High Temperature Oxidation Behavior of Nb-20Mo-15Si-5B-20Cr Alloy

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HIGH TEMPERATURE OXIDATION BEHAVIOR OF Nb-20Mo-15Si-5B-20Cr ALLOY

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Dedicated to my parents, Raul & Rosa
and to my sisters, Grisel & Tania.
HIGH TEMPERATURE OXIDATION BEHAVIOR OF
Nb-20Mo-15Si-5B-20Cr ALLOY

By

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THESIS

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Special thanks to my co-workers, friends and family for their help, friendship and support. Thanks Pilar and Ben for sharing all your knowledge with me. Thanks to Karina and Lucet for their advice and guidance and to my sister Grisel for her constant motivation, and for helping me with the schematics. To my parents, Raul and Rosa; thanks for your guidance, advice, support, encouragement and for being my role models.
Materials for high temperature applications, such as jet engines, gas turbines and turbine blades, require a balanced combination of physical and chemical properties to withstand the aggressive environments in which they are utilized. Some of the properties required are high strength, low density, high melting point and good oxidation resistance at elevated temperatures [1-3]. For this reason, the microstructure and oxidation behavior of the Nb-20Mo-15Si-5B-20Cr alloy (at. %) has been studied as a potential candidate to replace nickel-based alloys currently used in the aerospace industry.

Short term oxidation (STO) and long term oxidation (LTO) studies have been performed in air for this alloy over a temperature range from $700^\circ$C to $1400^\circ$C, for 24 and 168 hours respectively. Oxidation curves for this alloy were obtained by plotting the mass gain per unit area as a function of temperature and time to determine its oxidation resistance. STO was temperature dependent and oxidation curve shows a minimum mass gain per unit area between 900 and 1000°C. LTO was time dependent and curves show a minimum mass gain at 1200 and 1300°C. Parabolic behavior was observed at those temperatures.

Microstructure of the alloy and oxidized products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). According to results, the microstructure is composed of body center cubic (BCC) solid solution ($\alpha$), tetragonal $\text{Nb}_5\text{Si}_3$, $\text{Nb}_3\text{Si}$, hexagonal Laves phase $\text{NbCr}_2$ and a eutectic like microconstituent $\alpha$, $\text{Nb}_3\text{Si}$ and $\text{NbCr}_2$. The oxidation products
at 700 to 1300°C show the presence of Nb$_2$O$_5$, SiO$_2$, CrNbO$_4$, among others. The parabolic and linear oxidation rate constants values indicate that the studied alloy is competitive when compared to the values for Nb-based alloys reported by different authors.
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CHAPTER 1

INTRODUCTION

Materials for high temperature applications, such as jet engines, gas turbines and turbine blades, require a balanced combination of mechanical and chemical properties to withstand the aggressive environments in which they are utilized. Some of the properties required are high strength, low density, high melting point and good oxidation resistance at elevated temperatures [1]. Currently, the aerospace industry utilizes nickel-based super alloys to manufacture these aircraft components. However, in past years, working temperatures of these engines have been increasing and they are approaching the limit of nickel-based superalloys (1150°C). For this reason, new metallic systems and alloys that can survive above the 1150°C are investigated [1-3].

Niobium silicide-based alloys are studied as potential candidates to replace nickel super alloys because of their high melting point (~1750°C), low density (6.6 to 7.2 g/cc) and high temperature strength [1,4] however their poor oxidation resistance at elevated temperatures prevents them use for various applications. Studies have shown that additions of alloying elements such as chromium, titanium, aluminum, molybdenum and hafnium to these alloys improve their oxidation resistance at temperatures up to 1300°C due to the formation of intermetallic phases [3, 5-8]. Among the alloying elements, Cr is the most promising because it promotes the formation of Laves phase NbCr$_2$ [1, 9-15].

The alloy considered in this study is the Nb-20Mo-15Si-5B-20Cr (composition given in atomic percent). The composition of the alloy was given by Naval Air Warfare Center and it relies on the basis for developing oxidation resistant microstructures. The
addition of silicon promotes the formation of niobium silicides Nb$_5$Si$_3$ and Nb$_3$Si while chromium provides the Laves phase NbCr$_2$ to the alloy. These additions improve the oxidation resistance of the alloy. Boron is added as a phase stabilizer. The addition of molybdenum strengthens the solid solution of niobium Nb$_{ss}$ and provides the tensile ductility and fracture resistance at room temperature to the alloy.

The purpose of this research is to study the oxidation behavior of the Nb-20Mo-15Si-5B-20Cr alloy in a temperature range from 700 to 1400°C. The effect of oxidation temperature and time has been studied as well as the effect of alloying elements during exposure. Previous research has been performed on Nb-W-Cr systems with B and C modifiers to understand the oxidation behavior of single-phase and two-phase ternary alloys. This study has a similar approach to study the oxidation behavior of a multi-phase niobium based alloy.
CHAPTER 2

BACKGROUND

2.1 Oxidation Principles

Engineering metals and alloys react chemically when exposed to air especially at high temperatures because the susceptibility of the metal to chemical attack increases with increasing temperature. The most common reactant is the air or oxygen, therefore this chemical reaction is called oxidation. Oxidation is defined as the interaction of the metal with the oxygen producing an oxide [16]. The oxidation mechanisms, which a metal or alloy can be subjected to, are as follows:

1. Metal surface adsorbs atomic oxygen.
2. Oxide nucleates at multiple sites that are thermodynamically favorable and grows to form a continuous film.
3. As the oxide layer grows it provides a protective scale that prevents the metal from further oxygen attack.
4. Growth stresses develop cracks and porosity in the oxide that modify the oxidation mechanism and may cause failure to protect the metal from the oxygen.

There are three main laws by which the metal or alloy oxidizes at high temperatures: linear, parabolic and logarithmic. At high temperatures, metals and alloys have a combination of linear and parabolic oxidations. Linear oxidation occurs when the metal’s surface is not protected by a layer of oxide; with prolonged time exposure the metal would continue to oxidize at a constant rate and it would never slow down causing
the destruction of the metal. Several factors cause linear oxidation: the formation of volatile or molten oxides, the spallation or breakaway of oxides due to growth and internal stresses or the growth of porous non protective oxide. Parabolic oxidation is controlled by the diffusion of atoms and the driving force is the chemical potential. If a compact oxide layer is formed and it continues to grow at prolonged time exposure, the diffusion distance of atoms increases causing a decrease in the diffusion rate. Most metals and alloys exhibit parabolic behavior at elevated temperatures. This type of oxidation is of great importance because the oxide growth occurs with a decreasing oxidation rate. Logarithmic behavior is observed at the initial stage of oxidation of metals at low temperatures, where a thin oxide layer is formed. It is characterized by a rapid rate of reaction at the beginning of the process followed by a decrease in rate or vice versa [16-18].

2.1.1 Protective Oxides and Oxide Volatilization

Oxide morphology depends on the environment, exposure time and composition of the metal or alloy. It is desirable to have a protective oxide that is adherent, slow forming and self-healing [18]. Some oxides have this protective nature, such as \( \text{Cr}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) because they are slow growing, dense and chemically stable. At temperatures up to \( \sim 1000^\circ \text{C} \) \( \text{Cr}_2\text{O}_3 \) is very stable and resists oxidation. At higher temperatures \( \text{Cr}_2\text{O}_3 \) transforms to \( \text{CrO}_3 \) and volatilizes [12, 13, 20-22]. However, it is been reported that the presence of \( \text{Cr}_2\text{O}_3 \) at \( 1100^\circ \text{C} \) occurs as a result of oxide entrapment in the oxide scale [9-11]. The volatilization of oxides is an important issue particularly at high temperatures. Molybdenum, tungsten and boron oxides are known
for their volatile behavior and low melting point. Molybdenum oxide MoO$_3$ sublimes at 704 °C and it starts to vaporize above 500 °C [18, 23]. Even though the presence of MoO$_3$ at higher temperatures is not expected, Semmel [24] observed the formation of MoO$_3$ in pure Mo oxidized from 900-1300 °C during the cooling period.

2.2 Refractory Metals and their Intermetallics

The refractory metals are characterized by the high strength of their interatomic bond which provides high melting point, mechanical strength and electrical resistance. Among them, niobium and molybdenum are the most promising refractory metals for high temperature applications. Niobium has a combination of high strength, ductility, low density and high melting point. Molybdenum also has high melting point, higher density, low coefficient of linear thermal expansion and good heat resistance [25]. Table 2.1 summarizes some of the physical properties for niobium and molybdenum.

<table>
<thead>
<tr>
<th>Property</th>
<th>Niobium</th>
<th>Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>BCC</td>
<td>BCC</td>
</tr>
<tr>
<td>Melting point, °C</td>
<td>2496</td>
<td>2623</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>8.57</td>
<td>10.2</td>
</tr>
<tr>
<td>Young's modulus, 10$^6$ psi</td>
<td>16</td>
<td>42</td>
</tr>
<tr>
<td>Coefficient of thermal expansion 10$^6$ /°C</td>
<td>7.1</td>
<td>5.4</td>
</tr>
<tr>
<td>Ductile-to-brittle transition temp, °C</td>
<td>-120</td>
<td>-20</td>
</tr>
</tbody>
</table>

However, both niobium and molybdenum exhibit poor oxidation at elevated temperatures in their monolithic form and they depend on their intermetallic phase to
improve the oxidation resistance [1, 2, 27]. Intermetallic compounds are usually stoichiometric; possess high strength and low deformability at low temperatures. Current efforts are focused in the development of multiphase niobium alloys with solid solutions and substantial amounts of refractory intermetallics such as niobium silicides (Nb$_3$Si, Nb$_5$Si$_3$), borosilicides (Mo$_5$SiB$_2$, Nb$_5$Si$_3$B$_2$) and Laves phase (NbCr$_2$) [12].

2.2.1 Solid Solutions

As mentioned before, alloys containing niobium silicides also contain solid solutions for toughness and ductility and intermetallics for oxidation resistance. When compared to other refractory metals, niobium retains its ductility even when it is highly alloyed with other metals and it is less susceptible to interstitial impurities. The strengthening of niobium alloys is due to the formation of substitutional solid solutions and studies show that at 1095°C the most effective strengthening elements are molybdenum, tungsten, vanadium, and zirconium [25].

