**Oxidation behavior and chlorination treatment to improve oxidation resistance of
Nb-Mo-Si-B alloys**

by

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CHAPTER 1

GENERAL INTRODUCTION

This thesis is written in an alternate format. The thesis is composed of a general introduction, two original manuscripts, and a general conclusion. References cited within each chapter are given at the end of each chapter. The general introduction starts with the driving force behind this research, and gives an overview of previous work on boron doped molybdenum silicides, Nb/Nb₅Si₃ composites, boron modified niobium silicides and molybdenum niobium silicides. Chapter 2 focuses on the oxidation behavior of Nb-Mo-Si-B alloys. Chapter 3 contains studies on a novel chlorination technique to improve the oxidation resistance of Nb-Mo-Si-B alloys. Chapter 4 summarizes the important results in this study.

Literature Review

For civilian and military applications, there is an increasing need for materials, which can be used at high temperature to improve energy efficiency. Potential uses for high temperature materials include industrial furnace elements, power generation components, aircraft turbine engine hot section components such as blades, combustors, nozzles, and so on. In terms of candidate materials for high temperature structural application, there is a temperature cut off at ~1000°C [1]. Below this temperature, it is possible to use nickel and cobalt-base superalloys and aluminide intermetallics. However, above 1000°C, for oxidation and strength reasons, one must shift to the silicon-based ceramics, advanced intermetallics, and silicide-based materials. Transition metal silicides show good potential for use as structural materials in excess of 1000°C. Silicides can provide exceptional high-temperature corrosion resistance under oxidizing and sulfidizing conditions characteristic of many fossil energy environments and thus are potential candidate materials for protective coatings. Especially, M₅Si₃ type compounds are attractive due to their high melting temperature, relatively low density and good creep resistance [2]. Drawbacks of single phase M₅Si₃ include brittle fracture at ambient temperature. However, some of these silicides can be equilibrium with the terminal refractory metal (or alloy) phase, and therefore offer the potential for ductile phase toughening

by forming M/M_5Si_3 composite. Extensive studies [3,4] have demonstrated that two-phase Nb/NbSi₃ alloys have a good balance of low temperature toughness and high temperature strength. However, Nb/Nb₅Si₃ alloys still suffer from catastrophic oxidation upon exposure to air at temperature above 500°C.

It was previously reported that the addition of boron to Mo₅Si₃ results in substantial improvement in high-temperature oxidation resistance [5,6]. Boron doped molybdenum silicides provide good oxidation resistance and high strength at elevated temperature, but low fracture toughness limits its use as the high temperature structural material.

Nb-Si-B ternary phase diagram suggests a large phase field, which offers a possibility of ductile-phase toughening of the brittle niobium silicide; however, past research in this group as well as elsewhere showed that boron modified niobium silicide does not have a good oxidation resistance at high temperature [8,9]. Because of the complete solid solubility between Nb and Mo, two-phase structure, (Nb, Mo) metal plus boron modified (Nb, Mo) silicide, may exist and combine the good properties of low temperature toughness and high temperature oxidation resistance. Past work [8] on Nb-Mo-Si-B alloys showed that the quaternary system is not oxidation resistant as Mo-Si-B system. The difference in oxidation resistance between boron-doped Mo-Si and Nb-Si may be interpreted in terms of the volatility of oxide. MoO₃ volatilize forming pores and way for glass to flow and make protective glass layer but Nb₂O₅ does not volatilize and thus a thin protective borosilicate layer does not form[9]. It was thought that if Nb₂O₅ that form during exposure to air atmosphere is volatilized by gas phase reactions, the scale may behave like Mo-Si-B intermetallic and hence can be rendered oxidation resistant. This led us to chlorination process to selectively remove Nb₂O₅ from the oxide layer and study microstructure and oxidation behavior after chlorination.

Mo-Si-B System

Mo-Si-B system intermetallics have been attracting attention as promising candidate materials for high temperature applications, especially materials containing Mo₅Si₃ (T₁) phase. The Mo-Si-B phase diagram was first investigated by Nowotny [10] in the 1950's. The isothermal section of the phase diagram at 1600°C is shown in Figure 1. The crystal

structure of impurity-free Mo_5Si_3 is tetragonal W_5Si_3 having the space group $I4/mcm$. The Mo_5Si_3 unit cell is very large and complex, and contains four formula units. The homogeneity (~ 2.5 at% silicon) of Mo_5Si_3 makes the production of a single-phase material much easier compared to the line compounds Mo_3Si and MoSi_2 .

Because of the stability of Mo_3Si , terminal solid solution Mo can not co-exist with the brittle Mo_5Si_3 in thermodynamic equilibrium. Small amount of boron is incorporated into the Mo_5Si_3 and yields a ternary phase, T_1 , with the tetragonal W_5Si_3 -type structure. Nowotny reported that T_1 ($\text{Mo}_5\text{Si}_3\text{B}_x$) has a maximum solubility of 4.5 at.% boron, but recent work performed by Huebsch[11] suggests that the boron solubility is much lower, approximately 2 at%. Nowotny also reported another ternary phase, T_2 , with higher boron content (Mo_5SiB_2). The structure was determined to be tetragonal Cr_5B_3 -type. Oxidation of Mo_5Si_3 is characterized by porous scale formation and active oxidation below about 1650°C .

Scale porosity allows oxygen transport via a short circuit path to the underlying silicide, allowing faster oxidation than would be expected from a diffusion-controlled process.

Figure 1 Isothermal cut of the Mo-Si-B ternary phase diagram at 1600°C

Bartlett et al explained the oxidation of Mo by the partial pressure of oxygen at the oxidation interface [12]. The model is based on the premise that, in order to maintain P_{O_2} at the level thermodynamically indicated by Si/SiO₂ equilibria, the rate of Si supply to the oxidation interface must be faster than the rate of Si consumption due to reaction with O₂. If the Si supply rate is slower than Si consumption rate, the oxidation interface become silicon-depleted and oxygen partial pressure at interface increases. An increasing in P_{O_2} will lead to oxidation and volatilization of Mo, causing the scale to rupture and become non-passivating . When temperature is higher, Si diffusion rate is sufficiently high and no Mo is oxidized. A protective SiO₂ layer is formed [12].

It has been shown by Meyer et al [5,6] that doping Mo₅Si₃ 1-2 wt% boron significantly improves the oxidation resistance of Mo₅Si₃ by several orders of magnitude [5]. Mechanism of high oxidation resistance of boron-doped Mo₅Si₃ is also explained by Meyer et al. At 600°C, the scale is composed of three distinct areas: small pockets of borosilicate glass and almost pure MoO₃ are surrounded by a matrix of mixed molybdenum and silicon oxides. At 633°C, larger MoO₃ crystals begin to form around “pure” MoO₃. At 750°C, MoO₃ begins to sublime, which leads to the decrease of both number and size of MoO₃ crystals. Viscous flow starts at 1000°C and then a coherent protective layer is formed.

Oxygen pressure at oxidation interface, porosity and viscosity are the keys for forming a protective layer. If oxidation is limited by oxygen diffusion, oxygen partial pressure will be fixed by the Si/SiO₂ equilibria. SiO₂ has a much lower free energy of formation than any molybdenum oxide. The dominant oxidation reaction will be:

A silicon depleted and molybdenum rich interlayer will thus form.

On the other hand, if the partial pressure of oxygen at the interface is high enough to oxide molybdenum, oxidation will be:

It predicts a mass loss due to volatilization of MoO₃. A metallic Mo interlayer will not form [5].

When viscous flow doesn't close pores, porosity of the layer determines the steady state oxidation rate. When viscous flow forms a coherent layer, oxidation is controlled by diffusion rate of oxygen through the layer [5,6].

Boron doping of Mo_5Si_3 does not appear to decrease the high creep strength of Mo_5Si_3 due to the complex unit cell. The creep rate for a three-phase microstructure consisting of T_1 matrix and Mo_3Si and T_2 is $1.1 \times 10^{-6} \text{ s}^{-1}$ at 1300°C under 140MPa. No dislocation motion was observed in T_1 phase. Only a few dislocations were noted in T_2 . The average activation energy was determined to be $\sim 400 \text{ kJ/mol}$. [5]

Mo_5Si_3 single crystal has significant thermal expansion anisotropy along the a and c directions. The measured thermal expansion coefficient of Mo_5Si_3 single crystal is: $\alpha_a = 5.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, $\alpha_c = 11.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $\alpha_a/\alpha_c = 2.2$ [13]. This can result in a substantially high residual thermal stresses, up to 1.8 GPa, due to thermal expansion mismatch between different grains in the polycrystalline Mo_5Si_3 materials. These large stresses can fracture weakly bonded grain boundaries in cooling processes during fabrication, resulting in grain boundary cracking.

Recent study in this group [13,14] indicates the addition of boron or change of the Mo:Si ratio have minor effects on the thermal expansion anisotropy behavior of T_1 phase. This was the motivation of recent studies [8,15] to incorporate Nb into Mo-Si-B system to improve mechanical properties while retaining oxidation resistance.

Nb-Si System

Niobium silicide base alloys have a strong potential as high temperature structural materials due to their high melting point over 2000°C and excellent strength [16] even at temperature above 1200°C. There are three silicides of Niobium: Nb₃Si, which is only stable between 1765°C and 1975°C; NbSi₂ and Nb₅Si₃, with the highest melting point in the Nb-Si system[17].

Nb₅Si₃

The correct stoichiometry of Nb₅Si₃ was first identified by Knapton [18] in 1955. The latest Nb-Si binary phase diagram is shown in Figure 2 [19] The Nb₅Si₃ compound has the highest melting temperature of 2515°C in Nb-Si system and low density (7.11gm/cm³) [16]. Nb₅Si₃ has very limited range of solubility in with niobium and NbSi₂. It has two tetragonal equilibrium phases with a transition at 1940°C. α-Nb₅Si₃ is stable below 1935°C, while β-Nb₅Si₃ is stable above 1645°C. Owing to their complex crystal structures, plastic deformation of monolithic Nb₅Si₃ will be limited even in the high temperature range. An incorporation of a ductile phase to brittle Nb₅Si₃ phase resulting in two-phase silicide alloy will be one way to improve room temperature deformability.

Nb₅Si₃ shows brittle fracture behavior at low temperatures. However, from Nb-Si phase diagram, the terminal niobium solid solution and Nb₅Si₃ coexist up to temperature of 1645°C. So the Nb-Si system offers a possibility of ductile-phase toughening of the brittle Nb₅Si₃ with the niobium solid solution. This concept has led to alloy development efforts oriented toward two-phase/multi-phase systems, wherein the goal is to achieve a balance of properties for structural use such as high melting temperatures, high stiffness, low densities, and good high-temperature strength/creep resistance.

