The Effect of Al and B Additions on the Oxidation Behavior of Alloys from the Nb-Cr-Si System

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THE EFFECT OF AL AND B ADDITIONS ON THE OXIDATION BEHAVIOR OF ALLOYS FROM THE Nb-Cr-Si SYSTEM

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Dedication

Dedicated first and foremost to God Almighty, my source of strength. To Him be all the glory and honor. To my amazing parents, Ruben and Biviana Esparza for their love, support, hard work and for always believing in me.
THE EFFECT OF AL AND B ADDITION ON THE OXIDATION BEHAVIOR
OF ALLOYS FROM THE NB-CR-SI SYSTEM

by

NYDIA JUDIT ESPARZA, B.S.

THESIS

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Abstract

Nickel based superalloys have been developed to perform substantially in industry however as technology develops, the need and desire to increase service temperatures to improve efficiency and performance is pushing the capabilities of these alloys. These aspired requirements entail the research and development of new structural materials that surpass the abilities of nickel alloys. Research in Nb-based alloys is underway as Nb alloys have shown to be a promising alternative with similar density but higher melting temperatures than the Ni alloys. However, because Nb has poor oxidation properties extensive studies are necessary to develop an alloy that can perform as highly as the Ni alloys in industry.

This study will focus on the effect of Al and B on oxidation resistance by subjecting five alloys from the Nb-Cr-Si system to isothermal static and cyclic conditions. Oxidation in air for 24 hours at temperatures ranging from 700°C to 1400°C has been conducted on alloys with composition of Nb-30Cr-10Si, Nb-30Cr-10Si-5Al, Nb-30Cr-10Si-10Al, Nb-30Cr-10Si-5B, and Nb-30Cr-10Si-10B (at%). The weight gain per unit area as a function of temperature was determined and samples were analyzed using SEM, EDS, XRD, and x-ray mapping. Better oxidation resistance was observed in the low temperature range in the Nb-30Cr-10Si and in alloys with boron additions. At higher temperatures, the 5Al and boron additions were beneficial to the oxidation response of the alloys. Complete oxidation occurred in all the alloys at 900°C except in the 10B alloy. The 10Al addition was detrimental at all temperatures. Alloys with boron addition yielded better oxide adherence compared to the Nb-30Cr-10Si and aluminum alloys. Cyclic oxidation for 168 hours was also performed which resulted in spalling of the oxides and limited amounts of metal left.
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Chapter 1. Introduction

New developments in high temperature technology continuously increase the need of high temperature materials and their enhanced behavior. These materials used in applications such as structural applications, turbines, energy and aerospace industry, and nuclear systems are required to withstand extreme high temperatures and maintain a suitable oxidation resistance in corrosive environments. The most capable material used in industry is nickel-based superalloys due to their high oxidation resistance in aggressive conditions under high temperatures and pressures. Although the mechanical and oxidation properties of these nickel-based superalloys have proved to be superior to any other alloys, they are gradually reaching their maximum potential due to their upper temperature limit to be used in applications. The need and desire to increase service temperatures to improve efficiency and performance will exceed the melting temperature of Ni and will require the development of new structural materials.

A promising alternative to nickel based super alloys are Niobium based super alloys because of higher melting temperatures, and low density comparable to that of nickel and high strength at elevated temperatures. Niobium however, requires development through alloying to enhance the oxidation resistance in aggressive environments and reach the performance capabilities of Ni-based superalloys. The issue with these Nb-based superalloys is that they suffer catastrophic oxidation in certain temperature range and demonstrate poor oxidation at others since niobium is highly soluble in oxygen and forms a voluminous oxide that does not offer protection to the alloy at high temperatures.  

For these reasons, extensive research has been conducted in addition of alloying elements including Al, Cr, Si, Ti, Hf, Ge, and Fe in order to enhance its oxidation resistance. These Nb-
based alloys can be processed to yield a multiphase microstructure of intermetallic phases that improve the oxidation resistance of the material. As a result of previous studies, it has been determined that through these additions the oxidation resistance of Nb-based alloys is improved but oxidation mechanisms such as pesting and spallation still remain a problem. The core of these issues deal with the phases and oxides formed during oxidation. When there is a mismatch or large difference of coefficients of thermal expansions between two phases, or a phase and an oxide, cracks tend to form and give way to the spalling and pesting mechanisms which hinder the alloys performance.

The current effort is to develop intermetallic phases such as the Laves phase that will form a protective oxide layer which will reduce the oxygen diffusion rates and decrease the oxidation of high temperature alloys in service. The Laves phase can be obtained by alloying Nb with Cr. Additionally, alloying Nb with Si result in the formation of silicides, which provide high temperature strength and improve the oxidation resistance.\(^5\) The alloying elements that are currently of great interest include Al and B. These two elements have been reported to support the formation of an adherent, highly protective oxide scale.

The purpose of this research is to observe the oxidation behavior and kinetics of five alloys in the Nb-Cr-Si system and define the effect of Al and B on the oxidation behavior of these alloys. The Cr and Si alloying elements were selected to form intermetallic phases (NbCr\(_2\)) and silicides which improve oxidation resistance.\(^1\) The addition of Al was to promote a protective Al\(_2\)O\(_3\) layer which has been reported to highly enhance the oxide scale adhesion and decrease spalling. Boron is expected to reduce the pest susceptibility in the low temperature range.\(^7\) The alloys selected for this study include:
- Nb-30Cr-10Si
- Nb-30Cr-10Si-5Al
- Nb-30Cr-10Si-10Al
- Nb-30Cr-10Si-5B
- Nb-30Cr-10Si-10B

A study of the effect of Al and B on the oxidation for the alloys of this system will be performed by characterizing and observing microstructural response and behavior to oxidation along with characterization of oxide scale formation. The understanding of these effects will provide a clearer perspective on the enhancement or detrimental contribution of these alloying elements in the Nb system and will add progress on the studies of Nb-based alloys.
Chapter 2. Literature Review

2.1 Oxidation

Oxidation occurs when metals are heated in a highly oxidizing atmosphere including stagnant air or oxygen which are common conditions in service of many metals and alloys in industry. Oxidation is defined as the interaction of metal with oxygen to form an oxide. This process occurs by the absorption of oxygen molecules from the atmosphere and initiating the nucleation of oxides which is followed by the formation of a thin oxide layer on the surface of the metal that grows thicker as oxidation continues.

In thermodynamic terms, oxidation follows when the oxygen potential in an environment is higher than the partial pressure of oxygen in equilibrium with the oxide. The rate at which it occurs has been characterized into several forms which include linear, parabolic, and logarithmic oxidation.

Parabolic Oxidation is described as oxide growth occurring with a decreasing oxidation rate continuously. The oxidation rate of a reaction is inversely proportional to the scale thickness (x) or the weight of the formed oxide in this parabolic pattern. This relation can be noted by:

\[ \frac{dx}{dt} = \frac{K_p}{x} \]

And integrated as:

\[ x^2 = 2K_pt + C \]

where \( K_p \) is the parabolic rate constant.

Most metals and alloys are observed to follow this trend at high temperatures where the growth of the oxide occurs by the diffusion of ions or electrons in the first formed scale
composed of the stable oxides.\textsuperscript{6} This behavior is desired over linear oxidation as it delays the rate after a layer is formed on the surface of the metal. This oxidation function is observed when the oxide scale is compact and continuous making the diffusion of oxygen into the metal difficult and providing protection to the unoxidized metal.

Linear oxidation occurs when the oxidation rate is constant with time and is independent of the amount of gas or metal used up in the reaction. In this case, the reaction rate is controlled by diffusion through the gas phase.\textsuperscript{8} Linear oxidation is represented by the following equation:

\[ \frac{dx}{dt} = K_1 t \]

Integrated it becomes:

\[ x = K_1 t + D \]

\( x \) is the thickness of the oxide scale, \( t \) represents time of oxidation, and \( K_1 \) represents the linear rate constant at which oxidation occurs.\textsuperscript{8} This linear behavior allows for oxygen to continue diffusing into the metal consuming by the formation of oxide. This is observed with the formation of a porous incoherent oxide scale. The continuous diffusion of the oxygen into the metal eventually results in complete oxidation.

Logarithmic oxidation follows the logarithmic law and has been observed to form very thin films of oxides and is generally occurring at low temperatures up to about 400°C.\textsuperscript{8} This oxidation rate occurs quickly in the initial reaction but reduces to a very low rate rapidly. Because of a rapid initial oxide formation, this type of oxidation is ideal as it results in the lowest oxidation rates however; it is not observed or obtainable at high temperatures.
2.2 Oxidation of Niobium

Niobium has become of great interest in research for high temperature applications because of its melting temperature of 2468°C exceeding that of nickel of ~1453°C and service temperature of 1150°C. Regardless of its high temperature, Niobium exhibits very poor oxidation resistance behavior making it necessary to alloy with other elements to enhance its oxidation resistance. One of the phases resulting from Nb is the Nb solid solution which is not beneficial for the oxidation resistance of the alloy but offers ductility to an alloy which may be needed for crack arrest and bridging. The poor oxidation properties of Nb in part are due to the formation of the Nb₂O₅ oxide from this phase. This process along with the oxidation of Nb is explained as follows.

