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Diffusional Analysis of a Multiphase Oxide Scale Formed on a Mo-Mo_3Si-Mo_5SiB_2 Alloy

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Diffusional analyses were performed to understand the oxidation at 1300 °C of a multiphase Mo-13.2Si-13.2B (at.%) alloy. During oxidation, a protective glass scale formed with an intermediate layer of (Mo + glass) between the base alloy and external glass scale. Compositional profiles across the (Mo + glass) layer and the external glass scale were determined, and interdiffusion fluxes and effective interdiffusion coefficients for the various components were determined by using "*Multi*DiFlux" software. The motion of the (alloy/Mo + glass) and (Mo + glass/glass) interphase boundaries after passivation was examined. Additionally, vapor-solid diffusion experiments at 1300 °C were carried out with single-phase Mo_3Si and T2 specimens in addition to a multiphase Mo-10Si-10B (at.%) alloy. These specimens were exposed to vacuum to induce silicon loss resulting in the formation of a Mo layer. An average effective interdiffusion coefficient of Si in Mo at 1300 °C was estimated from the Mo_3Si-vapor couple to be in the order of 8×10^{-17} m^2/s.

Keywords Mo_3Si, Mo_5SiB_2, multicomponent diffusion, oxidation

1. Introduction

Alloys in the Mo-Si-B system consisting of a body-centered cubic (bcc)-(Mo) solid solution and the intermetallics phases Mo_3Si and Mo_5SiB_2 (T2) are candidate materials for high-temperature structural applications.[1-7] A balance of toughness, oxidation, and creep resistance of the multiphase, Mo-Mo_3Si-Mo_5SiB_2 (T2), alloys is sought from the mixture of bcc metal and silicide phases. The oxidation at 600 to 1400 °C can be described by the competition between the volatilization of Mo oxide and the formation of borosilicate glass scale from the intermetallic phases.[3,8]

The fracture toughness of the Mo-Mo_3Si-Mo_5SiB_2 (T2) alloys is expected to increase with increasing volume fraction of the metal phase. On the other hand, the oxidation resistance is expected to decrease.[6,7] From a previous study,[2,5] a protective borosilicate glass scale was found to form at 1300 °C for the three-phase Mo-Mo_3Si-T2 alloys if the volume fractions of the Mo_3Si and T2 phases were adjusted so that a Si/B = 1 ratio was maintained. Additionally, a fine dispersion of the three phases can be produced by arc melting compositions near the $L \rightarrow \alpha$(bcc)-T2 eutectic trough[9] such as the Mo-13.2Si-13.2B (at.%) alloy that is shown in Fig. 1.

The main objective of this study is to examine the oxidation layers formed on a Mo-13.2Si-13.2B (at.%) alloy exposed to air at 1300 °C and assess the interdiffusion behavior of the various components from experimental concentration profiles determined in the diffusion zone. The diffusion layers included an external, continuous glass scale, an intermediate (Mo + glass) layer over the base Mo-Si-B alloy. A compositional analysis of these layers as well as a diffusional analysis of the concentration profiles has been carried out with the aid of the "*Multi*DiFlux" program[10,11] developed for the determination of interdiffusion fluxes and interdiffusion coefficients in multicomponent systems. Effective interdiffusion coefficients for the various components determined in the (Mo + glass) layer are reported. In addition, disks of Mo_3Si, Mo_5SiB_2 (T2), and multiphase Mo-10Si-10B (at.%) alloys were exposed to vacuum or flowing argon gas environment for various times at 1300 °C; they were examined for silicon loss and the formation of a Mo layer at the surface. Interdiffusion coefficients of the components in the Mo layer were determined from the compositional information of such vapor-solid couples and are reported in this paper.

2. Diffusion in Multiphase Alloys

The diffusion analysis used in this study is based on the methods developed by Dayananda and his group.[10-17] For isothermal multicomponent, solid-solid and vapor-solid diffusion couples, the interdiffusion flux of each component can be determined directly from the concentration profiles.

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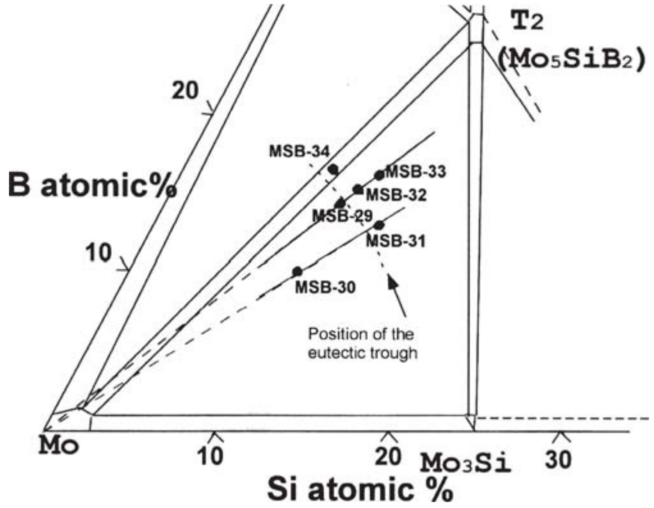

Fig. 1 Schematic of the Mo-T2-Mo_3Si ternary section with the position of the eutectic trough at 1600 °C marked (constructed from data presented in Ref 9). Alloy No. 31 has a Si/B ratio of 1 and lies near the L = (Mo) + T2 eutectic trough.

