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Microstructures and Oxidation Behavior According to Nb:Mo Ratio in a Nb–Mo–Si System with Si Pack Cementation Coatings

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Abstract: Research is being conducted on Mo- and Nb-based alloys that are used in the aerospace sector, including those used for advanced gas turbines and aircraft engines. There is a limit to using Mo, which has a high density among refractory metals, and a few studies exist describing the addition of Nb to Mo–silicide alloys. There is a lack of guidance research on the basic Nb:Mo ratio of alloys, and it is necessary to study how to improve oxidation resistance. Therefore, this study aims to improve oxidation resistance by controlling the ratio of Nb and Mo in $(\text{Nb}_x, \text{Mo}_y)\text{Si}_2$ coating layers with Si pack cementation coatings on Nb–Mo alloys. Static oxidation tests were carried out at 1200 °C for 6 h to confirm the oxidation characteristics. As a result, a SiO_2 or $\text{SiO}_2 + \text{Nb}_2\text{O}_5$ ceramic protective layer was formed on the surface. After the oxidation tests, alloys with a Nb content of less than 35 at.% were found to protect the surface. The ratios of Nb and Mo in the Nb–Mo alloy and silicide coating layer were compared, and the improvement of oxidation resistance is discussed in terms of microstructural evolution.

Keywords: coatings; oxidation; SEM

1. Introduction

In recent years, next-generation technology has become preoccupied with eco-friendly and economic factors, and many studies in various fields have focused on improving efficiency. Typically, the aerospace industry focuses on engine efficiency, including advanced gas turbines and aircraft engines [1,2]. Among the methods of improving the efficiency of an engine, much research has been conducted on increasing the operating temperatures of materials [1,2]. When selecting a new high temperature material, various factors such as melting point, density and oxidation resistance should be considered. For example, Ni-based Haynes 230 and/or Inconel 718 alloys, which have been used as turbine engine materials for decades, have an operating temperature below ~1100 °C [3]. However, by reaching a service temperature of ~1300 °C without a cooling system, the output power of an engine can be improved by about 50%. In this regard, Mo-based alloys have been considered as alternatives [2]. Many studies have been conducted on high-temperature alloys with designs that can enhance the material properties [4–8]. For example, it has been documented that Mo–Si–B alloys showed excellent high temperature strength. Much research has been carried out on Mo–Si–B alloys of Mo_3Si (A15) + Mo (ss) + Mo_5SiB_2 (T2) phases by adding Si and B to the ductile Mo component to increase strength at high temperatures [2,9–11]. While Mo-based alloys showed excellent mechanical properties, attempts were made to lower their densities. One route for adjusting density was to design Mo–Nb-based alloys, since the density of Nb is lower than that of Mo. Research has been

conducted on Nb–Mo-based alloys with lowered densities and improved mechanical properties at room temperature [12,13]. K. Chattopadhyay et al. investigated the microstructure and mechanical properties of Nb–Si–B alloys [14]. N. Takata et al. investigated the microstructures of Nb–Mo–Si–B alloys in Bcc/T1/T2 three phases by fixing the Nb content at 32.6 at.% and then adjusting the Si and B contents [15]. J.M. Byun et al. tried to improve the mechanical properties by adding Nb to a Mo–Si–B alloy with powder metallurgy, and compared the manufactured Nb–Mo–Si–B alloy with a Mo–Si–B counterpart [13].

While they have high melting points and excellent strength at high temperatures [2,12,13,16], the alloys are known to show serious defects upon exposure to high temperatures under ambient atmosphere [4,16,17]. For Mo-based alloys, the Mo component is known to have poor oxidation resistance as a result of the formation of volatile oxides MoO_3 (g) at temperatures above about 500 °C [16–19]. When Mo-based alloys were exposed to high temperatures in air, they usually disintegrated. For Mo–Si–B alloys, while the oxidation behavior is enhanced due to the formation of borosilicate, the surface still needs protection. In addition, Nb-based alloys also have been reported to have poor oxidation behavior due to Nb_2O_5 (s) oxides having non-protective properties at high temperatures, and because oxidation rapidly forms porous layers instead of continuous oxide layers [20–22]. In order to enhance the oxidation behavior, many studies have been reported, such as pack cementation, spray coatings, plasma coatings, etc. [16,23,24]. Among the examined coating routes, pack cementation processing appears to be an effective manner to produce oxidation resistant coatings. The pack cementation process can provide mass production and ensure high bond strength between the coating materials and substrates. Further, complex-shaped component parts can be uniformly coated, since the coating method adopts gas diffusion to substrates [16].