Figure 2 Nb-Si Phase Diagram [19]

Nb/Nb₅Si₃ composites

Niobium silicide in-situ composites have been extensively studied for high temperature applications. Its properties are discussed in brief as follows:

1. Creep Behavior

There have been several recent studies on the creep resistance of Nb-Si in-situ composites [16, 20, 21, 22, 23, 24, 25]. In a series of papers [22, 23, 24, 25], Henshall and co-workers investigated the primary and steady state creep response of ductile-phase toughened Nb₅Si₃/Nb in-situ composites through a combination of analytical modeling and numerical simulation, using experimental data generated by Subramanian et al. [16,20]. These studies, which treated the Nb₅Si₃ as the continuous phase, demonstrated that the creep behavior of the in-situ composites is dominated by the silicide phase, which is stronger and bears a higher load than the weaker Nb solid solution. At a given stress, the steady state creep rate of the niobium silicide in-situ composites [20,21] is significantly lower than that of the Nb_{ss} phase, even though it is higher than that exhibited by monolithic silicides [16]. The creep exponent of the in-situ composite is about 2 [20,21], compared with ≈ 1 for Nb₅Si₃ [16] and 5.8 for Nb [22,23] or Nb(Si) solid solution [25].

3. Thermal expansion

The thermal expansion coefficients of niobium ($7 \times 10^{-6}/^{\circ}\text{C}$ for pure Nb) and niobium silicide (Nb₅Si₃) ($6.2 \times 10^{-6}/^{\circ}\text{C}$) are not appreciably different [3], so the interface between composite phases will not suffer excess stress during thermal cycling.

4. Strength

The strength increases and ductility decreases for Nb/Nb₅Si₃ with increasing Si content in the Nb-10 to 16Si range[28]. In the as-cast + heat-treated alloys, a high level of strength is retained in the temperature range of 1400⁰C to 1600⁰C, even though these alloys are totally brittle at temperature below 1000⁰C.

5. *Fracture toughness*

The room temperature fracture toughness of the Nb-Si system ranged from 13 MPam^{1/2} for a Nb-16.5Si alloy to about 21 MPam^{1/2} for a Nb-10Si alloy [29]. However, we know the monolithic Nb₅Si₃ intermetallic shows a room temperature fracture toughness of only ~3 MPam^{1/2}. The results show that the room temperature fracture toughness of the composite is considerably greater than that of the intermetallic and that the toughness of the composite can be affected by the way it is processed.

6. *Oxidation Resistance*

It is well recognized that all Nb-based alloys suffer from catastrophic oxidation and oxygen penetration embrittlement upon exposure to air at temperatures above 500°C. [28] High metal recession rates, spalling, and general structural disintegration typically characterize the high-temperature oxidation behavior of the Nb-Nb₅Si₃ alloys. Further, the fast diffusion of oxygen throughout the oxide layers or through the grain boundaries, followed by dissolution of oxygen within the Nb phase, results in substantial hardening and embrittlement of the Nb phase. The oxidation of α -Nb₅Si₃ crystal was measured by Okada [30] with TG and DTA. The oxidation begins to proceed in the temperature range of about 430°C. The oxidation product was found to be Nb₂O₅. Although a SiO₂ was not detected in his experiment, he suggested the noncrystalline or amorphous SiO₂ was probably formed during the oxidation reaction. Jackson et al [31] also reported the single phase Nb₅Si₃ oxidized rapidly, and formed a very voluminous, thick scale. The oxidative instability of Nb-Si alloys led researchers [7,8,9] to add small amount of boron in Nb-Si alloys as to imitate the Mo-Si-B system to form a protective borosilicate glass layer

Nb-Si-B System

Nowotny[32] determined the isothermal section of Nb-Si-B at 1600°C (Figure 3). He reported the boron will be interstitially built into Nb₅Si₃ and form Nb₅Si₃(B) with D8₈ structure (Mn₅Si₃-type, hexagonal). The lattice parameters for 5 at. % boron [33] are: a=7.54, c=5.25. When B/Si substitution takes places, Nb₅(Si,B)₃ is formed. Nb₅(Si,B)₃ has a body-centered tetragonal Cr₅B₃-type structure which is called T₂ phase by Nowotny. The lattice parameters of Nb₅(Si,B)₃ for 5 at. % boron are: a=6.46, c=11.75Å.

Murakami et al [9] studied the microstructure, mechanical properties and oxidation behavior of powder compacts, prepared by spark plasma sintering, of the Nb-Si-B system in the Nb₅Si₃-NbB₂-NbSi₂ triangle, which contains ternary phase D8₈ (Figure 4)

Compacts of the system was found to consist of two or three of NbB₂, Nb₅Si₃, Nb₅Si₃B₂ and NbSi₂ phases depending on the composition unless a large amount of silicon is consumed by forming SiO₂. It was found that compacts with compositions on the line of Nb₅Si₃-Nb₅Si₃B₂-NbB₂ generally exhibit high micro vickers hardness (~1.5-2.0KHv) at room temperature and a high compressive strength at high temperatures(~1700°C). The oxidation results (Figure 6) showed that oxidation resistance increases in the sequence NbB₂, Nb₅Si₃, D₈₈ (56Nb-34Si-10B) and NbSi₂. The oxide layer of D₈₈ (56Nb-34Si-10B) is as thick as 230 µm after exposing to air at 1250°C for 5 hours, and is composed of Nb₂O₅, SiO₂ and a large number of pores. The oxidation resistance of Nb₅Si₃B₂ is found to be better than that of Nb₅Si₃ for the short duration oxidation experiment, but not as good as that of NbSi₂ by the boron addition responsible for the formation of Nb₅Si₃B₂. Figure 5 shows the oxidation induced mass change for compositions studied by Murakami et al [9].

Liu et al [7,8] studied the oxidation behavior of Nb-Si-B compacts at 1000°C (Figure 6). Boron-containing phases, T₂ and D8₈, showed better oxidation resistance than Nb₅Si₃, but they are still extremely poor compared to boron-modified Mo₅Si₃. The oxide scale was composed of a fine mixture of Nb₂O₅ and borosilicate glass. The inferior oxidation resistance of Nb₅Si₃B_x against boron-doped Mo₅Si₃ may be attributed to the fact that contrary to MoO₃, Nb₂O₅ does not volatilize and thus a thin protective borosilicate layer does not form on Nb₅Si₃B₂ [7,8,9].

Figure 3 Isothermal section of Nb-Si-B Phase diagram at 1600°C [32]

Figure 4 Compositions of Nb-Si-B compacts investigated by Murakami et al (open circles)[9]

Figure 5 Oxidation-induced mass change of Nb-Si-B powder compacts with five different compositions at 1250°C in air as a function of time[9]

Figure 6 Oxidation-induced mass change of Nb-Si-B arc melted powder compacts different compositions at 1000°C in air as a function of time[7,8]

Nb-Mo-Si-B System

As discussed earlier, Mo-Si-B system offers a good combination of properties for high temperature application. But its low fracture toughness and thermal expansion anisotropy need to be improved before they can find practical applications. This is the motivation of a recent study to incorporate Nb into Mo-Si-B system to improve mechanical properties while retaining good oxidation resistance. Nb-Si system offers possibility of ductile phase toughening and Nb metal can coexist in equilibrium with boron containing silicides. Since there is a complete solubility between Nb and Mo (Figure 7), the Nb/Mo substitution may avoid the formation of Mo_3Si and then improve the toughness of T_1 ($\text{Mo}_5\text{Si}_3\text{B}_x$) by ductile phase toughening. In addition, Nb/Mo substitution may change the lattice parameter of T_1 and subsequently affect the thermal expansion behavior of T_1 . Thermal expansion anisotropy of Nb-Mo-Si alloys has been studied by Fu et al [34]. They found that the CTE (coefficient of thermal expansion) anisotropy of Mo_5Si_3 can be significantly reduced through ternary alloying additions that alter interatomic distance and bonding strength along the atom chains in the c -direction. Nb was found to reduce $\text{CTE}(c)/\text{CTE}(a)$ ratio to a value of 1.5 for MoNb_4Si_3 from the 2.2 for Mo_5Si_3 as reported previously [35,36,37]. Isothermal oxidation behavior and microstructure of Nb-Mo-Si-B intermetallic compacts with different compositions and at different temperatures has been studied recently by Liu et al [8] (Figure 8). Desired compositions were prepared by arc melting process and compacts were obtained by grinding followed by pressing and sintering. It is reported that that when metal content (Nb + Mo) is fixed, the relative density increases as the Mo content increases. In addition, the relative density also increases with the metal content when Nb/Mo is fixed. The microstructure depends on the Nb/Mo ratio. The co-existence of T_2 or T_1 with metal phase was obtained in 53Nb-17Mo-23Si-7B and 35Nb-35Mo-23Si-7b systems. The lattice dimensions reported for T_1 , T_2 and $D8_8$ increased linearly with Nb/Mo ratio. Also formation of the M_3Si was suppressed by substitution of Nb for Mo. Oxidation studies of Nb-Mo-Si-B alloys with nominal compositions of Nb/Mo = 1/3, 1 and 3 show that alloys with Nb/Mo=3 gained mass at a very rapid rate and eventually converted to powder when exposed to air. On the other hand alloys with Nb/Mo = 1/3 lost mass due to MoO_3 vaporization. Nb_2O_5 was present in scale of all alloy compositions. Large oxidation rate constants suggest that Nb-Mo-

Si-B alloys are not oxidative stable as confirmed by absence of continuous protective glass layer. Formation of non-volatile Nb_2O_5 is speculated to be the primary reason behind the oxidative instability of Nb-Mo-Si-B alloys. Selective removal of Nb_2O_5 that forms during initial stages of oxidation was thought to result in improved oxidation resistance by forming continuous glass layer as oxide scale would behave like Mo-Si-B alloys. The idea led us to design the chlorination process to selectively remove Nb_2O_5 as volatile NbCl_5 .

Figure 7 Nb-Mo phase diagram

Figure 8 Oxidation induced mass change of Nb-Mo-Si-B powder compacts at 1000°C in air as a function of time [8]

Chlorination

Statement of Problem

The non-volatile Nb_2O_5 , which is one of the oxidation products during oxidation of Nb-Mo-Si-B alloys, seems to be the main reason for its poor oxidation resistance. In Mo-Si-B system, MoO_3 volatilization leads to formation of pores which in turn gets healed by the viscous flow of borosilicate glass and leading to formation of the protective layer or barrier to oxygen diffusion and prevents further oxidation of alloy. But in Nb-Mo-Si-B system, non-volatile Nb_2O_5 grains not only increase the viscosity of the borosilicate glass but also possibly allows oxygen to diffuse through grains and grain boundaries and further oxidizes the alloy.

Hypothesis

If we can design a procedure to selectively volatilize the Nb component from the scale and enrich the scale of the quaternary alloy in borosilicate glass, it may be possible to affect oxidation resistance that is on par with the Mo-Si-B alloys.

Approach

To test the hypothesis stated above, the following will be attempted in Nb-Mo-Si-B system:

1. Pre-oxidize alloy to form an oxide layer containing Nb_2O_5 embedded in borosilicate glass layer.
2. Convert the Nb_2O_5 formed during oxidation to a volatile phase and remove from the scale leaving behind a borosilicate glass which would flow on heat treatment and form a protective layer.

Review of literature indicates that halides and oxyhalides of Niobium are volatile. The primary purpose of the present study is to design an experimental setup to selectively remove Nb_2O_5 by converting to a halide and study the oxidation behavior of the treated material.

