The Effects Of Uncommon Silicides On The Oxidation Of Alloys From The Nb-Cr-Si System

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THE EFFECTS OF UNCOMMON SILICIDES ON THE OXIDATION OF ALLOYS FROM THE NB-CR-SI SYSTEM

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Dedication

This thesis is dedicated to my wife, whose support and understanding were the pillars of stability needed to reach the end. I would also like to dedicate this thesis to my parents who never gave up believing in me.
THE EFFECTS OF UNCOMMON SILICIDES ON THE OXIDATION OF ALLOYS FROM THE Nb-Cr-Si SYSTEM

by

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THESIS

Presented to the Faculty of the Graduate School of The University of Texas at El Paso in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

Department of Metallurgical and Materials Engineering

THE UNIVERSITY OF TEXAS AT EL PASO

May 2012
Acknowledgements

It is my honor to express my deep and sincere appreciation to my thesis advisor Dr. S.K. Varma for giving me the opportunity to work on this research. Dr. Varma’s support and guidance were invaluable and I am forever grateful. I would also like to thank Dr. Stafford on Dr. Bronson for being members of my thesis committee. I appreciate their advice and the help. To Dr. Stafford in particular I extend my most profound gratitude for not only being a mentor, but for pointing me toward a most interesting future. Special consideration is due to Dr. David Schifler and the office of Naval Research for their financial support (Project #: N00014-08-0506).

I would like to acknowledge the Department of Metallurgical and Materials Engineering for without them I would not be here. I would like to thank David Brown for many amazing conversations and for his support on many of my projects. Special thanks go to Ben Portillo, Nydia Esparza and Victoria Rangel, for their time, knowledge, and friendship. I would also like to thank Amanda, Brenda, Katey, and Eduardo for their support.

Finally, I would like to thank my wife, who tirelessly put up with my eccentric ways, and gave me support and strength when I needed it most. I would like to thank my family: my father for his advice and dedication, my mother for her support, and my sister for being an inspiration to strive toward.
Abstract

Niobium based alloys are being tapped as potential successors to current nickel base superalloys in high temperature applications. In the aerospace industry, high temperature materials are constantly being pushed to higher temperature regimes in order to improve engine efficiency however current superalloys cannot be pushed further due to melting temperature limitations. Niobium, being a refractory metal, can withstand much higher temperatures than nickel however its oxidation properties are woefully inadequate.

The purpose of this study is to ascertain whether increased silicon additions can improve niobium oxidation properties by: forming ternary silicides with better oxidation properties and by preventing the formation of Nb$_2$O$_5$. Chromium is shown to form CrNbO$_4$ which protects niobium alloys better than Nb$_2$O$_5$. If the concentrations of chromium found in all phases can be increased, the likelihood for a complete CrNbO$_4$ scale increases as well. Increased silicon concentrations could allow this to happen by forming ternary silicides.

Four compositions of Nb-Cr-Si alloys where chosen: Nb-20Cr-10Si, Nb-20Cr-20Si, Nb-20Cr-30Si and Nb-20Cr-42Si. These alloys were tested in temperature ranges between 700° to 1400°C. Gravimetric data was taken and plotted in order to assess weight gain per unit area versus temperature. Oxidation properties were variable based on alloy except for the 42Si alloy which showed very little oxidation. Increased silicon content pushed the pesting regime toward higher temperatures. The highest concentrations of silicon eliminated bulky oxide formation. The alloys and oxides were characterized by XRD, SEM, BSE, and EDS.
# Table of Contents

Acknowledgements

Abstract

Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

Chapter 2: Literature Review

  2.1 Oxidation Principles
  2.2 Oxidation of Niobium
  2.3 Oxidation of Chromium
  2.4 Niobium-Silicon Alloys
  2.5 Niobium-Chromium Alloys
  2.6 Nb-Cr-Si
  2.7 Nb-Cr-Si Ternary Silicides

Chapter 3: Methods and Materials

  3.1 Alloy Preparation
  3.2 Sample Preparation
  3.3 Oxidation
  3.4 XRD
  3.5 SEM
  3.6 Pandat™

Chapter 4: Results and Discussion

  4.1 As-Cast Characterization
  4.2 Static Oxidation
  4.3 Cyclic Oxidation
  4.4 Oxidation Initiation
List of Tables

Table 2.1: Physical properties of niobium, chromium and silicon..........................11

Table 3.1: Alloy compositions in atomic percent.....................................................13
List of Figures

Figure 4.1: Simulated ternary phase diagram of the Nb-Cr-Si system showing corresponding alloy compositions and phases.................................................................18

Figure 4.2: As-cast X-ray diffraction patterns for the 10Si-42Si alloys.................................................................19

Figure 4.3: Backscatter micrographs in the as-cast condition. a) Nb-20Cr-10Si, b) Nb-20Cr-20Si, c) Nb-20Cr-30Si, d) Nb-20Cr-42Si. .................................................................21

Figure 4.4: Pandat™ phase fraction chart for the 10 and 20Si alloys.................................................................23

Figure 4.5: Pandat™ phase fraction chart for the 30 and 42Si alloys.................................................................24

Figure 4.6: 24 hour static oxidation results. .................................................................26

Figure 4.7: XRD phase intensity for the 20Si alloy.................................................................27

Figure 4.8: XRD phase intensity chart for the 30Si alloy.................................................................28

Figure 4.9: XRD phase intensity chart for the 42Si alloy.................................................................30

Figure 4.10: Bse images of the metal-oxide interface for the 10, 20 and 42Si alloys. a) 10Si alloy demonstrates an oxide scale with large voids and cracking and separation from the metal-oxide interface. b) 20Si alloy shows little pest oxidation. c) 42Si alloy has no apparent oxide on the surface of the metal.................................................................32

Figure 4.11: BSE images of microstructures for the 10, 20 and 42Si alloys at 1100°C. a) 10Si alloy shows bulky scale of Nb₂O₅ and CrNbO₄. b) 20Si alloy’s scale is highly porous. c) 42Si, undergoing pest damage, showed two different oxide structures based on the location of the oxide.........................34

Figure 4.12: Elemental X-Ray mapping of the 42Si alloy at 1100°C. Chromium is concentrated around the edges of external oxides and in a layered structure in internal layers .................................................................35

Figure 4.13 X-ray elemental maps at 1500x magnification. Chromium is concentrated at the external edges of the oxide.................................................................36

Figure 4.14: BSE images of microstructures for the 10 - 42Si alloys at 1200°C. a) 10Si alloy shows a eutectic like structure of Nb₂O₅ and CrNbO₄. b) 20Si alloy shows similar characteristics to the 10Si alloy however there are nodules of CrNbO₄ growing from the eutectic like structure. c) 30Si demonstrates a thick scale with a mixture of three oxides. d) 42Si scale forms into two oxide structures which are highly porous.................................................................38

Figure 4.15: Elemental X-ray map demonstrating the concentration of chromium along the edges of the oxide scale. Silicon is concentrated in the interior of the scale.................................................................39
Figure 4.16: BSE and Elemental X-ray maps of the 30 and 42Si alloys showing the chromium depleted region in the metal-oxide interface.

Figure 4.17: a) 30Si alloy at 1300°C showing internal oxidation of the Nb$_5$Si$_3$ grains near the metal-oxide interface. b) 42Si alloy at 900°C with oxidation occurring on the surfaces of internal shrinkage cavities. c) 1000°C the oxidation that was occurring on the internal surfaces spreads out to nearby grains. d) 1200°C the oxidation completely surrounds internal pores.

Figure 4.18: 7 day cyclic oxidation curves for the 42Si alloy.

Figure 4.19: BSE images of the 42Si alloy after 15 minutes of oxidation. a) 900°C shows no evidence of oxidation. b) 1100°C forms Nb$_2$O$_5$ and SiO$_2$ c) 1300°C forms larger oxides than the 1100°C specimen.

