Microstructures and oxidation behavior of some Molybdenum based alloys

by

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Dedicated to my parents

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Abstract

The advent of Ni based superalloys revolutionized the high temperature alloy industry. These materials are capable of operating in extremely harsh environments, comprising of temperatures around 1050°C, under oxidative conditions. Demands for increased fuel efficiency, however, has highlighted the need for materials that can be used under oxidative conditions at temperatures in excess of 1200°C. The Ni based superalloys are restricted to lower temperatures due to the presence of a number of low melting phases that melt in the 1250 – 1450°C, resulting in softening of the alloys above 1000°C. Therefore, recent research directions have been skewed towards exploring and developing newer alloy systems. This thesis comprises a part of such an effort.

Techniques for rapid thermodynamic assessments were developed and applied to two different systems – Mo-Si alloys with transition metal substitutions (and this forms the first part of the thesis) and Ni-Al alloys with added components for providing high temperature strength and ductility. A hierarchical approach towards alloy design indicated the Mo-Ni-Al system as a prospective candidate for high temperature applications. Investigations on microstructures and oxidation behavior, under both isothermal and cyclic conditions, of these alloys constitute the second part of this thesis. It was seen that refractory metal systems show a marked microstructure dependence of oxidation.

1. Introduction

The discovery of Ni based superalloys in early 1940s revolutionized the field of high temperature alloys. These alloys were instrumental in rapid increases in operating temperatures of gas turbines and aircraft engines resulting in increased Carnot efficiencies. However, towards the turn of the century, progress in superalloys slowed down. These alloys could no longer be tweaked to meet the higher temperature requirements, and the researchers started looking at alternative materials systems for a solution.

The present thesis is one such attempt at exploring newer materials system for prospective usage in gas turbines and makes a short but critical contribution in the larger goal of using a combination of hierarchical screening tools, both theoretical and experimental, in search for new materials.

1.1 The “ideal” alloy

In order to arrive at the requirements for the “ideal” alloy, let us briefly consider the service environments in which the turbine is expected to function. The chemical nature of the environment arises due to the fuel and the flue gases. Coal and steam are the two crucial types of fuels used. Burning of coal results in the production of gases like CO and CO₂, along with ancillary gases resulting from the sulfur content and other impurities in the coal. In case of steam-based turbines, the turbine blades also get exposed to supercritical steam containing H₂O in gaseous form. Hence the materials in the turbine blades need to be extremely resistant to oxidation.

The physical environment is chiefly characterized by the operating temperature and the nature of fluid flow. The operating temperatures have a direct link with the efficiency of the turbines. As a rather simplistic approximation, one can consider the turbines to be a Carnot engine, which would indicate increasing efficiencies with increasing temperatures. The fluid flow in gas turbines is often supersonic. As a result of irreversible flow discontinuities in supersonic flow fields, the inlets and the walls can be subjected to a series of normal and oblique shocks [1]. In addition, the combination of elevated temperatures and loads result in grain boundary sliding and creep in the turbine materials. Therefore, the alloys used should have good creep resistance, fracture toughness and fatigue resistance in order to withstand loads at high temperatures as well as shocks due to the flow field of the fluids, over and above the ductility required for easy processing. Microstructure plays a crucial role in the mechanical properties of these alloys.

Hence, to summarize, the “ideal” alloy is one that has good oxidation resistance, a high melting point, has good phase stability and microstructural stability. It should also have adequate ductility, creep resistance, fracture toughness and a high fatigue limit. To complicate the alloy development further, often these properties change in a conflicting manner with alloying additions.

1.2 Phase stability

A phase is said to be thermodynamically stable when it has the lowest Gibbs energy or Helmholtz energy under given conditions [2]. In other words, the phase is in global equilibrium. This definition works well for single phase or single component materials. However, this is not necessarily the case for multi-phase or multicomponent alloys. The concept of equilibrium, for multicomponent materials, is defined in terms of the chemical potential. The chemical potential can mathematically be defined as the gradient of the Gibbs free energy with respect to composition:

$$\mu_i^\alpha = \left. \frac{\partial G^\alpha}{\partial x_i} \right|_{x_1, x_2, \dots, x_n, n \neq i} \quad (1.1)$$

Therefore, unless the chemical potential of a given species remains the same in different phases, a free energy gradient will result in diffusion of species leading to changes in the composition. In other words, for a stable phase assemblage:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots \quad (1.2)$$

where i is the chemical species under consideration and $\alpha, \beta, \gamma, \dots$ are the different phases present in the stable phase assemblage. Graphically, this is equivalent to drawing common tangents between the phases present. The points lying on the curves and the tangents give the chemical composition of the phases in equilibrium, as shown in figure 1.1 [3].

Figure 1.1: Equilibrium mixture of α and β

1.2.1 Significance of phase stability in high temperature applications

Phase stability is one of the crucial metallurgical problems for high temperature alloys. The processes determining the microstructures and phase assemblages of these materials often result in presence of phases that may be metastable at service temperatures. Consequently, the phase assemblage and structure of these materials can change in service conditions resulting in undesirable phases. Often, the presence of oxidative environments adds to the complexities. Therefore, it is important to know (i) the stable phases, (ii) the rate at which the metastable microstructures transform to the equilibrium phase fields and (iii) the stable oxides, their morphology and rate of formation of these oxides at service temperatures.

High temperature alloys have been known to fail under service conditions. Often, this is a result of precipitation of topologically closed packed intermetallic phases [4]. These phases have a large degree of non-metallic directional bonding, and result in alloy embrittlement,

especially if they precipitate in a continuous network on the grain boundaries. This can occur when the material is in service, or even during repairs, especially if post-welding heat treatments are not carried out carefully.

The significance of phase stability can therefore be easily judged. Principles of phase stability can help us design alloys and microstructures tailored for different applications; at the same time, a lack of stability can also prove to be dangerous if the new phases forming during phase transformations are brittle or have large volume changes and result in catastrophic failure of the components.

1.2.2 Computational methods for studying stability

A theoretical understanding of phase stability often involves estimating the free energy or enthalpy of the system. In this section we briefly discuss the various techniques for theoretical estimation of free energy and enthalpy. Computational techniques for assessment of free energy/enthalpy can broadly be classified into two categories, i.e. continuum approaches like CALPHAD [5] and atomistic approaches [6].

The CALPHAD method is based on expressing the thermodynamic variables as a polynomial function of temperature. These functions are stored in databases, e.g. Scientific Group Thermodata Europe (SGTE) database [7]. In this method, random substitutional solution models are typically used for solid solutions, where components can take up any position available to the phase. While the original approach was used exclusively for binary alloys, a number of researchers have extended this approach for multicomponent alloys as well. The most commonly used extrapolations are based on the equations of Muggianu, Kohler and Toop; for a concise summary see [5]. Muggianu's expression holds good if the alloy is dilute in two of the components. Kohler's equation allows for composition dependence of binaries. Toop's equation considers that two of the binaries behave in the same way while the third is different and is more applicable for ionic solids rather than metallic materials.

For modeling ordered structures, appropriate sublattice models [8] have to be formulated. Solubility range of the phase and the crystallographic data for the phase are the two crucial inputs in sublattice models [9]. The crystallographic information is required to determine the number of sublattices required as well as the species allowed on different

sublattice. Corresponding to different sublattices are different “end-members”. These end-members are intermetallics having a stoichiometry very close to the composition under consideration. A weighted composition of these end-members can then model the intermetallic phase. This results in allowing for a degree of solubility and substitution in the phase under consideration.

An alternative to CALPHAD approach is the semi-empirical Miedema model, which doesn't rely on experimental data. The model requires very few inputs in the form of some fundamental information like electro-negativity, Wigner-Seitz electron density and volume of formation. This model will be discussed in more detail in the next section.

Atomistic simulations of free energy can be carried out in a number of methods like harmonic methods, ab-initio calculations, molecular dynamics simulations and Monte Carlo methods. The harmonic methods can be used only for solid phases since they are based on broken translational and rotational symmetries and localized atomic vibrations. Here, the Helmholtz energy is calculated as a sum of the static potential energy and the vibrational energy. The vibrational frequencies used in the sum can be obtained from the quasiharmonic lattice theory. For ab-initio calculations, Hartree-Fock theory is used. The implicit assumption in Hartree-Fock theory is that the N-body wavefunction can be approximated by a single Slater determinant. Then, based on the variational principle, a solution can be obtained for the wavefunctions and the energy of the system [10].

1.2.3 Miedema's semi-empirical model for binary alloys

The Miedema model is built on the “macroscopic atom” picture [11]. The basic assumption in this case is that the reference can be chosen as atoms embedded in a metal, instead of free atoms. The essence of the model lies in estimating quantitatively the effects of the change in the Wigner-Seitz cell boundary electron density. Dissimilar cells, in contact with each other, would tend to shift their electron densities such as to remove the cell boundary discontinuities in order to form the alloy. Elimination of such discontinuities is expected to require energy; hence the electron density difference Δn_{ws} accounts for a positive contribution to the interface energies. The enthalpy is given by:

$$\Delta H_{ch} = c_A c_B \{ f_B^A \Delta H_{ic}^{AB} + f_A^B \Delta H_{ic}^{BA} \} \quad (1.3)$$

f_B^A represents the degree to which A is surrounded by B, and is given as:

$$f_B^A = c_B^s [1 + \gamma (c_A^s c_B^s)^2] \quad (1.4)$$

where c_A^s represents the concentration of A at the surface and ΔH_{ic}^{AB} represents the interfacial enthalpy for A surrounded by B. The factor γ takes the values 8, 5 and 0 for intermetallics, metallic glasses and solid solutions respectively. The surface concentrations may be given as –

$$c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \quad (1.5)$$

This expression can be easily extended to multicomponent alloys as well. The interfacial enthalpy is given by –

$$\Delta H_{ic}^{AB} = \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \{-P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2\} \quad (1.6)$$

The values of P and Q are dependent on the type of metals forming the alloy / intermetallic compound. Usually, the value of P is taken as 14.2 for metals with valency higher than 2, and 10.7 for metals with valency of 1 or 2. The P/Q ratio is maintained at 9.4 [12]. Equation 1.6 has to be modified for alloys of a transition metal with a non-transition metal due to an additional enthalpy term arising out of filling of Brillouin zones of a particular crystal structure. The modified relation may be expressed as –

$$\Delta H_{ic}^{AB} = \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \{-P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R^*\} \quad (1.7)$$

If the model equations are analyzed it can be seen that introduction of surface concentrations in equation 1.5 results in the deviation from the regular solution behavior. The quantity $(n_{ws}^{-1/3})_{av}$ in equation 1.7 is supposed to reflect the influence of the electronic screening length on the width of the dipole layer at the A-B interface [13].

As Pettifor points out [14], while the model provides very simple and useful rules for alloy formation, the physical concepts upon which it is based finds no justification in quantum mechanics. The attractive contribution in Miedema model is assumed to be ionic in nature [15]. This clearly is not the case for metallic systems. Despite this, the Miedema's model is still capable of yielding fast and fairly accurate estimates of the formation enthalpy.

The usefulness of Miedema's theory has led to extensive studies on understanding the microscopic origins of the theory [16], as well as numerous applications like eliciting structural information [17, 18], diffusion of impurity elements [19], glass formation and crystallization [20-23], estimation of bulk modulus [24, 25] and formation of point defects [26].

1.2.4 Extending Miedema's approach to multi-component systems

A number of investigators have attempted to extend Miedema's approach to multicomponent systems [21, 27-33]. Gallego et. al. [21] approximated the formation enthalpy as a sum of the formation enthalpies of the respective binary systems. Such an approach however neglects the role of ternary interaction parameters and the relative compositions of the individual binaries, since the partitioning coefficients need not be the same for all the binaries. Goncalves and Almeida [27] devised an ingenious approach for estimation of enthalpies based on the relative positions of atoms. This approach was devised for MgCu_2 , MgZn_2 , CaCu_5 structure types. In principle the approach can be extended to other structure types as well, once the crystallographic information is available. However, the model can't be applied in absence of relevant crystallographic information.

Zhang and Jesser [28] attempted to extend the Miedema model using the same approach as Gallego et. al. [21] while incorporating an additional strain energy component. The strain energy was calculated using Eshelby's model [34]. However, Eshelby's model is a continuum approach, devised especially to treat the stresses arising due to inclusions and hence, in the strictest sense, be applied to alloying at atomistic levels. Herbst [29] used an extended version of Miedema model to predict the hydrogen content in ternary hydrides. However, he had to establish and incorporate polynomial fits based on the data for a large number of hydrides. Hence this approach is not a general approach and can't be applied directly to multi-metallic systems.

De Tandler et. al. [30] adopted an approach similar to Gallego et. al. [21] while adding an entropy component to estimate the Gibbs free energy. Ouyang et. al. [31, 32] used a geometric approach similar to Toop's approach [5]. However, it is known that Toop's approach is largely applicable to ionic solids rather than metallic materials. Bera et. al. [33] estimated the

formation enthalpies using a pseudo-binary approach. However, their approach was based on crystallography and hence can't be used in absence of crystallographic information.

1.2.5 Correlating enthalpy and bulk modulus

The versatility of the phase stability approach to alloy design can be better appreciated when we consider that a number of engineering properties can be estimated to a first degree of approximation based on the enthalpy for formation. One such property is the bulk modulus of alloys and compounds. A number of authors have proposed different empirical models for correlating bulk modulus with enthalpy [24, 25, 35]. Li et. al. suggested that the bulk modulus is related to enthalpy according to the following equation [25]:

$$B = n_{wS}^2 V \left[1 + \frac{\Delta H}{E_{AB} + \Delta H} \right] \quad (1.8)$$

where E_{AB} is the cohesive energy of the solid and can be expressed in terms of cohesive energies of the elements as a simple weighted average. Li et. al. have reported that this empirical relation can predict the bulk modulus within an error limit of $\pm 8.5\%$ [24, 25].

Raju et. al. [35], on the other hand, suggested a logarithmic relation:

$$\ln(B) = \ln(B_0) + k\Delta H \quad (1.9)$$

where B_0 is the bulk modulus at absolute zero and k is a material-dependent thermoelastic constant. The relationships between enthalpy and bulk modulus is indeed important since the bulk modulus can be related to the Young's modulus as [36]:

$$E = 3(1 - 2\nu)B \quad (1.10)$$

where E is the Young's modulus and ν is the Poisson's ratio which typically lies in the 0.25-0.3 range for metallic materials. Young's modulus, being a measure of stiffness of a material, is an important design parameter for materials selection in industry.

1.3 Refractory metal silicides

Recent research shows that refractory metal silicides, especially Mo and Nb based silicides, have excellent potential for ultra-high temperature applications [37-40]. This section focuses on the key physical properties of silicides, namely, thermodynamic stability, oxidation

Figure 1.2b: Nb-Si binary phase diagram [44]

Figure 1.2c: Ti-Si binary phase diagram [44]

Figure 1.2d: Ta-Si binary phase diagram [44]

Figure 1.2e: V-Si binary phase diagram [44]

Figure 1.2f: Si-Zr binary phase diagram [44]

Figure 1.2g: Si-Y binary phase diagram [44]

Figure 1.2h: Si-W binary phase diagram [44]

Amongst all the 4d and 5d transition metal silicides, only Mo_3Si forms in a cubic structure. Speier et. al. noted that this is mainly related to the effect of increased overlap of metal d states with its surroundings [45]. Mo_3Si forms in an A15 structure belonging to the space group $Pm-3n$ and Laue class $m3m$ [46]. In an M_3X A15 structure, the M atoms form in three orthogonal chains [47]. Based on this arrangement, Geller devised an approach for estimating lattice parameters of these compounds according to the following relation [48]:

$$a_0 = \frac{4}{\sqrt{5}} \left(R_M + R_X \right) \quad (1.11)$$

The M_5Si_3 phase is present in all of the binaries. In case of Zr-Si, the Zr_5Si_3 phase is present over a small temperature range. Table 1.1 summarizes the structures of the 3-1 and 5-3 compounds found in important transition metal-silicon systems.

Alloy system	3-1 compounds		5-3 compounds	
	Pearson symbol	Space Group	Pearson symbol	Space Group
Mo-Si	cP8	Pm-3n	tI38	I4/mcm
Nb-Si	tP32	P4 ₂ n	tI32	I4/mcm
Ti-Si*	tP32	P4 ₂ n	hP16	P6 ₃ /mcm
Ta-Si	tP32	P4 ₂ n	tI32	I4/mcm
V-Si*	cP8	Pm-3n	hP16	P6 ₃ /mcm
Zr-Si	tP32	P4 ₂ n	hP16	P6 ₃ /mcm
Y-Si	absent	absent	hP16	P6 ₃ /mcm
W-Si	absent	absent	tI32	I4/mcm

Table 1.1: Crystal structures of 3-1 and 5-3 compounds in some of the important transition metal-silicon systems. * indicates that the metal is a 3d transition metal [49].

The equilibrium structure for Mo_5Si_3 is the $D8_m$ structure (space group I4/mcm). However, often, a competing hexagonal structure $D8_8$ (space group $P6_3/mcm$) is also observed [50]. Fu et. al. reported that the bonding in Mo_5Si_3 was characterized by pronounced multi-centered covalent components. Their calculations showed that $D8_m$ had a much lower formation enthalpy as opposed to $D8_8$ ($\sim 0.7\text{eV}/\text{formula unit}$). Furthermore, it is known that the $D8_8$ structure can be stabilized only through interstitial alloying elements like carbon.

McMahan et. al. have reported the variation in bonding characteristics, formation enthalpies and density of states with a change in Si content in Mo-Si alloys [51]. Their results are summarized in figure 1.3 (a)–(c). It can be seen from figure 1.3(a) that the Si-Si bonds in an A15 structure tend to appear at only larger separations (and hence are presumably weaker). In contrast, the $D8_m$ structure has a slightly higher amount of Si-Si bonds. The number of Mo-Si bonds is comparable for both A15 and $D8_m$. From figure 1.3(b), it is apparent that the $D8_m$ phase has a lower formation enthalpy than the A15 phase. From figure 1.3(c), it can be seen that the DOS at the Fermi level decreases with higher Si content, with the exception of the $D8_m$ phase, which shows a slightly higher value than the A15 phase.

Figure 1.3: (a) Number of bonds per atom as a function of separation; (b) Variation of formation enthalpy with Si content; (c) DOS of different compounds in Mo-Si system [51].

In case of Nb-Si alloys, Nb_5Si_3 can exist in two major forms – the $\alpha\text{-Nb}_5\text{Si}_3$, which is stable at relatively lower temperatures ($<1650^\circ\text{C}$), and $\beta\text{-Nb}_5\text{Si}_3$, which is the high temperature phase. It has been reported that the key difference between the two variants is existence of antibonding orbitals [52, 53]. $\beta\text{-Nb}_5\text{Si}_3$ contains antibonds whereas the $\alpha\text{-Nb}_5\text{Si}_3$ does not. The change in nature of bonding becomes especially significant when ternary alloying elements are added.

Figure 1.4 (a)-(d) shows the liquidus projections/ternary phase equilibria for Mo-Si-B [54, 55], Nb-Si-B [54] and Mo-Nb-Si. Addition of B to metal rich regions in the Mo-Si system results in the formation of the T2 phase (Mo_5SiB_2). The T2 phase also forms with B addition to Nb-Si system, as can be seen from figure 1.4(c). In fact, the T2 phase has a greater compositional tolerance in the Nb-Si system compared to Mo-Si system. An isothermal section for Mo-Nb-Si at 800°C is shown in figure 1.4(d). It can be seen that this system exhibits M_3Si phase up to 25 atom% Nb substitution. Mo_5Si_3 and the low temperature variant of Nb_5Si_3 have the same structure type (W_5Si_3 type) while the low temperature MoSi_2 and the NbSi_2 phase have the same structure type (C11_b). Since Nb_3Si phase is not stable below 1700° , it doesn't appear in the phase diagram.

Figure 1.4: (a) Liquidus projections in Mo-Si-B system [55]; (b) Ternary phase equilibria for Mo-Si-B [56]; (c) Ternary phase equilibria for Nb-Si-B [57]; (d) Ternary phase equilibria for Mo-Nb-Si [44]

Unlike the Mo-Si and Nb-Si system, the W-Si system does not exhibit any equilibrium 3-1 phase. Studies on Mo-W-Si alloys have been mainly restricted to alloys with higher Si content [58], where MSi_2 phase forms. Studies on Nb-Mo-W-Si systems have been carried out at high Nb content [59]. The microstructures consist of Nb_{ss} and $\alpha\text{-(Nb,Mo,W)}_5\text{Si}_3$ when boron doping is below 1%, and $\beta\text{-(Nb,Mo,W)}_5\text{Si}_3$ when boron doping is higher than 1%. However, there appears to be a paucity of experimental data on the role of W in stabilizing/destabilizing the A15

structure when added to Mo-Si system. Studies on Mo-Nb-Si-B quaternary alloys showed that for a Mo:Nb ratio less than 1:1, the microstructure consisted of the T1 ($\text{Mo}_5\text{Si}_3\text{B}_x$), T2 and D8_8 phases [60, 61]. For Mo:Nb ratios of approximately 2.75, the phase assembly comprised of T1, T2 and M_3Si (A15) phase [61]. Therefore, this seems to suggest that the A15 phase can be destabilized below certain critical Mo:Nb ratios. Similar studies on role of Mo:W ratios are not available to the best of my knowledge.

