Original Article

Short-term oxidation response of Nb–15Re–15Si–10Cr–20Mo alloy

Ruth Melody Dasary, Shailendra Kumar Varma*

Department of Metallurgical and Materials Engineering, University of Texas, El Paso, TX, United States

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The Nb–15Re–15Si–10Cr–20Mo alloy was subjected to 24 h of air exposure in a temperature range from 700 to 1400 °C. Re addition to the Nb–Si–Cr–Mo alloy has been found to control the pesting at lower temperatures and spalling at higher temperatures. The curve in a graph of weight gain per unit area as a function of temperature was used to determine the oxidation resistance. Re, Si formation around a solid solution phase reduces the infusion of oxygen into the metal, controlling the kinetics of the alloy system. Oxidation characterization was carried out using XRD and back scattered imaging, EDS, and X-ray mapping modes on the SEM. Mo addition promotes the formation of oxidation resistance Nb3Si2.

Keywords: Oxidation, Niobium, Rhenium, Molybdenum, High temperature phases

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1. Introduction

Numerous studies have been conducted to challenge the existing alloy systems to provide better oxidation resistance at elevated temperatures. Niobium was chosen as the base metal due to its low density and high melting point. However, one of the major drawbacks is the poor oxidation resistance of Nb. Therefore, alloying elements are added to Niobium not only to improve the oxidation resistance at high temperatures but also to impart properties such as high temperature strength, and creep for applications such as aircraft engines, missiles and turbines [1,2].

Previous studies have shown that minor quantities of addition of alloying elements such as Hf, Cr, Si, Ti, Al, Re to produce “RMIC’s” – refractory metal inter-metallic composites, contain multiple phases including silicides. The microstructure of these alloys consists of Nb solid solution, Laves phases (NbCr2) and many other highly desirable silicides. The alpha solid solution imparts ductility to the alloy and silicides help to resist oxidation and improve strength at higher temperatures [2–4].

Cr and Si can provide the basic oxidation protection criteria for the development of Nb alloys. Highly desirable NbSiCr4, Nb5Si3Cr and Nb5Si3Cr4 matrices for the oxidation resistance up to 1300 °C have been used in several studies [5,6]. One the most desirable oxide, CrNbO4, was formed in combination with Nb2O5 during the oxidation of such alloys. Mo, Cr and Si are the alloying elements promoting the formation of oxides such as SiO2 and CrNbO4 in preference to Nb2O5 [7].

Gokhale and Abbaspian [8] investigated Re–Si phase equilibrium, which was modified by Knapton [9] and again later...
on by Jordà et al. [10] whose work is considered to be the most reliable. The system has been characterized by the following key features:

(a) Monoclinic intermetallic \( \text{Re}_2\text{Si} \), richest in Re out of the other Re silicides, melts at 1810 °C [10–13].
(b) Cubic intermetallic \( \text{ReSi} \) is a high-temperature phase that forms peritectically at 1820 ± 10 °C and decomposes eutectoidally at 1650 °C [10–13].
(c) Tetragonal intermetallic \( \text{ReSi}_{1.8} \) melts at 1940 °C.

All three intermetallics appear to be nearly stoichiometric, with homogeneity ranges of less than 1.5 atomic percentage of Si [10–13].

Addition of Re forms a Re silicide rich layer, which acts as a protective phase at high temperature. Often Re is added to achieve “The Rhenium Effect”, which is defined as contribution to an overall improvement of strength, plasticity, weldability, lower ductile to brittle transition temperature and reduced degree of recrystallization embrittlement [11]. Generalized conclusions cannot be made due to limited literature. The alloying elements used in this study were added to form the intermetallics such as \( \text{Mo}_3\text{Si}_2 \), \( \text{Nb}_3\text{Si}_3 \) in combination with \( \text{Re}_2\text{Si} \). Also, in addition, \( \text{SiO}_2 \) is formed and as a protective coating at higher temperatures. Thus the formation of the silicides is considered as the best way to avoid the formation of Nb oxides besides \( \text{CrNbO}_4 \) [1,8,5,13].

Of all the refractory metals, Nb and Mo have been considered as having the greatest potential for turbine applications [14–16]. Nb is inherently ductile at room temperature and has relatively low density of 8.56 g/cm³, while Mo has a higher density (10.2 g/cm³) and relatively low ductility at room temperature. Both Nb and Mo have wide solubility for a number of common alloying additions. But Nb and Mo have substantial oxidation limitations in their monolithic form. Their refractory metal-intermetallic composites (RMICs) depend on an intermetallic phase to provide the high-temperature oxidation resistance. For the high-temperature applications envisioned for the next advances in jet engines, Nb and Mo silicide based composites are considered to be the most likely candidates [6–10]. The melting points of the silicide-containing composites based on these systems are in excess of 1750 °C. Densities of the Nb-silicide based composites are in the range of 6.6–7.2 g/cm³, while for the Mo-RMICs, the range is 8.6–9.4 g/cm³ [14–16].