A number of studies have been conducted to improve oxidation resistance by forming SiO_2 or Al_2O_3 oxide on the surface in a high temperature oxidation environment with pack cementation coatings [16,17,20,21,25]. K. Choi et al. discussed the growth and oxidation behavior of coating layers after Si pack cementation coatings on Mo–3Si–1B (wt.%) alloys [16]. K. Choi et al. also investigated the oxidation behavior under the condition of 1350 °C after forming a MoSi_2 -silicide layer on the surface of TZM alloys. In addition, the oxidation behavior was discussed in terms of the diffusion pathway and microstructure changes in the Mo–Si–O system [17]. J. Cheng et al. investigated the microstructures and oxidation behavior of the coating layers at 1100 °C after forming silicide layers in Nb–Si–B alloys [20,21]. Y. Liu et al. investigated the oxidation behavior in terms of microstructures by controlling the Nb:Mo ratio in the Nb–Mo–Si–B system [26].

It has been reported that after pack cementation coatings, the oxidation resistance increased for Mo-based alloys at high temperatures. For example, when Mo–Si–B alloys were coated via a Si pack cementation process, a MoSi_2 layer was produced at the surface, and the coated alloy showed excellent oxidation resistance up to about 1400 °C. At the same time, when Nb–Si–B alloys were Si pack coated, the NbSi_2 layer was produced at the surface. It should be noted that the oxidation resistance of the coated NbSi_2 layer was not excellent due to the formation of non-protective oxides, indicating that an optimum composition of the coated layer should be determined. Further, since the surface coating layer of (Mo or Nb) Si_2 is directly affected by the substrate composition, various substrate compositions should be investigated; this is the primary objective of this study.

In this study, in order to identify the optimal composition for the coating layer, various Mo–Nb alloys which directly affect the surface coating layer were investigated. After Si pack cementation coatings were applied to Nb–Mo alloys, oxidation resistance at 1200 °C (that is, a higher temperature than that previously reported for the oxidation limits of NbSi_2 -coated alloys) was investigated from the viewpoint of microstructures. Based on the results, we offer guidelines for the appropriate Nb:Mo ratio of substrates for potential Mo and Nb-based alloys at 1200 °C.

2. Experimental Details

The alloys were prepared by arc-melting using a tungsten electrode under an Ar atmosphere with six compositions in the Nb–Mo system. Table 1 shows the compositions of the alloys. Prior to coating the samples, each sliced piece was polished with SiC paper and then ultrasonically cleaned. For the Si pack cementation coatings, three powders of Si, NaF, and Al₂O₃ were prepared. The weight ratio of the powder mixture was selected as 25Si–5NaF–70Al₂O₃ (wt.%). Then, the powder was mixed together and dried for 24 h at 70 °C. The sliced alloy piece embedded in the mixed powder were placed in alumina crucibles and sealed with alumina-based ceramic bonds. The sealed alumina crucibles were dried at room temperature for 24 h, then placed in a furnace and annealed at 1100 °C for 24 h under an Ar atmosphere. A more detailed description of the specimen preparation procedure is given elsewhere [16]. The temperature of the furnace was raised at a rate of 5 °C/min and then held for the desired time. After heat treatment, the alumina crucibles were cooled to room temperature in the furnace.

Isothermal static oxidation tests to examine the oxidation behavior of the coating layer were carried out for 6 h at a temperature of 1200 °C in air. When the desired oxidation time was reached, the specimen was pulled out the furnace and air cooled. After the oxidation tests, the samples were polished with SiC paper and then polished with 0.5 µm Al₂O₃ powder. In order to observe microstructural changes, scanning electron microscope (SEM, Hitachi SU5000, Ibaraki, Japan) was used, and energy-dispersive X-ray spectroscopy (EDS) (NanoAnalysis, High Wycombe, UK) was used for composition measurements. For phase analysis, X-ray diffraction (XRD, Rigaku, Akishima, Japan) was performed for the specimens without polishing (after coatings and after oxidation).