1.3.2 Oxidation behavior

The oxidation behavior of the Mo based alloys at temperatures below 800°C is poor due to the formation of MoO_3 , which volatilizes easily resulting in formation of a porous scale [62]. The high degree of scale porosity allows oxygen transport via a short-circuit path to the underlying silicide leading to rapid oxidation. The oxidation resistance can be improved markedly with a small amount of boron doping [62-65]. This improvement is primarily due to the formation of borosilicate glass. Viscous flow starts above 1000°C .

The major factors affecting the oxidation pathways are the oxygen pressure at the oxidation front, the porosity of the scale being formed, and the viscosity of the scale. A lower oxygen pressure leads to the following reaction:

A higher oxygen pressure will lead to the following reaction:

The second situation will result in rapid oxidation since MoO_3 is highly volatile. Porosity of the oxide scale will provide for oxygen paths to the underlying silicide and cause catastrophic oxidation. Recently, pack cemented MoSi_2 coatings were applied on a Mo-4.3Si-1.1B alloy to suppress oxidation up to 1300°C [66].

The oxidation behavior of Niobium silicides is poorer than Molybdenum silicides. Single phase Nb_5Si_3 has been observed to oxidize rapidly resulting in the formation of a thick voluminous scale [67]. Consequently, studies have been carried out by boron doping of Nb-Si alloys [60, 61, 68]. From these studies, it appears that the T2 phase has better oxidation resistance than the other phases present in the system.

Studies on oxidation behavior of quaternary Mo-Nb-Si-B alloys was found to be relatively poor compared to Mo-Si-B, due to the presence of the D8₈ phase, which has poor oxidation resistance. This is borne out when we consider that alloys with less D8₈ volume fraction showed improved oxidation behavior [60].

A comparison of the oxidation behavior of refractory metal disilicides showed MoSi₂ to have the best oxidation resistance with NbSi₂ having a much poorer oxidation resistance. WSi₂ was also seen to have poor oxidation resistance up to 1200°C. It was also reported that a mixture of MoSi₂ and WSi₂ followed a parabolic oxidation law, and the overall oxidation behavior was not highly affected by the presence of WSi₂ [69]. Recent studies, however, showed that at 1300°C, WSi₂ has excellent oxidation resistance, since at this temperature, the SiO₂ formed a continuous scale [70]. Other transition metal silicides like Ti-Si alloys show high oxidation rates when exposed to air, and might not be suitable candidates for high temperature applications [71].

1.3.3 Mechanical behavior

Metal rich Mo-Si alloys usually have poor mechanical properties due to the presence of the brittle A15 phase. Single crystal studies on Mo₃Si showed anomalous yield behavior and a lack of plastic deformation due to the fact that only three independent slip systems can occur [72]. MoSi₂-Mo₅Si₃ composites have superior creep behavior as compared to monolithic MoSi₂ [73]. Mo₃Si-Mo₅Si₃ composites showed excellent hardness, due to the presence of Mo₃Si, but had a low toughness [74]. Nb_{ss}-Nb₅Si₃ alloys, on the other hand, have good low temperature toughness, as well as reasonable high temperature strength and creep resistance [37, 75-77].

The effect of boron doping on mechanical properties of Mo-Si and Nb-Si alloys have also been studied by a number of investigators [59, 68, 78, 79]. The overall effect of boron on creep behavior in Mo-Si alloys was found to be small and dislocation climb was found to be the key deformation process during creep [78]. In case of Nb-Si alloys, it was found that B resulted in a significant increase in the hardness of 5-3 phase while the Nb_{ss} phase remains unaffected. The overall high temperature strength appears to increase with boron additions [59].

1.4 Nickel aluminides

Aluminides have found widespread applications as high temperature materials, especially at temperatures below 1000°C [80]. The most common aluminides in practice are nickel aluminides, titanium aluminides and iron aluminides. Usually, the aluminides are not used in single phase form; rather, they are present as precipitates in superalloys [4]. Ti based alloys are known to suffer ignite at higher temperatures [81]. On the other hand, nickel aluminides offer better high temperature resistance, and are found in the microstructures of superalloys. In this section we focus primarily on nickel aluminides and related alloys.

1.4.1 Phase stability

Figure 1.5 shows the Ni-Al phase diagram. This system has 5 intermetallics. The Ni_3Al intermetallic (known as the γ' phase) forms via a eutectic reaction. It has a narrow solubility range and crystallizes in a cP4 structure (Pm-3m space group). This is also known as the L_{12} structure. The Ni_5Al_3 intermetallic forms as a mixture of Ni_3Al and NiAl is cooled below 700°C through a peritectoid reaction. This intermetallic belongs to the Cmmm space group.

Figure 1.5: The Ni-Al phase diagram [44].

The NiAl intermetallic has a wide composition range and forms directly from the liquid. It has a very high melting point (1640°C) and forms in the B2 structure (Pearson symbol cP2,

space group $Pm-3m$). The Ni_2Al_3 intermetallic forms through a peritectic reaction at 1133°C . It belongs to the $P-3m_1$ space group and has the Pearson symbol $hP5$. The $NiAl_3$ intermetallic forms through a peritectic reaction at well at 854°C . It belongs to the space group $Pnma$ and has the Pearson symbol $oP16$.

In Ni base superalloys, the microstructure consists of an FCC Ni based solid solution (known as the γ phase), the γ' phase which forms as a precipitate, often coherently with the matrix alongwith a number of other phases depending on the overall chemistry of the superalloy [4, 82]. Alloying additions are often chosen such that the melting temperature of the alloy increases. Hence, the enthalpy of the solid solution formed by alloying, the structure and the solubility of the alloying element are key considerations for the γ phase. Figure 1.6 shows a schematic of the microstructures of Ni based alloys with aluminide phases.

Figure 1.6: A schematic microstructure of a Ni based alloy with γ' precipitates [4]

For the γ' phase, addition of ternary alloying elements shifts the phase boundary as shown in figure 1.7 [4, 83]. In an Ni-Al-X alloy, elements like Co and Pt shift the γ' phase fields parallel to the Ni-X axis, implying a substitution in Ni sites, with a constant Al content. Elements like Ti and Ta do the opposite. A few elements like Cr, Fe and Mn can result in mixed behavior.

Figure 1.7: Effect of alloying additions on γ' phase field [4]

First principles studies have indeed shown that Pt preferentially goes to the Ni sub-lattice while elements like Cr and Hf prefer the Al sub-lattice [84-86]. Whenever available, calorimetric studies on Ni-Al-X intermetallics can be used as a guide for stability of that phase [87].

γ' also undergoes order-disorder transformations. It has been shown that for pure γ' , the disordering temperature is roughly the same as its melting temperature, although it does depend to a small extent on the doping level and stoichiometry [88-90]. Other phases in these systems include the γ'' phase, which forms as a result of Nb addition to Ni-Al alloys [4]. Additionally, excessive quantities of Cr, Mo, W and Re can promote the formation of topologically close-packed phases [91].

1.4.2 Oxidation behavior

Oxide growth requires an upward diffusion of the oxide forming metal atoms. The upward diffusing metal atoms react with oxygen at the outer surface to form the oxide layer. Alternatively, the oxygen can diffuse down through the oxide layer, and react with the metal atoms in the sub-surface. In some cases, both oxygen and metal atoms diffuse resulting in further oxide formation [92].

Ideally, for high temperature applications, it is desired to have diffusion controlled slow, parabolic oxidation kinetics [93]. In this case, the thickness of the metal consumed is given by the relation:

$$x = \left(\frac{V_m}{vM_x} \right) \Delta W_s \quad (1.12)$$

where x is the thickness of the metal consumed, V_m is the molar volume of the alloy, v is the stoichiometric factor for the scale product, M_x is the atomic weight of oxygen and ΔW_s is the weight change due to oxidation.

Formation of a thin film of oxide also results in accumulation of stresses within the oxide scale. The origin of the stresses lies in the volume changes within the scale as a result of oxidation. A Pilling-Bedworth ratio less than unity (volume of the oxide is less than the volume of the alloy forming the oxide) would indicate a porous and non-protective oxide. A Pilling-Bedworth ratio substantially higher than unity indicates a large volume of oxide and hence, a significant volume increase. This introduces compressive stresses and leads to spallation of the oxide scale. These stresses interfere with the diffusion process, by affecting the vacancy flux of oxygen ions. In addition to oxidation, such stresses can also arise as a result of the Kirkendall effect resulting from a large differential of diffusing species [94].

Efforts have been made by many to tailor the oxidation behavior of nickel aluminides by addition of alloying elements (most commonly with Cr and Y, or Pt, depending on the end usage of the alloy) [95, 96]. The choice of alloying element additions are influenced by several considerations including the adherence of oxide scale to the substrate; the crystallographic matching of the modified alloy with the base alloy; modifications in diffusion rates of Al atoms, and hence, the growth rate of the oxide.

In case of a binary nickel aluminide, the isothermal oxidation behavior is largely dependent on the Al content. Lower Al content results in formation of nickel oxides, which are not as stable as alumina. This results in greater metal loss. Higher Al content, in addition to lower the fraction of nickel oxides formed, also promotes an adherent scale [97]. Ternary additions to nickel aluminides aim to improve the oxidation resistance and/or mechanical behavior. For higher temperature regimes, the two most important alloying elements are Hf

and Pt. The key advantage of Hf is claimed to promote an adherent slow growing alumina scale, whereas Pt addition presumed to modify the diffusion behavior of various refractory elements while decreasing the chemical activity of Al simultaneously increasing its interdiffusion coefficient. Jackson et. al. have reported that Pt retards the diffusion of refractory metal elements [98]. In addition, Pt is also known to promote adherence of the oxide scale [96].

The interdiffusion behavior of alloying elements has been studied extensively using diffusion couples. These studies largely dealt with binary systems, or with diffusion of a given element in a specific alloy phase field. Recently, however, the trends in diffusion studies have shown a shift towards diffusion multiple studies, where, with an appropriate choice of sample geometry, interdiffusion data and phase equilibria can be mapped out using a microprobe [99, 100].

1.4.3 Mechanical behavior

The mechanical properties of these alloys are strongly dependent on microstructures. Strengthening can occur via the solid solution strengthening of the FCC γ matrix or by the precipitation of γ' phase. Hence, the key microstructural parameters are as follows [82] –

- (i) Particle size
- (ii) γ' volume fraction
- (iii) Crystal orientation

In addition, certain alloying elements like Rhenium can promote rafting [101]. This occurs during microstructural coarsening, when the γ' precipitates start to coalesce. This results from of misfit stresses and affects the strength of the alloys.

The Ni based superalloys containing Ni aluminides are known to retain their strength up to a large fraction of their melting temperature. It has also been reported that creep properties of two phase superalloys are much superior to single phase superalloys [102]. The figure 1.8 summarizes the mechanical behavior of Ni base superalloys.

Figure 1.8: Tensile behavior of Ni based superalloys [102]

Addition of alloying elements can result in solid solution hardening as well as a change of bulk modulus. Jiang et. al. carried out first principles studies on effect of Pt on bulk modulus and shear modulus [103]. Often Improvements in mechanical properties of superalloys at ever increasing temperatures of the already optimized microstructures are achieved by the addition of elements like Rh, W, Mo, Ta or Ti, although addition of these elements result in reduced oxidation resistance [104]. Table 1.2 shows the high temperature strength of a number of alloys, intermetallics and pure metals.

Alloy	Strength (MPa)	Remarks
Pure Mo [105]	1000	Yield strength at 1000°C
Inconel 740 [106]	750	Yield strength at 200°C
Inconel 740 [106]	625	Yield strength at 800°C
Inconel 740 [106]	40	Yield strength at 1000°C
CMSX-3 [102]	950	Yield strength at 200°C
CMSX-3 [102]	1000	Yield strength at 800°C
CMSX-3 [102]	450	Yield strength at 1000°C
NiAl [107]	900	Yield strength at 200°C

Alloy	Strength (MPa)	Remarks
NiAl [107]	750	Yield strength at 800°C
NiAl [107]	400	Yield strength at 1000°C
Ni ₃ Al [108]	600	Yield strength at 1000°C
Ni ₃ Al + MoSi ₂ [108]	1250	Yield strength at 1000°C. Alloys were arc-melted in 1:1 ratio

Table 1.2: High temperature strength of different alloys

1.5 Problem formulation and approach

The literature review carried out in the preceding section highlights the dual nature of the high temperature alloy development. On one hand, these alloys are expected to show good stability at elevated temperatures; on the other hand, they are expected to be fairly ductile.

1.5.1 Black and white

To sum up the known body of literature, nickel based alloys, especially the alumina formers, are relatively good for oxidation resistance. However, given melting temperatures of around 1350°C, they are restricted to applications under 1050°C, above which they are unable to retain sufficient strength for structural applications.

The refractory metal silicides have fairly good oxidation resistance at elevated temperatures, but are susceptible to moisture. These alloys also have good creep strength; however they are brittle due to the presence of a large amount of brittle intermetallics which neither contributes towards strength nor towards oxidation resistance.

1.5.2 Shades of gray

It remains to be seen if nickel aluminides can be alloyed with refractory metals in a significantly larger amounts while retaining the oxidation resistance of the alumina scale even at higher temperatures. Similarly, it needs to be elucidated whether appropriate alloying additions can get rid of at least some of the brittle intermetallics from the refractory metal silicides phase assemblage without compromising the oxidation resistance of these alloys.

The two grand questions in alloy design would be to find efficient methods that can be used to either (a) tweak existing systems for improved performance or (b) find a new alloy system that offers improved performance. As a general approach, fast semi-empirical techniques can be used to down-select promising candidate materials, which can then be worked on using a combination of careful experimentation and more involved calculations.

In this particular case, Miedema's semi-empirical model was used to improve the refractory metal silicides on one hand and develop a new alloy system on the other. The former has been discussed in greater details in the second and third chapters of this thesis, primarily by destabilizing the A15 phase with appropriate alloying additions. While the oxidation resistance of refractory metal silicides has been extensively studied, the oxidation behavior in absence of the A15 phase from the phase assemblage has not been tackled extensively. The latter was approached using a combination of thermodynamic calculations and known data on melting temperatures, which will be discussed later in this section.

A high temperature alloy needs not only to be high melting but also have adequate oxidation resistance at elevated temperatures. This requires the presence of an oxidatively stable phase that can help in forming a passivating scale during the oxidation process. The well known passivating elements at high temperatures would be Cr, Si and Al. Cr and Si can form extremely good oxide scales; however, they can function only in dry environments. For typical power plant applications, alumina formers would be a better choice. Hence, the first clue towards the process of alloy design would be to have a good alumina forming phase in the system.

Amongst the many alumina formers, nickel aluminide was chosen as the oxidation resistant phase for our system. The choice of nickel aluminide was influenced by three factors – (i) A large Al content (50 atomic %) ensures easier formation of a hermetic alumina scale; (b) nickel aluminide has a fairly high melting temperature (1638°C) for an aluminum containing alloy; (c) alumina is relatively slow to nucleate. Hence to prevent large metal loss it is useful to have a second oxide that nucleates fast and provides initial protection, but can then be reduced by Al to form alumina, which is more thermodynamically stable, dense and provides better

protection to subsequent oxidation. NiO fulfils all of these criteria and hence alloying Ni with Al is a logical way to approach this issue.

Once the oxidation resistant phase has been chosen, a second metal rich solid solution phase would be required that could provide the high temperature strength and ductility to the alloy system. At the same time, this metal should not react with aluminum and destabilize the nickel aluminate. Hence, this metal was selected by looking at elements with cubic structure, and extremely high melting temperature ($> 2000^{\circ}\text{C}$) with formation enthalpies of their aluminides being significantly lower than NiAl. Mo and W were prospective candidates, with the former being chosen due to its relatively better ductility and lower density.

Oxidation behavior of Mo-Ni-Al is a relatively unknown territory. Some studies have been carried out in the hypo-eutectic region, with the amount of Mo being fairly low (< 9 atom %). However, to my knowledge, no studies on oxidation resistance have been carried out with larger amounts of Mo. Fortunately, the phase equilibria in the Mo-Ni-Al system is relatively well known. Raghavan carried out a review of the phase diagram literature for this particular ternary system in 2006 [109]. The most complete phase diagram at an elevated temperature was done by Lu et al in 1999 [110]. Partial assessments in the Ni rich regions were carried out by Miracle et al [111], while partial assessments in the Al rich region were carried out by Grushko et al [112]. It could be seen from these studies that Mo rich regions contained alloys with higher melting temperatures, whereas the Ni and Al rich regions had relatively lower melting regions. Given the volatile nature of MoO_3 , a lower Mo content is likely to benefit the alloy. Given the constraints of high melting and good oxidation resistance, the area that would be most likely of interest would lie in the 15 to 30 atom % Mo in the Mo + NiAl two-phase field region. However, given the paucity of data, studies are still required to establish the variation of oxidation in the two-phase region.

1.5.3 Problem formulation and approach

Designing a new alloy system is a herculean task, and the complete development of an usable alloy system is outside the scope of a single thesis. Hence, only a part of this problem will be attempted. Given that Mo based systems have been identified as potential candidates, we will be dealing with alloys having two phases showing completely contrasting oxidation

behavior. Hence, it is plausible that the phase assemblages and the microstructures of these elements could have a significant bearing on the oxidation resistance. The goal of this thesis would be to develop alloys having different microstructures and phase assemblages and then examine their effects on the oxidation behavior. Two alloy systems will be considered for the purpose of this study – Mo-Si-B and Mo-Ni-Al.

1.6 Dissertation organization

This dissertation has been written in an alternate format, with seven of the chapters being written in form of papers that have been / will be submitted for publication (chapter 2 being the notable exception, which has been published in Journal of Alloys and Compounds). The current chapter provides an introduction to the body of work contained in these seven chapters, while the last chapter sums up the entire work, and draws upon the conclusions to devise a path for future work.

Chapter 2 deals with extending the Miedema's semi-empirical model to ternary system and uses it to demonstrate the possibility of Nb and W additions in destabilizing the A15 Mo₃Si phase. *Chapter 3* deals with the experimental studies on phase stability of A15 with Nb and W additions as well as density of states of the substituted compounds. *Chapter 4* sees a shift in focus from silicides to the Mo-Ni-Al system. The central issue addressed in this chapter is the isothermal oxidation behavior of cast Mo-Ni-Al alloys. *Chapter 5* follows up on the work done in chapter 5 and focuses on the cyclic oxidation of the Mo-Ni-Al alloys. *Chapter 6* explores liquid phase sintering as a processing technique for synthesis of Mo-Ni-Al alloys and explores the oxidation behavior of the sintered alloys. *Chapter 7* sums up the general conclusions and contains suggestions for future work in this field. The *Appendix* consists of a paper published in *JOM*. This paper presents a wider picture of our on-going research program, and has been included for providing a broader perspective on this topic.

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2. Applications of an extended Miedema model for ternary alloys

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2.1 Abstract

The extension of Miedema's semi-empirical model to ternary systems by means of an energy minimization scheme was implemented to demonstrate a number of physical phenomena associated with select ternary alloys. In order to gain a thermodynamic understanding of glass-forming ability of Zr based alloys, a combination of extended Miedema's model and lattice strain energies has been invoked. The extended Miedema approach has also been used to study the phase selection during crystallization for amorphous Zr-Cu-Ni alloys. Also extended Miedema's model was used to illustrate its applicability to study the phase stability of Mo-Nb-Si alloys around M_3Si composition ($M=Mo, Nb$), by predicting the amount of Nb (30 atom percent) required to destabilize the structure.

2.2 Introduction

During the 1970s and early 1980s, Miedema and his colleagues developed a semi-empirical approach that could predict formation enthalpies of binary alloys [1-7]. The Miedema model is built on the "macroscopic atom" picture. The basic assumption in this case is that the reference can be chosen as atoms embedded in a metal, instead of free atoms. The essence of the model lies in estimating quantitatively the effects of the change in the Wigner-Seitz cell

boundary electron density. Dissimilar cells, in contact with each other, would tend to shift their electron densities such as to remove the cell boundary discontinuities in order to form the alloy. Elimination of such discontinuities is expected to require energy; hence the electron density difference Δn_{ws} accounts for a positive contribution to the interface energies. Following the development of Miedema's model, a number of research groups tried to use this model for a variety of metallurgical problems ranging from glass formation to lattice defects [8-19].

Miedema's model, in its original form, is applicable only to binary alloys. Hence, in order to use it for multicomponent systems, a number of different extensions have been proposed [10, 11, 20, 21]. The energy minimization approach which is presented in the following sections involves treating the formation enthalpy as a weighted sum of constituent binary systems, with the weights and the individual binary compositions being chosen such that the net formation enthalpy of the system is minimized. In this paper, we will illustrate application extended Miedema model to study several physical phenomena associated with ternary alloys.

