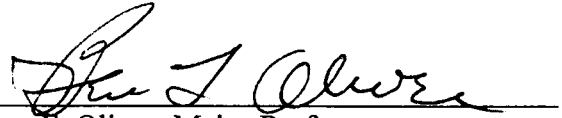


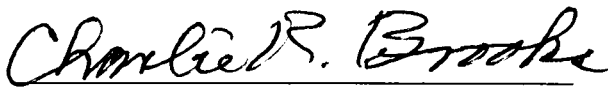
To the Graduate Council:

I am submitting herewith a thesis written by Kerry Lee Henry entitled "Preliminary Investigation into the Effects of Microalloying on a NiAl-31Cr-3Mo Eutectic Alloy." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Metallurgical Engineering.

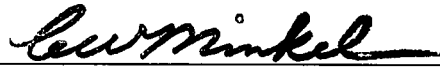


Ben F. Oliver, Major Professor

We have read this thesis
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor and
Dean of The Graduate School

**PRELIMINARY INVESTIGATION INTO THE
EFFECTS OF MICROALLOYING ON A
NiAl-31Cr-3Mo EUTECTIC ALLOY**

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Kerry Lee Henry
December 1998

DEDICATION

This thesis is dedicated:

In loving memory of Christopher A. Richardson
Nov. 1, 1978 - Jan. 3, 1998

I miss you so much little brother.

My mother, Ruth R. Cunningham

Thank you for all your love, support and belief in me.

My husband, Edward G. Henry

Thank you for always pushing me to excel. I love you.

ACKNOWLEDGMENTS

Many people are deserving of thanks for their help on this project. Dr. Ben Oliver, thank you for taking me onto your team and teaching me about NiAl-based composites and directional solidification. Thank you for your patience with my background and taking the time to teach me what I did not know. Dr. Ron Noebe of NASA Lewis Research Center, thank you for supplying the necessary materials as well as machining the bend specimens.

Dr. Charlie Brooks and Dr. Ray Buchanan, thank you for being part of my committee. Thank you both for the knowledge I obtained in your classes. I enjoyed them both.

Dr. Allen Yu, thank you for your knowledge of mechanics of composites. Thank you for all the time you spent answering my questions. You were always very helpful and welcoming. Dr. David Joy, thank you for all the knowledge about the SEM and TEM. I learned a lot in those classes. Thank you also for all the time you spent helping me get fabulous images.

Doug, Larry, and Ray (machine shop), thank you for getting my samples done efficiently. I am sure you will miss the cookies; I will miss the conversations.

Carla and Sandy, thank you for all the help and support. You are both very special ladies and I will miss you and our talks. Thank you for always finding a smile for me.

The electronics shop, thank you for all the help with the mechanical testing. Thank you also for the help rendered while teaching MSE 201. C.J., Bill, Tang, and my fellow TAs. Your friendships and sense of humor has been greatly appreciated. I will miss you all. To anyone I missed, I apologize.

ABSTRACT

The intermetallic NiAl shows promise for development as a high temperature material. Some of its properties, particularly its room temperature fracture toughness and elevated temperature creep strength, must be improved before NiAl can substitute for the Ni-based superalloys. Past work has focused on creating NiAl-based eutectic in-situ composites. While these composites improved the properties of NiAl, they did not improve those properties enough.

This study investigates the possibility of microalloying to improve the properties further. A based eutectic alloy of composition NiAl-31Cr-3Mo (atomic percent) was chosen because it has the best combined properties of any of the in-situ composites. Microalloy additions were selected based on phase diagram information and the effects of the additions on binary NiAl. Five additions were chosen for preliminary investigation: Hf, Ta, Ti, V, and W. Since the effect of microalloying was to be studied, none of the samples contained more than 2 atomic percent of any alloy.

After the preliminary investigation, V and W were chosen for a more in-depth study. Ingots containing 1 atomic percent of V or W were directionally solidified. Room temperature fracture toughness tests and microscopy were performed on the samples. The V alloys had improved fracture toughness over the base eutectic alloy. The W alloys decreased the fracture toughness. The NiAl-32Cr-1Mo-1V alloy had a very fine lamellar spacing. The W alloys had a very coarse and cellular eutectic structure.

This study was only a beginning investigation of these alloys. Its purpose was to

provide preliminary information about the effects of microalloying additions on NiAl-based eutectics. While these initial findings are promising, more work must be completed before conclusive results are established.

TABLE OF CONTENTS

1.	INTRODUCTION AND NiAl REVIEW	1
	Introduction.....	1
	Properties of Nickel Aluminide	1
	Physical Properties.....	1
	Elastic Properties	6
	Slip Systems.....	10
	Yield Strength	10
	Fracture Toughness.....	11
	Creep Strength	15
2.	IN-SITU COMPOSITES AND ALLOYING REVIEW	19
	In-Situ NiAl-based Eutectics	19
	General Review.....	19
	NiAl-Cr,Mo System.....	21
	Alloying and Microalloying.....	26
	General Alloying Techniques	26
	Alloying in Binary NiAl	27
3.	PRELIMINARY INVESTIGATIONS	29
	Introduction.....	29
	NiAl-X and Cr-X Phase Diagrams.....	29
	Hf Systems.....	29
	Ta Systems.....	31
	Ti Systems.....	31
	V Systems	31
	W Systems	35
	Sample Preparation	35
	Arc-Melt Procedures	35
	Polishing Procedures.....	36
	Preliminary Results.....	36
	NiAl-Cr,Mo-Hf	36
	NiAl-Cr,Mo-Ta	41
	NiAl-Cr,Mo-Ti.....	45
	NiAl-Cr,Mo-V	49
	NiAl-Cr,Mo-W.....	53
	Summary of Preliminary Investigation.....	53

4.	PROCESSING AND TESTING PROCEDURES.....	55
	Directional Solidification Procedure.....	55
	Four-Point Flexure Testing.....	55
5.	RESULTS AND DISCUSSION.....	59
	Introduction.....	59
	Results.....	59
	Room Temperature Fracture Toughness.....	59
	Microscopy and Lamellar Spacing	62
	Discussion.....	80
	Fracture Toughness.....	80
	Lamellar Spacing	81
6.	SUMMARY AND FUTURE WORK	83
	REFERENCES	85
	VITA.....	91

LIST OF TABLES

TABLE	PAGE
1. Elastic constants for NiAl at room temperature	9
2. Characterization of NiAl-based eutectics directionally solidified at the University of Tennessee	20
3. Compositions of arc-melts processed by NASA Lewis Research Center	38
4. Nominal compositions of arc-melted Ti buttons processed at the University of Tennessee	47
5. Composition of directionally solidified ingots	60
6. Room temperature fracture toughness results	61
7. Average lamellar spacing for the five directionally solidified ingots	73

LIST OF FIGURES

FIGURE	PAGE
1. Crystal structure of NiAl	2
2. The Ni-Al phase diagram	3
3. Density and lattice parameter as a function of composition	5
4. Heat of formation as a function of composition for several Ni-Al alloys	7
5. Yield stress as a function of temperature for single crystal NiAl	12
6. Yield stress as a function of temperature for polycrystalline NiAl	13
7. Yield stress as a function of composition at various temperatures	14
8. Room temperature fracture toughness of NiAl alloys	16
9. Creep behavior of stoichiometric NiAl at 1175K	18
10. Properties of various NiAl-based eutectic systems directionally solidified at the University of Tennessee	22
11. Adjusted properties of various NiAl-based eutectic systems directionally solidified at the University of Tennessee	23
12. Microstructure of directionally solidified (a) NiAl-34Cr and (b) NiAl-Cr,Mo at 400x	25
13. Ni-Al-Hf ternary system at 1073 K	30
14. a) Ni-Al-Ta ternary system phase diagram at 1272 K. b) Cr-Ta binary phase diagram	32
15. a) Ni-Al-Ti ternary system phase diagram at 1073 K. b) Cr-Ti binary phase diagram	33
16. a) Ni-Al-V ternary system phase diagram at 1073 K. b) Cr-Ti binary phase diagram	34

17.	a) Ni-Al-W pseudo binary phase diagram. b) Cr-W binary phase diagram . .	36
18.	Optical micrographs of NiAl-30.5Cr-3Mo-0.5Hf alloy at a) 200x b) 400x	39
19.	Optical micrographs of NiAl-30Cr-3Mo-1Hf alloy at a) 200x b) 400x . . .	40
20.	Optical micrographs at 100x for a) NiAl-30.5Cr-3Mo-0.5Ta alloy b) NiAl-30Cr-3Mo-1 Ta alloy c) NiAl-29Cr-3Mo-2Ta alloy	42
21.	Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5Ta alloy b) NiAl-30Cr-3Mo-1 Ta alloy c) NiAl-29Cr-3Mo-2Ta alloy	43
22.	Backscattered SEM micrograph of NiAl-29Cr-3Mo-2Ta alloy at 3000x	44
23.	Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5Ti alloy b) NiAl-30Cr-3Mo-1Ti alloy c) NiAl-29Cr-3Mo-2Ti alloy	46
24.	Optical micrographs at 400x for a) NiAl-Cr,Mo-1Ti b) NiAl-Cr,Mo-4Ti alloys processed at the University of Tennessee, Knoxville	48
25.	Optical micrographs at 400x for a) NiAl-Cr,Mo-6Ti b) NiAl-Cr,Mo-8Ti c) NiAl-Cr,Mo-10Ti alloys processed at the University of Tennessee, Knoxville	50
26.	Microhardness as a function of composition for NiAl-Cr,Mo-Ti alloys processed at the University of Tennessee	51
27.	Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5V alloy b) NiAl-30Cr-3Mo-1V alloy c) NiAl-29Cr-3Mo-2V alloy	52
28.	Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5W alloy b) NiAl-30.25Cr-3Mo-0.75W alloy c) NiAl-30Cr-3Mo-1W alloy	54
29.	Schematic of the liquid zone and control actions of directional solidification process	56
30.	4-point bend fixture geometry and specimen size	57
31.	Fracture surfaces of NiAl-31Cr-3Mo alloy at a) 100x b) 500x c) 1000x .	63

32.	Fracture surfaces of NiAl-30Cr-3Mo-1V alloy at a) 100x b) 500x c) 1000x	64
33.	Fracture surfaces of NiAl-32Cr-1Mo-1V alloy at a) 100x b) 500x c) 1000x	65
34.	Fracture surfaces of NiAl-30Cr-3Mo-1W alloy at a) 100x b) 500x c) 1000x	66
35.	Fracture surfaces of NiAl-32Cr-1Mo-1W alloy at a) 100x b) 500x c) 1000x	67
36.	BSE images of transverse section of NiAl-31Cr-3Mo alloy at a) 1000x b) 3000x	68
37.	BSE images of transverse section of NiAl-30Cr-3Mo-1V alloy at a) 1000x b) 3000x	69
38.	BSE images of transverse section of NiAl-32Cr-1Mo-1V alloy at a) 1000x b) 3000x	70
39.	BSE images of transverse section of NiAl-30Cr-3Mo-1W alloy at a) 1000x b) 3000x	71
40.	BSE images of transverse section of NiAl-32Cr-3Mo-1W alloy at a) 1000x b) 3000x	72
41.	Optical micrograph of longitudinal section of NiAl-31Cr-3Mo alloy at 400x	74
42.	Optical micrograph of longitudinal section of NiAl-30Cr-3Mo-1V alloy at a) 200x b) 400x	75
43.	Optical micrograph of longitudinal section of NiAl-32Cr-1Mo-1V alloy at 400x	76
44.	Optical micrograph of longitudinal section of NiAl-30Cr-3Mo-1W alloy at 400x	77
45.	Optical micrograph of longitudinal section of NiAl-32Cr-1Mo-1W alloy at 400x	78

CHAPTER 1

INTRODUCTION AND NiAl REVIEW

1. INTRODUCTION

Current superalloys have reached their serviceable upper temperature limits ($\sim 80\% T_m$). This fact has sparked recent investigations into new high temperature materials, particularly intermetallic compounds containing aluminum. The intermetallic nickel aluminide (NiAl) shows much promise. This general discussion reviews the properties of NiAl as well as some of the developments made in improving some of the properties. A comprehensive review of all the mechanical and physical properties of NiAl and its composites is not intended. An extensive review of NiAl compiled by Noebe, Bowman, and Nathal [1] may be consulted for more complete coverage.

2. PROPERTIES OF NICKEL ALUMINIDE

2.1 Physical Properties

The nickel aluminide, NiAl, has an ordered B2 lattice structure. This structure is a Hume-Rothery β -phase electron compound. It has a valence electron to atom ratio of 3/2 making NiAl a member of the intermetallic family that crystallizes in the primitive cubic CsCl structure [1-3]. This crystal structure can be described as two interpenetrating primitive cubic lattices where Al atoms occupy one sublattice and Ni atoms occupy the second. This structure is shown in Figure 1 [1].

NiAl has a wide non-stoichiometric range as shown in Figure 2. The single phase

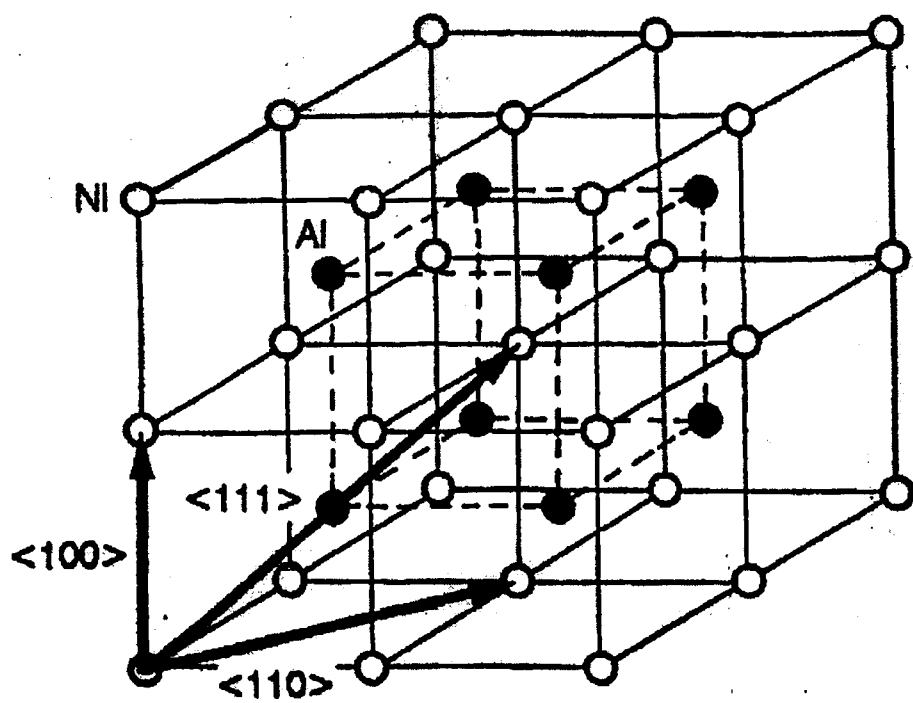


Figure 1: Crystal structure of NiAl [1]

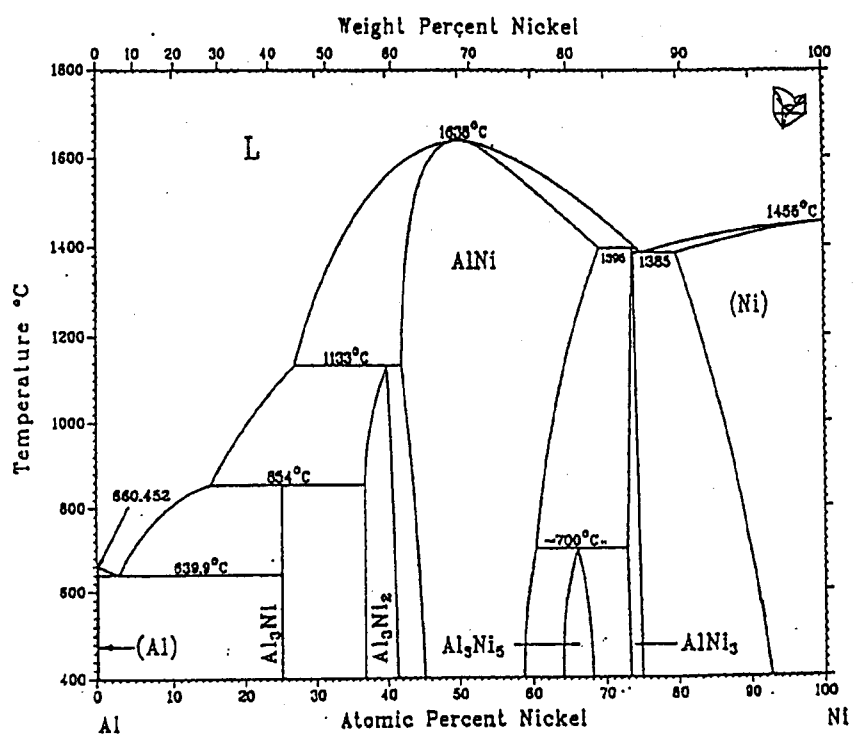


Figure 2: The Ni-Al phase diagram [4]

composition field of NiAl exists from about 45 to 60 atomic percent nickel at room temperature. Stoichiometric Ni-50Al melts congruently at 1911 K, the highest temperature of the NiAl single phase field [1,4]. The lattice constant for NiAl is a function of stoichiometry. The maximum lattice constant has been reported at the stoichiometric composition[5-8] as well as at slightly Al-rich compositions [9-10]. Figure 3 [11] shows the relationship between composition and the lattice parameter. The maximum as reported by Taylor and Doyle occurs at Ni-50Al and has a value of 0.2887 nm [5]. The lattice parameter on either side of stoichiometry can be described by a linear relationship of the form [1]:

$$a_0(\text{nm}) = 0.299839 - 0.000222(\text{at. \% Ni}) \quad \text{for 50 to 60 at. \% Ni}$$

$$a_0(\text{nm}) = 0.266819 + 0.000438(\text{at. \% Ni}) \quad \text{for 45 to 50 at. \% Ni}$$

Another physical property of NiAl which is dependent on composition is density. The density increases linearly with decreasing Al content [5,6,12]. At the stoichiometric composition the density has been measured to be about 5.90 g/cm³. At this composition the slope of the linear density function changes. The relationships between density and composition are given by the linear functions [1]:

$$\rho(\text{g/cm}^3) = 3.15 + 0.055(\text{at. \% Ni}) \quad \text{for 50 to 60 at. \% Ni}$$

$$\rho(\text{g/cm}^3) = 0.118(\text{at. \% Ni}) \quad \text{for 45 to 50 at. \% Ni}$$

The lattice parameter and density relationships have been used to understand the defect structure which occurs in NiAl. On the nickel rich side of stoichiometry, the excess nickel atoms substitute on the aluminum sites. This forms antistructure atoms Ni_{Al} [8,12]. When the NiAl is Al-rich then nickel vacancies, V_{Ni}, are formed. These

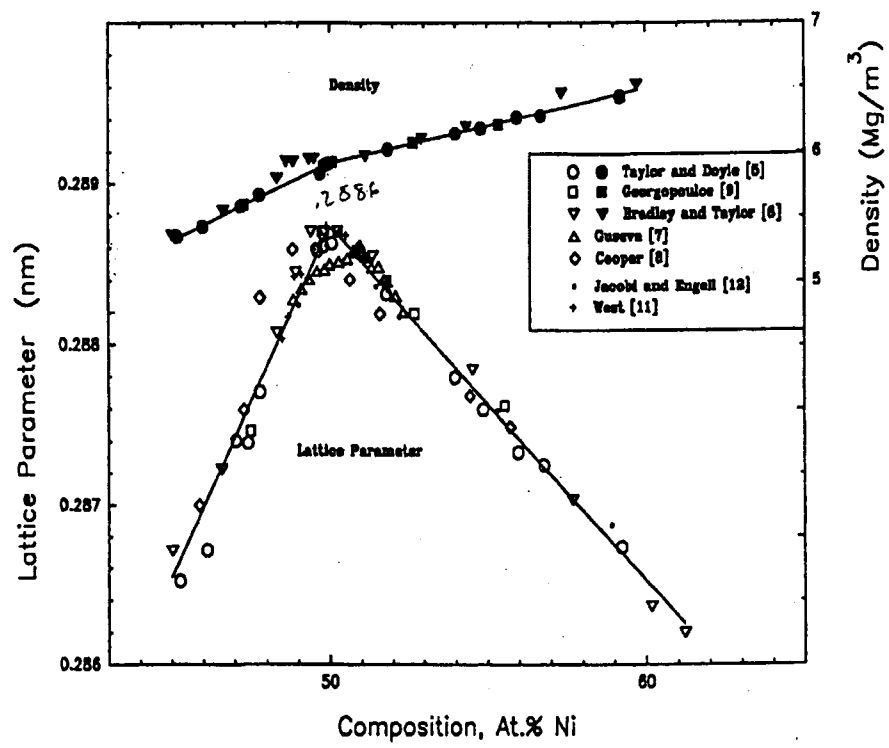


Figure 3: Density and lattice parameter as a function of composition [1]

defect structures occur in other β -phases like CoAl, NiGa, and CoGa. Several explanations have been given for the formation of vacancies in β -Hume-Rothery phases. They range from effects of electronic structure to atomic size-factor to the degree of intrinsic disorder measured from the variation of chemical activity of aluminum with respect to composition[13-15].

NiAl has a high Ni-Al bond strength. There appears to be no ionic contribution to bonding. The controlling mechanism is the d-band filling through Al-to-Ni charge transfer. The directional d-bonding charge builds up along the nearest-neighbor Ni-Al direction. This build-up leads to the high Ni-Al bond strength. It is thought that the NiAl bonding is a mixture of metallic and covalent type bonding [16-19].

NiAl is thermodynamically stable as indicated by the very large negative heat of formation. The heat of formation has been measured in the range of -59 to -72 kJ/mol near stoichiometry. The heat of formation is dependent on composition and is at its peak at stoichiometric NiAl [1] as shown in Figure 4. Of the β -type compounds, NiAl has one of the highest heats of formation.