2.2.2 Niobium Silicides, Nb$_5$Si$_3$ and Nb$_3$Si

The addition of silicon to niobium improves the creep and oxidation resistance at elevated temperatures, typical additions ranges from 12 to 25 at % [1, 2]. The principles for niobium silicide formation rely on the Nb-Si binary system shown in Figure 2.1. In this niobium rich portion there are five stable phases present: liquid (L), Nb, Nb$_3$Si, β-Nb$_5$Si$_3$ and α-Nb$_5$Si$_3$. At a composition of ~18 % Si Nb$_3$Si is formed by a eutectic reaction L$\leftrightarrow$Nb+Nb$_3$Si at 1932°C; this silicide has a tetragonal Ti$_3$P-type crystalline structure. With further cooling, α-Nb$_5$Si$_3$ is formed by a eutectoid reaction Nb$_3$Si$\leftrightarrow$Nb+
α-Nb₅Si₃ at 1700°C; α-Nb₅Si₃ has a tetragonal Cr₅Si₃-type crystalline structure. There is also third reaction Nb₅Si+β-Nb₅Si₃↔α-Nb₅Si₃ at 1946°C.

**Figure 2.1.** Binary phase diagram for Nb-Si system calculated using Pandat™ 8.1 software [28].

Silicides α-Nb₅Si₃ and β-Nb₅Si₃ have a tetragonal crystal structure. The differences between these two phases rely on their lattice parameters (α-Nb₅Si₃ a: 6.5698Å c: 11.887Å, β-Nb₅Si₃ a: 10.028Å c: 5.0698Å) and composition. However, the stoichiometry range for both phases is less certain [29, 30]. Nb₃Si has a tetragonal structure. The equilibrium microstructure of niobium-silicide based alloys consists of niobium solid solution and α-Nb₅Si₃. Several authors reported the presence of Nb₅Si
and $\beta$-Nb$_5$Si$_3$ in the as cast microstructure of alloys with 18 at.% Si [3, 5, 7, 31, 32]. Chan et al. [12] showed the possible presence of Nb$_3$Si in the microstructure of multiphase alloys. The silicon addition to these alloys ranged from 1.0-17.3 at. %. Geng et al. [5] reported the presence of Nb$_3$Si and $\beta$-Nb$_5$Si$_3$ phases in the Nb–18Si–5Al–5Cr–5Mo as cast alloy. After heat treatment, $\beta$-Nb$_5$Si$_3$ transformed into $\alpha$-Nb$_5$Si$_3$ but Nb$_3$Si was still present. The author concluded that the presence of Nb$_3$Si in the heat treated alloy at 1500°C for 100 hr indicated equilibrium microstructure was not reached. Equilibrium microstructure was observed when the alloy underwent a heat treatment of 200 hr at 1500°C.

### 2.2.3 Laves Phase, NbCr$_2$

Chromium is a common alloying element because it improves the oxidation resistance of a metal at high temperature. Its melting point (1845-1903°C), low density (7.15g/cc) and its resistance to deformation at elevated temperatures makes it suitable for high temperature applications [15, 33]. The addition of Cr improves the oxidation resistance of niobium silicides by stabilizing the Laves phase (NbCr$_2$) [1, 2, 5, 34]. It has been shown that additions of chromium greater than ~5 at. % stabilizes the chromium-rich Laves phase [1-5]. Laves phases with an AB$_2$ stoichiometry are the most common intermetallic compounds, as shown by Nb-Cr binary phase diagram in Figure 2.1. There are 3 types of Laves phases: Low temperature cubic C-15 structure (MgCu$_2$-type), high temperature hexagonal C-14 (MgZn$_2$-type), which is only stable at temperatures above ~1624°C, and the dihexagonal C-36 (MgNi$_2$-type) [34-36]. The equilibrium microstructure consists of chromium or niobium rich solid solutions and C-15
NbCr$_2$. Thermodynamic modeling from the Nb-Si-Cr system as well as experimental studies on alloys from the Nb-Ti-Si-Al-Cr-Mo-Hf system has shown the presence of the C-14 Laves phase NbCr$_2$ in the as cast microstructure. Researchers attributed the phase stabilization to the presence of silicon [3, 5, 6-8, 12, 14, 15, 37-39]. Zhao et al. [15] reported the stabilization of C-14 phase at lower temperatures promoted by silicon; its stability ranges from ~6 to ~26% Si. It also was reported that the C-14 Laves appears with variable Si/Cr concentration but with little variation in niobium. Geng et al. [3,5,7,8] reported the presence of C-14 Laves phase in heat treated samples from the Nb-Si-Al-Cr system at 1000 and 1500°C.

![Binary phase diagram for Nb-Cr system](image)

**Figure 2.2.** Binary phase diagram for Nb-Cr system calculated using Pandat™ 8.1 software [28].
2.2.4 Mo Silicides and Borosilicides

Molybdenum silicides are also potential intermetallics for high temperature applications due to its strength retention and high melting point. MoSi$_2$ is a widely used compound in the heating elements of furnaces. It provides good oxidation resistance up to 1700°C by developing a SiO$_2$ layer; however, its low creep strength at high temperature and poor fracture toughness are its limitations. The addition of boron to the Nb-Si and Mo-Si systems creates ternary intermetallics such as Nb$_5$Si$_2$B and Mo$_5$SiB$_2$ and Mo$_5$Si$_3$B$_x$. It has been shown that as little as 6.5 at. % of boron addition to alloys from the Mo-Si-B system improves the oxidation resistance and creep resistance of these alloys over monolithic Mo$_5$Si$_3$ [40]. Several authors have focused their attention to develop Mo-Si-B silicide alloys because Mo$_3$Si and Mo$_5$SiB$_2$ have melting points on the order of 2000°C and have potential as high temperature structural materials. When combined with molybdenum solid solution, the fracture toughness and creep resistance are improved [41-43]. The oxidation behavior of these intermetallics will be discussed later.

2.3 Oxidation of Niobium

Since the 1950’s there have been numerous investigations of the oxidation of pure niobium. The oxidation behavior of niobium is complex because it forms several polymorphic oxides. Some of the oxides that have been observed are NbO, NbO$_2$ and several forms of Nb$_2$O$_5$. The principal oxide is porous Nb$_2$O$_5$, which is non volatile at ~1373°C, melts around 1440°C and tends to break during cooling [16, 24].
The oxidation of niobium above 650°C can be described as follows: It starts with a protective oxidation stage (induction period) followed by oxide spallation caused by the formation of Nb$_2$O$_5$ at prolonged time exposures. The induction period, which decreases with increasing temperature, exhibits a slow oxidation. This behavior is attributed to the adsorption and dissolution of oxygen by the niobium. NbO and NbO$_2$ are forming from the solid solution formed by the niobium and oxygen. After this stage, accelerated oxidation is observed created by the transformation of NbO/NbO$_2$ to Nb$_2$O$_5$ [24]. Hurlen [44] performed an extensive study of the reaction of niobium with oxygen at different pressures and temperatures from 150-1000°C. It was stated that the sequential stages in the oxidation of Nb were: linear (I), parabolic (II), a rate-increasing transition, linear (III), parabolic (IV) and parabolic (V).

Arbuzov et al. [45] observed structural transformations in Nb$_2$O$_5$ at different ranges of temperature. A $\alpha \rightarrow \beta$ transition in Nb$_2$O$_5$ was reported. Alpha-niobium pentoxide ($\alpha$-Nb$_2$O$_5$) was present at a temperature range from 500-800°C and $\beta$-Nb$_2$O$_5$ formed from 900-1000°C. Both oxides exhibited an orthorhombic crystal structure with different lattice constants. It was also observed that single crystals of $\beta$-Nb$_2$O$_5$ grow as whiskers, and these become less in number but longer as temperature is increased. Khanna [16] explained that a transition from $\gamma \rightarrow \alpha$ occurs in Nb$_2$O$_5$ at 800-850°C and the whisker growth is attributed to the growth of single crystal $\alpha$-Nb$_2$O$_5$. Goldschmidt [46] investigated the polymorphic forms of Nb$_2$O$_5$ and reported two types of niobium oxide: a low temperature $\alpha$-Nb$_2$O$_5$ and a high temperature $\beta$-Nb$_2$O$_5$. Alpha-niobium pentoxide is metastable and transforms suddenly to $\beta$-Nb$_2$O$_5$. This oxide exhibits an orthorhombic
crystal structure. Beta-niobium pentoxide has a monoclinic structure and it is the stable between 600°C and 1230°C.

2.4 Oxidation of Refractory metal-silicide alloys

The addition of silicon and chromium to niobium, as previously mentioned, creates intermetallics and these improve the oxidation of monolithic niobium at high temperatures. Extensive oxidation studies have been performed to improve the oxidation of niobium by trying to develop protective layers of oxides [1-15, 21, 22]. Y. Murayama et al. [47] showed that the oxidation of three-phase (\(\text{Nb}_{\text{ss}}+\text{Nb}_3\text{Al}+\text{Nb}_5\text{Si}_3\)) alloys from the Nb-Si-Al-Ti system was greatly improved by the addition of Ti at 1300°C.

J. Geng et al. [3] studied the oxidation behavior at 800 and 1200°C of several niobium-silicide based alloys with modifiers. The base composition of these alloys consisted of Nb-18Si-5Cr-5Al with additional amounts of molybdenum, titanium and hafnium. The authors reported that the oxidation resistance of the base alloy was significantly improved at 800°C by the addition of titanium and the decrease in amount of molybdenum present (from 5 to 2 at %) in the alloy. Oxidation at 1200°C resulted in the spallation of oxide scales in alloys with titanium, low molybdenum and hafnium additions; titanium oxides (\(\text{TiNbO}_4\), \(\text{TiNb}_2\text{O}_7\) and \(\text{Ti}_2\text{Nb}_{10}\text{O}_{29}\)) and \(\text{SiO}_2\) were present in the oxide scales. No protective oxide scale was observed by the authors at 800 and 1200°C. On the other hand, pesting oxidation occurred in some alloys at 800°C temperature. Pesting oxidation is observed at intermediate temperatures and it preferentially attacks the intermetallic compounds. Pesting is characterized by the disintegration of alloys into small oxide particles and powder [48]. Zelenistas [6] stated
that even though NbCr$_2$ Laves phase was stabilized by silicon in the Nb-Si-Ti system it did not prevent the alloys from pesting oxidation at 800°C. Several authors have reported the pesting phenomenon at temperatures from 700-900°C [3, 6, 8, 49].