Figure 4.20: X-ray maps of the 1100° and 1300°C specimens. There is no indication of a chromium depleted region however the 1300°C does show concentrations of chromium in the oxide.
Chapter 1: Introduction

The demand for new high temperature materials to surpass current service temperature requirements has increased due to a desire for higher efficiency turbines. Superalloys, particularly the nickel and cobalt based, are used due to their corrosion resistance, high temperature strength and relatively low density (~7gm/cm$^3$). The problem with these superalloys is that they have reached their maximum operating temperature. Elevating service conditions runs the risk of having the materials operate at temperatures where their liquid phase would be present.\textsuperscript{[1]} It is therefore imperative that materials that are able to withstand higher temperatures than current superalloys are the key to improved efficiency.\textsuperscript{[2]} This means that these new materials must perform in a manner similar or better than current superalloys. The replacement alloys must be able to maintain strength at temperatures above 1200°C while providing good resistance to oxidation and thermal cycling.\textsuperscript{[2]}

Niobium, which is a refractory metal due to its high melting temperature, has the potential to replace current superalloys due to its comparable density and adequate high temperature strength. Unfortunately the Nb$_2$O$_5$ oxide layer, which gives niobium some corrosion resistance, tends to spall off at higher temperatures and therefore strips the metal of its protection.\textsuperscript{[3]} Spalling which is a condition where the protective oxide layer of a metal separates from the metal-oxide interface occurs in niobium when the thermal stresses created in the metal-oxide interface are no longer accommodated by plastic deformation as it cools. The stresses created by this condition creates cracks that propagate into the oxide.\textsuperscript{[4]} In order to combat the spalling, alloying elements have been used. Elements such as Mo, Ti, Hf, and Al have been used
prevent spalling and improve oxidation resistance, however, the addition of these alloying agents introduce a form of oxidation known as pest damage.[5-8] Two elements, silicon and chromium, have shown great promise due to the nature of the phases they form and the characteristic oxidation products they form.

The Nb-Cr-Si system is comprised of various phases that are able to provide better oxidation resistance than that of niobium. The system was first investigated by Goldschmidt and Brand in 1961 by the use of about 220 alloys.[9] The phase diagram was then further refined by Zhao et al who managed to pinpoint the tie lines of various phases.[10] The Nb-Cr-Si system received considerable amount of attention due to the Nb$_5$Si$_3$ phase, which has excellent creep properties and high temperature strength but has a tendency to pest.[11] The system also forms the NbCr$_2$ Laves phase which has good oxidation properties due to the formation of CrNbO$_4$.[12]

Most of the research done on the Nb-Cr-Si system concentrates on the niobium rich corner of the phase diagram thus little is known of the ternary silicides found in the system. These silicides come in different configurations, such as CrNb$_4$Si$_3$, CrNbSi, (Cr,Nb)$_6$Si$_5$, and (Cr,Nb)$_{11}$Si$_8$. Little is known about their oxidation and mechanical properties.[13-14]

The focus of this thesis work is to study the effects of oxidation on the ternary silicides found in the Nb-Cr-Si system. The study also allows the opportunity to test the effects of silicon on oxidation properties. The Nb alloys in this study contain 20at% chromium while the silicon content is varied from 10 to 42 at%. The modification of the silicon content allows for the formation of various ternary phases while allowing for an effective study of the effects of silicon on phase transformations and oxidation resistance. While various compositions from the Nb-Cr-Si system have been investigated, such as the Nb-20Cr-30Si alloy previously studied by Varma, and have characterized oxide formation oxidation resistance; however the studies have not
delineated the effect of silicon on the oxidation behavior nor have they tested uncommon ternary silicides.\textsuperscript{[15-18]} Of particular interest is the opportunity to test the oxidation response of CrNb$_4$Si$_3$ and (Cr,Nb)$_{11}$Si$_8$. 
Chapter 2: Literature Review

2.1 Oxidation Principles

The formation of oxides is dependent on oxygen partial pressures and the free energy of the metal.\footnote{This is important because changes in partial pressures can change oxidation rates, products, etc.} Oxides form scales on the base metal which can be either protective or non-protective depending on several factors; which include differences between density, structure, and interface coherency. The process of oxidation occurs in three steps: adsorption of oxygen, formation of the oxide which grows laterally, and finally, the growth of an oxide film.\footnote{According to Wagner’s theory of oxidation, this is further compounded by metal ions preferentially migrating to the surface as opposed to oxygen moving into the interior.}

In order to protect a metal from complete oxidation, it must fulfill several requirements based on its environment. Most important is the metal’s ability to form a protective oxide layer. This layer must then act as a barrier to substrate diffusion while maintaining structural stability.\footnote{This means that the oxide layer cannot spall off, form cracks, pores, or evaporate away.} Pillings and Bedworth created an equation whose ratio could predict if a metal’s oxide layer would be passive.\footnote{The equation is given as:}

\[
R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}
\]

where \(R_{PB}\) is the Pilling-Bedworth ratio, \(M\) is the atomic or molecular mass, \(n\) is the number of atoms per molecule of oxide, \(\rho\) is the density and \(V\) is the molar volume. If \(R_{PB}\) is less than 1, the oxide forms an oxide layer that is too thin to protect the metal. A \(R_{PB}\) greater than 2 then the oxide layer will spall off. Therefore, a \(R_{PB}\) number between 1 and 2 is ideal.
2.1.1 Oxidation Kinetics

Oxidation kinetics controls the rate at which oxidation occurs and is affected by material properties as well as temperature, i.e. higher temperatures may increase the speed of oxidation. There are three mechanisms by which oxidation may occur: parabolic, linear, and logarithmic. The parabolic mechanism is a state where oxygen diffusion into the material decreases as the oxide layer increases. The decrease in diffusion rate is usually due to the thickness of the scale; therefore oxidation rate is inversely proportional to the thickness of the oxide scale.\[20\]

The parabolic behavior is given as follows:

\[
\frac{\Delta x}{dt} = k'_p \quad \text{where } k'_p \text{ is the parabolic constant}
\]

Integration of the equation gives the parabolic rate equation

\[
x^2 = \frac{k'_p t}{2}
\]

x then becomes the thickness of the oxide, t is time.

Pilling and Bedworth derived an equation that measured the advancement of oxidation based on the mass increase per unit area.\[23\]

\[
\left(\frac{\Delta m}{A}\right)^2 = k''_p t
\]

where \(\Delta m\) is the mass gain, A is the surface area, \(k''_p\) is the parabolic rate constant in gm\(^2\) cm\(^{-4}\) sec\(^{-1}\) and t is time.

Linear oxidation kinetics occurs when the oxide scale on the surface of the metal is non-protective. If the scale cracks, spalls, volatilizes, is porous or produces a molten oxide then the oxygen is free to diffuse into the material with little impediment. This leads to a linear rate of oxidation and given time the metal will completely oxidize. The behavior is characterized by the equation
\[
\frac{dx}{dt} = k_L
\]
when integrated gives
\[
x = k_L t
\]
where \(x\) is the mass of the oxide formed, \(t\) is the time of exposure and \(k_L\) is the linear rate constant.

The final type of oxidation kinetics involves logarithmic oxidation rates. Logarithmic oxidation is seen when a metal begins to oxidize and is characterized by having a thin oxide film or occurs at low temperatures. Logarithmic behavior was first reported by Tammann and Köster who found that many metals initially oxidized by logarithmic kinetics. An equation for logarithmic behavior was derived by the assumption that oxidation rate is controlled by the flow of electrons from the metal into the oxide film.

\[
\frac{dy}{dt} = k'' \frac{t}{e^{k' t}} \quad \text{or} \quad y = k'' \ln \left( \frac{t}{\text{const}} + 1 \right)
\]

2.1.2 Volatilization

Volatilization is a process where the oxide layer of a sample evaporates. This affects the metal by creating porosity in the passivation layer and allows the influx of oxygen into the system. This is readily apparent in chromium oxide which undergoes volatilization when \(\text{Cr}_2\text{O}_3\) transforms into \(\text{CrO}_3\) at temperatures above 1000°C. This effect occurs at lower temperatures when \(\text{Cr}_2\text{O}_3\) is exposed to large concentrations of water vapor. The volatilization prevents the use of \(\text{Cr}_2\text{O}_3\) as a protective oxide but this effect can be mitigated by alloying with other elements in order to reduce the creation of \(\text{Cr}_2\text{O}_3\).
2.1.3 Pest Damage

Pestling is a unique form of oxidation and was first coined by Fitzer when he observed its occurrence in molybdenum disilicide. Pestling is described as the disintegration of intermetallic compounds into powder. Westbrook and Wood investigated the causes of pest damage and concluded that the majority of cases, pesting occurred due to intergranular attack. This attack occurred only in non-inert environments and could occur under isothermal or thermal cycling. The attack was due to preferential oxidation of the grain boundaries due to the diffusion of oxygen.