Table 1. Chemical composition of arc-melted Nb_xMo_y alloys (at.%).

Element.	Nb (at.%)	Mo (at.%)
Alloy 1	100	0
Alloy 2	73.6	26.4
Alloy 3	51.2	48.8
Alloy 4	35.1	64.9
Alloy 5	25.7	74.3
Alloy 6	0	100

3. Results and Discussion

Each Nb_xMo_y alloy prepared by arc-melting was identified by EDS analysis to determine the atomic percentage of the compositions (in Table 1). Figure 1 shows the results of the XRD patterns of the fabricated Nb_xMo_y alloys. Figure 1 shows the XRD results of Alloy 1 (Nb), Alloy 2 (Nb_{73.6}Mo_{26.4}), Alloy 3 (Nb_{51.2}Mo_{48.8}), Alloy 4 (Nb_{35.1}Mo_{64.9}), Alloy 5 (Nb_{25.7}Mo_{74.3}), and Alloy 6 (Mo), respectively. As the Mo content increases, the XRD peak shifts to the right. It appears that the peak shift is a well-known effect which occurs due to lattice parameter difference. While an analysis of the peak shift is needed, a detailed analysis will be shown elsewhere.

Figure 1. XRD patterns of the as-cast Nb–Mo alloys with the compositions of (a) Alloy 1 (Nb), (b) Alloy 2 (Nb_{73.6}Mo_{26.4}), (c) Alloy 3 (Nb_{51.2}Mo_{48.8}), (d) Alloy 4 (Nb_{35.1}Mo_{64.9}), (e) Alloy 5 (Nb_{25.7}Mo_{74.3}), and (f) Alloy 6 (Mo).

Figure 2 shows SEM BSE images of a cross section of the Si-coated Nb_xMo_y alloys heated at 1100 °C for 24 h. When the substrate was pure Nb (Figure 2a), the coated layer was identified as NbSi₂ with a thickness of ~27 μm; another coated layer was identified as MoSi₂ with a thickness of ~39 μm at the surface (Figure 2f). However, when the composition of the substrate was changed, the coating layer composition was different. For the Nb–Mo alloys (Alloys 2, 3, 4, and 5), a mixture of Nb and Mo silicide was identified, i.e., (Nb_x, Mo_y)Si₂. Furthermore, another (Nb_x, Mo_y)₅Si₃ layer formed between the substrate and the outer (Nb_x, Mo_y)Si₂. Notably, in Alloy 3 (Nb_{51.2}Mo_{48.8}), Alloy 4 (Nb_{35.1}Mo_{64.9}), and Alloy 5 (Nb_{25.7}Mo_{74.3}), the (Nb_x, Mo_y)₅Si₃ phases were distributed in the (Nb_x, Mo_y)Si₂ layer. The (Nb_x, Mo_y)₅Si₃ phases of Alloy 5 (Nb_{25.7}Mo_{74.3}) were generally distributed, but the (Nb_x, Mo_y)₅Si₃ phases of Alloy 3 (Nb_{51.2}Mo_{48.8}) and Alloy 4 (Nb_{35.1}Mo_{64.9}) were distributed close to the substrate.

In fact, since the outer coating layer is significant for surface protection during oxidant exposure, the outer (Nb_x, Mo_y)Si₂ layer was specially focused. Table 2 shows the results of the EDS measurements of the outer (Nb_x, Mo_y)Si₂ coating layer. The Nb:Mo ratio in the (Nb_x, Mo_y)Si₂ layer is shown for the Si-pack-coated alloys. The EDS measurements of the NbSi₂ coating layer in Figure 2a and the MoSi₂ coating layer in Figure 2f were confirmed to be about Nb:Si = 34.8:65.2 (at.%) and about Mo: Si = 35.3:64.7 (at.%), respectively. Also, the EDS measurements of the (Nb_x, Mo_y)Si₂ coating layers in Figure 2b–e were confirmed to be about Nb:Mo:Si = 26.9:8.5:64.6 (at.%), 18.9:16.4:64.7 (at.%), 12.5:23.1:64.4 (at.%), and 9.0:27.4:63.6 (at.%), respectively. Additionally, the Nb:Mo ratios in the silicide coating layers of each specimen were about 100.0/0, 76.0/24, 53.5/46.5, 34.8/64.2, 24.8/75.2, and 0/100.0 (at.%), indicating that the outer coating layer may be expressed as (Nb_x, Mo_y)Si₂.