Although all the halides of niobium are volatile at ambient temperature, niobium pentachloride is the best choice as it is easy to form. Formation of niobium iodide requires

iodine vapors at high pressure and temperature (1300-1600°C) for complete reaction [38]. No method for preparing pentabromides from pentoxides was found in literature. Niobium pentafluoride reacts readily with silica or glass (which is present in system) to form niobium oxyfluoride and silicon tetrafluoride.

This reaction is undesirable as it removes the protective SiO_2 from the scale. Considering these factors, niobium pentachloride appears to be composition of choice to convert niobium pentoxide to volatile niobium compound.

The melting point of niobium pentachloride as reported range between 205-210°C [39,40,41]. The boiling point of NbCl_5 was reported to be 254°C [39].

Chlorination of Nb_2O_5

Conversion of Nb_2O_5 to NbCl_5 can be accomplished by one of several ways as briefly described below:

1. By heating pentoxide in Carbon tetrachloride (CCl_4) as illustrated by the following chemical reaction,

2. By introducing carbon in the samples during processing. Then heating the sample in chlorine gas to convert niobium pentoxide to niobium pentachloride as shown by the following reaction,

3. By flowing a mixture of carbon monoxide and chlorine through the Nb_2O_5 at elevated temperature. It undergoes a reaction of the type:

Although all three methods have been used to convert non-volatile Nb_2O_5 to volatile NbCl_5 , thermodynamic calculations have been performed on possible reactions and reactants to select the best method for conversion. From the calculations (Figure 9), all

three reactions are possible at the test temperature, but third method is preferred, as it is the most recent method used for chlorination of pentoxide to pentachloride. Moreover, this method does not involve introduction of any fourth element (i.e. as Carbon in second method) to the Nb-Mo-Si-B system to form the undesirable phases in alloy to alter its properties. Also, the formation of carbon tetrachloride in gaseous form at test temperature is thermodynamically not favored ($\Delta G_f > 0$ at $T > 700^\circ\text{C}$). Other two methods (using carbon and carbon tetrachloride) are low temperature methods ($300\text{-}400^\circ\text{C}$), so there is possibility of formation of other non-volatile compounds of niobium at that temperature range (NbOCl_3), which may further dissociate back to form pentoxide and chlorine. Considering these factors, third method using carbon monoxide and chlorine mixture was chosen for this study.

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CHAPTER 2

MICROSTRUCTURE AND OXIDATION BEHAVIOR OF Nb-Mo-Si-B ALLOYS

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Abstract

Microstructure and oxidation behavior of sintered M-Si-B alloys, where M = Nb, Mo and (Nb,Mo) with phase assemblies $T_1(\text{Mo}_5\text{Si}_3\text{B}_x)\text{-MoSi}_2\text{-MoB}$, $T_1\text{-}T_2(\text{Mo}_5\text{SiB}_2)\text{-Mo}_3\text{Si}$, $\text{Mo-T}_2\text{-Mo}_3\text{Si}$ in Mo-Si-B system, $T_2(\text{Nb}_5(\text{Si,B})_3)$, $\text{D8}_8(\text{Nb}_5\text{Si}_3\text{B}_x)$ in Nb-Si-B system, and $T_1\text{-}T_2\text{-D8}_8$ in (Nb,Mo)-Si-B system were investigated. Alloys were oxidized at 1000°C in flowing dry air. In Mo-Si-B compositions, alloys showed excellent oxidation stability and initial mass loss of alloy varied according to Mo content. Minor quantities of MoO_2 were observed in Mo-Si-B scales. Nb-Si-B and Nb-Mo-Si-B alloys displayed large parabolic rate constants (in the range of 0.5-120 $\text{mgs}^2/\text{cm}^4\cdot\text{hr}$) indicating that these systems are not as oxidatively stable as Mo-Si-B alloys. Oxidation kinetics was significantly dependent on initial heating atmosphere. In the Nb-Si-B system T_2 and D8_8 alloys were more resistant to oxidation when heated to test temperature in ultra high pure argon. Quaternary Nb-Mo-Si-B alloy containing less D8_8 phase was more oxidation resistant than that containing more D8_8 phase. Scales on the order of 20-80 μm were observed on Mo-Si-B alloys and relatively thicker scales (on the order of 200-600 μm) were observed on Nb-Si-B and Nb-Mo-Si-B alloys. Initial heating in argon resulted in denser scale and reduced the parabolic rate constants of ternary alloys by ~17-22% and quaternary compositions by ~30-40%.

I. Introduction

For civilian and military applications, there is an increasing need for materials, which can be used at high temperature to improve energy efficiency. Among the current materials for high temperature structural application, there is a temperature cut off at $\sim 1000^{\circ}\text{C}$ [1]. Below this temperature, nickel and cobalt-base superalloys and aluminide intermetallics are being used. However, above 1000°C , one must shift to other materials systems such as silicon-based ceramics and advanced intermetallics to meet oxidation and strength requirements. Transition metal silicides show good potential for use as structural materials above 1000°C . Silicides can provide exceptional high-temperature corrosion resistance under oxidizing and sulfidizing conditions characteristic of many fossil fuel environments and thus are potential candidate materials for protective coatings. Especially, M_5Si_3 type compounds are attractive due to their high melting temperature and good creep resistance [2]. The creep rate of Mo_5Si_3 is lower than that of even whisker reinforced MoSi_2 at high stress level [3]. Recently Mo-rich multiphase alloys have received considerable attention [4-10]. Drawbacks of single-phase M_5Si_3 materials included brittle fracture at ambient temperature and poor oxidation resistance at elevated temperature. Some of these silicides coexist with the terminal refractory metal solid solution phase, and therefore offer the potential for ductile phase toughening by forming M- M_5Si_3 composite. It was previously reported that the addition of boron to Mo_5Si_3 results in substantial improvement in high-temperature oxidation resistance [11, 12]. The oxide scale is $\sim 50\text{ }\mu\text{m}$ thick for undoped Mo_5Si_3 oxidized at 1000°C for 80 hours, whereas the boron-doped Mo_5Si_3 forms a continuous, non-porous scale that is less than $10\text{ }\mu\text{m}$ thick after 400 hours exposure at 1000°C . Boron doping of Mo_5Si_3 does not appear to decrease the high creep strength of Mo_5Si_3 due to the complex unit cell. The creep rate for a three-phase microstructure consisting of T_1 matrix and Mo_3Si and T_2 was found to be $1.1 \times 10^{-6}\text{ s}^{-1}$ at 1300°C under 140 MPa. No dislocation motion was evident in T_1 phase and only a few dislocations were noted in T_2 . The average activation energy of creep was $\sim 400\text{ kJ/mol}$ [13]. Recently Choe et al [14] studied the fracture toughness and fatigue crack behavior in Mo- Mo_3Si - T_2 alloys at ambient and elevated temperatures. They found that micro cracking and extensive crack trapping by the primary α -Mo phase are the principal mechanisms of toughening. Moreover, the fatigue crack growth resistance of Mo- Mo_3Si - T_2 alloy was found

to be superior to monolithic MoSi_2 at ambient temperature. Figure 1(a) shows the isothermal section of Mo-Si-B phase diagram at 1600°C [15] for the area of interest. Boron doped molybdenum silicides provide good oxidation resistance and high strength at elevated temperature, but low fracture toughness limits its potential use as a high temperature structural material.

Extensive studies [16, 17] have demonstrated that two phase Nb-Nb $_5\text{Si}_3$ alloys have a good balance of low temperature toughness and high temperature strength. The toughness of Nb-Nb $_5\text{Si}_3$ composites increases with Nb content [16]. However, Nb-Nb $_5\text{Si}_3$ alloys still suffer from catastrophic oxidation upon exposure to air at temperature above 500°C . Nb-Nb $_5\text{Si}_3$ alloys oxidize mainly by oxygen diffusion, with the rapid formation of stratified and porous layers which spall off easily [18].

Addition of boron to the Nb-Si system results in two ternary phases with large homogeneity regions, T_2 ($\text{Nb}_5(\text{Si},\text{B})_3$) and $D8_8$ ($\text{Nb}_5\text{Si}_3\text{B}_x$), as shown in the isothermal section of Nb-Si-B phase diagram (Figure 1(b)) at 1600°C [19]. This diagram suggests that Nb-rich boundary of the T_2 phase varies over a large B/Si range but nearly constant Nb concentration, whereas $D8_8$ phase shows a broader compositional variability with respect to niobium. Recently Murakami and Yamaguchi [20] studied the oxidation behavior of compositions in the Nb $_5\text{Si}_3$ -NbB $_2$ -NbSi $_2$ phase triangle containing $D8_8$. Oxidation resistance of $D8_8$ at 1250°C in air was found to be poor compared to NbSi $_2$, but superior to Nb $_5\text{Si}_3$. The scale microstructure is consisted of Nb $_2\text{O}_5$, SiO $_2$ and large number of pores. No continuous glass layer was observed. Liu et al [21] also studied the microstructure and oxidation behavior of single phase Nb $_5\text{Si}_3$, T_2 ($\text{Nb}_5(\text{Si},\text{B})_3$) and $D8_8$ ($\text{Nb}_5\text{Si}_3\text{B}_x$) alloys in Nb-Si-B system. They reported that oxidation behavior of Nb-Si-B system is inferior to that of Mo-Si-B.

Because of the complete solid solubility between Nb and Mo, one can reasonably expect the existence of (Nb, Mo) alloy with boron modified (Nb, Mo) silicide. Such a composite may be designed to possess the desired properties of low temperature toughness and high temperature oxidation resistance. The free substitution of Nb for Mo may suppress the formation of Mo $_3\text{Si}$ (Figure 1) and thereby improve the fracture toughness of T_1 ($\text{Mo}_5\text{Si}_3\text{B}_x$) by ductile Nb/Mo phase toughening. In addition, Nb/Mo substitution may change the metal-metal and metal-silicon bonding of T_1 and subsequently affect the thermal expansion

behavior of T_1 phase. This concept has led to alloy development efforts with the goal of achieving an acceptable balance of mechanical properties and environmental resistance.

As proposed [20,21], the dominant factor for low oxidative stability of Nb-Si-B alloys appears to be formation of non-volatile Nb_2O_5 and high porosity on exposure to air. The motivation behind this work is to reduce the porosity in the oxide scale by initially heating alloys in an inert atmosphere to by-pass the “pecking region” and investigate the oxidation behavior and scale formation at 1000°C, and study the oxidation behavior of Nb-Mo-Si-B alloys to develop possibility of alloys with acceptable mechanical properties. Specifically, we studied the oxidation resistance of boron modified molybdenum silicides, niobium silicides and molybdenum-niobium silicides in order to better evaluate the Nb-Mo-Si-B quaternary silicides as high temperature material.