The mechanism of high temperature oxidation of niobium is explained by inward diffusion of oxygen. There are two steps in the oxidation of niobium: the protective layer oxidation stage and the breakaway oxidation stage. The process begins by the formation of a protective layer on the surface of the alloy which takes place through dissolution of oxygen into the metal and forming Nb stable oxides which include NbO, NbO₂, and Nb₂O₅. In this first stage which is observed below 300°C oxidation occurs following the logarithmic law of oxidation as oxygen is absorbed into the Nb metal. The second stage of oxidation in Niobium, the breakaway stage, begins when the formation of Nb₂O₅ occurs which follows the parabolic oxidation law and is observed in the rage of 300 to 500°C. The Nb₂O₅ oxide exists in three forms which will be discussed later. When the Nb₂O₅ oxide grows, it becomes very porous and provides no oxidation resistance or protection to the metal from further oxidation. Particularly, the Nb₂O₅ oxide forms under tension because the Pilling-Bedworth ratio (PBR) for this metal-
oxide interface is less than one. This tension causes oxide cracking to occur exposing unoxidized metal to further oxidation.\textsuperscript{8}

The Nb\textsubscript{2}O\textsubscript{5} oxide occurs in three forms; the monoclinic, which is the high temperature form, the body centered monoclinic mid-temperature form, and the orthorhombic form which is the low temperature form. The growth of this oxide and the transformation of Nb\textsubscript{2}O\textsubscript{5} from gamma to the alpha structure in the range of 800-850°C produce stresses which will cause cracking of the oxide layer when the layer of oxide will begin to breakaway. This transformation has also shown pesting behavior at the intermediate temperature range from 900-1100°C.\textsuperscript{12} The time of initiation of the second stage of oxidation in niobium will decrease as temperature and oxygen pressure increases.\textsuperscript{6} At temperatures ranging from 500 to 1250°C where spalling and cracking of the Nb oxide layer occurs, linear oxidation is then observed.\textsuperscript{11}

The oxidation behavior in the Nb system is very temperature dependent. Crystal orientation is also an important factor in this system due to the breakaway mechanism. At temperatures below 650°C, localized and uneven attack of the metal surface occurs along preferred lattice planes in individual grains.\textsuperscript{6} At high temperatures, the mechanism undergoes a drastic change in which initial oxides include NbO or NbO\textsubscript{2} and are formed from the solid solution and oxygen.\textsuperscript{6} This allows for a uniform layer of oxide on the surface yielding protection for the metal. As mentioned before, the Nb\textsubscript{2}O\textsubscript{5} oxide can exist in three polymorphic forms which display different structures. This is particularly important as the transformation between structures has shown to affect the oxidation layer and cause cracking between the oxide and the metal leading to spallation.\textsuperscript{13} At low temperatures, Nb\textsubscript{2}O\textsubscript{5} exists in an orthorhombic form then transforming into a face centered body cubic monoclinic structure in the mid temperature range. This mid temperature form has a very high volume expansion compared to the low temperature
form and this transformation has resulted in complete oxidation of the metal. This form harms the formed oxide scale because it is the least fitting and least similar to the existing metal.\textsuperscript{6} At high temperatures, Nb\textsubscript{2}O\textsubscript{5} is observed in the monoclinic form which has a lower volume expansion than the mid temperature polymorph.\textsuperscript{6} The Nb\textsubscript{2}O\textsubscript{5} oxide is one of the most detrimental oxides in the Nb system as it has a very high volume expansion of 169\% which forms very high stresses and is released by oxide cracking.\textsuperscript{1} This oxide cracking results in spalling of the oxide scale as explained in detail later.

2.3 PHASES AND INTERMETALLICS

Multiphase Nb-based alloys, particularly in the composition mentioned for this study, are of great interest because of its formation of the silicides, Nb solid solution, and Laves phase. Each of these phases enhances the performance of the alloy in some way although some of these phases may be more damaging for the alloy for their lack of oxidation of resistance. Nb solid solution phase is an example of this case as it has a crystal structure of body centered cubic and is known for providing tensile ductility and fracture resistance, however, it is not beneficial for oxidation resistance.\textsuperscript{14} The Silicide and Laves phases will be discussed in greater detail as follows.

2.4 Nb-Si SYSTEM

Silicon is an alloying element commonly used in the Nb-system because of its formation of intermetallic phases and silicides which exhibit high temperature strength, high melting point, and good creep resistance.\textsuperscript{9} A common silicide formed in the Nb-Cr-Si alloys is the Nb\textsubscript{5}Si\textsubscript{3} as it exhibits the highest melting temperatures of the silicides formed with Nb. Although this silicide has good mechanical properties including a melting temperature of 2515°C (addition of Silicon
is added with the intention of providing creep resistance) it does not have a balance of properties needed in high temperature applications.\textsuperscript{1,10,15} Aside from its good mechanical properties, this silicide has very poor oxidation resistance which is thought to be attributed to the formation of Nb$_2$O$_5$ oxide that forms from this phase in a very porous.\textsuperscript{6} The desired contribution of the Nb$_5$Si$_3$ silicide aside from its very high melting point is that it tends to form a eutectic-like microstructure with the Nb$_{ss}$ phase.\textsuperscript{9,15-17} This lamellar structure has shown great thermo-chemical stability and has high coarsening resistance.\textsuperscript{18} This composite phase may have the potential of higher (by 200°C) service temperature requirements because of this lamellar structure.\textsuperscript{17} Additionally this silicide provides low density with high temperature strength and its oxidation resistance can be improved by alloying with Cr, Al, Ti and Hf.\textsuperscript{2} The Nb$_5$Si$_3$ silicide is a result of the decomposition of the Nb$_3$Si silicide into Nb and Nb$_5$Si$_3$ and can be useful in the Nb system if alloyed to enhance its oxidation resistance.\textsuperscript{15,18}

Another silicide phase that is currently being explored and is present in the Nb-30Cr-10Si alloy is the Nb$_9$Si$_2$Cr$_3$ also noted as the Nb$_9$(Cr, Si)$_5$. This phase formed through invariant reactions based on Nb$_5$Si$_3$, Nb$_{ss}$, and NbCr$_2$ phases.\textsuperscript{10} It can be seen in existence with other silicides such as the Nb$_3$Si$_3$. This phase has been reported to have high aluminum solubility and concentration in the intermediate temperature range of 900-1200°C yielding in internal oxidation occurring along the interface of the silicide and the Laves phase.\textsuperscript{1} There have been no other reports of studies of the 923 silicide to determine a formation of a protective layer.

2.5 Nb-Cr System and Laves Phase

Alloying Nb with Cr has proven to enhance the oxidation of Nb. Cr is of interest in high temperature applications because like niobium, Cr has a high melting point and offers high
chemical stability which is convenient when alloying other elements.\textsuperscript{19,20} The Laves phase or NbCr\textsubscript{2} phase in the Nb-Cr-Si system is a very desirable phase as it has good properties including low creep rate, relatively low density, high oxidation resistance, and high melting point of 1720\textdegree{}C.\textsuperscript{3,7,14,21-22} The Laves phase also has high strength at elevated temperatures of 1200\textdegree{}C and maintains its mechanical properties at higher temperatures.\textsuperscript{19,23-24} The Laves phase exists in three structures including the C15 which is the cubic form, C14 the hexagonal form, and the C36 dihexagonal form.\textsuperscript{24-25} These structures and their stability depend on the temperature range. The C15 low temperature form of the Laves phase is observed to be stable at temperatures below 1650\textdegree{}C and the C14 high temperature form is observed to be stable above 1650\textdegree{}C.\textsuperscript{26-28}

The limiting factor for this phase in structural application is its low fracture toughness which can be improved though stress assisted phase transformation to maintain phase stability.\textsuperscript{24} It has been reported that the stability and amount of Laves phase present increases with an increase of Cr content in an alloy.\textsuperscript{4} In the same study, it was reported that oxidation resistance increased with higher volume of NbCr\textsubscript{2} present. The results of various studies reported NbCr\textsubscript{2} to form a two oxide layer structure and its high oxidation resistance is thought to be attributed to the formation of the Cr\textsubscript{2}O\textsubscript{3} and CrNbO\textsubscript{4} layers.\textsuperscript{19,21,23} The CrO\textsubscript{3} oxide layer is formed in the outer portion of alloys and is lose and porous so it does not provide high oxidation resistance. The CrNbO\textsubscript{4} layer, however, formed in the inner portion of the scale has shown good adhesion with a compact structure reducing the oxidation rate and improving the protection of the metal.\textsuperscript{20-21}
2.5 Al-Addition

Oxidation resistance of Nb silicide based alloys has been reported to be improved by elemental additions of Al. Because Nb has high oxygen solubility, pesting is commonly observed. This is particularly the case for Chromium rich oxide scales which suffer from spalling but the addition of Al has shown to significantly reduce scaling and spalling from this oxide.\(^2\) Due to these findings, alloying additions are further being incorporated in the alloys to suppress the spalling behavior.\(^2\) The aluminum content seen in alloying additions is usually kept below 15% as high Al content promotes cleavage fracture in the Nb solid solution.\(^7\) It has been reported by previous studies that Al additions improve spallation resistance which occurs from the formation of the Cr\(_2\)O\(_3\) and CrNbO\(_4\) oxide scales and volume expansion from Nb\(_2\)O\(_5\).\(^2\) When Al is added to an alloy Al\(_2\)O\(_3\) forms which is desired as its volume expansion is only 4.9%.\(^2\) This volume expansion is very low in comparison to 107% volume expansion of Cr\(_2\)O\(_3\) and 169% volume expansion of Nb\(_2\)O\(_5\).\(^1\) The lower expansion volume decreases the stresses and difference of CTE reducing the susceptibility of spallation. The formation of the protective Al\(_2\)O\(_3\) layer has been reported to be forming along the Laves phase and has also been reported to increase the oxidation resistance of the Nb\(_5\)Si\(_3\) silicide.\(^1,3\) For the protective continuous oxide layer to form from Al, Al must be soluble in the phases of the alloy as seen in a study by Alvarez and Varma in the Nb-20Si-20Cr-5Al alloy.\(^1\) For the stability of the Al\(_2\)O\(_3\) to occur, the Al flux to the oxide scale must be greater than the flux of Nb or Cr which would lead to the formation of other alloys.\(^2\) Additionally, alloying with Al up to 12 at% has shown good adhesion of the developed oxide layer making it protective to alloy.\(^2\) The addition of Al may also aid in decreasing the initial cracks and defects present in the sample which lowers the oxygen diffusion rate at the oxide/metal interface.\(^2\)
2.6 B-Addition

The addition of boron as an alloying element has proven to increase the oxidation resistance of alloy in the Nb-Si and Mo-Si systems. The addition of boron has shown to form a borosilicate glass layer that enhances oxidation resistance.\textsuperscript{33-36} Moreover, the addition of boron has been reported to eliminate the pest oxidation in the lower temperature range because of the formation of the same borosilicate glass which flows into the cracks of the oxide layer.\textsuperscript{34} Alloying B with Nb and Si is of particular interest because of the possible development of a two-phase microstructure consisting of Nb and T2 (Nb5SiB) in hope of balancing oxidation resistance and fracture toughness. This T2 structure has proven to have better oxidation resistance compared to the Nb5Si3 silicide alone, a common silicide observed in the Nb-Si system.\textsuperscript{36} Most of the enhancement reported by B addition has been made in the Mo-Si system. Another direction taken with the research in Mo is making the same additions of B anticipating similar results due to the similarity of atomic sizes of Mo and Nb. Studies by Meyer et al. have reported the formation of a porous borosilicate glass with a lacy network structure. The borosilicate glass has been observed to fill pores left by the volatilization of Mo. Although this borosilicate glass is still prone to oxygen diffusion, it has been observed to slow oxidation rates by filling the pores left by Mo.\textsuperscript{33} In the case of Nb, the formation of Nb2O5 does not occur in a continuous scale, rather it occurs with the presence of pores and voids between Nb2O5 and other oxides. The formation of a borosilicate layer would fill the voids left by the Nb2O5 oxide and offer additional protection to the alloy.
2.7 Oxidation Issues in Nb Alloys

