $c = 4 \cdot 736 \pm 0 \cdot 002$
$Mo_{73}Si_{13}C_{14}$	Mo		
	Mo_3Si	cubic	$a = 4 \cdot 890 \pm 0 \cdot 001$
	Mo_2C	hexagonal	$a = 3 \cdot 009 \pm 0 \cdot 001$; $c = 4 \cdot 734 \pm 0 \cdot 002$

Figure 3. Diffusion layer in an Mo/SiC couple prepared by CVD, annealed for 96 h at 1200 °C.
Total diffusion layer thickness 36 μm.

related to the {100}⟨011⟩ texture component in the coarse-grained molybdenum substrate. Table 2 lists x-ray diffraction results for an Mo/SiC couple annealed for 48 h at 1200 °C, taken from a section parallel to the substrate surface immediately below the SiC coating. From a comparison with texture-free materials it follows that in the Mo_5Si_3 and Mo_5Si_3C phases in the diffusion layer only those planes which make angles of <35° with the c axis come to reflection.

x-Ray diffractograms of SiC-coated molybdenum after short annealing times (0, 1, 4, and 12 h at 1200 °C) only revealed the existence of Mo_5Si_3 and Mo_2C; thus the Mo_5Si_3C layer is either very thin or absent at this stage of the process.
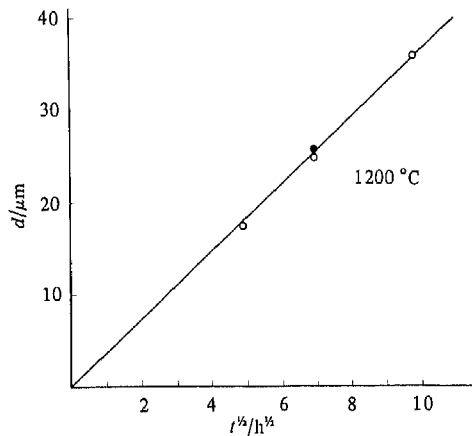

Figure 4. Total layer thickness in Mo/SiC couples versus the square root of annealing time at 1200 °C. The black circle refers to a couple prepared by resistance welding, open circles to couples prepared by CVD.

Table 2. Intensities, I, of reflections from Mo_5Si_3 and Mo_5Si_3C in diffractograms from texture-free (TF) compounds, and from the diffusion layer (DL) in an Mo/SiC couple prepared by CVD and annealed for 48 h at 1200 °C, immediately below the SiC coating.

Mo_5Si_3 $(a = 9\cdot647$ Å; $c = 4\cdot909$ Å$)^a$				Mo_5Si_3C $(a = 7\cdot303$ Å; $c = 5\cdot057$ Å$)^b$			
Reflection plane	Angle with (001)/°	I(TF) (ASTM 17-415)	I(DL)	Reflection plane	Angle with (001)/°	I(TF) (ASTM 8-429)	I(DL)
211	48·7	20		110	90	10	
310	90	20		200	90	40	
002	0	10	100	111	54·2	50	
400	90	10		002	0	30	100
112	19·8	60	20	210	90	70	
202	27·0	20	20	102	21·8	50	~50
420	90	60		211	64·7	100	
411	64·5	50		300	90	70	
222	35·7	100	10	112	34·7	80	~10
213	17·0	<2	5	400	90	10	
620	90	10		113	24·8	10	
512	52·4	10		222	54·2	50	
323	31·4	10	5	320	90	10	
631	73·7	10		312	55·2	30	
532	56·0	10		321	74·0	40	
413	35·0	20	2	213	35·2	40	
602	56·8	20		410	90	40	
004	0	<2	80	402	58·0	50	
642	61·4	10		004	0	30	~10

^{a} Tetragonal; ^{b} hexagonal.