2.2 Oxidation of Niobium

The oxidation of niobium occurs due to the saturation of the niobium lattice with oxygen which eventually leads to the formation of oxides. The saturation time decreases as temperature rises above 500°C. As temperatures increase to 600°C, NbO and NbO₂ begin to form along grain boundaries. Above 650°C, Nb₂O₅ forms from NbO₂. Nb₂O₅ becomes non-protective above 700°C. Nb₂O₅ is polymorphic, as first discovered by Brauer who saw three structures when testing niobium between 400°-1250°C. The polymorphs later showed that αNb₂O₅ forms first and is a low temperature (below 800°C) orthorhombic oxide while β Nb₂O₅ is a high temperature orthorhombic oxide with a lattice constant that is almost twice that of α. The formation of a monoclinic form of Nb₂O₅ has been reported as well. The process of oxidation of niobium occurs by the formation of NbO and NbO₂. A layer of Nb₂O₅ then grows over the layer of NbO and NbO₂ at approximately 600°C. An investigation of the high temperature oxide scale of Nb₂O₅ discovered that the oxide spalled due to compressive stresses that occurred in the oxide scale during which tensile stresses were occurring in the metal. Cracking in the
oxide also occurred due to accelerated oxidation of the metal’s edges. The accelerated oxidation also created concentrations of heat that increased the diffusion of oxygen into the metal thus forming thicker oxides. This resulted in curvature of the oxide where cracks could eventually form.\cite{33} This leads to the recognition that the formation of \( \text{Nb}_2\text{O}_5 \) is dominant and non-protective. Alloying to reduced oxidation kinetics of the oxide has thus far proven unsuccessful.\cite{34}

2.3 Oxidation of Chromium

Chromium forms a passive layer of \( \text{Cr}_2\text{O}_3 \) that has a hexagonal close-packed crystal structure. Chromium also forms \( \text{CrO}_2 \) and \( \text{CrO}_3 \) which are stable only at low temperatures. The \( \text{Cr}_2\text{O}_3 \) oxide is most important as it imparts protection against corrosion due to being thermodynamically stable in a temperature range of up to 1000°C. When exposed to high oxygen partial pressures, the \( \text{Cr}_2\text{O}_3 \) oxide begins to volatilize at temperatures above 1000°C into a gaseous \( \text{CrO}_3 \). This volatilization can lead to porosity and the subsequent breakdown and reformation of the protective scale.\cite{35} In wet environments, the volatilization leads to the formation of channels in the oxide layer. These channels are caused by the buildup of internal pressures due to the formation of chromic acid and cause cracks to form in the oxide layer.\cite{36}

2.4 Niobium-Silicon Alloys

The Nb-Si system has three stable intermetallics that are \( \text{Nb}_3\text{Si} \), \( \text{Nb}_2\text{Si} \) and the most well-known \( \text{Nb}_5\text{Si}_3 \). The \( \text{Nb}_3\text{Si} \) phase occurs from a peritectic reaction at 1915°C. It then undergoes a eutectic reaction into \( \text{Nb}_{\text{ss}} \) and \( \text{Nb}_5\text{Si}_3 \) at 1765°C. The \( \text{Nb}_2\text{Si} \) phase occurs with higher
concentrations of silicon and has a melting temperature of 1935°C. The Nb₅Si₃ is usually found in a eutectic with Nb₆S. It is polymorphic and has a low temperature and high temperature forms known as α and β respectively and both phases are tetragonal.\textsuperscript{[37]} Nb₅Si₃ has good mechanical properties at high temperatures, particularly its creep resistance. At issue with Nb₅Si₃ are its poor oxidation properties. The Nb₅Si₃ phase forms an oxide of Nb₂O₅ with some SiO₂ which does not protect the metal. Instead, between 700-1000°C undergoes pesting and will completely disintegrate in less than 3 hours when exposed to temperatures of 1000°C. The oxide will pest at temperatures above 1000°C due to the large volumetric expansion that occurs when Nb₂O₅ transforms from an orthorhombic crystal structure to a base-centered monoclinic structure. There is also a mismatch in the coefficient of thermal expansion between the Nb₂O₅ and Nb₅Si₃ by about one fourth.\textsuperscript{[38]} Other phases present in the Nb-Si system include Nb₃Si and Nb₂Si.

2.5 Niobium-Chromium Alloys

The importance of the Nb-Si alloy in high temperature oxidation is due to the Nb₅Si₃ phase. The Nb-Cr alloy is also important due to the formation of the Cr₂Nb Laves phase. A Laves phase is a combination of two metals in an AB₂ configuration. The classification of a Laves phase is done based on its crystalline structure. The Nb-Cr system has two Laves phases labeled C(14) and C(15). The C(15) Laves phase is found at low temperatures and is cubic whereas the C(14) phase is hexagonal and occurs at high temperatures.\textsuperscript{[39]} The Laves phase is important in that it has better oxidation properties than Nb₅Si₃. Cr₂Nb forms a CrNbO₄ oxide which protects the metal better than Nb₂O₅. Unfortunately the protection of CrNbO₄ is not complete and at best will protect the metal for up to 500 hours at 1100°C.\textsuperscript{[12]} This is due to the volatilization of Cr₂O₃ that forms alongside CrNbO₄. This volatilization leaves pores that are
prone to cracking during changes in temperature. One issue with the Laves phase is its poor fracture toughness at room temperature (1.5MPa m^{1/2}).

2.6 Nb-Cr-Si

The Nb-Cr-Si alloy system has been heavily studied over the last 50 years. The phase diagram was first established by Goldshmidt and Brand in 1961 by creating 220 separate cast samples.\textsuperscript{[9]} The phase diagram was then further improved by Zhao et al. by the use of a diffusion multiple technique followed by backscatter diffraction for phase verification.\textsuperscript{[10]} Shao used a CALPHAD based thermodynamics modeling software in order to model a possible phase diagram which proved to be similar to that of Zhao’s.\textsuperscript{[40]}

This system is favorable due to the formation of the NbCr\textsubscript{2} Laves and Nb\textsubscript{5}Si\textsubscript{3} phases that protect niobium better than the metal by itself. Chan determined that high concentrations of silicides and Laves phases improved oxidation resistance compared to higher concentrations of solid solution.\textsuperscript{[40]}

Recent oxidation work on the Nb-Cr-Si system involved alloys with low concentrations of chromium and silicon (between less than 20 at\% for each element). The oxidation properties of the Nb-Cr-Si system, with low concentrations of Cr and Si, are unfavorable for many reasons. Between 700 and 850°C, undergoes pest damage due to the intermetallics formed in the structure.\textsuperscript{[28]} Bulky oxide formation becomes an issue in a temperature range from 900 to 1100°C and spalling occurs at 1200°C. Evidence points to the changes in the crystal structure of the Nb\textsubscript{2}O\textsubscript{5} oxide as the reason for the change in oxidation behavior as different temperatures are reached.\textsuperscript{[18]} Studies indicate that higher amounts of Cr provide better oxidation resistance due to
the formation of Cr$_2$O$_3$ and CrNbO$_4$ compared to higher concentrations of Si which allows for the formation of Nb$_2$O$_5$.\textsuperscript{[41]} Physical properties for Nb, Cr, and Si are presented in a table below.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Atomic Weight</th>
<th>Density at 25°C (g/cm$^3$)</th>
<th>Melting Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium</td>
<td>41</td>
<td>92.906</td>
<td>8.60</td>
<td>2467°C</td>
</tr>
<tr>
<td>Chromium</td>
<td>24</td>
<td>51.996</td>
<td>7.19</td>
<td>1860°C</td>
</tr>
<tr>
<td>Silicon</td>
<td>14</td>
<td>28.086</td>
<td>2.34</td>
<td>1412°C</td>
</tr>
</tbody>
</table>