2.2 Elastic Properties

Studies on elastic modulus have been conducted by several investigators[20-22]. Harmouche and Wolfenden studied the effects of both temperature and composition on Young's modulus[20]. They determined that composition had a small effect on the value of Young's modulus. At room temperature a maximum for Young's modulus was noted at 48 atomic percent Al. Harmouche and Wolfenden had predicted the maximum to

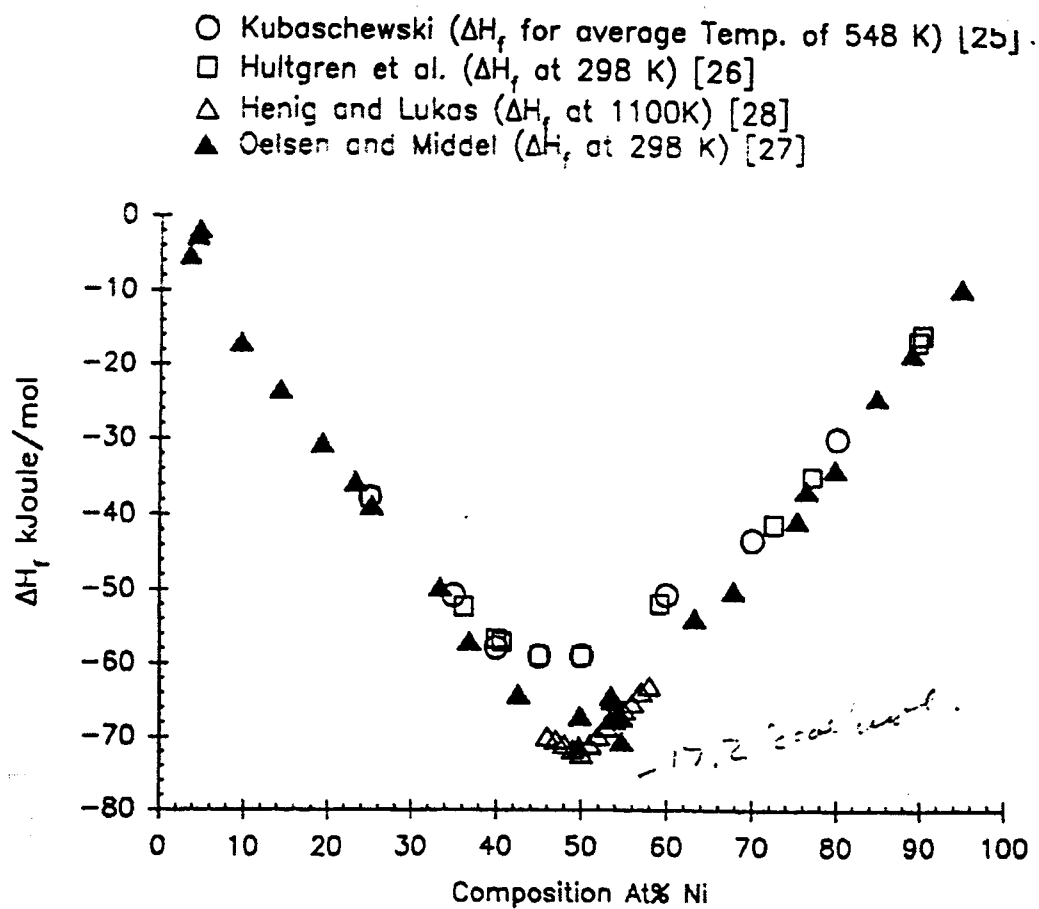


Figure 4: Heat of formation as a function of composition for several Ni-Al alloys [1]

have occurred at stoichiometric composition. They believe the deviation to be caused by the large concentration of point defects that are present in Ni-rich NiAl. Rusovic and Warlimont [23] found similar results for these compositions at temperatures below 673K.

The results of these two groups differ in the shape of the modulus vs composition plots. Rusovic and Warlimont found that beyond 673K, the data had a substantial change in curvature whereas Harmouche and Wolfendern did not. This difference appears to be related to different processes used to prepare the samples.

Harmouche and Wolfendern arrived at a single equation to represent Young's modulus. They used a statistical model of the form $E = E(X, T, X^2, T^2, XT)$, where X is composition and T is absolute temperature. Since the effect of stoichiometry variation on the modulus is small, Harmouche and Wolfendern found the following equation gave the best fit for the data points which they obtained[20]:

$$E = 259.31 - 0.072(T) + 3 \times 10^{-5}(T^2) - 6 \times 10^{-4}(XT) \text{ GPa}$$

Rusovic and Warlimont[23] on the other hand determined that Young's modulus was only linearly dependent on temperature and given by the following equation:

$$E = 204.9 - 0.041(T) \text{ GPa}$$

NiAl is anisotropic. Unlike Young's modulus, the anisotropy of NiAl depends on both composition and temperature. The value of anisotropy, A, ($A = 2C_{44}/(C_{11}-C_{12})$), ranges from 1.85 for Ni-55Al to 5.67 for Ni-45Al [23,24]. For temperatures ranging from room temperature to 873K, A goes from 3.3 to 2.94 [22,23].

Joslin [25] did an excellent job of summarizing the elastic constants of NiAl at room temperature. The results are found in Table 1. The references in the table are

Table 1: Elastic constants for NiAl at room temperature [25]

PROPERTY	ORIENTATION	VALUE (GPa)	REF.
E	<100>	94.46	21
E	<110>	184.51	21
E	<111>	270.43	21
G	<100>	112.1	21
G	<110>	52.5	21
G	<111>	44.5	21
C11	–	197	23
C12	–	102	23
C44	–	88	23
v	–	0.313	28

references in Joslin's work.

2.3 Slip Systems

Experimental determination of the operative slip system in NiAl has been a major focus for many researchers[26-28]. Theoretical explanations of the slip behavior of NiAl have not been very successful [26,29,30]. Studies have shown that NiAl exhibits two distinguishable types of slip behavior depending on the orientation. Soft orientations include all non- $\langle 001 \rangle$ loading directions. The hard orientations are those which are close to the $\langle 001 \rangle$ loading direction.

Single crystals in the soft orientation have been observed to slip in $\langle 001 \rangle \{110\}$ and $\langle 001 \rangle \{100\}$ at all deformation temperatures [27,31,32]. Polycrystalline NiAl also evidences these same slip systems. For hard oriented single crystals, the slip mode is dependent on temperature. For temperatures near liquid nitrogen temperature, observed slip is $\langle 111 \rangle \{123\}$ or $\{-1,-1,2\}$ [27,31]. Between room temperature and about 600K, kinking and uniform deformation by $\langle 111 \rangle \{-1,-1,2\}$ and $\{-1,1,0\}$ occurs [27,31]. At temperatures higher than 600K deformation occurs as a result of $\langle 110 \rangle$ and $\langle 001 \rangle$ dislocations [33-35] or by a combination of glide and climb of $\langle 100 \rangle$ and $\langle 110 \rangle$ dislocations [31,36].

2.4 Yield Strength

Many investigators have reported yield stress values for NiAl. There are many inconsistencies in the reported values. These differences can be attributed to many

variables such as composition, strain rate, grain size, cooling rate, surface finish and specimen fabrication [1,37-40]. Most of these conditions are not noted by the investigators, which makes comparing the results difficult.

The yield stress of NiAl has a temperature dependence which is similar to that of BCC metals. Figure 5 shows the dependence of yield stress on temperature for single crystals. It is also evident from Figure 5 that yield stress for single crystals depends on the orientation of the crystals, with $\langle 100 \rangle$ -oriented crystals having the highest yield stress. Commonly reported figures of yield stress range from 980 to 1400 MPa for $\langle 100 \rangle$ -oriented stoichiometric single crystals and from 165 to 190 MPa for $\langle 110 \rangle$ -oriented single crystals. These values are from about room temperature to 700 K. Polycrystalline NiAl also exhibits a relation between yield strength and temperature. The results for several polycrystalline NiAl samples are shown in Figure 6.

Stoichiometry also affects the yield stress. Typically, the lowest yield stress is obtained at Ni-50Al. Off-stoichiometric alloys show an increase in yield stress, with Al-rich alloys having the greater increase. Figure 7 shows the effect of composition on the yield stress. From the data in Figure 7 the hardening rate for Ni-rich alloys averaged about 120 MPa/at% while Al-rich compositions averaged about 350 MPa/at%.

2.5 Fracture Toughness

Fracture Toughness of NiAl is highly anisotropic. At room temperature, $\langle 110 \rangle$ -oriented single crystals have a reported fracture toughness of $4\text{--}5 \text{ MPa}\sqrt{\text{m}}$ [24,40]. For $\langle 001 \rangle$ -oriented crystals, fracture toughness has been reported of about $8 \text{ MPa}\sqrt{\text{m}}$ [40].

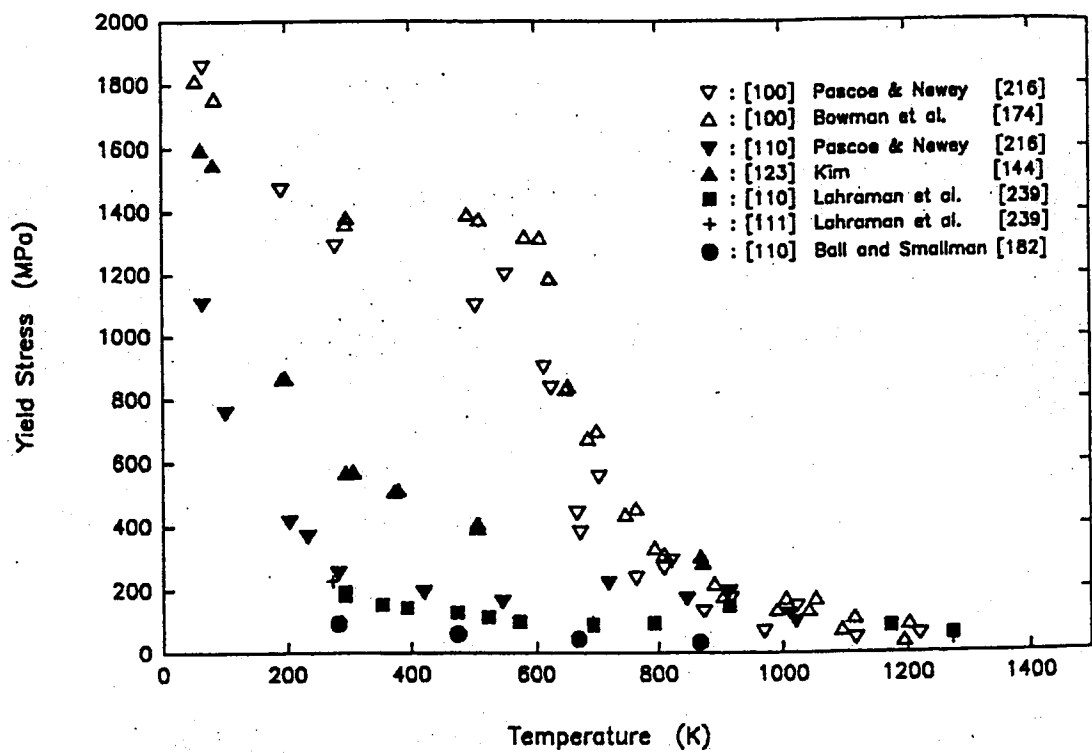


Figure 5: Yield stress as a function of temperature for single crystal NiAl [1]

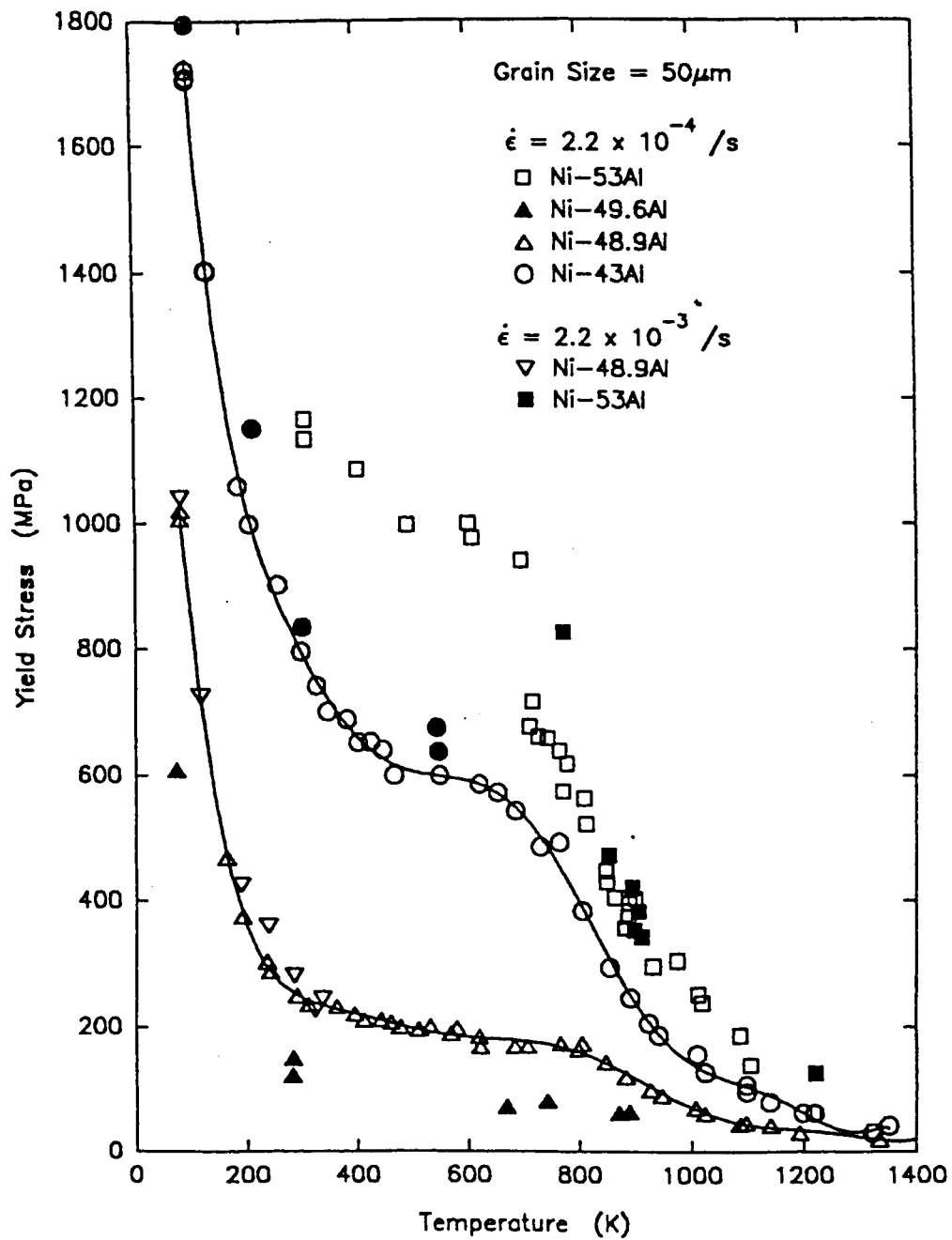


Figure 6: Yield stress as a function of temperature for polycrystalline NiAl [1]

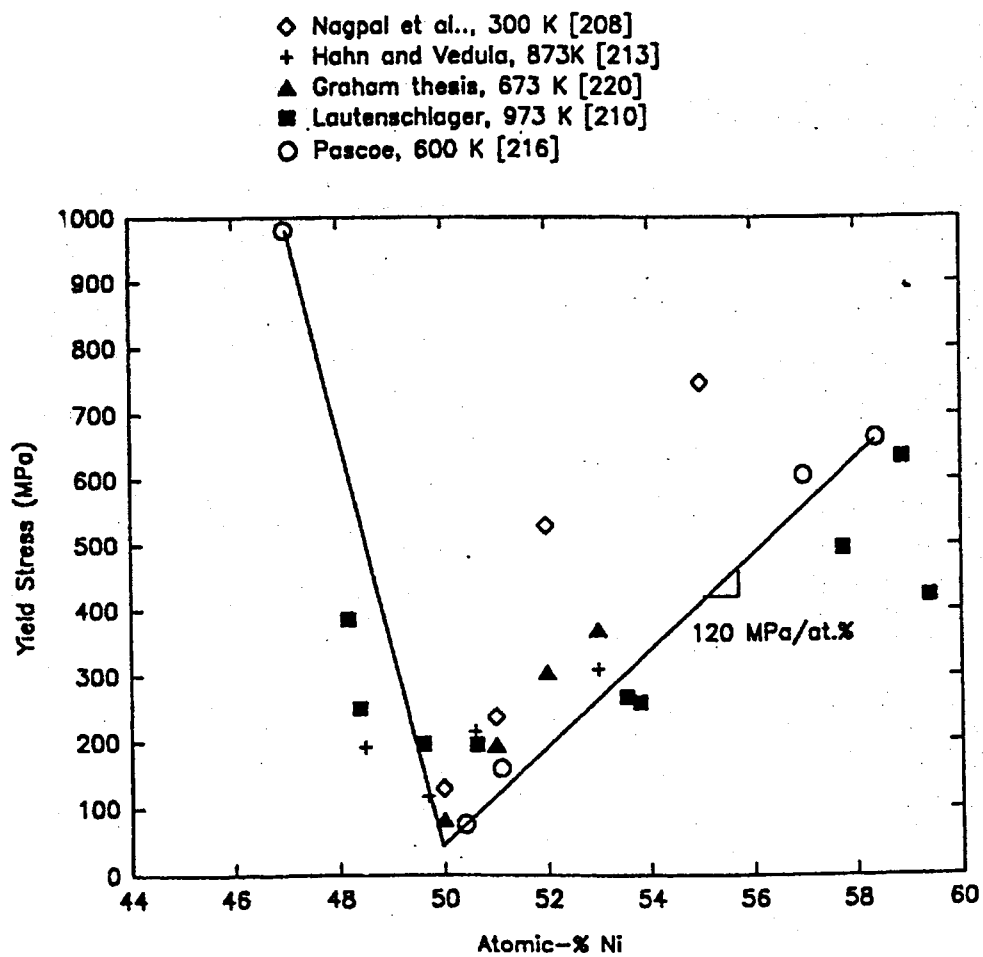


Figure 7: Yield stress as a function of composition at various temperatures [1]

The cleavage plane for NiAl is $\langle 110 \rangle$ but there can also be cleavage on the $\langle 115 \rangle$ or $\langle 117 \rangle$ planes prior to the cleavage on the $\langle 110 \rangle$ plane [37].

Fracture toughness is influenced by both stoichiometry and temperature. Room temperature fracture toughness increases when the composition is Ni-rich. Small deviations from stoichiometry do not have much of an effect. The relationship between composition and fracture toughness is shown in Figure 8 [1]. Reuss and Vehoff have performed most of the investigations of fracture toughness at higher temperatures [41,42]. Their studies showed that fracture toughness for polycrystalline NiAl increased with increasing temperature. The transition from brittle to ductile behavior occurred between 550 to 650 K with corresponding fracture toughness values of from 20 to approximately 50 MPa $\sqrt{m}$. These increased fracture toughness values were sensitive to both microstructure and grain size.

2.6 Creep Strength

Creep behavior in metals and alloys can be divided into three stages. These stages are primary, secondary, and tertiary. The secondary stage or steady-state stage is of primary interest when studying creep in NiAl. The steady-state creep rate is given by the equation:

$$\dot{\epsilon} = A \sigma^n \exp(-Q/RT)$$

where σ is the applied stress, n is the stress exponent, Q is the activation energy for creep, R is the gas constant, T is the absolute temperature, and A is a constant which incorporates variables like microstructure and stacking faults [1]. Normally, steady-state

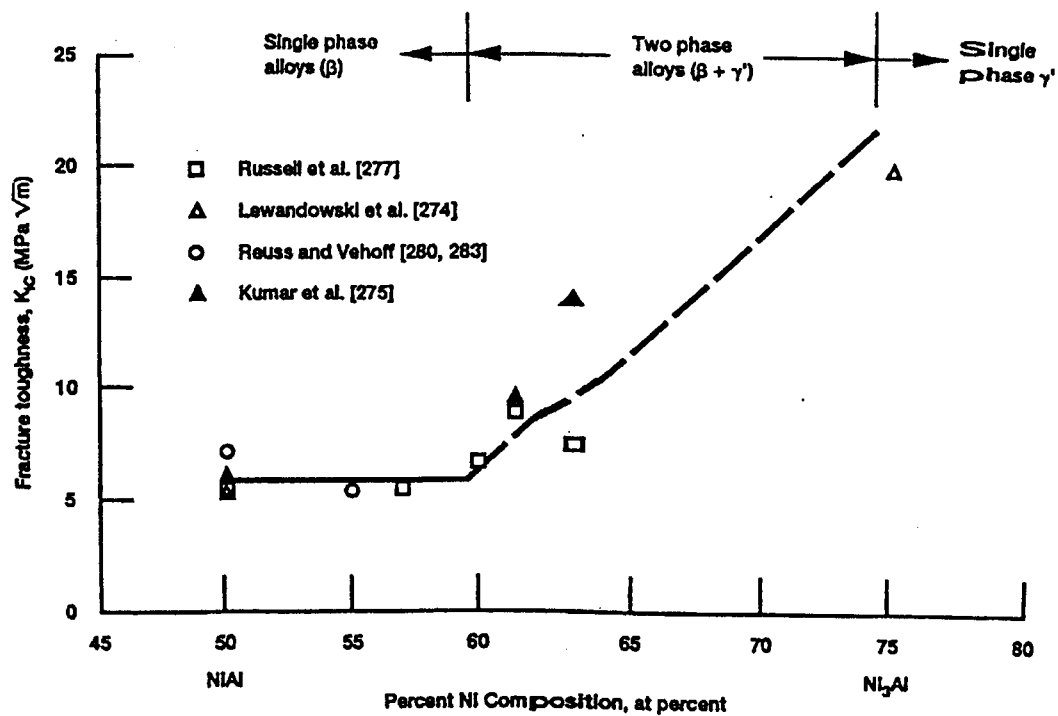


Figure 8: Room temperature fracture toughness of NiAl Alloys [1]

creep tests are performed under constant load or stress and creep rate is the dependent variable. The creep tests can also be performed for constant strain rates with steady state flow stress as the dependent variable. The creep behavior of stoichiometric NiAl at 1175K can be seen in Figure 9 [1].