2.3 Theoretical Calculations

In this paper, we adopt an approach similar to that of Gallego, with each of the binaries having a certain weight. These weights are determined by numerical minimization of enthalpy. In this approach, the formation enthalpy is given as:

$$\Delta H = \phi_1 \Delta H_{AB}(c_A) + \phi_2 \Delta H_{BC}(c_B) + \phi_3 \Delta H_{CA}(c_C) \quad (2.1)$$

where c_A , c_B and c_C are atom fraction of species A, B and C in the AB, BC and CA binaries respectively and ϕ_1 , ϕ_2 and ϕ_3 are weights assigned to each of the binaries. These weights are found by minimizing ΔH under the following set of constraints:

$$\begin{aligned} \sum_{i=1}^3 \phi_i &= 1 \\ \phi_1 c_A + \phi_3 (1 - c_C) &= x_A \\ \phi_2 c_B + \phi_1 (1 - c_A) &= x_B \\ \phi_3 c_C + \phi_2 (1 - c_B) &= x_C \end{aligned} \quad (2.2)$$

Once the values of the weights and binary compositions have been determined, the formation enthalpy can be easily computed.

The formation enthalpies of the constituent binary systems are calculated using Miedema's semi-empirical model [1-3, 5-7, 22]. According to this model, the net enthalpy of mixing is given by the relation:

$$\Delta H_{tot} = \Delta H_{ch} + \Delta H_{el} + \Delta H_{st} \quad (2.3)$$

where ΔH_{ch} , ΔH_{el} , ΔH_{st} represent the chemical, elastic and structural contributions respectively. The chemical enthalpy may be evaluated as follows –

$$\Delta H_{ch} = c_A c_B \{ f_B^A \Delta H_{ic}^{AB} + f_A^B \Delta H_{ic}^{BA} \} \quad (2.4)$$

f_B^A represents the degree to which A is surrounded by B, and is given as:

$$f_B^A = c_B^s [1 + \gamma (c_A^s c_B^s)^2] \quad (2.5)$$

where c_A^s represents the concentration of A at the surface and ΔH_{ic}^{AB} represents the interfacial enthalpy for A surrounded by B. The factor γ takes the values 8, 5 and 0 for intermetallics, metallic glasses and solid solutions respectively. The surface concentrations may be given as –

$$c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \quad (2.6)$$

The interfacial enthalpy is given by –

$$\Delta H_{ic}^{AB} = \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \{ -P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 \} \quad (2.7)$$

The values of P and Q are dependent on the type of metals forming the alloy / intermetallic compound. Usually, the value of P is taken as 14.2 for metals with valency higher than 2, and 10.7 for metals with valency of 1 or 2. The P/Q ratio is maintained at 9.4 [1, 7]. Equation 2.7 has to be modified for alloys of a transition metal with a non-transition metal due to an additional enthalpy term arising out of filling of Brillouin zones of a particular crystal structure. The modified relation may be expressed as –

$$\Delta H_{ic}^{AB} = \frac{V_A^{2/3}}{(n_{ws}^{-1/3})_{av}} \{ -P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R^* \} \quad (2.8)$$

The volume changes associated with charge corrections effects may be given as [6] –

$$\Delta V_i = \frac{1.5 c_j^s V_i^{2/3} (\phi_i^* - \phi_j^*)}{2 (n_{ws}^{-1/3})_{av}} (n_{ws,i}^{-1} - n_{ws,j}^{-1}) \quad (2.9)$$

$$V_i^* = V_i + \Delta V_i \quad (2.10)$$

Valence state of element determines the preferred crystal structure that it forms. Hence, during the process of alloying, if the elements are forced to form an alloy having a different crystal structure, an additional structural enthalpy term, needs to be added to the chemical enthalpy term. Miedema et. al. proposed that the total structural enthalpy when an element “A” is dissolved in “B” is given by [23]:

$$H_{AinB}^{struct} = \left(\epsilon_A - Z_B \frac{\partial E^{struct}(B)}{\partial Z} \right) + \left(\epsilon_B^{struct} - E_A^{struct} \right) \quad (2.11)$$

Once the structural contribution to the enthalpy is estimated, the formation enthalpy of an A-B binary would be given as:

$$\Delta H(A, B) = x_A x_B \left[f_B^A H_{AinB}^{i/c} + f_A^B H_{BinA}^{i/c} \right] + \left(\epsilon_B H_{AinB}^{struct} + x_A H_{BinA}^{struct} \right) \quad (2.12)$$

In order to study the lattice strain energies of solid solutions we have used the approach developed by Miracle and Senkov [24, 25], and extended to ternary systems by Ray et. al. [8, 26]. According to this approach, the lattice strain energy of a multicomponent system can be expressed as:

$$E_{molar}^{el} = \sum_{\substack{j=1, j \neq i \\ p=s, i}}^n \frac{c_j^2}{1 - c_i} E_{ij}^{bin} \quad (2.13)$$

where E_{ij}^{bin} is the lattice strain energy of a binary i - j solid solution (i as the matrix species and j as the solute species).

2.4 Results and Discussion

The relations presented in the above section were used to study a number of physical phenomena ranging from glass forming ability in ternary alloys to equilibrium phase assemblage in ternary systems.

2.4.1 Glass forming ability

Over the years, a number of approaches have been proposed to understand glass formation in metallic systems [8-11, 24, 27-33]. A number of factors like the e/a ratio [30, 31],

lattice strain [8, 9, 24, 26], formation enthalpy [8-11, 26] and local geometry [8, 27-29] have been proposed to explain the phenomena. In this paper, we have focused on the thermodynamics of glass formation. Assuming the frustration of nucleation of intermetallic crystalline phase, the competing phase for the metallic glass is the solid solution. The driving force for crystallization can therefore be given as:

$$\Delta H^{cryst} = (H_{mg}^{ch} + H_{mg}^{str}) - (H_{ss}^{ch} + H_{ss}^{str} + H_{ss}^{lse}) \quad (2.14)$$

where H_{ss}^{ch} is the chemical contribution to enthalpy of a solid solution, H_{ss}^{str} is the structural contribution to enthalpy of the solid solution, H_{ss}^{lse} is the lattice strain energy of the solid solution, H_{mg}^{ch} is the chemical contribution to the enthalpy of a metallic glass and H_{mg}^{str} is the structural contribution to the enthalpy of a metallic glass. Since glasses are thermodynamically treated as liquids, it is assumed that they have zero lattice strain energy. The higher the value of this driving force for crystallization, the easier it is for the glass to form.

Several experimental approaches have been postulated for measuring glass forming ability (GFA). Ideally, lower the critical cooling rate with which the liquid can still transform to glass, the better is the glass forming ability. With this in mind, a number of parameters involving the liquidus temperature (T_l), the crystallization temperature (T_x) and the glass transition temperature (T_g) have been formulated to assess the GFA of an alloy. The first parameter for assessing GFA was formulated by David Turnbull who used the reduced glass transition temperature (T_{rg}), the ratio of T_g and T_l , as a measure of GFA [34]. Subsequently, it has been debated [35-37] whether a ratio based on T_g/T_l is a better measure or T_g/T_m is a better measure where T_m is the onset of the melting. In 1978, Donald and Davies suggested [38] the use of T_l^{mix} as an alternative for T_l in the expression for T_{rg} . Here T_l^{mix} represents the weighted average of the melting points of the individual components. This results in a simple parameter given as:

$$\Delta T^* = \frac{T_l^{mix} - T_m}{T_l^{mix}}, \quad T_l^{mix} = \sum_{i=1}^n x_i T_m^i \quad (2.15)$$

Recently, Inoue et al. [39] have proposed a new parameter for GFA. It was suggested that ΔT_x be used as a parameter for GFA. Better glass formers are expected to exhibit a wider

supercooled range or a higher value of ΔT_x . Lu and Liu [40] suggested the use of γ parameter, defined as:

$$\gamma = \frac{T_x}{T_g + T_l} \quad (2.16)$$

as a better glass forming criterion. It is widely accepted that the critical cooling rate (R_c) is a good measure of GFA. On this basis, the γ parameter shows lesser scatter as opposed to the parameters suggested by any of the earlier researchers. Mondal and Murty [41] have suggested an even more simplified and effective approach towards GFA. They suggested two parameters:

$$\alpha = (T_x/T_l) \quad (2.17)$$

$$\text{and } \beta = T_x/T_g + T_g/T_l \quad (2.18)$$

using these parameters GFA can be assessed effectively. The former parameter, in fact, doesn't even require the knowledge of T_g for predicting GFA. Figure 2.1 shows a comparison of α , β and γ parameters with respect to the reduced glass transition temperature. It can be seen that the trend is consistent for all of them.

Figure 2.1 Comparison of different glass-forming parameters.

Figures 2.2 (a) and (b) show plots of the driving force for crystallization vis-à-vis the α and the γ parameter respectively. The γ parameter has been estimated using the experimental data available on Zr based metallic glasses available in the literature [42-44]. The figure is

consistent with our expectation that a more negative driving force will aid glass forming ability. Hence, given a glass-forming system, the extended Miedema approach can be used to identify good glass forming composition regimes.

Figure 2.2: (a) Comparison of the driving force for crystallization with α parameter; (b) Comparison of the driving force for crystallization with γ parameter.

2.4.2 Crystallization pathways in metallic glasses

Experimental studies on crystallization behavior of $Zr_2Cu_{1-x}Ni_x$ metallic glasses have shown that the Zr_2Ni (c16) based phase crystallizes for $x \leq 0.625$ [45, 46]. In the range $0.625 \leq x \leq 0.375$, both Zr_2Cu and Zr_2Ni based phases can be observed, while for $x \leq 0.375$ Zr_2Cu (c11b) is the preferred phase. Table 2.1 shows a list of the optimized parameters (c_A , c_B , ϕ_1 , and ϕ_2). The Cu-Ni binary has a negligible contribution to the formation enthalpy, and the fraction contribution of this binary (ϕ_3) is 0.01. The major contributions to the formation enthalpy comes from the Zr-Cu binary for values of x lower than 0.375, with the binary composition being approximately Zr_2Cu , whereas the major contribution for values of x higher than 0.625 is due to the Zr-Ni binary.

Cu and Ni have a difference of one valence electron with a minor difference in size. According to Miedema's model, the interaction parameter between different species is governed by volume differences and differences in electron density at the Wigner-Seitz cell boundary. The volume difference being negligible, the difference in the number of valence electron and consequently, a difference in the Wigner-Seitz cell boundary electron density plays a key role in Zr-Cu and Zr-Ni systems having different interaction parameters. Since the

formation enthalpy of alloys in the Cu-Ni binary is fairly small, the formation enthalpy of the ternary glass is mainly decided by contributions of the Zr-Cu and Zr-Ni binaries. A more negative Zr-Ni interaction parameter should result in the enthalpy minimization routine favoring a relatively greater phase width for the c16 (Zr₂Ni) structure as compared to the c11b (Zr₂Cu) structure. This has already been verified experimentally by Kramer et. al. [45]. This indicates that at least in this system, the electronic structure plays an important role in GFA, a fact ignored in other parameterization schemes.

Composition	Fraction cluster A (Zr-Ni) ϕ_1	Cluster comp (atom fraction Zr) c_A	Fraction cluster B (Zr-Cu) ϕ_2	Cluster comp (atom fraction Cu) c_B
Zr ₂ Ni _{1/8} Cu _{7/8}	0.11	0.7	0.88	0.33
Zr ₂ Ni _{1/4} Cu _{3/4}	0.19	0.6	0.80	0.31
Zr ₂ Ni _{3/8} Cu _{5/8}	0.29	0.6	0.70	0.30
Zr ₂ Ni _{1/2} Cu _{1/2}	0.40	0.6	0.59	0.28
Zr ₂ Ni _{5/8} Cu _{3/8}	0.50	0.6	0.49	0.25
Zr ₂ Ni _{3/4} Cu _{1/4}	0.60	0.6	0.39	0.21
Zr ₂ Ni _{7/8} Cu _{1/8}	0.71	0.6	0.28	0.14

Table 2.1: Fraction of Zr-Ni and Zr-Cu binary in the Zr-Cu-Ni ternary and their respective compositions.

2.4.3 Phase stability in ternary alloy system

Mo-Si based alloys constitute an important class of ultra-high temperature alloys [47-49]. However, a key impediment to widespread usage of these materials is the relatively low fracture toughness. Microstructural investigations show the presence of a three-phase alloy, with the three phases being a Mo based solid solution, a M₃Si (M=metal) phase and M₅Si₃ phase [50-52]. It has been shown that the M₃Si phase has poor mechanical properties [53, 54]. It was surmised that the removal of this phase could lead to improved toughness. Using the present model, formation enthalpies of the M₃Si phase and a phase mixture of Mo based solid

solution and M_5Si_3 was calculated. Assuming limiting conditions, when M_3Si exists in equilibrium with Mo and M_5Si_3 [55]:

Here, x_a and x_b represent the atom percentage of Mo and Nb, λ and ψ denote the phase fraction of the solid solution and M_5Si_3 , ϕ_1 and ϕ_2 represents the atom percentage of Mo and Nb in the solid solution and μ_1 and μ_2 represent the atom percentage of Mo and Nb in the M_5Si_3 phase. Using principles of mass balance, we have the following set of equations:

$$x_a + x_b = 75 \quad (2.19a)$$

$$\lambda\phi_1 + \psi\mu_1 = x_a \quad (2.19b)$$

$$\lambda\phi_2 + \psi\mu_2 = x_b \quad (2.19c)$$

$$\lambda + 37.5\psi = 25 \quad (2.19d)$$

$$\phi_1 + \phi_2 = 99 \quad (2.19e)$$

$$\mu_1 + \mu_2 = 62.5 \quad (2.19f)$$

Solving the equations, we obtain $\psi = 2400/3650$ and $\lambda = 1250/3650$. The remaining variables can be expressed in terms of ϕ_1 .

$$\mu_1 = (x_a - \lambda\phi_1)/\psi \quad (2.20a)$$

$$\phi_2 = 99 - \phi_1 \quad (2.20b)$$

$$\mu_2 = 62.5 - (x_a - \lambda\phi_1)/\psi \quad (2.20c)$$

Using these relations, the enthalpy difference between the A15 phase and an assemblage of solid solution and M_5Si_3 phases and plotted in Figure 2.3. From this figure it can be seen that the difference in formation enthalpy of the $(Mo,Nb)_3Si$ phase and the phase assemblage of (Mo,Nb,Si) solid solution + $(Mo,Nb)_5Si_3$ decreases with increasing Nb addition and tends to zero at approximately 30 atom percent Nb. Experimental studies have indicated that the $(Mo,Nb)_3Si$ phase does indeed get destabilized when further Nb is added [55].

Figure 2.3: Plot of enthalpy difference between M_3Si phase and a phase mixture of Mo based solid solution and M_5Si_3 as a function of Nb addition. The shaded region indicates the composition range where the M_3Si phase gets destabilized.

2.5 Conclusions

In this paper we have successfully applied the extension of Miedema's semi-empirical model in our previous work to a number of physical phenomena. We were able to understand glass forming ability of a number of alloy systems using thermodynamic parameters based on the formation enthalpies estimated using the extended Miedema model. Based on the individual binaries, we could obtain trends in the predominant clusters present in glasses and thus gain an understanding of the crystallization pathways. The model could also be used to understand phase stability issues in the refractory metal silicides. Thus it can be seen that the model is capable of giving good approximate predictions and has the potential to be applied in diverse areas.

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2.7 References

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3. Effect of Nb and W additions on the stability of the A15 Mo₃Si phase

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3.1 Abstract

A combination of theoretical and experimental studies on the stability of Mo₃Si with Nb and W additions has been presented in this paper. Theoretical studies suggest that the formation enthalpy of the A15 Mo₃Si decreases initially with Nb addition, but starts increasing beyond 37.5 atom %, thereby suggesting that the A15 structure can be destabilized by Nb addition. In case of W additions, the formation enthalpies increase monotonically. Experimental studies show that the A15 phase becomes destabilized when approximately 27.5-30 atom percent Nb is added. The corresponding value for W additions was found to be approximately in the 12.5-15 atom % range.

3.2 Introduction

The drive for greater efficiencies requires the modern day gas turbines to operate at as high a temperature as possible, in highly oxidative environments. This requires the development of novel alloys that can withstand such harsh conditions. Ni based superalloys have been the workhorse material for the high temperature industry for several decades. However, these alloys are intrinsically restricted to temperatures under 1050°C due to their relatively low melting temperatures [1]. Refractory metal silicides have long been known to have high melting temperatures, and in some cases, excellent oxidation resistance. These

properties have been exploited in MoSi_2 based alloys for a variety of applications like heating elements in furnaces. Hence, molybdenum silicides have slowly emerged as an attractive candidate for some ultra-high temperature applications [2-4]. The oxidation stability of these alloys, especially the compositions with relatively low Si content has been further improved by controlled boron additions. Boron doped Mo_5Si_3 has been shown to form a borosilicate scale that provides excellent oxidation resistance at high temperatures [5-9]. However, the oxidation resistance of these materials is largely due to intermetallics that are fairly brittle [10]. In order to develop adequate ductility and toughness, it becomes essential to have a metal rich solid solution phase in thermodynamic equilibrium with these intermetallics. Therefore, in order to obtain an optimal level of oxidation resistance and toughness, a two phase microstructure consisting of a Mo rich solid solution and the $\text{Mo}_5\text{Si}_3\text{B}_x$ compound is a potentially attractive alloy.

The Mo-Si binary phase diagram [11], shown in figure 3.1, will show that obtaining a phase mixture of Mo based solid solution and the oxidation resistant Mo_5Si_3 phase would have to include the A15 $\text{Pm}\text{-}3\text{n}$ Mo_3Si phase. Studies on the Mo-Si-B ternary system [12] indicates that boron addition does not destabilize the A15 phase up to 1800°C [13]. The A15 phase is undesirable due to its very low fracture toughness due to very few active slip systems [14-16] and is therefore not desirable. Mo oxidizes in air to undergo a pesting reaction at temperatures in excess of 700°C . The amount of Si in Mo_3Si is not sufficient to form a completely hermetic oxide scale and protect the alloy. Consequently, this phase has very poor oxidation resistance [17-19]. Therefore, the presence of this phase is quite undesirable for ultra-high temperature applications. Studies on Mo-Nb-Si-B alloys seem to indicate that the A15 phase can be removed from the microstructure if a large amount of Nb is added to the alloy [20, 21]. This has been further corroborated thermodynamically using an extension [22] of the semi-empirical Miedema model [23-30] for multicomponent alloys. However, it has also been demonstrated that the addition of Nb adversely affects the oxidation resistance [20, 21]. Hence, it is important to destabilize the A15 phase with the minimum amount of Nb.

Figure 3.1: Phase diagram of binary Mo-Si [11].

Figure 3.2 Ternary isotherm of Mo-Si-B alloys at 1600°C [12].

In this paper, we attempt to estimate the effect of Nb on the phase stability of the A15 Mo_3Si structure and the minimum amount of Nb needed to destabilize the A15 phase. The limited solubility of boron in the A15 Mo_3Si [31] would indicate that the results from studies on the A15 compound in the Mo-Nb-Si and Mo-W-Si can be easily extrapolated to a higher order boron containing system. Previously, the Mo-Nb-Si phase equilibria had been experimentally assessed at 800°C , and it was found that up to 20 atom percent of Nb could be incorporated in the A15 phase [32]. However at temperatures in excess of 1770°C , the phase diagram is significantly different from that at 800°C and hence information from the above cited work cannot be extrapolated. Only recently has an assessment of phase equilibria been attempted at these temperatures, and that is largely theoretically calculated with no experiments being done in the vicinity of the M_3Si composition ($\text{M} = \text{metal}$) [33]. At 800°C , Mo_3Si exists in the Mo-Si binary phase diagram, but Nb_3Si does not exist in the Nb-Si phase diagram. Therefore, even in the absence of a ternary isotherm, it is quite clear that the $(\text{Mo,Nb})_3\text{Si}$ phase cannot exist beyond a certain Nb content. At temperatures above 1780°C , however, the Nb_3Si phase is present in the binary Nb-Si phase diagram [34] shown in figure 3.3.

Figure 3.3: Phase diagram of the binary Nb-Si system [34].

The atomic sizes of Mo and Nb are comparable, and the Mo-Nb system exhibits complete solid solubility [35]. Therefore, unlike 800°C , the destabilization of Mo_3Si with Nb addition should not be taken as granted. Since the phase diagram changes significantly with temperature, it is critical to investigate whether Nb indeed destabilizes the A15 phase at a higher temperature. At higher temperatures, the ternary isotherm has been calculated using the CALPHAD method recently [33], which showed a limited range of existence of the A15 structure. These results are in accordance with our own work using a very approximate thermodynamic model [22]. However, experimental studies are still required to validate these calculations.

Figure 3.4: Phase diagram of the binary Si-W system [36].