The interdiffusion flux $\tilde{J}_i(x)$ of component i at anytime t is given by:

$$\tilde{J}_i(x) = \frac{1}{2t}\int_{C_i^+ \text{ or } C_i^-}^{Ci(x)} (x - x_o)\,dC_i \quad (i = 1, 2, \ldots, n) \tag{Eq 1}$$

where C_i^+ and C_i^- are the concentration in the multiphase alloys away from the diffusion zone. The symbol x_o refers to the location of the Matano plane. The use of Eq 1 requires[11-17] that the concentration profiles of the various components be functions of the Boltzmann parameter λ, expressed by $(x - x_o)/\sqrt{t}$. The validity of the Boltzmann parameter requirement has been illustrated for both solid-solid[17] and vapor-solid ternary diffusion couples.[18,19] An integrated interdiffusion coefficient, $\tilde{D}^{\text{int}}_{i,\nabla C}$[12,16] is defined over a concentration ranges $C_i(x_1)$ to $C_i(x_2)$ in the diffusion zone by:

$$\tilde{D}^{\text{int}}_{i,\Delta x} = \int_{x_1}^{x_2} \tilde{J}_i\,dx \qquad (i = 1, 2, \ldots, n) \tag{Eq 2}$$

On the basis of Onsager's formalism[20] of Fick's law for multicomponent diffusion $\tilde{J}_i(x)$ is defined by:

$$\tilde{J}_i(x) = -\sum_{j=1}^{n-1} \tilde{D}^n_{ij} \frac{\partial C_j}{\partial x} \qquad (i = 1, 2, \ldots, n-1) \tag{Eq 3}$$

where $\partial C_j/\partial x$ is the concentration gradient of component j and $\tilde{D}^n_{ij}$ are the $(n - 1)^2$ composition-dependent interdiffusion coefficients. On the basis of Eq 3, Eq 2 becomes:[16]

$$\tilde{D}^{\text{int}}_{i,\Delta x} = \sum_{j=1}^{n-1} \int_{C_j(x_2)}^{C_j(x_1)} \tilde{D}^n_{ij}\,dC_j \tag{Eq 4}$$

An average effective interdiffusion coefficient $\tilde{D}^{\text{eff}}_i$ for the component i over the interval is defined by:[16]

$$\tilde{D}^{\text{eff}}_i = \frac{\tilde{D}^{\text{int}}_{i,\Delta x}}{C_i(x_1) - C_i(x_2)} \tag{Eq 5}$$

3. Experimental

Microstructure and composition profiles were analyzed from a previous set of cast and heat treated (1600 °C, 24 h) Mo-13.2Si-13.2B (at.%) samples that had been cyclically oxidized at 1300 °C in air for 48 h to form a protective borosilicate glass scale. The Mo-13.2Si-13.2B (at.%) alloy (Fig. 1, alloy No. 31) was prepared by arc melting elemental Mo, B, and Si pieces under a partial pressure (70 kPa) of argon as described elsewhere.[2] Disk-shaped specimens having a 12.5 mm diameter with a 7 mm thickness were machined from the arc melted ingot and heat treated in vacuum at 1600 °C for 24 h to coarsen the cast microstructure. Specifically, the heat treatment resulted in the coarsening of the fine binary and ternary eutectic microstructures that resulted upon arc melting. Even after heat treating at 1600 °C, evidence of the solidification microstructure and microsegregation were visible. By areal analysis the volume fractions of Mo, Mo_3Si, and Mo_5SiB_2 were determined to be 28, 27, and 45%, respectively. Cyclic oxidation tests were conducted at 1300 °C in an air-atmosphere tube furnace for 48 h. An initial period of rapid weight loss occurred within the first 6 h, after which a protective glass scale formed and no further weight loss was measured.[2] The thickening of the intermediate layers that formed between the protective glass scale and the bulk Mo-13.2Si-13.2B (at.%) alloy was measured at 1300 °C as a function of time. This was accomplished by sectioning the oxidized specimen (1300 °C, 48 h) and placing half in the furnace at 1300 °C for an additional 48 h. Furthermore, two new disk-shaped specimens of the cast and heat treated (1600 °C, 24 h) Mo-13.2Si-13.2B (at.%) alloy were oxidized at 1300 °C for 12 and 24 h, respectively. The cross sections of all these specimens were viewed using light optical microscopy, and the thickness of the observed interlayer of (Mo + glass) was measured to the nearest 5 μm. Ten measurements at different locations were taken for each specimen.

Vapor-solid desiliconizing experiments were carried out with Mo_3Si, Mo_5SiB_2 (T2), and the multiphase Mo-10Si-10B (at.%) alloys prepared by arc melting. Specimens of Mo_3Si were prepared by arc melting Mo powder with Si pieces together. The Mo_3Si specimens consisted of three phases: Mo_3Si as a matrix, Mo_5Si_3 (T1) as a second phase, and a trace of Mo. The presence of these three phases was confirmed by x-ray diffraction (XRD) techniques. By areal analysis the volume fractions of Mo_3Si and Mo_5Si_3 were determined to be 92.98% and 7.02%, respectively. The volume fraction of Mo was negligibly small and was difficult to determine.