II. Experimental Procedure

Three compositions in the Mo-Si-B system, two compositions in Nb-Si-B system and two quaternary Nb-Mo-Si-B compositions were chosen for study (Table 1). Starting materials used for Mo-Si-B samples were powders of desired composition provided by Exotherm Corporation (Camden, NJ) and for Nb-Si-B samples were 99.8% niobium rod (MPC of Ames Laboratory, Ames, IA), 99.99 % lump silicon (Alpha Chemicals, Danvers, MA) and 99.5% lump boron (AESAR, Ward Hill, MA). All processing operations were carried out under ultra high purity argon atmosphere. Nb-Si-B and Nb-Mo-Si-B samples were prepared by arc melting the starting materials on a copper hearth with a tungsten electrode. Each sample was melted at least three times to ensure homogeneity. Powders were ground in a tungsten carbide lined container (Model 8000 Mixer/Mill, SPEX Industries, Edison, NJ) with 0.2~0.3 wt% stearic acid. Powders were sieved through a -635 mesh stainless steel sieve, with a nominal opening size of 20 μm , and uniaxially dry pressed into 0.95 cm diameter pellets at 186 MPa using stearic acid as lubricant. The samples were heated in a tube furnace at 550°C to remove the stearic acid. Pellets were then sintered at 1900°C for 2 hours in a high temperature furnace with tungsten heating elements (Model M60, Centorr/Vacuum Industries, Nashua, NH). The furnace was heated at a rate of 20°C/min and cooled at a rate of 5°C/min. Phase identification and microstructure characterization were performed using X-

ray diffraction (XRD, Scintag XDS 2000,Cupertino,CA), scanning electron microscopy (SEM, JEOL, JSM 6100,Peabody,MA) and energy dispersive spectroscopy (EDS, Oxford Instruments,Valley,CA). Rietveld refinement of XRD patterns was performed using Rietica (Lucas Height Research Laboratory, Menai, Australia) to determine the lattice parameters and fraction of phases present. Peak profile coefficients, thermal parameters, specific atom sites, and lattice parameters were varied to obtain the best numerical fit for the X-ray data.

The oxidation coupons (~0.8cm in diameter and ~0.1cm in thickness) were polished (final polish with 0.05 μm Al_2O_3). A 0.18mm diameter hole was drilled through coupons prior to polishing from which the coupons were suspended from a sapphire wire in a vertical tube thermo-gravimetric analyzer using an electrobalance accurate to 0.01mg (Cahn-2000,Cahn Instruments,Inc., Cerritos,CA).

Samples were heated to the test temperature either in argon or compressed breathing air and subsequently oxidized in breathing air at 1000°C. All gas flow were set at 100ml/min. Specimen temperature was increased at a rate of 20°C/min to 1000°C and held up to 100 hours for Mo-Si-B alloys, and for 5-7 hours for Nb-Si-B and Nb-Mo-Si-B alloys. The oxidation-induced mass changes were continuously recorded as a function of time. The oxide scale was characterized using XRD, SEM and EDS.

III. Results and Discussion

(a) *Microstructure analysis*

Phase characterization was performed to confirm the composition of sintered alloys. Samples A,B and C formed the expected composition as predicted by the Mo-Si-B phase diagram (Figure 1(a)) with densities greater than 95%. Table 2 summarizes the phase composition of alloys from Reitveld refinement with the error in the range of $\pm 2\%$. BSE images of alloy cross sections are shown in Figure 2. Microstructure of alloy A shows connected grains of T_1 with isolated grains of MoB and MoSi_2 within the matrix. Similarly, alloy B shows connected grains of T_1 matrix with dispersed Mo_3Si and T_2 . Alloy C shows microstructure of connected network of Mo grains with Mo_3Si and T_2 . Although T_1 and Mo phases are clearly visible in

backscattered electron images but it is difficult to distinguish between Mo_3Si and T_2 phases as they have similar contrast. Some grain pullouts occurred during the preparation of metallographic samples. Small pores, grain pullouts and/or silica packets are visible as dark circles.

Alloys D and E were intended to form single phase T_2 and D8_8 respectively as shown in Nb-Si-B phase diagram (Figure 1(b)). Alloy D contains ~3-5% Nb metal phase in T_2 matrix. Alloy E is nearly single phase D8_8 with minor NbB (3-5%) phase. Alloy D was 95% dense whereas E was only 85% dense. Unlike Mo-Si-B alloys, which can be sintered to near theoretical density at 1800°C [22], the densities of Nb-Si-B samples were low, even after sintering at 1900°C for 2 hours. The difference in sintering behavior can be attributed to the high melting temperature of Nb-Si-B alloys. Single phase Mo_5Si_3 melts at 2180°C whereas Nb_5Si_3 melts at 2515°C. Slower diffusion is expected from niobium silicides. Fitzner [23] reported that silicon diffusion in Mo_5Si_3 is 1000 times higher than in Nb_5Si_3 at 1700°C. On the other hand Liu et al [21] reported that Nb-Si-B alloys are denser than boron free- Nb_5Si_3 and they suggested that diffusion in boron-containing T_2 phase is faster because B is smaller than Si.

Sample F and G showed very similar microstructure with mixture of T_1 , T_2 and D8_8 phases. Sample F is richer in D8_8 ($(\text{Nb},\text{Mo})_5\text{Si}_3\text{B}_x$) phase (~20%) than sample G (~11%). Absence of the M_3Si phase in quaternary Nb-Mo-Si-B compositions shows that the appropriate substitution of Nb for Mo suppresses the formation of M_3Si phase. The reduction in the amount of M_3Si phase is attributed to the expansion of two-phase field by Nb substitution. In particular, the Nb substitution results in a shift in T_2 composition towards Nb-Mo-Si side or to regions with lower B to Si ratio in the quaternary system. X-ray diffraction data clearly points to the expansion of the lattice dimensions of the T_1 and T_2 phases as suggested by the shift in corresponding peaks lower angles. Table 3 shows lattice parameters of constituent phases of Nb-Mo-Si-B alloys along with the published data [15, 19, 24-27] of ternary Mo or Nb T_1 and T_2 phases. Reitveld analysis confirmed that in both samples, Nb substitution for Mo in Mo-Si-B causes lattice expansion. This is to be expected based on the larger atomic radius of Nb. Quaternary D8_8 lattice parameters are in agreement with that of D8_8 phase of Nb-Si-B system implying that D8_8 phase in Nb-Mo-Si-B alloys is Nb rich. This is consistent

with the observation that the existence of a large homogeneity region for the hexagonal D8₈ in Nb-Si-B system and absence of a D8₈ type phase in Mo-Si-B system. Results show that lattice parameters of T₁ and T₂ phases after substitution of Nb for Mo vary between the values of single phase Mo and Nb free T₁ and T₂ compositions respectively. Isolated porosity was observed in all compositions.

(b) Isothermal oxidation

Mo-Si-B

Oxidation behavior of Mo-Si-B alloys represented as change in mass as a function of time is shown in Figure 3(a). Results show that oxidation of Mo-Si-B occurs in three distinct stages. Stage I refers to the initial uptake of oxygen and formation of oxide layer containing Mo oxide, B₂O₃ and SiO₂ (Fig. 3(b)). During this stage the temperature is lower than the vaporization temperature of MoO₃. As temperature reaches vaporization temperature of MoO₃, a sharp drop in mass was observed, which is referred as stage II. [11]

In the stage III mass change with time slows down considerably. In this stage the oxidation is diffusion controlled. Oxidation kinetics in this stage was reported in detail by Meyer et al (REF) and found to be limited by diffusion of MoO₃ through the scale. The scale after 100 hours of oxidation ranges between 10 and 20 µm depending upon the alloy composition. During stage II, mass loss due to MoO₃ volatilization increases as Mo content of the sample increases. Alloy C lost ~40mg/cm² compared to A and B which lost 1 and 3 mg/cm² respectively. These mass losses correlate, at least qualitatively, with the Mo contents of the samples (Table 1). Parabolic oxidation behavior in the steady state (Stage III) oxidation is illustrated in Figure 3(c). Parabolic rate constant, K_p, for stage III has been calculated from the slope of straight line on the plot of (Δm/A)² vs time.

$$\left(\frac{\Delta m}{A}\right)^2 = K_p t + C \quad (1)$$

where, A is surface area of sample and C is a constant. Rate constant and correlation coefficients (R²) are given in Table 4.

Linear oxidation rate constants on the order of $10^{-5} \text{ kg}^2/\text{m}^4 \text{ hr}$ are in agreement with the values reported previously [11, 12, and 22]. Figure 4 shows the secondary electron images of oxide layer on Mo-Si-B alloys after 100 hours of oxidation in dry air. Energy dispersive spectroscopy detected presence of Mo along with Si. X-ray diffraction patterns of the scale after 100 hours of oxidation in flowing air at 1000°C is shown in Figure 5. All the three Mo-Si-B composition showed presence of MoO_2 in the scale. This is believed to be MoO_2 trapped in borosilicate glass layer. After formation of glass layer, oxygen partial pressure at oxide/alloy interface must be reduced to a level that only partial oxidation of Mo occurs forming MoO_2 . Its content in the scale varies with the phase composition of alloy. Comparing the relative intensities of MoO_2 peaks, alloy C forms more MoO_2 than alloy A and alloy B forms least amount of MoO_2 . This observation is evident from the SEM analysis of scale. Presence of base alloy silicide peaks in the XRD patterns also indicative of a thin scale in alloy A. Silicide peak intensities were low for alloy B and almost negligible for alloy C, showing that alloy C forms a thicker scale than alloy B. XRD also detected Mo element in the oxide scales of alloy A and B. Intensities of Mo peaks in alloy B is stronger than that of A. Probable oxidation reactions for the formation of MoO_2 and Mo for alloy A and B which contains significant amount of T_1 phases are:

Obviously, overall oxidation reaction involves formation of both MoO_2 and Mo, relative amounts of which depends on the partial pressure of oxygen at the scale/alloy interface. For alloy C, two Mo bearing phases, and in particular T_2 phase must be involved in oxidation:

Very low rate constants indicated the tendency for all alloys to undergo either a small steady state mass gain or mass loss. For alloy C with highest molybdenum content, large MoO_2 peaks coupled with absence of Mo peaks implies that the oxygen partial pressure at the interface is large enough to convert all Mo into MoO_2 and MoO_3 .