In contrast to the Mo-Nb-Si systems, relatively very few studies exist on Mo-W-Si systems. A review of the W-Si phase diagram (figure 3.4) shows the absence of a W_3Si phase over the entire temperature range above 1000°C [36]. The Mo-W system, on the other hand, forms a continuous isomorphous solid solution [37]. Additionally, there is very little difference in the atomic radius of Mo and W. This would suggest that while the A15 Mo_3Si could possibly dissolve a finite amount of W additions, relatively larger additions should result in

destabilization of the A15 phase. Given the higher density of W as compared to Mo, it would be desirable to keep the levels of W substitutions to a minimum. The oxidation behavior of WSi_2 has been studied by a number of researchers [38-41]. The oxidation kinetics are faster than that for MoSi_2 at lower temperatures; however, at temperatures of 1300°C or higher, the kinetics slow down. Therefore, possibly W additions will not damage the oxidation resistance of the Mo-Si-B alloys. Therefore, a second goal of this paper is to estimate a composition range over which W additions can destabilize the A15 phase. Given that all the three binaries Mo-Nb, Mo-W and Nb-W form continuous solid solutions across the entire composition range (and can consequently be assumed to have relatively weak interaction parameters) [35, 37, 42], it is reasonable to expect that a critical Nb:W ratio can be established in order to destabilize the A15 phase for a given level of transition metal substitution in the Mo site once the solubility limits of Nb and W additions have been established using a simple rule of mixtures. Hence, the final part of this work will focus on the influence of Nb:W ratios on the phase evolution in Mo-Nb-W-Si quaternary alloys.

3.3 Theoretical calculations

The first principles calculations carried out in the present work using the Vienna *ab-initio* simulation package (VASP) within the framework of the density functional theory (DFT). The calculation is conducted in a plane-wave basis, using the projector-augmented wave (PAW) method with ultra-soft pseudo-potentials [43]. The exchange and correlation items are described by the generalized gradient approximation (GGA), and the cutoff energies are 320 and 535 eV for the plane wave basis and augmentation charge respectively. During the relaxation calculation, the energy criteria are 0.01 and 0.1meV for electronic and ionic relaxations respectively, while for calculation of the density of states (DOS), the criterion is 0.001 meV. The k-point grid used for structural relaxation was 6×6×6, chosen according to the Monkhorst-Pack scheme [44], and symmetry reduced to the irreducible Brillouin zone. The calculations for the M_3Si ($\text{M}=\text{Mo}_{1-x}\text{Nb}_x$ or $\text{M}=\text{Mo}_{1-x}\text{W}_x$) phase were carried out assuming the A15 structure to hold across the entire range of x. The amounts of Nb and Mo as well as W and Mo

were varied to calculate the formation enthalpies. The DOS for this structure was also calculated as a function of Nb content.

3.4 Experimental details

Alloys were synthesized by arc-melting of pure elemental chips (Alfa Aesar, +99.5%) on a water cooled copper hearth in an inert argon atmosphere. The alloy buttons were re-melted a minimum of four times in order to ensure adequate homogeneity. In addition to the Mo_3Si , six alloys in the Mo-Nb-Si system, five alloys in the Mo-W-Si system and two alloys in the Mo-Nb-W-Si quaternary system were synthesized. Table 3.1 shows the nominal compositions of the alloys synthesized for this study. The Mo-Nb-Si alloys were heat treated at 1850°C in an atmosphere of flowing ultra-high purity argon in tantalum containers. The heating as well as the cooling rates were controlled at 20°C/min.

Alloy	Mo	W	Nb	Si	Alloy	Mo	W	Nb	Si
Mo_3Si	75	0	0	25	MWS1	70	5	0	25
MNS1	65	0	10	25	MWS2	65	10	0	25
MNS2	55	0	20	25	MWS3	62.5	12.5	0	25
MNS3	50	0	25	25	MWS4	60	15	0	25
MNS4	47.5	0	27.5	25	MWS5	57.5	17.5	0	25
MNS5	45	0	30	25	MWNS1	55	10	10	25
MNS6	40	0	35	25	MWNS2	55	15	5	25

Table 3.1: Nominal compositions of the alloys studied. All compositions are in atomic %.

Microstructures of the alloys were studied using a JEOL 5910LV scanning electron microscope at an accelerating voltage of 20KV. Phase analyses of the alloys were carried out using a Philips PANalytical x-ray diffractometer with a Bragg-Brentano geometry using a monochromatic Cu $K\alpha$ radiation (wavelength = 1.54059 Å) with a step size of 0.0167 degrees. The x-ray data was then Rietveld refined using GSAS [45] to quantify the change in lattice parameters of various phases due to Nb and W substitution for Mo and to assess the relative

amounts of different phases present in the sample. Additionally, wavelength-dispersive spectra (WDS) were recorded on the A15 grains to estimate the Nb and W substitution in these alloys. Approximately 100 points were collected for each sample using automated data analysis. The WDS studies were carried out using JEOL JXA-8200 microprobe. Data was acquired at an accelerating voltage of 20KV, with a beam current of 20 nA. Si- K_α , Mo- L_α and Nb- L_α lines were used for analysis. A counting time of 10 seconds on the peak and 5 seconds on the background on either side of the peak was used.

3.5 Results and Discussion

3.5.1 Effect of Nb substitution

Recent calculations by Geng et. al. [33] indicated a finite phase width of the Mo_3Si phase with Nb additions, beyond which a three phase region comprising of a bcc Mo based solid solution, the A15 $(\text{Mo,Nb})_3\text{Si}$ and the T1 $(\text{Mo,Nb})_5\text{Si}_3$ phase should form. In general, our experimental work presented in this paper and previous calculations using an extension of the semi-empirical Miedema's model [22] agree well with these results. However, the three phase region quite possibly has a slightly narrower phase width than predicted by Geng et. al. [33]. Figure 3.5 shows the variation of formation enthalpy of $(\text{Mo,Nb})_3\text{Si}$ in the A15 structure from our *ab-initio* calculations. In order to check the accuracy of the calculations, the formation enthalpy values estimated using the *ab-initio* calculations were compared with the experimentally determined values available in the literature. The formation enthalpy of Mo_3Si , from first principles calculations, was found to be -0.3108 eV/atom or -120 kJ/mol. Fujiwara and Ueda estimated a value of $-122.1 + 0.0027T$ (K) ± 0.15 kJ/mol [46] while Tomaszewicz et. al. estimated a value of -125 ± 5.8 kJ/mol from fluorometric calorimetry [47]. These experimental results compare favorably with the values obtained from first principles calculations in this work.

Miedema described the interactions occurring at the interface of the Wigner-Seitz cell of an element being solved in another using an interfacial enthalpy term [25, 28, 29], which is a function of the electronegativity difference between the elements and the difference in the electron density at the Wigner-Seitz cell boundary of the elements. This term has a parallel in

the interaction parameter as it is defined in the CALPHAD approach. Essentially, this is a measure of the strength of interaction between two atoms when brought together. This value, for solvation of Si in Mo was determined to be -120 kJ/mol of Si, whereas the corresponding value for solvation of Si in Nb was determined to be -195 kJ/mol [28-30]. Similarly, the interfacial enthalpy for solvation of Mo in Si is -126 kJ/mol of Mo while that for solvation of Nb in Si is -216 kJ/mol of Nb [28-30]. Therefore, the Nb-Si interaction is stronger compared to the Mo-Si interaction. With increasing levels of Nb addition at the cost of Mo content, the contribution of Nb-Si interactions becomes more as compared to the Mo-Si interactions. In addition to the Mo-Si and Nb-Si interactions, there is a third interaction to be considered, i.e. the Mo-Nb interactions. The interfacial enthalpy values estimated for solvation of Mo in Nb is -22 kJ/mol of Mo, while the corresponding value for Nb in Mo is -23 kJ/mol of Nb. This metal-metal interaction is significantly weaker than the two metal-metalloid interactions. Consequently, initial Nb addition serves to stabilize the Mo_3Si compound as evidenced by an initial reduction in formation enthalpy estimated from the *ab-initio* calculations. However, once the number of Nb-Si pairs get saturated, further addition of Nb leads to Nb-Nb interactions replacing the Mo-Nb interactions, which, by definition have interfacial enthalpy of zero kJ/mol. Consequently an increase in the formation enthalpy can be observed. Since the Nb-Si interactions are stronger than the Mo-Si interactions and much stronger than the Mo-Nb interactions, the increase in formation enthalpy beyond a critical amount of Nb occurs with a slope that is shallower than the slope observed during the initial decrease in the formation enthalpy. This is in fact observed in our *ab-initio* calculations (figure 3.5), where it can be seen that there is an initial decrease in the formation enthalpy followed by an increase. This would indicate an initial stabilization of the A15 compound followed by a subsequent destabilization beyond a certain amount of Nb additions.

Unlike unary systems, however, phase stability in multicomponent systems can't be explained comprehensively by considering only a single phase. In order to address this issue one needs to carefully assess the different possibilities of phase selection. In this case, the binary phase diagrams would suggest that should the A15 get destabilized, it would decompose into a metal rich solid solution and the $(\text{Mo,Nb})_5\text{Si}_3$ T1 (space group) phase. In line with our

argument, we need to consider the change in population of different types of interactions with progressive Nb additions in the competing phases. In case of the metal rich solid solution, an increase in Nb content should result in the increase in the number of Mo-Nb interactions at the cost of Mo-Mo interactions. The Mo-Nb interactions have lower energy and should result in increasing the stability of the solid solution with respect to one having a lower Nb content. Therefore, an increase in Nb addition would further stabilize the solid solution. Similarly, an increase in the Nb addition at the cost of Mo will increase the number of Nb-Si interactions with a corresponding decrease in the number of Mo-Si interactions. This would stabilize the T1 phase. Additionally, it has been shown by McMahan et. al. that the number of metal-metal bonds per atom is higher in the A15 structure than the T1 structure, whereas the number of metal-silicon bonds per atom is higher for the T1 structure as opposed to the A15 structure [48]. This would indicate that the stabilization effect due to Nb addition is much more prominent for the T1 structure as compared to the A15 structure even in the initial stage. Consequently, it would be expected that beyond some stage due to increasing stabilization of the T1 phase and the solid solution vis-à-vis the A15, the single phase A15 would decompose to form T1 and the solid solution.

Figure 3.5: Variation of formation enthalpy with increasing Nb additions.

In addition to the estimation of formation enthalpies, density of states plots were calculated for different levels of Nb substitutions. These plots are shown in figure 3.6. The location of the Fermi surface on a DOS plot provides some indications on the structural stability of these compounds. It can be seen that at the enthalpy minima, the Fermi surface has moved out of the gap at the equiatomic Mo:Nb ratio. This would suggest that there is a possibility for the structure to be unstable at this composition level despite the lowering of formation enthalpy.

Figure 3.6: density of states of $\text{Mo}_{1.5}\text{Nb}_{1.5}\text{Si}$

It should be kept in mind that the calculated results are being used to guide the subsequent experiments and should not be used as a stand-alone evidence for understanding phase stability. In case of unary systems, energetic can be used to give an accurate idea of phase stability. For multicomponent alloys, while the formation enthalpies and density of states provide useful indicators, they can't be treated as conclusive evidence of stabilization or destabilization of a phase. Therefore, we don't use the *ab-initio* calculations to predict *a priori* the composition limits; rather these calculations are performed with the sole aim of reducing

Edisonian experimentation while providing some physical insights towards the phase evolution in these alloy system. In this case, the Fermi surface moving out of the pseudo-gap at the equiatomic Mo:Nb despite a reduction in formation enthalpy is strongly suggestive that destabilization of the compound occurs near this region, and hence acts as a good starting point for experiments.

Figure 3.7: X-ray diffraction patterns from selected compounds in the Mo-Nb-Si series of alloys.

Figure 3.7 shows the X-ray diffraction patterns for different compositions. The data was collected in the 2θ range between 20° and 90° since a relatively larger spread of 2θ values would help in obtaining a better refinement fit. However, given the major peaks of interest fall at values less than $2\theta = 55^\circ$, only the region between $2\theta = 25^\circ$ and 55° have been shown here. The diffraction pattern at the bottom of the stack corresponds to the single phase pure Mo_3Si . The refined lattice parameter of this compound was found to be $4.8921 \text{ \AA}$ which is in good agreement with the values reported in the literature [11, 15]. As Nb is added to the system, a

slight progressive shift of the Mo₃Si peaks can be seen towards the lower 2θ values indicating an increase in the lattice parameters, which would be expected with Nb substitutions in the Mo sites, since Nb is slightly larger than Mo (2.08 Å vs. 2.01 Å). It is also clear that as we move from the Mo₅₀Nb₂₅Si₂₅ composition to the Mo_{47.5}Nb_{27.5}Si₂₅ composition, the single phase A15 structure decomposes to form a two phase mixture comprising of a Mo based solid solution and the T1 (Mo,Nb)₅Si₃ phase. Even as low as the Mo₅₀Nb₂₅Si₂₅ alloy composition, minor traces of the T1 (Mo,Nb)₅Si₃ phase and the b.c.c. solid solution can be observed in the diffraction pattern.

Refinement of the diffraction pattern of the alloy with nominal composition Mo_{47.5}Nb_{27.5}Si₂₅ showed a presence of a minor amount of the A15 (< 5%). Phase analysis of Mo₄₅Nb₃₀Si₂₅ failed to show any amount of the A15 phase. This would seem to indicate that the three phase region is extremely narrow spanning in a range of 27.5 to 30 atom% of Nb addition along the Mo₃Si-Nb₃Si tie-line, which is slightly narrower than the values obtained by Geng et al. [33]. In addition to the formation enthalpy and density of states, the *ab-initio* calculations were also used to calculate the lattice parameters of the Mo₃Si compound with increasing Nb substitutions. The results obtained from the first principles calculations were compared with experimental results in order to verify the accuracy of the calculations. Table 3.2 shows the lattice parameters obtained from first principles calculations, as well as the lattice parameters obtained experimentally. The agreement between calculated and observed lattice parameters is excellent which further supports the possibility of the larger Nb is occupying only the Mo site.

Alloy	Experimental value (Å)	First principles (Å)
Mo ₃ Si	4.8921	4.89
Mo _{2.5} Nb _{0.5} Si	4.9443	4.95
Mo ₂ NbSi	4.9812	4.98

Table 3.2 Comparison of lattice parameters obtained from our experimental studies and calculated lattice parameters from first principles.

Figure 3.8 show the microstructures of the alloys with and without the A15 phase. It can be seen from these alloys that the A15 phase, as long as it exists, forms in sufficiently large

phase fraction to obtain statistically significant measurements from compositional analysis with the microprobe using WDS. These measurements were able to confirm that the composition of the A15 phase in each case was close to the loaded compositions.

Figure 3.8: Microstructures of Mo-Nb-Si alloys. (a) Alloys with the composition $\text{Mo}_{25}\text{Nb}_{25}\text{Si}_{25}$ have a largely single phase microstructure with very small amounts of b.c.c. Mo rich solid solution phase and the T1 $(\text{Mo,Nb})_5\text{Si}_3$ phase. (b) Alloys with compositions $\text{Mo}_{45}\text{Nb}_{30}\text{Si}_{25}$ show an exclusively two phase microstructure consisting of the b.c.c. Mo rich solid solution and the T1 phase.

Mo_3Si is a line compound. Therefore marginal composition variations while melting the nominal composition is quite likely, leading to the formation of small amount of second and third phases. As the molten alloy cools down, it first passes through the liquidus curve resulting in the formation of a minor amount of the Mo rich solid solution. The remaining liquid along with the Mo solid solution that was already formed solidifies following a peritectic reaction path resulting in formation of the Mo_3Si compound [49]. In the higher Nb content alloy, where the Mo_3Si is unstable, the solidification follows a different path, with an eutectic microstructure evolving in place of the peritectic solidification product resulting in a two phase mixture of Mo based solid solution and the $(\text{Mo,Nb})_5\text{Si}_3$ phase. Figure 3.8(a) shows a region having a small amount of the T1 $(\text{Mo,Nb})_5\text{Si}_3$ phase embedded in a Mo_3Si matrix. It is quite clear from the micrograph that Mo_3Si is still the primary phase that was formed. Figure 3.8(b) shows the

formation of a two phase mixture once the A15 phase gets destabilized. The bright phase is the Mo rich solid solution whereas the dark phase is the (Mo,Nb)₅Si₃ phase.

Figure 3.9: Variation of lattice parameter with increasing Nb content.

Figure 3.9 shows the variation of lattice parameters with increasing Nb content. The refined lattice parameters show a fairly consistent trend of lattice expansion with increasing Nb content. A linear lattice expansion trend suggests that the Vegard's law holds for Nb addition as expected since Nb forms an isomorphous solid solution with Mo. The Vegard's law can be used to determine the actual fraction of Nb in the A15 phase using the lattice parameter of 5.15 Å for A15 Nb₃Si [50]. The values determined from Rietveld refinement and WDS are in fairly good agreement. Microprobe analysis was also carried out on the T1 phase in the multiphase alloys. It was seen that the T1 phase had an equiatomic Mo:Nb ratio, which would correspond to a Nb level that is much higher than the nominal composition, thereby indicating a preferential partitioning of the Nb to the T1 intermetallic as opposed to the metal rich solid solution. Such a result is in good agreement with our rationale at the beginning of this section, where we suggested implicitly that a larger amount of Nb in the T1 phase would bring about rapid

stabilization of the two phase T1 + solid solution phase assemblage as opposed to the A15 compound.

3.5.2 Effect of W additions

The interfacial enthalpy for solvation of Si in W has been reported as -102 kJ/mol whereas the corresponding value for solvation of W in Si has been reported as -110 kJ/mol [28-30]. This would indicate that W-Si interactions are weaker than Mo-Si interactions. Additionally, the interfacial enthalpy for solvation of Mo in W, as well as that of W in Mo has been reported as -1 kJ/mol [28-30]. Therefore, W addition resulting in W-Si interactions at the expense of Mo-Si interaction will only serve to raise the formation enthalpy of the A15 compound. The Mo-W interactions are only marginally stronger than the Mo-Mo interaction; hence the marginal decrease in formation enthalpy due to an increase in Mo-W interactions will be far outweighed by the significant increase in formation enthalpy due to the increased number of weaker W-Si interactions. Therefore, in this case, unlike the Mo-Nb-Si system, a monotonic increase in formation enthalpy is to be expected.

Figure 3.10: Variation of formation enthalpy with increasing W additions.

Figure 3.10 shows the variation of formation enthalpy with W additions. It can be seen that W additions does in fact result in a strictly monotonic increase in the formation enthalpy. With progressive W additions, the two competing phases would be the Mo-W solid solution and the $(\text{Mo,W})_5\text{Si}_3$ T1 phase. Using similar arguments, it would appear that W additions would not reduce the formation enthalpy of either of these phases. However, the phase assemblage could still be more stable than the A15 structure if the W preferentially partitioned into the solid solution, leaving only a relatively small amount of W available to substitute Mo in the T1 phase. In such an event, the T1 structure would still contain a fairly large amount of Mo-Si interactions in comparison to the A15 phase resulting in the destabilization of the A15 structure. We shall return to this point later in this section while studying the microprobe and x-ray diffraction results. This, combined with the W-Si phase diagram [36] shown in figure 3.4 would suggest that beyond a certain amount of W addition, the A15 phase is likely to become destabilized.

Figure 3.11: Density of states of $\text{Mo}_{62.5}\text{W}_{12.5}\text{Si}_{25}$.

Figure 3.11 shows the density of states of the $\text{Mo}_{62.5}\text{W}_{12.5}\text{Si}_{25}$ alloy. It can be seen that at this composition the Fermi surface has moved out of the pseudo-gap leading to a possibility

that the structure might be unstable at this composition. As with the previous set of Mo-Nb-Si alloys, we use these calculations as a guide for selecting experimental compositions rather than for making any conclusive comments on the phase stability. These results indicated that the destabilization of the A15 structure was likely to be possible with a much smaller level of substitution with W as compared to Nb. Hence, the experimental studies were focused largely in the lower W substitution regions.

Figure 3.12 shows the x-ray diffraction patterns with different levels of W substitutions. The diffraction data was collected in the 2θ range between 20° and 90° . However, given the major peaks of interest fall at values less than $2\theta = 75^\circ$, only the region between $2\theta = 25^\circ$ and 75° have been shown here. It can be seen that the T1 peaks start appearing at 10 atom % W additions itself, although only around 15 atom % substitution is the A15 phase finally removed from the phase assemblage almost completely.

Figure 3.12: X-ray diffractograms with progressively increasing W content.

Figure 3.13 shows the variation of lattice parameters with increasing W additions. The initial increase in lattice parameter is relatively linear, almost in accordance with Vegard's law. However, at higher levels of W additions there is a significant deviation from linearity. Microprobe analyses on these samples indicate a maximum W content of 7 atom percent, even for alloys with 10 and 12.5 atom% of W additions. Such a result, along with the diffractograms shown in figure 3.12 would indicate that W solubility in the A15 structure is approximately 7 atom %, further addition beyond which leads to the decomposition of the A15 phase partially to form a mixture of the b.c.c. Mo rich solid solution and the T1 $(\text{Mo,W})_5\text{Si}_3$ phase. As the W content is increased above 15 atom %, the A15 is no longer observed, with a two phase field comprising of the metal rich solid solution and the T1 phase taking its place.

Figure 3.13: Variation of lattice parameters with progressive W additions.

Microprobe analysis carried out on the two phase alloy with 15 atom% W indicated a W substitution level of approximately 26 atom % in the metal rich solid solution (which also contained around 70 atom % Mo and 4 atom % Si). W composition in the T1 $(\text{Mo,W})_5\text{Si}_3$ on the other hand, was found to be under 5 atom %. This corresponds to a 12:1 Mo:W ratio in the T1

phase and approximately 3:1 Mo:W ratio in the solid solution. This would clearly seem to support our line of reasoning developed the beginning of the section and indicate a preferential partitioning of the W to the solid solution rather than the T1 intermetallic compound.