2.7.1 Internal Oxidation

Internal oxidation is the formation of oxide precipitates within the alloy along the interface of phases or on the phases below the surface of the metal.\textsuperscript{6, 37} Internal oxidation happens from the oxygen dissolution into the alloy and along the metal/oxide interface. Internal oxides will form if the outward diffusion of the elements in the alloys is slower than inward diffusion.\textsuperscript{6} The process of internal oxidation entails the diffusion of oxygen at the surface of the metal or at the alloy-oxide scale interface. Oxygen will then diffuse in through the metal matrix and an oxide precipitate will form growing until there is no more solute atoms to supply into the precipitate.\textsuperscript{8} The size of the internal oxides forming depends on the nucleation rate which depends on the diffusion coefficient of the atoms and the diffusion coefficient of oxygen moving into the alloy. If the nucleation rate is high, then small oxides form and if it is low large oxides are observed.\textsuperscript{6} This is better explained by:

In order for the internal oxidation mechanism to take place, the following conditions must be met during oxidation\textsuperscript{8}:

- The free energy of formation per mole of O\textsubscript{2} for the solute metal oxide must be more negative than the free energy of formation for the base metal oxide.

- The free energy for the reaction of M + νO = BO\textsubscript{ν} must be negative. The base metal must have the sufficient solubility and diffusivity for oxygen to establish the needed activity of dissolved oxygen to begin the reaction

- The concentration of solute atoms in the alloy should be lower than the required amount for conversion from internal to external oxidation.
• There should be no protective surface layer to prevent the dissolution of oxygen in the alloy in order to begin the internal oxidation.

2.7.2 Pesting

Pesting is a mechanism recognized as the oxidation of alloys resulting in degradation of the metal in the form of powders. Pesting causes damage to the alloy and has been observed in refractory metals at intermediate temperatures greater than 800°C. The pest oxidation mechanism has been observed in intermetallic compounds as early as 1899 and has been studied in an effort to understand the cause of powder formation. Pesting was attributed by Westbrook and Wood to grain boundary hardening. They reported that the concentration of gasses such as oxygen increased grain boundary embrittlement which caused hardening and explained that at lower temperatures, oxygen diffused at a slower rate reaching only the external surfaces of oxidized samples. Furthermore, oxygen was able to diffuse through the grain boundary and that oxygen embrittled the material by increasing the hardness. This increase in hardness in turn creates internal stresses which result in the sample fragmenting along those hardened grain boundaries. In a study by Zhang in 2005, it was reported that pest oxidation could more closely be related to pre-existing defects such as pores or cracks. Zhang reported that large stresses at the tip of preexisting cracks resulted in the initiation of new cracks and propagation of existing cracks referred to as the wedging effect and found that cracks would open and propagate further with increasing oxidation and created a preferential site for high stress concentration. Additionally, the number of preexisting cracks and pores in the samples is related to the time for fragmentation to occur as these defects are ascribed to rapid oxidation. Previous studies by Bewlay have shown that pesting can be controlled in Nb alloys by the alloying with Al and Hf. Other alloying additions that have been reported to reduce pesting in Nb alloys are Al and
Hf. The addition of B has also shown to reduce the pest behavior in Niobium alloys in the low temperature regime. The pesting mechanism is still under research and is not fully understood or explained in detail.

2.7.3 Stresses in Oxides Scales

Stresses within the metal and the metal oxide are created during the oxidation process which has an effect on the adherence and compact level of the oxide scale with the metal. One of the stresses that form during oxidation are those caused by volume differences between the oxide and the metal. This can be represented by the Pilling-Bedworth ratio (PBR) which is the ratio of the volume of the oxide versus the volume of the metal. This ratio states that the oxide is in compression if the PBR is greater than one and in tension if it is less than one. A second type of stress pertaining to the experimentation presented in this project is thermal stresses. These stresses produce during the cooling process after oxidation. The thermal stresses can be attributed to the difference in the coefficient of thermal-expansion between the metal and the oxide. Due to the formation of these stresses, the oxide scale formed and the protection they will offer to the metal are affected. In reaction to these stresses several mechanisms occur which jeopardize the protection of the metal which are most commonly observed as cracking of the oxide scale and spalling.

2.7.4 Spalling

Spalling is another issue with high temperature materials, especially in Nb-based materials commonly observed in the 800-1100°C range. This mechanism entails the breakaway of formed oxide scales from the metal alloy leaving the unoxidized metal unprotected. Interfacial spallation has been attributed to the thermal expansion mismatch. Thermal compressive stresses
form cooling of the oxide because the coefficient of thermal expansion for the oxide is generally
less than that of the metal. This difference in the coefficient of thermal expansion along with the
mismatch stresses result in breakaway between the metal and the oxide causing the oxide scale to
spall off.\textsuperscript{8, 13, 37} Moreover, protective oxides formed with compressive stresses, spalling will
occur when the elastic strain energy which is stored in the oxide scale is greater than the fracture
resistance. This mechanism can be generalized to occur for alloys which form thick oxide scales
with high volume expansion, alloys that form high stresses, and alloys which do not form well
adhered oxide scales which is the case for \(\text{Cr}_2\text{O}_3\) and \(\text{Nb}_2\text{O}_5\) oxides.\textsuperscript{8,14, 21, 38}

This study will be concentrated on enhancing the oxidation resistance with Aluminum
additions to the Nb-Cr-Si system for the Nb-30Cr-10Si composition. Aluminum has been added
as an alloying element for its formation of a protective \(\text{Al}_2\text{O}_3\) layer during oxidation which has
been observed to form in the Laves phase. Al has also been seen to improve the oxidation
resistance of some particular silicides in some studies and decrease the pesting mechanism in
some intermetallic phases present.\textsuperscript{39-41} In order to achieve this desirable properties from
aluminum, however, it is important that aluminum is soluble in the present phases in order to
attain a protective continuous oxide layer.

In order to carry out this investigation, three alloys in the Nb-Cr-Si system will be
compared in the following compositions: Nb-30Cr-10Si, Nb-30Cr-10Si-5Al, and Nb-30Cr-10Si-10Al (at%). The experiments will include oxidation for 24 hours in temperatures ranging from
700°C to 1400°C to evaluate the behavior of these alloys for the first 24 hours of service.
Furthermore, cyclic loading oxidation will also be performed to observe the behavior in heating
and cooling conditions at selected temperatures between 700°C to 1400°C.
Chapter 3: Experimental Details

3.1 Alloy Fabrication

The alloys used in this study were fabricated by Ames Laboratory of Iowa State University. Alloys were processed using arc-melting technique in an inert high purity argon gas atmosphere and were re-melted three times for homogeneity. The cast ingots were then cut into 5 x 5 x 5 mm cubes using electrical discharge machining (EDM). The compositions of the alloys under study are as listed in table 1 in atomic percent.

Table 3.1: Atomic percent compositions of alloys used in this study

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nb (at%)</th>
<th>Cr (at%)</th>
<th>Si (at%)</th>
<th>Al (at%)</th>
<th>B (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-30Cr-10Si (30-10)</td>
<td>60</td>
<td>30</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb-30Cr-10Si-5Al (5Al)</td>
<td>55</td>
<td>30</td>
<td>10</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Nb-30Cr-10Si-10Al (10Al)</td>
<td>50</td>
<td>30</td>
<td>10</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Nb-30Cr-10Si-5B (5B)</td>
<td>55</td>
<td>30</td>
<td>10</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Nb-30Cr-10Si-10B (10B)</td>
<td>50</td>
<td>30</td>
<td>10</td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

3.2 Sample Preparation

Once received, the alloy cubes were polished using SiC paper to a 600 grit surface finish on all six surfaces. To acquire an accurate surface area exposed to oxidation, the samples were measured to a thousandth of a millimeter on each surface using a micrometer. The cubes were then ultrasonically cleaned in ethanol for 15 minutes to ensure removal of particles or debris present on the surface from the polishing process.

Leco 528 hp (SiO₂) crucibles were used for oxidation experiments. The crucibles along with the crucible tops were furnace dried at a temperature of 300°C for 2 h to remove moisture that may affect oxidation. The samples were placed in the crucibles to prevent material loss and protect the samples from environment particles that could affect oxidation. Crucibles and
samples were weighed before and after oxidation experiments to observe the weight gain after oxidation using Sartorius analytical balance model MC210S.

3.3 OXIDATION

3.3.1 Isothermal Static Oxidation

The alloys were subjected to short term static oxidation referred to as STO to observe the oxidation behavior of the alloy during the first 24 h in service. Static Oxidation experiments consisted of exposing the sample to a desired oxidation temperature ranging between 700°C to 1400°C. The samples were heated to the preselected oxidation temperature at a ramp rate of 10°C/min, held at the oxidation temperature for 24 h, and furnace cooled to room temperatures. STO was conducted in static air. Once the 24 h oxidation was complete, the samples were weighed to monitor the weight gain per unit area and were plotted as a function of temperature. This thermogravimetric method was used to monitor the oxidation behavior by evaluating the weight gain and oxidation at each temperature.

