

# **Relationship Between Pack Chemistry and Growth of Silicide Coatings on Mo–TZM Alloy**

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A theoretical model equation has been derived to relate the growth kinetics of silicide coating with the pack chemical composition and other processing conditions for siliconizing of Mo–TZM (Mo–0.5Ti–0.1Zr–0.02C) alloy to improve its oxidation resistance at high temperatures. A series of experiments conducted with varying pack Si (1–10 wt %) and NH<sub>4</sub>F (2–20 wt %) content, time (1–25 h), and temperature (800–1200°C) confirmed the validity of the model. MoSi<sub>2</sub> was the main coating layer formed during the siliconizing process. Optimum processing conditions were derived for doping of Al in MoSi<sub>2</sub> to form Mo(Si,Al)<sub>2</sub> in the outer layer of the coating.

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There is an increasing demand for materials capable of withstanding environments with respect to temperature, stress, radiation, oxidation, and liquid metal corrosion for a prolonged duration. Molybdenum and niobium base alloys are the most promising materials for such kinds of applications.<sup>1-3</sup> Mo–TZM (Mo–0.5Ti–0.1Zr– 0.02C) is a molybdenum base alloy containing 0.5 wt % Ti, 0.1 wt % Zr, and 0.02 wt % C. Solid solution and carbide strengthening improve the high-temperature mechanical properties of the alloy making it suitable as a potential candidate material for advanced high-temperature nuclear reactors operated beyond 1000°C.<sup>4</sup> However, the major problem with Mo base alloys is their inadequate oxidation resistance due to the formation and rapid volatilization of the oxide MoO<sub>3</sub> around 704°C that also melts at 794°C.<sup>5,6</sup>

In order to improve the oxidation resistance of the Mo base alloys, formation of a protective coating is necessary.<sup>7</sup> Coating of molybdenum di-silicide (MoSi<sub>2</sub>) on the outer surface of the alloy component is the most promising because it has an outstanding oxidation resistance up to a temperature of 1700°C.<sup>8,9</sup> The excellent oxidation resistance of MoSi2 at high temperatures is due to the formation of a self-healing, glassy silica (SiO<sub>2</sub>) layer that protects the substrate from further attack by oxygen. However, for porous MoSi<sub>2</sub> product, the SiO<sub>2</sub> layer formed in the lower temperature range of 400-600°C is not continuous, leading to the oxygen penetration and pest disintegration.<sup>10-13</sup> Recently, a lot of studies have been done to improve the oxidation behavior of  $MoSi_2$  by doping boron in the multiphase Mo–Si–B alloy.<sup>5,14,15</sup> The other ways of preventing the low-temperature pesting are formation of theoretically dense MoSi<sub>2</sub> or addition of Al to form Mo(Si,Al)<sub>2</sub>.<sup>16</sup> In Mo(Si,Al)<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> formation is preferred to that of SiO<sub>2</sub>, involving a minor volume expansion of 4.9% compared to 85.6% in the case of SiO<sub>2</sub>.<sup>17</sup> Maruyama and Yanagihara<sup>18</sup> conducted detailed oxidation studies of Mo(Si,Al)<sub>2</sub> at different temperatures. Formation of protective Al<sub>2</sub>O<sub>3</sub> scale below 1595°C, which is the eutectic temperature in the SiO<sub>2</sub>-3Al<sub>2</sub>O<sub>3</sub> 2SiO<sub>2</sub> system, has been reported. Above the eutectic temperature, a liquid scale of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (mullite) rich in Al<sub>2</sub>O<sub>3</sub> content forms.<sup>18-20</sup> Therefore, a coating of the dense MoSi<sub>2</sub> or Mo(Si, Al)<sub>2</sub> compound on Mo-TZM alloy will increase its oxidation resistance at high temperatures.

Pack cementation process is most widely used for applying protective coatings on materials, such as steels,<sup>21-23</sup> superalloys,<sup>24</sup> TiAl,<sup>25-27</sup> and refractory metals alloys<sup>28,29</sup> suitable for hightemperature applications. It is a diffusion coating process<sup>30</sup> involving embedding the substrate into a sealed or vented refractory container with a powder mixture called the pack, which is then heated at 800–1200°C in an inert atmosphere for 8–36 h. The pack is composed of a master alloy or pure element powder to be enriched at the substrate surface, a halide salt activator, and inert filler. The halide activator decomposes at high temperature to produce volatile halide vapors of the elements. The chemical potential gradient drives the gas phase diffusion of the metallic halides to result in surface deposition followed by solid-state diffusion, which is considered as the rate-limiting step.<sup>31</sup> The process is easy to operate, inexpensive, can accommodate substrates of varying size and shape, and can produce a uniform and smooth coating of desired thickness. Formation of alumoreinide<sup>32</sup> and silicide<sup>33,34</sup> coating on Mo–Si–B alloy using this process has been reported. Our recent studies on the continuous and cyclic oxidation behavior of MoSi<sub>2</sub> and Mo(Si,Al)<sub>2</sub> coated Mo– TZM alloy showed the protective nature of both the coatings under oxidizing conditions up to 1300°C.<sup>35</sup>