Table 2. EDS results of the $(\text{Nb}_x, \text{Mo}_y)\text{Si}_2$ coating layer of Si-pack-coated Nb_xMo_y alloys (at.%).

Element	Nb (at.%)	Mo (at.%)	Si (at.%)
Alloy 1	34.8	0	65.2
Alloy 2	26.9	8.5	64.6
Alloy 3	18.9	16.4	64.7
Alloy 4	12.5	23.1	64.4
Alloy 5	9.0	27.4	63.6
Alloy 6	0	35.3	64.7

Figure 2. SEM BSE image of cross sections of Si-pack-coated specimens at 1100 °C for 24 h showing the formation of $(\text{Nb}_x, \text{Mo}_y)\text{Si}_2$ and $(\text{Nb}_x, \text{Mo}_y)_5\text{Si}_3$ coating layers on the surface with substrate compositions of (a) Alloy 1 (Nb), (b) Alloy 2 ($\text{Nb}_{73.6}\text{Mo}_{26.4}$), (c) Alloy 3 ($\text{Nb}_{51.2}\text{Mo}_{48.8}$), (d) Alloy 4 ($\text{Nb}_{35.1}\text{Mo}_{64.9}$), (e) Alloy 5 ($\text{Nb}_{25.7}\text{Mo}_{74.3}$), and (f) Alloy 6 (Mo).

Figure 3 shows the compositions of the substrates and the coated layer marked in the Nb–Mo–Si ternary phase diagram. Since the isothermal diagram was reported only both at 800 °C and 1300 °C, a schematic isothermal phase diagram was presented to show the locations of the present alloy compositions and the coated layer compositions. The dotted arrows do not show a real diffusion pathway, but indicate that the coated layer compositions are closely related to the substrate compositions. As shown in Figure 3, the coated layer of $(\text{Nb}_x, \text{Mo}_y)\text{Si}_2$ was changed with respect to the substrate compositions. It should be noted that the absence of the $(\text{Nb}_x, \text{Mo}_y)_5\text{Si}_3$ phase in some alloys is possibly due to nucleation difficulties of resolution limitation, as indicated in previous papers [2,16]. Again,

the dots in the phase diagram are from the EDS measurements from Tables 1 and 2. In turn, the present observations can be used in the design of coating layers with control of the substrate.

Figure 3. Schematic diagram of Nb–Mo–Si ternary phase diagram showing EDS measurements of substrates and coated layers. The points corresponding to the Nb–Mo–Si ratio of the Si-pack-coated Nb_xMo_y alloys are shown in the Nb–Mo–Si systems with the compositions of (a) Alloy 1 (Nb), (b) Alloy 2 ($\text{Nb}_{73.6}\text{Mo}_{26.4}$), (c) Alloy 3 ($\text{Nb}_{51.2}\text{Mo}_{48.8}$), (d) Alloy 4 ($\text{Nb}_{35.1}\text{Mo}_{64.9}$), (e) Alloy 5 ($\text{Nb}_{25.7}\text{Mo}_{74.3}$), and (f) Alloy 6 (Mo).

Figure 4 shows the XRD patterns of Si-pack-coated specimens at 1100 °C for 24 h. When the alloy composition of Nb increased from 100 to 0 weight percent, the peak was changed. For example, with Alloy 1 (Nb), only NbSi_2 peaks were observed. With Alloy 6 (Mo), only MoSi_2 peaks were identified. However, when the substrate composition was between Nb and Mo, peaks of the $(\text{Nb}_x, \text{Mo}_y)\text{Si}_2$ and $(\text{Nb}_x, \text{Mo}_y)_5\text{Si}_3$ phase layers were detected. Further analysis will be given elsewhere.