It should be noted that one of the possible pitfalls of W addition to the system, for such a study, arises due to the extremely high melting temperature of W. Given the large atomic sizes (relative to interstitial vacancies) and the extremely high melting temperatures, the diffusion kinetics is extremely sluggish, which is likely to cause a relatively high amount of segregation resulting in local inhomogeneity which can be a source of inaccuracy in determining the solubility limits. Therefore, SEM analysis becomes extremely important in this case to ascertain the uniformity of the microstructure.

Figure 3.14: SEM micrographs of Mo-W-Si alloys. (a) Microstructure of a $\text{Mo}_{67.5}\text{W}_{7.5}\text{Si}_{25}$ alloy. (b) Microstructure of a $\text{Mo}_{60}\text{W}_{15}\text{Si}_{25}$ alloy.

Figure 3.14(a) shows a micrograph of an alloy with 7.5 atom% W addition. According to the x-ray diffraction patterns, this alloy is comprised largely of single phase $(\text{Mo},\text{W})_3\text{Si}$. This fact is further corroborated by the micrograph which shows a gray matrix of $(\text{Mo},\text{W})_3\text{Si}$ with smaller phase features embedded in it. The bright phase was determined to be a (Mo,W) solid solution using WDS whereas the darker features were identified to be the $(\text{Mo},\text{W})_5\text{Si}_3$ phase. Figure 3.14(b) shows the microstructure of $\text{Mo}_{60}\text{W}_{15}\text{Si}_{25}$ alloy. The x-ray diffraction patterns revealed an almost complete removal of the A15 phase from this alloy resulting in a phase mixture of a

metal rich solid solution and the T1 phase. The microstructure indeed confirms this with the bright phase being identified as the (Mo,W) solid solution and the dark phase being identified as the $(\text{Mo,W})_5\text{Si}_3$ T1 phase. While scanning through microstructures from different regions of the samples, very little obvious W segregation could be found.

3.6 Conclusions

Ab-initio calculations were used as a guideline for designing experiments to study the phase stability of the A15 phase with different substitutions. It was seen that both Nb and W substitutions destabilize the A15 phase beyond a certain critical level of substitution. In case of Nb additions, it was seen that 30 atom% substitutions is required to remove the A15 phase. In case of Mo-W-Si alloys, 15 atom% W additions were sufficient to remove the A15 phase from the microstructure. In case of Mo-Nb-Si alloys, the three phase region comprising of A15, T1 and the metal rich solid solution is possibly narrower as compared to the corresponding three phase region in the Mo-W-Si alloy system.

3.7 Acknowledgements

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4. Isothermal oxidation of a cast $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy

A paper to be submitted to *Scripta Materialia*

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4.1 Abstract

In this paper we report the isothermal oxidation behavior of a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ which lies in the two phase (Mo + NiAl) region of the Mo-Ni-Al ternary system. The oxidation kinetics in terms of specimen mass change and evolution of the oxide scale was studied at 1200°C. The effects of temperature and alloy microstructures were also investigated. Alloys with a finer microstructures showed improved oxidation resistance.

4.2 Introduction

Gas turbines in thermal power plants reliant on fossil fuels follow the well known Brayton cycle [1]; consequently, their energy efficiency increases with an increase in operating temperatures. Improvements in Ni-based superalloys have enabled a significant rise in operating temperatures leading to higher efficiencies. However, this trend of improvements in operating temperatures have slowed down considerably over the last couple of decades, with only an approximately 15°C rise in operating temperatures being realized over the last decade [2]. The marginal increases in operating temperatures for Ni based superalloys is largely a consequence of the relatively low melting temperatures of Ni (~1455°C) as well as the other constituent phases (for instance, the γ' Ni_3Al melts around 1395°C) and this restricts the operating temperatures to under 1050°C. Refractory metal silicides have been widely studied as

prospective materials at higher temperatures [3-16]; however the issues with their brittleness and the degradation of the borosilicate scale in moist environments are well documented [17-20].

Our earlier work involving a hierarchical screening method had shown some prospect in Mo-Ni-Al alloys for high temperature applications [21]. NiAl has the highest melting temperature of all nickel aluminides and is known to have good oxidation resistance. Mo was added in order to provide adequate toughness and high-temperature strength to the alloy. A significant body of research literature is available in the Mo-Ni-Al system with relatively low amounts of Mo [22-28]. However, the higher Mo region in this system has been largely left unexplored, especially in terms of oxidation behavior. From a scientific point of view, this system presents a new challenge as well, with the alloy system comprising of a two phase microstructure, of which Molybdenum shows a rapid mass loss upon oxidation, following linear kinetics, at high temperatures, whereas the NiAl shows a slow mass gain, following parabolic kinetics. In this paper, we attempt to explore this system in greater detail and understand the intricacies of this system under quasi-isothermal conditions. Subsequent articles will focus on the cyclic oxidation behavior of these alloys.

4.3 Experimental details

4.3.1 Materials and alloy synthesis

Pure elemental powders of Mo (Alfa Aesar, 99.5%), Ni (MPC, 99.6%) and Al (Alfa Aesar, 99.8%) were mixed in appropriate ratios in a high energy SPEX 8000 mixer/shaker mill for 15 minutes. The mixed powders were then pelletized using a hydraulic press. The pellets were arc-melted in an atmosphere of ultra-high purity argon on a water cooled copper hearth using a Zr getter. The arc-melted buttons were then either drop-cast 10 mm- or suction cast 6.25mm-diameter rods in a water cooled cylindrical copper mould in an ultra-high purity (99.99% pure) argon atmosphere. Some of the drop-cast rods thus prepared were heat treated in a Centorr furnace at 1550°C for 6 hours under an atmosphere of flowing ultra-high purity argon atmosphere in alumina crucibles.

4.3.2 Oxidation testing

Coupons for oxidation tests were cut from the drop-cast/suction cast rods using a high speed saw with an alumina blade. The isothermal oxidation tests were carried out at 1000, 1100 and 1200°C. Oxidation of the alloys results in the formation of volatile MoO_3 . In a standard oxidation rig, the volatile MoO_3 would condense on the furnace walls and the wires suspending the coupons leading to erroneous mass measurements. Hence, the oxidation tests in this study were carried out in a horizontal tube furnace. The coupons were exposed to air at the desired temperatures for a given time and pulled out for weighing. These alloys showed a tendency of significant spallation while cooling down to room temperature. Hence the mass measurements after cooling are not an accurate measure of the mass under strict isothermal conditions. Hence, the coupon was immediately transferred into a pre-weighed alumina boat in order to collect all the material lost due to spallation and cracking upon cooling inside the alumina boat, and the mass was measured upon cooling representing a more accurate mass change under isothermal conditions. Three coupons were used for each reading.

4.3.3 Characterization

The alloys were characterized using scanning electron microscopy. A JEOL 5910Lv scanning electron microscope (SEM) was used to characterize the microstructures of the alloys. Semi-quantitative chemical analysis was done to identify the different phases in the microstructure using energy dispersive spectroscopy (Noran-Vantage). Oxidized samples for scanning electron microscopy were prepared by first coating a thin layer of gold on the oxidized coupon. The coupon was then copper-plated and cut to obtain cross-sections and polished for the SEM studies. X-ray diffraction (XRD) was carried out using an x-ray diffractometer (PANalytical, Philips) with a Bragg-Brentano geometry using a monochromatic Cu K_α radiation (wavelength = 1.54059 Å), with the data being collected over the range $2\theta = 10^\circ$ to 90° .

4.4 Results and Discussion

4.4.1 The oxide scale

The oxidation behavior of the binary nickel aluminide has been extensively studied and reviewed [29]. It is well-known that NiO is kinetically preferred over Al_2O_3 and forms initially

during oxidation of nickel aluminides; however Al_2O_3 is the more stable oxide, and hence forms eventually with Al reducing the NiO. Additionally, as an intermediate step, a spinel NiAl_2O_4 has been known to form as well. Depending on the oxygen availability, Mo can oxidize to form either MoO_3 or MoO_2 [30]. Therefore, it would be reasonable to expect the formation of Al_2O_3 , NiAl_2O_4 , MoO_2 and MoO_3 during the oxidation of a Mo-Ni-Al alloy. Figure 4.1 shows the x-ray diffraction pattern taken from the surface of the oxidized alloy at 1000°C after 10 hours of isothermal oxidation. While the x-ray diffraction data was collected between $2\theta = 10^\circ$ to 90° , only the $20^\circ - 60^\circ$ range is shown here. As expected, the Al_2O_3 , NiAl_2O_4 and MoO_2 show up in the pattern. Additionally, MoO_3 needles were observed to have condensed in the cooler regions of the furnace tube. The x-rays from the oxidized surface also showed the base alloy (Mo and NiAl) and NiMoO_4 phase in the scale.

Fig 4.1: X-ray pattern of the oxide scale

All of these phases were observed in oxidized microstructures as well. In general, the oxide layer was extremely non-uniform, with regions of very high oxygen penetration ($> 100 \mu\text{m}$), as well as regions of very low oxygen penetration ($\sim 10 \mu\text{m}$). A careful observation of the

microstructure shows that the sharp inroad of oxygen into the alloy is often a consequence of a large Mo feature exposed to the atmosphere at the surface as seen in figure 4.2(a). In general, the alumina scale is 5-10 μm thick. However, other phases (MoO_2 , NiAl_2O_4 and NiMoO_4) contribute to the thickness, as can be seen in Figure 4.2(b). Figure 4.1(d) shows the overall morphology of the scale using secondary electrons, whereas figure 4.1(e) shows the granular morphology of the NiAl_2O_4 spinel.

Figure 4.2: (a) Breakaway oxidation due to the presence of a large Mo feature at the surface; (b) Back-scattered image showing the large variety of phases in the scale; (c) Secondary electron image showing the scale morphology; (d) Secondary electron image showing the granular structure of the spinel NiAl_2O_4 .

4.4.2 Effect of oxidation temperature

Figure 4.3 shows the microstructures of the drop-cast alloy after oxidation at 1000 and 1200°C for 10 hours. As temperature increases by 200°C, the scale thickness increases by an

order of magnitude as expected. Reports on the parabolic rate constant for growth of the alumina scale show a clear dependence on temperature, with lower temperatures ($\sim 1000^\circ\text{C}$) favoring thinner scales as compared to higher temperatures ($\sim 1200^\circ\text{C}$) [31].

Figure 4.3: Comparison of the scale formed (dark layer over the base alloy) on 10 mm cast alloys at (a) 1000°C and (b) 1200°C after 10 hours of isothermal oxidation.

4.4.3 Isothermal oxidation kinetics

Figure 4.4(a) shows the kinetics of isothermal oxidation. Figure 4.3(b) shows the corresponding evolution of the oxide scale for the 10 mm-diameter as-cast drop-cast alloy. The SEM micrographs were taken roughly at the center of the coupon. The non-uniformity of the scale makes quantification a challenge. However, the thickness averaged over multiple locations has been plotted alongside the mass change results in figure 4.3(a). By and large, this figure suggests that the mass change converges into a steady state value. However, this was not conclusively observed during the current set of experiments. This trend can be understood better when one looks at the interface between the base alloy and the oxide scale. Alumina shows up in the back-scattered images as a very thin dark line, and usually forms just below the bright phase in the scale (MoO_2). Hardly any alumina forms within the first hour of oxidation. However, with increasing time, the amount of alumina increases steadily and covers a large area of the alloy. Therefore, despite the initial mass loss due to volatilization, indications are that the alumina will eventually seal the alloy surface.

The scale thickness increases in proportion to the mass change; this would be an expected result for alloys that gain mass on oxidation. In this case however, the fact that the scale thickens irrespective of the mass loss indicates that the mass change plots can be deceptive and the actual amount of Mo lost due to formation and subsequent volatilization of

MoO_3 may actually be more than indicated by the mass change vs. time plot. The microstructures shown in Figure 4.4(b) were taken from different coupons. Hence it is difficult to map one on to the other; even then, it suggests that oxidation proceeds by formation of initial “seeds” or regions of undulation that penetrate the alloy to a larger extent than the rest of the scale, and this is followed by “growth” or “coarsening” of these undulations with time.

4.4.4 Effect of alloy microstructures

Figure 4.5 (a) and (b) shows the oxide scale formed at 1200°C for alloys processed using two different routes. The alloy shown in figure 4.5(a) was made by suction-casting a 6.25 mm-diameter rod, whereas the alloy in figure 4.5(b) was an annealed drop-cast rod (also of 6.25 mm diameter). Figure 4.5 (c) and (d) show the microstructures of the suction-cast and the annealed alloys respectively. It can be seen that the suction cast alloy is characterized by very fine features, while the annealed alloy has relatively coarser features. It appears that finer microstructures exhibit better isothermal oxidation resistance. Such an observation has, in fact, already been made for Mo-Si-B alloys by Rioult et. al. [32]. Finer the size of the Mo phase, the less the amount of Mo lost due to volatilization, as long as the Mo phase does not have a high degree of connectivity.

A finer feature with a high aspect ratio would also require a longer diffusion path per unit volume of oxygen, thereby resulting in a greater pressure drop. At lower oxygen pressures, MoO_2 , rather than MoO_3 is formed, and this has been confirmed from the SEM images shown in figure 4.2(b) as well as x-ray diffraction patterns. MoO_2 , less volatile than MoO_3 is likely to offer improved oxidation resistance. In fact, Ellingham diagram indicates that MoO_2 is even more stable than NiO [33]. Absence of NiO can also help in suppressing the NiAl_2O_4 spinel formation. Formation of the spinel is highly undesirable since it impedes the oxidation resistance of the material. Moreover, recent work has shown that, once the spinel grows beyond a critical cluster it can erupt from the sub-surface thereby causing mechanical damage in the oxide scale [34].

Figure 4.5: Effect of microstructural length scales. (a) Oxide scale formed on a suction-cast alloy after oxidation at 1200°C for 10 hours; (b) oxide scale formed on an annealed alloy after oxidizing for the same duration; (c) microstructure of the suction-cast alloy and (d) microstructure of the annealed alloy.

4.5 Conclusions

We studied the isothermal oxidation behavior of a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy and found it to be a strong function of the oxidation temperature and the microstructure. The time dependent evolution of the alumina scale at 1200°C suggests that it might eventually seal off the surface. The trends in mass change of the specimen points in a similar direction as well. As such, this alloy system appears to hold out promise for high temperature applications.

4.6 Acknowledgements

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5. Cyclic oxidation of cast Mo-Ni-Al alloys

A paper under preparation

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5.1 Abstract

The cyclic oxidation behavior of Mo-Ni-Al alloys was studied for different alloy compositions ($\text{Mo}_{2x}\text{Ni}_{50-x}\text{Al}_{50-x}$, with $x = 7.5, 10, 12.5$ and 15), in as-cast and annealed conditions. As expected, oxidation resistance degrades with increasing Mo content. A relatively steady state effect could be observed at 1100°C for annealed alloys under 20 atom% Mo. The sizes of Mo features were seen to have a significant impact on the oxidation resistance, with the annealed alloys showing superior oxidation resistance especially at higher temperatures. The effect of oxidation and thermal shocks during cycling were addressed both from an experimental viewpoint as well as with the help of Griffith's model for stress intensification at crack tips.

5.2 Introduction

The discovery of superalloys in 1940s provided a tremendous boost for high temperature alloys. Over the years, the operating temperatures of superalloys have been increased from 400°C to approximately 1050°C [1]. However, improvements in operating temperatures have been considerably harder to come by, with the last decade seeing a rise in the temperatures by a mere 15°C . A significant constraint arises due to the relatively low melting temperatures of some of the constituent phases [1]. Additionally, pure nickel melts

around 1450°C. The major phase of the superalloys being comprised of a γ Ni based solid solution, the mechanical behavior of these alloys reduce drastically over the current operating temperatures. Refractory metal silicides were proposed as candidate materials at higher temperatures [2, 3], but issues with their brittleness [4, 5] and poor oxidation in wet environments [6] limit their implementation commercially. Currently, the operating temperatures are boosted with the addition of a thermal barrier coating (TBC), bond coats and cooling systems, with the land-based turbines being regularly operated at temperatures of 1150-1200°C. The US Department of Energy envisages turbines functioning at even higher temperatures as a part of their FutureGen program in order to boost the fuel efficiencies while reducing emissions. Such a goal calls for significant improvements in high temperature alloys. We adopted a multi-scale hierarchical sieving approach towards alloy design [7] in order to explore the phase space for prospective high temperature alloys using a combination of semi-empirical [8], *ab-initio* and experimental techniques.

Initial studies using such an approach suggested that Mo-Ni-Al system could have fairly good potential for applications at elevated temperatures. The presence of Mo is expected to help improve the fracture toughness. In fact, toughness of NiAl alloy increased from 5 to 14 MPam^{1/2} with the addition of 9 atom% Mo [9]. Isothermal oxidation behavior of a 20 atom % Mo containing NiAl alloy indicated the formation of a continuous alumina scale. However, studies on cyclic oxidation behavior of this alloy have not been reported. The phase diagram of this ternary system has been reasonably well assessed [10]. A ternary isothermal section for 1100°C is shown in figure 5.1 [11]. Alloys in the Al and Ni rich regions would conceivably have good oxidation behavior since both Ni and Al form passivating oxide scales (NiO and Al₂O₃ respectively). These alloys however would have relatively low melting temperatures. The Mo rich region, on the other hand, would offer high melting temperatures but very poor oxidation resistance due to the volatile nature of MoO₃. We report oxidation behavior of two phase alloys comprising NiAl + Mo (s.s.) with the Mo content ranging between 15 and 30 atom % with the Ni:Al ratio kept constant at 1:1. The alloys were tested in as-cast as well as annealed forms. The microstructural characteristics of these alloys and their effect on cyclic oxidation behavior were investigated.

mm respectively. Some of the cast rods were heat treated at 1550°C for 5 hours under an atmosphere of flowing ultra-high purity (99.99% pure) argon atmosphere in alumina crucibles.

5.3.2 Oxidation testing

Oxidation tests were carried out at 1000, 1100 and 1200°C. Temperatures lower than 1000°C don't favor the formation of $\alpha\text{-Al}_2\text{O}_3$. Temperatures higher than 1200°C result in massive scale spallation, even for the pure NiAl. Consequently, the test temperature range was chosen between 1000 and 1200°C. For each alloy composition six discs, approximately 1 mm thick, from two different castings of each size were cut and used for subsequent oxidation tests at 1000, 1100 and 1200°C. The results were then averaged. Use of multiple coupons was essential due to the stochastic nature of the process, a feature that will be discussed in greater details later. The oxidation process was carried out using ambient air in a horizontal cylindrical furnace. The discs were taken out every 2 hours and allowed to cool for 15 minutes, weighed and put back in the furnace for the next cycle. This led to a cyclic oxidation schedule whereby the discs were exposed to the target temperatures for 2 hours followed by exposure to ambient conditions for 30 minutes. The mass change was normalized to initial geometric area and plotted against oxidation time to obtain a measure of the oxidation kinetics.

5.3.3 Characterization

The alloys were characterized using scanning electron microscopy and x-ray diffraction. A JEOL 5910Lv scanning electron microscope (SEM) was used to characterize the microstructures of the alloys. A thin layer of gold was sputtered on the oxidized coupons to make them electrically conducting. The gold coated coupons were then copper plated and cut along their cross-section. These were then polished well for the SEM work. The phases present in the coupons as well as the oxide scale were obtained from discs cut out from the drop-cast alloy using an x-ray diffractometer (PANalytical, Philips) with a Bragg-Brentano geometry using a monochromatic Cu K_α radiation (wavelength = 1.54059 Å). The data collected over $20^\circ < 2\theta < 90^\circ$ with a step size of 0.0167 degree.

5.4 Results and Discussion

5.4.1 Microstructures and phase analysis

Figure 5.2: X-ray diffraction pattern of an as-cast $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy. The open circles denote the Mo peaks while the solid circles denote the NiAl peaks.

Figure 5.2 shows the XRD patterns for a 10 mm diameter as-cast $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy. It can be clearly seen that this pattern corresponds to a mixture of β -NiAl and Mo. While the pattern shown in this figure corresponds to the $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy in as-cast condition, it is representative of all the alloys studied in this work, with all of them showing a two phase mixture of Mo rich solid solution and the NiAl intermetallic. The full pattern refinement of the diffraction pattern was carried out using the GSAS software [12] and the lattice parameters of Mo and NiAl were found to be 3.16 and 2.89 Å respectively, which is in good agreement with literature data [13, 14]. This indicates that quite possibly, there is very little solubility of Ni and Al in Mo or of Mo in the β -NiAl. The lattice parameters don't change much as Mo content

increased from 15 to 30 atom% Mo, with the only significant change in the diffraction pattern being the relative phase fractions of Mo and β -NiAl.

Figure 5.3 shows the variation in microstructure as we move from the edge of a 10mm casting to the center of a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy. Heat transfer occurs in an outward radial during the drop casting process. Since the heat transfer is much more efficient through the walls of the water cooled copper mold as compared to the liquid melt itself, the Mo dendrites are much finer and have a higher aspect ratio at the edge of the casting than the center albeit the variation in the aspect ratio is much less after the initial 1.25 mm.