Specimens of Mo_5SiB_2 (T2) were prepared via powder processing method from the starting powder of Mo, Mo_5Si_3, and B. The hot-pressed microstructure consisted of T2 and glass inclusions. A multiphase alloy of composition Mo-

10Si-10B (at.%) was also prepared by arc melting in flowing Ar-5%H_2 gas. The as-cast alloy consisted of Mo, Mo_3Si, and Mo_5SiB_2 (T2) phases.

Disk-shaped specimens were sectioned from the Mo_3Si, Mo_5SiB_2 (T2), and the multiphase Mo-10Si-10B (at.%) alloys using a slow-speed diamond saw. Parallel faces of the alloy disks were ground and polished through 0.05 μm alumina paste. The alloy disks were heated under vacuum until the temperature reached 1000 °C; then, the Ar-5%H_2 gas was let into the furnace. The specimens were held at testing temperatures for a specific period of time. Partial pressure of oxygen in the diffusion furnace was evaluated to be in the ranges of 10^{-16} to 10^{-19} atm at 1300 °C.[21]

After diffusion annealing (desiliconizing treatment), specimens were electroless nickel plated, sectioned, and characterized for diffusion structure and chemical composition by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). Concentration profiles for diffusion study were determined both at Purdue University and at Oak Ridge National Laboratory (ORNL) using electron microprobe analyzers (EPMA) equipped with wave dispersion spectrometers (WDS).

The "*Multi*DiFlux" program[10,11] developed for the analysis of multicomponent diffusion couples was used to calculate average effective interdiffusion coefficients on the basis of Eq 1 to 5. The program fits the raw data obtained by microprobe analysis with cubic hermite interpolation polynomials to generate concentration profiles over each layer. From the fitted concentration profiles, interdiffusion flux profiles were generated by the program; from these profiles, the program calculates the integrated and average effective interdiffusion coefficients for the individual components.

4. Results

4.1 Diffusion Analysis of an Oxidized Sample

Multicomponent diffusion analysis was carried out for an Mo-13.2Si-13.2B (at.%) alloy that had been oxidized at 1300 °C for 48 h to form a protective glass scale. Figure 2 presents the cross section from a disk of the oxidized three-phase Mo-13.2Si-13.2B (at.%) alloy. It reveals an external, protective glass scale and an inner layer consisting of Mo and borosilicate glass (Mo + glass) layer, formed on the base alloy consisting of Mo, Mo_3Si, and T2 phases. For the diffusion analysis, the oxidized alloy was treated as a solid-solid diffusion couple with terminal layers consisting of the base alloy and the passive glass layer sandwiching the intermediate (Mo + glass) layer. While the vapor/solid interface of the passive glass layer is free to communicate with the environment, including the loss of silicon and boron and the intake of oxygen, parabolic growth of the (Mo + glass) inner layer with time can still occur, provided the composition at the moving vapor/glass interface varies negligibly with time. Presented in Fig. 3 are results of the variation in thickness of the intermediate (Mo + glass) layer with the square root of time. While scatter in the data is evident, a linear curve fit of the averaged values resulted in a good fit with a correlation coefficient of $R = 0.98$. This observation suggests that the growth of the (Mo + glass) layer between the base alloy and the external passive glass layer can be treated as a function of the Boltzmann parameter, $(x - x_o)/\sqrt{t}$ and that the concentration profiles on either side of the intermediate (Mo + glass) layer may be considered to vary parabolically with time. In addition, the composition at the external vapor/glass interface is assumed to vary little after the formation of the passive glass layer. On the basis of above observations and assumptions, Eq 1 was used for the determination of interdiffusion fluxes from the concentration profiles of Mo, Si, and B.

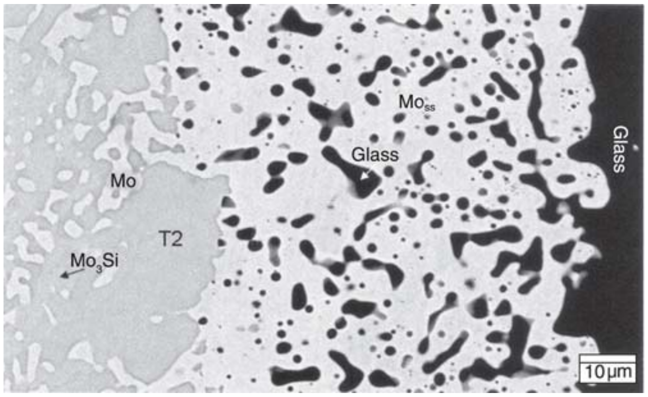

Fig. 2 Back-scattered electron micrograph of Mo-13.2Si-13.2B (at.%) after oxidized at 1300 °C for 48 h showing the three-phase matrix consisting of Mo, Mo_3Si, and Mo_5SiB_2 (T2), an intermediate layer consisting of Mo and glass, and the outer glass scale