As mentioned, Nb-based alloys and/or NbSi_2 -coated Nb-based alloys do not maintain their original shape during oxidation exposure at 1200 °C [21], in contrast to MoSi_2 -coated Mo-based alloys [16]. In order to examine the oxidation resistance, oxidation tests were carried out at 1200 °C. Figure 5 shows the appearance of the Si-pack-coated specimens before and after the oxidation tests at 1200 °C for 6 h. After the oxidation tests, the Si-pack-coated Alloy 1 (Nb) and Alloy 2 ($\text{Nb}_{73.6}\text{Mo}_{26.4}$) appeared to be white due to the formation of $\text{SiO}_2 + \text{Nb}_2\text{O}_5$ on the surface. Notably, the surface oxide was peeled off from the surface, showing serious defects. Also, it can be seen that Alloy 3 ($\text{Nb}_{51.2}\text{Mo}_{48.8}$) shows cracks on the surface after oxidation tests, and is not smooth, indicating that Alloy 1 (Nb), Alloy 2 ($\text{Nb}_{73.6}\text{Mo}_{26.4}$), and Alloy 3 ($\text{Nb}_{51.2}\text{Mo}_{48.8}$) do not show oxidation stability. However, it was noted that Alloy 4 ($\text{Nb}_{35.1}\text{Mo}_{64.9}$), Alloy 5 ($\text{Nb}_{25.7}\text{Mo}_{74.3}$), and Alloy 6 (Mo) show no changes in appearance, because the surface is protected by the formation of a stable SiO_2 protective layer.

Figure 4. XRD patterns of Si-pack-coated specimens at 1100 °C for 24 h with the compositions of (a) Alloy 1 (Nb), (b) Alloy 2 (Nb_{73.6}Mo_{26.4}), (c) Alloy 3 (Nb_{51.2}Mo_{48.8}), (d) Alloy 4 (Nb_{35.1}Mo_{64.9}), (e) Alloy 5 (Nb_{25.7}Mo_{74.3}), and (f) Alloy 6 (Mo).

Figure 5. Images of Si-pack-coated specimens before and after oxidation tests at 1200 °C for 6 h.

Figure 6 shows SEM BSE images of the surface of the Si-pack-coated Nb_xMo_y alloys after the oxidation tests at 1200 °C for 6 h. Regarding the pure Nb and pure Mo substrates, Figure 6a,f show SEM BSE images of the surface of the coated Alloy 1 (Nb) and Alloy 6 (Mo) after the oxidation tests, respectively. The phase sequence was identified as SiO₂+Nb oxide for the coated Alloy 1 (Nb) and SiO₂+Mo oxide for the coated Alloy 6 (Mo), respectively. Figure 6b–e show SEM BSE images of the surface of the coated Alloy 2 (Nb_{73.6}Mo_{26.4}), Alloy 3 (Nb_{51.2}Mo_{48.8}), Alloy 4 (Nb_{35.1}Mo_{64.9}), and Alloy 5 (Nb_{25.7}Mo_{74.3}) after the oxidation tests. Different from Figure 6a,f, mixed oxides of SiO₂ and Nb₂O₅ with some Mo content were produced at the surface for the alloys of Alloy 2 (Nb_{73.6}Mo_{26.4}), Alloy 3 (Nb_{51.2}Mo_{48.8}), Alloy 4 (Nb_{35.1}Mo_{64.9}), and Alloy 5 (Nb_{25.7}Mo_{74.3}) as shown Figure 6b–e.

Figure 6. SEM image of the surface of Si-pack-coated specimens after oxidation tests at 1200 °C for 6 h with substrate compositions of (a) Alloy 1 (Nb), (b) Alloy 2 (Nb_{73.6}Mo_{26.4}), (c) Alloy 3 (Nb_{51.2}Mo_{48.8}), (d) Alloy 4 (Nb_{35.1}Mo_{64.9}), (e) Alloy 5 (Nb_{25.7}Mo_{74.3}), and (f) Alloy 6 (Mo).

Figure 7 shows SEM BSE images of a cross section of the Si-pack-coated Nb_xMo_y alloys after the oxidation tests at 1200 °C for 6 h. Figure 7a,f show SEM BSE images of cross sections of the coated Alloy 1 (Nb) and Alloy 6 (Mo) after oxidation tests, consisting of several layers. The phase sequence was identified as SiO₂ + Nb₂O₅/NbSi₂/Nb₅Si₃/Nb for the coated Alloy 1 (Nb) and SiO₂/MoSi₂/Mo₅Si₃/Mo for the coated Alloy 6 (Mo). In the case of the coated Alloy 1 (Nb), a Nb₅Si₃ phase was also formed as a layer with a thickness of about 10 µm between the NbSi₂ layer and the substrate. Similarly, the Mo₅Si₃ layer in the coated Alloy 6 (Mo) was also formed with a thickness of about 17 µm between the MoSi₂ layer and the substrate.