NiAl exhibits dislocation creep. Dislocation creep can be produced by either dislocation glide or climb. If creep is controlled by dislocation climb as in pure metals (class M type), the stress exponent will be 4 or 5. For alloys with stress exponents of 3 (class A type), creep is controlled by dislocation glide. In the case of dislocation climb there is a well defined subgrain structure. Dislocation glide has no subgrain formation [43]. NiAl exhibits class M type creep behavior.

When discussing creep behavior in NiAl it is common to use the term creep strength. Creep strength is here defined as the stress necessary to produce a secondary creep rate of 10^{-7} s^{-1} . The creep strength of binary NiAl falls short of the standards set by the Ni-based superalloys. In order for NiAl to be a viable alternative to the superalloys, this property must be improved.

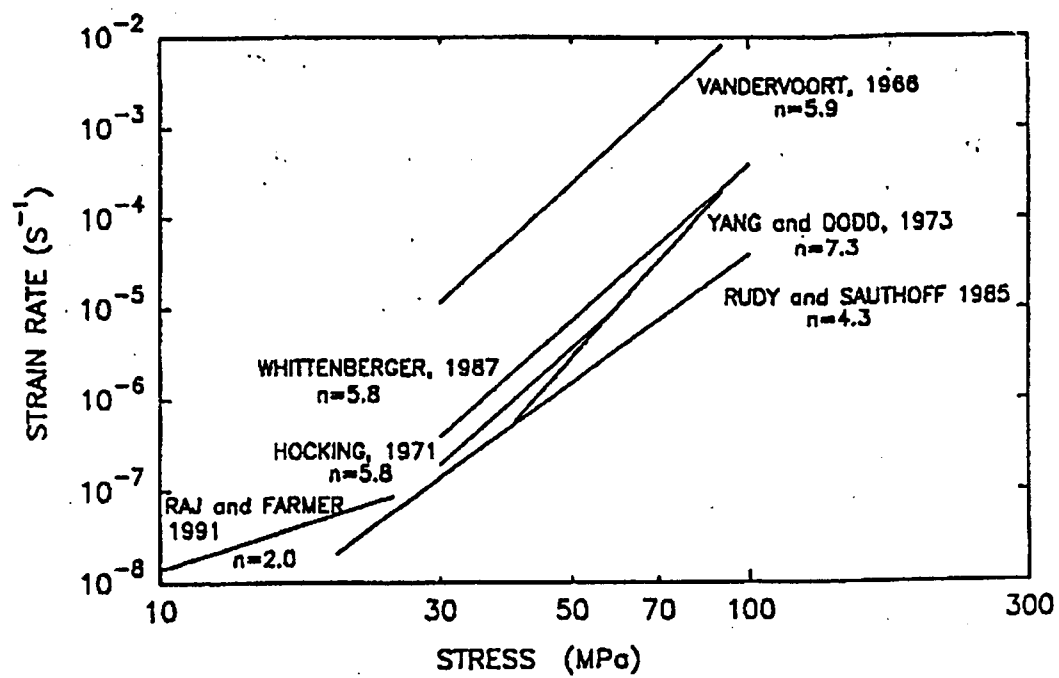


Figure 9: Creep behavior of stoichiometric NiAl at 1175K [1]

CHAPTER 2

IN-SITU COMPOSITES AND ALLOYING REVIEW

1. IN-SITU NiAl-BASED EUTECTICS

1.1 General Review

One approach for improving the properties of NiAl has been the formation of in-situ, NiAl-based eutectic composites. In these eutectics, NiAl serves as the matrix with refractory metals, Heusler-type phases, and/or Laves-type phases as the reinforcement. Many of the systems have been successful in improving the creep strength and the room temperature fracture toughness of NiAl.

There are various types of eutectic morphologies. The three classic categories of binary eutectics are lamellar, rod-like, and irregular (needle-like). There is also the possibility of having mixed eutectic structures. A common mix is partial lamellar and partial rod-like or blade-like. The morphology of an eutectic appears to be highly dependent on both chemical composition and the freezing rate. Crocker et al [44] classified the binary eutectic structures and gave some "rules" for predicting eutectic growth. Tiller discussed the important physical requirements for solidification of eutectics [45]. The most frequent morphologies are rod and lamellar types. In rod eutectics the discontinuous phase, here the metal phase (rods), would reinforce the continuous intermetallic (NiAl) phase. In lamellar structures, the reinforcement would come in the form of alternate layers of the metal phase with the intermetallic phase.

Table 2 lists the eutectic alloys which have been examined at the University of

Table 2: Characterization of NiAl-based eutectics directionally solidified at the University of Tennessee

Eutectic (atomic %)	Phases	T _{Eut} (K)	Type	V _f	Strength ^a (MPa)
β-9Mo	β-α	1778	rod	0.11	80
β-34Cr	β-α	1723	rod	0.34	140
β-28Cr-6Mo	β-α	1723	lam.	0.34	160
β-40V	β-α	1633	lam	0.50	40
β-16.5Nb	β-L	1710	lam	0	150
β-15.5Ta	β-L	1833	lam	0	280
β-12.5Ta-7Mo	β-L-α	1800	rod-lam	0.1	155
β-33Cr-6Ta	β-L-α	1698	rod-lam	0.35	135
β-15Zr-15V	β-H-hex	1494	lam-int	0	9.8
β-33V-10Ta	β-L-α	1578	rod-bla	0.44	50
β-33.3Cr-11.1Nb	β-α-L	1633	rod-lam	0.3?	99

^a Creep strength (compression): strain rate 10^{-6} per second at 1% true strain, 1300 K.

β: NiAl	V _f : Volume fraction metal phase
α: solid solution metal phase	bla: blades
lam: lamellar	int: interfacial rod
L: Laves phase	hex: hexagonal intermetallic (ZrV ₂)
H: Heusler phase	

Tennessee. The materials listed have all been directionally solidified using a containerless method. After processing, the materials were tested for creep resistance and room temperature fracture toughness. The results of the testing are graphed in Figure 10 [25,46,47].

Included with the eutectics and binary NiAl as a property attainment goal is NASAIR 100, a nickel-based superalloy. As shown in Figure 10, the NiAl-based eutectics examined to date show a considerable improvement of properties over binary NiAl. Although the properties of the in-situ composites still fall short of the current superalloys, the results obtained thus far encourage further investigation. For many of the composites, the melting temperatures are higher than for the superalloys. Another consideration is the density of the composites. Figure 11 shows a density-adjusted graph of the systems of Figure 10. It is evident that when density is accounted for, the composites are even more promising.

1.2 The NiAl-Cr,Mo System

One of the most promising in-situ eutectic composite systems explored at the University of Tennessee is the NiAl-Cr,Mo eutectic [47]. The alloys studied by Johnson had compositions of 66 at.% NiAl with the balance of Cr and Mo. The Mo content in these alloys ranged from 0.6 at.% to 6 at.% Mo. The NiAl-Cr,Mo eutectic exhibits a lamellar structure, a melting temperature of 1723K, a creep strength at 1300K of 160 MPa, and a room temperature fracture toughness of about 22 MPa% $\sqrt{\text{m}}$ [47].

The NiAl-Cr,Mo eutectic was an improvement over the NiAl-34Cr eutectic. The

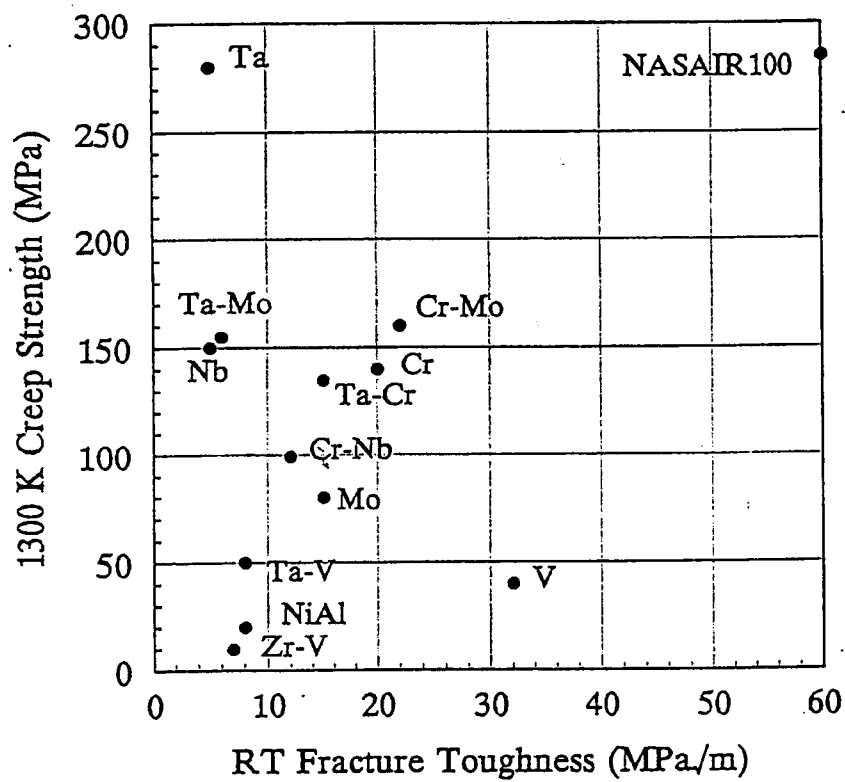


Figure 10: Properties of various NiAl-based eutectic systems directionally solidified at the University of Tennessee [25, 46,47]

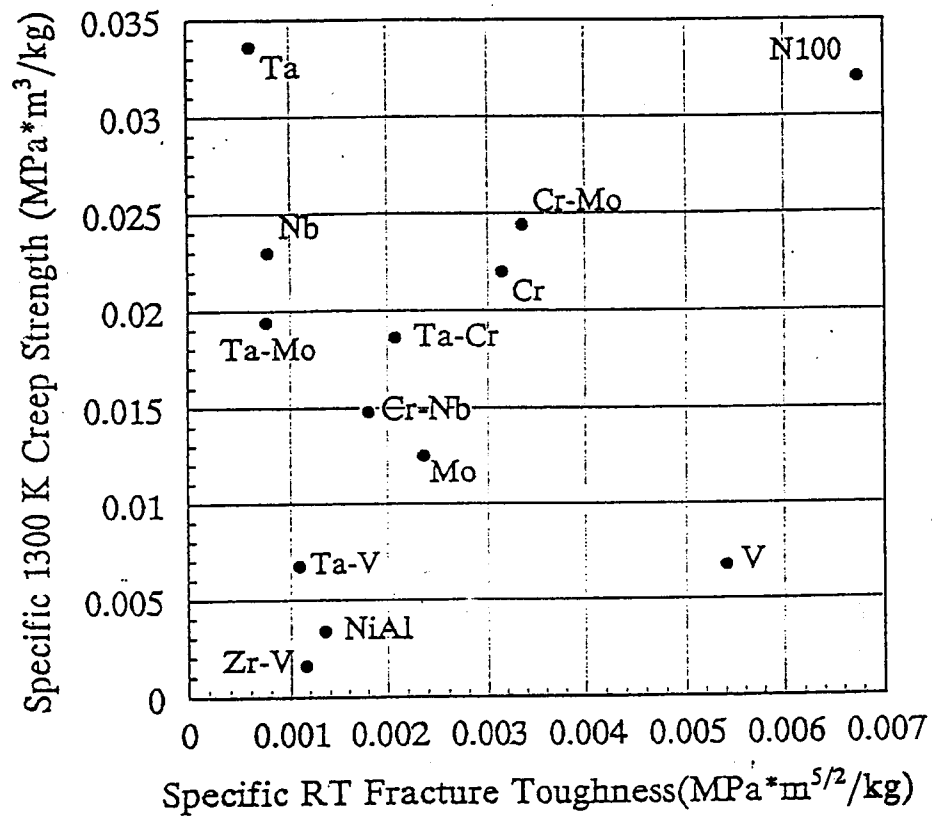
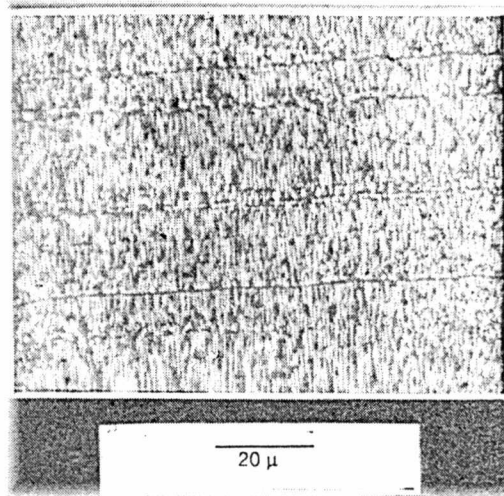


Figure 11: Adjusted properties of various NiAl-based eutectic systems directionally solidified at the University of Tennessee [25, 46, 47]

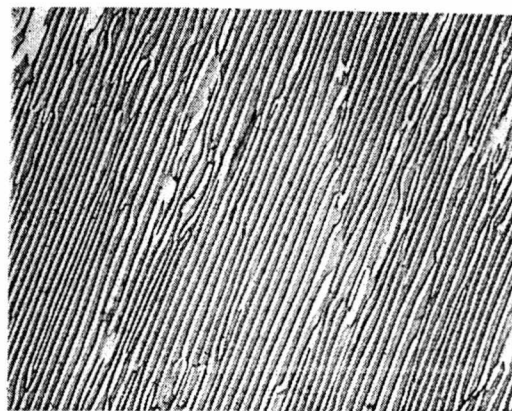
NiAl-34Cr eutectic was also studied by Johnson at the University of Tennessee. The NiAl-34Cr eutectic exhibited a rod-like eutectic structure, a melting temperature of 1723K, a creep strength at 1300K of 140 MPa, and a room temperature fracture toughness of about 20 MPa%*m*. Figure 12 shows the microstructure for both the NiAl-34Cr and one of the NiAl-Cr,Mo alloys. Both alloys have been processed using directional solidification.

The study of the NiAl-Cr,Mo system is not a new one. The system was initially studied by Cline and Walter [48], who examined the effects of quaternary additions on the NiAl-Cr eutectic system. They concluded that at 0.6 at.% Mo, the morphology of the NiAl-Cr,Mo structure transitioned from a rod to a lamellar morphology. Below 0.6 at.% Mo, the structure was mixed rod and lamellar. The other changes that occurred with the addition of Mo was a change from a $\langle 100 \rangle$ growth direction to a $\langle 111 \rangle$ growth direction.

While the NiAl-Cr,Mo alloy system has useable properties, it is still short of the standards set by the Ni-based superalloys. Continued investigation of this eutectic is warranted to see if the properties can be improved. If the fracture toughness of the alloys can be maintained and the high temperature creep resistance improved, the NiAl-Cr,Mo eutectic would be a good candidate for some current applications. If the fracture toughness can be improved and the high temperature creep resistance maintained, the material could see use in many low temperature applications.



a) NiAl-34Cr



b) NiAl-Cr,Mo

Figure 12: Microstructure of directionally solidified (a) NiAl-34Cr and (b) NiAl-Cr,Mo at 400x [47]

2. ALLOYING AND MICROALLOYING

2.1 General Introduction to Alloying Techniques

The question remains on how to improve on the NiAl-Cr,Mo eutectic. One option would be to microalloy the eutectic with another element. When looking to promote promising alloying additions, two routes can be taken. First an alloying addition should strengthen the NiAl matrix and/or the Cr-rich metal phase. The other route for improved properties using alloying would be to find additions that change the lattice parameter of either phase. The difference in the lattice parameter would change the interface coherency between the NiAl and the Cr-rich phase. This would create obstacles for mobile dislocations as well as promote crack delamination.

A popular alloying technique which might prove favorable to the NiAl-based eutectics is solid-solution hardening. There are two ways to obtain solid-solution hardening: substitutional solid solutions and interstitial solid solutions. Substitutional solid solutions are formed when the solute atoms replace the solvent atoms in the crystal lattice. This replacement distorts the crystal lattice which then further impedes the movement of dislocations in the crystal. When forming interstitial solid solutions, the solute atoms fit in the interstices of the structure. The solute atoms fit best at dislocations and the areas surrounding the dislocations. The dislocations are then lined with the interstitial atoms. In order for the dislocations to move, they need to either drag all the solute atoms with them or tear themselves away from them. The result is usually that the dislocations are locked in place [49].

Another alloying approach is to strengthen with additional phases. Two possible scenarios can occur with the addition of a new phase. The first would be to strengthen using large particles of a second phase. These particles are distributed randomly in the matrix phase. They serve as stronger than average grains. The second way to strengthen would be to dispersion harden with strong particles of a second phase. The particles interfere with the movement of dislocations. In this case the morphology of the second phase can be very important [49].

2.2 Alloying in Binary NiAl

Alloying has been applied to binary NiAl (the matrix of the eutectic) in hopes of improving the properties of the intermetallic. Many intensive studies have been conducted in this area. Most have met with limited success. The effects of alloying in-situ composites, however, have not been extensively studied. The following discussion reviews some of the alloying studies of binary NiAl.

Darolia and Walston examined the effects of alloying on binary, single-crystal NiAl [50]. Their efforts resulted in alloys with improved high temperature strength; however, the alloys lost ductility and toughness. Both solid solution effects and precipitation hardening play into the strengthening. From the results of the alloys that were studied, Darolia and Walston felt that two types of second phases warranted further investigation. The two types are Heusler (β') Ni_2AlX , where X is a Group IVB or VB element, and NiAlX Laves phase where X is Hf, Ta, Ti, Nb, V, or Zr. Another promising high temperature alloy reviewed by Darolia and Walston was that containing Ti β'

precipitates. In order to obtain good strength, 7.5-10 at. % Ti was needed. Some the other promising alloys contained small additions (<1 at. %) of Ta or Hf.

Darolia, Lahrman, and Field improved on the room temperature ductility of binary, single-crystal NiAl slabs with small additions of Fe, Ga, and Mo [51]. The mechanisms for the improvements are still under investigation. The effect was apparent in the "soft" (non- $\langle 100 \rangle$) orientations.

Kaysser, Laag, Murray, and Petzow used powder metallurgy techniques to improve both the fracture toughness and creep strength of binary, polycrystalline NiAl. They used additions up to 10 at. % of Ti and Nb. Besides the alloying additions, the very fine grain size of the alloys likely contributed to the improved properties [52].

As previously mentioned, Cline and Walter [48] studied the effects of Mo on the NiAl-Cr eutectic. In that same study the effect of V, W, and Fe were also documented. Both V and W affected the morphology and growth direction of the NiAl-Cr eutectic. There was a transition from rod-like to lamellar structure. The compositions at which the transition occurred were different from that of Mo. When adding V, the morphology became lamellar around 1.3 at. %. In comparison, W exhibited that behavior around 0.7 at. %. The other effect that was observed was that the growth direction changed from $\langle 100 \rangle$ to $\langle 111 \rangle$ for both the V and W additions.

CHAPTER 3

PRELIMINARY INVESTIGATIONS

1. INTRODUCTION

Microalloying appears to be a viable route to improve the NiAl-Cr,Mo eutectic. Based on the work of previous investigators and the known phase constitutional relationships, 5 elements were chosen for microalloying. The amount of the microalloying elements are small (2 at. % or less). The elements chosen were Hf, Ta, Ti, V, and W.

2. NiAl-X AND Cr-X PHASE DIAGRAMS

2.1 Hf Systems

The first element to be reviewed was Hf. Small additions of Hf were shown to improve the properties of binary NiAl [50]. Figure 13 is the ternary phase diagram for the Ni-Al-Hf system at 1073 K [53]. While this diagram does not show solubility of Hf in NiAl, diagrams at higher temperatures do. This implies that as the alloys cooled, there could be precipitation. From Figure 13, the precipitate would most likely be of the composition of the Laves phase NiAlHf.

Phase diagram information for Cr-Hf could not be found. The only information that was obtained for the Cr-Hf system was that there is an alloy of composition HfCr₂ [54]. From the information available, it appears that Hf would likely segregate to the NiAl phase.