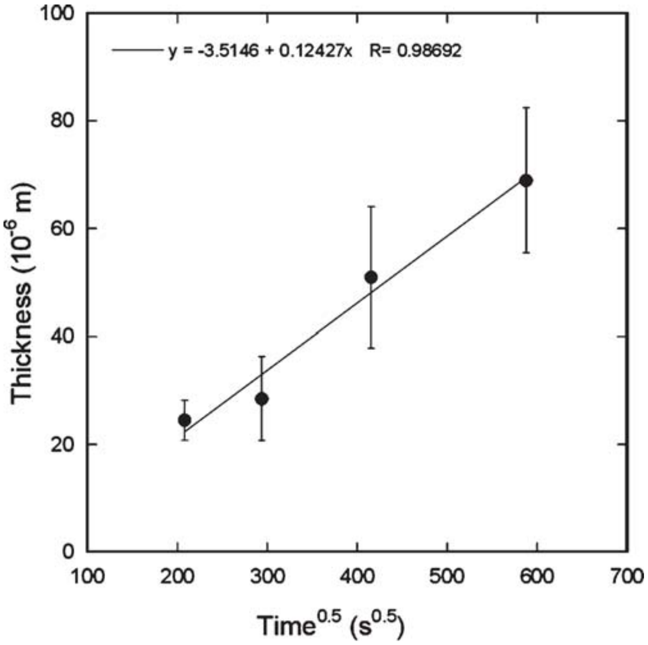

Fig. 3 Variation of the thickness as a function of $\sqrt{t}$ of the intermediate Mo + glass layer in a Mo-13.2Si-13.2B (at.%) alloy that has been oxidized at 1300 °C between 12 and 96 h

Volume fractions of the phases in the base alloy were determined by systematic point count techniques and are

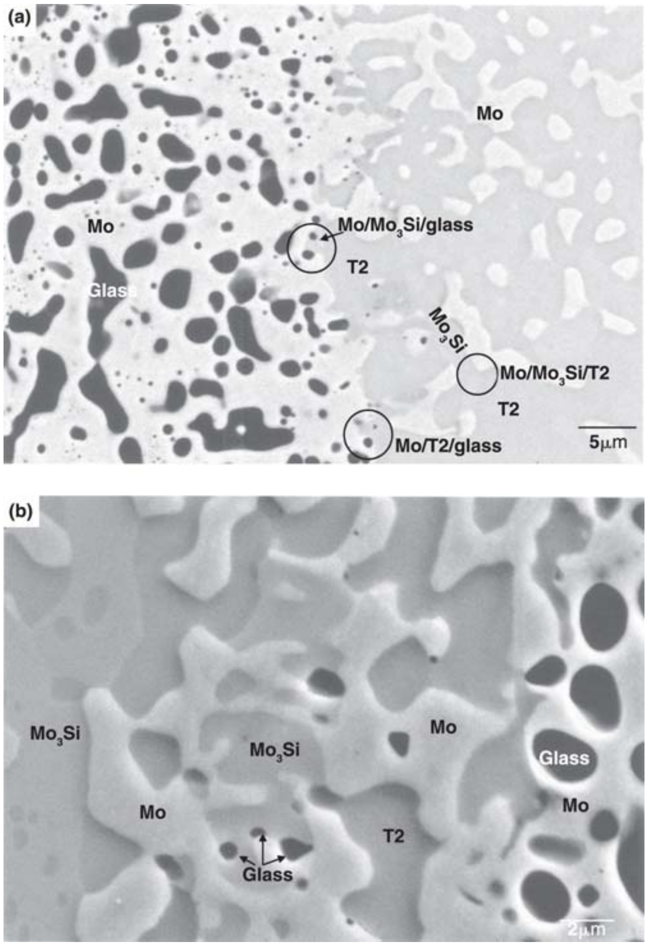

Fig. 4 Backscattered electron micrograph of heat treated Mo-13.2Si-13.2B (at.%) alloy oxidized at 1300 °C for 48 h showing the combination of phases that were in contact. Mo is the brightest phase, Mo_3Si phase shows up as light gray, Mo_5SiB_2 (T2) phase is the darkest phase in the metal matrix, and glass is the darkest/black area and is mostly at a Mo + glass layer or near its interface.

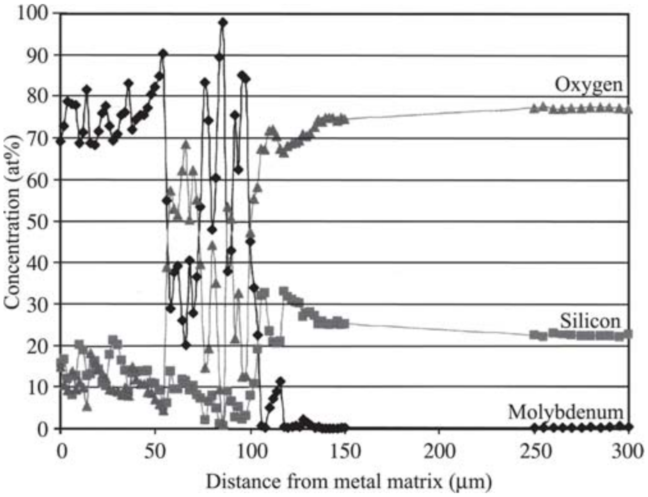

Fig. 5 Concentration profile from EPMA analysis of Mo-13.2Si-13.2B (at.%) alloy oxidized at 1300 °C for 48 h in air atmosphere.