However, the objective is to not only promote the formation of intermetallic such as \( \text{Nb}_3\text{Si}_3 \) and \( \text{NbCr}_2 \) but also increase their phase fractions by adjusting the compositions of alloying elements such as Cr, Mo and Si [10,13]. The confrontation of the challenges in this study includes:

(a) To reduce the \( \alpha \) solid solution.
(b) To promote the formation of rhenium-silicide (Re_2Si) layer.
(c) To stabilize the microstructure.

The 3, 5 (\( \text{Nb}_5\text{Si}_3 \)) silicide phase is protected from oxidation in \( \text{Nb-Si-Mo} \) alloys [16–18]. The 3, 5 silicide is an intermetallic with 3 Si atoms and 5 metal atoms. Authors showed that the oxidation behavior was controlled at intermediate temperatures by the hypo- and hyper-eutectic character of the alloy due to the accelerated oxidation of large volume fractions of (\( \text{Nb-Mo}_2\)Si) in hypereutectic alloys. Molybdenum content increases the oxidation resistance by improving the sinterability of the oxide scale at 1000 °C which lowers porosity and reduces oxygen diffusion and increases the activity of silicon leading to the development of a layer of \( \text{SiO}_2 \). Also when Re is added to Mo the strength of the Mo matrix is increased. It is controlled by the cooling process especially for the silicide dispersions which can impart toughness to the material [16–20].

The oxidation behavior of Nb–15Re–15Si–10Cr–20Mo (at%) alloy has been reported in this paper. Effects of Rhenium addition as well as chromium content on the oxidation behavior in the temperature range between 700 and 1400 °C have been examined. Oxidation behavior was studied in air for periods of 24 h at selected temperatures. Isochronal experimental results and oxidation characterization by scanning electron microscopy (SEM) and X-ray diffraction (XRD) will be presented.

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Fig. 1 – Isothermal section of Nb–Re–Si–Cr–Mo (using PANDAT™).

Fig. 2 – As cast micrograph of the alloy.
2. Experimental details

Nb–15Re–15Si–10Cr–20Mo (in atomic percentages) alloy was fabricated by the Ames Laboratory of Iowa State University using an arc melting process in a high purity argon atmosphere. Button samples of alloy were melted several times to ensure homogeneity. The alloy samples were cut into 5 mm cubes using electric discharge machining (EDM). As-received samples were polished to a 600 grit finish to remove surface contamination from the machining process and then ultrasonically cleaned in methanol before oxidation experiments. Oxidation was carried out in standard lab air from 700 to 1400 °C. Programmed furnaces were used at a ramp rate of 10 °C/min and all samples were furnace cooled. They were weighed after cooled in furnace to room temperature. Static oxidation involved exposure at each temperature for 24 h using only one cycle of heating and cooling.

Oxidation products were characterized by XRD in a Bruker D8 Discovery using JCPDS data. Samples were mounted in an epoxy resin, sectioned, and polished to a 1200 grit finish to examine cross sections containing the scale. Oxide metal interfaces were characterized by secondary scanning electron microscopy imaging (SE), backscatter electron microscopy (BSE), Energy Dispersive X-ray Spectroscopy (EDS), and X-ray mapping in a Hitachi S-4800 UHR FE-SEM.

3. Results and discussion

Pandat™, a thermodynamic modeling software, developed by CompuTherm LLC, was utilized to study the isothermal sections for temperature range used in this study. The isothermal sections were calculated by holding Rhenium and Silicon content at 15 atomic percents shown in Fig. 1. Predicted microstructural components include: CrNbSi, sigma phase, α solid solution and Nb5Si3. However, the as-cast
microstructure of the alloy as shown in Fig. 2 depicts the presence of Re$_2$Si, (Nb,Mo)$_5$Si$_3$, NbCr$_2$ and α solid solution. Re$_2$Si is formed around the solid solution and is expected to prevent the infusion of oxygen when subjected to the oxidation process. The Laves phase was formed in limited amounts, on a relative scale, throughout the structure. The important aspect is to understand how rhenium silicide layer can act as a protective barrier preventing the diffusivity of oxygen into the metal. Elemental distribution was determined using X-ray mapping shown in Fig. 3 for the as cast structure.