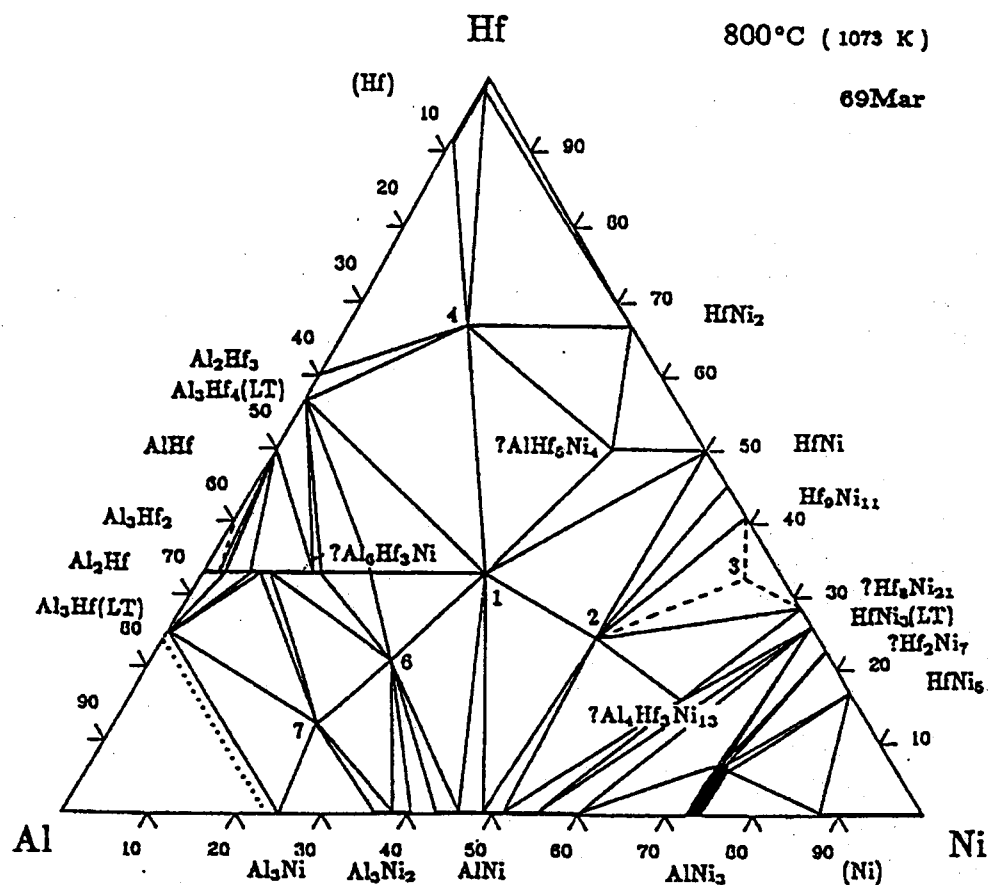


Figure 13: Ni-Al-Hf ternary system at 1073 K [53]

2.2 Ta Systems

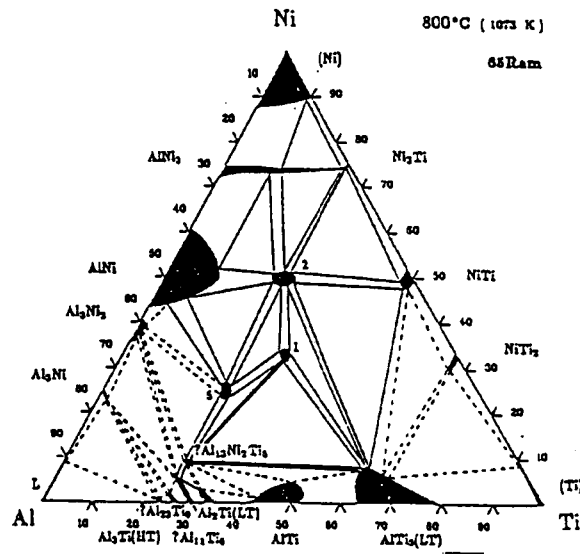
Ta was another addition that somewhat improved the properties in NiAl [50]. Figure 14a shows a ternary diagram for Ni-Al-Ta system at 1273 K [53]. Ta has some solubility in NiAl at this temperature. Figure 14b is the binary Cr-Ta phase diagram[55]. Ta is soluble in Cr up to about 5 wt. % at 1773 K. Since additions of only 2 at. % Ta or less are of interest here, it is possible that Ta may enter both phases.

2.3 Ti Systems

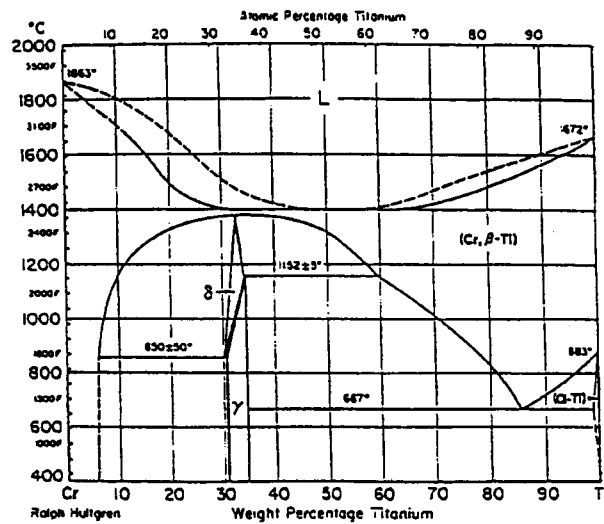
Both Kaysser et al. [52] and Darolia and Walston [50] saw property improvement with Ti additions to NiAl. Figure 15 shows the Ni-Al-Ti and the Cr-Ti systems [53, 55]. Ti is soluble in both NiAl and Cr. The solubility in NiAl at 1073 K is about 15 at. %. The solubility in Cr at 673 K is around 7 at. %. It is likely that the Ti will segregate to both NiAl and Cr.

2.4 V Systems

As mentioned in the previous chapter, V tends to act like Mo in the NiAl-Cr eutectic promoting a change from a rod-like to a lamellar morphology [48]. The phase diagrams in Figure 16 show that V is very soluble in NiAl and Cr [53,55]. Once again the V could segregate to either phase or both. A drawback to V is the possibility that it could depress the melting temperature of the alloy.

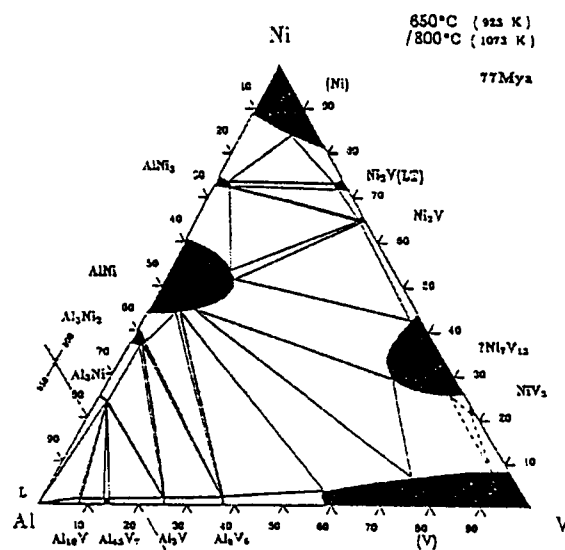


a) Ni-Al-Ti ternary at 1073K

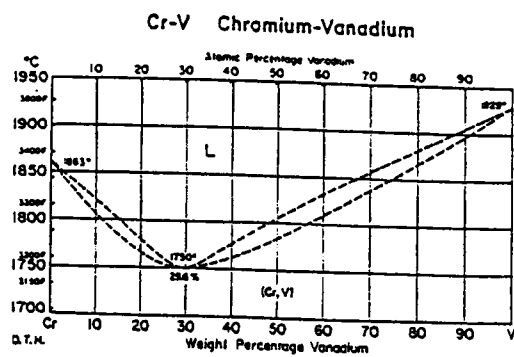


b) Cr-Ti binary phase diagram

Figure 15: a) Ni-Al-Ti ternary system phase diagram at 1073 K [53]. b) Cr-Ti binary phase diagram [55]



a) Ni-Al-V ternary at 1073 K



b) Cr-V binary phase diagram

Figure 16: a) Ni-Al-V ternary system phase diagram at 1073 K [53]. b) Cr-Ti binary phase diagram [55]

2.5 W Systems

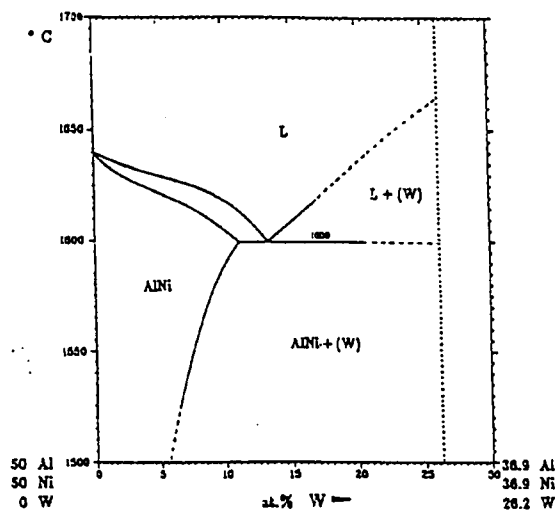
W is another solute that promotes the lamellar structure of the eutectic [48]. Figure 17 shows a pseudo-binary NiAl-W and the binary Cr-W diagrams [53,55]. W has good solubility in both phases. A possible problem with W going into Cr is the miscibility gap that forms. At the low additions (2 at. % or less), the miscibility gap should not pose any problems. As mentioned with previous alloys, the W could segregate to either phase or both phases.

3. SAMPLE PREPARATION

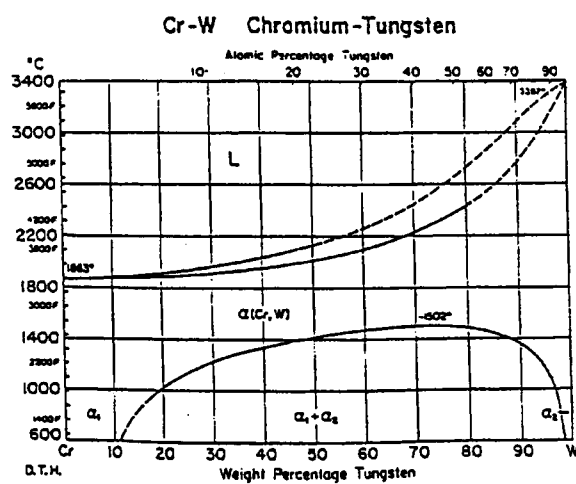
3.1 Arc-Melt Procedures

While some of the effects of the alloying additions on binary NiAl are known, little is known about their effects on the NiAl-based NiAl-Cr,Mo eutectic. The initial microalloying additions were done experimentally utilizing the economical method of small arc-melt buttons.

The buttons were 25 grams in weight. The raw materials were melted simultaneously on a water-cooled copper hearth in one atmosphere positive pressure of argon. The melting source was a non-consumable tungsten electron controlled by a 400 amp welder. Additional arc-melts were supplied by NASA Lewis. Their melts were arc-melted and drop cast into small rods. The material received from NASA Lewis was in the form of 3/8 inch diameter, 3 inches long rods.



a) NiAl-W pseudo binary phase diagram



b) Cr-W binary phase diagram

Figure 17: a) NiAl-W pseudo binary phase diagram [53]. b) Cr-W binary phase diagram [55]

3.2 Polishing Procedures

Once the material was processed, optical and electron microscopy was used to examine the microstructure. In order to view the structure, the materials had to be prepared using standard polishing procedures. A piece of material from each button or pin was sectioned off with a standard high speed cut-off wheel. The specimens were then mounted in conductive Bakelite mounts. The samples were ground using a high speed grinding wheel with 200 grit paper. The samples were further polished using 3 steps of diamond paste: 15 μm , 6 μm , and 1 μm . The last polishing step was using a 0.06 μm Al_2O_3 slurry. Once polished the samples were etched using a 90 vol. % H_2O , 5 vol. % HNO_3 , 5 vol. % HF solution.

4. PRELIMINARY RESULTS

4.1 NiAl-Cr,Mo-Hf

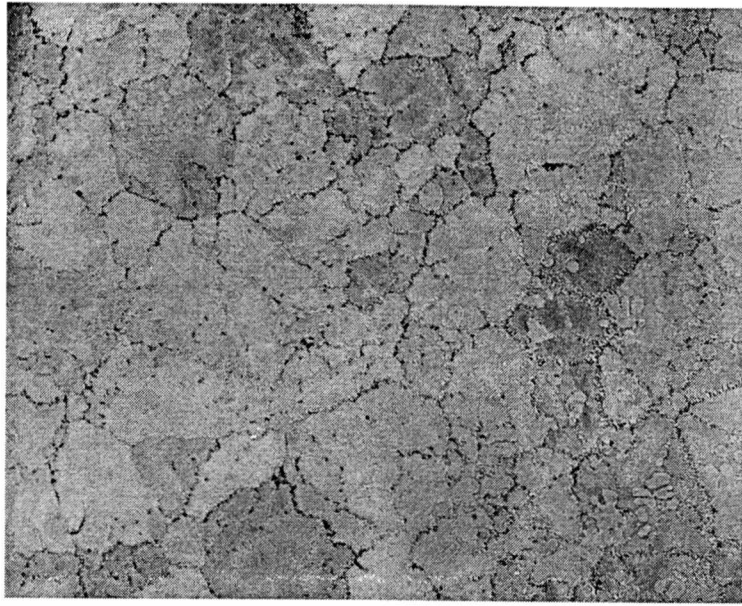
Table 3 shows the compositions of all of the arc-melt pins which were processed by NASA Lewis. All of the alloys contained 66 at. % NiAl, and 34 at. % additions. The Mo was kept constant at 3 at. %. Two compositions containing Hf were investigated.

The microstructures of the alloys were observed with optical microscopy. Both compositions had similar structures as seen in Figures 18 and 19. The alloys both have eutectic colonies and primary phase. Also in evidence is a dark phase along the boundaries.

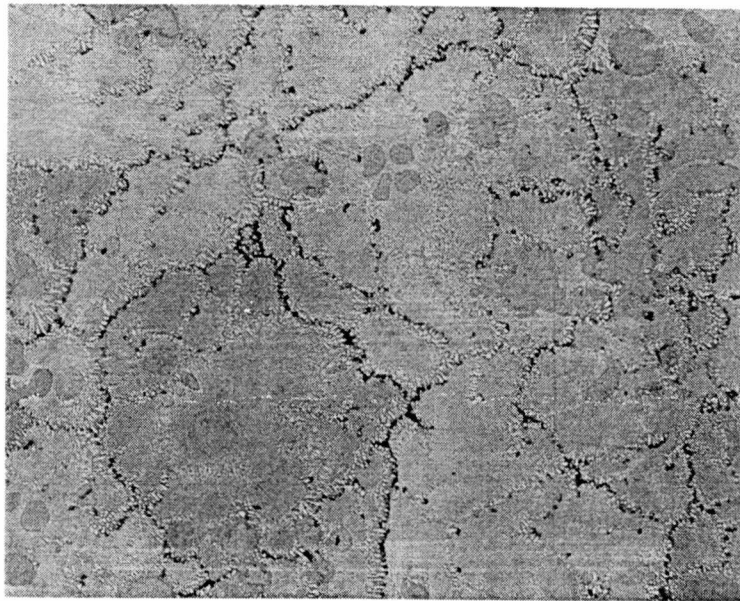
When the alloys were studied using Scanning Electron Microscopy (SEM), the

Table 3: Compositions of arc-melts processed by NASA Lewis Research Center

Ni at. %	Al at. %	Cr at. %	Mo at. %	X at. %
33	33	30.5	3	0.5 Hf
33	33	30	3	1 Hf
33	33	30.5	3	0.5 Ta
33	33	30	3	1 Ta
33	33	29	3	2 Ta
33	33	30.5	3	0.5 Ti
33	33	30	3	1 Ti
33	33	29	3	2 Ti
33	33	30.5	3	0.5 V
33	33	30	3	1 V
33	33	29	3	2 V
33	33	30.5	3	0.5 W
33	33	30.25	3	0.75 W
33	33	30	3	1 W

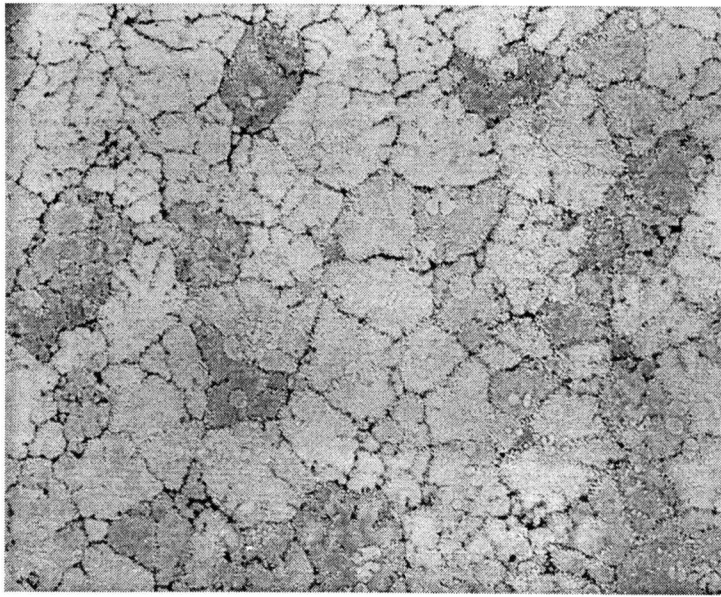


a) 200x

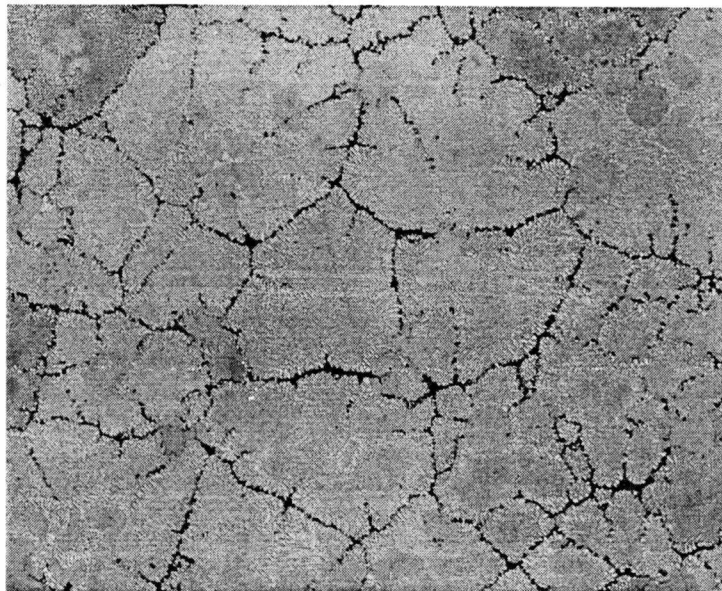


b) 400x

Figure 18: Optical micrographs of NiAl-30.5Cr-3Mo-0.5Hf alloy at a) 200x b) 400x



a) 200x



b) 400x

Figure 19: Optical micrographs of NiAl-30Cr-3Mo-1Hf alloy at a) 200x b) 400x

dark phase was not in evidence. Since the alloys were studied using SEM in an unetched condition, it is probable that the dark areas are an etching effect. The primary phase was determined to be NiAl.

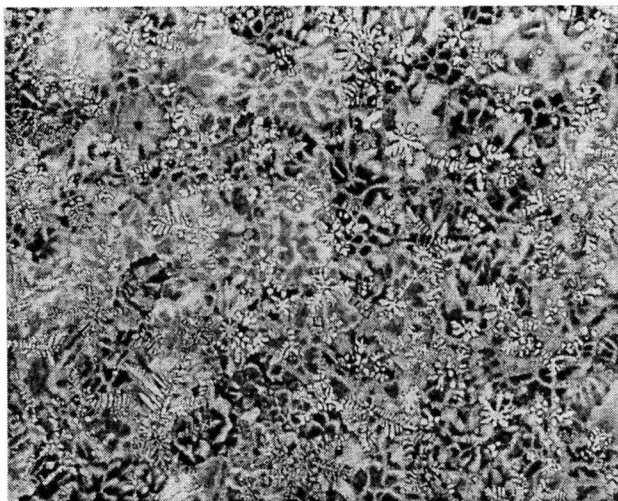
4.2 NiAl-Cr,Mo-Ta

Three compositions which contained Ta were studied. Using optical microscopy, all the Ta alloys had NiAl dendrites present. Figure 20 shows the Ta alloys at 100x. As the Ta increases, the quantity of dendrites decreases. The length of the dendrites also decreases. Figure 21 shows the alloys at 400x. At higher percentages of Ta the eutectic structure is not as well defined. Also as the amount of Ta increases, more primary phase is present.

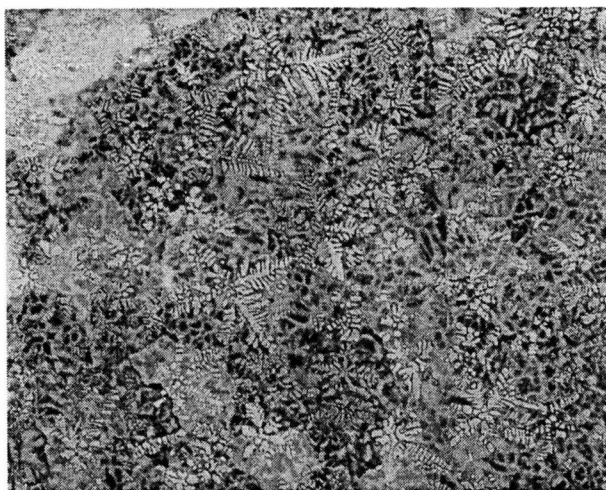
The Ta alloys were examined in the SEM on Backscatter Electron mode (BSE). BSE shows any atomic number contrast in the alloys. While examining the samples an additional phase was discovered. Figure 22 shows this new phase (bright phase) at high magnification. Using Energy Dispersive Spectrometry (EDS) analysis this new phase was determined to be Ta rich. The other areas of the sample do not contain much Ta. EDS also confirmed that the primary phase was NiAl.