Nb-Si-B

Oxidation induced mass change for Nb-Si-B compositions exposed to air at 1000°C are shown in Figure 6. Figure 6(a) shows mass gain as a function of time when samples were initially heated to the test temperature in flowing air and 6(b) shows the same in argon. Both Nb-Si-B compositions (i.e. T₂ and D8₈) showed mass gain irrespective of initial heating atmosphere. The curves were fitted to a parabolic model, and the fit of the model. Rate constants, K_p , along with correlation coefficient, R^2 , are summarized in Table 5. The large parabolic rate constants compared to Mo-Si-B system indicates that the scale formed was not protective in nature. Figure 7(c),(d) and (e) shows the microstructure of oxide scale formed on Nb-Si-B alloys after oxidation at 1000°C when heated in flowing air and Figure 8(c),(d) and (e) shows the same when heated in pure argon. T2 showed more resistance to oxidation than D88 under same conditions irrespective of initial heating atmosphere. This can be attributed to the denser microstructure of T₂ (95% theoretical density) then D8₈ (85% theoretical density). Porosity of the alloys has significant effect on the oxidation behavior and oxide scale microstructure. Similarity of the pore size within the scale and base alloy indicates that the pores in the oxide are predominantly those from the base alloy after oxidation. One can expect improvement in oxidation resistance by reducing the porosity of the base alloys. Plausible methods may be to form dense alloys using processing techniques like HIP (Hot isostatic pressing) and plasma spray sintering. Yamaguchi et al reported [20] densities greater than 90 % of theoretical density by plasma spray sintering between 1500°C and 1800°C . XRD detected Nb_2O_5 in the scale. The mixed oxide product very likely formed by the simultaneous oxidation of Nb, Si and B since these three elements have similar standard free energies of formation [28]. T₂ and D8₈ alloys showed more resistance to oxidation when heated to test temperature in argon atmosphere. When samples are heated to test temperature parabolic rate constant was reduced by 17-22%. The scale formed on Nb-Si-

B alloys was porous and spalled off easily when heated in air. Exposure of alloys to inert atmosphere (i.e. argon) during heating by-passes the "pesting" region (i.e. 650-850°C) and the scale forms is less porous and thin as evident in Figure 8(c),(d) and (e). However, it has been shown that T₂ and D8₈ have much better oxidation resistance than binary Nb₅Si₃ [21], suggesting that addition of boron can improve oxidation resistance, although only modestly in comparison to the Mo-Si-B system. The difference in oxidation resistance between boron modified Mo₅Si₃ and boron modified Nb₅Si₃ is most likely due to the formation of non-volatile Nb₂O₅ and the high porosity of oxide scale observed in the latter. The presence of Nb₂O₅ impedes flow of borosilicate glass. As a result a continuous protective glass layer does not form on the alloy surface. Moreover, the non-volatile Nb₂O₅ facilitates the diffusion of air to scale/alloy interface through grain boundaries. The coefficient of oxygen diffusion in Nb₂O₅ ($8.7 \times 10^{-11} \text{ cm}^2/\text{sec}$) is almost 1000 times higher than in silica glass ($1.8 \times 10^{-14} \text{ cm}^2/\text{sec}$) at 1000°C [29,30,31].

Nb-Mo-Si-B

Oxidation behavior of Nb-Mo-Si-B compositions (sample F and G) is shown in Figure 6. Sample G was more resistant to oxidation than sample F irrespective of initial heating atmosphere, which is due to presence of more D8₈ phase in composition F (20 %) than in composition G (11 %). There is no D8₈ phase in Mo-Si-B system, therefore it is believed that D8₈ phase present in Nb-Mo-Si-B compositions is essentially Nb rich, thus on exposure to air it forms more non-volatile Nb₂O₅ and increases the oxidation rate. Porosity in scale is mainly left behind pores from the base alloy. Mostly scale was consisted of connected network of Nb₂O₅ particles in glass. This connected matrix of Nb₂O₅ is expected to diffuse oxygen to the alloy surface.

The initial heating atmosphere significantly affected scale microstructure. When heated in air, sample F and G formed a four-layered scale microstructure as shown in Figure 7(d,e). Layer 1 consists of Nb₂O₅ with a small amount SiO₂. Layer 2 is mainly the coarse Nb₂O₅, silica glass and some large pores. EDS detected Mo-element in layer 3. This is believed to be condensed MoO₃ in the scale. This implies that layer 2 may act as a diffusion barrier for volatile MoO₃. This layer may also hinder the inward diffusion of oxygen. The fourth layer,

adjacent to base alloy consists of a mixture of Nb_2O_5 and amorphous SiO_2 . Severe cracks were observed in base alloy. The cracks are believed to be due to large tensile stresses induced on the base alloy by formation of Nb_2O_5 and SiO_2 . XRD detected Nb_2O_5 on the surface but no crystalline MoO_3 , SiO_2 and B_2O_3 . When heated in air, oxidation of quaternary compositions can be described by two stages, an initial transient period followed by a region of steady state oxidation. At initial stage, Nb, Mo, and Si were all oxidized because of the high oxygen partial pressure. Above 700°C , the evaporation of MoO_3 resulted in a surface containing Nb_2O_5 , amorphous SiO_2 or and a large amount of pores. Four layered microstructure was absent in scale when heated in argon (Figure 8e). Scale mainly consists of Nb_2O_5 dispersed in glass, with a very thin layer at alloy/oxide interface, which may be internal oxidation layer. Porosity was much less for alloys heated in argon (porosity ~9%) than alloys heated in air (porosity ~30%). This can be attributed to formation of MoO_3 pockets during heating in air, which remains in the scale until temperature reaches the volatilization temperature of MoO_3 . As MoO_3 volatilizes, it leaves behind large pores. Heating in argon by-passes this step and direct exposure to air at 1000°C vaporizes Mo as MoO_3 leaving scale of Nb_2O_5 and glass. Oxide scales on F and G showed very little spallation.

IV. Summary

1. Powder compacts of Mo-Si-B, Nb-Si-B and Nb-Mo-Si-B intermetallics system were prepared by arc melting and sintering at 1900C for 2 hours. Mo-Si-B alloys were almost fully dense, while Nb-Si-B and Nb-Mo-Si-B were porous. This shows that diffusion process is slower in Nb-Si-B system. Substitution of Nb for Mo suppresses formation of Mo_3Si phase.
2. As reported previously [11,12] , Mo-Si-B alloys displayed excellent oxidation stability at 1000°C in air. The scale was found to be essentially borosilicate glass layer with minor content of MoO_2 near the alloy/scale interface. MoO_2 content varied according to composition and was maximum for composition Mo-T₂-Mo₃Si
3. Substitution of Nb for Mo resulted in expansion of T₁ and T₂ lattice dimensions, where as D8₈ lattice constants were in agreement with pure Nb-Si-B. Unit cell dimensions observed for T₁ and T₂ were between single phase Nb and Mo free compositions.
4. T₂ alloy showed more resistance to oxidation than D8₈ alloys. Oxidation behavior of Niobium containing alloys i.e. Nb-Si-B and Nb-Mo-Si-B alloys depends on initial heating atmosphere. T₂ and D8₈ compositions were more resistant to oxidation than when heated in argon to test temperature. Quaternary alloy containing less D8₈ phase was more resistant. Initial heating of alloys in argon displayed thinner and low porous scales formation than that of alloys heated in air. Parabolic fit for oxidation suggests that process is primarily governed by diffusion of air through porous scale containing niobium pentoxide dispersed in borosilicate glass.
5. Large rate constants indicate that scale formed from Niobium containing alloys was not protective as compared to Mo-Si-B alloys. Substitution of Nb for Mo drastically decreased the oxidation resistance of Nb free T₁ alloys. The difference in oxidation stability of boron modified Mo-Si and Nb-Si may be attributed to the non-volatile nature of oxide formed and high porosity of the scale.

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Sample	Weight %			
	Mo	Nb	Si	B
A	84.0	-	13.4	2.6
B	88.6	-	9.9	1.5
C	94.6	-	4.3	1.1
D	-	87.1	11.3	1.6
E	-	83.7	14.6	1.7
F and G	44.0	42.6	12.3	1.1

Table 1: Nominal compositions of alloys studied

Sample	Phase Composition						
	Molar %						
	M	MSi ₂	T ₁	T ₂	D8 ₈	M ₃ Si	MB
A	-	12	66	-	-	-	22
B	-	-	45	31	-	24	-
C	43	-	-	30	-	27	-
D	3-5	-	-	95-97	-	-	-
E	-	-	-	-	92-97	-	3-8
F	-	-	42	38	20	-	-
G	-	-	60	29	11	-	-

Table 2: Phase compositions of alloys studied after Rietveld refinement of X-ray diffraction patterns

Sample	T ₁		T ₂		D8 ₈	
	a	c	a	c	a	c
F	9.816	5.002	6.138	11.356	7.480	5.161
G	9.815	5.007	6.077	11.410	7.519	5.208
Mo*	9.642	4.904	6.013	11.034		
Nb*	10.040	5.081	6.571	11.887	7.554	5.247

Table 3: Lattice parameters of individual phases in Nb-Mo-Si-B system (Å)

Nb* : without Mo in composition

Mo* : without Nb in composition

Sample	Phase Composition	K_p ($\text{mgs}^2/\text{cm}^4.\text{hr}$)	R^2
A	MoSi ₂ -T1-MoB	0.15	0.95
B	T1-T2-Mo ₃ Si	0.18	0.95
C	Mo-T2-Mo ₃ Si	0.24	0.94

Table 4: Steady state parabolic rate constants for Mo-Si-B alloys oxidation at 1000°C

Sample	Phase Composition	Air*		Ar*	
		K_p ($\text{mgs}^2/\text{cm}^4.\text{hr}$)	R^2	K_p ($\text{mgs}^2/\text{cm}^4.\text{hr}$)	R^2
D	T ₂	20.15	0.99	18.79	0.98
E	D8 ₈	114.83	0.99	54.12	0.99
F	T ₁ -T ₂ -D8 ₈	0.58	0.93	0.33	0.99
G	T ₁ -T ₂ -D8 ₈	0.78	0.98	0.53	0.99

Table 5: Parabolic rate constants for oxidation of Nb-Si-B and Nb-Mo-Si-B alloys at 1000°C . * Atmosphere during the heating cycle to 1000°C

Figure 1

Figure 2

Figure 2

Figure 2

Figure 3

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure captions

1. (a) Isothermal section of Mo-Si-B at 1600°C; compositions studied in this work are showed as 1,2 and 3.
 (b) Isothermal section of Nb-Si-B at 1600°C; composition studied in this work are showed as 4 and 5
2. BSE images of alloy compositions studied
 Where, $T_1(\text{Mo}_5\text{Si}_3\text{B}_x)$, $T_2(\text{Mo}_5\text{SiB}_2)$ for A,B and C ; $T_2(\text{Nb}_5(\text{Si,B})_3)$, $D8_8(\text{Nb}_5\text{Si}_3\text{B}_x)$ for D and E ; T_1 (tetragonal $(\text{Nb,Mo})_5\text{Si}_3\text{B}_x$) , $T_2(((\text{Nb,Mo})_5(\text{Si,B})_3)$, $D8_8$ (hexagonal $(\text{Nb,Mo})_5\text{Si}_3\text{B}_x$) for F and G. Grain pullouts, silica pockets and pores are visible as dark circles.
3. (a) Oxidation kinetics of Mo-Si-B alloy compositions at 1000°C in flowing air
 (b) Steady state oxidation kinetics at 1000°C in flowing air
 Curves have been shifted for better comparison.
4. Secondary electron images of scale on Mo-Si-B alloys after exposure to air for 100 hours at 1000°C
 (a) Alloy A
 (b) Alloy B
 (c) Alloy C
 Protective borosilicate glass layer is visible as dark contrast. Bright contrast phase is MoO_2 formed during oxidation reaction due to low partial pressure of oxygen at alloy/scale interface.