The studies on formation of aluminide coating have been extensively focused in comparison to the effect of the processing condi-tions on growth kinetics.<sup>21,24</sup> More systematic studies have been reported in the literature on the formation of aluminide coating on nickel base super alloys,<sup>24</sup> steels,<sup>21</sup> etc., by the pack aluminizing process in relation to determining the effects of processing conditions on the growth kinetics. Formation of aluminide and silicide coatings on molybdenum base alloys using pack cementation process with some specific conditions has been reported earlier. Systematic studies on the formation of silicide coatings on Mo-base alloy by pack cementation process are nonexistent in the literature. In the present work, model calculations of the pack cementation process has been performed for deriving the corelation between the growth of silicide coatings on Mo-TZM alloy substrate with pack composition and other processing conditions. The theoretical model equation corelating the coating thickness with pack composition and processing conditions has been obtained from the thermodynamic and kinetic analysis. The validity of the analysis is subsequently confirmed by experiments. Process optimization has also been done on formation of alumino-silicide coating on the alloy substrate.

### Experimental

Initially pure molybdenum powder was prepared by conducting hydrogen reduction of MoO<sub>3</sub> at 900°C for 2.5 h. Mo powder was milled with pure Ti, Zr, and C powder of required quantity. The powder mix was subsequently compacted to 20 mm diam pellets and sintered at 1000°C for 4 h. Finally Mo–TZM alloy was produced by arc melt consolidation of the sintered pellets prepared from a milled powder mixture containing Mo, Ti, Zr, and C. Alloy was hot rolled into sheets and annealed at 1650°C for 1 h followed by cutting into small buttons of dimensions  $15 \times 10 \times 2$  mm. The surfaces of the buttons were ground and polished to 1 µm diamond finish. The specimens were then degreased and cleaned by ultrasonic

cleaning. The cleaned samples were weighed accurately and placed in the pack. The pack mixtures were prepared by mixing appropriate amounts of Si, Al<sub>2</sub>O<sub>3</sub> (filler), and NH<sub>4</sub>F (activator) powder. The pack cementation experiments were conducted by following the standard techniques.<sup>35</sup> The average particle size of powder of each material was  $<75 \mu m$ . The packs were prepared by filling and tapping the powder mixture around the Mo-TZM substrates in a cylindrical alumina crucible of 36 mm diam and 48 mm length. The crucible was then sealed with an alumina lid using alumina base cement. The cement sealing was dried for 24 h at room temperature followed by controlled heating inside a tubular furnace under argon flow. Initial curing treatment was given at 150°C for 2 h followed by heating at 250°C for 2 h to facilitate further curing of the cement and to remove any residual moisture. Subsequently, the temperature of the furnace was raised to the actual coating temperature at a rate of 4°C min<sup>-1</sup> and held for a desired time. The furnace was subsequently cooled to room temperature at a slow rate. Experiments were conducted by varying process parameters, such as temperature (800–1200°C), dwell time (1–25 h), pack Si and activator ( $NH_4F$ ) contents, and different activators (NH<sub>4</sub>F, NaF, and NH<sub>4</sub>Cl). A similar set of experiments were carried out to form an adherent and uniform alumino-silicide coating of sufficient thickness. The preliminary set of experiments was conducted at five different temperatures between 800 and 1200°C for 10 h using a fixed pack composition of Al<sub>2</sub>O<sub>3</sub>-80%, Si-10%, and NH<sub>4</sub>F-10%, by weight. Applying the same pack composition, the next set of experiments was carried out at 1100°C by varying the dwell time from 1 to 25 h. Subsequent experiments were conducted at 1100°C for 10 h with varying Si and NH<sub>4</sub>F content in the pack, keeping constant NH<sub>4</sub>F and Si percentages in respective cases. Studies were also conducted using the other activators (NH<sub>4</sub>Cl and NaF) of same weight percent at the similar coating conditions. The experiments of Al doping in the silicide coating were conducted using different pack compositions, and the pack composition producing adherent and uniform coating of sufficient thickness at 1100°C was found to be Al<sub>2</sub>O<sub>3</sub>-60%, Si-10%, Al-10%, and NH<sub>4</sub>F-20% by weight. Using this pack composition, the effects of time and temperature on alumino-silicide coating were studied by carrying out a series of experiments. After cooling and taking the samples out of the furnace, the coated samples were washed in a water jet to remove any residual powder from the surface. Weight and thickness measurements of the coated specimens were conducted. The specimen weight gain in milligrams per centimeters squared was estimated from the weight difference and the surface area of the specimens. The coated surface was examined by X-ray diffraction (XRD) (Pananalytical X'pert Pro) for identifying the phases. The cross-sectional microstructure and chemical composition of the coated specimens were analyzed using optical (Olympus), scanning electron microscopy (SEM) (Hitachi), and energy dispersive X-ray spectroscopy (EDS) (Thermo Electro Corporation). The thicknesses of silicide and aluminosilicide layers were estimated from Si and Al diffusion profiles measured by EDS.