Metallography was carried out on the metal remaining after oxidation to understand the formation of various phases. At 700 °C (Nb,Mo)$_5$Si$_3$, Re$_2$Si and Nb solid solution were formed and found to be present in equal proportions. There was no formation of Laves phase at this temperature. Starting from 800 °C, a decrease in the grain size of silicides and increase in the amount of Re$_2$Si around Nb solid solution was observed. Also an increase in the amounts Nb solid solution was noticed. NbCr$_2$ started to appear beyond 800 °C. An evolution of eutectic like microstructure has been observed at 1000 °C as shown in Fig. 4(d).

Fig. 4 – Microstructures of remaining metal (a) 700 °C, (b) 800 °C – showing solid solution in light gray area and 5, 3 silicides in dark gray regions, (c) 900 °C – showing solid solution, 5, 3 silicides and NbCr$_2$, medium gray regions, (d) 1000 °C – showing eutectic like microstructure, (e) 1100 °C, (f) 1200 °C, (g) 1300 °C, (h) 1400 °C – showing a eutectic microstructure of Re$_2$Si layer.
At 1100 °C a noticeable increase in Re₂Si and NbCr₂ is observed. The amount of 3, 5 silicides is found to decrease due to the formation of the eutectic structure. The same effect takes place at 1400 °C, but only in the Re₂Si layer surrounding the solid solution phase. At this temperature, the 3, 5 silicides might play a major role during oxidation, as the Re₂Si begins to diffuse toward the oxidized layer, to form rhenium-silicide rich zone. A magnified view of this zone in Fig. 5 shows the growth of eutectic structure.

The oxide-metal interfaces were studied for the alloy at all temperatures. Fig. 6 shows the microscopic images at (a) 700 °C, (b) 900 °C, (c) 1200 °C and (d) 1400 °C. The formation of allotropes of Nb₂O₅ has been observed depending on the oxidation temperature. The bulky base centered monoclinic (β) form was present at 700 and 800 °C and then replaced by monoclinic form at 900, 1000, 1100, 1200 °C which eventually converts to CrNbO₄ at 1300 °C and 1400 °C. The formation of bulky oxide form of Nb₂O₅ at all the temperatures can be attributed to the presence of relatively large amounts of solid solution in the alloy. The oxide at 700 °C consists of β-Nb₂O₅ and SiO₂. Although the β-Nb₂O₅ is converted into monoclinic Nb₂O₅ from 900 °C, it is speculated that the formation of monoclinic Nb₂O₅ occurs first followed by the formation of SiO₂ at the pore surface. At 1000 °C, CrNbO₄ begins to form in minimal amounts along with monoclinic Nb₂O₅ and SiO₂ as shown in Fig. 7. The identification
has been carried out by the combination of XRD and X-ray mapping procedures to show a difference between a pore and SiO₂ depositions. Due to the similarity in the contrast, difficulties were faced to confirm this point. However, as shown in Fig. 8(b) and (c), the SiO₂ particles exist very close to the pore area, in the very dark regions. The concentrations of Si and O, shown in Fig. 8(b) and (c) confirm this.

At 1200 °C a monoclinic form of Nb₂O₅ is present, along with CrNbO₄ and SiO₂. There was a greater amount of porosity in the oxide layer, compared to other oxide products at different temperatures of this study. Fig. 9 shows a micrograph of oxide layer at 1200 °C, emphasizing the growth of the CrNbO₄, SiO₂ and also the formation of the pores. An elemental distribution of the oxide layer shown in Fig. 10(a) clearly indicates that there are localized Nb₂O₅ oxide regions unlike oxide products at other temperatures. This can explain that as the temperatures increase the formation of Nb₂O₅ becomes localized, and eventually is replaced by CrNbO₄. This combination of three oxides, CrNbO₄, Nb₂O₅ and SiO₂ continues up to 1300 °C. An important point to note is that although the formation of CrNbO₄ starts to appear from 900 °C, it becomes more prominent from 1200 °C.

At 1400 °C the formation of an extended residual molybdenum oxide rich area is observed as shown in Fig. 11. This area also consists of evenly distributed CrNbO₄ matrix with localized regions of SiO₂ and Re₂Si. However, Re₂Si distributes itself uniformly as shown in Fig. 12(b). The uncharacteristic presence of SiO₂ (Fig. 12(e) and (f) respectively) shows confined concentrated points of Si and O. The maps point to the fact that CrNbO₄ is the most dominant oxide at this temperature. At this temperature also noticeable pores are formed, moving toward the CrNbO₄ region. The pores tend to dominate, as shown in Fig. 13. However, the CrNbO₄ zone does not consist of any pores.