Further study should be conducted on this alloy system. More detailed analysis should be done on the new phase to determine if it is pure Ta or a Ta compound. Only a simple survey was done in this investigation. The higher Ta alloys did not show the promising eutectic structure that is of interest in this research.

a)



b)



c)

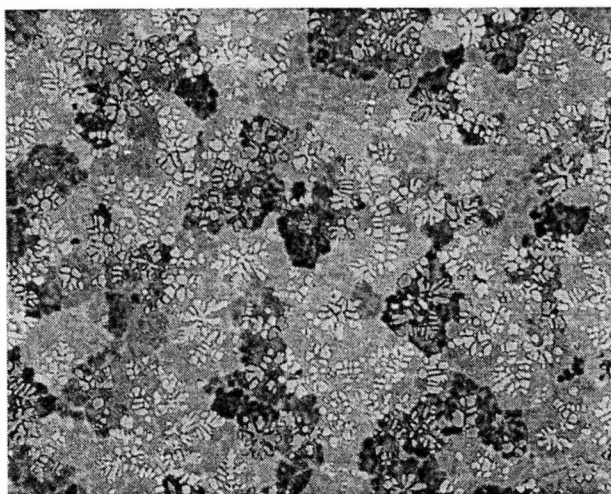
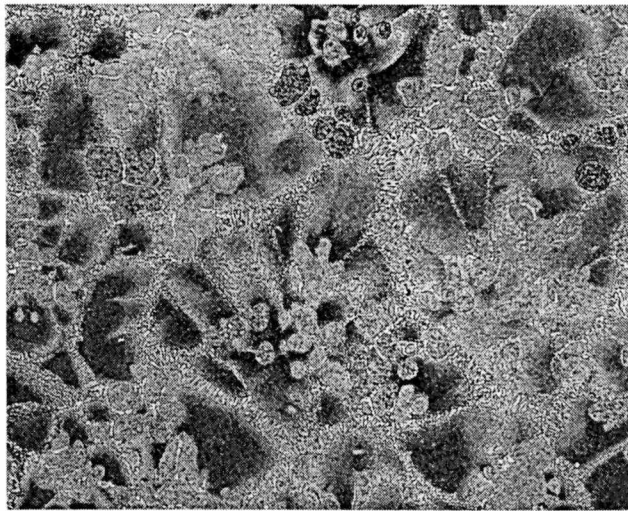
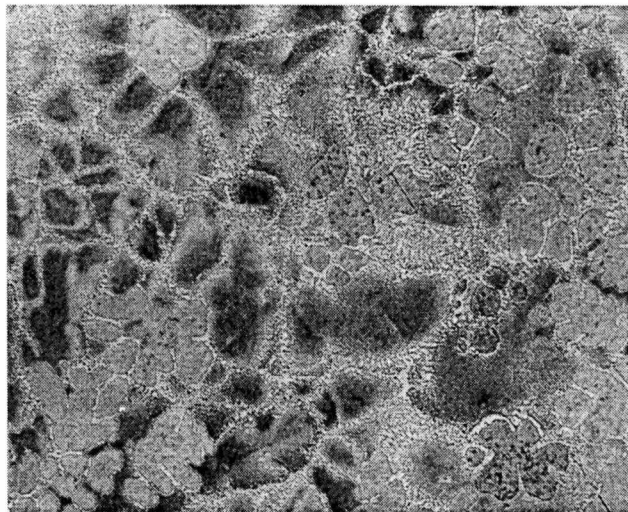


Figure 20: Optical micrographs at 100x for a) NiAl-30.5Cr-3Mo-0.5Ta alloy b) NiAl-30Cr-3Mo-1Ta alloy c) NiAl-29Cr-3Mo-2Ta alloy

a)



b)



c)

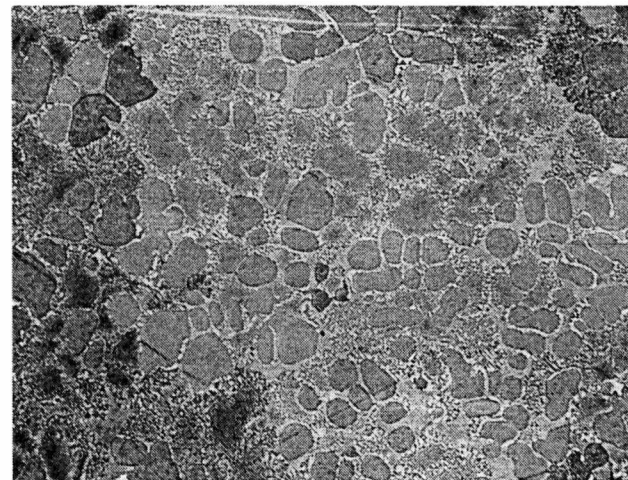


Figure 21: Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5Ta alloy b) NiAl-30Cr-3Mo-1Ta alloy c) NiAl-29Cr-3Mo-2Ta alloy

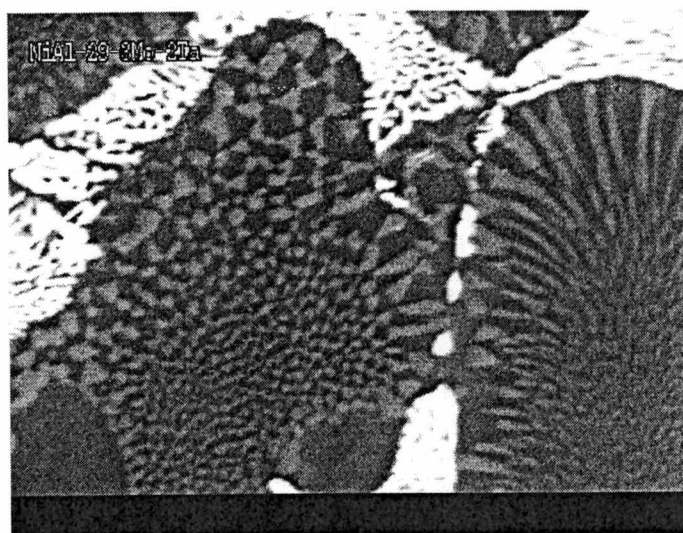


Figure 22: Backscattered SEM micrograph of NiAl-29Cr-3Mo-2Ta alloy at 3000x

4.3 NiAl-Cr,Mo-Ti

Two sets of Ti samples were studied. The first set were processed at NASA Lewis and is included in Table 3. Optical microscopy showed a good lamellar eutectic structure as seen in Figure 23. The structures also show primary phase. The alloy with 1 at. % Ti has the most well defined eutectic structure. At 2 at. % Ti, the microstructure shows a dark phase in the colony boundaries.

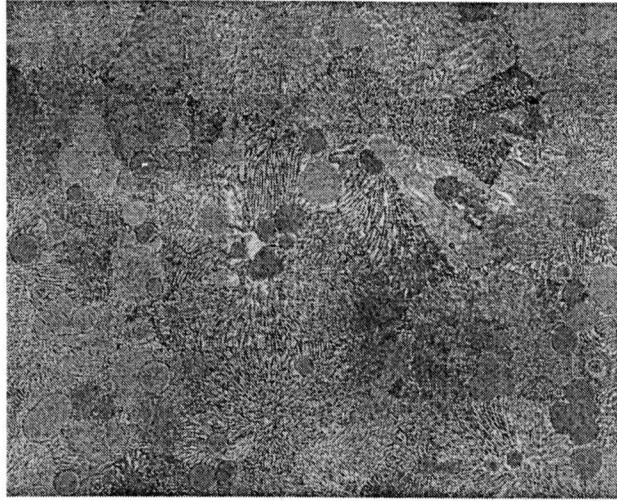
SEM and EDS analysis confirm that the primary phase is NiAl. The dark phase does not show up very well in the BSE mode. However, EDS mapping shows that the boundary areas are Ti rich.

The alloys processed at NASA Lewis did have a problem. All three compositions contained pieces of unmelted Mo. Therefore, the results in the preliminary study are not conclusive. New alloys should be processed and reinvestigated.

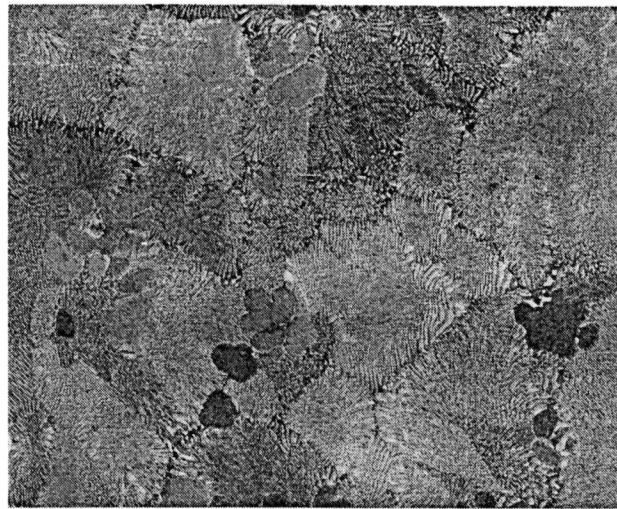
The second series of NiAl-Cr,Mo-Ti arc-melts were successfully processed at the University of Tennessee using the arc-melt process previously described. These alloys were made from a NiAl-28Cr-6Mo material with Ti added. Table 4 lists the nominal compositions for these alloys.

For the alloys of composition 1- 4 at. % Ti, the microstructure consisted of well-defined eutectic colonies and primary phase. Figure 24 shows the microstructure of the 1 at. % Ti and the 4 at.% Ti alloys. At 4 at. %, the microstructure begins to show a dark phase in the colony boundaries similar to that seen in the NASA alloys. The alloys containing 6 - 10 at.% Ti do not exhibit the same structure as the lower Ti alloys. There is no definite eutectic structure. There continues to be two phases but no order or

a)



b)



c)

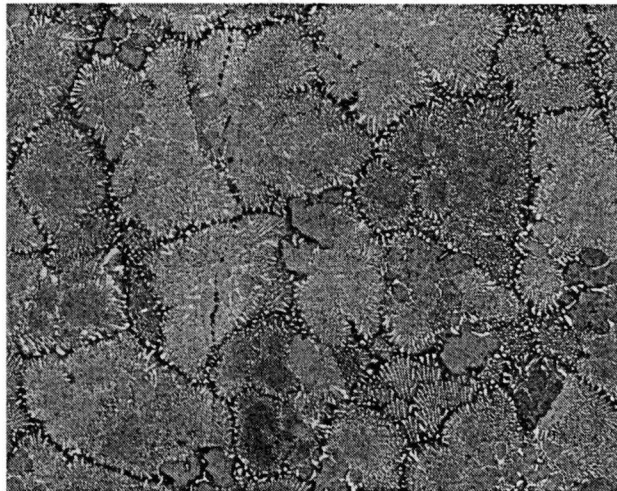
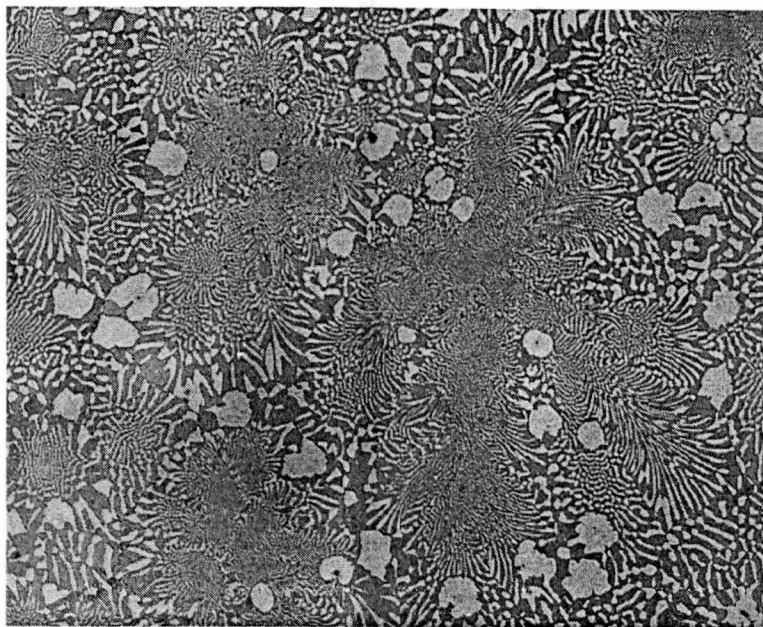


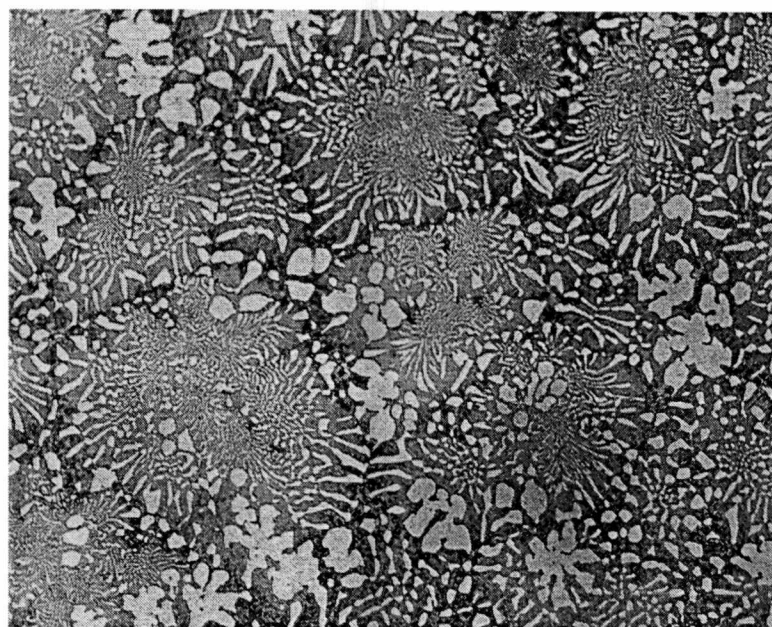
Figure 23: Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5Ti alloy b) NiAl-30Cr-3Mo-1Ti alloy c) NiAl-29Cr-3Mo-2Ti

Table 4: Nominal compositions of arc-melted Ti buttons processed at the University of Tennessee

Atomic % Ni	Atomic % Al	Atomic % Cr	Atomic % Mo	Atomic % Ti
32.5	32.5	28	6	1
32	32	28	6	2
31	31	28	6	4
30	30	28	6	6
29	29	28	6	8
28	28	28	6	10



a) 1 at. % Ti



b) 4 at. % Ti

Figure 24: Optical micrographs at 400x for a) NiAl-Cr,Mo-1Ti b) NiAl-Cr,Mo-4Ti alloys processed at the University of Tennessee, Knoxville

periodicity to the structure. Figure 25 shows the higher Ti alloys at 200x.

Vickers microhardness tests were also conducted on these samples. Figure 26 is a graphical representation of those hardness results. With the addition of 1 at. % Ti, the microhardness has an initial raise in hardness from 450 Hv to 575 Hv. The hardness plateaus around 2 at. % until 4 at. %. After the addition of 4 at. % Ti, the hardness continues to increase reaching a value of 735 Hv at 10 at. % Ti.

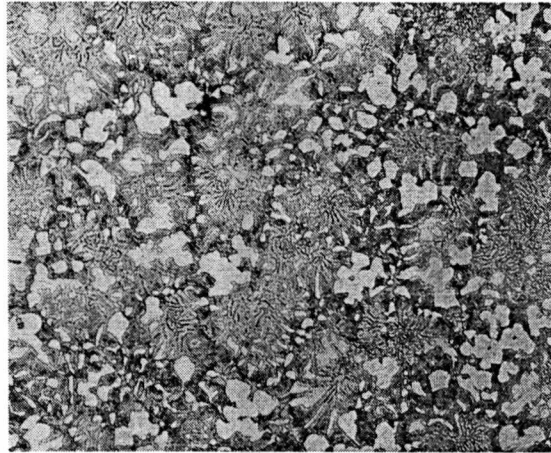
While there is a correlation between hardness and mechanical properties in steels, none has yet been determined for intermetallic compounds and alloys. The increase in hardness indicates that some type of change is occurring in these alloys. The second increase in hardness is possibly caused by the changes of microstructure in the higher Ti alloys.

4.4 NiAl-Cr,Mo-V

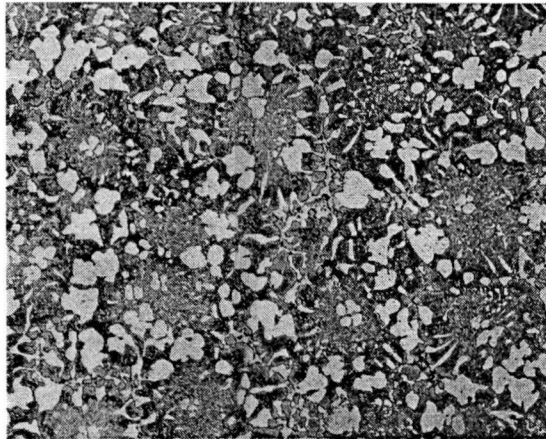
Three compositions of V alloys were studied. Optical microscopy was also conducted on these alloys. Figure 27 shows the alloys at 400x. In all the alloys, the microstructure has well defined eutectic colonies and primary phase present. The eutectic structure appears finer in these alloys than in the NiAl-Cr,Mo alloys.

SEM and EDS analysis confirms that the primary phase is NiAl. EDS mapping also confirms that the V is present in the eutectic structure. However, the structure is too fine to resolve at the working distance needed to do EDS. It has not been determined which phase of the eutectic contains the V.

a)



b)



c)

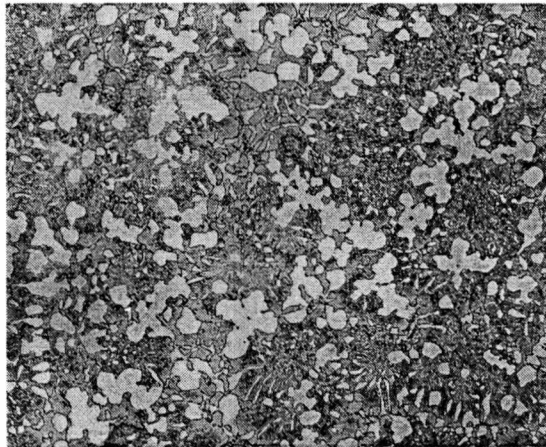


Figure 25: Optical micrographs at 400x for a) NiAl-Cr,Mo-6Ti b) NiAl-Cr,Mo-8Ti
c) NiAl-Cr,Mo-10Ti alloys processed at the University of Tennessee, Knoxville

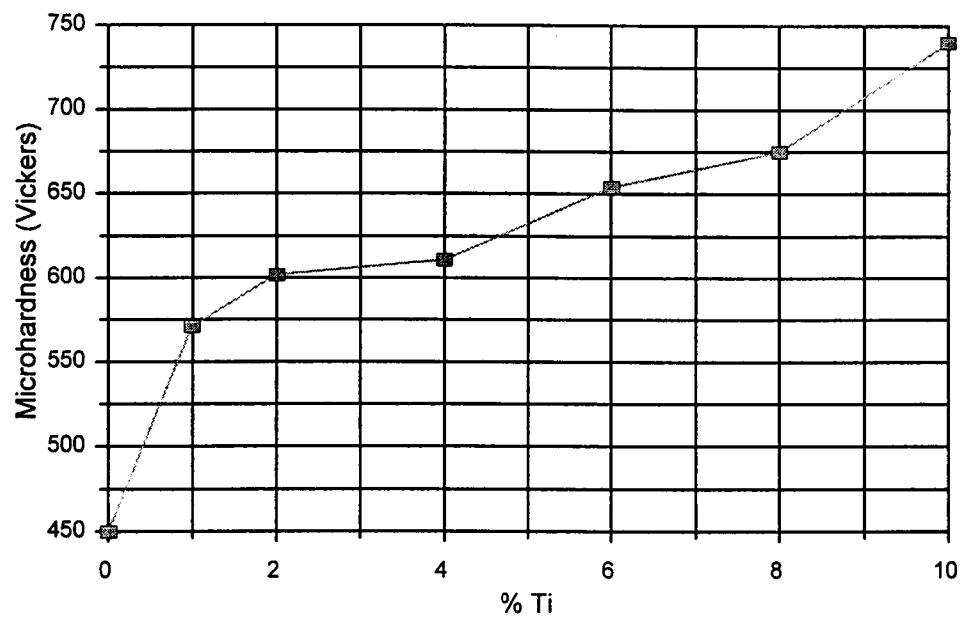
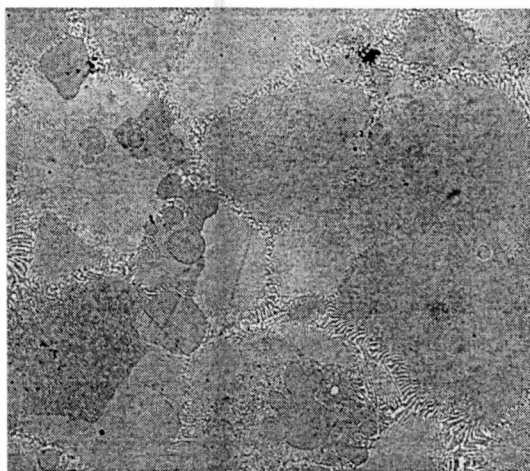


Figure 26: Microhardness as a function of composition for NiAl-Cr,Mo-Ti alloys processed at the University of Tennessee

a)



b)



c)

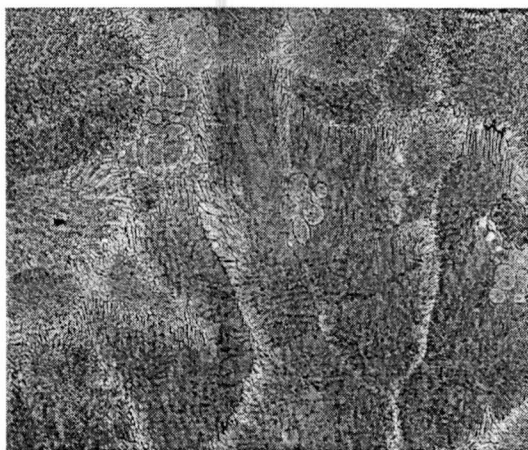


Figure 27: Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5V alloy b) NiAl-30Cr-3Mo-1V alloy c) NiAl-29Cr-3Mo-2V alloy

4.5 NiAl-Cr,Mo-W

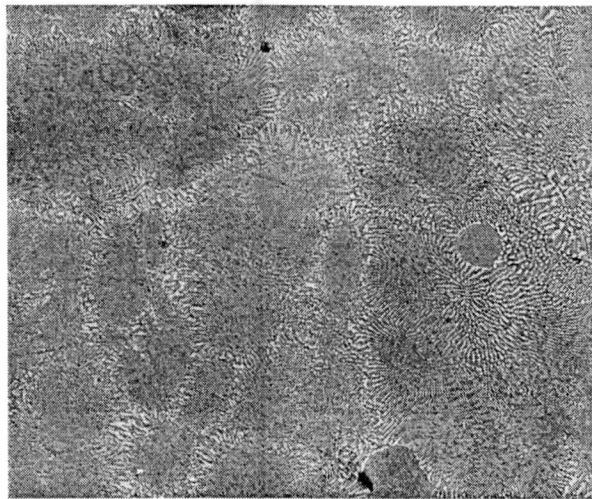
Like the V alloys, the W alloys had a regular eutectic structure. The structure is not as fine as the V alloy but also consists of eutectic and primary phase. Figure 28 shows the optical micrographs for the W alloys at 400x. The eutectic structure in the 1 at. % W alloy exhibits a better aligned eutectic structure.