Figure 7b–e show SEM BSE images of cross sections of the coated Alloy 2 (Nb_{73.6}Mo_{26.4}), Alloy 3 (Nb_{51.2}Mo_{48.8}), Alloy 4 (Nb_{35.1}Mo_{64.9}), and Alloy 5 (Nb_{25.7}Mo_{74.3}) after the oxidation tests. Generally, the layer sequence was observed as an oxide layer/(Nb, Mo)Si₂/(Nb, Mo)₅Si₃/substrate after the oxidation tests; the (Nb_x, Mo_y)₅Si₃ layer was thicker than before the oxidation tests. In Figure 7a–c, some surface pores were found in the SiO₂ oxide layer, indicating that the surface oxide was unprotected. However, Alloy 4 (Nb_{35.1}Mo_{64.9}), which has a higher Mo content than Alloy 3 (Nb_{51.2}Mo_{48.8}), was well protected by a SiO₂ protective layer, indicating that the outer coating layer composition originating from substrates is a critical factor for the protection of the substrate.

Figure 7. SEM BSE image of cross section of Si-pack-coated specimens after oxidation tests at 1200 °C for 6 h with substrate compositions of (a) Alloy 1 (Nb), (b) Alloy 2 (Nb_{73.6}Mo_{26.4}), (c) Alloy 3 (Nb_{51.2}Mo_{48.8}), (d) Alloy 4 (Nb_{35.1}Mo_{64.9}), (e) Alloy 5 (Nb_{25.7}Mo_{74.3}), and (f) Alloy 6 (Mo).

In order to examine the surface oxides after the oxidation tests, XRD was carried out for all of the coated alloys. Figure 8 shows the XRD patterns of the Si-pack-coated specimens after oxidation tests at 1200 °C for 6 h. As shown in Figure 8a, SiO₂ and Nb₂O₅ phases were observed when the content of Nb was increased in the Nb–Mo alloys.

Figure 8. XRD patterns of Si-coated specimens after oxidation tests at 1200 °C for 6 h with substrate compositions of (a) Alloy 1 (Nb), (b) Alloy 2 (Nb_{73.6}Mo_{26.4}), (c) Alloy 3 (Nb_{51.2}Mo_{48.8}), (d) Alloy 4 (Nb_{35.1}Mo_{64.9}), (e) Alloy 5 (Nb_{25.7}Mo_{74.3}), and (f) Alloy 6 (Mo).

The weight changes after the oxidation tests with and without coatings are shown in Figure 9. When the specimens were not coated, about a 50 % specific weight change was observed after oxidation. However, the coated specimens did not show any abrupt weight changes after oxidation for any of the alloys, as shown in Figure 9. It should be noted that for Alloy 1 (Nb), Alloy 2 (Nb_{73.6}Mo_{26.4}), and Alloy 3 (Nb_{51.2}Mo_{48.8}), the oxides were composed of mainly SiO₂ + Nb₂O₅. When the substrate was alloys of Alloy 4 (Nb_{35.1}Mo_{64.9}), Alloy 5 (Nb_{25.7}Mo_{74.3}), and Alloy 6 (Mo), the surface oxides were mainly SiO₂ with some Mo oxides. As shown in Figure 5, after oxidation, the surface roughness increased for the coated pure Nb and Nb-rich alloys, indicating that specific weight changes do not directly indicate the soundness of the alloys. Regarding this relationship, the oxidation of the coated surface (Nb_x, Mo_y)Si₂ layers often undergoes a weight increase due to oxide formation at the surface, together with a weight reduction due to sublimation and/or pore formation, which affects weight changes after oxidation. Further investigation will be reported in order to identify structural evolution upon long-term exposure to high temperatures.