Chan [12] studied the cyclic oxidation of niobium alloys with titanium, chromium, silicon, hafnium and germanium additions from 900-1400°C. It was found that the oxidation products for alloys was a mixture of CrNbO$_4$, Nb$_2$O$_5$, TiNb$_{10}$O$_{29}$ and Nb$_2$O$_5$·TiO$_2$ and small amounts of SiO$_2$ and GeO$_2$. The best oxidation resistance was exhibited by the alloy (35.8Nb-22.5Ti-4Hf-15.6Cr-17.3Si-4.8Ge at.%), which contains higher concentrations of Laves phase NbCr$_2$ and niobium silicides than the other alloys and little amount of niobium solid solution. Even though the formation of protective oxide was not observed, the oxidation resistance of the alloys was attributed to the chromium, which promoted the formation of ternary oxide CrNbO$_4$.

Moreover, several studies have been performed on the oxidation behavior of alloys from the Nb-W-Cr with carbon modifiers. Carbon addition to the alloy with low chromium content, 5 at.% has been shown to improve its oxidation resistance. However, carbon is detrimental to the oxidation resistance of alloy with higher chromium concentration (10 at.% Cr). Also, It is been stated that there is a relationship between phase transformation and oxidation resistance for alloys with 5 and 10Cr additions. The 10Cr shows better oxidation behavior than 5Cr because at temperatures above 1100°C it suffers a phase transformation: from two-phase ($\text{Nb}^{\text{ss}}$+NbCr$_2$) it is converted to single phase ($\text{Nb}^{\text{ss}}$) reducing its oxidation drastically [9-11].
Some studies have shown the presence of thin protective scales, such as Al$_2$O$_3$, in niobium-based alloys. T. Murakami et al. [50, 51] observed the formation of such layer in powder compacts with an Nb$_3$Si$_5$Al$_2$ matrix (alloy Nb-47Si-20Al) in a temperature range from 1100-1300˚C. The authors concluded that the oxidation resistance was improved at those temperatures due to the formation of protective Al$_2$O$_3$. Brady et al. [13] studied the oxidation behavior of Laves phase (NbCr$_2$ and TaCr$_2$) composites at 1100˚C and it was concluded that TaCr$_2$ was better than NbCr$_2$ for high temperature applications. Laves phase formed by tantalum and chromium, TaCr$_2$, exhibited a parabolic oxidation and formation of protective Cr$_2$O$_3$ while NbCr$_2$ suffered from accelerated oxidation and oxide breakaway.

Recent studies have been focused in the oxidation of alloys from the Nb-Mo-Si, Mo-Si-B and Nb-Mo-Si-B systems. Chattopadhyay et al. [52] conducted an isothermal and non-isothermal oxidation study of hypo- and hyper-eutectic alloys from the Nb-Mo-Si system. At 800˚C hypereutectic alloys (Si content more than 17.5 at. %) were more susceptible to oxidation. At 1000 and 1150˚C a continuous layer of amorphous SiO$_2$ was observed in alloys with higher Mo content (more than 15 at. %) regardless of the hypo or hyper character. Nb$_2$O$_5$ and SiO$_2$ were observed in the oxide scales. A niobium oxide, Nb$_{12}$O$_{29}$, also appears in the oxide scale and the authors explained that Nb$_{12}$O$_{29}$ appears to be an intermediate reaction product of niobium and oxygen, caused by oxygen deficiency.

A different oxidation scenario occurs when boron is added to Mo-Si systems; the oxidation resistance is greatly improved by the boron addition [53-61]. Akinc et al. [57]
describes the oxidation behavior of alloys containing the Mo$_5$Si$_3$B$_x$ phase as follows: Initial oxidation of surface forms borosilicate glass and crystalline MoO$_3$. With further oxidation, MoO$_3$ volatilizes, viscous borosilicate flows and covers the pores left by MoO$_3$ and promotes a type of protective scale. Several authors [55-59] had reported the formation of borosilicate glass in the oxide scale. Liu et al. [56] reported the formation of four different oxide layers when niobium was added to the Mo-Si-B system. Alloy (31.5Nb-31.5Mo-30Si-7B) oxidized at 1200°C showed the presence of these oxide scales. Layers located away of metal (layer 1 and 2) consisted of Nb$_2$O$_5$ crystals, borosilicate glass and large pores; the layer near metal (layer 3) consisted of molybdenum rich oxides MoO$_3$ and internal oxidation. Finally, the layer located at interface (layer 4) was identified as internal oxidation region with oxides and silicides. On the other hand, other authors reported the presence of MoO$_2$ near the alloy/oxide interface instead of MoO$_3$ [55] and the formation of amorphous silicon oxide matrix instead of borosilicate glass as the protective oxide [60].
CHAPTER 3
EXPERIMENTAL DETAILS

3.1 Alloy Preparation

The Nb-based alloy was prepared by Ames National Laboratory at the Iowa State University using arc melting technique in an argon atmosphere to prevent oxidation of metals. The metals used to prepare this alloy had a minimum of four nines in purity. The compositions of niobium, molybdenum, silicon, boron and chromium for this alloy are listed in table 3.1 in atomic percent. The composition of the investigated alloy was given by Naval Air Warfare Center. After casting, the sample ingots were electrically discharged machined (EDM) into 10 x 10 x 6 mm samples and then delivered for oxidation studies.

Table 3.1. Composition of alloy given in atomic percent

<table>
<thead>
<tr>
<th>Niobium</th>
<th>Molybdenum</th>
<th>Silicon</th>
<th>Boron</th>
<th>Chromium</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>20</td>
<td>15</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

3.2 Sample Preparation

The received alloy and crucibles were prepared for oxidation experiments as follows:

1. Samples were polished down to a 600-grit finish to remove any initial oxide layer.
2. Square samples were electrically discharged machined (EDM) into 5 x 5 x 5 mm samples.
3. The samples were re-polished down to a 600-grit finish to remove any scratches and imperfections left by the EDM process.

4. Samples were measured using a micrometer and finally they underwent an ultrasonic bath for 10-15 minutes in ethanol to remove any debris or contaminants.

5. Caps were made out of Leco 528 HP crucibles in order to prevent any material loss during the oxidation process.

6. Leco 528 HP crucibles and caps were furnace dried at 300°C for 2 hrs previous to oxidation.

### 3.3 Sample Oxidation

The alloy was subjected to oxidation in air using box furnaces over a temperature range from 700-1300°C. A furnace (Linderberg/Blue M model 1100) was used for experiments performed at 700-900°C, and a computer-controlled high temperature furnace (Sentro Tech. Corp model ST-1600-888) was used from 1000-1300°C. The ramp time for both furnaces was set to 10°C per minute. Two oxidation studies were performed in this alloy: short term oxidation (STO) and long term oxidation (LTO). STO consisted of one cycle of 24 hr., while LTO consisted of seven cycles of 24 hours giving a total exposure time of 168 hr. After each cycle, samples were furnace cooled to room temperature. Initial weight and final weight after each cycle was recorded using a Sartorius Analytical balance (model MC210S) with precision up to six decimal places. Weight gain/loss per unit area recorded for each sample indicates the amount of oxidation at a given temperature.
3.4 Sample Characterization

After the oxidation was completed, oxidized samples were stored in glass vials waiting for sample characterization. Sample characterization for as cast alloy and oxidized samples consisted of optical microscopy (OM), scanning electron microscopy (SEM), which includes energy dispersive spectroscopy (EDS) and x-ray mapping, and x-ray diffraction (XRD). Sample characterization was performed in facilities provided by the University of Texas at El Paso.

3.4.1 Optical Microscopy, OM

Samples (as cast and oxidized) for OM were ground through a series of silicon carbide papers: 240, 400, 600, 800, 1000 and 1200. Final polishing was performed only in as cast samples with a series of 1μm, 0.3μm and 0.5μm alumina slurries and a felt cloth. Samples were rinsed in water and dried using ethyl alcohol. Sample etching was carried out by swabbing sample for 2 to 10 s using ASTM 66 etchant: 6mL hydrofluoric acid (HF), 3mL nitric acid (HNO₃) and 6mL hydrochloric acid (HCL). An optical microscope (Reichert MEF4 A/M) equipped with a digital camera (DCM500) and Scope Photo Software 3.0 was utilized to obtain micrographs of alloy and oxidized samples.

3.4.2 Scanning Electron Microscopy, SEM

Samples for SEM analysis were sputter coated with gold using a SPI-MODULE sputter coater to prevent charging effects. All SEM studies were performed on a Hitachi S-4800 Scanning Electron Microscope equipped with EDS and BSE (Back Scatter Electron) detectors. Sample characterization included BSE imaging, EDS analysis and
x-ray mapping. BSE imaging was used to identify the different phases present in the microstructure and in the oxide scale. EDS analysis was performed in the base metal and in the oxide scale; at least five readings were taken for each phase and the average of these was reported. The elapsed live time for each reading was set to 30-50 seconds. Calibration of EDAX detector was performed periodically to ensure proper readings. The ratio of readings gave us an estimated oxide and phase stoichiometry, which was confirmed by XRD technique. X-ray mapping was performed to locate the elements present in the alloy. To obtain contrast between element maps the dwell time was set to 15-18 seconds, which gave a mapping time of 13-16 minutes. All SEM and EDS characterization was performed at an accelerating voltage of 20kV, probe current of 20µA and a working distance from 12.0-15.5 mm.