The molybdenum oxide rich area is sandwiched between a thick layer of CrNbO₄ and a rhenium silicide rich (Re₂Si) zone. All the three layers were intact and the remaining metal was tightly encapsulated within. A series of micrographs are stitched to show a clear view of the formation of three distinct layers in Fig. 13. According to Chan [21] the oxidation resistance is improved by the formation CrNbO₄ alone rather than the formation of oxide combination. At 1000 and 1100 °C, the oxide was found to be very hard and brittle, causing the metal and oxide to scratch while polishing.
The Cr depleted layer was not observed in this alloy, as expected. The reason could be the low percentage of Cr addition in the alloy. The combination of CrNbO$_4$ and SiO$_2$ is considered to be advantageous, compared to Nb$_2$O$_5$, as the oxide layers prevent the diffusivity of the oxygen and lower the oxidation kinetics of the metal [21]. But large amounts of Nb$_2$O$_5$ often tend to form pores and thus increase the flow of oxygen, resulting in pesting at lower temperatures. Cracks formed between the oxide and the metal have been observed at all temperatures except 900 °C. This effect is usually the result of the mismatch of specific volumes and stresses brought on by the differences in the thermal expansion coefficients of oxides.

Oxide products were subjected to X-ray diffraction to characterize the oxide products formed as shown in Fig. 14. Trends of the samples vary accordingly between low (700–900 °C), mid (1000 and 1100 °C) and high temperature ranges (1200–1400 °C). Nb$_2$O$_5$ and SiO$_2$ have been detected, from 700 to 1300 °C at all temperatures. However the forms of Nb$_2$O$_5$ were different. At 900 °C, the set of Nb$_2$O$_5$ peaks seems to slightly shift to the left indicating the change in the form, compared to the peaks obtained at 700 °C. Also a noticeable increase in the intensity has been observed. At 900 °C, CrNbO$_4$ starts to form along with the formation of Nb$_2$O$_5$ and SiO$_2$. Molybdenum oxide rich zone (MoO$_3$ or other forms of MoO$_{2x}$) is present at 1400 °C.

The curve in Fig. 15 shows the weight gain per unit area as a function of oxidation temperature. This curve shows that there has been a negative weight loss throughout the temperature range from 700 to 1400 °C except at 1100 °C. The constant weight loss observed is due to the formation of volatile molybdenum trioxide MoO$_3$ (and/or various forms of MoO$_3$). Noticeable evidence from the crucibles was also detected, as the alumina crucibles changed their color to a greenish-blue, suggesting the escape of the oxide. The mass-gain at 1100 °C may be due to the formation of the bulky oxide which includes Nb$_2$O$_5$, CrNbO$_4$, and SiO$_2$. The surface of the oxide formed at this temperature is shown in Fig. 7 followed by its elemental X-ray mapping in Fig. 8. An estimated 75–90% of the metal was remaining after the samples were subjected to oxidation procedure. The metal-oxide interface was fairly intact at all temperatures, indicating good oxidation resistance.
Fig. 12 – Elemental analysis of oxide layer at 1400°C. Showing concentration of Nb in (a), Re in (b), Mo in (c), Cr in (d), Si in (e) and O (f) (in reference to Fig. 11).

Fig. 13 – Series of micrographs stitched to show a clear view of the formation of three distinct layers at 1400 °C. Encircled area is the zoomed part, used in Fig. 11.
The microconstituents observed in the as-cast structure were Nb$_{2}$s, (Nb, Mo)$_{3}$Si$_{3}$, Re$_{2}$Si and NbC$_{2}$. The Pandat$^\text{TM}$ predicts the formation of Nb, Nb$_{5}$Si$_{3}$, sigma-phase and CrNbSi. The difference in the microconstituents was observed.

The morphology of the phases for oxidized samples from 700 to 1300 $^\circ$C does not appear to change drastically. However, at 1400 $^\circ$C many locations of Re$_{2}$Si have been found to be transformed into a eutectic like structure.

Re$_{2}$Si provides a very good oxidation resistance except at 1400 $^\circ$C.

Base centered monoclinic form of Nb$_{2}$O$_{5}$ (bulky oxide), has been observed at 700 and 800 $^\circ$C.

The improved oxidation resistance of the alloy can be attributed to the formation of CrNbO$_{4}$ which starts to form at 900 $^\circ$C.

Mass loss at temperatures from 700 to 1000 $^\circ$C and 1200 to 1400 $^\circ$C is attributed to the formation of volatile molybdenum trioxides, and the weight gain at 1100 $^\circ$C is due to the formation of Nb$_{2}$O$_{5}$, SiO$_{2}$ and CrNbO$_{4}$. XRD and X-ray mapping confirm these observations.

**Conflicts of Interest**

The authors declare no conflicts of interest.

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**References**