3.3.2 Cyclic Oxidation

Cyclic Oxidation experiments were also conducted to observe the oxidation behavior of the alloys in cyclic conditions. One cycle of cyclic oxidation consisted of heating the samples to an oxidation temperature ranging between 700°C to 1400°C for 24h at a ramp rate of 10°C/min and then allowed to furnace cooled. Once the cycle was complete the samples were weighed to record the weight gain. The cycle was then repeated for seven days for a total of 168 h of oxidation. The metal left was mounted for microstructure characterization and the oxide product which resulted in pesting or spalling was collected for XRD analysis. The weight gain per unit area was plotted as a function of time to observe the oxidation trend at each temperature.
3.4 CHARACTERIZATION AND ANALYSIS

3.4.1 SEM

Scanning Electron Microscopy was used for characterization and phase identification of as-cast microstructure. Surface analysis via SEM was conducted using a Hitachi FESEM 8700 which is equipped with a backscatter electron detector (BSE). BSE mode was used to identify the phases present in the as-received samples as it allows atomic number contrast to better observe the difference of contrast in the phases present. Secondary mode was useful in observing surface topography for defects and pores.

Oxidized samples were mounted in an epoxy resin for SEM analysis. Once mounted, the samples were polished to a 1200 grit finish. The surface of these samples were also analyzed under SE and BSE modes for phase identification and morphology along with oxide characterization. Another SEM capability used was energy dispersive spectrometry (EDS) to confirm the elemental composition and ratio of each phase and oxide in accordance to XRD analysis. X-ray mapping was also used during SEM analysis to observe the elemental distribution in the phases and oxides. Most of the SEM analysis was conducted at 20KeV and a working distance of 15 mm.

3.4.2 X-Ray Powder Diffraction

The oxide scales that spalled off or pest were ground using a ceramic mortar to perform X-Ray powder diffraction (XRD). X-ray diffraction detects and identifies phases present in the alloys and the oxides formed during oxidation and gives details such as crystal structure, lattice parameter, and d-spacing. The XRD system used was a Bruker D8 Discovery with a monochromatic Cu Kα radiation. The scattered slit used was 0.2mm and the receiving slit was 6mm. The x-ray diffraction scan conditions used were a step size of 0.02mm, increment of 0.05
degrees, and a scan speed of 5 deg/min. To analyze the phases in the alloys present, the mount samples, that were polished and used for SEM analysis, were used in the same conditions for XRD.

3.5 Isothermal Phase Diagrams

Prior to characterization, Pandat™ software was used for isothermal section calculations. Pandat™ is a software which uses thermodynamic data to construct isothermal section of multicomponent systems and uses data to predict phases at various compositions and temperatures. This software was used in this study to observe the predicted phases present at room temperatures and determine phase stability by comparing the isotherms of the range of temperatures between 700°C to 1400°C. This software also provided the fraction amount expected of each predicted phase to explain any phase transformation that were expected to occur.
Chapter 4 Results and discussion

4.1 AS CAST

4.1.1 Isothermal Sections

Isothermal sections of the ternary and quaternary alloys were constructed using Pandat™ software at room temperature for the as-cast conditions. Figures 4.1a-4.1c shows the isothermal sections at 25°C for the Nb-30Cr-10 (30-10) alloy, Nb-30Cr-10Si-5Al (5Al) alloy, and the Nb-30Cr-10Si-10Al (10Al) alloy respectively.

Figure 4.1: Isothermal sections constructed for 25°C. a.) Nb-30Cr-10Si alloy b.) Nb-30Cr-10Si-5Al alloy and c.) Nb-30Cr-10Si-10Al alloy
The isothermal section of the 5Al and 10Al quaternary alloys were calculated based on the Nb-Cr-Si system by maintaining the atomic percent of 5 and 10 Al as fixed concentrations. The composition of each alloy is indicated by the square symbol on each respective isotherm. The point calculation on the 30-10 alloy isotherm (fig. 4.1a) indicates that a ternary phase microstructure consisting of NbCr$_2$, commonly known as the Laves phase, Nb$_9$Cr$_2$Si$_3$ (923-silicide), and the Nb solid solution (Nb$_{ss}$) is predicted. The same phases are expected to be present in the 5Al alloy (fig. 4.1b), however the formation of the Nb$_3$Al aluminide was additionally predicted. The 10Al alloy (fig. 4.1c) predicted the Nb$_9$Si$_2$Cr$_3$ silicide, the NbCr$_2$ phase, and the Nb$_3$Al phase. No Nb$_{ss}$ was predicted to be present in the 10Al alloy.

Pandat™ was also used to determine the phase stability of the predicted phases by constructing isothermal section in a range of temperatures between 700-1400° for each alloy. Pandat™ was also used to determine the predicted phase stability. The software indicated that there were no phase changes in the Nb-30Cr-10Si and the Nb-30Cr-10Si-10Al alloys at temperatures between 700°-1400°C. In the Nb-30Cr-10Si-5Al alloy, however, a phase change from Nb$_9$Si$_2$Cr$_3$ to Nb$_5$Si$_3$ is expected to occur at 1100°C.

Isotherms for the quaternary Nb-30Cr-10Si-5B (5B) and the Nb-30Cr-10Si-10B (10B) alloys were not calculated. The Pandat™ software database is not yet equipped with B thermodynamic data for the isotherm calculations.

4.1.2 Microstructural Characterization by Scanning Electron Microscopy

The microstructures of both as-cast alloys are presented in Figure 4.2. Figure 4.2a shows that the Nb-30Cr-10Si alloy consists of four phases rather than three as predicted. It contains the Nb$_9$Cr$_2$Si$_3$ phase as light grey, the Nb$_5$Si$_3$ as dark grey, the Laves phase in black, and the Nb$_{ss}$ in white. The Nb-30Cr-10Si-5Al (Figure 4.2b) consists of a three phase microstructure composed
of Nb$_9$Cr$_2$Si$_3$, NbCr$_2$ and the Nb$_{ss}$ phases. The 5Al addition suppresses the Nb$_5$Si$_3$ which is no longer present in this alloy. Additionally, the Al addition decreases the amount of Nb$_{ss}$ and transforms it from a primary phase as observed in the 30-10 alloy into a microconstituent in the lamellar structure. In both alloys, a eutectic-like microstructure can be observed consisting of Nb$_{ss}$, NbCr$_2$, and the Nb$_9$Cr$_2$Si$_3$ silicide. The Nb-30Cr-10Si-10Al (Figure 4.2c) alloy shows a similar microstructure to the 30-10 alloy in that it contains the Nb$_5$Si$_3$ and the Laves phase. However, no Nb$_{ss}$ solution was detected in this alloy; instead a second silicide Nb$_3$Si is present. The increase of Al from 5 at% to 10 at%, has suppressed the presence of the Nb$_9$Si$_2$Cr$_3$ and favored the formation of the Nb$_5$Si$_3$ and Nb$_3$Si. The Nb$_9$Cr$_2$Si$_3$ is the preferred silicide as it has been reported to form a more oxidation resistant scale than the Nb$_2$O$_5$ formed by the Nb$_5$Si$_3$. A pronounced eutectic-like microstructure is not observed in this alloy. The inconsistency of the fourth phase present in the Nb-30Cr-10Si and the Nb$_3$Al phase not present in the 5Al and 10Al alloy as calculated by Pandat™ may be attributed to the non-equilibrium conditions present during casting of these alloys.
Figure 4.2: As-cast microstructures of (a.) Nb-30Cr-10Si, (b.) Nb-30Cr-10Si-5Al, (c.) Nb-30Cr-10Si-10Al, (d.) Nb-30Cr-10Si-5B, and (e.) Nb-30Cr-10Si-10B
4.1.3 X-Ray Diffraction and X-Ray Mapping

The phases observed by SEM analysis were confirmed using XRD analysis as shown in Figure 4.3a and 4.3b. Most of the peaks for the 30-10 alloy were identified and labeled corresponding to the phases detected with EDS, however, peaks 35 and 36 were not identified. Similarly in the 5Al (Figure 4.3a) alloy, most phases match with the EDS analysis, however, peaks 35, 40, and 75 remain unidentified. Currently, there is no diffraction data or a diffraction card for the Nb$_9$Cr$_2$Si$_3$ silicide therefore it is highly possible that the unidentified peaks correspond to this silicide. To confirm the presence of the Nb$_9$Si$_2$Cr$_3$ phase, EDS and X-ray mapping were used. An X-ray map of the as cast 5Al alloy is presented in Figure 4.4. The purpose of the X-ray map is to detect the elemental distribution throughout the phases by relating the intensity of color with each element. The concentration of Cr is high indicated by the bright intensity of green in the regions where the NbCr$_2$ phase is present which is indicated on the backscatter image. Conversely, the concentration of Si is high in the regions where the silicide is present and depleted in other phases. The presence of Nb is observed in all phases but is highly concentrated in the Nb$_{ss}$ phase.

The important region to note is the Nb$_9$Si$_2$Cr$_3$ silicide. The light grey regions where the 923-silicide is present has a high concentration of Nb which represents the 61.94 at% Nb detected by E-Dispersive Spectrometry in this phase. The Si concentration can also be appreciated in the silicide where the EDS detected 13.47 at%. Cr was detected to be 21.6 at% and is also observed to be present in the silicide regions on the X-ray map. The elemental distribution in the 923-silicide (light grey phase) is consistent with the EDS composition analysis confirming the presence of the Nb$_9$Si$_2$Cr$_3$ phase.
Figure 4.3: XRD scans of the Nb-30Cr-10Si, Nb-30Cr-10Si-5Al, and Nb-30Cr-10Si-10Al as cast alloys confirming the phases present as found by EDS.

Figure 4.4: Map of Nb-30Cr-10Si-5Al as cast alloy showing the elemental distribution in each phase confirming the presence of the 923-silicide (light grey phase).
The XRD patterns for the 5B and 10B alloys are presented in Figure 4.5 and are compared to the Nb-30Cr-10Si alloy. Some of the peaks in the alloys with boron addition were not identified and the corresponding phases for those peaks are unknown as the only three phases found in the alloys were confirmed with XRD. The presence of the Nb$_3$Si in the alloys with B addition can be observed in comparison to the Nb$_5$Si$_3$ found in the 30-10 alloy.

Elements with low atomic weight, usually below carbon, are difficult to detect thus, it was difficult to get an accurate reading on the B content within each phase. For that reason, X-Ray Mapping was performed on the 5B and 10B alloys to detect the elemental distribution of B in the microstructure. In Figure 4.6a, the x-ray map of the 5B alloy exhibits high Nb concentration in the Nb$_{ss}$ and in the Nb$_3$Si but depleted in the Laves phase. Accordingly, the concentration of Cr is high in the Laves phase while Si is highly concentrated in the Nb$_3$Si. Boron is distributed uniformly throughout the Nb$_{ss}$ and Nb$_3$Si however, the concentration
appears lower within the Laves phase. The same is observed in the 10B x-ray map (Figure 4.6b) where the concentration of B is less in the Laves phase and higher in the Nb rich phases.