Table 1 Volume fractions of Mo, Mo_3Si, and Mo_5SiB_2 (T2) present in the Mo-13.2Si-13.2B (at.%) alloy after cyclically oxidized in air at 1300 °C for 48 h

Phase	Mo	Mo_3Si	Mo_5SiB_2
Bulk materials	0.28 ± 0.03	0.27 ± 0.03	0.45 ± 0.03
Near alloy/Mo + glass interface	0.29 ± 0.03	0.17 ± 0.02	0.54 ± 0.03

reported in Table 1. Volume fractions of the phases in the alloy adjacent to the (Mo + glass) layer were also determined and reported in Table 1. Volume fraction of the Mo_3Si phase in the base alloy close to the (Mo + glass) layer appears to be lower than that in the bulk, while the opposite is true for the volume fraction of T2, which appears to be larger in the vicinity of the base alloy/(Mo + glass) interphase region. A magnified image of this region is presented in Fig. 4 where the various phases in contact with each other have been identified. The various combinations of two phases or three phases in contact with each other are: Mo/Mo_3Si, Mo/T2, Mo_3Si/T2, Mo/Mo_3Si/T2, Mo/glass, Mo_3Si/glass, T2/glass, Mo/Mo_3Si/glass, and Mo/T2/glass.

A concentration profile determined by microprobe analysis through a trace across the diffusion zone is presented in Fig. 4; here the compositions fluctuate consistent with the phase and its composition during analysis. The compositions of the individual phases were also measured separately in the two-phase (Mo + glass) layer. In addition the volume fractions of the individual phases, Mo and glass, were determined in the (Mo + glass) layer by the point-count technique. Average concentration profiles were then calculated over the (Mo + glass) layer from the data on volume fractions and compositions of Mo and glass phases, and the average concentration profiles were constructed as presented in Fig. 5. The profiles in Fig. 5 formed the basis for calculation of interdiffusion fluxes and effective interdiffusion coefficients for Mo, Si, and O in the (Mo + glass) layer by the *Multi*DiFlux program.

For the purpose of analysis, the (Mo + glass) layer was considered to form after the passive glass layer has initially developed on the base alloy and that the growth of the (Mo + glass) layer is dictated by the interdiffusion of the various components between the terminal base alloy and the passive glass layer. The composition of all glass inclusions within the (Mo + glass) layer was considered to be identical and was based on an average measured composition of Si-8.3B-66.7O (at.%) from EPMA analysis at ORNL. The compositions of Mo solid-solution in the (Mo + glass) layer were measured as Mo-3Si (at.%) from EPMA analysis at Purdue University. Diffusion of Mo in glass was considered negligible.

The effective interdiffusion coefficients calculated for the various components from Fig. 6 are reported in Table 2. The positive and negative numbers listed in Table 2 reflect the flux direction of the species in question with respect to its concentration gradient. A negative number represents uphill diffusion against the concentration gradient.

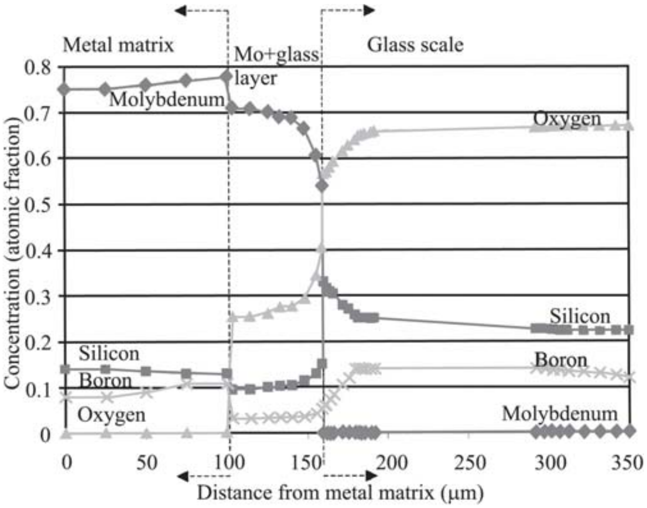

Fig. 6 Concentration profile of Mo-13.2Si-13.2B (at.%) alloy oxidized at 1300 °C for 48 h determined from volume fraction of each phase and EPMA results. The Matano planes of molybdenum, silicon, boron, and oxygen were at 151.8, 155.9, 142.7, and 140.5 μm, respectively.

Table 2 Summary of the effective interdiffusion coefficients of Mo, Si, B, and O calculated utilizing the *Multi*DiFlux program (data from Fig. 6).
The Mo + glass layer was split into two areas for convenience when using the *Multi*DiFlux software.