# Results

*Process model.*— In the pack cementation process, the fluoride activator (NH<sub>4</sub>F, NaF, etc.) reacts with Si and forms a number of gaseous fluorides such as SiF<sub>4</sub>, SiF<sub>3</sub>, SiF<sub>2</sub>, and SiF. NH<sub>4</sub>F activator initially dissociates into NH<sub>3</sub> and HF at ~300 °C. Subsequent reactions between HF and Si lead to the formation of the fluoride vapors. It is assumed that a depletion zone of depth  $\Delta x$  exists near the substrate surface where the Si is completely consumed. The chemical potential gradient developed due to the formation of the depletion zone drives the gas phase diffusion of silicon fluorides to result in surface deposition. The flux  $J_i^v$  of the migrating fluoride vapor is given by



Figure 1. Equilibrium partial pressures of the major vapor species in the  $10Si-10NH_4F-80Al_2O_3$  (in weight percent) pack.

$$J_{i}^{v} = \left(\frac{D_{i}}{RT}\right) \frac{\Delta P_{i}}{\Delta x}$$
[1]

where  $D_i$  is the gas phase interdiffusion coefficient, R is the gas constant, T is the temperature, and the derivative is the partial pressure gradient at the substrate surface. The change in partial pressure  $\Delta P_i$  for each species "i" is defined as the partial pressure of the species in the bulk pack ( $a_{\rm Si} = 1$ ) minus the partial pressure of the species at the substrate. Levine and Caves<sup>24</sup> have shown that for this kind of migration and deposition process, the amount of element (Si) being deposited on the metal or alloy surface of a unit area (m in milligrams per centimeters squared) at a time interval t can be given by

$$m^{2} = \left(\frac{2\rho\varepsilon M_{\rm Si}}{lRT}\sum D_{\rm i}\Delta P_{\rm i}\right)t$$
[2]

where  $\rho$  is the Si concentration (in grams per cubic centimeter) in the pack,  $\varepsilon/l$  is the correction factor due to the pack porosity and pore length, and  $M_{\text{Si}}$  is the atomic weight of Si. From Eq. 1 and 2, it is clear that the difference in the partial pressures ( $\Delta P_i$ ) of silicon fluoride vapors is the driving force for the migration of the vapors to the outer surface of the substrate and formation of the coating by deposition or reduction at the surface.

The metal-deficient fluoride SiF<sub>4</sub> is assumed to be a depleted species, and its deposition is thermodynamically unfavorable, rather it carries fluorine back to the pack to reform the lower fluoride species that support deposition. Considering total pressure inside the pack as one atmosphere and applying mass balance approach, the equilibrium partial pressure of different fluorides in a pack mixture consisting of 10 wt % Si, 10 wt % NH4F, and 80 wt % Al2O3 at different coating temperatures have been calculated and plotted in Fig. 1. Among the fluorides, the partial pressure of  $SiF_2$  is the maximum in this temperature range. The standard free energies for the formation of different fluorides are presented in Table I. Like SiF<sub>4</sub>, SiF<sub>3</sub> is also a very stable fluoride and as per Fig. 1 SiF has a very low vapor pressure. Therefore, the coating process is mainly dictated by the migration and dissociation of SiF<sub>2</sub>. Now, considering  $\rho$  is proportional to the pack Si content in weight percent  $(W_{Si})$ , Eq. 2 can be written as

$$m^{2} = \left(\frac{2\varepsilon M_{\rm Si} D_{\rm SiF_{2}}}{lRT}\right) W_{\rm Si} P_{\rm SiF_{2}} t$$
[3]

 $SiF_2$  is formed as per the chemical reaction  $Si + 2MF = SiF_2 + M$ (M = NH<sub>4</sub>,Na, etc.). The partial pressure of  $SiF_2$  is given by

| $T(\mathbf{K})$ | SiF <sub>4</sub> | SiF <sub>3</sub> | SiF <sub>2</sub> | SiF      | AlF <sub>3</sub> | $AlF_2$  | AlF      |
|-----------------|------------------|------------------|------------------|----------|------------------|----------|----------|
| 1100            | -1457.08         | -1037.8          | -622.103         | -132.837 | -1141.77         | -722.925 | -351.771 |
| 1200            | -1442.69         | -1033.22         | -624.685         | -142.578 | -1134.12         | -723.693 | -357.754 |
| 1300            | -1428.31         | -1028.62         | -627.201         | -152.246 | -1126.42         | -724.356 | -363.627 |
| 1400            | -1413.94         | -1023.98         | -629.651         | -161.844 | -1118.66         | -724.924 | -369.397 |
| 1500            | -1399.58         | -1019.32         | -632.036         | -171.372 | -1110.85         | -725.401 | -375.072 |
| 1600            | -1385.22         | -1014.63         | -634.359         | -180.834 | -1102.99         | -725.795 | -380.659 |