### 3.4.3 X-Ray Diffraction, XRD

A Sintag XDS 200 x-ray diffractometer with monochromatic CuKα radiation ($\lambda=1.54056\text{Å}$), voltage of 45kV and current of 45mA was used to characterize the phases present in the as received alloy and the oxides formed in the oxide scale at various temperatures. The parameters used for XRD diffraction analyses are shown in table 3.2.
Table 3.2. Parameters used for XRD diffraction analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generator voltage</td>
<td>45kV</td>
</tr>
<tr>
<td>Generator current</td>
<td>40 mA</td>
</tr>
<tr>
<td>Step size</td>
<td>0.3 s</td>
</tr>
<tr>
<td>Start angle</td>
<td>5°</td>
</tr>
<tr>
<td>Stop angle</td>
<td>90°</td>
</tr>
<tr>
<td>Preset time</td>
<td>0.5 s</td>
</tr>
<tr>
<td>Tube divergence slit</td>
<td>2</td>
</tr>
<tr>
<td>Tube scatter slit</td>
<td>4</td>
</tr>
<tr>
<td>Detector divergence slit</td>
<td>0.1</td>
</tr>
<tr>
<td>Detector receiving slit</td>
<td>1</td>
</tr>
</tbody>
</table>

Sample preparation for XRD analysis was done by pulverizing oxidation products until a fine powder was obtained. The powder was adhered to a glass slide by using petroleum jelly. Once a pattern was obtained, the most intense peaks were matched to the oxides using powder diffraction files PDF from a Powder Diffraction Database. As received alloy analysis was performed using the same procedure mentioned above but it was not converted into powder.

3.4.3 Phase Diagram Modeling

A phase diagram calculation software for multicomponent systems Pandat™8.1 provided by CompuTherm LLC (Madison, WI) was used to calculate the isothermal sections of the alloy at various temperatures. This software predicts the phases present in the alloy based on the crystal structures and amount of alloying elements. The stability of these phases is calculated based on thermodynamic data.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 As Cast Characterization

4.1.1 Scanning Electron Microscopy, SEM

A backscatter (BSE) image of the as cast or as received microstructure of Nb-20Mo-15Si-5B-20Cr alloy is shown in Figure 4.1(a); contrast indicates the different phases present in the alloy. The alloy consisted of four phases, solid solution ($\alpha$), silicides $\text{Nb}_5\text{Si}_3$, $\text{Nb}_3\text{Si}$ and Laves phase $\text{NbCr}_2$. White areas represent the solid solution ($\alpha$) of Nb and Mo. Light gray areas represent a mixture of silicides $\text{Nb}_5\text{Si}_3$ and $\text{Nb}_3\text{Si}$, while dark gray areas are $\text{NbCr}_2$. Also, the alloy contained a eutectic like microconstituent showing $\alpha$, $\text{Nb}_3\text{Si}$ and $\text{NbCr}_2$. Figure 4.1(b) shows a high magnification (3500x) image of the eutectic like region where again white areas are ($\alpha$), light gray areas correspond to silicide, $\text{Nb}_3\text{Si}$, and dark gray areas are $\text{NbCr}_2$. Boron was added to the alloy as a phase stabilizer. However, the characterization techniques used in this investigation, such as XRD, SEM and EDS analysis could not detect the presence of boron in the alloy. Therefore, the effect of boron addition in the as received microstructure of the alloy and in its oxidation behavior will not be discussed. Other characterization techniques, such as wave dispersive spectrometry (WDS) also called electron probe microanalysis (EPMA) or EDS analysis with boron detection capabilities are recommended to study the boron effect. Figure 4.2 shows the elemental x-ray mapping of the alloy. The concentration or contrast of elements is related to the phases that are forming. X-ray mapping of elements shows that chromium is highly concentrated in the Laves phase $\text{NbCr}_2$ with significant amounts of silicon. Little chromium concentration is
observed in the $\alpha$ phase as well as in the silicide $\text{Nb}_5\text{Si}_3$, but higher chromium concentration is shown in eutectic $\text{Nb}_3\text{Si}$. As expected, silicon is mostly concentrated in silicides and little concentration of this element is found in the $\alpha$ phase. Molybdenum is mostly located in the $\alpha$ phase. Table 4.1 shows the elemental analysis performed in each phase. It can be observed that chromium concentration in the $\alpha$ phase and $\text{Nb}_5\text{Si}_3$, 9.91 and 2.34 at% respectively, is lower than in the eutectic like microconstituent. Chromium concentration in the eutectic $\alpha$ phase and $\text{Nb}_3\text{Si}$ is 17.25 and 9.83 at%, respectively. Also, silicon concentration increases in the eutectic $\alpha$ and Laves phase $\text{NbCr}_2$ exhibits a silicon concentration of 15.65 at%.

![Figure 4.1. BSE micrographs of as cast alloy: Microstructure consists of solid solution $\alpha$ (white area), $\text{Nb}_3\text{Si}$ and $\text{Nb}_5\text{Si}_3$ (light gray areas), $\text{NbCr}_2$ (dark gray areas) and eutectic like microconstituent formed by $\alpha$, $\text{Nb}_3\text{Si}$ and $\text{NbCr}_2$. (b) shows a magnified view of eutectic microconstituent.](image)

<table>
<thead>
<tr>
<th>Element</th>
<th>Solid solution</th>
<th>Silicide</th>
<th>Phases</th>
<th>Eutectic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$ (at.%)</td>
<td>$(\text{Nb}_5\text{Si}_3$ (at.%)</td>
<td>$\alpha$ (at.%)</td>
<td>$(\text{Nb}_3\text{Si})$ (at.%)</td>
</tr>
<tr>
<td>Si</td>
<td>2.93</td>
<td>31.60</td>
<td>5.72</td>
<td>22.35</td>
</tr>
<tr>
<td>Nb</td>
<td>48.15</td>
<td>55.52</td>
<td>44.58</td>
<td>37.25</td>
</tr>
<tr>
<td>Mo</td>
<td>39.01</td>
<td>10.54</td>
<td>32.45</td>
<td>17.02</td>
</tr>
<tr>
<td>Cr</td>
<td>9.91</td>
<td>2.34</td>
<td>17.25</td>
<td>9.83</td>
</tr>
</tbody>
</table>
Figure 4.2. Elemental x-ray mapping of Si, Cr, Nb and Mo performed on the as cast microstructure. High concentration or contrast of elements is related to the phases that are forming.
4.1.2 X-Ray Diffraction, XRD

The XRD pattern obtained for the as cast alloy is shown in Figure 4.3. Individual phases and their crystal structures were identified by matching the characteristic XRD peaks against powder diffraction files. The presence of four phases was confirmed by this characterization technique, body centered cubic BCC solid solution ($\alpha$), tetragonal $\text{Nb}_5\text{Si}_3$, tetragonal $\text{Nb}_3\text{Si}$ and hexagonal Laves phase $\text{NbCr}_2$. The solid solution ($\alpha$) is rich in Nb and Mo and a BCC structure was observed since both Nb and Mo possess this crystal structure. The Laves phase $\text{NbCr}_2$ found in the alloy corresponds to the high temperature hexagonal structure (C14), which was stabilized by the presence of Si.

![XRD pattern of the as cast alloy](image)

Figure 4.3. XRD pattern of the as cast alloy.
4.1.3 Phase Diagram Modeling

The calculated isothermal sections at 800°C, 1000°C, 1200°C and 1300°C from the Nb-Mo-Si-Cr system are presented in Figure 4.4. The isothermal sections were modeled by using Pandat™ 8.1 software, which calculates the phase stability based on the most recent thermodynamic data.

The quaternary isothermal sections were calculated by fixing the amount of chromium at 20 percent and setting the amounts of niobium, molybdenum and silicon at 80 percent. The alloy’s composition was set to 45Nb-20Mo-15Si-20Cr. Boron was not included in the software’s database. The software predicted the phases found in the alloy, which are, the solid solution (α), Nb₅Si₃ and NbCr₂. The presence of Nb₃Si was not observed in the calculated isotherms. However, the software confirmed the presence of the hexagonal C-14 Laves phase NbCr₂. It can be observed that the phases present in the alloy remained stable at all temperatures and the alloy remained in the four-phase region.
Figure 4.4. Isothermal sections calculated at 800°C, 1000°C, 1200°C and 1300°C for the Nb-Mo-Si-Cr system.
4.2 Short Term Oxidation, STO

The short term oxidation curve, obtained after 24 hours of exposure in air for a temperature range from 700-1400°C, is shown in Figure 4.5. This curve was calculated by plotting the mass gain per unit area as a function of oxidation temperature. The oxidation behavior of the alloy can be described in stages. The first stage occurs at 700°C, this stage is characterized by an increase in mass gain per unit area. The second stage occurs at 800°C, and a decrease in mass gain can be observed. The oxidation products at these two stages consist of a small amount of loose powder and a thin oxide layer surrounded the metal. The third stage shows better oxidation resistance than stage one and occurs at 900 and 1000°C. This stage shows the least weight gain by the alloy. Oxidation products for this stage are thin layers of oxide surrounding the metal with no loose oxide. The fourth stage occurs at temperatures from 1100-1300°C and the mass gain per unit area at that temperature was constant. Spallation of oxides was observed at 1100°C and a thick bulky oxide layer surrounded the metal at 1100, 1200 and 1300°C. The fifth and final stage occurred at 1400°C; at this temperature the metal was completely transformed into a swollen bulky oxide. The most weight gain per unit area was observed at this temperature.