Analyzed area	Elements	Effective interdiffusion coefficients, m^2/s
Mo + glass layer (0-31 μm)	$\tilde{D}^{eff}_{Mo}$	$+1.7 \times 10^{-19}$
	$\tilde{D}^{eff}_{Si}$	-3.2×10^{-18}
	$\tilde{D}^{eff}_{B}$	-3.9×10^{-19}
	$\tilde{D}^{eff}_{O}$	$+1.7 \times 10^{-18}$
Mo + glass layer (31-60 μm)	$\tilde{D}^{eff}_{Mo}$	$+1.1 \times 10^{-19}$
	$\tilde{D}^{eff}_{Si}$	-4.2×10^{-19}
	$\tilde{D}^{eff}_{B}$	-8.5×10^{-20}
	$\tilde{D}^{eff}_{O}$	$+3.0 \times 10^{-19}$

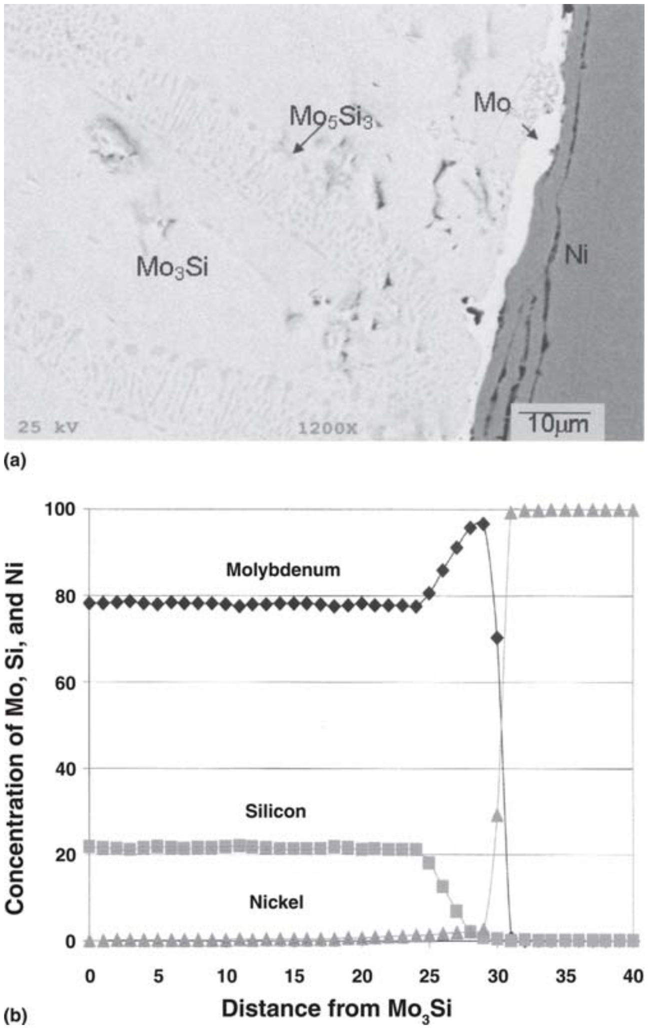

Fig. 7 Results from the vapor-solid desiliconizing of Mo_3Si showing (a) the cross section of the vapor-solid couple that was diffusion annealed at 1300 °C for 70 h (SEM backscattered electron image) and (b) the corresponding concentration profile as measured for Mo, Si and Ni

4.2 Diffusion Studies with Mo_3Si, T2, and Multiphase Mo-10Si-10B (at.%) Alloy

Vapor-solid desiliconizing experiments were carried out with disks of Mo_3Si, T2, and multiphase Mo-10Si-10B (at.%) alloy. The main idea for these experiments was to explore the formation of Mo layer at the surface of the various alloy disks and to evaluate Si interdiffusion coefficients in the Mo-rich phase. The main results of these experiments are described below.

Specimens of Mo_3Si prepared as described in the experimental section were heated from room temperature to 1300 °C within 15 min and held at 1300 °C for a specific period. Specimens were then cooled to 200 to 300 °C within 5 min. A preliminary analysis by XRD revealed that a Mo layer formed on the specimen surface for all of the specimens annealed at 1300 °C. Backscattered electron SEM micrographs of the cross section of the vapor-solid diffusion couple of Mo_3Si annealed at 1300 °C for 70 h are presented in Fig. 7(a); the concentration profiles determined by microprobe analysis are presented in Fig. 7(b). Figure 7(a) reveals that the Mo solid-solution layer formed on the Mo_3Si surface was of an average thickness of 2.6 μm. The composition of this layer was determined by both EDS and WDS analyses. The integrated and effective interdiffusion coefficients of silicon, $\tilde{D}^{int}_{Si}$ and $\tilde{D}^{eff}_{Si}$ were determined from the profiles with the aid of the *Multi*DiFlux program[10,11] using Eq 5 and are reported to be $+1.0 \times 10^{-12}$ g · mole/m · s and $+8.1 \times 10^{-17}$ m^2/s, respectively.