SEM and EDS confirmed the primary phase as NiAl. W is present in the eutectic structure. Once again it was not determined where in the eutectic structure the W is. This difficulty is most likely related to the limited resolution of the SEM in BSE mode.

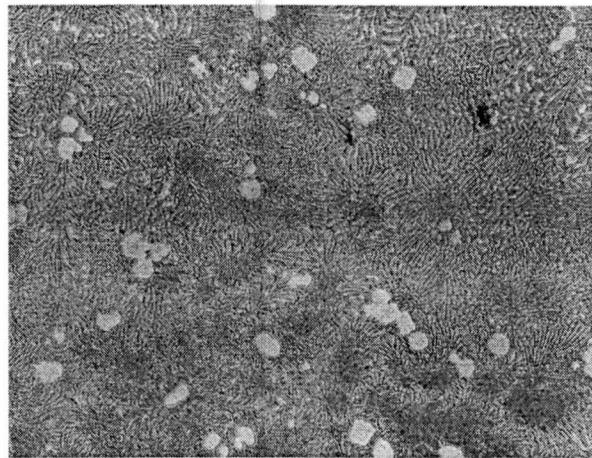
4.6 Summary of Preliminary Investigation

All the alloys surveyed exhibited a primary phase which was identified by EDS to be NiAl. Most of the alloys also retained the NiAl-Cr,Mo eutectic structure. The V and W alloys have the best eutectic microstructures for directional solidification (DS) processing. The 1 at. % alloys of both V and W were chosen for DS and further investigation.

a)



b)



c)

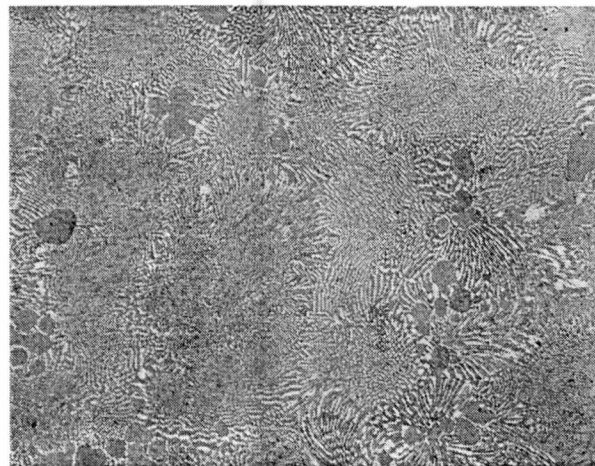


Figure 28: Optical micrographs at 400x for a) NiAl-30.5Cr-3Mo-0.5W alloy b) NiAl-30.25Cr-3Mo-0.75W alloy c) NiAl-30Cr-3Mo-1W alloy

CHAPTER 4

PROCESSING AND TESTING PROCEDURES

1. Directional Solidification Procedure

Directional solidification (DS) is the most promising of processing techniques for eutectic composites. DS allows for control of microstructure orientation and thus the anisotropic properties of the eutectics. Classic Czochralski and Bridgman techniques are useful [56-59]. These techniques can introduce impurities from the crucible at the needed processing temperatures. For alloys where high purity is a necessity, contamination must be avoided.

Oliver et al. [25,47] have developed containerless methods of directional solidification. The basis of the method involves induction heating and melting within a chemically controlled environment (high purity helium). A molten zone forms and is levitated by the induction field. Computer control of the molten zone allows stable processing. The goal during processing is to maintain a constant ingot diameter as well as a steady state microstructure. These two properties are maintained using power control and diameter stretch/squeeze control. Figure 29 shows a schematic of the liquid zone and some of the possible control actions. A detailed description of the process, equipment and its operation is available elsewhere [25,47].

2. Four-Point Flexure Testing

Four-Point flexure tests on notched samples were used to determine the room temperature fracture toughness of the DS specimens. Figure 30 shows the specimen size

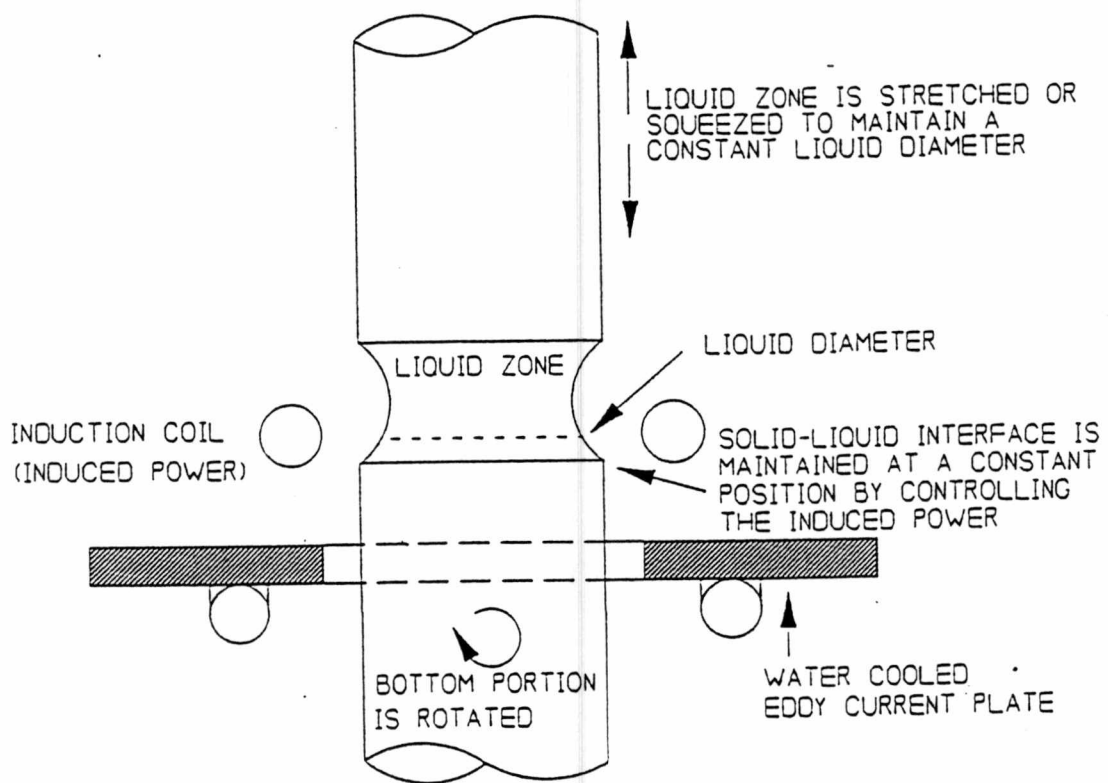
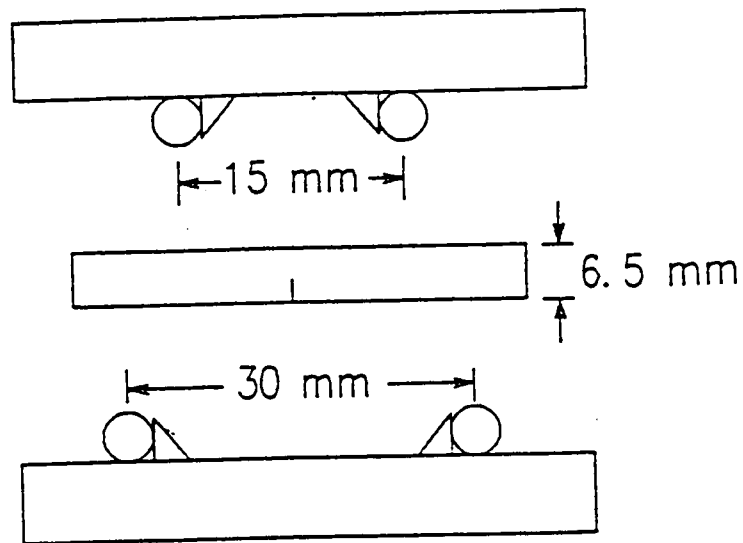


Figure 29: Schematic of the liquid zone and control actions of directional solidification process



SAMPLE SIZE: 4.5 mm x 6.5 mm x 40 mm
NOTCH: 2.00 mm x 0.35 mm

Figure 30: 4-point bend fixture geometry and specimen size

and geometry. NASA Lewis machined the bend specimens using electrical discharge machining. The samples were notched perpendicular to the growth direction using a slow speed, diamond-impregnated saw. The tests were run using a screw driven test frame using displacement control at a rate of 1.4×10^{-4} mm/s. K calibration for pure bending was used to calculate the fracture toughness [60].

CHAPTER 5

RESULTS & DISCUSSION

1. INTRODUCTION

Based on the preliminary results discussed in Chapter 3, V and W were chosen as microalloying additions. Five ingots were processed using the directional solidification method described in Chapter 4. All the ingots were processed under the same conditions and at the same freezing rates. The compositions of those ingots are found Table 5. The NiAl-31Cr-3Mo ingot was included as a reference. All the alloys contained 66 atomic percent NiAl.

The amount of V and W remained constant at 1 atomic percent, and the Cr and Mo content was varied to keep the NiAl content constant at 66 atomic percent. A lamellar structure was expected even in the reduced Mo ingots since both V and W promote that structure in NiAl-Cr alloys [48].

2. RESULTS

2.1 Room Temperature Fracture Toughness

Room temperature fracture toughness tests were conducted on the five DS specimens using the procedure describe in Chapter 4. The results are listed in Table 6. The NiAl-32Cr-1Mo-1V ingot had the highest fracture toughness with an average of 26.6 MPa√m. This was a measurable increase over the straight NiAl-31Cr-3Mo eutectic (23.5 MPa√m). The 3Mo-1V alloy also showed an increase in fracture toughness, but less than

Table 5: Composition of directionally solidified ingots

Ni at. %	Al at. %	Cr at. %	Mo at. %	X at. %
33	33	31	3	—
33	33	30	3	1 V
33	33	32	1	1 V
33	33	30	3	1 W
33	33	32	1	1 W

Table 6: Room temperature fracture toughness results

Sample Number	Break Stress (MPa)	K_I (MPa/m)	KI Average (MPa/m)
31Cr3Mo-1	310.12	24.8	23.5
31Cr3Mo-2	271.20	23.8	
31Cr3Mo-3	235.99	21.8	
31Cr3Mo-4	291.59	24.7	
31Cr3Mo-5	263.17	22.9	
31Cr3Mo-6	287.27	23.1	
3Mo1V-1	310.12	25.4	24.3
3Mo1V-2	298.39	24.4	
3Mo1V-3	306.42	24.2	
3Mo1V-4	266.26	23.6	
3Mo1V-5	302.71	24.1	
3Mo1V-6	268.73	24.0	
1Mo1V-1	310.12	24.8	26.6
1Mo1V-2	342.25	25.3	
1Mo1V-3	371.28	27.3	
1Mo1V-4	305.18	26.6	
1Mo1V-5	358.93	24.6	
1Mo1V-6	316.30	27.6	
1Mo1V-7	339.16	27.9	
1Mo1V-8	326.19	27.7	
3Mo1W-1	277.38	19.7	18.0
3Mo1W-2	218.69	19.0	
3Mo1W-3	226.72	15.5	
3Mo1W-4	220.55	18.6	
3Mo1W-5	223.02	19.8	
3Mo1W-6	175.45	17.7	
3Mo1W-7	222.40	15.7	
1Mo1W-1	201.40	22.4	22.2
1Mo1W-2	239.70	20.6	
1Mo1W-3	211.28	19.0	
1Mo1W-4	261.94	22.4	
1Mo1W-5	274.29	24.4	
1Mo1W-6	228.58	22.5	
1Mo1W-7	251.44	25.5	
1Mo1W-8	229.81	20.4	

the 1Mo-1V alloy. Both of the W alloys had a lower fracture toughness than the unalloyed eutectic.

The fracture surfaces of the five alloys were examined. Figures 31-35 show the fracture surfaces at various magnitudes. The NiAl-31Cr-3Mo eutectic, the 3Mo-1V alloy, and the 1Mo-1V alloy, all show river patterns (Figures 31-33). This indicates that the specimens did have some ductility before fracture. The 3Mo-1W and 1Mo-1W alloys show signs of a more brittle fracture. Figures 34-35 have cleavage areas throughout the surfaces.

2.2 Microscopy and Lamellar Spacing

Both optical and BSE images were taken of the bend specimens. The transverse section of the specimen was polished and etched using previously describe techniques. The BSE micrographs for the five alloys are shown in Figures 36-40. The 31Cr-3Mo, 3Mo-1V, and 1Mo-1V alloys had similar structures. The 3Mo-1V appears to have the most primary phase of the three. The 1Mo-1V appears finer than the straight Cr-Mo. The two W alloys have a much coarser structure with a lot of primary phase areas.

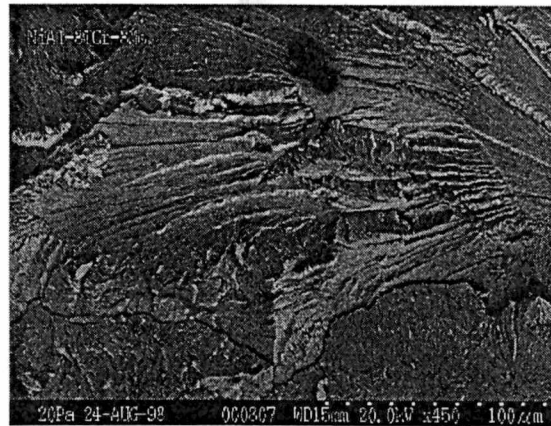
Figures 36-40 were used to determine the lamellar spacing of the eutectic. The results are found in Table 7. A line integration method was used to calculate the lamellar spacing. At least 10 measurements on each micrograph was taken. Those measurements were then averaged to get the spacing listed in Table 7.

A longitudinal section of each specimen was also polished and studied. Figures 41-45 show the structure of the ingots in the direction of growth. Figure 41 indicates that

a)



b)

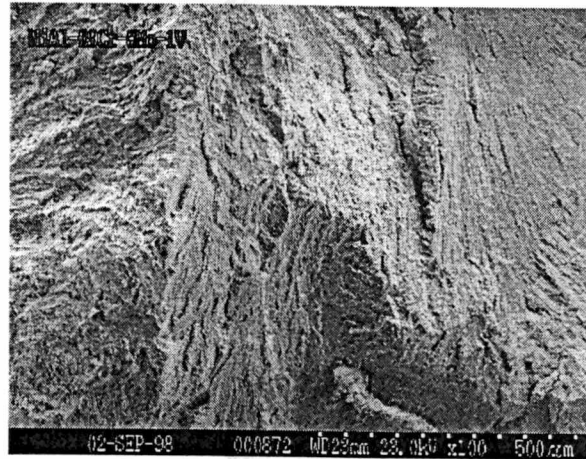


c)

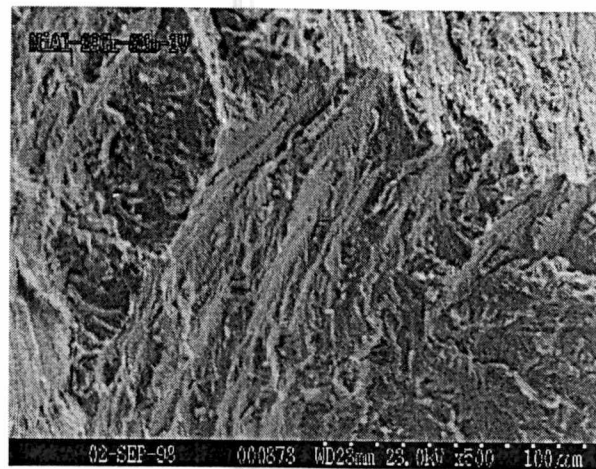


Figure 31: Fracture surfaces of NiAl-31Cr-3Mo alloy at a) 100x b) 500x c) 1000x

a)



b)



c)

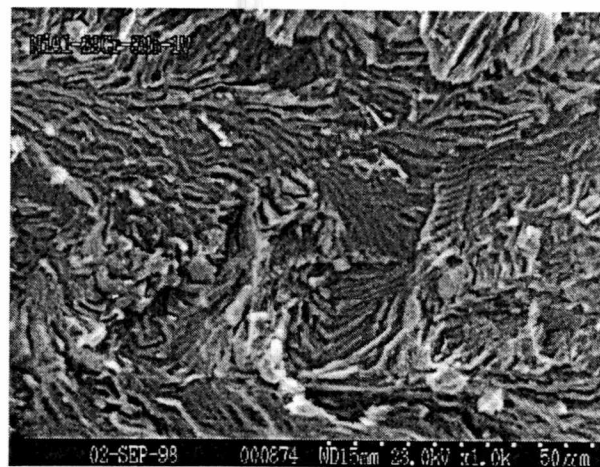
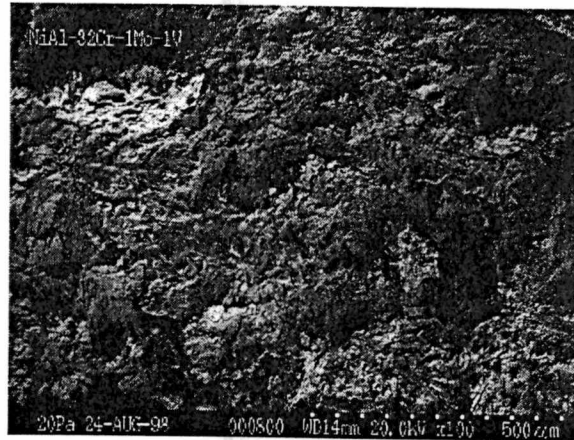


Figure 32: Fracture surfaces of NiAl-30Cr-3Mo-1V alloy at a) 100x b) 500x c) 1000x

a)



b)



c)

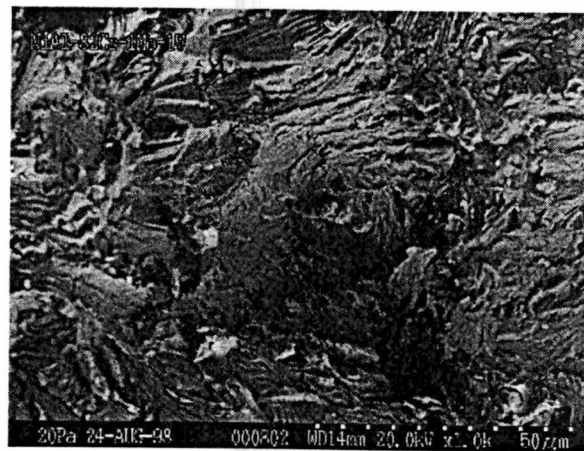
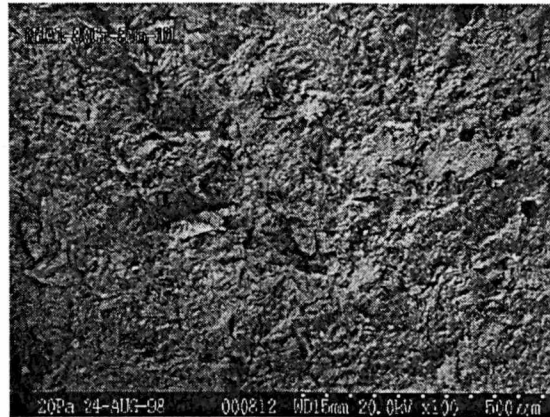
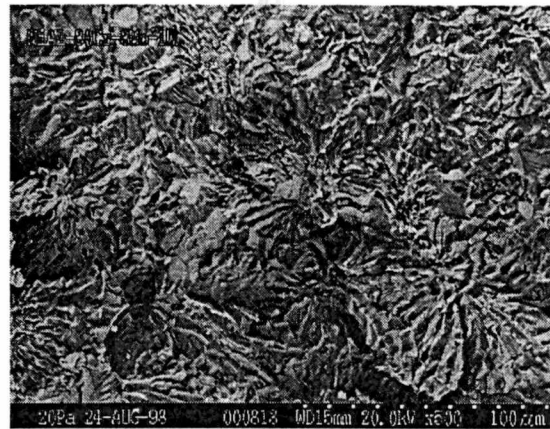


Figure 33: Fracture surfaces of NiAl-32Cr-1Mo-1V alloy at a) 100x b) 500x c) 1000x

a)



b)

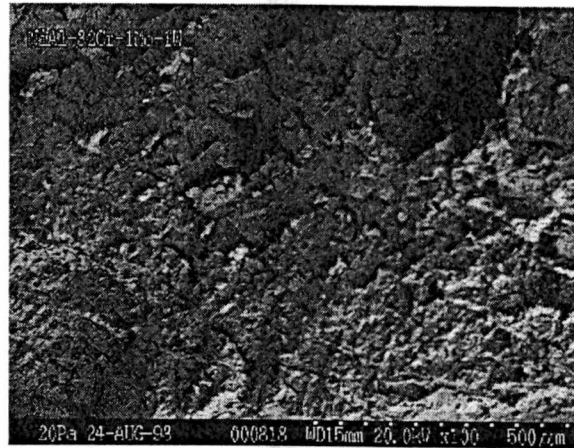


c)



Figure 34: Fracture surfaces of NiAl-30Cr-3Mo-1W alloy at a) 100x b) 500x c) 1000x

a)



b)



c)