According to the oxidation behavior observed at different temperatures and the stages identified, detailed short term oxidation experiments at 800, 1000, 1200 and 1300°C were conducted to determine the oxidation kinetics at 24 hours of exposure. This study was performed by periodic removal of a specimen, weighing and re-insertion for further exposure at constant temperature. The alloys were oxidized up to 24 hours.
in six cycles of 2, 3, 4, 5 and 10 hours and cooled inside the furnace to room temperature. Figure 4.6 shows the short oxidation curve obtained by plotting the mass gain per unit area as a function of oxidation time. The oxidation kinetics of the alloy follows a parabolic behavior at all temperatures (800, 1000, 1200 and 1300°C.) The parabolic oxidation rate constants \( k_p \) were calculated by the least-square method, linear-regression analysis of the mass gain data and the equation

\[
\left( \frac{\Delta m}{A} \right)^2 = k_p t \quad (4.1)
\]

where, \( \Delta m \) is the mass change of the specimen, \( A \) is the surface area and \( t \) is the exposure time. Table 4.2 shows the calculated parabolic oxidation rate constants and the mass gain per unit area at 24 hours of exposure at each temperature. The oxidation rate constant determines the rate of material consumption. From Figure 4.6, it can be observed that the mass gain and the oxidation rate are proportional to the oxidation temperature. The highest oxidation rate and mass gain was observed in the alloy oxidized at 1300°C. The values for oxidation rate constant and mass gain per unit area at 1300°C are 143.7 mg²/cm⁴/hr and 57.07 mg/cm² respectively. The alloy exhibited better oxidation resistance at 800°C with an oxidation rate constant of 4.84 mg²/cm⁴/hr and a mass gain per unit area of 11.4 mg/cm². Oxidation product at 800°C consisted of loose powder and thin oxide scale and metal. The spallation of oxides was observed at 1000, 1200 and 1300°C.
Figure 4.5. Short term oxidation curve (weight gain per unit area vs. oxidation temperature) obtained after 24 hours of exposure in air. Curve indicates oxidation products final state (△ powder-thin oxide scale/metal, ■ thin oxide scale/metal, ○ bulky oxide/metal and ♦ bulky oxide.)

Figure 4.6. Short term oxidation curve (weight gain per unit area vs. oxidation time) obtained after 24 hours of exposure in air. Oxidation at all temperatures followed a parabolic behavior.
Table 4.2. Oxidation rate constants and mass gained after 24 hours of exposure at 800, 1000, 1200 and 1300°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Total mass gain per area (mg/cm²)</th>
<th>Oxidation rate constant (mg/cm²/hr)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>11.4</td>
<td>4.84</td>
<td>0.957</td>
</tr>
<tr>
<td>1000</td>
<td>20.8</td>
<td>16.64</td>
<td>0.986</td>
</tr>
<tr>
<td>1200</td>
<td>37.8</td>
<td>54.15</td>
<td>0.974</td>
</tr>
<tr>
<td>1300</td>
<td>57.07</td>
<td>143.7</td>
<td>0.943</td>
</tr>
</tbody>
</table>

4.2.1 Characterization of Short Term Oxidation Products

4.2.1.1 Scanning Electron Microscopy, SEM

Figure 4.7 shows BSE micrographs of the oxide-metal interfaces formed on alloy after 24 hours of exposure at 700-1200°C. Oxidation scales formed at 700 and 800°C, Figures 4.7(a) and (b) respectively, show a highly porous oxide scale with dense mixture of oxides. Light gray oxides observed at 700°C, Figure 4.7(a), consist of a mixture of Nb₂O₅ and MoO₃, while dark gray areas represent a mixture of SiO₂, CrNbO₄ and Cr₂O₃. Oxide scale formed at 800°C, Figure 4.7(b), was composed of Nb₂O₅ (light gray areas) and CrNbO₄ (dark gray areas.) Figure 4.7(c) shows the oxide scale formed at 900°C. It can be observed that the oxide scale was less porous than at lower temperatures. Dense light gray areas were composed of Nb₂O₅, while dark gray areas are a mixture of SiO₂ and CrNbO₄. A porous gray oxide was also observed, which corresponds to CrMoO₄. Oxide scales formed at 1000-1200°C, Figures 4.7(d-f), were similar. Scales were composed of fine oxide particles and porous oxides. A mixture of CrMoO₄ and SiO₂ was observed in oxide scales formed at 1000°C and 1100°C, Figures 4.7(d) and (e) respectively. CrNbO₄ is located at the oxide-metal interface in alloy oxidized at 1000°C. At 1100°C, a layer of SiO₂ and Nb₂O₅ (dark gray areas) also
appears at the interface and a mixture of Cr$_2$O$_3$, SiO$_2$ and Nb$_2$O$_5$ conforms the oxide scale. Figure 4.7(f) shows the oxide-metal interface of alloy oxidized at 1200°C. The oxide scale was composed of Nb$_2$O$_5$, CrNbO$_4$ and MoO$_3$.

Figure 4.7. BSE micrographs of the oxide-metal interfaces formed on alloy oxidized for 24 hours of exposure at (a) 700°C, (b) 800°C, (c) 900°C, (d) 1000°C, (f) 1100°C and (d) 1200°C. Nb$_2$O$_5$, CrNbO$_4$ and SiO$_2$ were the common oxides present at all temperatures.
SEM analysis of the oxide scale formed at 1300°C showed that the scale is composed of three layers. Figure 4.9 (a) shows an overall view of the oxidized specimen and the oxide layers formed. Magnification of micrograph is 300x. Figure 4.9 (b) shows a high magnification (1000x) micrograph of the oxide-metal interface and the first oxide formed in contact with the metal. This oxide layer (layer 1) consists of a mixture of Nb and Mo rich oxides. Elemental analysis on these oxides revealed the presence of MoO$_2$ and MoO$_3$ (light gray areas) and Nb$_2$O$_5$ (gray areas). SiO$_2$ (dark gray areas) was observed as a thin layer located at the interface; however this oxide layer was not continuously formed. The layer 2; shown in Figure 4.9(c), consists of globular particles of CrNbO$_4$ (gray areas) oxide embedded in a SiO$_2$ matrix (black areas). Figure 4.9 (d) illustrate the outermost layer (layer 3) formed in oxidized alloy. This layer is mainly composed of elongated Nb$_2$O$_5$ particles (white areas) with some regions or spots of CrNbO$_4$ (gray areas) embedded in a SiO$_2$ matrix (black areas). The SiO$_2$ matrix was only found in oxide layers formed at 1300 and 1400°C. Sample oxidized at 1400°C was completely transformed into a swollen oxide. Figure 4.11(a) shows a low magnification (300x) BSE image of the oxide formed at 1400°C. Figure 4.11(b) shows a detailed view of sample. Magnification of micrograph is 500x. The oxide microstructure consisted of elongated Nb$_2$O$_5$ particles (white areas), globular CrNbO$_4$ particles (gray areas) embedded in a SiO$_2$ matrix (dark areas).

Table 4.3 shows the composition of oxides obtained from the elemental analysis performed on oxide scales. The elemental analysis made possible the location of oxides. The presence of these oxides was later confirmed by XRD.
Figure 4.8. A schematic representation for oxide layer formed in samples oxidized at a) 700-800°C and b) 900-1200°C after 24 hours of exposure. Oxide layer formed at 900-1200°C was less porous than at lower temperatures.

Figure 4.9. BSE micrographs of alloy oxidized at 1300°C for 24 hrs: (a) shows an overall view of the oxidized sample and the distinct oxide layers, (b) illustrates the oxide-metal and first oxide layer in contact with metal. Layer 1 consists of MoO$_3$, Nb$_2$O$_5$ and SiO$_2$, while layer 2 (c) is formed by globular particles of CrNbO$_4$ embedded in SiO$_2$ matrix. Layer 3 (d) shows elongated particles of Nb$_2$O$_5$ with CrNbO$_4$ regions in a SiO$_2$ matrix. Magnification of micrographs is (a) 300x and (b-d) 1000x.
Figure 4.10. A schematic representation for the three oxide layers formed in sample oxidized at 1300°C after 24 hours of exposure.

Figure 4.11. BSE micrographs of oxide formed at 1400°C for 24 hrs: (a) shows an overall view of the oxide; oxide microstructure (b) consisted of elongated particles of Nb₂O₅ and globular particles of CrNbO₄ regions in a SiO₂ matrix. Alloy oxidized completely at this temperature.
Table 4.3. EDS analysis of oxide scales developed in alloy after 24 hours of oxidation at 700-1400°C.