Table I. The standard free energies ( $\Delta G^{\circ}$ ) of formation in kilojoules per molecule for different fluorides at different temperatures.

$$P_{\text{SiF}_2} = k[\text{MF}]^2 = kW_{\text{MF}}^2 \qquad [4]$$

where k is the equilibrium constant and  $W_{\rm MF}$  is the weight-percent activator (NH<sub>4</sub>F or NaF) used. Substituting Eq. 4 into Eq. 3, one obtains

$$m^{2} = \left(\frac{2\varepsilon M_{\rm Si} D_{\rm SiF_{2}} K}{lRT}\right) W_{\rm Si} W_{\rm MF}^{2} t$$
[5]

or

$$n = \frac{k_{\rm m}}{T^{1/2}} W_{\rm Si}^{1/2} W_{\rm MF} t^{1/2}$$
 [6]

where  $k_m$  is a constant at constant temperature. As the final stage of the coating growth is inward diffusion of Si in Mo base matrix, the linear relationship between *m* and  $t^{1/2}$  at constant temperature and other parameters is obvious and also observed by many researchers<sup>21,24</sup> during the diffusion controlled pack cementation process. Now, if there is no loss of substrate material into the pack and the silicide compound of well-defined stoichiometry (Mo<sub>x</sub>Si<sub>y</sub>) forms in the coating layer, the relationship between the substrate weight gain (*m* in milligrams per centimeters squared) and coating thickness (*h* in microns) is given by

r

$$h = \frac{10M_{\rm c}}{yM_{\rm Si}\rho_{\rm c}}m = k_1m$$
[7]

 $k_1$  is a constant incorporating  $M_{Si}$  atomic weight of Si,  $M_c$ , and  $\rho_c$  are molecular weight and the density (in grams per cubic centimeters) of the coated compound Mo<sub>x</sub>Si<sub>y</sub>, respectively. Substituting Eq. 7 into Eq. 6 one gets

$$h = \frac{k_h}{T^{1/2}} W_{\rm Si}^{1/2} W_{\rm MF} t^{1/2}$$
 [8]

where  $k_h$  is a constant at constant temperatures. The variation of  $k_h$  with temperature can be given by

$$k_h = k_0 \, \exp\!\left(-\frac{E_a}{RT}\right) \tag{9}$$

where  $E_a$  is the activation energy for the coating growth process and  $k_0$  is a constant. Finally, substitution of Eq. 9 into Eq. 8 yields

$$h = \frac{k_0}{T^{1/2}} W_{\rm Si}^{1/2} W_{\rm MF} t^{1/2} \exp\left(-\frac{E_{\rm a}}{RT}\right)$$
[10]

Equation 10 is the ultimate kinetic equation for the coating growth process, which relates the growth rate of the coating with temperature (*T*), time (*t*), and pack composition, such as Si ( $W_{Si}$ ) and fluoride activator content ( $W_{MF}$ ) of the pack. The main assumption made in deriving Eq. 10 is constant composition in the coating layers with the variation of pack Si and activator contents, time, and temperature of coating experiments. From Eq. 10, it is clear that thickness of the coating would increase if the pack Si and activator content is increased at constant *T* and *t*. Equation 10 suggests that coating thickness would increase linearly with  $W_{Si}^{1/2}$  at constant *T*, *t*, and activator content in the pack. Most importantly, a linear relationship between the coating thickness (*h*) and pack activator content ( $W_{MF}$ ) is predicted by Eq. 10. Such a relationship between the

coating growth rate and pack chemistry for the formation of silicide coatings on molybdenum base alloys is not available in the literature. Our experimental results presented in the following sections strongly supported this derived relationship (Eq. 10), confirming the validity of the assumptions for the coating process.

Coating formation.— In general, the surfaces of the coated samples were smooth and free from the entrapment of pack particles. The appearance of the silicide coating specimens was metallic whitish gray. The cross-sectional SEM image of a representative silicide coated sample is presented in Fig. 2a. The coating (Fig. 2a) was prepared at 1100°C for 17.5 h using a pack composition of 10Si–10NH<sub>4</sub>F–80Al<sub>2</sub>O<sub>3</sub> (in weight percent). The specimen weight gain (*m*) and coating thickness (*h*) for this coating experiment was ~16.95 mg cm<sup>-2</sup> and 82.68  $\mu$ m, respectively. The diffusion profile (Fig. 2b) of major elements measured by EDS along the line marked on the micrograph revealed the formation of a thick (~79  $\mu$ m) outer layer followed by a thin (~3.7  $\mu$ m) inner layer in the coating. Elemental analysis and XRD studies confirmed that the thick outer



Figure 2. (Color online) (a) Cross-sectional SEM image and (b) diffusion profiles of major elements in the coating layer formed during silicide coating formation at  $1100^{\circ}$ C for 17.5 h.