### 2.7 Nb-Cr-Si Ternary Silicides

#### 2.7.1 Nb$_9$(Cr,Si)$_5$

Very little is known about this phase. It is the only ternary phase to occur at low concentrations of chromium and silicon. The phase has variable stoichiometric composition ranges depending on the availability of Cr, or Si but the niobium does not change.\textsuperscript{[42,43]} The silicide, also referred to as 9-2-3 silicide from its stoichiometric composition of Nb$_9$Si$_2$Cr$_3$, is seen in quaternary compositions as well.\textsuperscript{[7]}

#### 2.7.2 CrNbSi

Very little is known of this phase other than its discovery by Goldshmidt and Brand in the 1961.\textsuperscript{[9]} The phase underwent XRD and EPMA study in 1975. The issue with the CrNbSi phase
is that it cannot be in direct equilibrium with Nb$_{65}$ due to the higher stability of αNb$_5$Si$_3$.\textsuperscript{[40]} There is no oxidation information on this phase.

\textbf{2.7.3 (Cr,Nb)$_{11}$Si$_8$}

This ternary phase can have stoichiometric compositions of Cr$_7$Nb$_4$Si$_8$, Cr$_4$Nb$_7$Si$_8$, Cr$_5$Nb$_6$Si$_8$ and Cr$_6$Nb$_5$Si$_8$.\textsuperscript{[44]} This phase underwent crystallographic studies in the 1970’s.\textsuperscript{[45]} The (Cr,Nb)$_{11}$Si$_8$

\textbf{2.7.4 (Cr,Nb)$_6$Si$_5$}

Much like the (Cr,Nb)$_{11}$Si$_8$ phase, not much is known about the (Cr,Nb)$_6$Si$_5$ family. It can have composition: Nb$_2$Cr$_4$Si$_5$, Nb$_3$Cr$_3$Si$_5$ and Nb$_4$Cr$_2$Si$_5$. The phase was first characterized in 1968.\textsuperscript{[46]}
Chapter 3: Methods and Materials

3.1 Alloy Preparation

Four alloys were studied in this project. These alloys were fabricated at the Ames Laboratory at Iowa State University. The alloys were prepared by the arc-melting technique in an inert argon atmosphere. The chamber was first evacuated and a zirconium button oxygen getter was used. The alloys were melted three times in order to ensure homogeneity and then were Electron Beam Discharge (EBM) machined into 5x5x5 millimeter cubes. Table 3.1 shows the compositions of the alloys in atomic percent.

Table 3.1: Alloy compositions in atomic percent.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Niobium</th>
<th>Chromium</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Si</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>20Si</td>
<td>60</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>30Si</td>
<td>50</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>42Si</td>
<td>38</td>
<td>20</td>
<td>42</td>
</tr>
</tbody>
</table>

3.2 Sample Preparation

As-received cubes arrived with a dark grey sheen. The samples from the 30Si and 42Si specimens also contained various cracks and pores. The samples had not undergone hot isostatic
pressing (HIP). The samples were polished to a 600 grit finish with SiC polishing paper. The cubes were then measured in order to calculate a surface area and were placed in an ultrasonic cleaner with methanol as the liquid bath solution for 15 minutes. This removed possible SiC particle contamination. Quartz crucibles from the LECO Corporation (528-018 HP) were used. The crucibles were baked at 300°C for 3 hours in order to remove any possible moisture and furnace cooled. The samples and crucibles were then weighed in a Sartorius MC 210S (accuracy of 0.01mg). The samples were weighed in three configurations: the samples by themselves, the crucibles by themselves (2 were used to protect the sample) and the two crucibles with each sample inside.

3.3 Oxidation

Three different oxidation tests were used: Static, Cyclic, and Oxidation initiation. In static oxidation, the samples were placed in a SentroTech (St-1500-678-YU) box furnace for temperature ranges between 700°C-800°C. For temperature ranges between 900°C-1400°C a SentroTech (ST-1600-888-N) furnace was used. The samples were placed in the furnace for 24 hours with a ramp time of 10°C/min and then furnace cooled. The samples were then weighed with the crucibles. In cyclic oxidation the same regimen as the static oxidation was used except that the samples were placed in a furnace a total of 7 times. After each cycle the samples and crucibles were then weighed to measure oxidization weight gain. The final oxidation test regimen involves placing samples in a furnace and allowing it to ramp up to the final temperature. The samples are then left in the furnace for 15 minutes and then air quenched to room temperature. After cooling, the samples and their crucibles are weighed.
3.4 XRD

Phases and crystal structures were identified and confirmed by x-ray diffraction (XRD). A Bruker D8 Discover diffractometer was used at a setting of 40mA with a voltage of 40kV. A scatter slit with a 0.2mm was used as well as a receiving (divergence) slit of 6mm. The x-rays came from CuK\textsubscript{α} radiation ($\lambda=1.54056\text{	extbar}$$) with a step size of 0.05mm. Both the as received alloys and their oxide powders were analyzed with the as-received having been polished to 1200 grit.

3.5 SEM

Samples were characterized via Scanning Electron Microscopy (SEM). A Hitachi S-4800 was used along with a Robinson backscatter detector (BSE) as well as an EDAX detector for energy-dispersive spectroscopy. The BSE detector was used in order to identify different phases by contrast due to the differences in atomic weights. BSE works by detecting the electrons that are scattered by phases as heavier atomic masses tend to scatter more electrons. The EDS was used in order to roughly quantify atomic percentages in individual phases as well as for verifying alloy composition. The EDS functions by counting x-rays produced as a result of the photoelectric interaction that occurs when an electron is removed from an atomic orbital. These x-rays have varying energies based on the atom from which the electron was removed. The EDS can roughly quantify atomic percentages by counting the x-rays given off from various phases and or alloys. The EDS accuracy is based on calibration and atomic number size. Atomic numbers below sodium (Z=11) is poor unless a thin window detector is used. Even so sensitivity below oxygen (Z=8) is poor.\textsuperscript{[47]}
SEM analysis was done by mounting the samples in an epoxy resin (Kold Mount) and then polished with SiC paper to 1200 grit. Charging was prevented by coating the specimen with gold particles using a Gatan Precision Etching Coating System (Model 682) before being observed in the SEM. The samples were affixed to the SEM holder with graphite tape with a piece of graphite tape extending to the sample to further prevent charging. The SEM was run at an acceleration voltage of 20kV with a probe current of 20μA. The 42Si sample was analyzed at 30kV and 20μA in order to improve the contrast between the phases. The working distance was set at 15mm ±2mm.

3.6 Pandat™

Pandat™[^48] is a modeling program used to construct isothermal phase diagrams. The software is capable of modeling multi-component phase diagrams by calculating potential phases based on Gibbs free energy curves. Pandat™ is capable of giving quantitative data by giving compositions of phases or calculating predicted phase volume fractions. Isothermal sections were created in the following temperatures ranges: 25°C and 700°C-1400°C.[^49,^50]
Chapter 4: Results and Discussion

4.1 AS-CAST CHARACTERIZATION

4.1.1 Phase Diagram

A ternary phase diagram was constructed using Pandat™ 8.2 modeling software. The isothermal section was taken at 25°C and at 1 atm. Figure 4.1 demonstrates the result of the phase diagram modeling. The Nb-20Cr-(10-42)Si alloys are represented on the phase diagram along with calculated phases expected to be present. The 10Si and 20Si alloys are predicted to have Nb3n, the C(15) Laves phase, and the Nb9Si2Cr3 ternary silicide. The first uncommon ternary silicide, CrNbSi, is predicted at 30Si as well as the C(14) Laves phase, which is a high temperature form of NbCr2. The phase composition changes completely in the 42Si alloy. Pandat™ predicted the formation of the Nb5Si3 (5-3 silicide) phase as well as two compositions of the (Cr,Nb)11Si8 family, Cr4Nb7Si8 and Cr6Nb5Si8. CrNb4Si3 is assumed to form alongside the 5-3 silicide.
Figure 4.1: Simulated ternary phase diagram of the Nb-Cr-Si system showing corresponding alloy compositions and phases.