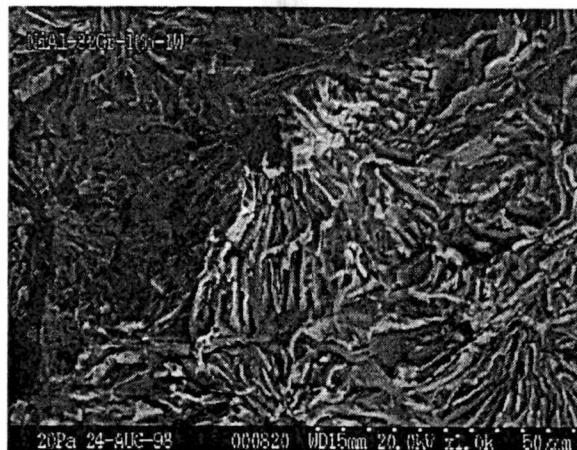
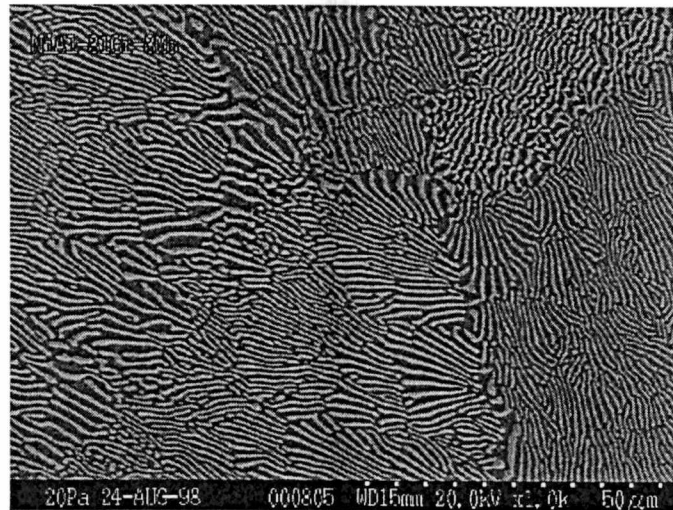
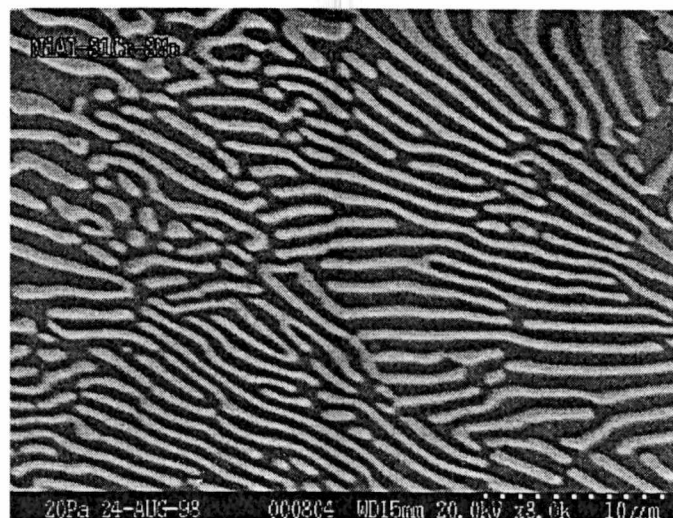


Figure 35: Fracture surfaces of NiAl-32Cr-1Mo-1W alloy at a) 100x b)500x c) 1000x

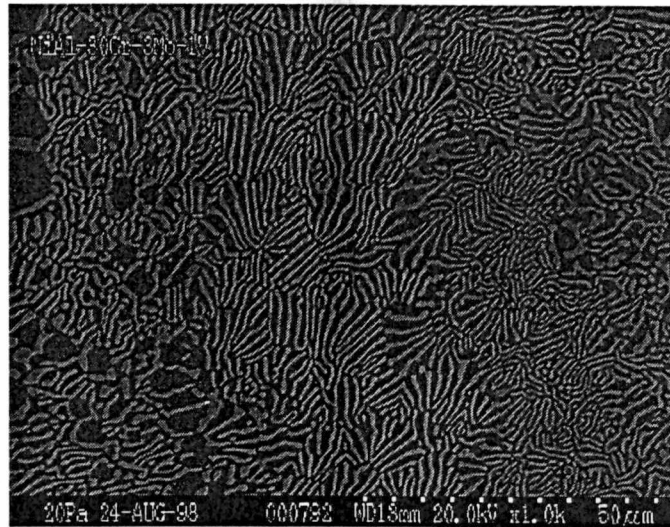


a) 1000x

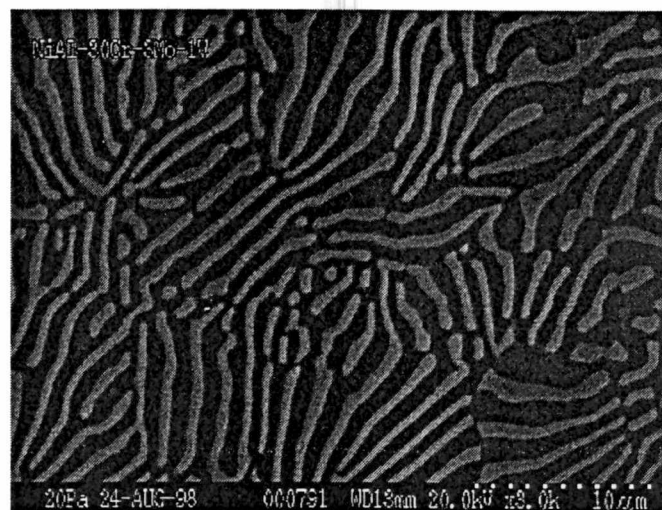


b) 3000x

Figure 36: BSE images of transverse section of NiAl-31Cr-3Mo alloy at a) 1000x
b) 3000x

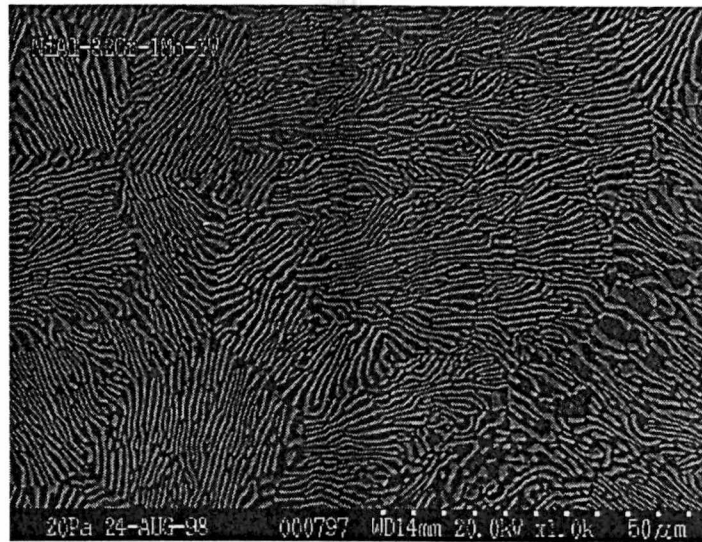


a) 1000x

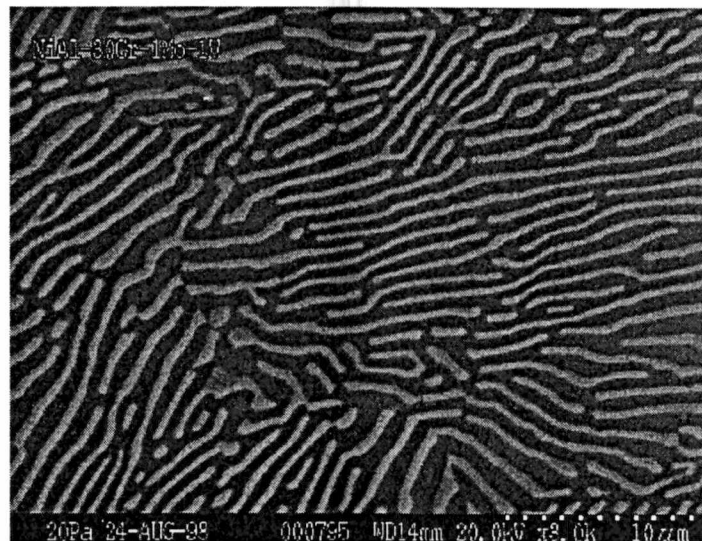


b) 3000x

Figure 37: BSE images of transverse section of NiAl-30Cr-3Mo-1V alloy at a) 1000x
b) 3000x

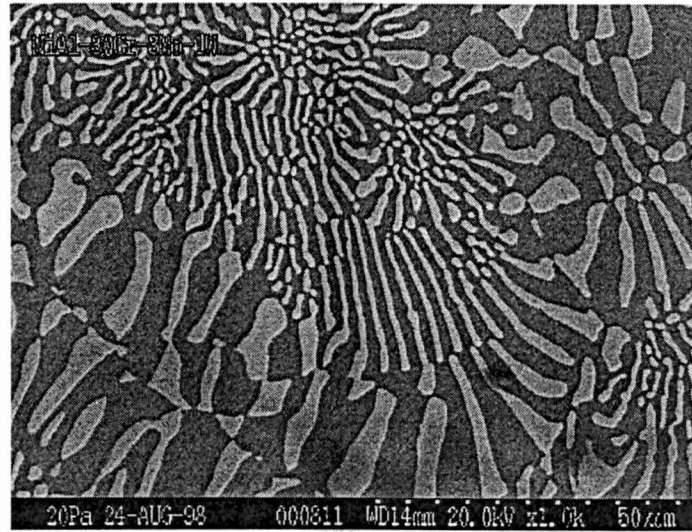


a) 1000x

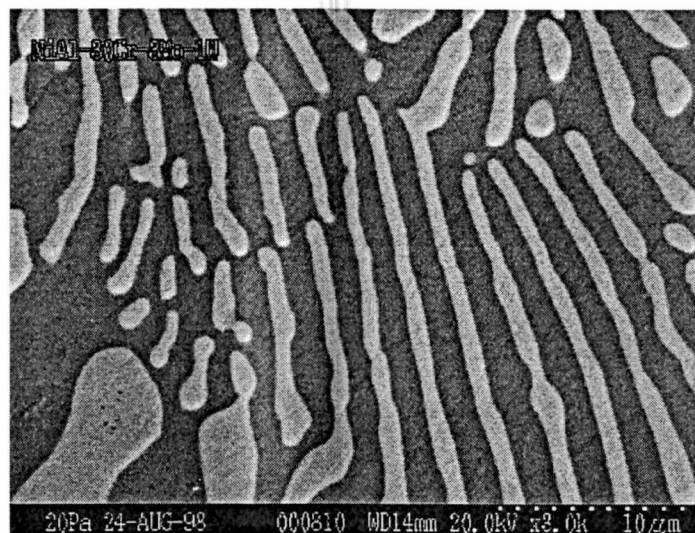


b) 3000x

Figure 38: BSE images of transverse section of NiAl-32Cr-1Mo-1V alloy at a) 1000x
b) 3000x

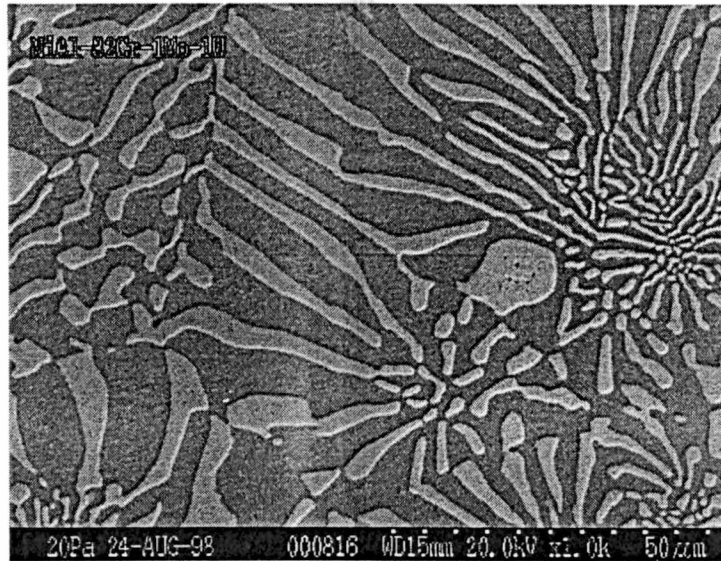


a) 1000x

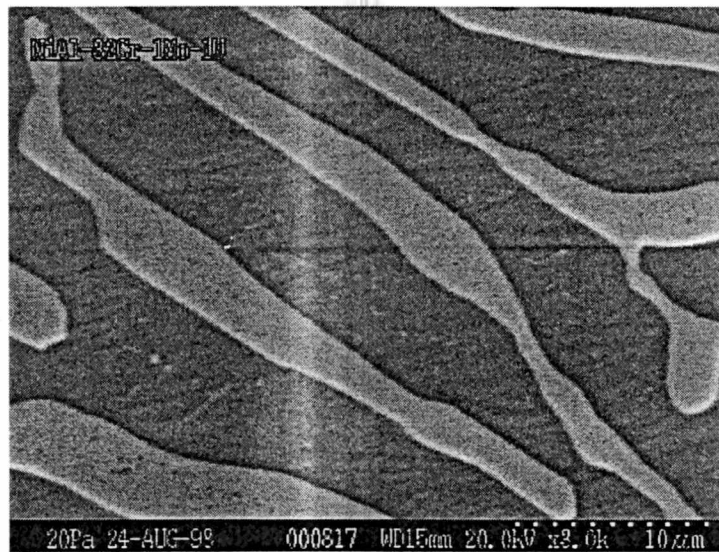


b) 3000x

Figure 39: BSE images of transverse section of NiAl-30cr-3Mo-1W alloy at a) 1000x
b) 3000x



a) 1000x



b) 3000x

Figure 40: BSE images of transverse section of NiAl-32Cr-1Mo-1W alloy at a) 1000x
b) 3000x

Table 7: Average lamellar spacing for the five directionally solidified ingots.

Ingot Composition	Average Lamellar Spacing (μm)
NiAl-31Cr-3Mo	1.0
NiAl-30Cr-3Mo-1V	1.1
NiAl-32Cr-1Mo-1V	0.8
NiAl-30Cr-3Mo-1W	1.9
NiAl-32Cr-1Mo-1W	3.0

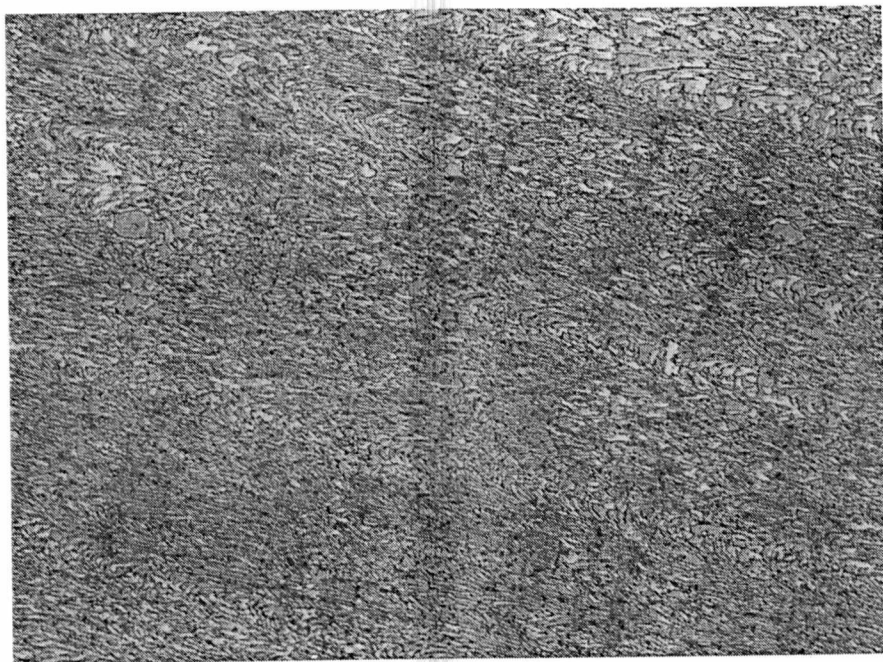
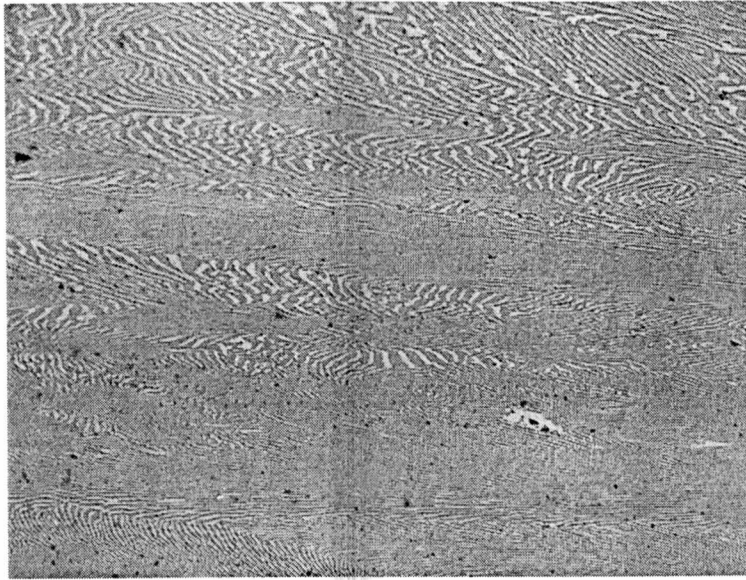
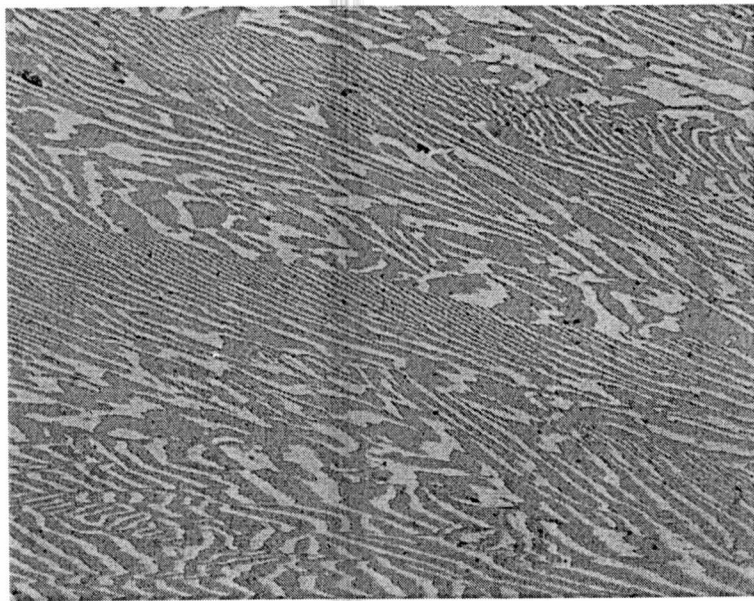


Figure 41: Optical micrograph of longitudinal section of NiAl-31Cr-3Mo alloy at 400x



a) 200x



b) 400x

Figure 42: Optical micrograph of longitudinal section of NiAl-30Cr-3Mo-1V alloy at
a) 200x b) 400x

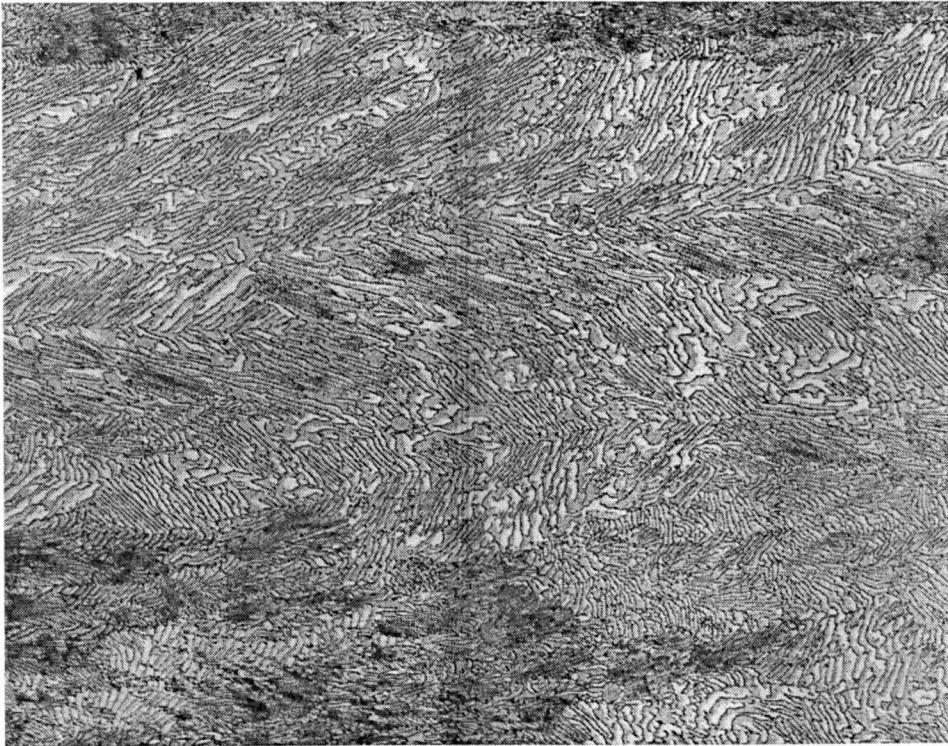


Figure 43: Optical micrograph of longitudinal section of NiAl-32Cr-1Mo-1V alloy at 400x