5. X ray diffraction patterns for oxide scales after oxidation of alloy A, B and C for 100 hours at 1000°C in flowing air. MoO_2 was observed in all three compositions. Alloy A and B shows base alloy silicide peaks suggests that scale is thin whereas alloy C suggests thick scale as silicide peaks are absent.
6. Oxidation kinetics of Nb-Si-B and Mo-Nb-Si-B alloy compositions
 - (a) Initial heating to test temperature in flowing air
 - (b) Initial heating to test temperature in flowing ultra pure argon
7. Oxide scale after oxidation at 1000°C, with initial heating to test temperature in flowing air
 - (a) Alloy D after 7 hrs oxidation in flowing air at 1000°C. Thick scale on alloy D consists of Nb_2O_5 in glass and large pores. Scale spalled off easily.
 - (b) , (c) Alloy E after 7 hrs oxidation at 1000°C.
 - (d) Alloy F after 5 hrs of oxidation; four layers microstructure of scale. Layer 1 consists of Nb_2O_5 particle in silica glass. Layer 2 and 3 is coarse Nb_2O_5 in silica glass and large pores formed due to volatilization of MoO_3 . Layer 4 is mixture of Nb_2O_5 and amorphous silica.
 - (e) Layer 3 which consists of Nb_2O_5 rod shaped crystals (white) dispersed in borosilicate glass (dark matrix)

Pores are mainly left behind on the base alloy after formation of respective oxides.
8. Oxide scale after oxidation at 1000°C, with initial heating to test temperature in ultra high pure argon
 - (a) Alloy D after 10 hrs oxidation

(b), (c) Alloy E after 10 hrs oxidation

(d),(e) Alloy F after 10 hours of oxidation. Four layered microstructure was absent when heated in argon. Scale mainly consists of Nb_2O_5 and borosilicate glass.

CHAPTER 3

CHLORINATION TREATMENT TO IMPROVE OXIDATION RESISTANCE OF Nb-Mo-Si-B ALLOYS

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Abstract

Recent studies have shown that the quaternary Nb-Mo-Si-B system is not oxidation resistant. The difference in oxidation resistance between Mo-Si-B and Nb-Mo-Si-B may be interpreted in terms of the volatility of the metal oxide that forms. MoO_3 evaporates from the surface scale at about 650°C , leaving an oxidation resistant borosilicate glassy scale. Nb_2O_5 persists as a rapidly growing condensed phase that overwhelms the ability of the borosilicate glass to form a protective layer. A novel chlorination processing was employed to selectively remove Nb_2O_5 from the scale of the quaternary alloy as volatile NbCl_5 . Present work investigated the chlorination of oxidized Nb-Mo-Si-B alloy of nominal composition 63(Nb, Mo)-30Si-7B with Nb/Mo=1 (at%) comprised of a three phase microstructure of $(\text{Nb},\text{Mo})_5\text{Si}_3\text{B}_x(T_1)$ - $(\text{Nb},\text{Mo})_5(\text{Si},\text{B})_3(T_2)$ - $(\text{Nb},\text{Mo})_5\text{Si}_3\text{B}_x(D_8)$. Oxidation behavior of these alloys in air has been studied both before and after chlorination. Results show that Nb_2O_5 can be selectively removed from the scale to leave a borosilicate rich scale. The chlorinated scale forms a dense scale after heat treatment at 1000°C in argon. Oxidation rate of the chlorinated alloys was about one-third that of the unchlorinated alloy under identical conditions. Alloy oxidation during heating to test temperature has been studied and a plausible mechanism for formation of porosity in oxide scale has been offered.

I. Introduction

The rate of oxidation depends primarily on the oxidation product formed, which in turn is determined by the combination of composition, microstructure and surface condition of alloy. Transition metal M_5Si_3 type compounds are attractive due to their high melting temperature and good creep resistance [1]. Mo-Si-B system offers a good combination of properties for high temperature applications such as excellent oxidation stability [2,3] and superior creep resistance [4]. But its low fracture toughness and thermal expansion anisotropy need to be improved before the alloys can find practical applications. This was the motivation of recent studies [5,6,7,8] to incorporate Nb into Mo-Si-B system to improve mechanical properties while retaining oxidation resistance. Nb-Si-B system offers the possibility of ductile phase toughening since Nb metal can coexist in equilibrium with boron containing silicides. Since there is a complete solubility between Nb and Mo, the Nb/Mo substitution can suppress Mo_3Si formation, and this may enable the toughness of $T_1(Mo_5Si_3B_x)$ to be improved by ductile phase toughening. In addition, Nb/Mo substitution may favorably affect the thermal expansion behavior of T_1 phase. Thermal expansion anisotropy of Nb-Mo-Si alloys has been studied by Fu et al [8]. They found that the CTE (coefficient of thermal expansion) anisotropy of Mo_5Si_3 can be significantly reduced through ternary alloying additions that alter interatomic distance and bonding strength along the atom chains in the c -direction. Nb was found to reduce $CTE(c)/CTE(a)$ ratio to a value of 1.5 for $MoNb_4Si_3$ from the 2.2 as reported previously[9,10,11,12]. Isothermal oxidation behavior and microstructure of Nb-Mo-Si-B intermetallic compacts with different compositions and at different temperatures has been studied recently by Liu et al [5,7]. Results show that Nb-Mo-Si-B alloys have poor oxidation resistance as compared to Mo-Si-B alloys. This poor oxidation resistance was attributed to the formation of the fast growing Nb_2O_5 that interferes with formation of a continuous scale of the protective borosilicate glass layer. The non-volatile nature of Nb_2O_5 and the highly porous scale formed after evaporation of MoO_3 are the proposed reasons for its poor oxidation resistance. In the Mo-Si-B system, volatile MoO_3 facilitates the formation of a continuous borosilicate glass layer that acts as a barrier to oxygen diffusion and prevents further oxidation of alloy.

We recently reported [6] that initial heating of unoxidized quaternary alloy in argon can significantly decrease the porosity of the scale (30% to 9%). This improves the oxidation resistance but not to the limit of Mo-Si-B. The purpose of the present research is to understand the mechanism of oxidation of Nb-Mo-Si-B alloys during initial heating in air and to design a procedure to volatilize the Nb component from the scale. By enriching the scale of the quaternary alloy in borosilicate glass, it may be possible to affect oxidation resistance that is on par with the Mo-Si-B alloys. Although all the halides of niobium are volatile by 1000°C, niobium pentachloride was chosen for this study, as it is relatively easy to form. Formation of niobium iodide requires iodine vapors at high pressure and temperature (1300-1600°C) for complete reaction [13]. No method for preparing niobium pentabromides from niobium pentoxides is available in literature. Niobium pentafluoride reacts readily with silica or glass to form niobium oxyfluoride and silicon tetrafluoride. Considering these factors, NbCl₅ reaction route was selected to convert niobium pentoxide to a volatile niobium compound. The reported melting point of niobium pentachloride ranges between 205°-210°C while the boiling point is only slightly higher, 254°C. [14]

Conversion of Nb₂O₅ to NbCl₅ has been studied previously [15,16,17] to obtain pure niobium from impure ores. The present work will use a similar method to remove Nb₂O₅ from the scale of the oxidized Nb-Mo-Si-B samples. The direct reaction of niobium pentoxide and chlorine is not thermodynamically favorable at temperatures <1000°C. For this reason chlorination is performed in the presence of reducing agents like carbon [15] or carbon monoxide [16, 17]. Inclusion of carbon in the alloy can produce undesirable phases, thus CO is chosen as reducing agent for this study. Heating Nb₂O₅ in the presence of a flowing mixture of carbon monoxide (CO) and chlorine leads to the following reaction:

The present work investigated the extent of Nb₂O₅ removal from the oxidized scale by reaction (1). If Nb₂O₅ can be selectively removed from the oxide scale of the quaternary alloy, its oxidation resistance may also be suitably improved. Based on the previous work of Liu [7], alloys with high content of Nb gained mass and those with high content of Mo lost

mass at a very rapid rate with alloys converting to oxides powder. Alloys with Nb/Mo=1 showed a small mass change in long-term oxidation tests. Thus, alloy composition from the Nb-Mo-Si-B system with Nb:Mo =1:1 was selected for the present investigation.

II. Experimental Procedure

Starting materials were 99.8% niobium rod (MPC of Ames Laboratory, Ames, IA), 99.9% molybdenum rod (Mi-Tech Metals, Indianapolis, IN), 99.99 % lump silicon (Alpha Chemicals, Danvers, MA) and 99.5% lump boron (AESAR, Ward Hill, MA). Nb-Mo-Si-B samples were prepared by arc melting the starting materials on a copper hearth with a tungsten electrode under argon. Each sample was melted at least three times to ensure homogeneity. Melted buttons were then ground in a tungsten carbide lined container (Model 8000 Mixer/Mill, SPEX Industries, Edison, NJ) with 0.2~0.3 wt% stearic acid. Powders were sieved through a -635 mesh stainless steel sieve, with a nominal opening size of 20 μm , and uniaxially pressed into 0.95 cm diameter pellets at 186 MPa. The samples were heated in a tube furnace to 550°C under flowing high purity argon to remove the stearic acid. Pellets were then transferred to the sintering furnace and sintered at 1900°C for 2 hours (Model M60, Centorr/Vacuum Industries, Nashua, NH) under flowing high purity argon. The furnace was heated at 20°C/min and cooled at 5°C/min. Phase identification and microstructure characterization were performed using X-ray diffraction (XRD, Scintag XDS 2000, Cupertino, CA), scanning electron microscopy (SEM, JEOL, JSM 6100, Peabody, MA) and energy dispersive spectroscopy (EDS, Oxford Instruments, Valley, CA). Rietveld refinement of the XRD patterns was performed using Rietica (Lucas Height Research Laboratory, Menai, Australia) to determine the fraction of phases present and the lattice parameters. Peak profile coefficients, thermal parameters, specific atom sites, and lattice parameters were varied to obtain the best numerical fit for the X-ray data. Oxidation samples were polished using standard metallographic techniques including a final polish with 0.05 μm Al_2O_3 . The oxidation coupons (~0.8cm in diameter and ~0.1cm in thickness) were suspended from a sapphire wire in a vertical tube thermo-gravimetric analyzer using an electrobalance accurate to 0.01mg (Cahn-2000, Cahn Instruments, Inc., Cerritos, CA). A 0.18mm diameter hole was

drilled through coupons prior to polishing from which the coupons were suspended. The experimental setup for chlorinating the pre-oxidized Nb-Mo-Si-B alloy is shown in Figure 1. High purity argon was initially flowed through the system to purge all ambient gases. The furnace was heated at the rate of 20°C/min to 1000°C under flowing argon atmosphere, and then gas flow switched to the reactive gas mixture (Chlorine, 99.5%, Praxair, Danbury, CT and Carbon monoxide, 99.5%, Praxair, Danbury, CT). Chlorine and carbon monoxide gas flow were both set to 25ml/min and flowed for 30 min. Gas flow was switched back to argon to purge the reaction tube at 1000°C, followed by cooling to room temperature. A two-stage scrubber containing NaOH was used to neutralize excess chlorine exiting the tube. The gas flow was first bubbled through water to convert volatile NbCl_5 carried down stream into Nb_2O_5 and HCl. Microstructure of the oxide scale was characterized after chlorination using XRD, Auger, SEM and EDS. Treated samples were then oxidized in the TGA apparatus to determine the effect of chlorination on the alloy oxidation behavior. Parabolic rate constants were calculated to compare the effect of chlorination on alloy oxidation, where mass change during oxidation was normalized to geometrical area of sample.