<table>
<thead>
<tr>
<th>Temperature (C°)</th>
<th>Oxide</th>
<th>O</th>
<th>Si</th>
<th>Nb</th>
<th>Mo</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>(\text{Nb}_2\text{O}_5/\text{MoO}_3)</td>
<td>46.12</td>
<td>3.07</td>
<td>23.89</td>
<td>17.81</td>
<td>9.11</td>
</tr>
<tr>
<td></td>
<td>(\text{Cr}_2\text{O}_3/\text{SiO}_2/\text{CrNbO}_4)</td>
<td>39.10</td>
<td>11.89</td>
<td>22.27</td>
<td>11.05</td>
<td>15.68</td>
</tr>
<tr>
<td>800</td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>40.38</td>
<td>7.61</td>
<td>35.90</td>
<td>10.33</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td>(\text{CrNbO}_4)</td>
<td>21.88</td>
<td>12.52</td>
<td>25.88</td>
<td>8.99</td>
<td>30.73</td>
</tr>
<tr>
<td>900</td>
<td>(\text{SiO}_2/\text{CrNbO}_4)</td>
<td>46.51</td>
<td>11.58</td>
<td>22.00</td>
<td>4.58</td>
<td>15.33</td>
</tr>
<tr>
<td></td>
<td>(\text{Nb}_2\text{O}_5/\text{CrMoO}_4)</td>
<td>47.71</td>
<td>2.25</td>
<td>33.59</td>
<td>8.18</td>
<td>8.28</td>
</tr>
<tr>
<td></td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>47.01</td>
<td>2.74</td>
<td>39.33</td>
<td>8.42</td>
<td>2.51</td>
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<tr>
<td>1000</td>
<td>(\text{CrNbO}_4)</td>
<td>49.92</td>
<td>4.52</td>
<td>20.71</td>
<td>5.13</td>
<td>19.72</td>
</tr>
<tr>
<td></td>
<td>(\text{CrMoO}_4/\text{SiO}_2)</td>
<td>52.76</td>
<td>15.83</td>
<td>21.67</td>
<td>4.90</td>
<td>4.84</td>
</tr>
<tr>
<td></td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>51.06</td>
<td>2.93</td>
<td>34.77</td>
<td>7.85</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>(\text{Cr}_2\text{O}_3/\text{SiO}_2)</td>
<td>51.05</td>
<td>10.19</td>
<td>17.75</td>
<td>7.00</td>
<td>14.02</td>
</tr>
<tr>
<td>1100</td>
<td>(\text{SiO}_2/\text{CrMoO}_4)</td>
<td>49.29</td>
<td>12.35</td>
<td>18.68</td>
<td>10.64</td>
<td>9.05</td>
</tr>
<tr>
<td></td>
<td>(\text{SiO}_2/\text{CrNbO}_4)</td>
<td>48.90</td>
<td>14.26</td>
<td>23.52</td>
<td>7.73</td>
<td>5.59</td>
</tr>
<tr>
<td></td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>50.76</td>
<td>2.38</td>
<td>35.99</td>
<td>7.70</td>
<td>3.17</td>
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<tr>
<td>1200</td>
<td>(\text{CrNbO}_4)</td>
<td>43.73</td>
<td>4.11</td>
<td>23.72</td>
<td>4.95</td>
<td>23.49</td>
</tr>
<tr>
<td></td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>51.36</td>
<td>4.88</td>
<td>31.45</td>
<td>9.59</td>
<td>2.72</td>
</tr>
<tr>
<td>1300 first oxide layer</td>
<td>(\text{MoO}_2/\text{MoO}_3)</td>
<td>44.76</td>
<td>&lt;1</td>
<td>13.58</td>
<td>29.69</td>
<td>11.96</td>
</tr>
<tr>
<td></td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>49.39</td>
<td>&lt;1</td>
<td>40.02</td>
<td>10.24</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>(\text{SiO}_2)</td>
<td>55</td>
<td>31.75</td>
<td>4.61</td>
<td>5.84</td>
<td>2.81</td>
</tr>
<tr>
<td>1300 last oxide layer</td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>51.14</td>
<td>&lt;1</td>
<td>40.98</td>
<td>7.88</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>(\text{CrNbO}_4)</td>
<td>50.12</td>
<td>&lt;1</td>
<td>22.41</td>
<td>5.51</td>
<td>20.13</td>
</tr>
<tr>
<td></td>
<td>(\text{SiO}_2)</td>
<td>55.57</td>
<td>36.52</td>
<td>5.75</td>
<td>1.71</td>
<td>&lt;1</td>
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<tr>
<td>1400</td>
<td>(\text{Nb}_2\text{O}_5)</td>
<td>57.8</td>
<td>&lt;1</td>
<td>35.2</td>
<td>6.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td></td>
<td>(\text{CrNbO}_4)</td>
<td>55.02</td>
<td>0.51</td>
<td>20.54</td>
<td>4.93</td>
<td>19.01</td>
</tr>
<tr>
<td></td>
<td>(\text{SiO}_2)</td>
<td>64.62</td>
<td>28.03</td>
<td>1.87</td>
<td>4.11</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Figure 4.12 through 4.14 illustrates the elemental x-ray mapping of samples oxidized at 800, 1000 and 1300°C, respectively. Analysis was performed along the oxide-metal interface at a magnification of 1000x. Maps show the distribution of niobium, molybdenum, silicon and oxygen along the metal and oxide scale. At 800°C, Figure 4.12, oxide scale is mainly formed by niobium and molybdenum oxides. Chromium and silicon concentrations along the oxide scale were observed in localized areas. Figure 4.13 shows the maps for sample oxidized at 1000°C. At this temperature, the oxide scale is mainly composed of silicon and chromium rich oxides.
Niobium concentration was limited to some areas and low molybdenum concentration was observed. Elemental mapping at 1300°C, Figure 4.14 shows that, indeed, first oxide layer in contact with metal contains molybdenum and niobium rich oxides. Chromium concentration was low and formation of SiO$_2$ along the interface can be appreciated.

4.2.1.2 X-Ray Diffraction, XRD

The oxidation products in powder form were characterized by XRD. Figure 4.15 presents the XRD patterns of oxides obtained from samples oxidized at 700, 800, 1100, 1200 and 1300°C 24 hours of exposure. XRD analysis at 900 and 1000°C was not performed since insufficient oxide products were formed at those temperatures. XRD technique detected the presence of Nb$_2$O$_5$, CrNbO$_4$, Mo$_4$O$_{11}$, MoO$_3$, MoO$_2$, CrMoO$_4$ and SiO$_2$. The predominant oxides formed at all temperatures were tetragonal CrNbO$_4$ and monoclinic Nb$_2$O$_5$. XRD patterns were similar at all temperatures except at 700 and 800°C. An extra peak of Nb$_2$O$_5$ appeared at those temperatures at a 2θ value of 23°. Examination of pattern revealed that the reflection corresponds to the orthorhombic form of Nb$_2$O$_5$. Figure 4.16 shows the XRD patterns for samples oxidized in six cycles up to 24 hours at 800, 1000, 1200 and 1300°C. Again, the presence of CrNbO$_4$ and Nb$_2$O$_5$, MoO$_3$ among other oxides was confirmed. Table 4.4 summarized the oxides identified by XRD at different temperatures.
Figure 4.12. Elemental x-ray mapping of O, Si, Cr, Nb and Mo performed on the oxide-metal interface obtained at 800 °C.
Figure 4.13. Elemental x-ray mapping of O, Si, Cr, Nb and Mo performed on the oxide-metal interface obtained at 1000°C.
Figure 4.14. Elemental x-ray mapping of O, Si, Cr, Nb and Mo performed on the oxide-metal interface obtained at 1300°C.
Figure 4.15. XRD patterns of the oxidized products obtained after 24 hours of exposure at 700-1300 °C.

Figure 4.16. XRD patterns of the oxidized products obtained after oxidizing samples in six cycles up to 24 hours at 800, 1000, 1200 and 1300 °C.
Table 4.4. Summary of oxides identified by XRD formed during short term oxidation.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Oxides identified by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>Nb₂O₅ orthorhombic, Nb₂O₅ monoclinic, SiO₂, MoO₃, MoO₂, CrNbO₄, Cr₂O₃</td>
</tr>
<tr>
<td>800</td>
<td>Nb₂O₅ orthorhombic, Nb₂O₅ monoclinic, SiO₂, MoO₂, CrNbO₄, Cr₂O₃</td>
</tr>
<tr>
<td>1000-1100</td>
<td>Nb₂O₅ monoclinic, SiO₂, CrMoO₄, Mo₄O₁₁, CrNbO₄</td>
</tr>
<tr>
<td>1200-1300</td>
<td>Nb₂O₅ monoclinic, SiO₂, MoO₃, MoO₂, Mo₄O₁₁, CrMoO₄, CrNbO₄, Cr₂O₃</td>
</tr>
</tbody>
</table>

4.3 Long Term Oxidation, LTO

Long term oxidation studies consisted of seven cycles of 24 hours, which gave a total exposure time of 168 hours in air at temperatures ranging from 700-1300°C. Figures 4.17 and 4.18 represent the long term curves obtained by plotting the mass gain per unit area as a function of oxidation time at 700-900°C and 1000-1300°C, respectively. Oxidation kinetics revealed linear and parabolic behaviors at different temperatures and at different interval of time. Both oxidation rates were calculated by the method previously mentioned. Equation 4.1 was used to calculate the parabolic oxidation rate constant \( k_p \) and linear oxidation rate constant \( k_l \) was calculated using the equation

\[
\left( \frac{\Delta m}{A} \right) = k_l t \quad (4.2)
\]

where, \( \Delta m \) is the mass change of the specimen, \( A \) is the surface area and \( t \) is the exposure time. The parabolic and linear oxidation rate constants of the alloy as well as the mass gain after 168 hours at different temperatures are given in Table 4.5.

At 700°C, the alloy followed a linear oxidation throughout the entire exposure time. A faceted oxide and metal was the end oxidation product. The alloy exhibited linear oxidation for the first 120 hours at 800°C. This linear rate was less than the one
observed at 700°C. Further exposure, more than 120 hours, resulted in a rapid increment of the mass gain. At the end of the oxidation test, the sample disintegrated completely into powder and the most mass gain per unit area (223.1 mg/cm²) was displayed at this temperature.

Oxidation at 900°C followed a linear rate for the first 72 hours and for the next two cycles (up to 120 hours) a rapid mass gain per unit area was experimented by the alloy. Further exposure resulted in mass loss. At 900°C, the alloy gained the second most significant mass gained (191.2 mg/cm²) when compared to other temperatures. At 1000°C, the oxidation kinetics of the alloy was linear during the entire oxidation test. Bulky oxide with no metal was the end product of alloy oxidized at 900 and 1000°C. Alloy followed a parabolic rate at 1100-1300°C. This parabolic rate was only observed in the first 72 hours of oxidation at 1100, while at 1200 and 1300°C it was maintained throughout the entire oxidation test. At 1100°C the alloy was completely oxidized. The oxidation product obtained was a swollen bulky oxide with no metal. Alloy showed better oxidation resistance at 1200 and 1300°C since the least mass gained of 48.3 mg/cm² was observed at 1200°C, followed by 1300°C with a value of 71.3 mg/cm². Also, the parabolic rates decreased when compared to short term oxidation. A thick oxide scale surrounding the metal was the end product at these two temperatures. Several cracks were observed in the oxide scale. The oxide scale formed at 1200-1300°C was slightly deformed, and cracks parallel to the surface of the oxide were noticed.
Figure 4.17. Long term oxidation curve (weigh gain per unit area vs. oxidation time) obtained after 168 hours of exposure in air at 700, 800, 900 and 1000°C.