Figure 5.3: Microstructure variation across the cross-section of $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy coupon from the edge to the center. (a) Microstructure at the edge; (b) Microstructure at a depth of 1mm; (c) Microstructure at the center.

Figure 5.4 (a)-(d) shows the microstructures of the as-cast alloys as a function of composition. These microstructures are representative of the bulk of the alloy, at a distance of about 1.5mm from the mold walls. It can be seen that the microstructures consist of two phases – a dendritic Mo rich phase and an interdendritic NiAl phase. The inter-dendritic region also contains some Mo + β -NiAl eutectic microstructure. Energy dispersive spectroscopy (EDS) showed that Mo rich phase is almost pure Mo with rest being a combination of Ni and Al.

The NiAl phase showed an approximately equiatomic composition of Ni and Al. This result is in complete agreement with the results obtained from x-ray diffraction as well as the Mo+NiAl two-phase field in the ternary isotherms corresponding to the nominal composition of the alloys. Mo is the higher melting of the two phases and is the primary solidifying phase during the casting process. As the Mo dendrites grow with very little Ni and Al solubility, the

surrounding interdendritic liquid becomes enriched in Ni and Al and greatly depleted in Mo. Upon further cooling, the liquid freezes following a eutectic reaction to result in an interdendritic matrix of NiAl with a small amount of eutectic lamellae of Mo. As the composition of Mo is increased in the alloy, it can be seen that the fraction of eutectic phase in the inter-dendritic region goes down. Given that the eutectic composition is at approximately 9 atom % of Mo, this reduction in the amount of the eutectic can be easily explained on the basis of the lever rule. Additionally, with an increase in the Mo content, the Mo dendrites grow progressively thicker.

Figure 5.4: Scanning electron micrographs of alloys with (a) 15% (b) 20% (c) 25% and (d) 30% Mo, with the balance being equiatomic NiAl.

Figure 5.5 shows the microstructures of a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy in as-cast and annealed conditions. Annealing was done at 1550°C for 10 hours. It can be seen that the interdendritic eutectic lamellae in the alloy undergoes a significant amount of coarsening as a result of the annealing process. Visually, this coarsening is much more prominent at the radial edge of the cast coupons and in the interdendritic regions as opposed to the core of the cast coupons or the Mo rich primary dendrite arms. In other words, the finer the features, the more are they likely to coarsen. This suggests the coarsening to be predominantly as surface energy driven process, with the reduction in specific surface area (and consequently surface energy) being the key driving force. The minimum Mo size observed in the annealed microstructure was on the order to 2-3 microns suggesting that features coarser than this would be relatively resistant to coarsening.

Figure 5.5: Microstructures of (a) as-cast alloy and (b) annealed alloy after annealing at 1550°C for 6 hours.

5.4.2 Oxidation reactions

The binary Mo-O phase diagram was developed by Brewer and Lamoreaux [15]. From this phase diagram, it can be seen that MoO_3 is easy to volatilize; however, a small oxygen deficit can push the composition towards the liquid region. This would result in formation of some amount of liquid as the alloy cools down during the cyclic oxidation process. The Mo_8O_{23} , Mo_9O_{26} and Mo_4O_{11} phases are stable only below 820°C . Hence, depending on the amount of oxygen available, the oxidation products are likely to be either MoO_3 or MoO_2 . Additionally, the

MoO₂ and the MoO₃ thus formed would react with the other oxides that are formed during the oxidation process.

Figure 5.6: Ternary isotherms of (a) Ni-Mo-O; (b) Ni-Al-O; (c) Mo-Al-O and (d) pseudo-binary phase diagram of NiO-Al₂O₃ [16]

Jacobs et. al. studied the ternary isothermal section of Ni-Mo-O system at 1100°C [17]. The isothermal section shown in figure 5.6(a) indicates that NiO, MoO₂ and MoO₃ can indeed coexist. Furthermore, with a slightly off-stoichiometric MoO₃ condensing to a liquid phase, the liquid MoO₃ and NiO can react, with the presence of liquid favoring the kinetics of the reaction

in order to yield NiMoO_4 . Kuznetsov [18] states that the only ternary compound formed in the Ni-Al-O system is the NiAl_2O_4 spinel and is stable over the temperature range of interest in this study, with a significant amount of off-stoichiometry being allowed on the Al_2O_3 side of this structure, as seen in figure 5.6(b). An isothermal section of the Mo-Al-O system at 1400°C , shown in figure 5.6(c), was calculated by Gubbels et. al. [19]. Assuming that no further compound formation occurs at lower temperatures, it can be seen that no ternary compound forms in this system. Therefore, based on the information gleaned from the isothermal sections, the oxidation of Mo-Ni-Al alloys would be expected to result in the formation of MoO_3 , MoO_2 , NiO , Al_2O_3 , NiAl_2O_4 and NiMoO_4 .

Among these reactions, only the first three reactions contribute to the mass change of the alloy during the oxidation process. NiO eventually gets reduced resulting in the formation of alumina. As such, the kinetics of alumina formation or NiO formation is considerably slower than the volatilization of Mo. The parabolic rate constant for oxidation of NiAl has been estimated to be $2 \times 10^{-5} \text{ mg}^2 \cdot \text{cm}^{-4} \cdot \text{s}^{-1}$. On the other hand, Mo oxidation follows a linear kinetics with a rate constant of $-16.4 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ at 1100°C [20]. Therefore clearly, the kinetics of the process will be influenced to a larger extent by the MoO_3 formation and its subsequent volatilization.

Figure 5.7 shows the x-ray diffraction pattern collected from the scale that spalled off during the oxidation process. The pattern was seen to contain a number of phases, principal amongst them being NiO , NiAl_2O_4 , NiMoO_4 , NiAl , Mo and small amounts of Al_2O_3 . It is well known that the initial oxidation product of nickel aluminides is NiO . With time, the NiO gets reduced to Ni by the Al since Al_2O_3 is an oxide that is thermodynamically more stable than NiO , although its formation in the initial stages is not favored by relatively sluggish kinetics [21]. Therefore cracks in NiAl could result in spalling off of some Ni. Additionally, the formation of the NiAl_2O_4 spinel in the alloy subsurface could contribute to the spallation. It has been demonstrated that nucleation of the spinel, followed by growth beyond a certain critical cluster size results in “eruptions” of the spinel through the surface [22], which could be yet another cause for spallation.

Figure 5.7: X-ray diffraction pattern obtained from the spalled scale.

5.4.3 Stochastic nature of the process

Figure 5.8 shows the oxidation kinetics under cyclic conditions of the nine coupons cut from a 6.25 mm diameter as-cast $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy at 1200°C. A significant amount of spread can be seen in this data. The oxidized microstructures shown in the subsequent sections will correspond to the coupons that show mass change kinetics that are closest to the average values. It should be further noticed from Figure 5.8 that the curves can be divided into three distinct categories with the differently colored data points corresponding to different castings. Minor differences resulting in small changes in microstructures from one casting to another (even for same diameter castings) can result in significant changes in the oxidation kinetics, although for the most part, coupons from a single casting are fairly comparable. The amount of Mo lost due to volatilization will depend on two factors – the size of Mo grain and the connectivity of the Mo grains. Hence, a small change in the connectivity of Mo, especially that of the larger phase features will have a fairly significant bearing on the oxidation kinetics, leading to a relatively large spread in the oxidation data.

Figure 5.8: Variation in oxidation kinetics for different coupons of an as-cast $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy. The alloy coupons were oxidized at 1200°C under cyclic conditions in as-cast conditions.

5.4.4 Effect of oxidation temperature

Figure 5.9: Effect of oxidation temperature on oxidation kinetics of as-cast alloys.

Figure 5.9 shows the oxidation behavior of as-cast alloys at three different temperatures. As the oxidation temperature increases, the rate of MoO_3 volatilization increases resulting in a more rapid mass loss at elevated temperatures, with the effect becoming more prominent at higher temperatures. The vapor pressure of MoO_3 exceeds one atmospheric pressure at 1100°C [23]. Consequently, it becomes much easier to volatilize MoO_3 above 1100°C , and the difference in oxidation kinetics at 1000 and 1100°C is much less than the difference in kinetics at 1100 and 1200°C .

Figure 5.10 shows low magnification images of the oxide scale of cast alloys oxidized at different temperatures. The oxidation behavior of the alloy can be considered in terms of loss of Mo as MoO_3 and the formation and growth of the alumina scale. Mo is known to start pesting at 700°C and the vapor pressure of MoO_3 rapidly increases with temperature. This explains why the variance in oxide scale thickness is significantly more between alloys oxidized at 1100°C and 1200°C as compared to the variance in scale thickness between alloys oxidized at 1000°C and 1100°C .

Figure 5.10: Low magnification SEM images of the oxide scales of as-cast and annealed alloys having a diameter of 6.25mm. These images correspond to as-cast alloys oxidized at (a) 1000°C; (b) 1100°C; (c) 1200°C.

5.4.5 Effect of alloy composition

Figure 5.11: Effect of composition on oxidation kinetics.

Figure 5.11 shows the effect of alloy composition on the oxidation kinetics at 1200°C. It is quite clear that oxidation resistance is favored by a lower Mo composition. A lower Mo content leads to a sparser Mo distribution within the alloy resulting in a lower degree of

connectivity. Additionally, in the higher Mo alloys, MoO_3 volatilization opens up new pores and pathways into the alloy. A lower Mo content also corresponds to a higher NiAl content, with more Al being available to form a protective alumina scale.

5.4.5 Effect of annealing and alloy microstructures

Figure 5.12 shows a comparison between the oxidation kinetics of annealed and cast alloys. It becomes clear that annealed alloys perform significantly better than cast alloys especially at 1200°C. At the lowest test temperature (1000°C), the cast alloys show a better oxidation resistance as compared to the annealed alloys. At 1100°C, both cast and annealed alloys show a very similar oxidation behavior. At lower temperatures, the overall oxidation kinetics is relatively sluggish. The oxidation behavior is largely dominated by the size of the Mo grains and consequently, the cast alloys show a much slower mass loss due to significantly finer Mo features. With slow oxidation kinetics, the size of the surface Mo grains is more significant than their connectivity. At 1100°C, a fine balance exists between the size of the Mo features and the degree of connectivity. As a result, the oxidation behavior is largely similar beyond the initial mass loss.

Figure 5.12: Higher magnification SEM images of the oxide scale and the internal regions of the coupons for a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy, with 10mm diameter, oxidized cyclically at (a) 1000°C; (b) 1100°C and (c) 1200°C.

Figure 5.13 shows a comparison of the scales formed in cast and annealed alloys at 1000 and 1100°C. It can be seen that at 1000°C, the annealed alloys have lost a greater amount of

Mo due to volatilization of the relatively larger Mo features. The features in the cast alloys are finer, with a significantly larger amount of eutectic present at the surface. The eutectics consist of very fine parallel lamellae. Consequently, only a small amount of mass was lost due to exposure with air. The lack of interconnectivity amongst the eutectic lamellae also prevents the formation of oxygen pathway into the alloy. In Figure 5.13(c) and (d) it can be seen that the oxide scale looks roughly the same which is consistent with the nature of the mass change seen in the oxidation plots in figure 5.12.

Figure 5.13: SEM micrographs of the oxide scales in (a) cast alloys at 1000°C; (b) annealed alloys at 1000°C; (c) cast alloys at 1100°C and (d) annealed alloys at 1100°C.

Figure 5.14: SEM images of the oxide scale and the internal regions of the coupons for a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy 1200°C.

(a) Oxide scale of an as-cast alloy; (b) microstructure of an as-cast alloy prior to oxidation; (c) image of crack network in the scale; (d) oxide scale of an annealed alloy; (e) internal features of an as-cast alloy and (f) internal features of an annealed alloy.

Figure 5.14 shows SEM micrographs of the cast and annealed alloys oxidized at 1200°C. The first three micrographs deal with the oxide scale whereas the last two deal with the interior of the alloys post oxidation. Figure 5.14(a) shows a large network of cracks at the surface of the alloy that was exposed to air during the oxidation tests. The crack network can be best described as a tree-like structure. The average distance between the cracks is approximately 10 μm . The second micrograph shows the dendrites in an alloy prior to oxidation. Coincidentally, the secondary dendrite arm spacing is approximately 10 μm as well. Micrograph in Figure 5.14(c) shows fine cracking around a region where significant mass loss occurred (as shown with an arrow). Figure 5.14(d) shows the micrograph of the annealed alloy. The degree of cracking in the scale subsurface of the annealed alloy was much less than the cast alloy.

Figure 5.14 (e) and (f) show images of the central region of the cast and annealed alloys post-oxidation. These regions were able to maintain their integrity throughout the oxidation testing and did not show any matrix cracking at all. It suggests that during oxidation at 1200°C all the cracking is confined largely in the scale region at the surface of the alloy and to a very small extent in the immediate subsurface. The coefficient of thermal expansion (CTE) of pure Mo varies between 5.25×10^{-6} and $7.25 \times 10^{-6} \text{ K}^{-1}$ [24] whereas that of NiAl varies between 14×10^{-6} and $16 \times 10^{-6} \text{ K}^{-1}$ [25, 26]. Bei et. al. have also studied the thermal expansion of a directionally solidified eutectic NiAl-Mo alloy in both longitudinal and transverse directions (with respect to the Mo fibers grown during DS of this alloy), and found the values to be roughly 10 % within the values predicted by using a rule of mixtures [25]. Given the significant difference between the CTEs, it is possible that the observed cracking is induced by thermal cycling. However, the alloy core, which has been subjected to thermal cycling but not exposed to air, has maintained its integrity and did not show up any cracking. This leads us to believe that while thermal cycling can indeed generate significant misfit stresses, they are not sufficient to result in cracking in the alloy on its own. This observation, coupled with the cracks observed at the surface in the oxide scale region would lead us to suggest that the cracking could in fact result from an interaction of thermally induced stresses due to thermal cycling and the oxidation process. Furthermore, given that the major difference between cast and annealed alloys is in their microstructures,

there is a strong possibility of the alloy microstructure being yet another significant contributor towards the cracks observed.

Figure 5.15 shows a schematic description of a possible mechanism for understanding the cyclic oxidation behavior at 1200°C. The Mo dendrites in the alloy are oxidized and volatilize leaving a notch like void in the NiAl matrix. The degree of stress intensification is dependent on the sharpness of the notch tip according to Griffith theory.

Alloys in as-cast conditions have features that are much sharper with a higher aspect ratio as compared to annealed alloys. Annealing results in coarsening of the microstructure assuming a relatively nodular shape, thereby reducing the stress intensity factor. This may explain why annealed alloys show relatively improved cyclic oxidation resistance in comparison to the cast alloys.

Figure 5.15: (a) A schematic representation of the alloy, pre-oxidation; (b) An idealized post-oxidation scenario, with the Mo dendrite volatilizing completely; (c) schematic representation of stress intensification at dendrite arm tip, with the discontinuity due to the volatilized Mo acting as a notch.

In addition to thermal stresses, the oxidation process itself would contribute to the stress build up due to the Pilling-Bedworth ratios (expressed as the volume ratio of oxidized-to-unoxidized material) of most of the oxides is greater than one. Additionally, formation of NiMoO_4 would stress the alloy significantly. In the temperature range of interest, a slight deficit of oxygen would drive the Mo-O phase space into the liquid region between MoO_2 and MoO_3 .

Additionally, NiO can form at the interface between a Mo dendrite/lamellae/nodule and the NiAl matrix. Reaction between oxides of Mo in liquid form with the NiO results in formation of a solid NiMoO_4 phase, which should result in a volume contraction. A phase forming with volume contraction at the interface of two phases will induce tensile stresses that can result in cracks occurring at the Mo/NiAl interfaces. With part of the Mo already volatilized, it is also conceivable that these stresses would then be accommodated by spallation of any remaining un-volatilized Mo itself, in addition to the matrix cracking in NiAl.

5.5 Conclusions

We studied the cyclic oxidation behavior of Mo-Ni-Al alloys in the Mo + NiAl phase field and found that the oxidation behavior is a strong function of the alloy composition, oxidation temperature and microstructure. As expected, a higher amount of Mo was found to be detrimental to the oxidation behavior. The oxidation behavior at 1200°C was observed to be significantly higher than expected based on oxidation behavior at 1000 and 1100°C. This was attributed to the extensive matrix cracking that occurred during the thermal cycling at this temperature. It was further observed that annealing, leading to subsequent blunting of the Mo features, resulted in significantly improved cyclic oxidation response. Based on this, a simple phenomenological model was proposed using Griffith's theory of crack growth.

5.6 Acknowledgements

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5.7 References

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6. Microstructures and oxidation behavior of sintered Mo-Ni-Al alloys

An article being prepared for submission

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6.1 Abstract

A 2D model was used to assess a composition region where a continuous oxide scale could be formed for Mo-Ni-Al alloys. The alloys were synthesized using reactive liquid phase sintering. Microstructures of these alloys were studied as a function of composition and sintering parameters. The alloys were oxidized under isothermal conditions at 1100 and 1200°C for 10 hours. Furthermore, cyclic oxidation tests were carried out in the 1000 – 1200°C temperature ranges for 8 hours, with each cycle comprising of 2 hours at the target temperature followed by a 30 minute exposure to the ambient atmosphere. It was seen that isothermal oxidation behavior of these alloys was significantly better than cyclic oxidation. Comparisons with previous work done with cast alloys showed that sintered alloys show an improved oxidation resistance under cyclic conditions.

6.2 Introduction

A number of intermetallics in Al and Si containing systems have been considered as prospective candidates for ultra-high temperature applications [1-5]. However, most intermetallics are extremely brittle; despite having high melting temperatures and good oxidation and creep resistance, they lack adequate ductility and toughness, with the K_{IC} being usually lower than $10 \text{ MPa}\cdot\text{m}^{1/2}$ for most. Therefore, these alloys can't be used as a single phase

material for high temperature structural applications, and would need to be alloyed in order to have a second phase that can impart the requisite ductility and toughness.

This is also the basic architectural framework of a number of Ni-Al and Mo-Si based alloys for high temperature applications. The Ni based alloys, however, are restricted to under 1050°C due to the relatively low melting temperature of Ni, Ni₃Al and a number of other constituent phases [6]. Mo-Si based alloys, on the other hand can't provide a simultaneous combination of strength, ductility and oxidation resistance, especially in moist environments [7-9]. Hence, we attempted to develop a new alloy system building on the knowledge base available for nickel aluminides and silicides. The multi-stage hierarchical sieving technique that led us to the Mo-Ni-Al system has been described elsewhere [10].

Mo-Ni-Al alloys show a tendency of forming a protective alumina scale under isothermal conditions. However, under cyclic oxidation conditions, they fail to form a permanent oxide scale. It was surmised that the poor performance of cast alloys was largely due to the presence of stress raisers, as a result of volatilized Mo dendrite tips that act as cracks within the NiAl matrix. In order to better understand if sharp cracks formed by oxidative volatilization of Mo, and potentially eliminate it, we processed alloy microstructures with nodular features and tested them under cyclic oxidation conditions. Prior to the oxidation experiments, we used a simple 2D model to assess the composition range where the alloys would tend to form a protective oxide scale, and used the computational results to determine the composition range and processing conditions to produce the desired microstructure.

6.3 Preliminary calculations

6.3.1 Model formulation

A simplified 2D probabilistic Cellular Automata model, with the following set of assumptions, were used for the preliminary calculations –

- a) Mo reacts with oxygen to form MoO₃, which volatilizes leaving the space exposed to fresh oxygen from the air.
- b) If NiAl surface gets exposed due to volatilization of MoO₃, Al₂O₃ forms and seals the surface preventing further oxidation.

- c) Once formed, Al_2O_3 does not spall.
- d) A 2D picture is representative of the alloy cross-section and the microstructure is invariant across the sample.
- e) Each grid in the lattice depicting the microstructure represents a single grain. Periodic boundary conditions are assumed at the vertical edges of the cell.
- f) Oxygen present in a given grid can penetrate a maximum of one grain diameter in any direction in a single time-step.

A microstructure was created using random numbers generated by the computer code. The computer clock was used to seed the random sequence, which otherwise would have been a pseudo-random sequence with same numbers being generated for every run under identical conditions. The upper bound of the random sequence was set to 100. The computation was performed on a 150 x 150 square lattice.

Two lists were created, one of which stored the location of the oxygen, while the other contained a description (in terms of the assigned number value) of the phases. The calculations were carried out assuming a Von Neumann neighborhood, with only the edge sharing cells will lead to oxygen penetration. Each oxidation step consisted of scanning the neighborhood around the oxygen cells, with the appropriate oxidation steps being carried out. In event of the oxygen cell being adjacent to both NiAl and Mo cells, Mo was preferentially oxidized.