Figure 4.6a: Map of Nb-30Cr-10Si-5B as cast alloy showing the elemental distribution of B in each phase.

Figure 4.6b: Map of Nb-30Cr-10Si-10B as cast alloy showing the elemental distribution of B in each phase.
4.2 EFFECT OF AL ADDITION

4.2.1. Static Oxidation Curves and Oxidation Behavior of Nb-30Cr-10Si and Al Alloys

Short-term static oxidation was conducted to observe the behavior of the alloy during the first 24 hours of service. Figure 4.7 shows the short term oxidation curves for the Nb-30Cr-10Si, Nb-30Cr-10Si-5Al, and Nb-30Cr-10Si-10Al alloys. These curves were obtained by plotting weight gain per unit area as a function of oxidation temperature. Table 2.1 indicates the percent metal left at each temperature to describe the resistance to oxidation of the alloys while the symbols on the graph indicate the oxidation mechanism observed at each temperature as follows; ● -represents pesting, ▲ -represents the complete oxidation by the formation of a swollen oxide, ■ - represents spalling of the oxide scale, and ◆ -represents cracking of the metal. Because Nb has high oxygen solubility, pest oxidation and spalling of the oxide scale is commonly observed as discussed in section 2.7.2 and 2.7.4.23

In the low temperature range between 700-800°C, pest oxidation is the dominant mechanism. This oxide powder formation was observed in all three alloys but occurred most severely in the 5Al alloy. The 5Al alloy had the worst oxidation resistance with only 10-20% metal left after oxidation at lower temperatures. The 30-10 alloy exhibited the best oxidation response on the basis of least weight gain and 90-95% metal left. This shows that Al addition has proven to be detrimental at low temperatures. The 10Al showed similar weight gain to the 30-10 alloy however, this alloy suffered from cracking of the metal due to the formation of Nb$_2$O$_5$ from the Nb$_5$Si$_3$ and Nb$_3$Si silicides as shown in Figure 4.8. The differences of thermal expansion between the phases and oxides forming were too high to maintain the integrated shape of the sample.
Figure 4.7: Oxidation curves for Nb-30Cr-10Si, Nb-30Cr-10Si-5Al, and Nb-30Cr-10Si-10Al alloys exposed for 24 h at temperatures from 700 to 1400°C.

Table 4.1: Percent metal left in Nb-30Cr-10Si, Nb-30Cr-10Si-5Al, and Nb-30Cr-10Si-10Al after oxidation for 24 hours

<table>
<thead>
<tr>
<th></th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
<th>1100°C</th>
<th>1200°C</th>
<th>1300°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-30Cr-10Si</td>
<td>95%</td>
<td>90%</td>
<td>0%</td>
<td>0%</td>
<td>75%</td>
<td>80%</td>
<td>70%</td>
<td>55%</td>
</tr>
<tr>
<td>Nb-30Cr-10Si-5Al</td>
<td>20%</td>
<td>10%</td>
<td>0%</td>
<td>0%</td>
<td>90%</td>
<td>70%</td>
<td>90%</td>
<td>80%</td>
</tr>
<tr>
<td>Nb-30Cr-10Si-10Al</td>
<td>75%</td>
<td>65%</td>
<td>0%</td>
<td>0%</td>
<td>45%</td>
<td>30%</td>
<td>0%</td>
<td>70%</td>
</tr>
</tbody>
</table>
At mid-temperature range from 900-1000°C, the alloys showed a higher weight gain and exhibited different oxidation mechanisms. The 30-10 and 5Al alloys underwent complete oxidation resulting in the formation of a swollen oxide at 900°C while pest oxidation was still observed in the 10Al alloy. At 1000°C, the formation of a swollen oxide occurred in the 30-10 and 10Al alloys but the 5Al alloy formed a protective oxide scale which resulted in an apparent decrease in weight gain and 80% metal left. The swollen oxide product was analyzed by x-ray diffraction which detected the body-centered monoclinic form of Nb$_2$O$_5$. This form of Nb$_2$O$_5$ has the largest coefficient of thermal expansion of 167% from the three forms making it a very voluminous oxide. The formation of this oxide resulted in the complete consumption of metal into oxide product. Thus, the 5Al addition makes the alloy less susceptible to oxidation at
1000°C and the 10Al addition provides no benefit to oxidation resistance. This alloy shows the same cracking behavior which gives way to the pest mechanism.

In the high temperature range from 1100-1400°C less weight gain was observed in the alloys compared to the weight gain at mid-temperatures. The formation of oxide scales was observed in the 30-10 and 5Al alloys which provided some protection to alloys resulting in high percentages of amount of metal left. Nonetheless, spalling of the oxide occurred in this temperature range due to stress generation during oxide growth as a result of differences in molar volume or differences of thermal expansion between the metal and the oxide.\textsuperscript{23,30} These created stresses that are released by cracking in the oxide scale during the cooling process.\textsuperscript{28} Oxidation behavior was significantly improved with the addition of 5at\% Al as these alloys showed less cracking therefore less oxide spalling than the 30-10 alloy at high temperatures. Subsequently the 30-10 alloys suffered of more severe spalling which exposed a new surface area of metal to oxidation and resulted in a higher weight gain. Though the 10Al alloy exhibit less weight gain than the 30-10 alloy, it displayed very poor oxidation response and very little oxide scale formation due to the cracking that still persisted at higher temperatures.

On the basis of weight gain and oxidation kinetics from the static oxidation curves, the 30-10 alloy has proven to have better oxidation resistance at low temperatures. The addition of 5Al was beneficial at intermediate and high temperatures yielding less weight gain and protection of unoxidized metal. The 10Al addition was not favorable at any temperature range in this study.

\textbf{4.2.2 Microstructures after oxidation}

Figure 4.9, 4.10 and 4.11 shows the microstructures for the alloys after 24 hour oxidation at 700°C, 1100°C, and 1400°C where the most significant microstructural changes occurred.
The phases observed in the as cast microstructure of the Nb-30Cr-10Si alloy were the same phases observed after oxidation at all temperatures except for the Nb₅Si₃ phase. Figure 4.9a shows the microstructure observed at 700°C where the Nb₅Si₃ phase is no longer present but the Nb₆₇, Nb₉Si₂Cr₃, and Laves phases are still observed. Additionally, as can be observed, the eutectic-like microconstituent is less abundant at 700°C while the amounts of Nb₉Cr₂Si₃ and the Laves phases show growth as primary phases. In the Nb-30Cr-10Si-5Al alloy (Figure 4.9b), the three phase microstructure remains the same with no phase changes at any temperatures. There are no obvious microstructural changes observed between the oxidized alloy and the as cast sample from 700-800°C for this alloy. The 10Al alloy shown in Figure 4.9c also maintains a similar microstructure as observed in the as cast conditions. There are no other significant microstructural changes in the low or intermediate temperature ranges up to 1000°C.

Figure 4.9: Microstructures after 24 h oxidation at 700°C for (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5Al, and (c) Nb-30Cr-10Si-10Al.
After oxidation at 1100°C, an important change can be observed in the 5Al and 10Al microstructures, Figures 10b and 10c respectively. The nucleation of spherically shaped dark particles occurs which is categorized as internal oxidation. These particles were characterized as Al$_2$O$_3$ by EDS and were confirmed through X-ray elemental mapping analysis. A higher magnification of the presence of these particles is presented in Figure 4.12. In the 5Al alloy, internal oxidation occurs along the NbCr$_2$ and Nb$_{ss}$ phase. The 10Al alloy exhibits Al$_2$O$_3$ formation along the NbCr$_2$ and Nb$_3$Si interface. To understand the difference of interface formation and justify the formation of the particles in the mentioned interfaces, the Al content was analyzed in each phase of the 5Al and 10Al alloys. The Al content was the highest in the 30-10 alloy in the Nb$_{ss}$ phase and increased at higher temperatures. There was a corresponding decrease of Al content in the Laves phase. In the 10Al alloy, the Al content was higher in the silicide compared to the Laves phase but there was no trend in the Al content of each phase as a function of temperature. The observed Al content for each alloy is presented in Table 4.2 and 4.3. This Al content analysis explains the formation of the particles along the corresponding interfaces. The phase with the highest Al content promoted the nucleation Al$_2$O$_3$ along that interface. In the case of the 10Al alloy, the Al$_2$O$_3$ particles form an outline along the Laves phase. This occurs because the high Al content in the silicide gets transferred into the Laves phase favoring the internal oxidation along the NbCr$_2$. 
Table 4.2: Aluminum content in phases in the Nb-30Cr-10Si alloy.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Nb_{ss} (at%)</th>
<th>NbCr (at%)</th>
<th>Nb_{9}Si_{2}Cr_{3} (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>5.22</td>
<td>4.9</td>
<td>5.12</td>
</tr>
<tr>
<td>800</td>
<td>7.51</td>
<td>3.15</td>
<td>5.08</td>
</tr>
<tr>
<td>1000</td>
<td>6.08</td>
<td>3.47</td>
<td>5.64</td>
</tr>
<tr>
<td>1100</td>
<td>9.71</td>
<td>3.97</td>
<td>5.32</td>
</tr>
<tr>
<td>1200</td>
<td>10.11</td>
<td>2.5</td>
<td>5.83</td>
</tr>
<tr>
<td>1300</td>
<td>4.94</td>
<td>0.53</td>
<td>5.83</td>
</tr>
<tr>
<td>1400</td>
<td>15.85</td>
<td>5.67</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Table 4.3: Aluminum content in phases in the Nb-30Cr-10Si-5Al alloy.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>NbCr (at%)</th>
<th>Nb_{5}Si_{3} (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>6.18</td>
<td>***</td>
</tr>
<tr>
<td>800</td>
<td>8.57</td>
<td>10.74</td>
</tr>
<tr>
<td>1100</td>
<td>6.53</td>
<td>11.5</td>
</tr>
<tr>
<td>1200</td>
<td>4.85</td>
<td>13.29</td>
</tr>
<tr>
<td>1400</td>
<td>0.29</td>
<td>6.55</td>
</tr>
</tbody>
</table>

At 1100°C, the eutectic-like microstructure in the 30-10 alloy has been broken down and the Nb_{9}Si_{2}Cr_{3} and the NbCr are now observed as primary phases (Figure 4.10a). In the 10Al alloy, Figure 4.10c, the NbCr appears to coalesce with itself which results in the growth of that phase.
Figure 4.10: Microstructures after 24 h oxidation at 1100°C for (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5Al, and (c) Nb-30Cr-10Si-10Al.