The vapor-solid diffusion experiments with Mo_5SiB_2 (T2) were carried out at 1300 °C for two different times of 51 and 80 h and at 1600 °C for 28 h. The surface of the specimens after annealing at 1300 °C showed the presence of T2, Mo, and a trace of Mo_3Si. An analysis by SEM and EDS of the cross section of T2 specimens annealed at both

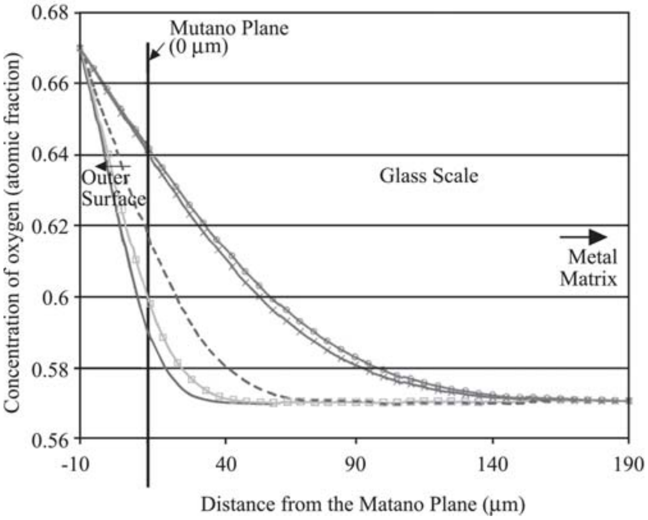

Fig. 8 Calculated concentration profile of oxygen in glass scale calculated using a value for the effective interdiffusion coefficient of oxygen in glass as 1.1 × 10^{-14} m^2/s. The diffusion times were varied as follows: 2.5 h (—), 4 h (—□—), 10 h (- - -), 42 h (—×—), and 48 h (—○—).

1300 and 1600 °C revealed that no immediate layer formed on the T2 surface. This observation suggested that the diffusion rates of silicon and boron in T2 were apparently low at both temperatures.

A diffusion study of the Mo-10Si-10B (at.%) multiphase alloy consisting of Mo, Mo_3Si, and Mo_5SiB_2 (T2) phases was conducted at 1300 °C for 10 h in flowing Ar-5%H_2 gas. After annealing the XRD of the specimen surface identified mainly Mo and T2 phases. Diffraction peaks for Mo_3Si were not detected. Surface layer of the annealed specimen consisted mostly of a solid solution of Mo and the products of oxidation. Evidence of internal oxidation and cracks were observed in the cross section of the annealed specimen. Cracks were mostly found in the brittle phase T2.

5. Discussion

5.1 Oxidation Layers at 1300 °C

The microstructure presented in Fig. 2 and 4 of the Mo-13.2Si-13.2B alloy oxidized at 1300 °C revealed the formation of an intermediate (Mo + glass) layer between the three-phase base alloy and the external silicate glass scale. At the Mo/glass interface, all three phases (Mo, Mo_3Si, and Mo_5SiB_2) were in contact with glass. However, the absence of the Mo_3Si/T2/glass contact indicated that one of the silicide phases preferred to react with oxygen to form glass (Fig. 4). The results from the vapor-solid diffusion experiments of single phase Mo_3Si and T2 revealed that the diffusion rate of Si in Mo_3Si was higher than that in T2 suggesting that in the passivated three-phase alloy, glass should initially start to form at Mo_3Si phase. Moreover, the data from the oxidized Mo-13.2Si-13.2B (at.%) alloy (1300 °C, 48 h) also showed that volume fraction of Mo_3Si substantially decreased near the (metal/Mo + glass) interface. The result indicated that, as Mo_3Si converted into glass, the volume fraction of Mo_3Si near the (Mo/Mo + glass) interface decreased. The vapor-solid diffusion couple of the Mo-10Si-10B (at.%) alloy annealed at 1300 °C also confirmed that volume fraction of Mo increased near the surface of the specimen.

Shown in Fig. 8 is an estimated concentration profile of oxygen in the outer glass scale that was calculated from the procedure developed by Sisson and Dayananda.[22] For the calculation, a value for the effective interdiffusion coefficient of oxygen in glass as 1.1 × 10^{-14} m^2/s was chosen.[21,23] As shown in Fig. 8, the concentration of oxygen in the glass scale increased near the surface of the specimen, which was consistent with the experimental data shown in Fig. 6.

5.2 Growth of the (Mo + Glass) Layer at 1300 °C

The (Mo + glass) layer growth rates were calculated from the fluxes and average concentrations of each element at the two interfaces, metal/(Mo + glass) and (Mo + glass)/glass. Such calculations are based on the assumption that the interfaces can be treated as planar and that they move parabolically with time. The instantaneous velocity of a planar interface (ϕ_I) is given by:[22]

$$\phi_I = \frac{\tilde{J}_i^{\beta} - \tilde{J}_i^{\alpha}}{C_i^{\beta} - C_i^{\alpha}} \qquad \text{(Eq 6)}$$

whereas $\tilde{J}_i^{\beta}$ and $\tilde{J}_i^{\alpha}$ are the interdiffusion fluxes of component i at the interface in the β and α phases, respectively, and $\tilde{C}_i^{\beta}$ and $\tilde{C}_i^{\alpha}$ are the concentrations of component i in the β and α phases at the interface. The instantaneous velocities of movement at 48 h for the two interfaces on either side of the (Mo + glass) layer were calculated from interdiffusion fluxes and average concentrations of silicon at the interfaces and reported in Fig. 9. These velocities dictate a thickening of the (Mo + glass) layer in the passivated sample. Furthermore, the velocity metal/(Mo + glass) interface of −1.4 × 10^{-10} m/s estimated from the diffusional analysis at 48 h (Fig. 9) is quite consistent with the thickening rate at 48 h of the (Mo + glass) layer (1.5 × 10^{-10} m/s) as determined from Fig. 3.