4.1.2 As-cast XRD

In order to ascertain whether the phases predicted by Pandat™ were reliable, x-ray diffraction was used on all of the as-cast alloys. Figure 4.2 shows the XRD patterns for all four alloys. The 10 and 20Si alloys show peaks corresponding to Nb$_{ss}$ however the Laves phase peaks correspond to the C(14) hexagonal configuration. Peaks for the Nb$_9$Si$_2$Cr$_3$ were not identified; instead peaks for both $\alpha$ and $\beta$ Nb$_5$Si$_3$ were seen. The 30Si alloy shows peaks for the C(14) laves phase which matches Pandat™’s predictions. Peaks for both 5-3 silicides were identified as well; however, peaks for the Nb$_9$Si$_2$Cr$_3$ phase were not present in the 30Si alloy.
The 42Si alloy did not show clearly defined peaks and this made identification of phases difficult. The only phase identified was the CrNb₄Si₃. Some peaks for the βNb₅Si₃ also appeared although some of these peaks coincided with those seen for CrNb₄Si₃. Both phases are tetragonal and have very similar lattice parameters (1.6% difference for the ‘a’ parameter and 3% difference for the ‘c’ parameter) so some overlap is be expected.\textsuperscript{[14]} Peaks for the Cr₆Nb₅Si₈, and Cr₄Nb₇Si₈ were not identified. The diffraction data shows some broad peaks at 2θ = 40, 42, 43, 45, 67 and 68. These peaks may correspond to the two (Cr,Nb)₁₁Si₈ phases however the XRD software, which is designed to update to the latest data set when opened, did not identify any diffraction data corresponding to the two phases.

![XRD for As-cast](image)

Figure 4.2: As-cast X-ray diffraction patterns for the 10Si-42Si alloys.
4.1.3 As-cast SEM

Backscatter Electron (BSE) micrographs of the 10 to 42Si alloys in as-cast condition are shown in Fig. 4.3. In Figures 4.3a and 4.3b, the 10 and 20Si alloys both show the presence of Nb\textsubscript{ss}, C(14) Laves, and αNb\textsubscript{5}Si\textsubscript{3}. The 10Si alloy shows concentrations of Nb\textsubscript{ss} represented by the white phase and Nb\textsubscript{5}Si\textsubscript{3} which is represented by the mid grey phase. There is also a eutectic like microstructure comprised of Nb\textsubscript{ss}, Nb\textsubscript{5}Si\textsubscript{3} and NbCr\textsubscript{2}. The 20Si alloy did not contain concentrations of solitary Nb\textsubscript{ss} phase. Instead, higher concentrations of free Nb\textsubscript{5}Si\textsubscript{3} are seen as well as the eutectic like microstructure in the 10Si alloys. The 20Si alloy also contains areas of C(14) Laves and is represented as a long dark phase in the micrograph. The 30Si alloy shown in Figure 4.3c demonstrates a two phase structure of βNb\textsubscript{5}Si\textsubscript{3} and C(14) Laves. At this silicon concentration there is no longer a eutectic like microstructure which is likely due to the absence of Nb\textsubscript{ss}. In Figure 4.3d, the 42Si alloy shows three phases consisting of β5-3 silicide, and the two compositions of (Cr,Nb)\textsubscript{11}Si\textsubscript{8}. The dark grey phase is composed of Cr\textsubscript{6}Nb\textsubscript{5}Si\textsubscript{8} and the lighter grey phase is Cr\textsubscript{4}Nb\textsubscript{5}Si\textsubscript{8}. The βNb\textsubscript{5}Si\textsubscript{3} phase is interesting in that there are areas of relatively high chromium concentrations. These areas are most likely regions of CrNb\textsubscript{4}Si\textsubscript{3}. 
4.1.4 Phase Fractions

There is a discrepancy between the data simulated by Pandat™ and that seen in XRD and SEM images. The formation of Nb$_5$Si$_3$ instead of Nb$_9$Si$_2$Cr$_3$ or the presence of C(14) Laves where C(15) was predicted for example. These discrepancies may be attributed to the lack of equilibrium conditions that occurred during the cooling of the alloy. In order to verify this, Pandat™ was used once more to calculate phase fractions from 25° to 1400°C. The phase fraction data would show if the phases represented in the XRD underwent phase transformations.
Figures 4.4 and 4.5 demonstrate the results of the Pandat™ simulation for the 10 through 42Si alloys. In Figure 4.4, the 10 and 20Si phase fractions are reproduced. While both show the presence of Nb₉Si₂Cr₃, which was not present in any form in the XRD data or SEM images, the 20Si prediction did allow for the formation of the 5-3 silicide at ~700°C. The phase fraction graph also shows the transformation temperature of C(15) to C(14) at 250°C in the 10Si alloy and 190°C for the 20Si alloy. In Figure 4.5, 30Si graph shows the disappearance of CrNbSi and Nb₉Si₂Cr₃ in favor for the formation of C(14) Laves at 160°C. This would be the reason that only two phases are present in the SEM micrograph. The 42Si alloy shows all phases present in the SEM micrographs but it is interesting to note that the chromium rich Cr₆Nb₅Si₈ decreases with increased temperature with a corresponding increase of Nb₅Si₃ and Cr₄Nb₇Si₈. This may be the reason for the dark blotches of CrNb₄Si₃ seen in the as-cast micrograph. The Pandat™ phase fraction data was able to predict most of the phases seen in the as-cast alloys. The only issue was the formation of Nb₉Si₂Cr₃ which was not present in any of the 3 phases where it was predicted. It may be that eutectic like structure is the ideal equilibrium structure instead of the Nb₉Si₂Cr₃ phase.
Figure 4.4: Pandat™ phase fraction chart for the 10 and 20Si alloys.
4.2. **Static Oxidation**

Static oxidation was done in order to test the oxidation resistance of the alloys. The tests involved oxidizing the specimens for 24 hours. The results were then graphically reproduced by weight per unit area versus temperature. The results of the oxidation tests were graphed and are shown in Figure 4.6. The graph also contains the type of oxidation all four alloys underwent at a certain temperature as well as a rough percentage of metal left (base on visual inspection). At 700°C it was observed that pest damage was the dominating oxidation mechanism as the area surrounding the sample contained powdered oxide. The 10 and 30Si alloys showed relatively
little pest damage while the 20Si alloy lost about 80% of its metal to pesting. The 42Si alloy showed no oxidation on the surface from 700° to 900°C. At 800°C the 10 and 20Si alloys showed some pesting while the 30Si alloy completely oxidized. The oxidation mechanism in the 10 and 20Si alloys changed at 900°C from pest to bulky oxide. Bulky oxide formation is an oxidation mechanism that results in an inverted pyramid structure that grows from each face of the metal until none is left. This occurrence may be due to the large volumetric expansion that occurs when Cr₂O₃ and Nb₂O₅ form, which is 107% and 169% respectively.[23] The 30Si continued to pest as opposed to the 10 and 20Si alloys. The 10-30Si alloys all underwent bulky oxide formation at 1000°C however some metal remained in the 20Si alloy. At this temperature, the 42Si alloy showed signs of pesting. It is known that Cr₂O₃ begins to volatilize at 1000°C.[35] It may be that the loss of the protection given by the Cr₂O₃ allowed the 42Si alloy to begin pesting. The results seen at 1100°C was the same as that observed at 1000°C however more metal remained for the 10 and 20Si alloys. From 1200° to 1400°C the dominant oxidation mechanism became spalling. Spalling occurs when differences in coefficients of thermal expansion cause the oxide to separate from the metal-oxide interface. This usually occurs during cooling as the stresses in the metal create a tensile force while the oxide creates a compressive stress. This results in the formation of cracks between the metal and oxide layer.[38] The oxide layer formed in these alloys was in general thicker than those seen at lower temperatures especially in the case of the 30Si alloy. This fact may be why oxidation resistance was also generally better in the spalling temperature range. In general, the 42Si alloy showed much better oxidation resistance and less weight gain than the other alloys. It is also important to note that in the 42Si alloy, the 1200°C temperature range did show some spalling occurring.
4.2.1 Static Oxidation XRD Analysis