Figure 4.11: Microstructures after 24 h oxidation at 1400°C for (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5Al, and (c) Nb-30Cr-10Si-10Al.
At 1400°C, the 30-10 alloy in Figure 4.11a shows a more abundant amount of Nbss which overpowers the Laves phase observed at lower temperatures. The eutectic microstructure reappears after oxidation at higher temperatures. In the 5Al alloy, the lamellar structure observed at 1100°C is no longer present and consequently, Nbss has transformed into a primary phase. The growth of the Al2O3 particles with increasing temperature can be observed in both the 5Al and 10Al alloys (Figures 4.11b and 4.11c). The particles are no longer present along the interfaces but have grown and now exist in the phases.

4.2.3 Oxide-metal interface

At 700°C a pronounced oxide layer is not observed in the Nb-30Cr-10Si or the Nb-30Cr-10Si-10Al alloy whereas the Nb-30Cr-10Si-10Al alloy forms a very thick but porous oxide layer that is not protective to the metal as it allows for oxygen to continue diffusing and react with the metal. Figure 4.13 shows the oxide scale formed after oxidation at 800°C where the main oxides observed were the CrNbO4 and Nb2O5. The 10Al alloy only showed the formation of the Nb2O5 oxide which is not beneficial for oxidation resistance. As mentioned, this oxide creates very
large stresses in the interface causing cracking which is very prominent in this alloy. The 5Al (Figure 4.13 b) alloy continues to form a very thick oxide scale at 800°C with large pores which allow further oxidation. The 30-10 (4.13 a) alloy formed the thinnest oxide scale at this temperature which was discontinuous but showed comparable amounts CrNbO$_4$ and Nb$_2$O$_5$ that provided some oxidation resistance.

Figure 4.13: Metal-oxide interface formed after oxidation at 800°C in the (a) Nb-30Cr-10Si alloy, (b) Nb-30Cr-10Si-5Al alloy, and (c) the Nb-30Cr-10Si-10Al alloy.
An oxide/metal interface can be clearly seen to form in the Nb-30Cr-10Si alloy at 1100°C as shown in Figure 4.14a. The oxide scale adhered well only in the regions closest to the surface, however, spalling of this scale was observed in the outer layer of the oxide scale. Un-reacted metal is also present in the oxide scale which is part of the NbCr$_2$ phase as identified by EDS and XRD. An interesting feature in this oxide scale is the formation of the CrNbO$_4$ oxide between the Nb$_2$O$_5$. The cracking observed in the oxide scale is due to this alternating formation as according to the Pilling Bedworth Ratio, these two oxides have different volume expansions. The 5Al (Figure 4.14 b) alloy yields a more compact, dense oxide scale which also contains unoxidized metal. This alloy promotes more amounts of the CrNbO$_4$ oxide which offers better protection to the metal. At this temperature, the 10Al alloy formed a very thick oxide scale in some pieces of the broken metal which was mostly comprised of Nb$_2$O$_5$. The Nb$_2$O$_5$ oxides present at this temperature in the oxide scale was confirmed to in the monoclinic form. Similar oxide scales with the same oxide formation were observed at 1200°C and 1300°C (not shown here). However, at these temperatures cracking was observed along the metal-oxide interface. The 5Al alloy shows a more continuous scale with better adherence compared to the 30-10 alloy.
Figure 4.14: Metal-oxide interface formed after oxidation at 1100°C in the (a) Nb-30Cr-10Si alloy, (b) Nb-30Cr-10Si-5Al alloy, and (c) the Nb-30Cr-10Si-10Al alloy.

The oxide/metal interface at 1400°C in Figure 4.15a shows severe cracking in the oxide scale for the 30-10 alloy with large sections of unoxidized metal. These are characteristics of poor oxidation performance by the oxide scale which is causing cracks to not only form along the interface but also at the surface of the unoxidized metal. Figure 4.15b presents the oxide scale formed at 1400°C for the 5Al showing a very compact scale with no cracks. Additionally, this oxide scale shows improved adherence with Al addition. The 10Al alloy oxide scale is still very porous and incoherent between oxides. Severe internal oxidation is occurring along the interface showing that the oxide scale is not providing adequate protection to the metal. The higher temperature oxide scales were composed of the CrNbO₄ protective oxide along with the monoclinic Nb₂O₅ oxide.
From the XRD patterns, the low orthorhombic form of Nb₂O₅ was observed in the oxide product powder at low temperatures, the body-centred monoclinic form was present at intermediate temperatures, and the monoclinic form was observed at higher temperatures. Figure 4.16 shows the XRD scans of the oxide product of the 30-10 alloy showing the transformation of Nb₂O₅ at each temperature range. The same transformation was observed in the alloys with Al addition.
Figure 4.15: XRD of oxide product formation for the Nb-30Cr-10Si alloy showing the transformation of Nb2O5 from orthorhombic form to monoclinic form.

4.3 EFFECT OF B ADDITION

4.3.1. Static Oxidation Curves and Oxidation Behavior of Nb-30Cr-10Si and B Alloys

Figure 4.16 shows the short-term static oxidation curves obtained for the Nb-30Cr-10Si-5B and Nb-30Cr-10Si10B in comparison to the Nb-30Cr-10Si. The observed metal left at each temperature is listed in Table 2 and the oxidation mechanism is represented on the graph as follows; ● -represents spalling, ▲ -signifies the formation of swollen oxide during complete oxidation, ■ -represents the spalling of the formed oxide scale, and ◆ -represents the formation of a protective adherent oxide scale. From 1000-1300°C, the 5B and 10B alloys formed a well adhered oxide scale which did not show the spalling mechanism which refers to the symbol
representing adherent oxide scale. This was a significant behavior to be noted as it signifies better oxidation resistance.

From 700°C to 800°C, the alloys showed the best oxidation response by the lowest weight gain though slight pest oxidation occurred. At 800°C the 5B alloy displayed an increase in weight gain and at 900°C, an even greater weight gain occurred in all three alloys. The 30-10 and 5B alloys completely oxidized by the formation the Nb$_2$O$_5$ swollen pyramid-like oxide. At this same temperature, the 10B alloy exhibited enhanced response to oxidation by forming an oxide layer that resulted in 80% metal left. Though this oxide scale was very thick and porous it provided some degree of protection and prevented complete consumption as observed in the other two alloys.

Weight gain continues to increase in the 10B alloy at 1000°C but it is important to note that in spite of the higher weight gain, the alloy formed a well adhered oxide scale which protected 80% of the metal signifying that the addition of 5 and 10B reduces the susceptibility of catastrophic oxidation in the studied Nb-based system. The 5B alloy at this temperature exhibits a dramatic decrease in weight gain and superior oxidation resistance compared to the other two alloys. The formation of a well-adhered protective oxide scale was observed. The 5B alloy maintained a very low weight gain at 1100°C and 1200°C where spalling of the oxide did not occur. The 10B alloy shows less favorable oxidation behavior due to the spalling of the oxide that occurred from 1100-1200°C though it was minimal compared to that observed in the 30-10 alloy.

At 1300°C, the oxidation mechanism shifts once again between the 5B and the 10B alloy. The 5B alloy shows oxide spalling and undergoes an increase in weight gain while the 10B alloy forms a well-adhered scale. At this temperature, oxidation response is highly improved in the
alloys with B addition resulting in 90% metal left compared to the 70% metal in the 30-10 alloy. Although the three alloys suffer from spalling at 1400°C, the B addition to this system evidently suppresses this behavior where it occurs less severely and forms more protective oxide scales.

The most favorable oxidation response at low temperatures was observed in the 10B alloy up to 900°C. In the range between 1000-1200°C, the oxidation resistance was enhanced in the 5B alloy on the basis of weight gain and amount of metal left. At high temperatures between 1300-1400°C, the oxidation behavior is comparable in the 5B and 10B alloys due to the spalling that was observed and much more favorable than in the 30-10 alloy.
Figure 4.16: Oxidation curves for Nb-30Cr-10Si, Nb-30Cr-10Si-5B, and Nb-30Cr-10Si-10B alloys exposed for 24h at temperatures from 700°C to 1400°C.

Table 4.4: Percent metal left in Nb-30Cr-10Si, Nb-30Cr-10Si-5B, and Nb-30Cr-10Si-10B after 24 hour oxidation

<table>
<thead>
<tr>
<th></th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
<th>1000°C</th>
<th>1100°C</th>
<th>1200°C</th>
<th>1300°C</th>
<th>1400°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-30Cr-10Si</td>
<td>95%</td>
<td>90%</td>
<td>0%</td>
<td>0%</td>
<td>75%</td>
<td>80%</td>
<td>70%</td>
<td>55%</td>
</tr>
<tr>
<td>Nb-30Cr-10Si-5B</td>
<td>95%</td>
<td>85%</td>
<td>0%</td>
<td>80%</td>
<td>95%</td>
<td>90%</td>
<td>90%</td>
<td>80%</td>
</tr>
<tr>
<td>Nb-30Cr-10Si-10B</td>
<td>95%</td>
<td>90%</td>
<td>80%</td>
<td>95%</td>
<td>90%</td>
<td>85%</td>
<td>95%</td>
<td>85%</td>
</tr>
</tbody>
</table>
4.2.2 Microstructures after oxidation

Phase changes were not observed in the 5B and 10B alloys after oxidation but an increase in the eutectic structure in the 5B alloy was evident at 700°C as can be observed in Figure 4.17b. At 800°C the Nb₃Si silicide decreased in size (not shown here) but remained as a primary silicide in the 5B alloy. The 10B alloy maintained the same structure and phases in this low temperature regime. Figure 4.17 shows that the addition of B appears to suppress the Nb₃s into the observed lamellar structure compared to 30-10 alloy. This may contribute to the enhanced oxidation displayed by the alloys with B addition as they have shown to form less Nb₂O₅ than the 30-10 alloy. Additionally, the B alloys have larger amounts of the Laves phase in the microstructure which provides more protection in the oxide formation favoring the CrNbO₄ oxide over the Nb₂O₅ resulting in suppressed spalling. The alloys containing the B additions also show a more pronounced arranged lamellar structure than the 30-10 alloy. The 10B microstructure at 700°C presented in Figure 4.17c appears to have larger amounts of Laves and primary phase Nb₃Si compared to the 5B alloy. These slight microstructural differences displayed an apparent effect on the oxidation response of the alloys at low temperatures.
At intermediate temperature ranges between 1000-1200°C, the 5B alloy loses stability of the eutectic like microstructure. At 1000°C, the eutectic becomes finer and then at 1100°C the amount present decreases and becomes largely comprised of the Nb<sub>ss</sub> with scarce amounts of silicide. Finally at 1200°C the amount of eutectic structure decreases drastically in some regions while in others it becomes broken up and the Nb<sub>ss</sub> becomes a primary phase surrounding the Laves phase. The 10B alloy generally maintains its phase and structure stability however, as presented in Figure 4.18c, the Laves phase is no longer present as a spherical shape but has become elongated. As can be observed in Figure 4.18, the Nb<sub>ss</sub> in the 5B alloy begins to coalesce and form larger phases while the 10B maintains a structured eutectic containing the
The higher amounts of Laves in the 5B were responsible for the better oxide formation in at these temperatures compared to that of the 10B which contains less amount of this phase.