III. Results and discussion

The starting phase composition of the as-sintered samples was determined using XRD and SEM. The detailed phase analysis and microstructure has been discussed previously [6]. The alloy composition contains three quaternary phases: 40 % T_1 (tetragonal $(\text{Nb},\text{Mo})_5\text{Si}_3\text{B}_x$; $x < 1$), 40 % T_2 ($(\text{Nb},\text{Mo})_5(\text{Si},\text{B})_3$) and 20 % $D8_8$ (hexagonal $(\text{Nb},\text{Mo})_5\text{Si}_3\text{B}_x$). Phase composition of base alloy has been calculated by Rietveld refinement of XRD data. BSE image of alloy studied is shown in Figure 2. Density of alloy was measured by Archimedes method and image analysis. Alloy was $97 \pm 1\%$ of theoretical density after sintering at 1900°C for 2 hours. The alloy has been tested for oxidation resistance by TGA before chlorination with different initial heating atmospheres (i.e. air, argon) and after chlorination. The effects of pre-heating and chlorination on initial mass change of the Nb-Mo-Si-B alloys at 1000°C are shown in Figure 3A. The mass change of the alloy when heated to the test temperature in either air or argon and then subsequently exposed to air is used to establish the base line behavior of the

alloy. A new sample is then pre-oxidized in air at 1000°C, chlorinated, and then tested in the TGA with initial heating in air. Heating in argon establishes the effect of residual oxygen in the system on alloy oxidation. Each curve is the result of two competitive mass change processes, mass gain due to the oxidation of Nb, Si and B, and mass loss due to the volatilization of MoO₃. XRD detected Nb₂O₅ on the surface of alloy exposed to air at 1000°C irrespective of initial heating atmosphere but no crystalline MoO₃, SiO₂ and B₂O₃ after 10 hours of oxidation at 1000°C. Figure 3 shows that when heated to test temperature in air alloy (Figure 3A) gained mass during initial heating (~2 mg). At steady state (Figure 3B) mass change at the rate of 0.76 mg²/cm⁴/hr² was observed. After heating in argon to the test temperature, alloy gained mass at the rate of 0.53 mg²/cm⁴/hr². These results show that pre-heating atmosphere has a significant effect on oxidation resistance of alloy at test temperature. The surface morphology of the oxide scales formed at 600°, 700°, 800° and 1000°C was studied to understand the initial oxidation during heating in air and argon to test temperature. Figure 4 shows SEM micrographs of scale surface formed after heating and exposure to air for 3 min at 600°, and 1000°C and then quickly cooled to room temperature by removing samples from the furnace. EDS detected Mo up to 700°C along with Nb and Si peaks. No Mo was detected above 800°C or above. Figure 5 compares the XRD patterns of the base alloy and the oxidized layer formed at 600°, 700°, 800°, 1000°C after 3 min. XRD patterns at 600° and 700°C do not contain any known Nb-oxide and Mo-oxide peaks. Meyer et al [2,3,4] observed needle shaped MoO₃ crystals growing from the scale during initial oxidation stages of Mo-Si-B alloys. The needle shaped MoO₃ crystals were not seen in the present work (Figure 4a), and the XRD pattern at 700°C indicates that Mo is present as Nb-Mo oxide solid-solution. Mo⁴⁺(0.70Å) and Mo⁵⁺ (0.66Å) ions are closer in size to Nb⁵⁺ (0.69Å) than Mo⁶⁺ ion (0.62Å) suggesting that molybdenum may dissolve into Nb₂O₅ as Mo⁴⁺ or Mo⁵⁺[18]. Prokoshkin [19] et al studied the oxidation behavior of Mo reinforced Nb for different Mo content and detected presence of (Nb,Mo)₂O₅ in oxide scales on Nb reinforced with 15-50 % of Mo .

As temperature increases, oxide solid-solution dissociates to MoO₃ and Nb₂O₅. At 800°C Mo-peaks disappeared from the EDS spectra, indicating dissociation of the oxide solid-solution and volatilization of MoO₃ and this was further evidenced by formation of volatile MoO₃ in

the furnace at temperature 800°C and 1000°C. Presence of Nb_2O_5 peaks and absence of any Mo-oxide peaks in XRD pattern after oxidation for 10 hours at 1000°C (Figure 5) further suggests that the solid-solution has completely dissociated.

Liu et al [7] studied the oxidation behavior of Nb-Mo-Si-B alloys with different Nb/Mo ratio. They observed that the pore size increases with the Mo content. Alloy with Nb/Mo = 3 showed pores on the order of 20 μm and Nb/Mo = 1/3 showed large pore channels on the order of 150-200 μm . Also channel microstructure of pores suggests that MoO_3 vapors coalesce to form a bubble before leaving the scale. MoO_3 volatilizes from the scale leaving behind the large pores and rod like Nb_2O_5 crystals in pores as evident from the cross-sectional SE images of oxide layer in Figure 6. As temperature increases to 800°C, micro cracks emerge from the pores, which may indicate the thermal expansion mismatch between the oxides formed. These large pores then facilitate the inward diffusion of oxygen to scale-alloy interface. Cross-sectional secondary electron images of alloy oxidized at 1000°C for 30 hours with initial heating in air are shown in Figure 6. Results show that scale consists of a four-layered microstructure of mixed oxides. The outer layer, which is called as Layer 4, is almost pore-free and is primarily fine Nb_2O_5 with a small amount of dispersed borosilicate glass. Beneath it, layer 3 exhibited coarse rod shaped Nb_2O_5 crystals within a borosilicate glass matrix and large number of pores. Layer 4 is considerably thinner (~50 μm) than Layer 2 and 3 (~600 μm) and the major difference between them is primarily morphology. The Mo content of the outer two layers (layer 3 and 4) was negligible, thus most of the molybdenum oxide has evaporated. Layer 2, which is considerably enriched in molybdenum, exists beneath Layer 3. This is believed to be condensed MoO_3 or MoO_2 trapped in the layer. The thick layer 3 likely acts as a barrier for outer diffusion of MoO_3 . EDS also detected some Nb in layer 3.

In Mo-Si-B system, borosilicate glass is believed to contain channels at the early stages of oxidation [20]. Vaporization of MoO_3 and healing of channels by viscous flow of borosilicate glass results in elimination of channels. This is not observed in Nb-Mo-Si-B system as Nb_2O_5 grains increases the viscosity of the borosilicate melt substantially. It has been reported that viscosity of lithia and soda glass increases by the factor of 10 by inclusion of 1-6% of M_2O_5 , where M is Vanadium and Tantalum [21]. Glass scale on quaternary alloys contains

significant amount of Nb_2O_5 , so we can expect viscosity of glass to increase sufficiently to hinder the viscous flow.

For all compositions in this study, severe cracks, which were attributed to formation of Nb_2O_5 , MoO_3 and borosilicate glass during oxidation were observed only in Layer 4. The scale formed upon heating in air was porous and spalled off, while the scale formed on heating in argon was adherent and without micro cracks.

Chlorination

Reactivity of pure Nb_2O_5 in the Cl_2+CO environment was measured to ensure gas mixture and reaction time was appropriately set. Starting with 100 mg of pure powder, 98.5% of Nb_2O_5 was removed from the reaction chamber after chlorination at 1000°C for 30 min. Pure SiO_2 and borosilicate glass were also tested to ensure their resistance to the chlorination process. A minimal loss of 1- 1.5% at 1000°C during chlorination is believed to be due to vaporization of some moisture and impurities. Figure 7 compares the oxide scale microstructure before and after chlorination. EDS (not shown), XRD (Figure 8) and Auger spectroscopy (Figure 9) have been used to investigate composition of oxide scale after chlorination. After 30 hours of oxidation the scale was $700\text{ }\mu\text{m}$ thick and exhibited four layers as observed previously. Layer 4, which was primarily Nb_2O_5 rich before chlorination, showed primarily SiO_2 by EDS. Layer 3 also showed more SiO_2 than Nb_2O_5 . Layer 2 was Mo-free but rich in Si and showed some Nb, suggesting that trapped MoO_3 formed Mo-chloride vapor and left the scale. There was no evidence of Cl in the oxide scale, indicating that all of the chloride phases had evaporated. Porosity comparison of the layered scale before and after chlorination suggests that glass flows to fill some of the voids but does not fill the large pores completely. This may explain why the chlorinated sample in Figure 3 showed significant reduction in mass gain. These results indicate that 30 minutes of chlorination was able to remove Nb_2O_5 from two-thirds of the scale. Remaining Nb_2O_5 is believed to be the grains that were completely covered with a borosilicate glass layer protecting them from coming in contact with the reactive gas mixture. Apparently 30 minutes of the chlorination time was not sufficient to adequately remove Nb_2O_5 from approximately $700\text{ }\mu\text{m}$ thick scale. The alloy was oxidized for 5 hours to study the effect of

chlorination on thinner scale. After 5 hours of exposure, $\sim 50\mu\text{m}$ thick scale was formed and 15 min of chlorination time was sufficient to remove most of Nb_2O_5 from the scale. No significant change in scale thickness was observed after chlorination. Scale after chlorination was adherent to the substrate unlike the 30 hour oxidation runs which spalled off easily. Auger analysis (Figure 9) of layer 2 shows that the scale is essentially borosilicate glass with a trace amount Nb.

Results show that after Nb_2O_5 removal, the oxidation resistance of alloy has been improved significantly after chlorination. After 10 hours of oxidation, the untreated alloy gained 2.6 mg/cm^2 weight. It was decreased to 1.3 mg/cm^2 after the chlorination. Table 1 shows the parabolic rate of oxidation for alloys oxidized before and after chlorination. Results show that the alloy oxidation rate after chlorination ($0.2\text{ mg}^2/\text{cm}^4/\text{hr}^2$) is one-third of the rate before the chlorination ($0.76\text{ mg}^2/\text{cm}^4/\text{hr}^2$). This rate is comparable to the oxidation rate of the alloy ($0.13\text{ mg}^2/\text{cm}^4/\text{hr}^2$) in argon with a residual oxygen pressure of $P_{\text{O}_2} = 10^{-4}\text{ atm}$. This suggests that oxygen diffusion through the glass layer is hindered reducing partial pressure of oxygen at alloy/scale interface.

Oxidation after chlorination occurred in three different stages. Stage 1 (Figure 3A) was a sharp gain in mass, which is believed to be due to oxidation of elements to their respective oxides. Stage 2 and 3 (Figure 3B) are small steady state mass change with linear rate on the order of $0.1\text{ mg/cm}^2/\text{hr}$. This stage indicates that the after initial incubation period, the scale becomes protective in nature. Figure 10 shows the microstructure of the scale oxidized for 10 hours after chlorination of pre-oxidized alloy for 30 hours. Cracks have been observed at layer1/layer2 interface. Layer 1 is believed to be an internal oxidation layer containing silicides and layer 2 consists primarily niobium oxide. Large mismatch between thermal expansion coefficients of Nb_2O_5 and silicides is responsible for mechanical failure of scale at the interface creating cracks during oxidation. EDS shows Nb-peaks near layer 1 indicating that only Nb_2O_5 is forming. Layer 4 and 3 were mostly glass after 10 hours of oxidation shows that Nb_2O_5 formed does not diffuse to other layers.