All samples (except for the 42Si alloy from 700°-900°C) produced an oxide that could be analyzed by XRD. Figure 4.7 shows the XRD pattern for the 20Si alloy from 900° to 1200°C. The XRD data is a good indicator of possible phase changes which could explain the changes in oxidation behavior. Also, the XRD data for the 10 and 20Si alloys were very similar as the oxide phases present were identical. CrNbO$_4$ is present at all temperatures and is stable whereas the Nb$_2$O$_5$ undergoes allotropic transformations. From 900° to 1000°C, the Nb$_2$O$_5$ is in an
orthorhombic configuration (oNb$_2$O$_5$). At 1100°C the oxide changes to a base-centered monoclinic form (βNb$_2$O$_5$) and then at 1200°C transforms again to the high temperature monoclinic form (mNb$_2$O$_5$). It is the high temperature Nb$_2$O$_5$ that may be the cause of spalling at temperatures above 1200°C. Each subsequent transformation from oNb$_2$O$_5$ to βNb$_2$O$_5$ to mNb$_2$O$_5$ appeared to protect the alloy better as there was some metal remaining. It is important to note, however, that the XRD patterns only represent the dominant oxide but that there is also some overlap between the oxides at the transition temperatures.

![XRD Data for 20Si Alloy](image)

Figure 4.7: XRD phase intensity for the 20Si alloy.
In the 30Si alloy, seen in Figure 4.8, the $\alpha$Nb$_2$O$_5$ transformation occurs 100° earlier at 1000°C. In this case, the $\beta$Nb$_5$Si$_3$ phase undergoes pesting at 900°C as opposed to forming a bulky oxide. This results in a suppression of bulky oxide formation while pushing the pesting regime toward higher temperatures. It also implies that the increased amount of silicon (as the only variable between the 20 and 30Si alloy is the amount of silicon) affected both the stabilization of the high temperature $\beta$Nb$_5$Si$_3$ phase as well as the stabilization of the $\beta$Nb$_2$O$_5$ phase.

Figure 4.8: XRD phase intensity chart for the 30Si alloy.
The XRD data for the 42Si alloy, shown in Figure 4.9, is different than that of the 20 and 30Si alloys. There is no evidence of the α or β forms of Nb₂O₅. Instead there is only the presence of the monoclinic high temperature form. Once more, the increase in silicon content may be acting as a stabilizer for the mNb₂O₅ phase. The data also shows evidence of the formation of SiO₂ which was not seen in the XRD data for the other alloys. Even though only the mNb₂O₅ phase was present in the data, it should be noted that pesting generally occurs at a set temperature range. This means that the phases in the 42Si alloy are better able to resist pesting whether by having a protective layer of Cr₂O₃ that prevents oxygen diffusion into the grain boundaries or by some other method. This would push the temperature range where pesting occurs to much higher temperatures, which is seen in the 42Si alloy.
Figure 4.9: XRD phase intensity chart for the 42Si alloy.
4.2.2 Static Oxidation SEM Analysis

SEM analysis was done on all samples with some metal remaining. This was done in order to characterize the metal-oxide interface. Temperatures of interest were those that represented a specific form of oxidation, i.e. pesting. In this study, these temperatures were 800°, 1100° and 1200° which showed pest damage, bulky oxide, and spalling respectively. It is also important to note that although the dominant oxidation mechanism for the 42Si alloy at 1200°C was pesting, spalling also occurred in small amounts.

The alloys tested at 800°C, except for the 42Si alloy, all showed pest damage as the main form of oxidation. At this temperature range, the 10 and 20Si alloys both retained 80% and 95% of their metal respectively; however the 30Si alloy retained no metal leaving only powder. The 42Si appeared to have all of its metal remaining as no oxide was seen on the surface. In Figure 4.10a, the 10Si alloy shows a highly porous oxide layer of oNb$_2$O$_5$ and CrNbO$_4$. Cracking occurs all along the interface and in the oxide structure. This cracking is also seen in the separation of the oxide from the metal-oxide interface. The metal itself shows some coarsening of the grain structure. The 20Si alloy, shown in Figure 4.10b has a very thin oxide layer of oNb$_2$O$_5$ and CrNbO$_4$. This alloy had only pested about 5% of its metal and this is indicated in the scale. The oxide scale that does remain shows instances of a eutectic-like oxide similar to the structure seen in the metal. The eutectic-like structure is composed of Nb$_2$O$_5$ and CrNbO$_4$. The microstructure itself does not show any cracking or much coarsening of the grain structure when compared to the as-cast sample. The 42Si alloy, in Figure 4.10c, is completely devoid of any oxide at its surface. There are, however, indications of cracking throughout metal-surface interface. These cracks are most likely due to differences in the coefficients of thermal expansion (CTE) between the various ternary phases.
Figure 4.10: Bse images of the metal-oxide interface for the 10, 20 and 42Si alloys. a) 10Si alloy demonstrates an oxide scale with large voids and cracking and separation from the metal-oxide interface. b) 20Si alloy shows little pest oxidation. c) 42Si alloy has no apparent oxide on the surface of the metal.

The microstructure of the samples observed at 1100°C is quite different from those seen at 800°C. At 1100°C the 10, 20 and 30Si alloys underwent bulky oxide formation whereas the 42Si alloy only experienced pesting. At this temperature the 30Si alloy had no metal remaining but the 10 and 20Si alloys did retain some metal. Figure 4.11a shows a cross section of the 10Si alloy. The oxide seen is quite thick and readily adherent to the metal interface. This corresponds to the visual inspection of the oxide that showed an inverted pyramid oxide structure.
originating from the retained metal. The oxide on the structure was readily adhered to the metal. Further inspection off the BSE image indicates that the scale demonstrates a large amount of porosity. This porosity probably allowed diffusion of oxygen to continue into the metal and allowing the scale to advance inward. The shrinking amount of retained metal and the constant diffusion of oxide are the reason for the appearance of an inverted pyramid oxide. The 20Si alloy, seen in Figure 4.11b, also demonstrates a thick oxide scale relative to the scale seen at the 800°C temperature. This sample also resulted in an inverted pyramid type of oxide formation. Both the 10 and 20Si oxides show the presence of the base centered monoclinic form of Nb₂O₅, or βNb₂O₅, which has a much larger volumetric expansion compared to the αNb₂O₅ form. The β is characterized more by its tendency to produce a bulky oxide. The 42Si alloy had quite a different oxide structure. There are two oxide structures apparent in Figure 4.11c. One oxide structure grows into the metal-oxide interface and is preferentially attacking the Nb₅Si₃/CrNb₄Si₃ phase while the other oxide type, which contains a mixed oxide structures, is in the process of breaking away. The oxide growing into the metal consists of layers of Nb₂O₅, CrNbO₄ and SiO₂. The other oxide structure consists of an inner and outer layer. The inner layer is made up of mostly Nb₂O₅ and SiO₂ whereas the outer layer consists of CrNbO₄ as well as Nb₂O₅ and SiO₂. There is also extensive cracking between the oxide scale layer and the metal interface.
Figure 4.11: BSE images of microstructures for the 10, 20 and 42Si alloys at 1100°C. a) 10Si alloy shows bulky scale of Nb$_2$O$_5$ and CrNbO$_4$. b) 20Si alloy’s scale is highly porous. c) 42Si, undergoing pest damage, showed two different oxide structures based on the location of the oxide.