Figure 4.18. Long term oxidation curve (weigh gain per unit area vs. oxidation time) obtained after 168 hours of exposure in air at 1100, 1200 and 1300°C.
Table 4.5. Oxidation rate constants and mass gained after 168 hours of exposure at 700-1300°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Total mass gain per area</th>
<th>Oxidation rate constant</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( m ) (mg/cm(^2))</td>
<td>( k_1 ) (mg/cm(^2)/hr)</td>
<td>( k_p ) (mg/cm(^2)/cm(^4)/hr)</td>
</tr>
<tr>
<td>700</td>
<td>188.5</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>223.1</td>
<td>0.52 (0-120 hr)</td>
<td>-</td>
</tr>
<tr>
<td>900</td>
<td>191.2</td>
<td>0.35 (0-72 hr)</td>
<td>-</td>
</tr>
<tr>
<td>1000</td>
<td>163.6</td>
<td>0.34 (0-72 hr)</td>
<td>-</td>
</tr>
<tr>
<td>1100</td>
<td>141.2</td>
<td>-</td>
<td>123.8 (0-72 hr)</td>
</tr>
<tr>
<td>1200</td>
<td>48.3</td>
<td>-</td>
<td>16.1</td>
</tr>
<tr>
<td>1300</td>
<td>71.3</td>
<td>-</td>
<td>31.76</td>
</tr>
</tbody>
</table>

Figure 4.19. Summary of long term oxidation process.
4.3.1 Characterization of Long Term Oxidation Products

4.3.1.1 Scanning Electron Microscopy, SEM

Figure 4.20 shows a BSE micrograph of sample oxidized at 700°C. Elemental analysis on oxides revealed that the scale conforms of a mixture of oxides. A mixture of Nb$_2$O$_5$ and MoO$_3$ are located in the light gray areas, while dark gray areas represent a mixture of SiO$_2$ and Nb$_2$O$_5$. The scale was highly porous with dense oxide mixtures. The scale was thicker than the one formed in short term oxidation. The thickness of the oxide scale was approximately 2mm. The presence of Cr$_2$O$_3$ and CrNbO$_4$ was not detected by elemental analysis.

As previously mentioned, the sample oxidized at 1000°C had transformed completely into oxide. Figure 4.21(a) shows an overall view of the oxide formed. The oxide was conformed to regions of chromium and niobium rich oxides. Elemental analysis showed that the white regions of oxide were mainly composed of Nb$_2$O$_5$. Gray regions corresponded to the stoichiometry of CrNbO$_4$. The presence of SiO$_2$ in the oxide scale was not detected by EDS. Figure 4.21(b) illustrates the morphology of these two oxides. The elongated particles correspond to Nb$_2$O$_5$ while small round particles are CrNbO$_4$. 
Figure 4.20. BSE images of sample oxidized at 700°C for 168 hours: (a) shows an overall view of the oxide metal interface. The oxide scale (b) is composed of mixed Nb$_2$O$_5$ and MoO$_3$ (light gray areas) and SiO$_2$ and Nb$_2$O$_5$ (dark gray areas). Magnification for both micrographs is 1000x.

Figure 4.21. BSE micrograph of oxide formed at 1000°C for 168 hours. Sample completely transformed into oxide at this temperature: (a) is an overall view of oxide scale (300x) while (b) shows the distinct oxides formed and its morphology (1000x).

SEM analysis revealed that sample oxidized at 1200°C formed two oxide layers and a diffused interface, Figure 4.22(b). Figure 4.22(a) is an overall view of the metal and oxide scale pointing to the two oxide layers formed. First oxide layer in contact with metal, Figure 4.22(c), consists of mixed Nb$_2$O$_5$, MoO$_2$ and MoO$_3$. Amounts of SiO$_2$ were also present in this layer. The second layer or outermost layer, Figure 4.22(d) consisted
of Nb$_2$O$_5$ and CrNbO$_4$ particles embedded in a SiO$_2$ matrix. The overall thickness of the oxide scale was 1 mm. The x-ray mappings of these two layers are shown in Figures 4.23 and 4.24. Molybdenum and niobium are richer in the first layer and it is chromium depleted. It can be also observed that the silicon and chromium have higher concentrations in the second layer.

Compared to short term oxidation, sample exposed to long term oxidation at 1300°C also formed a layered oxide scale. Figure 4.25(a) shows an overall view of the oxidized specimen and the location of the three oxide layers. Magnification of micrograph is 80x. Overall thickness of oxide scale is 1.5mm. Figure 4.25(b) shows a high magnification (1000x) micrograph of the diffused oxide-metal interface. Figure 4.25(c) shows the first oxide formed in contact with the metal. The layer 1 is composed of mixture of MoO$_2$ and MoO$_3$ (light gray areas) and elongated Nb$_2$O$_5$ (gray areas). Silicon dioxide SiO$_2$ (dark gray areas) matrix was also observed. The layer 2; shown in Figure 4.25(d), consists of globular particles of CrNbO$_4$ (gray areas) oxide embedded in a SiO$_2$ matrix (black areas). Figure 4.25(d) illustrate the outermost layer, layer 3, formed in alloy. This layer is mainly composed of Nb$_2$O$_5$ particles (white areas) with regions or spots of CrNbO$_4$ (gray areas) embedded in a SiO$_2$ matrix (black areas).

The x-ray mappings performed on layer 1-3 are shown in Figures 4.26 through 4.28 respectively. The location of oxides can be clearly distinguished. In layer 1, dark and gray particles represent the mixture of niobium and molybdenum rich oxides and higher silicon concentration surrounds the particles. The middle oxide layer or layer 2 is clearly composed of particles rich in niobium and chromium. This layer is molybdenum
The outermost layer is a combination of niobium, chromium and silicon and Si oxides. The matrix is silicon rich and the white areas are higher in niobium concentration, while chromium contrast is observed in the dark regions. Oxygen concentration is located throughout the entire oxide scale.

Figure 4.22. BSE micrographs of alloy oxidized at 1200°C for 168 hrs: (a) shows the oxide metal interface formed at this temperature, (b) illustrates the first oxide layer in contact with metal. This layer consists of MoO₃, Nb₂O₅ and SiO₂, while outermost layer (c) is formed by globular particles of CrNbO₄, elongated particles of Nb₂O₅ in a SiO₂ matrix. Magnification of micrographs is 1000x.
Figure 4.23. Elemental x-ray mapping of O, Si, Cr, Nb and Mo performed on the first oxide layer in contact with metal formed at 1200°C after 168 hours of exposure.
Figure 4.24. Elemental x-ray mapping of O, Si, Cr and Nb performed on the second or outermost oxide layer formed at 1200 °C after 168 hours of exposure.
Figure 4.25. BSE micrographs of alloy oxidized at 1300°C for 168 hrs: (a) shows an overall view of the oxidized sample and the three oxide layers formed, (b) illustrates the diffuse oxide-metal interface. Layer 1 (b) consists of MoO$_3$, Nb$_2$O$_5$ and SiO$_2$, while layer 2 (d) is formed by globular particles of CrNbO$_4$ embedded in SiO$_2$ matrix. Layer 3 (d) shows particles of Nb$_2$O$_5$ with CrNbO$_4$ regions in a SiO$_2$ matrix. Magnification of micrographs is (a) 80x and (b-e) 1000x.
Figure 4.26. Elemental x-ray mapping of O, Si, Cr, Nb and Mo performed on the first oxide layer, layer 1, in contact with metal formed at 1300°C after 168 hours of exposure.
Figure 4.27. Elemental x-ray mapping of O, Si, Cr and Nb performed on the middle oxide layer, layer 2, formed at 1300 °C after 168 hours of exposure.
Figure 4.28. Elemental x-ray mapping of O, Si, Cr and Nb performed on the outermost oxide layer, layer 3, formed at 1300°C after 168 hours of exposure.
4.3.1.2 X-Ray Diffraction, XRD

The oxidation products obtained after 168 hours of exposure were characterized by XRD. Figure 4.30 presents the XRD patterns of oxides obtained from samples oxidized at 700-1300°C. XRD analysis confirmed the presence of Nb₂O₅, CrNbO₄, Mo₄O₁₁, MoO₃, MoO₂, CrMoO₄ and SiO₂. The predominant oxides formed at all temperatures were CrNbO₄ and Nb₂O₅. XRD patterns were similar at all temperatures except at 700°C. An extra peak of orthorhombic Nb₂O₅ appeared at 2θ values of 23° and 29°. No orthorhombic Nb₂O₅ was observed at 800°C.
4.4 Oxidation Kinetics

Linear oxidation occurs when the metal’s surface is not protected by a layer of oxide; with prolonged time exposure the metal would continue to oxidize at a constant rate and it would never slow down causing the destruction of the metal. The formation of volatile or molten oxides, spallation or breakaway of oxides due to growth and internal stresses or the growth of porous non protective oxide are some of the factors that cause linear oxidation. Parabolic oxidation is controlled by the diffusion of atoms and the driving force is the chemical potential. If a compact layer of protective oxide is formed and it continues to grow at prolonged time exposure, the diffusion distance of atoms increases causing a decrement in the diffusion rate. This type of oxidation is of great importance because the oxide growth occurs with a decreasing oxidation rate. Table 4.6 shows a
comparison between parabolic and linear oxidation rate constants of the studied alloy and Nb alloys being developed for high temperature applications. The comparison of the values indicates that studied alloy is competitive compared to other Nb-based alloys previously reported.