The oxidized Mo-13.2Si-13.2B (at.%) alloy was treated as a diffusion couple satisfying the Boltzmann parameter requirement for the growth of the intermediate (Mo + glass) layer (Fig. 3); such treatment allowed the assessment of the effective interdiffusion coefficients for the components. Consistent with the Boltzmann parameter requirement, the concentration profiles were assumed to vary parabolically with time with little variation in the composition of the external glass/vapor interface. Composition at the vapor/glass interface can be considered to vary little, as the counterflows of boron, silicon, and oxygen at the interface decrease with the passivation of the oxidized specimen,[2] which exhibits little change in the net mass loss after passivation. The concentrations at the vapor/solid interface can be expected to remain invariant, provided the interdiffusion fluxes of all the components at the interface decrease as a function of $1/\sqrt{t}$, as required by the Boltzmann parameter

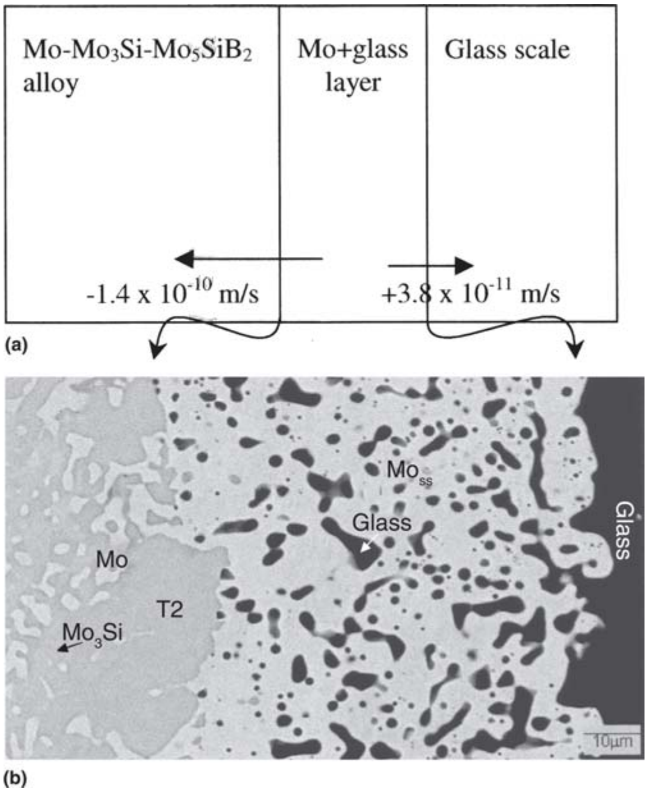

Fig. 9 Schematic of the movement of the Mo + glass layer showing (a) the estimated instantaneous velocities (at 48 h) of the interfaces and (b) corresponding electron micrograph. The arrows indicate directions and magnitudes of the movement of the Mo + glass layer.

requirement.[16] The main requirement for this is that the external glass/vapor interface position also changes parabolically with time consistent with an interface composition that changes little with time after passivation. The validity of the present analysis is subject to the above observations and assumptions.

While the present results were for a Mo-13.2Si-13.2B (at.%) alloy, previous work has shown that for higher boron contents (Si/B < 1), a nonprotective glass scale can form upon oxidation at 1300 °C. For these specimens (Si/B < 1), a thickening of the intermediate (Mo + glass) layer is not observed,[5,21] and the analysis of such specimens as a solid-solid diffusion couple would be inappropriate. For example, after 48 h at 1300 °C, the (Mo + glass) layer of the passivated alloy (Mo-13.2Si-13.2B, at.%) was observed to be significantly thicker than that in a nonpassivated alloy (Mo-8.6Si-16.6B, at.%)[2,24] that displayed continued weight loss with time.

6. Conclusions

The cyclic oxidation of a Mo-13.2Si-13.2B (at.%) alloy at 1300 °C in laboratory air resulted in the formation of a protective glass scale within 6 h. Microstructural analysis after 48 h revealed the presence of diffusion layers consisting of an external, continuous glass scale and an intermediate (Mo + glass) layer over the base Mo-Si-B alloy. Concentration profiles averaged over the mixtures of phases in each diffusion layer were estimated from the volume fractions of the individual phases in conjunction with EPMA data. Within the (Mo + glass) layer, the effective interdiffusion coefficients estimated using *Multi*DiFlux software indicated uphill interdiffusion of both B and Si in the (Mo + glass) layer. Additionally, desiliconization of a binary Mo_3Si specimen at 1300 °C for 70 h resulted in the formation of a bcc (Mo) layer on the Mo_3Si surface. From the desiliconization experiment, the average effective interdiffusion coefficient of Si in Mo at 1300 °C was determined to be 8×10^{-17} m^2/s.

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