Elemental X-ray mapping was done on the 42Si alloy in order to ascertain the types and location of individual oxides. The images in Figure 4.12 represent the oxide structures seen at the metal-oxide interface: the oxide growing preferentially into the 5-3 silicide and the oxide that undergoes pest damage. Concentrating on the oxide preferentially forming in the 5-3 silicide, it can be noted that both silicon and chromium form a layered structure. This layering may be the result of differences in kinetics in the formation of SiO$_2$ and CrNbO$_4$. There is also a
chromium depleted region between the oxide and the metal which could play a role in the formation kinetics. The oxide layer that is pested off also shows preferential concentrations of chromium in the outer edges of the oxide. This depletion region may also be to blame for the layered CrNbO$_4$/SiO$_2$ structure seen in Figure 4.12. Figure 4.13 is a magnified view of an oxide that was in the process of pesting. The BSE image shows the two different structures in the oxide; however x-ray does not help discern if the layering is due to differences in elemental composition. Instead the only observable feature is the chromium rich zones in the boundaries of the oxide.

Figure 4.12: Elemental X-Ray mapping of the 42Si alloy at 1100°C. Chromium is concentrated around the edges of external oxides and in a layered structure in internal layers.
The 1200°C allowed for a detailed comparison of all four alloys. At this temperature range all alloys underwent spalling (although for the 42Si alloy there was pest damage along with spalling). The 10Si alloy in Figure 4.14a shows two different oxide structures. There are large grains of pure Nb$_2$O$_5$ with sections of a eutectic like structure of Nb$_2$O$_5$ and CrNbO$_4$. This structure formed from the eutecticlike formation of Nb$_{5s}$/NbCr$_2$/Nb$_5$Si$_3$ seen in the 10Si as-cast BSE image in Figure 4.3. The 20Si alloy shown in Figure 4.14b is much more porous compared to the 10Si alloy however much of the same features remain, including the eutecticlike oxide structure. The difference in the oxide scale between 10 and 20Si specimens is in the formation of CrNbO$_4$ nodules seen scattered throughout the eutecticlike structure. This feature is not seen in the 10Si alloy. The 30Si alloy shows a thick scale that was made up of a mixture of Nb$_2$O$_5$, SiO$_2$ and CrNbO$_4$. There are also some areas that have higher concentration of Nb$_2$O$_5$ and these
areas have a similar appearance to the Nb₅Si₃ grains seen in the metal. The scale is much thicker than those of other alloys and was as porous as the scales seen in the 10 and 20Si alloys, however cracking did occur throughout the scale. There are also indications of preferential oxidation of the Nb₅Si₃ grains near the metal-oxide interface observed in Figure 4.14c. The 42Si alloy contained a porous scale which formed with what appears to be two different oxide types (as seen in the 42Si alloy at 1100°C). The oxide is very porous and cracking is apparent throughout the oxide and the metal-oxide interface. Elemental X-ray mapping was done as well to characterize the elemental composition of the two oxides. The mapping, shown in Figure 4.15, once again shows a strong concentration of chromium in the outer regions of the oxide scales (whether pested or spalled). There are also indications that silicon is being concentrated in the inner regions of the oxide. A large chromium depleted region is observed in the metal-oxide interface.
Figure 4.14: BSE images of microstructures for the 10 - 42Si alloys at 1200°C. a) 10Si alloy shows a eutectic like structure of Nb$_2$O$_5$ and CrNbO$_4$. b) 20Si alloy shows similar characteristics to the 10Si alloy however there are nodules of CrNbO$_4$ growing from the eutectic like structure. c) 30Si demonstrates a thick scale with a mixture of three oxides. d) 42Si scale forms into two oxide structures which are highly porous.
Figure 4.15: Elemental X-ray map demonstrating the concentration of chromium along the edges of the oxide scale. Silicon is concentrated in the interior of the scale.

The x-ray maps for the 30 and 42Si alloys points to areas that are depleted of chromium all along the metal-oxide interface. This depleted region occurs from 1000° to 1400°C with the thickness increasing as the temperature increases. Figure 4.16 demonstrates BSE images of the 30Si alloy at 1300°C and the 42Si alloy at 1200°C along with their corresponding elemental x-ray chromium maps. The 30Si alloy shows a chromium depleted region along the metal oxide interface. Its appearance in the BSE image displays a lower contrast compared to the metal and its phases and instead looks to be part of the oxide. The 42Si alloy also shows a chromium depleted region but with a brighter contrast. In the BSE image, the area looks to be highly porous but the elemental maps indicate high concentrations of silicon and may instead be SiO$_2$. The chromium depletion may be due to the formation of CrNbO$_4$. As the oxide is formed,
chromium is depleted from the surface, creating a concentration gradient. This gradient quickly strips the near surface metal of chromium.

The evidence then points to the ability of the uncommon ternary silicides to protect the metal by forming more CrNbO$_4$ than what is otherwise available to the 10-30Si alloys. This oxide is known to protect the metal and the ternaries, by the nature of containing chromium in their composition, can therefore form CrNbO$_4$. This protection is then found universally throughout the alloy as opposed to being limited to a few chromium containing binary phases, as
seen in the 10-30Si alloys. This protection is readily apparent at temperature ranges between 700° to 900°C where no oxidation took place in the 42Si alloy. The protection, however, is not absolute as is seen in the oxidation of the internal surfaces located in the 42Si alloy.

4.2.3 Oxidation of Internal Grains

The 30Si and 42Si alloys demonstrate oxidation of internal grains at various temperature ranges. This type of oxidation occurs when the outward diffusion of an element with a high affinity for oxygen is slower than the inward diffusion of oxygen into the metal.\textsuperscript{[22]} In the 30Si alloy, this oxidation is seen occurring close to the metal-oxide interface as seen in Figure 4.17a. Figures 4.17b-d demonstrate the evolution of oxide growth from the surfaces of internal pores and shrinkage cavities into the surrounding grains as temperatures increases. The effects of this type of oxidation on surrounding microstructure can be seen by the formation of cracks and as weight gain in gravimetric studies.

The data obtained by the static oxidation then leads to an interesting conclusion. Although the evidence indicates that there is diffusion of oxygen into the alloy it also becomes readily apparent that the 42Si alloy can resist oxidation in temperature ranges between 700° and 900°C. A reduction of shrinkage cavities and pores through post processing treatment may then render the metal able to resist internal weight gain.
Figure 4.17: a) 30Si alloy at 1300°C showing internal oxidation of the Nb$_5$Si$_3$ grains near the metal-oxide interface. b) 42Si alloy at 900°C with oxidation occurring on the surfaces of internal shrinkage cavities. c) 1000°C the oxidation that was occurring on the internal surfaces spreads out to nearby grains. d) 1200°C the oxidation completely surrounds internal pores.

4.3. CYCLIC OXIDATION

Cyclic oxidation behavior for the 42Si alloy was studied to determine the alloy’s oxidation response over a longer period. The results were then tabulated and plotted in an effort to not only quantify the alloy’s cyclic longevity but to determine its viability as well. Figure 4.18 plots the weight gain per unit area versus temperature with a temperature range of 900°C to
1400°C. 700°C and 800°C were not chosen under the assumption that much like their STO counterparts, there would be no oxidation on the surface of the metal. The experiment was done in 7 sets of 24 hour cycles for a total of 168 hours in which the specimen was allowed to furnace cool after every cycle.

The oxidation behavior of the 900°C sample showed the best response of all the samples tested. The sample appeared to oxidize linearly but the effect was so minute that there was almost no weight gain. The weight gain came from oxidation of internal pores and shrinkage cavities as the surface of the metal was free of oxidation. The 1000°C and 1100°C specimen, unlike the 900°C, were fully oxidized after 168 hours and had been converted completely into an oxide powder. This response was to be expected due to the results seen in static oxidation in which both 1000°C and 1100°C were subject to pesting. The pest oxide is not beneficial as it cannot form a protective scale. The 1200°C sample was interesting as the pesting/spalling seen in static oxidation occurred concurrently. The sample was able to survive the 168 hour cyclic oxidation however, as some metal remained. The curvature of the oxide showed that as the amount of metal decreased, oxidation accelerated. The 1300°C spalling was the dominant form of oxidation though some pesting occurred. The sample showed a linear growth in weight gain, compared to the ones tested at 1000°C to 1200°C and some of the metal remained. The sample at 1400°C spalled which was to be expected. Interestingly enough, oxidation also appeared to accelerate with the loss of surface area.