Figure 10 is a schematic illustration of the oxidation behavior of the coated Nb_xMo_y alloys at 1200 °C. For Alloy 1 (Nb), Alloy 2 (Nb_{73.6}Mo_{26.4}), and Alloy 3 (Nb_{51.2}Mo_{48.8}), a thick layer of SiO₂+Nb₂O₅ formed on the surface, resulting from the oxidation of NbSi₂. Nb₂O₅ is well known as a non-protective layer. The oxide produces pores when it forms at high temperatures, resulting in the severe damage that was observed for the Nb-based alloys (Figure 10a). Figure 10b is a schematic diagram showing the oxidation behavior of coated Alloy 4 (Nb_{35.1}Mo_{64.9}) and Alloy 5 (Nb_{25.7}Mo_{74.3}) after oxidation tests. Since the Nb content is relatively low, the Si in the (Nb, Mo)Si₂ layer reacted during oxidation to form a SiO₂ oxide layer on the surface to suppress further oxidation. When the alloy is exposed to air at high temperatures, the produced (Nb, Mo)Si₂ and (Nb, Mo)₅Si₃ coating layer protects the substrate. Figure 10c is a schematic diagram showing the oxidation behavior of the coated Mo alloy after oxidation tests. A thin layer of SiO₂ oxide formed on the surface, where the MoSi₂ and Mo₅Si₃ phases formed. In addition, as Si diffuses outward, the thickness of Mo₅Si₃ phase increases.

Figure 9. Specific weight of uncoated and coated specimens with respected to alloy compositions of (a) Alloy 1 (Nb), (b) Alloy 2 (Nb_{73.6}Mo_{26.4}), (c) Alloy 3 (Nb_{51.2}Mo_{48.8}), (d) Alloy 4 (Nb_{35.1}Mo_{64.9}), (e) Alloy 5 (Nb_{25.7}Mo_{74.3}), and (f) Alloy 6 (Mo).

Figure 10. Schematic diagram of oxidation behavior of Si-pack-coated (a) Alloy 1 (Nb), Alloy 2 (Nb_{73.6}Mo_{26.4}) and Alloy 3 (Nb_{51.2}Mo_{48.8}), (b) Alloy 4 (Nb_{35.1}Mo_{64.9}) and Alloy 5 (Nb_{25.7}Mo_{74.3}), and (c) Alloy 6 (Mo) after oxidation tests at 1200 °C.

It has been documented that Nb alloys usually do not have oxidation resistance at 1200 °C due to the formation of porous oxide phases of $\text{SiO}_2 + \text{Nb}_2\text{O}_5$. Severe oxidation behavior occurs when the substrate is even coated with NbSi_2 . However, the present results show that when a certain amount of Mo is present in the NbSi_2 layer, the surface $(\text{Nb}, \text{Mo})\text{Si}_2$ layer protects the substrate. While further investigation and phase analyses are needed, the present study clearly shows that an appropriate amount of Mo and Nb in the Nb_xMo_y substrates can protect the Si-pack-coated substrate at high-temperature exposure under an ambient atmosphere.

4. Conclusions

Refractory alloys, including Nb and Mo, are among the candidates for use in high temperature materials. While Mo-based alloys have better oxidation resistance at higher temperatures than Nb-based alloys, a high density of Mo often limits their application, resulting in the need for an optimum composition of Nb with Mo for high temperature applications. This study investigated the effect of oxidation behavior for silicide-coated alloys with various Nb/Mo compositions (Nb_xMo_y alloys). It was noted that the coating layer composition was significantly related to the substrate composition. With Si pack cementation coatings at 1100 °C for 24 h, NbSi_2 , $(\text{Nb}_x, \text{Mo}_y)\text{Si}_2$ + $(\text{Nb}_x, \text{Mo}_y)_5\text{Si}_3$, and MoSi_2 coating layers formed with respect to the substrate alloy compositions. In order

to examine the oxidation resistance, isothermal oxidation tests were carried out at 1200 °C for 6 h. When the composition of Nb was up to 50 at.%, the silicide layer did not protect the substrate due to the formation of porous SiO₂ with Nb₂O₅ oxides. However, when the composition of Nb in the substrate was lower than 35 at%, the silicide-coated substrates were successfully protected at 1200 °C. The present observations show that the Nb_xMo_y substrate compositions for retaining the oxidation resistance require a Mo content of at least Nb₃₅Mo₆₅ or higher for silicide pack coatings.

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