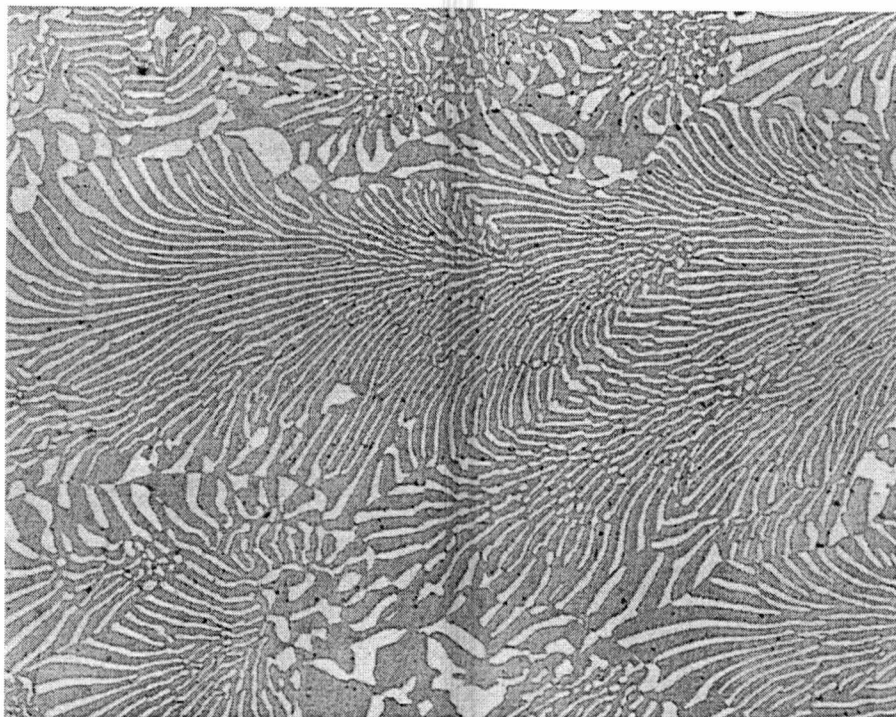


Figure 44: Optical micrograph of longitudinal section of NiAl-30Cr-3Mo-1W alloy at 400x

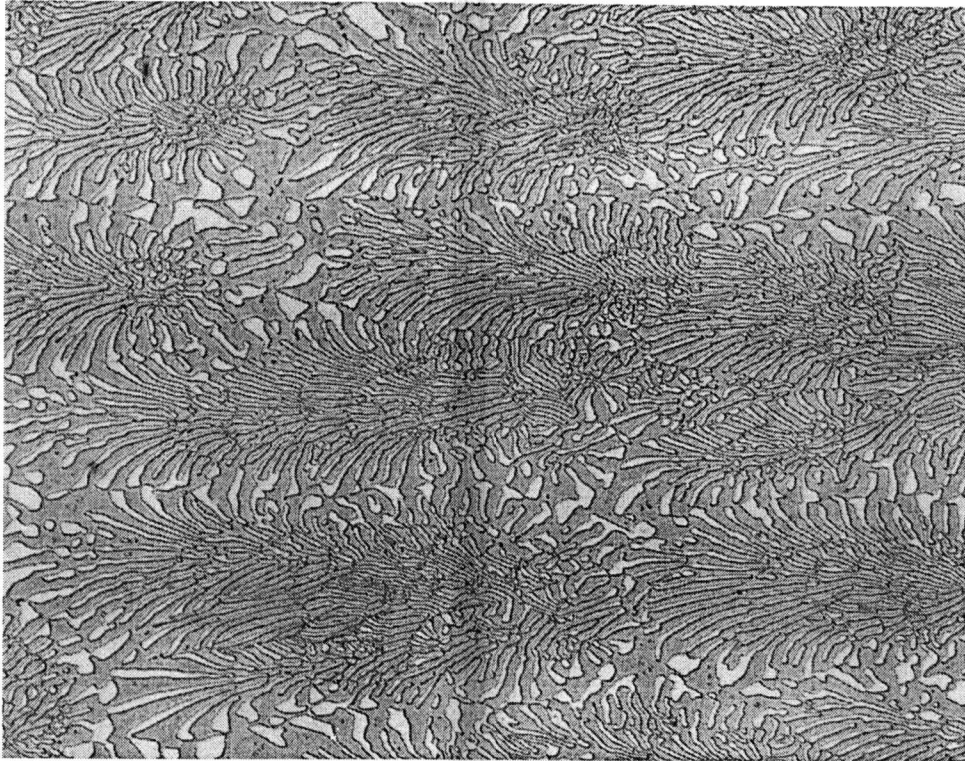


Figure 45: Optical micrograph of longitudinal section of NiAl-32Cr-1Mo-1W alloy at 400x

the 31Cr-3Mo has a well aligned eutectic structure. The eutectic colonies appear to be uniform. There are pockets throughout the structure which contain primary phase only.

The 3Mo-1V sample, Figure 42, varies greatly from the standard Cr-Mo. The eutectic colonies are not as cellular as in Figure 41. The structure appears banded with alternate bands of fine well-aligned eutectic and coarse less defined eutectic. Primary phase areas are not prevalent.

The 1Mo-1V, as seen in Figure 43, has a very fine structure. The overall structure is similar to the 31Cr-3Mo. Some of the eutectic colonies are more cellular than others. There are areas in the ingot with good lamellar alignment. There also are areas with a coarser structure than the rest of the ingot. Primary phase areas are not present to the extent they were in the 31Cr-3Mo ingot.

Figure 44 shows that the 3Mo-1W alloy has cellular shaped eutectic colonies. The laminates appear to branch out instead of aligning with any constancy. At the colony boundaries, the laminates become coarser and less defined. The overall structure is coarser than the 31Cr-3Mo.

Figure 45 indicates that the 1Mo-1W alloy has a structure similar to the 3Mo-1W alloy. The eutectic colonies are again cellular but within the colonies the laminates align better than in the 3Mo-1W ingot. The colonies are narrower than the ones in Figure 44.

3. DISCUSSION

3.1 Fracture Toughness

Of the samples studied, the NiAl-32Cr-1Mo-1V shows the most promise. This alloy had a considerable improvement in room temperature fracture toughness over the straight NiAl-31Cr-3Mo eutectic. It also had a considerable change in the laminate spacing.

One cause of the improved fracture toughness in the 1Mo-1V alloy might be related to the finer eutectic structure. The amount of brittle matrix (NiAl) present would be less. The reinforcements introduce energy-dissipating mechanisms which include debonding at the fiber/matrix interface, crack deflection, fiber bridging, and fiber pullout.

The NiAl-30Cr-3Mo-1V alloy also showed improved fracture toughness. The lamellar spacing, however, was greater in this alloy than in the NiAl-31Cr-3Mo. Looking at the longitudinal micrographs of these alloys (Figures 41,42) gives a possible explanation. As mention earlier, the 31Cr-3Mo alloy had many pockets of primary phase (NiAl matrix). In these areas, crack could propagate easily and quickly weaken the whole specimen. The 3Mo-1V alloy does not have primary phase areas. Also of importance is the alignment of the eutectic in the 3Mo-1V alloy. In many areas of the sample, the reinforcing phase is perpendicular to the breaking force. This orientation allows for more crack trapping or blunting.

Both of the W alloys had lower fracture toughness than the 31Cr-3Mo alloy. Both also had large lamellar spacings. While the volume fraction of the reinforcing phase may

be the same as in the V alloys, the size of the NiAl phase is larger in the W alloys. A crack which begins in one of these areas would be able to propagate longer and can reach a critical length causing the material to fail. The 3Mo-1W had a lower fracture toughness than the 1Mo-1W in spite of its smaller lamellar spacing. Again, the longitudinal view gives a possible explanation for this. The 3Mo-1W structure was very cellular in shape. Few of the reinforcement fibers are perpendicular to the crack growth. Any cracks could easily propagate through the sample. The 1Mo-1W alloy has more reinforcements aligned perpendicular to the crack growth direction which would frustrate the crack propagation.

3.2 Lamellar Spacing

A possible explanation of the decreased lamellar spacing in the 1Mo-1V alloy might be found by examining the equation for minimum lamellar spacing (λ^*). The minimum possible lamellar spacing occurs when the free energy change associated with the solidification of 1 mol of liquid equals zero. The minimum lamellar spacing can be determined using the following relation:

$$\lambda^* = \frac{2\gamma_{\alpha\beta}V_mT_E}{\Delta H \cdot \Delta T_0} \quad [61]$$

where $\gamma_{\alpha\beta}$ is the α/β interfacial energy, V_m is the molar volume of the eutectic, T_E is the equilibrium eutectic temperature, ΔH is heat of fusion of the eutectic, and ΔT_0 is the total undercooling. The undercooling can be calculated using the freezing point depression equation. Assuming that the molar volume, equilibrium eutectic temperature, and the

enthalpy term are known, only the interfacial energy and the amount of undercooling would effect the spacing.

The alloy was grown using direction solidification. Under such controlled solidification conditions, off-eutectic alloys (such 1Mo-1V) can be solidified as 100% eutectic with a composition the same as the overall composition instead of eutectic composition [61]. This is accomplished by raising the growth rate above a critical level which would allow the alloy to solidify at a temperature other than the eutectic temperature. Since a controlled solidification method was used, it is very possible that the lamellar spacing was mostly affected by the amount of undercooling. An alloy which has a high rate of undercooling would have a finer spacing than that which has a small undercooling.

CHAPTER 6

SUMMARY AND FUTURE WORK

1. Summary

NiAl has many characteristics that makes it a contender for high temperature material applications. NiAl limiting properties are its room temperature fracture toughness and its elevated temperature creep resistance. Both of these properties have been improved with the formation of in-situ NiAl-based eutectics; however, these properties need to be improved.

Microalloying was the technique used in this study. The best NiAl-based eutectic, NiAl-31Cr-3Mo, was chosen as the standard. Small arc-melt buttons were used as a fast method for preliminary investigation. All the initial alloys contained eutectic colonies and primary phase. The alloy containing Ta showed evidence of a possible second eutectic. The Ti arc-melts processed by NASA Lewis had unmelted Mo. EDS showed possible Ti segregation to the grain boundaries. The Ti arc-melts processed at the University of Tennessee had all the Mo in solution. At higher contents of Ti (> 4 at. %), the eutectic structure becomes less defined. There was also a significant increase in the Vickers microhardness of these arc-melts.

The V and W arc-melts had a microstructure most similar to that of the NiAl-31Cr-3Mo standard. V and W were chosen for further study. Five ingots were processed using directional solidification. The two V alloys showed an improvement in room temperature fracture toughness. The two W alloys had a lower room temperature fracture toughness. The NiAl-32Cr-1Mo-1V had a smaller lamellar spacing than the straight

eutectic. The W alloys had a coarser lamellar spacing.

2. Future Work

This investigation only touched on the effect of microalloying additions on NiAl-based eutectics. The results found thus far are promising. It is recommended that this problem be investigated further. Future work should include the following points:

- ◆ Elevated temperature creep tests
- ◆ Heat treatment tests
- ◆ Ti arc-melts that insure all the Mo is melted
- ◆ Identify the second structure in the Ta arc-melts
- ◆ Chemical analysis
- ◆ Corrosion tests
- ◆ Density calculations
- ◆ Similar tests with additional alloying elements

LIST OF REFERENCES

REFERENCES

- [1] R. D. Noebe, R. R. Bowman, and M. V. Nathal, NASA Technical Memorandum 105598, 1992.
- [2] C. Barrett and T. B. Massalski, Structure of Metals: Third ed., Chap. 10. Pergamon Press, New York, 1980.
- [3] J. H. Westbrook, Intermetallic Compounds. Chap. 10, Krieger Pub. Co., Huntington, New York, 1977.
- [4] M. F. Singleton, J. L. Murray, and P. Nash, "Al-Ni (Aluminum-Nickel)," Binary Phase Diagrams. T. B. Massalski, ed., American Society for Metals, Metals Park, OH, 1986, pp. 140-143.
- [5] A. Taylor and N. J. Doyle, "Further Studies on the Nickel-Aluminum System. I The β -NiAl and δ -Ni₂Al₃ Phase Fields," J. Appl. Cryst., vol. 5, 1972, pp. 201-209.
- [6] P. Georgopoulos, and J. B. Cohen, "The Defect Structure and Debye Waller Factors vs. Compositions in β Ni_{1+x}Al_{1+x}," Scripta Metall., vol. 11, 1977, pp. 147-150.
- [7] G. W. West, "Nuclear Magnetic Resonance and Lattice Parameter Measurements β -NiAl," Phys. Status Solidi, A, vol. 20, 1973, pp. 647-651.
- [8] H. Jacobi, and H. J. Engell, "Defect Structure in Non-Stoichiometric β -(Ni,Cu)Al," Acta Metall., vol. 19, 1971, pp. 701-711.
- [9] M. J. Cooper, "An Investigation of the Ordering of the Phases CoAl and NiAl," Philos. Mag., vol. 8, 1963, pp. 805-810.
- [10] T. Hughes, et. al., "X-ray Diffraction Investigation of β -NiAl alloys," J. Appl. Phys., vol. 42, 1971, pp. 3705-3716.
- [11] R. D. Noebe, R. R. Bowman, and M. V. Nathal, "Physical and Mechanical Properties of the B2 compound NiAl," Int. Mat. Rev., vol. 38, n. 4, 1993, p. 193.
- [12] A. J. Bradley and A. Taylor, "An X-ray Analysis of the Nickel-Aluminum System I. The β -NiAl and δ -Ni₂Al₃ Phase Fields," Proc. R. Soc.(London), vol. A159, 1937, pp. 56-72.
- [13] N. F. Mott and H. Jones, The Theory and Properties of Metals and Alloys, Dover, 1958.

- [14] H. Lipson and A. Taylor, Proc. R. Soc., vol. A173, 1939, p. 232.
- [15] M. Ettenberg, K. L. Komarek, and E. Miller, Trans. Metall. Soc., A.I.M.E., vol. 242, 1968, p. 1801.
- [16] A.G. Fox and M.A. Tabbernor, "Bonding and the Physical and Mechanical Properties of β -NiAl," High Temperature Intermetallics, The Institute of Metals, London, England, 1991, pp. 219-221.
- [17] M. J. Cooper, "The Electron Distribution in the Phases CoAl and NiAl," Philos. Mag., vol. 8, 1963, pp. 811-821.
- [18] A. G. Fox, "The electron Charge Distribution of β' -NiAl", Electron Microscopy and Analysis, G. J. Tatlock, ed., Adam Hilger Ltd., Bristol, England, 1985, pp. 379-382.
- [19] A.G. Fox and M.A. Tabbernor, "The Bonding Charge Density of β' -NiAl," Act Metall. Mater., vol. 39, 1991, pp. 669-678.
- [20] M. R. Harmouche, and A. Wolfenden, "Temperature and Composition Dependence of Young's Modulus in Polycrystalline B2 Ni-Al," J. Test Eval., vol. 15, 1987, pp. 101-104.
- [21] R. T. Pascoe and C. W. A. Newey, Metal Sci. J., vol. 12, 197, pp. 101-
- [22] R. J. Wasilewski, Met. Trans., vol. 236, 1966, pp.455-
- [23] N. Rusovic and H. Warlimont, Physics Status Solidi A, vol. 53, 1979, pp. 283-288.
- [24] D. B. Miracle, Acta Metall. Mater., vol. 41, n. 3, 1993, pp. 649-
- [25] S. M. Joslin, "NiAl and NiAl-Based Composites Directionally Solidified by a Containerless Zone Process," Ph.D. Thesis, University of Tennessee, 1995.
- [26] A. Ball and R. E. Smallman, "The Operative Slip System and General Plasticity NiAl-II," Acta Metall., vol. 14, 1966, pp. 1517-1526.
- [27] M H. Loretto and R. J. Wasilewski, "Slip Systems in NiAl Single Crystals at 300 °K and 770 °K," Philos. Mag., vol. 23, 1971, pp. 1311-1328.

- [28] J. T. Kim and R. Gibala, "Slip Transition in [001] Oriented NiAl at High Temperatures," High Temperature Ordered Intermetallic Alloys IV, L. A. Johnson, D. P. Pope, and J. O. Stiegler, eds., MRS, Pittsburgh, PA, 1991, pp. 261-266.
- [29] D. I. Potter, "Prediction of the Operative Slip System in CsCl Type Compounds Using Anisotropic Elasticity Theory," Mater. Sci. Eng., vol. 5, 1969, pp. 201-209.
- [30] W. A. Rachinger and A. H. Cottrell, "Slip in Crystals of the Caesium Chloride Type," Acta Metall., vol. 4, 1956, pp. 109-113.
- [31] J. T. Kim, "On the Slip Behavior and Surface Film Effects In B2 Ordered NiAl Single Crystals," Ph.D. Thesis, The University of Michigan, 1990.
- [32] R. J. Wasilewski, S. R. Butler, and J. E. Hanlon, "Plastic Deformation of Single-Crystal NiAl," Trans. Metall. Soc., A.I.M.E., vol. 239, 1967, pp. 1357-1364.
- [33] P. R. Strutt, R. A. Dodd, and G. M. Rowe, "Creep in Stoichiometric Beta-NiAl." Strength of Metals and Alloys, Proceedings of the 2nd International Conference, Vol III., ASM International, Metals Park, OH, 1970, pp. 1057-1061.
- [34] R. T. Pascoe and C. W. A. Newey, "Deformation modes of the Intermediated Phase NiAl," Phys. Status Solidi, vol. 29, 1968, pp. 357-366.
- [35] J. Bevk, R. A. Dodd, and P. R. Strutt, "The Orientation Dependence of Deformation Mode and Structure in Stoichiometric NiAl Single Crystals Deformed by High Temperature Steady-State Creep," Metall. Trans., vol. 4, 1973. Pp. 159-166.
- [36] R. D. Field, D. F. Lahrman, and R. Darolia, "Slip Systems in <001> Oriented NiAl Single Crystals," Acta Metall. Mater., vol. 39, 1991, pp. 2951-2959.
- [37] R. Darolia, "NiAl for High-Temperature Structural Applications," J. Metals, vol. 43, 1991, pp. 44-49.
- [38] K. Vedula, V. Pathare, I. Alanidis, and R. H. Titran, MRS Symp. Proc., vol. 39, 1985, pp. 411-421.
- [39] R. T. Pascoe and C. W. A. Newey, Metal Sci. J., vol. 12, 1968, pp.138-
- [40] K. -M. Chang, R. Darolia, and N. A. Lipsitt, "Cleavage Fracture in B2 Aluminides," Acta Metall. Mater., vol. 40, n. 10, pp. 2727-2737.

- [41] S. Ruess and H. Vehoff, "Temperature Dependence of the Fracture Toughness of Single Phase and Two Phase Intermetallics," Scripta Metall. Mat., vol. 24, 1990, pp. 1021-1026.
- [42] S. Ruess and H. Vehoff, "Mechanical Properties of Intermetallics at High Temperatures," High Temperature Aluminides and Intermetallics, S. H. Whang, ed., The Minerals, Metals, and Materials Society. Warrendale, 1990, pp. 329-352.
- [43] G. Sauthoff, "High Temperature Deformation and Creep Behavior of BCC Based Intermetallics," Proceedings of the International Symposium on Intermetallic Compounds, O. Izumi, ed., Japan Institute of Metals, Sendai, Japan, 1991, pp. 371-378.
- [44] M. N. Crocker, R. S. Fidler, and R. W. Smith, "The Characterization of Eutectic Structures," Proc. Roy. Soc. Lond., A, vol. 335, 1973, pp. 15-37.
- [45] W. A. Tiller, "Polyphase Solidification," Liquid Metals and Solidification, ASM, Cleveland, OH, 1958, pp. 276-318.
- [46] T. S. Newport, "Development and Processing of Nickel Aluminide-Carbide Alloys," M.S. Thesis, University of Tennessee, 1995.
- [47] D. R. Johnson, "Processing and Mechanical Properties of NiAl-Based In-Situ Composites," Ph.D. Thesis, University of Tennessee, 1994.
- [48] H.E. Cline, and J. L. Walter, Metall. Trans., vol. 1, n. 10, 1970, pp.2907-2917.
- [49] L. E. Samuels, Metals Engineering A Technical Guide, chap. 10, ASM, Metals Park, Ohio, 1988.
- [50] R. Darolia and W. S. Watson, "Development and Characterization of High Strength NiAl Single Crystal Alloys," Structural Intermetallics, TMS, 1997, pp. 585-594.
- [51] R. Darolia, D. Lahrman, and R. Field, "The Effect of Iron, Gallium, and Molybdenum on the Room Temperature Tensile Ductility of NiAl," Scripta Metallurgica and Materialia, vol. 26, 1992, pp. 1007-1012.
- [52] W. A. Kaysser, R. Laag, J. C. Murray, and G. E. Petzow, "Improvement of P/M-NiAl by Ti and Nb Additions," The International Journal of Powder Metallurgy, vol. 27, no. 1, 1991, pp. 43-48.

- [53] P. Villars, A. Prince, and H. Okamoto, Handbook of Ternary Alloy Phase Diagrams, ASM, vol. 4, 1995.
- [54] M. Hansen, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.
- [55] Metals Handbook, 8th ed., ASM, vol. 8, 1973.
- [56] P. W. Pellegrini and J. J. Hutta, J. Crystal Growth, vol. 42, 1977, pp. 536-539.
- [57] F. E. Heredia, M.Y. He, G. E. Lucas, A. G. Evans, H. E. Deve and D. Konitzer, Acta Metall. Mater., vol. 41, 1993, pp. 505-511.
- [58] Handbook of Crystal Growth 2 Bulk Crystal Growth Part A: Basic Techniques, ed. D. T. J. Hurle, North-Holland, Amsterdam, 1994.
- [59] H. E. Cline, J. L. Walter, E. Lifshin, and R. R. Russell, Metall. Trans., vol. 2, 1971, pp. 189-194.
- [60] W. F. Brown and J. E. Scrawley, Plane Strain Crack Toughness Testing of High Strength Metallic Materials, ASTM, n. 410, Baltimore, 1966, pp. 13-14.
- [61] D.A. Porter and K. E. Easterling, Phase Transformations in Metals and Alloys, Chapman and Hall, New York, 1992, pp. 222-231.

VITA

Kerry Henry was born in Englewood, New Jersey on June 27, 1971. She attended public schools in the Bethlehem Area School System in Bethlehem, Pennsylvania and graduated from Liberty High School in June, 1989. She enrolled at the Pennsylvania State University, University Park. She attended classes there from August, 1989 to May, 1993 when she received her Bachelor of Science in Mechanical Engineering. After graduation, Kerry worked as a Manufacturing Engineer at Telan Corporation in Hatfield, Pennsylvania. She later took a position with the United States Postal Service. In January, 1996 she enrolled full-time at the University of Tennessee, Knoxville. While working towards her Master of Science in Metallurgical Engineering, she worked as a Teaching Assistant. The Master's degree was received December, 1998.