Oxygen diffusion through non-volatile Nb_2O_5 grains and highly porous scale are the main reasons behind the oxidative instability of Nb-Mo-Si-B alloys as proposed in previous works [5,6,7,22]. It has been shown that chlorination is able to remove most of the Nb_2O_5 from

scale and parabolic oxidation rates of Nb-Mo-Si-B alloys have been significantly decreased after chlorination treatment. This suggests that presence of Nb_2O_5 affects the oxidation mechanism by altering the viscosity of glass melt and facilitating the diffusion of oxygen through grains. The coefficient of oxygen diffusion in Nb_2O_5 ($8.7 \times 10^{-11} \text{ cm}^2/\text{sec}$) is almost 1000 times higher than in silica glass ($1.8 \times 10^{-14} \text{ cm}^2/\text{sec}$) at 1000°C [23,24,25].

IV. Summary

Oxidation behavior of Nb-Mo-Si-B alloys with initial heating in air and argon has been investigated. Alloys heated in argon showed more resistance to oxidation than the same heated in air to the test temperature. Mechanism of oxidation with initial heating has been studied. Results showed the formation of Nb-Mo oxide solid-solution at lower temperature on exposure to air. This oxide solid-solution dissociated to Nb_2O_5 and MoO_3 at higher temperature. MoO_3 vapors can coalesce to form a bubble, which manifest as large pores as in the microstructure. A new processing technique of chlorination of oxidized alloys has been used to remove the non-volatile Nb_2O_5 from the oxidized scale and obtain a borosilicate glass rich layer. Chlorination was able to remove oxide from two-thirds of the scale of 30 hours pre-oxidized alloy. Oxidation rates were reduced to one-third after chlorination treatment. Steady state parabolic rate of oxidation after chlorination treatment were comparable to that of alloy oxidation in regular argon. This also suggests that oxidative instability of Nb-Mo-Si-B alloys can be attributed to presence of non-volatile Nb_2O_5 which increases the viscosity of the glass hence preventing the formation of a continuous glass and fast diffusion of oxygen through Nb_2O_5 grains. Low oxidation rates after chlorination indicate the formation of a protective scale.

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Oxidation process	K_p ($\text{mg}^2/\text{cm}^4/\text{hr}^2$)
Initial heating in air	0.76
Initial heating in argon	0.53
After chlorination of 5 hours pre-oxidized alloy	0.20
Oxidation in Argon ($P_{\text{O}_2} = 10^{-4}$ atm)	0.13

Table 1 : Steady state parabolic rate constants for oxidation of Nb-Mo-Si-B alloys (Data shown in Figure 3)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure captions

1. Experimental setup for chlorination of Nb-Mo-Si-B alloys at 1000°C
2. BSE images of alloy studied showing phases T_1 , T_2 and $D8_8$
 T_2 and $D8_8$ have similar contrast while T_1 is slightly brighter. Silica pockets and/or pores are visible as dark phase.
3. Comparison of the oxidation of the Nb-Mo-Si-B alloy at 1000°C in flowing air. Samples were pre-heated in air or argon to 1000°C then exposed to air. The chlorinated sample was preheated and exposed to air, while a sample was also preheated and exposed to argon only with $P_{O_2} = 10^{-4} atm$
 (A) Mass change on initial heat up
 (B) Steady state kinetics at 1000°C
4. Morphology of oxide scale of alloy after exposing alloys to air for 3 minutes to
 (A) 600°C
 (B) 1000°C
5. X-ray diffraction pattern comparison of base alloy compared to the alloy oxidized at 600°, 700°, 800° and 1000°C for 3 minutes. Nb-Mo oxide solid solution peaks are observed at 700°C. Appearance of Nb_2O_5 peaks and absence of Nb-Mo oxide solid solution peaks at 1000°C indicates the dissociation of Nb-Mo solid solution to Nb_2O_5 and MoO_3 . All other peaks are from base alloy.
6. Cross-section secondary electron image of alloy oxidized for 30 hours in flowing air at 1000°C
 (a) Four-layered scale
 (b) Layer 2 containing rod-shaped Nb_2O_5 dispersed in glass.
 Rod shaped Nb_2O_5 is visible as bright phase dispersed in glass.
7. Comparison of oxide scale, (a) Before chlorination, (b) After chlorination
 Nb_2O_5 is selectively removed from the scale as $NbCl_5$. No Cl peaks in EDS were observed suggesting all chlorides were volatile at the test temperature and removed from the scale.

8. XRD patterns of base alloy, oxidized alloy for 10 hours and scale after chlorination.
Disappearance of Nb_2O_5 peaks after chlorination and absence of any other peaks suggest that Nb_2O_5 has been removed from scale leaving an amorphous layer i.e. borosilicate glass
9. Auger analysis of layer 2 after chlorination and heat treatment at 1100°C for 1 hour
Presence of Boron and Silicon peaks suggests that amorphous phase present is borosilicate glass.
10. Microstructure of alloy oxidized at 1000°C in flowing air for 10 hours after chlorination.
 - (a) Four-layered microstructure of oxide scale.
 - (b) Microstructure of crack and layer 1. Nb_2O_5 growth is visible as bright phase.

CHAPTER 4

GENERAL CONCLUSIONS

Microstructure and oxidation behavior of sintered Nb-Mo-Si-B alloys has been investigated at 1000°C under flowing air. In the Mo-Si-B system, the phase assemblies investigated were $T_1(\text{Mo}_5\text{Si}_3\text{B}_x)\text{-MoSi}_2\text{-MoB}$, $T_1\text{-}T_2(\text{Mo}_5\text{SiB}_2)\text{-Mo}_3\text{Si}$, and $\text{Mo-}T_2\text{-Mo}_3\text{Si}$. Single phase $T_2(\text{Nb}_5(\text{Si,B})_3)$ and $\text{D8}_8(\text{Nb}_5\text{Si}_3\text{B}_x)$ were examined in Nb-Si-B system, along with three phase $T_1\text{-}T_2\text{-D8}_8$ in quaternary (Nb,Mo)-Si-B system. Substitution of Nb for Mo resulted in expansion of T_1 and T_2 lattice constants. Because of Nb/Mo substitution, the lattice parameters of T_1 , T_2 and D8_8 were all intermediate between corresponding Nb and Mo single-phase values.

Mo-Si-B alloys showed excellent oxidation resistance at 1000°C. In accordance with previous work, the scale was found to be essentially a borosilicate glass layer with minor a content of MoO_2 near the alloy/scale interface. MoO_2 content varied depending on the Mo-content of the alloy and was maximum for composition $\text{Mo-}T_2\text{-Mo}_3\text{Si}$. All Nb-Si-B compositions showed poor oxidative stability relative to Mo-Si-B alloys. In the Nb-Si-B system, T_2 alloy showed more resistance to oxidation than D8_8 alloys. This can be attributed to lower porosity levels achieved in T_2 (95% theoretical density) than D8_8 (85% theoretical density) upon sintering under identical conditions. Oxidation behavior of niobium containing alloys, i.e. Nb-Si-B and Nb-Mo-Si-B alloys, were found to depend on initial heating atmosphere. T_2 and D8_8 compositions were more resistant to oxidation when heated to test temperature in argon atmosphere. Quaternary alloy with lower D8_8 phase content was more resistant to oxidation, a consequence of the D8_8 phase having a lower oxidation resistance than T_2 . Initial heating of alloys in argon resulted in scales that are thinner and lower porosity than that formed on alloys heated in air. Parabolic fit for mass change on oxidation suggests a process that is primarily governed by diffusion (inward diffusion of oxygen or outward diffusion of gaseous MoO_3) through the porous scale containing niobium pentoxide dispersed in borosilicate glass. Although parabolic behavior was observed at 1000°C, the large rate constants indicate that scale was not protective in nature.

The mechanism of oxidation of Nb-Mo-Si-B during initial heating step was investigated. Results show the formation of Nb-Mo oxide solid solution at temperatures below 800°C, which later dissociates to Nb₂O₅ and MoO₃ higher temperatures. The latter vaporizes to leave a porous scale with Nb₂O₅ dispersed in borosilicate glass. Evolution of MoO₃ leaves large pores in the scale. Also, Nb₂O₅ presence in the scale appears to hinder the viscous flow of borosilicate glass at 1000°C. Since the diffusion coefficient of oxygen in Nb₂O₅ is three orders of magnitude higher than of oxygen in silica glass, Nb₂O₅ can facilitate the diffusion of oxygen through grains and grain boundaries to further enhance the alloy oxidation. Severe cracks were observed in the matrix and scale presumably due to a large volume expansion associated with the formation of oxides.

The primary factor contributing to the oxidative instability of Nb-Mo-Si-B alloys is believed to be the formation of Nb₂O₅ and the high scale porosity resulting from MoO₃ evaporation. A novel chlorination technique was used to remove non-volatile Nb₂O₅ from the scale as volatile NbCl₅ by flowing a mixture of chlorine and carbon monoxide over the pre-oxidized alloys. The chlorinated samples were then heat-treated to remove the scale porosity. A borosilicate glass rich layer with only minor amount of Nb₂O₅ was observed after chlorination. The oxidation rate of Nb-Mo-Si-B alloys was reduced by two-thirds after Nb₂O₅ removal (from 0.76 mg²/cm⁴/hr² to 0.20 mg²/cm⁴/hr²). The significant reduction in oxidation rate after chlorination indicates that the oxide scale became protective in nature on par with ternary Mo-Si-B (0.24 mg²/cm⁴/hr²).

In order to develop Mo-Si-B as an alloy with good environmental and mechanical properties at high temperature, future work might consider adding an element, which can eliminate the formation of Mo₃Si thus allowing oxidation resistant Mo₅Si₃B_x phase to be in equilibrium with Mo (to improve fracture toughness) and also forms a volatile oxide on exposure to air. Previous work at Ames Laboratory [1] has shown that V-Si-B forms a volatile V₂O₅ in scale, which evaporates by 1200°C allowing formation of passivating glass layer. In the 1960s, Scruggs found that powder metallurgical Cr is ductilized by addition of MgO particles that transform into MgCr₂O₄ spinel particles [2]. He determined that segregation of detrimental

impurities such as nitrogen to the particle-matrix interface is one of the factors responsible for ductilization. Scruggs found also that Mo may be ductilized by adding MgAl_2O_4 or NiAl_2O_4 spinel particles [3]. Schneibel et al at Oak Ridge National Laboratory have confirmed the ductilizing effect of Mo by spinel particles.

Also, recent work at Oak Ridge National Laboratory [4] has shown a significant reduction in the thermal expansion anisotropy of Mo-Si alloys with ternary vanadium additions. Future work can concentrate on studying the ductalization of vanadium by spinel addition and preparing a composition rich in $(\text{V},\text{Mo})_{\text{ss}}$ with spinel particles. The V-Mo-Si-B alloys with spinel particles might show a potential to form a protective glass layer with improved mechanical properties.

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