6.3.2 The stochastic nature of the process

Our preliminary calculations showed that the oxidation behavior in this system could be a highly stochastic process, with even minor changes in alloy microstructures playing a profound role. The stochastic nature of this process can be gauged from Figure 6.1. This figure shows the number of Mo grains lost for a Mo 30% alloy over the first 90 time steps. All the five curves represent the oxidation behavior of the same alloy, but represent different runs of the code. All parameters were kept constant except a new microstructure was generated for each run. The overall number of Mo grains was almost the same; however the number of Mo grains in the first layer of the microstructure ranged between 31 and 51. This illustrates the degree to which the randomness of the microstructure affects the oxidation results. The number of Mo grains lost varies significantly from low of about 60 to 110, nearly a two-fold variation. This

result is in fact in agreement with our experiments on cyclic oxidation behavior of cast Mo-Ni-Al alloys [11]. Under experimental conditions, microstructure of alloys could vary even for the same composition and processing routes. For a system like Mo-Ni-Al, where the phases have widely different oxidation behavior, it is not surprising that getting very similar readings would be impossible. At best, one can expect the results from different runs to be of the same order of magnitude, but they could still differ significantly.

Figure 6.1: Number of Molybdenum grains lost during different runs of the code, under same conditions, showing up the stochastic nature of the process.

In such a system, the mass change numbers, or even the metal recession rate is not likely to be a good indicator, especially if studies are carried out with very little variation in compositions. Even the time required to attain a steady state would not be an effective parameter. Analyzing Figure 6.1, it becomes evident that for different runs, the time required to attain steady state for different runs varied as much as by a factor of 2. It remains an open problem on ascertaining the limiting performance of a given alloy in this system for a given composition and processing route.

6.3.3 Effect of alloy composition

The code was run to test the effect of Mo content on the oxidation process. This was done by analyzing data and plotting it for Mo grains oxidized per time step, cumulative amount of Mo lost and Mo grains remaining at the end of each time step. The code was run for compositions varying from 10 to 90% Mo at intervals of 10% we also run compositions

corresponding to 2, 5, 55 and 65 % Mo. However, only the results for 20, 30, 60 and 80 % Mo has been shown in figure 6.2 for the sake of clarity.

Figure 6.2: Oxidation behavior of alloys with a wide range of Mo content. (a) Number of Mo grains oxidized at each time step; (b) Cumulative number of grains oxidized; (c); a blow up of the figure (b) for the lower Mo content alloys and (d) The number of Mo grains remains unoxidized in the alloy. All the legend numbers refer to the Mo content in the alloys.

Figure 6.2(a) shows the loss of Mo grains at each individual time step. It can be seen that the alloys with a lower Mo composition taper out to a very low value almost all at once. However, the number of grains lost at each step maintains a fairly constant value for higher Mo contents (60 and 80%). The presence of a large amount of Mo would provide easy oxygen

supply to Mo. Greater Mo loss also results in formation of connected pores, which allows for easier transport of oxygen through the material. At intermediate Mo contents, the probability of oxygen in contact with Mo grains, and connectivity of porosity are lower leading to decrease in number of Mo grains oxidized as well as higher fluctuations in the curve as manifested in the plots. Figure 6.2(b) shows the cumulative loss of Mo as a function of time. The alloys with low Mo content (< 30%) appear to reach a steady value relatively quickly. However, the 60 and 80% compositions show a steady linear loss. For 60% composition, the grain loss is somewhat non-linear especially at higher time steps reflecting the fluctuations seen in the previous figure. Figure 6.2(c) shows a magnified section of figure 6.2(b) in order to focus on the behavior of lower Mo content alloys. It can be seen that the lower Mo alloys tend to exhibit a steady state after only a few time steps, thereby indicating a possibility of forming a hermitic oxide scale, unlike the higher Mo content alloys that show monotonically increasing Mo loss. Figure 6.2(d) shows an interesting result. Due to the extremely interconnected network of Mo at higher alloy compositions, Mo content of the 80% Mo is lower after the oxidation process compared to 30% Mo alloy. Additionally, due to volatilization of the MoO_3 , porosity is higher, providing a connected path for continuous oxidation of the alloy.

6.4 Experimental details

6.4.1 Materials and alloy synthesis

Sintered alloys were prepared using pure elemental powders of Mo (Alfa Aesar, 3-7 μm , 99.95%), Ni (Materials Preparation Center (MPC), Ames Laboratory, < 45 μm , 99.9%) and Al (ALCOA, 1-5 μm , 99.95%). A number of compositions ranging from 15 atom% Mo to 30 atom% Mo, with the balance being equiatomic NiAl, were synthesized using this method. The powders were first blended for 15 minutes in SPEX 8000 high energy ball mill and then dry pressed at 24 MPa in a tool steel die to obtain compacted pellets of 8 mm diameter. The compacted pellets were then sintered in alumina crucibles having 9.5 mm inner diameter under an atmosphere of flowing ultra-high purity argon. Kubaschewski developed a pseudo-binary NiAl-Mo phase diagram, in the 0-20 % Mo range [12]. According to this phase diagram $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy will

melt at 1850°C and the eutectic is at 1600°C. Therefore an alloy with this composition exists in a mushy between 1600 and 1850°C, with the NiAl in liquid state and the Mo in solid state. For compositions that contain more than 20 atom % Mo, the liquidus temperature would be even higher than 1850°C. Therefore, a sintering temperature of 1800°C and a time of 30 minutes were used.

6.4.2 Oxidation testing

Oxidation tests were carried out at 1000, 1100 and 1200°C in ambient air in a cylindrical tube furnace. At each temperature- composition combinations, oxidation tests were run in triplicate and the data was averaged. The thicknesses of the discs were approximately 1 mm. The discs were taken out every 2 hours and allowed to cool for 30 minutes, following which they were weighed and put back in the furnace. This led to a cyclic oxidation schedule whereby the discs were exposed to the target temperatures for 2 hours followed by exposure to ambient conditions for 30 minutes. The mass change data and the initial surface area of the discs was used to calculate the mass change per unit area and plotted against oxidation time. For isothermal tests, the coupons were exposed to the desired temperature for a given duration and pulled out.

6.4.3 Characterization

A JEOL 5910Lv scanning electron microscope (SEM) was used to characterize the microstructures of the alloys. Oxidized samples for SEM were prepared by first coating a thin layer of gold on the oxidized coupon. The coupon was then copper-plated. The coupon was then cut to obtain a cross-sectional sample, which was polished well for the SEM work. The phases were confirmed using x-ray diffraction (XRD) using a (PANalytical, Philips) x-ray diffractometer with a Bragg-Brentano geometry using a monochromatic Cu K_{α} radiation (wavelength = 1.54059 Å. Data was collected between $2\theta = 20^{\circ}$ to 90° with a step size of 0.0167 degrees.

6.5 Results and Discussion

6.5.1 Microstructures and phase analysis

Figure 6.3: X-ray diffraction pattern from the sintered $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ compact. The solid circles represent NiAl whereas the open circles represent Mo.

Pure Al melts 660°C , while pure Ni melts 1455°C . The highest melting binary compound (β -NiAl) in the Ni-Al phase diagram melts at 1640°C . A comparison of formation enthalpies of intermetallics in the Ni-Al, Ni-Mo and Mo-Al binaries and the Mo-Ni-Al ternary shows that the most negative heat of mixing occur for the Ni-Al intermetallics [13, 14]. Hence it is reasonable to expect that a process like liquid phase sintering, where the compact is held for a reasonably long time at an elevated temperature, thermodynamics will prevail and the most stable compounds will tend to form. Additionally, given that Mo never melts completely while Ni and Al do (and consequently have greater atomic mobility during this process), from a kinetics standpoint, Ni-Al intermetallics would be preferred over any intermetallics involving Mo. A homogeneously dispersed stoichiometric mixture ensures that formation of any intermetallic other than the β -NiAl would require relatively long range diffusion. Even if there are local composition fluctuations, the large phase width of β -NiAl still favors the formation of this

compound. Hence, this was expected to turn out to be the final product even if there were some local compositional fluctuations.

Due to the relatively low fraction of Mo, the compact starts to soften and flows. The compact was held at the peak temperature for a while in order to attain a good degree of homogenization and densify. Figure 6.3 shows the x-ray diffraction pattern of a sintered compact ($\text{Mo}_{30}\text{Ni}_{35}\text{Al}_{35}$). The pattern clearly shows that the sintered alloy is a two phase mixture consisting of Mo and NiAl. Rietveld refinement carried out using the GSAS software [15] showed the presence of approximately 32 atom percent Mo, in agreement with the nominal composition, with the balance being NiAl.

Figure 6.4 shows the microstructures of sintered alloys with different compositions. It can be seen that these alloys tend to have nodular features, although the signature rod-like eutectic microstructure is also observed, especially for alloys containing lower levels of Molybdenum. The microstructure evolution can be better understood if we consider the Mo-Ni-Al system as a pseudo-binary system, with the pure Mo and pure NiAl being the two end members. The alloys are heated to a mushy region where both the liquid and the solid phase coexist together and held for 30 minutes in order to allow the liquid to penetrate the pores in the dry-pressed compacts. As the alloys cool down, partitioning occurs in accordance with the lever rule, with Mo forming as the solid phase, leaving the surrounding liquid rich in NiAl, corresponding to the eutectic composition ($\text{Mo}_9\text{Ni}_{45.5}\text{Al}_{45.5}$). The sintering temperature of 1800°C is well above the recrystallization temperature of Mo (1473°C) [16]. The initial particle size of Mo powders used was in the $3\text{--}7\text{ }\mu\text{m}$ range. The final grain size of the sintered compacts is in the $40\text{--}60\text{ }\mu\text{m}$ range. This indicates significant agglomeration and coarsening of the Mo powders during the sintering process. The lower the Mo content, the larger is the liquid fraction when the compact starts cooling. Consequently, it becomes easier for the Mo to grow in the liquid, opposite to the direction of heat extraction following a dendritic solidification pathway. Therefore a small amount of extremely coarse dendritic structure (dendrite thickness $\sim 30\text{ }\mu\text{m}$) can be observed. As the Mo content increases, the process starts resembling conventional liquid phase sintering more closely. A lower amount of liquid is available in which the Mo can

grow, and the Mo phase starts forming with even more nodular shapes. At the same time, the volume fraction of eutectics decreases significantly.

Figure 6.4: Sintered microstructures with compositions (a) $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$; (b) $\text{Mo}_{25}\text{Ni}_{37.5}\text{Al}_{37.5}$ and (c) $\text{Mo}_{30}\text{Ni}_{35}\text{Al}_{35}$.

6.5.2 Isothermal oxidation

Figure 6.5 shows the isothermal oxidation behavior of a sintered alloy with nominal composition $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ at 1200°C . It can be seen that the curve tends to converge towards a constant steady state value. The different phases formed during the oxidation process were identified using x-ray diffraction and found to consist primarily of Al_2O_3 , NiAl_2O_4 , NiMoO_4 , MoO_2 and MoO_3 , which is consistent with our previous results on oxidation of cast alloys.

Figure 6.5: Isothermal oxidation of a sintered $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy at 1200°C .

Figure 6.6: Oxide scale microstructures at (a) 1100°C and (b) 1200°C after isothermal oxidation for 10 hours.

These alloys developed an extremely irregular oxide scale. The overall morphology of the scale in a Mo-Ni-Al alloy is dependent on the initial microstructure, especially on the size and shape of Mo grains exposed on the surface. As can be seen from figure 6.4, Mo features of over $50\text{ }\mu\text{m}$ size are not uncommon. On the other hand, adjacent to these features are regions of eutectic phase (of comparable dimensions) that is rich in NiAl. The Mo features oxidize rapidly, resulting in a deep inward progress on the scale. The NiAl regions are oxidation

resistant, and show a very thin oxide scale. The isothermally oxidized microstructures can be seen in figure 6.6. Micrographs represent regions of the oxidized coupons that show a relatively uniform and thin scale. It can be seen that the total oxide scale and subsurface Al_2O_3 are much thicker at 1200°C as expected.

6.5.3 Effect of alloy composition on cyclic oxidation

Figure 6.7 shows a comparison of the cyclic oxidation kinetics for alloys with different levels of Mo content. It can be seen that the difference between 25 and 30 atom% alloys is much more than the difference between 15 and 20 atom % or 20 and 25 atom% at 1000°C , although at a higher temperature (1200°C), the gap between 20 and 25 atom % Mo widen up. These observations are in perfect agreement with the results from our 2D oxidation model discussed above.

Figure 6.7: Comparison of cyclic oxidation behavior with different Mo content at (a) 1000°C and (b) 1100°C .

6.5.4 Effect of temperature on cyclic oxidation

Figure 6.8 shows the effect of temperature on the cyclic oxidation behavior of a $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy. The mass loss with cyclic oxidation can be seen in figure 6.8(a). The alloy continues to lose mass at 1000°C and at 1200°C , while reaching a steady state at 1100°C . This behavior can be understood by considering the oxide scale growth rates. Brumm and Grabke reported the parabolic rate constants for the growth of alumina over a range of temperatures

[17]. At 1000°C, the growth rate of θ -Al₂O₃ is faster than that of α -Al₂O₃. As the alloy is placed in a furnace and subjected to heating in air, θ -Al₂O₃ forms first and starts growing but does not offer as good an oxidation resistance as α -Al₂O₃ since oxygen transport rate through θ -Al₂O₃ is higher in comparison to the α -Al₂O₃ (as evidenced from the oxide scale growth rates at this temperature for both the variants of alumina, 9×10^{-7} mg²/cm⁴ for θ -Al₂O₃ vis-à-vis 1×10^{-8} mg²/cm⁴ for α -Al₂O₃, nearly two orders of magnitude difference). However, the α -Al₂O₃ is thermodynamically more stable than θ -Al₂O₃ at this temperature and forms eventually. The slow growth rate of α -Al₂O₃ prevents formation of continuous protective scale in the experimental time frame studied in the current work. The growth rate of the α -Al₂O₃ is an order of magnitude higher at 1100°C ($\sim 9 \times 10^{-7}$ mg²/cm⁴), and hence forms a protective scale faster. The growth rate is even higher at 1200°C ($\sim 7 \times 10^{-5}$ mg²/cm⁴) leading to a considerably thicker scale as compared to 1100°C. As a result, the stress build-up at the interface is higher, resulting in scale spallation. In Mo-Ni-Al alloys, the issue gets more complicated with the presence of two additional oxides (MoO₂ and NiMoO₄) with coefficients of thermal expansion (CTE) mismatch. The mechanical stability of the scale reduces further due to the convoluted scale morphology. Additionally, the vapor pressure of MoO₃ exceeds 1 atmosphere at approximately 1125°C [18]. Hence, development of a protective oxide scale at 1200°C is more difficult than at 1100°C.

The oxidized microstructures can be seen in figure 6.9. The oxide scale at 1000°C does not show a continuous alumina layer as shown in figure 6.9(a). The scale formed at 1100°C, on the other hand, shows a continuous Al₂O₃ scale, shown in figure 6.9(b). At 1200°C, once again, a patchy, but thicker Al₂O₃ can be observed in figure 6.9(c), which supports the above discussion that a significantly higher growth rate combined with the presence of a variety of other oxides with different coefficients of thermal expansion could be responsible for the oxidation behavior observed at this temperature.

Figure 6.8: Effect of temperature on cyclic oxidation behavior

Figure 6.9: Oxide scale formed in cyclically oxidized alloys at (a) 1000°C, (b) 1100°C and (c) 1200°C.

Comparing the mass change plots shown in figures 6.5 and 6.8, it can be seen that the alloy shows lower mass loss under isothermal conditions as compared to the cyclic conditions.

Such a behavior has been observed numerous times for nickel aluminides, with the oxide scale spallation due to shock-induced thermal cycling being a key contributor. A comparison of the oxide scales for the two different cases, figures 6.6(b) and 6.9(c), shows that the oxide scale is better developed under isothermal oxidation. Under cyclic conditions, the overall scale thickness is higher largely due to the formation of a larger amount of secondary oxides like MoO_2 , NiAl_2O_4 and NiMoO_4 .

The as-cast Mo-Ni-Al alloys showed extensive cracking during cyclic oxidation at 1200°C [11]. Similar cracking was not observed in case of sintered alloys. In that respect, the latter resemble the annealed alloys that were previously studied [11]. This further suggests that the absence of sharp Mo features might play a major influence on the cyclic oxidation behavior of these alloys at temperatures around 1200°C.

6.6 Conclusions

A 2D model was used to assess a region of oxidatively stable compositions comprising of Mo + NiAl in the phase assembly. The calculations showed that the oxidation behavior of these alloys could be heavily stochastic with a significance dependence on the alloy microstructure. The model also indicated that the Mo content should be kept below 30% in order to obtain a continuous Al_2O_3 , and this guided the choice of the compositions for the experimental work. The Mo-Ni-Al alloys were prepared by reactive liquid phase sintering to yield microstructures with nodular Mo grains and fine eutectic phase. These alloys were studied under both isothermal and cyclic oxidative conditions. The oxidation behavior was strongly dependent on the alloy composition. It was seen that the performance of these alloys were better under isothermal conditions as compared to cyclic conditions. The cyclic oxidation behavior of these alloys was found to be comparable to the Mo-Ni-Al fabricated by casting followed by annealing in our previous work [11]. The cyclic oxidation behavior was significantly better with much lower mass loss (almost by a factor of six) and no cracking was observed in the scale subsurface in contrast to the as-cast. It appears that a fine nodular microstructure could result in significantly improved oxidation resistance in these alloys.

6.6 Acknowledgements

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7. Conclusions

7.1 The big picture

This work is part of a wider attempt at designing high temperature alloys that can operate at higher temperatures than the current Ni based superalloys under oxidizing conditions. For six decades since the discovery of Ni based superalloys, the operating temperatures have kept on increasing thanks to the efforts of various research groups. However, progress over the last decade has been extremely slow [1]. The key problem in further increasing the operating temperatures of Ni based superalloys arises from the melting temperatures of its different constituents. Pure Ni, which forms the matrix, melts at 1455°C, while the Ni₃Al precipitates melt at 1395°C.

Therefore, the key issues were – (a) is it possible to tweak existing systems to increase operating temperatures and (b) can we design a new high temperature alloy system that offer enhanced operating temperatures. In an attempt to address the first concern, we have studied the phase stability of Mo-Si alloys in order to remove the brittle phases from this alloy system. It is expected that removing the brittle phases will result in improved fracture toughness. The first part of the thesis largely focuses on this problem. The second part of the thesis deals with the second issue mentioned earlier, i.e. design of a new alloy system. In designing a new high temperature alloy system, a number of design criterion had to be met. The most important amongst these were melting temperature, oxidative stability, fracture toughness and high temperature strength. In this thesis, the focus remains on oxidative stability of an alloy system downselected using the melting temperature criterion.

Melting point has been known to have a correlation with formation enthalpy and cohesive energies [2-5]. Hence, a high negative enthalpy of formation was the first criterion

that any prospective alloy system had to meet. An experimental assessment of formation enthalpies of a large number of intermetallics is extremely time-intensive. Similarly, *ab-initio* calculations for a large number of intermetallics would be time intensive. Hence, an extension of Miedema's semi-empirical model was developed that could be used to rapidly assess the formation enthalpies of a large number of alloy systems.

Using this semi-empirical approach, a Mo + NiAl alloy was found to be suitable, with the additions of platinum group metals (PGM) like Rh, Ir and Pd showing further promise for enhanced melting temperature of the NiAl. The effect of PGM additions on the stability and oxidation behavior of NiAl is being studied separately, and the results of these studies will be utilized to expand the Mo-Ni-Al alloy system further. These studies, however, are beyond the purview of this thesis. Rather, we investigate the oxidation behavior of the base alloy system (Mo + NiAl).

7.2 General conclusions: silicides

An extension of Miedema's semi-empirical model was used to calculate the formation enthalpies of ternary alloys and applied to the Mo-Nb-Si and Mo-W-Si ternary systems. *Ab-initio* studies using the VASP software showed an increase in formation enthalpy with increasing levels of substitutions for W additions, and a decrease in formation enthalpy followed by a steady increase in case of Nb additions. Additionally, it was observed that increased levels of substitutions the Fermi surface started to move out of the pseudo-gap in the density of states. Based on these calculations, it was seen that Nb and W additions offer a possibility of destabilizing the A15 Mo₃Si phase.

Accordingly, experiments were carried out in both the ternary systems, and it was seen that Nb additions in 27.5 – 30 atom% range were adequate to remove the A15 phase. The corresponding value for W was determined to be in the 10 – 15 atom%. The W additions also seemed to result in a slightly wider three phase region where the A15, (Mo,W) solid solution and the (Mo,W)₅Si₃ co-exist. Wavelength dispersive spectroscopy indicated a preferential partitioning of Nb in the M₅Si₃ T1 phase (M=metal). On the other hand, a preferential partitioning of W into the metal rich solid solution was observed.

7.3 General conclusions: Mo-Ni-Al alloys

Miedema's semi-empirical model was used to downselect a new alloy system for ultra-high temperature applications, with alumina as the primary scale former. Preliminary calculations on a 2D grid suggested that alloys under 30% Mo content by volume would be worthwhile to explore for oxidative stability. Experimental studies showed that Mo levels in excess of 20 atom% (or approximately 25% by volume) resulted in poor oxidation resistance. The oxidative stability deteriorated with an increase in temperature over the range studied, with the difference between 1200 and 1100°C being much larger than the difference between 1100 and 1000°C. This was manifested in both, the mass losses observed during the oxidation tests, as well as the thickness of the oxide scales seen in the alloy microstructure.