Figure 3. (Color online) (a) Cross-sectional SEM image and (b) diffusion profiles of major elements in the coating layer formed during aluminosilicide coating formation at  $1100^{\circ}$ C for 17.5 h.

layer was formed by molybdenum di-silicide (MoSi<sub>2</sub>) and the inner layer consisted of Mo<sub>5</sub>Si<sub>3</sub>. The concentration of other alloying elements like Ti was found to be uniform ( $\sim 0.6$  wt %) throughout the cross section.

For the formation of alumino-silicide coatings, different pack compositions were tried at 1100°C with varying time. The pack composition yielding a sufficiently thick and desired coating composition was found to be 10Si-10Al-20NH<sub>4</sub>F-60Al<sub>2</sub>O<sub>3</sub> (in weight percent). Like silicide coating specimens, the coated surface was smooth and much brighter in appearance. Specimen weight gain of 14.83 mg cm<sup>-2</sup> corresponding to a coating thickness of  $\sim$  61.67  $\mu$ m was observed at 1100°C for 17.5 h. Figures 3a and b shows the cross-sectional SEM image and the concentration profiles of the Si, Al, and Mo measured by EDS along the marked line. The outer layer (~52  $\mu m)$  consisted of Mo(Si,Al)\_2 phase with a constant Al concentration of  $\sim 9.89$  at %. Reduction in Si (59.74–20.3 at %) concentration and increase in Al (9.89-34.35 at %), and Mo (30.54-45.35 at %) percentage was observed in the inner layer ( $\sim 10 \ \mu m$ ). According to the elemental composition, the inner coating layer could be constituted with a Mo(Al, Si) type of phase. The composition of the coated layers varied drastically at different processing conditions as two elements of different chemical nature deposited simultaneously during the coating process.

*Effect of time on coating thickness.*— The effect of time (1-25 h) on silicide coating thickness was studied at a constant temperature  $(1100^{\circ}\text{C})$  using a pack composition of  $10\text{Si}-10\text{NH}_4\text{F}-80\text{Al}_2\text{O}_3$  (in weight percent). The time was varied from 1 to 25 h. A linear relationship was obtained when the coating thickness (h) was plotted against  $t^{1/2}$  presented in Fig. 4. This result



**Figure 4.** (Color online) Kinetics of silicide and alumino-silicide coating growth at 1100°C.

is consistent with the prediction of Eq. 10 with constant temperature (T) and pack Si and NH<sub>4</sub>F content. The straight line in Fig. 5 is a least-squares fit to the data points, which gives

$$h = 16.97t^{1/2} + 14.12$$
 [11]

where *h* is in microns and *t* in hours. A relatively high offset value of 14.12 was probably due the slow heating and cooling rates, and a relatively higher temperature ( $1100^{\circ}$ C) for the coating process.

Linear relationship was also observed while *h* was plotted against  $t^{1/2}$  (Fig. 4) for alumino-silicide coating experiments conducted at 1100°C using a constant pack composition of 10Si–10Al–20NH<sub>4</sub>F–60Al<sub>2</sub>O<sub>3</sub> (in weight percent) for the time intervals of 1, 5, 10, 17.5, and 25 h. The least-squares fit of the data points yielded the following linear relationship

$$h = 10.94t^{1/2} + 21.99$$
 [12]

The lower slope (10.94) of the line for alumino-silicide coating compared to that (16.97) for silicide coating indicated a lower growth rate of the coating for the alumino-silicide coating process.

*Effect of temperature.*— The effect of temperature (800–1200°C) was studied using a pack of composition



Figure 5. Dependence of silicide coating thickness on temperature at constant coating composition and time of 10 h.



Figure 6. Dependence of coating thickness (*h*) on Si content  $(W_{Si}^{1/2})$  of the pack for siliconizing at 1100°C for 10 h using constant NH<sub>4</sub>F content.

 $10\text{Si}-10\text{NH}_4\text{F}-80\text{Al}_2\text{O}_3$  (in weight percent) at constant duration of 10 h. The pack composition used for these experiments was maintained as  $10\text{Si}-10\text{NH}_4\text{F}-80\text{Al}_2\text{O}_3$  (in weight percent). The coating thickness increased with increase in temperature. Si concentration in the outer layer was constant, and there was a marginal increase in the thickness of the inner Mo<sub>5</sub>Si<sub>3</sub> layer. As confirmed by XRD, the outer layer formed at all temperatures was found to be MoSi<sub>2</sub>. Therefore, the temperature affected only the coating thickness or the growth rate, not the Si concentration at the outer and the inner layer of the coating. It was observed that the temperature had a more significant effect than coating time (*t*), especially at higher temperatures. Equation 10 could be rewritten as

$$\ln(T^{1/2}h) = -\frac{E_a}{RT} + \ln k_0 + \frac{1}{2}\ln(W_{\rm Si}t) + \ln(W_{\rm NH_4F}) \qquad [13]$$