The cyclic oxidation experiment revealed the same deficiencies in the 42Si alloy as was seen in static oxidation. Pesting is the limiting factor in the viability of the alloys in use at high temperatures. The pest damage, which is seen only in the intermetallic phases of the Nb-Cr-Si system, is exacerbated during cyclic oxidation. There is also the issue that any scale, adherent or
not, is non-protective due to the porosity seen in the previous micrographs. Even if the scale is adherent, when the temperature cools the scale will spall off and cease to protect against further oxidation until a new scale is reformed.

![Cyclic Oxidation for the 42Si Alloy](image)

Figure 4.18: 7 day cyclic oxidation curves for the 42Si alloy.

### 4.4 Oxidation Initiation

The final experiment done was to assess the oxide kinetics of the 42Si alloy. The rationale being that the lack of a protective scale could be due to different nucleation times for the oxides. The 42Si alloy demonstrated a chromium depletion region and a layered substructure
of various oxides. The oxidation initiation test would be a significant factor in establishing whether the layered structure was due to chromium depletion or differences in oxidation kinetics.

Oxidation initiation was tested by placing samples in a furnace at three specific temperatures based on data seen in static oxidation. The sample would then be removed and air quenched in order to significantly slow down oxidation. The temperatures tested were 900°, 1100°, and 1300°C which were based on the pesting and spalling mechanisms present at those temperatures. It is also expected that no oxide would form at the 900°C sample however oxidation of the internal surfaces may occur.

The results of oxidation initiation are demonstrated in Figure 4.19 which displays the BSE images taken of each samples. Figure 4.19a is a BSE image of the sample tested at 900°C. There are significant amounts of voids along the surface but there is no oxidation present at the surface of the metal or in the free surfaces of the voids. The next image in Figure 4.19b demonstrates the growth of Nb2O5 and SiO2. There was no evidence of CrNbO4 formation. Also significant in the image is the cracking that is occurring throughout the matrix. The same can be said about the sample exposed to 1300°C. There was significantly more oxide on the surface however the cracking was less extreme. There also appears to be a layered structure in the Nb2O5/SiO2 oxide which points to very slight differences in the oxidation kinetics. Also importantly, there was no evidence of the formation of CrNbO4.

In order to verify the lack of formation of CrNbO4, elemental x-ray mapping was done in order to track the concentrations of chromium in both the metal and the oxide. Figure 4.20 shows the BSE and X-ray map of both the 1100° and 1300°C samples. The 1100°C sample shows almost no chromium in the oxide structure. The 1300°C sample shows a much stronger chromium presence in the oxide but the CrNbO4 structure observed in the static oxidation BSE
images is not present. The chromium depleted region found in the static oxidation maps was not observed.

The lack of chromium in the oxides points to the unobstructed formation of Nb$_2$O$_5$ in the initial stages of oxidation. CrNbO$_4$ is known to protect against further oxidation, however Nb$_2$O$_5$ does not as it is non-protective. This fact points to oxygen diffusing into the metal which can therefore begin the process of pesting in the 1100°C sample. The 1300°C sample also shows signs of Nb$_2$O$_5$ formation before CrNbO$_4$. The issue then becomes a matter of how the oxides form a scale. From the static oxidation BSE images, it appears that the scale created by CrNbO$_4$ and Nb$_2$O$_5$ contains voids which allow the diffusion of oxygen. Therefore the uncommon ternary phases, although allowing for the formation of more CrNbO$_4$ throughout the oxide-metal interface, are unable to produce a scale of CrNbO$_4$ that can protect the metal quickly enough to inhibit the formation of Nb$_2$O$_5$. 
Figure 4.19: BSE images of the 42Si alloy after 15 minutes of oxidation. a) 900°C shows no evidence of oxidation. b) 1100°C forms Nb₂O₅ and SiO₂ c) 1300°C forms larger oxides than the 1100°C specimen.
Figure 4.20: X-ray maps of the 1100° and 1300°C specimens. There is no indication of a chromium depleted region however the 1300°C does show concentrations of chromium in the oxide.
Chapter 5: Conclusions

Four alloys from the Nb-Cr-Si system with varying amounts of silicon were tested in order to ascertain the oxidation resistance of uncommon ternary silicides while also determining the effects of silicon on the overall oxidation resistance of the system. After static oxidation, the 42Si alloy showed the best oxidation response. The chromium concentration found in the ternary silicides of the 42Si alloy allowed for a more uniform scale containing CrNbO$_4$. The 42Si alloy demonstrated excellent oxidation properties in the 700° to 900°C as no oxidation was present on the metal-oxide interface. Oxidation did occur at these temperatures in the internal surfaces located inside the alloy. While the amount of weight gain caused by the oxidation of these pores and shrinkage cavities was minimal compared to the weight gain seen in the other alloys, improved post processing would reduce the amount of porosity seen in the metal. The 42Si alloy underwent pesting from the 1000° to 1100°C. The pest product consisted of Nb$_2$O$_5$, SiO$_2$, and CrNbO$_4$. The formation of the more uniform CrNbO$_4$ layer created a chromium depletion region in the metal-oxide interface. When compared to the 10-30Si alloys, the 42Si alloy was much better able to resist pest oxidation. The data points to lower oxidation kinetics compared to the binary phases seen in the 10-30Si alloy. In the 1200° to 1400°C range, the 42Si alloy underwent a different oxidation mechanism. The oxidation response here was better than what was seen in the 10-30Si alloys however the oxide scale was not protective due to its porosity and tendency to spall.

Cyclic and oxidation initiation studies were done in order to verify long term oxidation viability. Cyclic oxidation verified the oxidation resistance of the 42Si alloy at 900°C. The alloy proved to have a poor oxidation response to cyclic oxidation as little to no metal was left in the 1000° to 1400°C range. Data gathered during oxidation initiation pointed to the formation of Nb$_2$O$_5$ before CrNbO$_4$. Nb$_2$O$_5$ is a non-protective oxide and the failure to prevent its formation at first leaves the alloy vulnerable to oxygen diffusion into the lattice.
While the ternary silicides showed improved oxidation resistance overall, there are unfortunately many issues that need to be resolved. The alloy contained significant amounts of porosity and shrinkage cavities. The alloy also proved to be very brittle, although no mechanical testing was done. The alloy is also extremely susceptible to oxygen diffusion. Further testing is required in order to better characterize the ternary silicides found in the 42Si alloy. Mechanical testing, for example, could be done in order to measure fracture toughness at high temperatures. The ternary silicides may find future use as a dispersion product for production of CrNbO$_4$.

The effects of silicon were also taken into consideration in the study. The alloys were tested with 10, 20, 30, and 42 at% silicon. Oxidation resistance only improved at temperatures ranges above 1200°C. From the 700° to 1100°C range, silicon actually decreased oxidation resistance. Silicon also had an effect on the oxidation mechanism. An increase of silicon from 20% to 30% eliminated bulky oxide at 900°C causing the alloy to pest instead. XRD data pointed to the stabilization of different forms of Nb$_2$O$_5$. The higher concentrations of silicon also allowed for the formation of SiO$_2$ in the 30 and 42Si alloys. The SiO$_2$ could have acted as a diffusion barrier to oxygen, improving oxidation resistance above 1200°C as was seen in the static oxidation tests.
References


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Vita

Daniel Brendan Voglewede was born in Albuquerque, New Mexico. He entered the University of Texas at El Paso (UTEP) in the fall of 2006. While at UTEP, Brendan obtained an internship at Enterprise Products, a petroleum company located in Houston. He also worked as a consultant for Williams, also a petroleum company. After graduating from The University of Texas at El Paso in the summer of 2010 with a degree in Metallurgical and Materials Engineering, he enrolled in the graduate program in the fall of 2010 to obtain a Master of Science Degree in Metallurgical and Materials Engineering. While working on his Master’s Degree, he gave an oral presentation at TMS 2012, a national-level conference in Orlando Fl. He also published *The Effects of Uncommon Silicides on the Oxidation of Alloys from the Nb-Cr-Si System* in the journal Corrosion Science. After graduating in the spring of 2012, Brendan will be working at Halliburton Drill Bit Services.

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