Table 4.6. Comparison of parabolic and linear oxidation rate constants between studied alloy and Nb alloys.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Studied Alloy</th>
<th>Oxidation rate constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_p) (mg^2/cm^2/hr)</td>
<td>(k_l) (mg/cm^2/hr)</td>
</tr>
<tr>
<td>800</td>
<td>Nb-20Mo-15Si-5B-20Cr</td>
<td>4.84 (0-24 hr)</td>
<td>0.52 (0-120 hr)</td>
</tr>
<tr>
<td></td>
<td>Nb-18Si-5Cr-5Al-5Mo</td>
<td>-</td>
<td>684 (&lt;56 hr)</td>
</tr>
<tr>
<td></td>
<td>Nb-24Ti-18Si-5Cr-5Al-5Mo</td>
<td>-</td>
<td>205.2 (&lt;110 hr)</td>
</tr>
<tr>
<td></td>
<td>Nb-38Ti-12Hf-12Al</td>
<td>3.3 (&lt;10 hr)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nb-18Si-26Mo</td>
<td>746.7 (6-24 hr)</td>
<td>-</td>
</tr>
<tr>
<td>1000</td>
<td>Nb-20Mo-15Si-5B-20Cr</td>
<td>16.64 (0-24 hr)</td>
<td>0.61 (0-72 hr)</td>
</tr>
<tr>
<td></td>
<td>Nb-11Si-2B</td>
<td>20.3 (&lt;10 hr)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nb-15Si-2B</td>
<td>115 (&lt;10 hr)</td>
<td>-</td>
</tr>
<tr>
<td>1150</td>
<td>Nb-13Si-4Mo</td>
<td>203.1 (1-24 hr)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nb-12Si-15Mo</td>
<td>166 (5-19 hr)</td>
<td>-</td>
</tr>
<tr>
<td>1200</td>
<td>Nb-20Mo-15Si-5B-20Cr</td>
<td>54.15 (0-24 hr)</td>
<td>16.1 (0-168 hr)</td>
</tr>
<tr>
<td></td>
<td>Nb-24Ti-18Si-5Cr-5Al-2Mo-5Hf</td>
<td>396 (&lt;110 hr)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nb-25Ti</td>
<td>55.8 (&lt;10 hr)</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Nb-38Ti-12Hf-12Al</td>
<td>248.7 (&lt;10 hr)</td>
<td>-</td>
</tr>
<tr>
<td>1300</td>
<td>Nb-20Mo-15Si-5B-20Cr</td>
<td>143.7 (0-24 hr)</td>
<td>31.76 (0-168 hr)</td>
</tr>
</tbody>
</table>

4.5 Summary and Discussion of Results

This work presents the results obtained from the studies of the microstructure and high temperature oxidation behavior of the Nb-20Mo-15Si-5B-20Cr alloy.

The as cast microstructure of the alloy, Figure 4.1, consisted of the solid solution \(\alpha\), the silicides \(\text{Nb}_3\text{Si}_3\) and \(\text{Nb}_3\text{Si}\), the Laves phase \(\text{NbCr}_2\) and the eutectic like microconstituent formed by \(\alpha\), \(\text{Nb}_3\text{Si}\) and \(\text{NbCr}_2\). XRD analysis performed on the alloy, Figure 4.3, confirms the presence of these phases as well as their crystal structures.
Solid solution (α) has a BCC structure and Nb₃Si exhibited a tetragonal structure. Laves phase NbCr₂ was present in the alloy in the hexagonal C-14 form and tetragonal. Nb₅Si₃ was present in a tetragonal form. Pandat™ 8.1 software also confirmed the presence of (α), Nb₅Si₃ and high temperature C-14 Laves phase NbCr₂ and showed that the alloy remains in the four-phase region at different temperatures, see Figure 4.4. The presence of Nb₃Si in the as cast microstructure suggests that equilibrium microstructure was not reached during alloy solidification [3, 5, 7].

Short term oxidation, 24 hours of exposure, suggests that oxidation resistance is temperature dependent. Better oxidation resistance was observed at 900 and 1000°C as shown in Figure 4.5. This behavior can be attributed to the volatilization of molybdenum oxides. The oxidation product formed at 900 and 1000°C was a thin oxide layer composed of CrNbO₄, Nb₂O₅ and a mixture of SiO₂ and CrMoO₄. The oxide layer formed at 1000°C also revealed the presence of Cr₂O₃. As previously mentioned, MoO₃ volatilizes from 400 to 900°C (23, 52). MoO₃ was not detected by SEM and EDS analysis, Figure 4.7(b-d) and Table 4.3 respectively, of samples oxidized at those temperatures. X-ray mapping at 800 and 1000°C shows the existence of Mo in the oxide scale suggesting that molybdenum oxides, such as Mo₄O₁₁ and CrMoO₄, conforms the oxide scale and not MoO₃. The presence of these oxides was confirmed by XRD analysis, Figures 4.15 and 4.16.

The mass gain per unit area was constant from 1100-1300°C. Analysis of the oxide scale at those temperatures revealed that the oxide scale formed at 1300°C differs from the ones formed at 1100 and 1200°C. The porosity of the oxide scale was reduced and
it exhibited a layered fashion, Figure 4.9. The oxide scale consisted of three dense oxide layers. The layer 1 is composed of molybdenum and niobium oxides, MoO$_3$, MoO$_2$, and Nb$_2$O$_5$. The layer 2 is formed by CrNbO$_4$ particles embedded in a SiO$_2$ matrix. The layer 3 shows elongated particles of Nb$_2$O$_5$ with some regions of CrNbO$_4$ embedded in SiO$_2$ matrix. The formation of a SiO$_2$ matrix and molybdenum oxides was only observed at this temperature. The presence of molybdenum oxides in the layer close to the oxide-metal interface can be attributed to the oxide entrapment caused by the other layers or to formation during cooling [24]. The accumulation of MoO$_3$ in layer 1 below layer composed of CrNbO$_4$ and SiO$_2$ matrix indicated that layer 2 may have acted as a diffusion barrier for highly volatile MoO$_3$. This phenomenon has also been reported in alloys from the Nb-Mo-Si-B and Mo-Si-B systems [55-60].

Detailed oxidation experiments at 800, 1000, 1200 and 1300°C revealed that the oxidation behavior followed a parabolic trend. Better oxidation resistance was observed at 800°C. This can be attributed to spallation of the oxide scales during cooling. The oxidation product at 800°C consisted of a thin oxide scale with no powder and at higher temperatures the oxide layer detached from the metal causing further oxidation of the alloy.

The oxidation products at all temperatures are a mixture of CrNbO$_4$, Nb$_2$O$_5$ and SiO$_2$ among others; the predominant oxides formed at all temperatures were CrNbO$_4$ and Nb$_2$O$_5$ (refer to Table 4.5.).

Long term oxidation, 168 hours of exposure, shows that oxidation resistance is time dependent. Better oxidation resistance was observed at 1200 and 1300°C at the end of
168 hours. Oxidation at 700°C followed a linear oxidation throughout the entire test. Oxidation at 900 and 1000°C followed a linear behavior for the first 72 hours. Further exposure resulted in complete oxidation of sample. A parabolic trend was observed from 1100-1300°C. Complete oxidation was observed in sample oxidized at 800°C. The sample was completely transformed into powder at the end of 168 hours indicating that pesting had occurred. Pestling oxidation is observed at intermediate temperatures and it preferentially attacks the intermetallic compounds. Pestling is characterized by the disintegration of alloys into small oxide particles and powder [25]. Complete sample oxidation was also observed at 900-1100°C. Analysis of oxide scales formed at 1200 and 1300°C revealed the presence of different layers of oxides, Figures 4.22 and 4.25 respectively. The presence of SiO$_2$ matrix was observed at those temperatures. The improved oxidation resistance at higher temperatures can be attributed to the formation of SiO$_2$ matrix and CrNbO$_4$ particles. The combination of these two oxides acted as a barrier to prevent the alloy from further oxidation. Even though CrNbO$_4$ was the predominant oxide formed at all temperatures, its protective nature was not sufficient to prevent the alloy’s complete oxidation from 800-1100°C. Also, the formation of Nb$_2$O$_5$, a non-protective oxide, was too dominant to prevent complete oxidation of samples.
CHAPTER 5

CONCLUSIONS

- The microstructure of as cast Nb-20Mo-15Si-5B-20Cr alloy consists of four phases: Solid solution (α), silicides Nb$_5$Si$_3$ and Nb$_3$Si, Laves phase NbCr$_2$ and the eutectic like microconstituent (α), Nb$_3$Si and NbCr$_2$.
- The crystal structures of phases are: BCC (α), tetragonal Nb$_3$Si, hexagonal NbCr$_2$ and tetragonal Nb$_5$Si$_3$.
- Calculated isothermal sections showed that phases present in alloy remain stable at all temperatures.
- The presence of Nb$_3$Si in the as cast microstructure suggests that equilibrium microstructure was not reached during alloy solidification.
- Short term oxidation is temperature dependent.
- Short term oxidation curve showed that better oxidation resistance was displayed at 900 and 1000°C.
- CrNbO$_4$, Nb$_2$O$_5$ and SiO$_2$ were the main oxides present in oxide scales at all temperatures.
- The short term oxidation kinetics follows a parabolic behavior.
- Long term oxidation is time dependent.
- Samples oxidized at 1200 and 1300°C showed better oxidation resistance.
- Complete sample oxidation was observed in samples oxidized from 800-1100°C.
- Pesting oxidation behavior was exhibited by sample oxidized at 800°C.
- Oxidation kinetics followed a linear behavior from 700-1000°C and a parabolic behavior from 1100-1300°C.
• The presence of silicon oxide matrix and MoO$_3$ was observed at 1200 and 1300°C. The combination of CrNbO$_4$ and SiO$_2$ matrix provided oxidation resistance to the alloy.

• Parabolic and linear oxidation rate constants, obtained at 800, 1000, 1200 and 1300°C for both short and long term oxidation are competitive compared to the values for Nb-based alloys reported by different authors.
REFERENCES


CURRICULUM VITAE

Julieta Angelica Ventura Luna was born on August 12, 1983 in Celaya, Guanajuato, Mexico. She is the eldest of three daughters of Raul Arnoldo Ventura Loya and Rosa Ma. Luna Ramos. She completed her high school education at Colegio Arturo Rosenblueth, located in Celaya, Guanajuato, Mexico, in May 2001. In the fall of that year she enrolled at The University of Texas at El Paso and graduated in May 2006 with a B.S. degree in Mechanical Engineering. Upon graduation, she immediately enrolled for graduate studies to pursue a M.S. degree in Metallurgical and Materials Engineering. In the summer of 2007 she worked as a graduate intern for Lockheed Martin Space Systems Michoud Operations located in New Orleans, LA. She worked in the Materials Department for NASA’s Orion crew exploration vehicle. In the fall of that year she obtained a research assistant position with Dr. S.K. Varma under whom she authored several publications and made a poster and oral presentation at MAES and TMS conferences. She also was awarded with the Ray W. Guard Memorial Award for outstanding graduate student and graduate research.

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