Hence, at constant *t*,  $W_{\rm Si}$ , and  $W_{\rm NH_4F}$ , the activation energy of the silicide coating growth process in the temperature range of 800–1200°C can be obtained from the slope of the  $\ln(T^{1/2} h)$  vs 1/T plot. Figure 5 shows the good linear fit between  $\ln(T^{1/2} h)$  and 1/T (by least-squares method) to the experimental data points. The activation energy obtained from the slope was  $48.06 \pm 4.85$  kJ mol<sup>-1</sup>. This is a qualitative value for the overall coating process. Equation 13 could not be applied for alumino-silicide coating process due to the variation in composition observed in the outer and the inner layers of the coating formed at different temperatures.

Effect of Si content in the pack.— To study the effect of the pack Si content, the experiments were conducted at  $1100^{\circ}$ C for 10 h using a fixed NH<sub>4</sub>F (10 wt %) composition. Si content was varied between 1 and 10 wt %. In general, coating thickness was increased with increasing Si content, but the compositions at the outer and the inner surfaces were the same as Fig. 2a. Therefore, the variation in Si content in the pack did not affect the composition of the coating which was one of the key assumptions in deriving Eq. 10. The thick outer layer consisted of MoSi<sub>2</sub> and the inner layer was of Mo<sub>5</sub>Si<sub>3</sub>. The growth rate of the inner layer was marginal with respect to that of the outer layer. Figure 6 shows the linear relationship between h and  $W_{Si}^{1/2}$  as predicted by Eq. 10. The straight line is a least-squares fit of the experimental data points, which gives

$$h = 24.10W_{\rm Si}^{1/2} - 9.86$$
 [14]

The negative offset could be due to the slower initiation of the coating process.



Figure 7. Linear dependence of coating thickness on  $NH_4F$  (maximum up to 10 wt %) content in the pack.

Effect of NH<sub>4</sub>F content in the pack.— The effect was studied by varying the pack NH<sub>4</sub>F content from 2 to 20 wt % while keeping the pack Si content constant at 10 wt %. All the coating experiments were conducted at 1100°C for 10 h. The coating thickness increased with increasing NH<sub>4</sub>F content up to 10 wt %. A lower coating thickness was obtained for 20 wt % NH4F in the pack. As the NH4F content was increased, a lot of NH3 and HF were generated with increasing vapor pressure at higher temperatures. This caused cracks in the cement layer at the top of the crucible, and most of the vapors went out with the argon flow. Therefore, the quantities of halide vapors available for the coating to grow were very small. Coating thickness (h) was plotted against  $NH_4F$  content up to 10 wt % and presented in Fig. 7, which confirms the linear relationship predicted by Eq. 10. The straight line in Fig. 7 is a least-squares fit of the experimental data points producing the best fit ( $R^2 = 0.9994$ ) compared to the other results presented in the previous sections, giving

$$h = 2.95W_{\rm NH,F} + 32.57$$
 [15]

A positive offset could be due to a significantly high growth rate of the coating even at lower  $NH_4F$  content in the pack.

Considering all the results presented in the previous sections, the average value of  $k_0$  was calculated and found to be 984.89  $\mu$ m h<sup>-1/2</sup> K<sup>1/2</sup>. Thus for the formation of silicide coating on Mo–TZM alloy using NH<sub>4</sub>F (<10 wt %) activated pack in the temperature range of 800–1200°C, the final relationship of coating thickness with other process parameters becomes

$$h = \frac{984.89}{T^{1/2}} W_{\rm Si}^{1/2} W_{\rm NH_4F} t^{1/2} \exp\left(-\frac{5781.2}{T}\right)$$
[16]

where *h* is in microns,  $W_{\rm Si}$  and  $W_{\rm NH_4F}$  in weight percent, *t* in hours, and *T* in degrees Kelvin. Equation 16 may be used to predict the growth of a coating thickness at any specified values of Si (weight percent), NH<sub>4</sub>F (weight percent), time (in hours), and temperatures of <1200 °C.

Relationship between h and m.— Coating thickness (h) and specimen weight gain (m) obtained from various experiments on formation of silicide coating has been plotted against each other in Fig. 8 (open squares). The solid line is a least-squares fit ( $R^2$ = 0.994) of the experimental data points, which gives

$$h = 4.85m + 2.08$$
 [17]

Despite a little offset, the slope (4.85  $\mu$ m mg<sup>-1</sup> cm<sup>2</sup>) is close to the theoretical value of 4.24  $\mu$ m mg<sup>-1</sup> cm<sup>2</sup> calculated from Eq. 7 using



Figure 8. (Color online) Coating thickness against specimen weight gain of silicide and alumino-silicide coatings.

a theoretical density value of 6.24 g cm<sup>-3</sup> for MoSi<sub>2</sub>. It is observed, in all the coating conditions, that the thickness of the inner Mo<sub>5</sub>Si<sub>3</sub> layer is close to 5% of the total coating thickness. Applying this condition and using equivalent values of  $M_c$ ,  $\rho_c$ , and y in Eq. 7, the theoretical value of the slope  $(k_1)$  is calculated to be 4.62  $\mu$ m mg<sup>-1</sup> cm<sup>2</sup>, which is closer to the experimental value (4.85  $\mu$ m mg<sup>-1</sup> cm<sup>2</sup>). This result also confirms the validity of the proposed model in Eq. 10.