4 Evaluation of results

In figure 5 a cross section through the Mo–Si–C phase diagram at 1200 °C is given. It differs from that given by Nowotny et al (1954) for the system at 1600 °C in that it shows that the Mo_5Si_3 phase can coexist with SiC. In the 1600 °C cross section this is not the case and the $MoSi_2$ phase is claimed to coexist with the ternary compound 'T'. The results of Steinmetz and Roques (1976) seem to be inconsistent in this respect: they claim that $MoSi_2$ is in equilibrium with T at 1250 °C in $MoSi_2/Mo_2C$ couples, whereas at the same temperature in couples ($MoSi_2$-50 mol% SiC)/Mo they claim that the phases Mo_5Si_3 and SiC are coexistent.

The composition of the ternary compound T, we have found a much smaller homogeneity range than that found at 1600 °C by Nowotny et al (1954): the silicon content was certainly less than that corresponding to the previously used formula, Mo_4Si_3C (see, for example, Goldschmidt 1967; Nowotny et al 1954). Our values of the lattice parameters for T agreed with those given by Nowotny et al for the composition poorest in silicon, which corresponds closely to the formula Mo_5Si_3C found in our work.

The diffusion path for the couple Mo/SiC is also plotted in figure 5. The thinness of the Mo_5Si_3C layer suggests that carbon is withdrawn easily from this compound by molybdenum; this leads to the formation of Mo_2C and Mo_5Si_3.

The interwoven character of the ($Mo_5Si_3 + Mo_2C$) layer might be seen either as a typically ternary diffusion phenomenon as shown in figure 1c, or as a consequence of the pronounced texture in the Mo_5Si_3 phase. In the latter conception, crystals in which the c axis is oriented parallel to the diffusion direction are assumed to grow faster than others (Maas and Rieck 1978) and cause the serrated interface. However, we found the same texture in the Mo_5Si_3 layer present in $Mo/MoSi_2$ diffusion couples, although the layer is bounded by planar interfaces (Steinmetz and Roques 1976). We therefore believe that the serrated Mo_5Si_3/Mo_2C interface is governed by ternary diffusion kinetics and can possibly be explained if volume diffusion of carbon
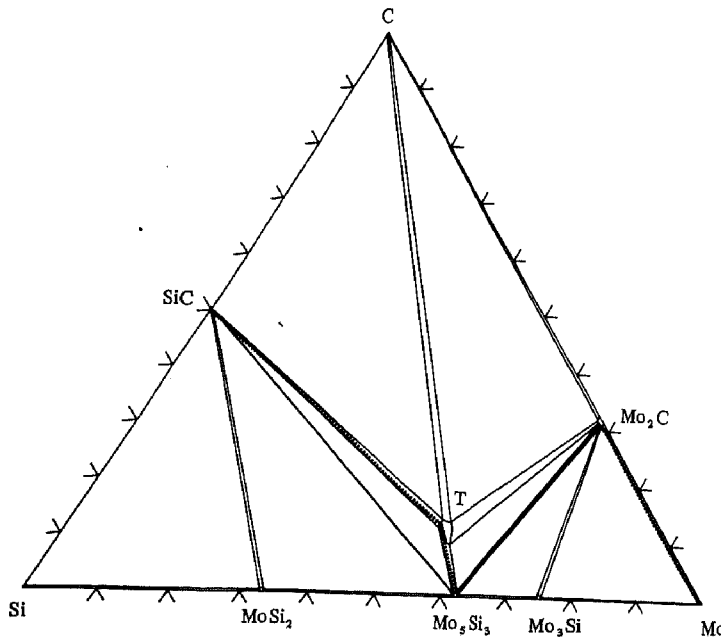

Figure 5. The 1200 °C cross section through the phase diagram Mo–Si–C. The diffusion path for the couple Mo/SiC is given by the thick lines (dashed and solid).

through the Mo_5Si_3 layer is taken as the rate-determining step. If this is the case, each accidental perturbation in the Mo_5Si_3/Mo_2C interface will be enlarged, since the reaction to Mo_2C will proceed more rapidly at those points where carbon has to travel the shortest distance through Mo_5Si_3; this will lead finally to a completely interwoven morphology. The same result would be observed if carbon diffuses along grain boundaries in the Mo_5Si_3 phase towards the molybdenum substrate, as suggested by Steinmetz and Roques (1976).

In future experiments we will investigate other types of couples, possibly at various temperatures, in order to obtain greater insight into the kinetics of this process.

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