Figure 4.18: Microstructures after oxidation for 24h at 1100°C for the (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5Al, and (c) Nb-30Cr-10Si-10Al.

Figure 4.19 presents the microstructures for the three alloys after oxidation at 1400°C.

The Nb_3Si phase in the 5B alloy (Figure 4.19b) has developed sharper and straighter edges signifying a more coherent interface than that observed at lower temperatures. In the 10B alloy (Figure 4.19c) the Laves phase has once again attained the circular shape and remains surrounded by the Nb_{ss}. Additionally, the eutectic structure is no longer observed and the growth of Nb_{ss} is apparent. Similarly in the 30-10 and 5B alloys, the amount of Nb_{ss} increases as
temperatures increase. Comparing the microstructures of the 30-10 alloy with the microstructures of the alloys with B additions in Figure 4.19, the presence of $\text{Nb}_{\text{ss}}$ remains less in the alloys with B content. Additionally, the 5B and 10B stabilize the presence of the silicide as a primary phase. Finally, the B content results in the presence of the Laves phase as a primary phase rather than embedded in the lamellar structure as is observed in the 30-10 alloy. These microstructural differences are the basis for the observed enhanced oxidation response of the B alloys.

Figure 4.19: Microstructures after oxidation for 24h at 1400°C for the (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5Al, and (c) Nb-30Cr-10Si-10Al.
4.2.3 Oxide-metal interface

At 700°C, no oxide formation is visible however, the addition of B results in an oxide-metal interface as shown in Figure 4.20. Figure 4.20b shows the oxide interface of the 5B alloy at this temperature containing a high volume of porosity. Adherence along the metal surface was not outstanding and the formation of two oxides was observed. The oxides formed in an alternating manner where the CrNbO$_4$ formed between the Nb$_2$O$_5$ which does not provide the most resistant scale but protection was still provided by this oxide layer. A very different oxide morphology is observed in Figure 4.20c by the 10B alloy. Distinct preferential oxidation can be observed where the formation of Nb$_2$O$_5$ grows out of the Nb$_3$Si maintaining the rectangular shape with sharp edges of the silicide. This is explained by the Silicon concentration observed in this oxide by x-ray mapping analysis. In between the formation of these pillar-like structures, the formation of CrNbO$_4$ along with unoxidized NbCr$_2$ particles is present. At 800°C, a more uniform oxide layer is formed but porosity is still severe. This porosity at this temperature and 700°C is attributed to the powder degradation observed at low temperatures. The coherency between the two oxides forming is still not superior but bonding between the metal and the oxide has begun. In the 10B alloy at 800°C, preferential oxidation observed at 700°C has decreased and a more continuous Nb$_2$O$_5$ rich scale is observed. The CrNbO$_4$ oxide is also present in small regions. Sections on the surface of the 10B alloy show some adherence but a continuous bonding is not yet attained. At 900°C, an oxide scale is only observed in the 10B alloy. This scale displays a sponge-like structure with large amounts of pores from pesting.
In the mid temperature range, from 1000°C-1100°C the oxide-metal interface provided oxidation resistance. In the 5B alloy the improvement is minor compared to the 10B alloy as the sponge-like structure is still observed. In the outer regions of the scale a more continuous morphology takes form in the 5B alloy although cracking is still severe. Bonding between the metal and the oxide in the 10B alloy is enhanced and the scale exhibits a more compact structure mostly comprised of Nb$_2$O$_5$. A more uniform oxide formation in the 10B alloy reduces the spalling due to less internal stresses as observed in the 30-10 alloy. The enhancement can be compared by the amount of metal left in this alloy.
A more apparent improvement in oxide scale is observed at intermediate temperatures and occurs at 1100°C. The thickness in the oxide scale decreased compared to the 30-10 alloy as can be observed in Figure 4.21. The oxide scale interface of the 5B alloy after oxidation at 1100°C is presented in Figure 4.21a. The oxide scale observed is more dense at the interface and more porous toward the outer region. There is superior adherence observed in this alloy which is largely the factor in oxidation resistance. Although the porosity in the outermost region of the oxide is not protective, the compact structure at the interface is beneficial as it reduces the oxidation rates slowing down diffusion of oxygen into the metal. X-ray mapping analysis was performed to observe the elemental distribution in the oxide scale and to understand the variance in color in the dense region.

Figure 4.21: Microstructures after oxidation for 24h at 1100°C for the (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5B, and (c) Nb-30Cr-10Si-10B.
Figure 4.22 shows the x-ray map of the 5B alloy which reveals a high content of B in the oxide scale. The x-ray map also shows a Cr depleted area at the interface signifying that Nb$_2$O$_3$ is the dominant oxide formation. However, a concentration of Si is also observed meaning that SiO$_2$ is mixed with the Nb$_2$O$_3$ oxide. After the Nb$_2$O$_3$ layer, a Cr rich layer follows which represents the presence of CrNbO$_4$. This layer contributes to the higher oxidation resistance at this temperature. From the x-ray map, it has been determined that the darker areas in the oxide scale are Cr rich regions while the light areas are rich in Si and Nb. The addition of B has resulted in the formation of horizontally continuous layers rather than the vertical preferential oxidation observed at lower temperatures. This behavior provides the compact and adherent oxide scale though outer regions are not as protective as desired.

Figure 4.22: X-ray Map of metal-oxide interface in 5B alloy after 24 h oxidation at 1100°C.
Similarly in the 10B alloy at 1100°C in Figure 4.21c a compact dense oxide scale with decreased amount of pores is observed. This scale also exhibits excellent adherence at the interface but displays cracking in the outer scale. Nonetheless, this oxide provided some oxidation resistance. The cracking in the outer layer of the oxide resulted in spalling. The formation of layers and color variance is apparent in this alloy therefore an x-ray map is presented in Figure 4.23. A thin oxide depleted region is once again observed at the interface along with light regions showing Nb rich areas and dark regions showing Cr rich areas. In this map, a round region of Nb$_2$O$_5$ is observed where cracking and porosity is observed. The difference of volume expansion is evident which explains the porosity in the vicinity of that region. The presence of silicide concentration is lower in those light contrast regions signifying less oxidation resistance by that oxide. If those Nb$_2$O$_5$ rich areas were not present in the oxide, cracking and porosity would not have occurred and spalling observed in this alloy would subside.

Figure 4.23: X-ray Map of metal-oxide interface in 5B alloy after 24 h oxidation at 1100°C.
The dense, uniform oxide structure and well bonded metal-oxide interface is observed in the high temperature regime from 1200°C-1300°C. At 1200°C in the 10B alloy more apparent layers alternating in Cr-rich and Nb-rich are observed. Compared to the 30-10 alloy, the adherence observed at the interface is excellent. The spalling mechanism is not observed in the 5B alloy at 1200°C as porosity is once again limited to the outer region of the oxide.

At 1400°C, the oxide scale is no longer observed as a continuous layer and a loss of adherence to the metal results in severe spalling which exposed the unoxidized metal to further oxidation. Adherence at the interface is lost in both the 5B and the 10B alloys however, these scales still performed better than the oxide formed in the 30-10 alloy. The loss of bonding between the metal and the oxide may be attributed to the Nb$_{ss}$ forming more Nb$_2$O$_5$ than that observed at lower temperatures. Since the Nb$_{ss}$ has become a primary phase, the formation of Nb$_2$O$_5$ will be highly favored which will creates internal stresses leading to the cracking observed.
Figure 4.24: Microstructures after oxidation for 24h at 1400°C for the (a) Nb-30Cr-10Si, (b) Nb-30Cr-10Si-5B, and (c) Nb-30Cr-10Si-10B.
4.4 Cyclic Oxidation

4.4.1. Cyclic Oxidation Curves and Oxidation Behavior

Alloys were subjected to long-term cyclic oxidation which consisted of seven 24-hour cycles for a total of 168 hours of oxidation. Cyclic oxidation was conducted to observe the behavior of the alloys after initial oxidation and observe the maintained integrity or disintegration of the formed oxide scales after the first 24 hours of service. Figure 4.25 presents the data collected from the cyclic oxidation for the Nb-30Cr-10Si alloy consisting of weight gain per unit area as a function of time. Only high temperature cyclic oxidation from 1100-1400°C was conducted for this alloy where it showed a formation of an oxide scale in static oxidation conditions. This alloy was not resistant to oxidation for seven cycles, and no metal was left at any temperature due to spalling which exposed unoxidized metal. This alloy showed similar behavior at all four temperatures where there was an initial high weight gain rate which reached steady state after 48 or 72 hours. The alloys only survived oxidation up to 72 hours, after which only oxide product was observed in the crucibles. At this point, steady weight gain was observed as there was no more metal to oxidize exhibiting poor oxidation response.

Cyclic oxidation results are not presented for the 10Al alloy due to the cracking of the metal in static oxidation experiments. Complete oxidation was observed after the first oxidation cycle since the shape of the metal was not maintained not allowing for an oxide scale to form and provide protection.
Figure 4.25: Cyclic oxidation curves for Nb-30Cr-10Si alloy exposed for seven 24-hour cycles at 1100°C-1400°C.