Figure 8 (solid circles) also shows the plot of h vs m for aluminosilicide coating experiments. It is evident from the figure that the least-squares linear fit is not very good ( $R^2 = 0.935$ ) and yields

$$h = 3.38m + 15.85$$
 [18]

which has a very high offset value. This could be due to the difference in vapor pressures of Si and Al fluorides producing the composition difference in the coating layers under different experimental conditions. As the coating composition and thickness of different layers vary with temperature, the validity of Eq. 7 has not been tested for alumino-silicide coating.

#### Discussion

In the pack cementation process, the chemical potential gradient is the main driving force for diffusion of halide vapors (e.g.,  $SiF_2$ ) from the surroundings to the substrate surface in the pack. It was observed in the case of silicide coating (siliconizing) experiments that the Si concentration in the outer layer remained constant at all time intervals. This indicates that Si concentration reaches a constant value within a very short time of the coating process, maintaining a thermodynamic equilibrium with the partial pressure of SiF<sub>2</sub> vapors at the vapor/coating interface during the process. After a certain time interval, a constant source of Si exists at the substrate surface forming a diffusion couple between Mo and Si. There are three silicide phases, Mo<sub>3</sub>Si,Mo<sub>5</sub>Si<sub>3</sub>, and MoSi<sub>2</sub>, identified on the Mo–Si binary equilibrium phase diagram.<sup>16</sup> Tortorici and Dayananda<sup>36,37</sup> did a detailed investigation on the Mo–Si diffusion couple and reported that the Mo<sub>3</sub>Si layer could not form below 1350°C due to nucleation difficulties. The thickness of the Mo<sub>5</sub>Si<sub>3</sub> laver formed near Mo surface was very small. The growth rate of the MoSi<sub>2</sub> was much faster than that of Mo<sub>5</sub>Si<sub>3</sub> in the temperature range of 900-1350°C. Our results were consistent with these earlier results. Thickness of the inner  $Mo_5Si_3$  layer was <5% of the major coating layer (MoSi<sub>2</sub>) in most of the coated specimens. Absence of pack particles in the coating (MoSi<sub>2</sub>) layer suggests that the inward diffusion of Si along tetragonal MoSi2 phase is the dominant diffusion mechanism. Figure 9a is an etched optical image of the cross



Figure 9. Cross-sectional optical image of etched silicide and aluminosilicide coated samples.

section of the silicide-coated sample, which shows that  $MOSi_2$  layer has a columnar microstructure due to a preferred direction of growth parallel to the diffusion direction. Mo–TZM substrate shows the annealed microstructure of average grain size 44  $\mu$ m adjacent to the thin  $Mo_5Si_3$  inner layer.

Assumptions made during derivation of Eq. 10 were validated from the experimental results. Equation 10 was derived on the basis of two major assumptions, namely: (*i*) the constant phase formation in the coating layer for all the experimental conditions and (*ii*) SiF<sub>2</sub> as the major vapor species responsible for Si migration and deposition of Si. Both the conditions were found to be satisfied from the experimental results. Therefore, Eq. 16 could be used to predict the thickness of the coating to be formed in a particular pack composition, time, and temperature of interest. A small deviation from the actual results may be observed for lower Si and NH<sub>4</sub>F contents (<1 wt %) due to the offsets in Eq. 14 and 15, which is inherent to any actual processes.

Codeposition of Si and Al on the Mo–TZM substrate resulted in formation of Mo(Si,Al)<sub>2</sub> and Mo(Al, Si) phases in the outer and the inner layers, respectively (Fig. 9b). The condition for codeposition of two (Al plus Si) or more elements by pack cementation is that the partial pressures of gaseous species in the pack for the elements to be deposited have to be comparable. Figure 10 shows the calculated equilibrium partial pressures of all Si and Al fluorides for a pack composition of  $10Al-10Si-10NH_4F-70Al_2O_3$  (in weight percent) at different temperatures. For the fluoride-activated process, AlF is responsible for deposition of Al on the metal surfaces.<sup>21</sup> It is evident from Fig. 10 that the partial pressures of SiF<sub>2</sub> and AlF are comparable at all the temperatures. But AlF is less stable compared to SiF<sub>2</sub> as dictated by the standard free energy of formation for different