Cyclic oxidation of these alloys resulted in much higher damage, especially in case of the cast alloys. A comparison of different microstructures showed a marked tendency for dendritic microstructure to perform poorly under cyclic conditions. Mo dendrites volatilize leaving behind discontinuities in the alloy. Based on the extensive cracking observed during cyclic oxidation of dendritic alloys it was concluded that the sharp discontinuities act as notches and raise the local stress levels during the cyclic oxidation process.

7.4 Scope for future work

7.4.1 The case for NiAl based coatings

The NiAl compound, with a minor amount of Hf (~0.05 atom%) and PGM additions, showed the formation of stable alumina scale at 1200°C [6]. This would suggest that a coating of the quaternary nickel aluminide (NiAl + PGM + Hf) on the base alloy with a higher amount of Mo would significantly improve the oxidation resistance. Unlike the B2 based coatings on Ni based superalloys, in this case there wouldn't be any chemical mismatch between the coating and the base alloy due to the presence of the binary NiAl in the base alloy.

7.4.2 Preliminary experimental studies

Preliminary studies were carried out to assess the microstructural stability with a NiAl shell on a Mo-Ni-Al core. A Mo-Ni-Al pellet with the nominal composition $\text{Mo}_{50}\text{Ni}_{25}\text{Al}_{25}$ was

encapsulated with Ni and Al powder (equiatomic ratio) in an alumina crucible and sintered at 1800°C for 30 minutes. The resulting microstructures are shown in figure 8.1. It can be seen that there is a fairly low diffusion of Mo outward into the NiAl rich region, despite the high sintering temperature. From the microstructure at the NiAl/Mo-NiAl interface, combined with a knowledge of the eutectic composition from the phase diagrams [7, 8], it appears that the amount of Mo diffusion outward is adequate to form a high melting ($\sim 1650^{\circ}\text{C}$) eutectic at the coating-base alloy interface, with the Mo content being 9 atom% in this region. More importantly, no physical interface between the external NiAl powder and the Mo-Ni-Al alloy could be observed. This implies that coating the alloy with PGM and Hf substituted NiAl would hold out promise for the future.

Figure 7.1: Microstructures of a Mo-Ni-Al alloy encapsulated with Ni and Al powders followed by sintering at 1800°C. (a) Overall microstructure at 100X magnification. (b) The interface between the external NiAl and the base alloy the showing signature rod eutectics of this alloy system.

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APPENDIX. A Multi-stage hierarchical approach to alloy design

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A1. Abstract

A multi-stage hierarchical sieving approach based on a combination of semiempirical and ab initio calculations along with selected experimental studies was used to down-select potential alloy systems for ultra-high-temperature applications. This approach indicates that the Mo-Ni-Al system has potential for applications at the target temperatures of 1,200-1,300°C. The Mo was selected for its high melting temperature, room temperature toughness, and creep resistance while the NiAl is a reservoir for the Al₂O₃ passivating scale. Microstructures based on casting and powder processing of the Mo-Ni-Al alloys were studied. Oxidation behavior of the Mo-Ni-Al alloys at 1,100 and 1,200°C in dry air was determined and those alloys with ≤ 20 at.% Mo were shown to be superior to the T2 (Mo₅SiB₂). Furthermore, the calculations predicted that small amounts of platinum group metals Pd, Ir, and Rh additions would increase the melting temperature without forming detrimental intermetallic phases, which results in improved oxidation stability of the NiAl phase.

A2. Introduction

Superalloys are the workhorse materials for land based gas turbine blades, which are required to operate under extremely harsh combustion environment while retaining their

mechanical integrity. Operating temperatures for Ni-based superalloys have been greatly increased by application of the thermal barrier coating along with a suitable Ni-Al based bond coat. Commercial turbine blades are routinely operated at temperatures up to 1150°C[1]. Even higher efficiencies such as envisioned in the DOE NETL's FutureGen gas turbine program will require alloys that can function at temperatures above melting point of today's commercial alloys. Hence, design of ultra high temperature alloys will require a major breakthrough. Refractory metal silicides in the metal-*T2-A15* phase field region can operate at high temperatures and retain their strength[2-5]. However, oxidation resistance of these alloys is significantly reduced. Alloys in the *T1-T2-A15* or disilicides of refractory metals offer improved oxidation resistance[6]. However, the presence of only brittle intermetallics in the phase assemblage renders them unusable in practice.

Significant increase in operating temperatures is not likely to be achieved by tweaking current Ni-based alloy compositions. A trial-and-error based approach towards the discovery of new materials is tedious; yet we lack the numerical tools to efficiently and accurately predict new phases and their properties. Potential phase space is enormous. For instance, a 4-component Ni based system, with all the elements selected from the transition metal elements, yields 3,654 possible combinations, and adding only one more constituent expands the number of combinations to 23,751. Considering that many commercial high temperature alloys can have in excess of 8 constituents, a systematic investigation of even a fraction of the potential phase space through computational thermodynamics or *ab initio* methods are unrealistic. Hence using rapid sieving techniques in an alloy design project is essential. Faster but lower accuracy approaches to quickly screen out the least favorable combinations followed by more rigorous methods to narrow the potential phase space offers an efficient alloy design approach.

Fortunately, we do have a few clues to pursue for developing fast screening methods. For instance, the melting temperature of a material can be taken as one of the guidelines for a prospective high temperature alloy. The melting temperature of a compound, in turn, correlates well with the interatomic bond strength and its formation enthalpy[7-9]. It has been demonstrated that the formation enthalpy of multicomponent system can be estimated with a reasonable degree of accuracy and extremely low computational cost using an extended

Miedema approach[10]. However, melting temperature is not the only requirement; only certain elements are known to promote the formation of protective oxide scales, most notably, Al, Cr and Si. Therefore, additional screening criteria include developing alloys comprising of a phase that will promote the formation of a slow growing protective oxide scale. Due to the low stability of chromia at the target operating temperatures, 1350 °C, and susceptibility of a silica based scales to moisture in coal combustion byproducts, we are left with an alumina forming alloy[11]. Alloys based on a mix of refractory metals (RM) and Ni-Al are believed to be the best candidates. The refractory metal forms the backbone of the alloy, providing toughness at low temperatures and creep resistance at high temperatures. The β -NiAl (B2 structure, SG 221), in turn, acts as a reservoir for the passivating alumina scale. However, alloying additions to the NiAl are required in order to boost its melting temperature ($T_m = 1640$ °C).

The primary focus of this study was to evaluate a series of alloy combinations narrowed down by the guidelines mentioned above, using semi-empirical, as well as *ab initio* calculations for their potential as a high temperature ($T \sim 1300$ °C), oxidation and fracture resistant material. Select alloy compositions predicted by the computational tools were then synthesized, characterized and tested for their high temperature oxidative stability as the first goalpost in the alloy development process.

A3. Theoretical calculations

The initial cut through the prospective phase space was performed using semi-empirical calculations based on an extended Miedema approach[10]. Briefly, this approach is based on using an energy minimization scheme by optimizing the compositions of the constituent binary systems under appropriate mass balance constraints. Our modified Miedema model was used for estimating the difference in formation enthalpies between Ni-Al and TM-Al (TM = transition metal). Twenty six elements from the transition metal block were tested over the entire composition range of their ternaries with Ni and Al. Three considerations were given for the selection of the TM : (1) high formation enthalpy, (2) absence of intermetallics with Ni or Al over a significant composition range and (3) a cubic crystal form to insure some ductility at lower temperatures. Using these criteria, Mo was clearly the best candidate. Molybdenum

retains its *bcc* structure up to its melting temperature and has a limited solubility with Al or Ni. While not possessing good oxidation stability in of itself, its low diffusivity and low solubility with NiAl suggests that a graded microstructure can be designed to minimize susceptibility for oxidation.

The next step in alloy design was to search for ternary addition to the NiAl to boost its melting temperature. As mentioned above, the ternary addition to the NiAl should not only raise the melting temperature but should be retained in solid solution with the NiAl. Again we used our modified Miedema model to down-select the most promising candidates based on their formation enthalpies. Of the late-transition elements, only Hf, Y, Zr, Nb, Pd, Rh and Ir showed the highest formation enthalpies with NiAl and a smaller affinity for Mo. It is critical that the ternary addition to NiAl do not exhibit high heat of mixing with Mo. At this point, more accurate calculations were required.

Ab initio methods are preferred at this stage. Unlike embedded atom methods, interatomic potentials do not have to be developed or in the case of computational thermodynamics, developing databases are not necessary. The disadvantage of *ab initio* methods is in instances where the crystal structure and its atomic decoration are not known so that a large number of prospective structures must be calculated. It should be stressed that unless specifically determined, *ab initio* provides only the most enthalpically stable structure (0 K). Entropically stable structures or highly complex low symmetry systems are very difficult to identify with this approach. In this particular system we suspected that the small platinum group metal (PGM) additions will not result in degeneracy of the β -NiAl, which was readily confirmed experimentally. Therefore the number of calculations required was small.

The *ab initio* calculations were carried out using the Vienna *ab initio* Simulation Package (VASP) [12-14] to get the thermodynamically stable structure of *B2* phase in the $\text{Ni}_{1-x}\text{AlTM}_x$ and $\text{NiAl}_{1-x}\text{TM}_x$ systems using a 54-atom supercell, where TM represents the transition metal element selected by the Miedema's model. The density functional calculations are performed using a plane-wave pseudo-potential representation, with ultra-soft pseudo-potentials [13] for all species and with a plane-wave energy cutoff of 300 eV. The *k*-point sampling was chosen to converge all of the total energies to an accuracy of 2 meV/atom. The *k*-point grid used for

structural relaxation was $6 \times 6 \times 6$, chosen according to the Monkhorst-Pack scheme [15], and symmetry reduced to the irreducible Brillouin zone.

A4. Experimental methods

A4.1 Mo-Ni-Al alloys

Mo-Ni-Al alloys are known to exhibit a two phase (*bcc* Mo + β -NiAl) microstructure over a limited range of compositions [16]. All the experiments in the present study were carried out in this phase field. Higher phase fraction of Molybdenum would be detrimental to the oxidation resistance; hence the phase fraction of Mo was kept below 35 at. % in all cases. The alloys were synthesized using powder metallurgical techniques as well as casting. The powder metallurgy involved mixing the pure metal powders ($\sim 10 \mu\text{m}$) in a mixer/shaker (SPEX 8000, SPEX CertiPrep Inc, Metuchen, NJ) for 10 minutes followed by compaction of the powders by dry pressing at a pressure of 3500 psi (24 MPa). The cylindrical pellets thus produced had a diameter of 10 mm and a height of 20 mm. The pellets were then sintered at 1750 °C for 45 minutes. The pellets synthesized by this route had nominal compositions of Mo = 15, 20, 25 and 35 at.%, with the balance in each case being equiatomic NiAl. Oxidation coupons having a diameter of 10 mm and a thickness of 1 mm were cut from the cylindrical samples and subjected to interrupted oxidation tests at 1100 °C which is the maximum temperature that current superalloys are exposed to in practice. Oxidation tests with multiple compositions allowed us to study the effect of Mo phase fraction and determine an appropriate composition range where the oxidation resistance was reasonably optimized.

The composition of the drop cast alloy ($\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$) was decided based on the oxidation behavior of the sintered alloys. Drop cast samples were prepared from pelletized elemental powder mixture of Mo (Alfa Aesar, 99.5% purity), Ni (MPC, 99.6% purity) and Al (Alfa Aesar, 99.8% purity) which were arc-melted. The alloys were re-melted thrice to achieve a greater degree of homogenization followed by drop-casting in order to obtain a cylindrical rod. The drop-cast alloy was subject to interrupted oxidation tests over a range of temperatures from 1000 °C to 1200 °C.

In this test, the samples were exposed to the target temperatures for a total of 20 hours with occasional interruptions for mass measurements at ambient temperature. The testing temperatures were deliberately kept at 1200 °C or lower since our work on oxidation of pure nickel aluminides at temperatures above 1200 °C (discussed below) has shown massive scale spallation. Microstructures of the as-prepared alloys as well as the oxidized coupons were studied using a JEOL 5910LV scanning electron microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 20 kV.

A4.2 Nickel aluminides with TM additions

The Ni-Al-TM alloys were produced from pieces cut from pure bulk metal sheets obtained from the Materials Preparation Center at Ames Laboratory, having a purity of 99.7% or more. Pure Ni and Al were first arc-melted together in an argon atmosphere to form β -NiAl. The *ab-initio* calculations suggested that the transition metals have a preference for the Ni site in the *B2* structure. Alloys with compositions $\text{Ni}_{50-x}\text{Al}_{50}\text{TM}_x$, ($x = 3, 6$ and 9) were then arc-melted in an argon atmosphere. The samples were re-melted thrice to achieve better homogenization before drop-casting. The rods were annealed at 1300 °C in an argon atmosphere for 6 hours to ensure homogeneity. SEM was used to characterize the microstructure while phase analysis was done using x-ray diffraction (XRD) on a Philips PANalytical x-ray diffractometer (Panalytical, Almelo, Netherlands) with a Bragg-Brentano geometry and $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The x-ray data was Rietveld refined using the GSAS software in order to estimate the lattice parameters of the phases as well as determine site preference for different elements [17]. Of the transition metals studied, it was observed that alloys with Platinum group metal (PGM) modifications formed single phase alloys while the other alloys showed a eutectic microstructure. Hence, further studies were carried out only on the PGM modified alloys. Oxidation coupons were prepared as described above, but more aggressive testing conditions, 1300°C for two hours and ambient for 30 min, were employed to determine if the PGM improved the oxidation stability of NiAl reservoir phase.

A5 Results and Discussion

A5.1 Oxidation behavior of Mo-Ni-Al alloys

Samples processed by liquid phase sintering showed the influence of alloy composition on the oxidation behavior. Alloys under 20 at% Mo, with equiatomic NiAl showed fairly good oxidation resistance, while the alloys with a higher volume fraction of Mo (e.g. $\text{Mo}_{35}\text{Ni}_{32.5}\text{Al}_{32.5}$) failed to form a passivating oxide layer (Figure A1). The strong composition dependence of oxidation is due to Mo's deleterious effect on the oxidation resistance. Minimizing the interconnected Mo network is required. Continuity of Mo phase depends on its volume fraction and the size of the Mo grains. Higher the volume fraction of the Mo phase, and larger the grain size, larger is the probability of connectivity and resulting in poorer oxidation resistance.

Figure A1: Interrupted flowing air oxidation of liquid phase sintered alloys with different Mo content at 1100°C.

Figure A2a shows a low magnification microstructure of the oxidized $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ cast alloy at 1200 °C. It can be seen that the alloy has developed a continuous alumina scale of about 5 μm thickness, albeit not uniform, across the length of the sample. A closer look at the oxide scale at higher magnification (Figure A2b) shows that the scale thickness fluctuations is due to presence of long Mo dendrites growing into the alloy.

Figure A2: (a) Low magnification image of the oxidized scale. The alumina scale appears to have formed continuously on the surface. (b) Higher magnification image of the oxidized alloy showing non-uniformity of scale thickness primarily as a result of the Mo phase at the surface. Mo gets oxidized and the resultant MoO_3 volatilizes allowing oxygen to penetrate relatively larger distances into the alloy.

Figure A3: Interrupted flowing air oxidation of an arc-melted and drop cast alloy ($\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$) at 1200°C .

It has been widely observed in case of nickel based alloys that the initial oxidation product of NiAl is the formation of NiO [18]. Subsequently, NiO is reduced by Al resulting in the formation of Ni and Al_2O_3 . Typically such a reduction results in linear rather than parabolic kinetics. Aluminum can also react with atmospheric oxygen to form Al_2O_3 which should exhibit parabolic oxidation kinetics. Additionally, NiO and Al_2O_3 can react to form a NiAl_2O_4 spinel [19].

All the reactions involving Ni and Al result in a slow mass gain, whereas the oxidation of Mo and the subsequent volatilization of MoO_3 results in a rapid mass loss [4]. Consequently, the overall oxidation rate is a sum of mass gain due to oxidation of Ni and Al and loss due to volatilization of MoO_3 . Figure A3 shows the oxidation kinetics during the interrupted oxidation process for the $\text{Mo}_{20}\text{Ni}_{40}\text{Al}_{40}$ alloy at 1200 °C. As a baseline comparison the steady state mass loss value for the T2- Mo_5SiB_2 compound is shown on the same figure for comparison. The preliminary data indicates that the oxidation behavior of Mo-Ni-Al alloy is comparable to the refractory metal silicides at fairly elevated temperatures.

Oxidation studies were limited to a temperature of 1200 °C because the alumina scale formed on nickel aluminides is prone to spallation above 1200 °C.

A5.2 Oxidation behavior of the nickel aluminide

X-ray diffraction studies on the nickel aluminides with Zr, Y, Hf and Nb additions indicated a two phase mixture. The PGM additions were shown to form a single phase with the same crystal system as the β -NiAl. A monotonic and approximately linear increase in the lattice parameter was observed with increasing PGM additions. Subsequent Rietveld refinement confirmed that PGM substitutions preferred the Ni site, which is in accordance with the *ab-initio* calculations (figure A4).

Figure A4 shows the variation of formation enthalpy of PGM substituted β -NiAl. It can be seen that substitution of PGM elements for Ni is energetically favorable. Also, controlled additions result in a monotonic change in formation enthalpy. This suggests that these PGM additions might be beneficial for obtaining an increase in the melting temperature of the nickel aluminide. The other transition metals that showed large negative formation enthalpies with the nickel-aluminide included Hf, Y, Zr, and Nb. All of these additions were experimentally found to produce deep eutectics. A high formation enthalpy can indicate high stability of both the solid and the liquid phase. The phase selection is decided by the relative stability of these two phases. Miedema's model is a structure-less model; hence it can't be used to predict which of these two phases will be more stable. Formation of a eutectic suggests that the liquid phase is relatively more stable compared to a single phase intermetallic with the same composition in

case of these alloying additions. Hence, further oxidation studies were carried out with only the PGM additions, since they were readily soluble in the β -NiAl.

Figure A4: Variation of formation enthalpy of β -NiAl with PGM additions.

Figure 5 shows the oxidation kinetics for the three PGM substitutions (all 6 at%) to the β -NiAl compared against undoped β -NiAl as a benchmark. It can clearly be seen that the Pd substitution performed worse than the β -NiAl during oxidation testing at 1300 °C. The oxide spallation of the Pd sample was noticeable early on during the test. The spallation flakes were large and discernable with the naked eye, just like the β -NiAl spallation. The Rh sample performed better than the base alloy NiAl, but worse than the alloy doped with Ir. The sample with Rh showed an adherent oxide scale initially, but after five hours oxide spallation was observed. From the oxidation resistance point of view, Ir substitution to β -NiAl appears to be superior. No sign of spallation was evident at times shorter than 20 h for alloys with 9 at% substitution. In all cases it should be noted that the best performing alloy at the end of 20 hours was always the alloy with highest fraction of the ternary substitution for all of the elements tested.

Figure A5: Cyclic oxidation of β -NiAl with and without PGM additions at 1300°C.

Figure A6: Microstructures of the oxidized alloys after oxidation at 1300°C for 24 hours. (a) β -NiAl and β -NiAl. With 6 atom% substitutions of (b) Rh, i.e. $\text{Ni}_{44}\text{Al}_{50}\text{Rh}_6$; (c) Ir, i.e. $\text{Ni}_{44}\text{Al}_{50}\text{Ir}_6$; (d) Pd, i.e. $\text{Ni}_{44}\text{Al}_{50}\text{Pd}_6$.

Figure 6a-d shows the oxidation microstructures of the baseline NiAl along with each ternary substitution set at 6 at%. These samples were oxidized for 24 hours at 1300 °C and then examined to better assess the evolution of the oxide scale formation. Figure 4 clearly displays that neither the benchmark β -NiAl alloy nor the β -NiAl doped with Pd additions show an

adherent oxide layer. Since both alloys had relatively significant mass loss, the surface would be devoid of a continuous oxide scale. The Rh doped β -NiAl showed an overall mass gain as well as signs of spallation. Looking at the oxide microstructure, it can be seen that the oxide layer is fairly continuous with a thickness of approximately 10 μm . The Ir addition showed an almost continuous oxide scale with a thickness of 8 microns. The only discontinuities were observed at the corners of the specimen where stresses in the oxide layer would be highest.

A6 Conclusions

We have shown that a hierarchical approach to alloy design starting with a less accurate but fast tool, followed by a more accurate but time consuming computational tools can be an efficient and effective means of down-selecting high temperature alloys. Our modified Miedema model is particularly effective in identifying regions of high (negative) formation enthalpies, indicative of high melting temperatures. Using the criteria of refractory base metal as the backbone of the alloy and identifying the NiAl as the most promising reservoir compound for alumina scale former, we demonstrated that Mo-Ni-Al-(PGM) shows good promise as a high temperature alloy. To further stabilize the reservoir compound, the most enthalpically stable ternary additions were determined. The most promising of the Ni-Al-(PGM) alloys based on *ab initio* calculations were synthesized and their oxidation behavior was studied. It was found that a few alloys in this system had enough potential to warrant further investigation of these materials for ultra-high temperature applications. The Mo phase fraction and its grain size play a critical role in the oxidation behavior of these alloys. Future work would be focused on developing PGM substituted Mo-Ni-Al alloys in the two phase *bcc*-Mo(ss) + β -NiAl phase fields.

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