Figure 4.26: Cyclic oxidation curves for Nb-30Cr-10Si-5Al alloy exposed for seven 24-hour cycles at 1100°C-1400°C.
Figure 4.26 presents the cyclic oxidation results for the Nb-30Cr-10Si-5Al alloy conducted from 1000-1300°C where the best oxidation response was observed in static oxidation experiments. The best oxidation response occurred at 1200°C, the only temperature where metal was observed after 168h. At this temperature, a steady weight gain is observed up to 144 h then a higher increase in weight is observed resulting in only 10% metal left. At 1000°C, the most detrimental oxidation behavior was observed where complete oxidation occurs after 48 hours resulting from a very steep weight gain rate. At 1100°C and 1300°C, the alloys completely oxidize after 120 hours. The alloy oxidized at 1100°C shows the lowest initial weight gain rate up to 72 hours but the drastic weight gain at 96 hours was detrimental to the alloy.

Figure 4.27: Cyclic oxidation curves for Nb-30Cr-10Si-5B alloy exposed for seven 24-hour cycles at 1100°C-1400°C.
Cyclic oxidation was conducted with the Nb-30Cr-10Si-5B alloy at temperatures ranging from 700-1400°C except 900°C since it had promising oxidation response in static oxidation by the formation of adherent oxide scale and high percents of metal left. The cyclic oxidation curves for the alloys are presented in Figure 4.27. The best oxidation behavior was observed at 700°C which resulted in the least weight gain and 70% metal left. Weight gain at this temperature occurred at a linear rate where weight gain was maintained constant throughout all cycles.

800°C was the temperature which exhibited the second best oxidation resistance resulting in 60% metal left. At this temperature, initial weight gain was higher than at 700°C and a linear weight gain was maintained up to 120 hrs where the curve shows a slight parabolic curve displaying a lower weight gain rate. Linear weight gain rate is not to be confused with linear oxidation which can only be determined using Thermogravimetric Analysis system not performed in this study.

No metal was left after 168 hours of oxidation at 1000, 1200, 1300, or 1400°C which show a parabolic curve that stabilize the weight gain rate at 96 hours. On the 96 hour cycle a slight decrease in weight gain is observed which can be attributed to several mechanisms, the most probable being volatilization of the oxides. 20% of the metal was left at 1100°C which displayed an interesting curve. From 24 to 72 hours, a linear behavior is observed and then stabilized at 96 hours. From 96 to 168 hours there is a large increase in weight gain which is attributed to spalling of the oxide. For the greatest oxidation resistance to be attained, it is essential to maintain a well adhered compact scale which is lost due to cracking during cooling between cycles in this alloy.

The cyclic oxidation behavior of the Nb-30Cr-10Si-10B alloy was also of high interest as large amounts of metal left were observed at all temperatures during short term oxidation. Figure 4.28 shows the oxidation curves for the 10B alloy from 700-1400°C. At 700°C, the best
oxidation resistance was observed on the basis of least weight gain. 65% metal was left and the weight gain observed occurred in linear behavior. At 800°C the 10B alloy also exhibited good oxidation resistance compared to other temperatures with 70% metal left. Weight gain was observed up to 72 hours then weight loss occurred at 96 hours. Steady weight gain was once again observed up to 168 hours. 55% metal left was observed at 1000°C which exhibited a linear weight gain behavior. At 1200°C a steady weight gain increase was not observed. The highest weight gain occurred at 48 hours and 96 hours which resulted in 40% metal left. Complete oxidation occurred at 900, 1100, 1300, and 1400°C which exhibited parabolic oxidation except for 1100°C which exhibited weight loss at 120 hours.

Figure 4.28: Cyclic oxidation curves for Nb-30Cr-10Si-10B alloy exposed for seven 24-hour cycles at 1100°C-1400°C.
A comparison of cyclic oxidation behavior between the 5B and 10B alloys at 700°C and 800°C where metal was observed after 168 hours was made to observe which B addition resulted in better oxidation resistance. Figure 4.29 presents the comparison. The best oxidation response was observed in the 10B alloy at 700°C on the basis of weight gain. Conversely, the least favorable oxidation behavior occurred in the 5B alloy at 700°C. At 800°C the 5B alloy showed slightly less weight gain making it a more favorable alloy at this temperature. The 10B alloy exhibited weight loss from oxide volatilization which is not a desired mechanism for oxidation resistance. Pest oxidation remains a problem in the alloys containing boron and is the root cause for detrimental oxidation observed in the cyclic oxidation analysis.

Figure 4.29: Comparison of cyclic oxidation curves between the Nb-30Cr-10Si-5B and the Nb-30Cr-10Si-10B alloys at 700-800°C.
4.4.1. Scanning Electron Microscopy

The formation of a protective oxide scale during initial oxidation and preserving adherence of an oxide scale through cycles of oxidation is essential for oxidation resistance. The oxide scales of the 5B and 10B alloys were analyzed using scanning electron microscopy to observe the condition of the oxide scale after long term oxidation. Figure 4.30 shows the oxide scales formed for the 5B alloy at 800°C and 1000°C. At low oxidation temperatures (Figure 4.30 a), a more adherent compact scale is observed though pores are still present within the oxide. The same oxides observed in static oxidation are still present during cyclic oxidation consisting of Nb$_2$O$_5$ and CrNbO$_4$. Figure 4.30 b shows the metal oxide interface at 1100°C. At higher temperatures, a continuous oxide scale is not present and voids are observed which are a result of the mismatch of coefficient of thermal expansion between the Nb$_2$O$_5$ and the CrNbO$_4$. Additionally, areas of unoxidized metal are observed within the oxide which as oxidation continues will be damaging to the protection of the metal as these regions will create stresses between the oxide which will result in cracking. Cracks are also observed in the oxide scale at higher temperatures which result in spalling of the scale.

![Figure 4.30: Metal-oxide interface of the Nb-30Cr-10Si-5B at (a.) 800°C and (b.) 1100°C.](image-url)
Figure 4.31 presents the metal-oxide interfaces formed for the 10B alloy. At 700°C (Figure 4.31a) the oxide scale formed is not compact or continuous exhibiting voids where oxygen can diffuse; however, this scale is largely comprised of CrNbO$_4$ which contributes to the better oxidation response observed at lower temperatures. Figure 4.31 shows the oxide scale at 800°C which exhibits a large volume of cracking along the interface. Pesting was observed at this temperature which caused the cracking and break off at of the oxide scale which resulted in powder deposit. At higher temperatures at 1000°C, a more continuous compact scale is observed. Large voids are present in the scale due to the large amount of Nb$_2$O$_5$ oxide which has a large volume expansion. Adherence was a problem at higher temperatures and crack initiation can be observed in Figure 4.31c. Large amount of spalling was observed at this temperature which resulted in more consumption of the metal into oxide than that observed at lower temperature.
Chapter 5. Conclusions

5.1 Conclusions

The following conclusions were made from the study of the effect of aluminum and boron additions to a Nb-30Cr-10Si alloy:

1. The as-cast microstructure of the Nb-30Cr-10Si consisted of the Nb\textsubscript{ss}, the Nb\textsubscript{3}Si\textsubscript{2}Cr\textsubscript{3}, the NbCr\textsubscript{2} and the Nb\textsubscript{5}Si\textsubscript{3}. The 5Al alloy exhibited the same phases excluding the Nb\textsubscript{5}Si\textsubscript{3}. An increase to 10Al supresses the Nb\textsubscript{3}Si\textsubscript{2}Cr\textsubscript{3} and forms the Nb\textsubscript{5}Si phase.

2. In static oxidation, the Nb-30Cr-10Si alloy shows better oxidation resistance at temperatures up to 800°C while the addition of 5Al is beneficial in the intermediate and high temperature range. The 10Al addition was detrimental at all temperatures.

3. At 900°C complete oxidation occurred in the Nb-30Cr-10Si alloy and the alloys with Al additions resulting in the formation of a swollen oxide largely comprised of the body centered monoclinic form of Nb\textsubscript{2}O\textsubscript{5}.

4. The formation of the Al\textsubscript{2}O\textsubscript{3} particles occurred between the Nb\textsubscript{ss} phase and the NbCr\textsubscript{2} phase in the 5Al alloy and along the Nb\textsubscript{ss} and Nb\textsubscript{3}Si interface in the 10Al alloy. The phase with highest Al content promotes internal oxidation along that interface.

5. The difference in the coefficient of thermal expansion between the CrNbO\textsubscript{4} and the Nb\textsubscript{2}O\textsubscript{5} oxide created cracking at the interface which resulted in spalling at higher temperatures.

6. The alloys with boron additions showed the same microstructure consisting of the Nb\textsubscript{ss}, NbCr\textsubscript{2}, and the Nb\textsubscript{3}Si phases.

7. The addition of boron was highly beneficial at all temperatures. The 10B alloy did not undergo complete oxidation at any temperature and showed the better oxidation resistance in the low and high temperature ranges. The 5B addition was most beneficial at intermediate temperatures.

8. The addition of boron results in better oxide adherence oxide scales compared to the alloys with aluminum additions.

9. In cyclic oxidation, the 5B alloy exhibits its best oxidation resistance at 700°C but completely oxidizes at 1000, and at the 1200-1400°C temperature range. Similarly, in cyclic oxidation, the 10B alloy exhibits its best oxidation response at 700°C but completely oxidizes at 900°C and 1100-1400°C.
References


[36] K. Chattopadhyay, Effect of Mo on microstructure and mechanical behavior of as cast Nbss-Nb5Si3 in situm composites


Vita

Nydia Esparza was born and raised in El Paso, Texas on August 11, 1988. She attended and graduated from Canutillo High School in 2006. She continued her studies at the University of Texas at El Paso and obtained her Bachelor of Science in Metallurgical and Materials Engineering in May 2010. After an internship with the Air Force Research Laboratory in the summer of 2010, she continued with her Master of Science in Metallurgical and Materials Engineering. Nydia did research in high temperature oxidation under the direction of Dr. S.K. Varma and presented part of her work at the MS&T Conference in Columbus, OH, in October 2011. Upon graduation, Nydia will be working for ONEOK, a natural gas company.

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