Figure 10. Equilibrium partial pressures of the major vapor species in the  $10Al-10Si-10NH_4F-70Al_2O_3$  (in weight percent) pack.

fluorides presented in Table I. Formation of the inner layer of Mo(AI, Si) rich in Al is due to the preferential dissociation of AlF at the initial stages of the coating process. The subsequent coating growth takes place by solid-state diffusion of both Al and Si. The final phase to form in the outer layer is of  $MoSi_2$  type [i.e.,  $Mo(Si,AI)_2$ ] because this is the most stable congruently melting compound.<sup>38</sup> The bright luster observed in the alumino-silicide-coated specimens was due to the presence of Al in the outer layer. As the composition of the inner layer varies with temperature<sup>35</sup> and pack composition, Eq. 10 is not strictly valid for multiple element (Si and Al) coating on Mo–TZM as observed under different experimental conditions. However, as reported earlier, both the silicide and alumino-silicide coatings showed excellent performance under oxidizing environment, even up to  $1300^{\circ}C.^{35}$ 

Fluoride activators, especially NH<sub>4</sub>F, is the most suitable activator for growing silicide coatings on Mo base alloys. To study the effect of different activators on the growth of the coating, the siliconizing experiments were conducted at 1100°C for 10 h using the same quantities (10 wt %) of NaF and NH<sub>4</sub>Cl. Si content of the pack was kept constant at 10 wt %. Figure 11 shows the cross section of the coatings formed for different activators using the same quantities (10 wt %). It is clear that NaF produced the lowest thickness (~19  $\mu$ m) followed by NH<sub>4</sub>Cl (~22  $\mu$ m) and coating growth was maximum ( $\sim 63 \ \mu m$ ) for NH<sub>4</sub>F under identical processing conditions. The lower partial pressure of the fluorides<sup>24</sup> formed in the case of NaF activated pack could be the reason for lower coating thickness. Similarly, the partial pressures of the chloride vapors of Si formed in NH<sub>4</sub>Cl activated pack are also lower compared to fluoride vapors in the NH<sub>4</sub>F-activated pack.<sup>39</sup> Si diffusion profiles for all the coatings are presented in Fig. 12, which shows that the inner and the outer layers are formed by Mo<sub>5</sub>Si<sub>3</sub> and MoSi<sub>2</sub> phases, respectively, for all the activators. Figures 11 and 12 confirm that the thickness of the inner (Mo<sub>5</sub>Si<sub>3</sub>) layer is maximum for the NaF-activated process and minimum for the NH<sub>4</sub>F-activated coating. The results indicate that in the NaF-activated process the supply of Si on the coating surface is reduced after a certain time interval. This causes reduction in the chemical potential gradient between the surface and the substrate. The inner Mo<sub>5</sub>Si<sub>3</sub> layer grows further due to the existence of a concentration gradient of Si between MoSi2 layer and Mo-TZM substrate. Whereas for the NH<sub>4</sub>F activated pack, a constant vapor pressure of SiF<sub>2</sub> is maintained at the vapor/substrate interface causing the growth of the outer MoSi<sub>2</sub> layer through out the processing time. This effect also confirms the validity of Eq. 10 for predicting the coating growth kinetics for the NH<sub>4</sub>F-activated siliconizing process.







**Figure 11.** (Color online) Cross-sectional optical images of silicide-coated samples using different activators (a) NaF, (b) NH<sub>4</sub>Cl, and (c) NH<sub>4</sub>F of the same quantity (10 wt %), 10 wt % Si, and coating at  $1100^{\circ}$ C for 10 h.

# Conclusions

The kinetic model Eq. 10 can be used to predict the growth of silicide coatings formed on Mo–TZM substrate by pack cementation



Figure 12. Si concentration profiles in the coating layers formed at 1100°C for 10 h in different activators.

process at temperatures below 1350°C, where MoSi<sub>2</sub> forms the main coating layer. The NH<sub>4</sub>F-activated process yielded the maximum coating growth compared to other activators under identical processing conditions. Equation 10 was found to be valid in the temperature range of 800-1200°C and the inter-relation between the coating thickness (h, in microns), siliconizing temperature (T, in degrees Kelvin), time (t, in hours), pack Si content ( $W_{Si}$  in weight percent), and NH<sub>4</sub>F activator content up to 10% ( $W_{\rm NH_4F}$ , in weight percent) can be given by  $h = 984.89T^{-1/2}W_{\text{Si}}^{1/2}W_{\text{NH}_4}Ft^{1/2}$  $\exp(-5781.2/T).$ 

The pack composition for growing Mo(Si,Al)<sub>2</sub> coating of sufficient thickness at 1100°C was found to be 10Si-10Al-20NH<sub>4</sub>F-60Al<sub>2</sub>O<sub>3</sub>. Both the diffusion-controlled silicide and alumino-silicide coating growth processes obeyed the lin-ear relationship between h and  $t^{1/2}$  at constant processing temperature (1100°C).

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