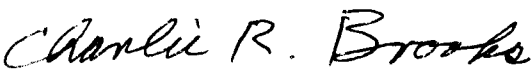


To the Graduate Council:

I am submitting herewith a thesis written by P. P. Smith entitled "Morphological Modification and Fracture Toughness of the Niobium Aluminide Eutectic." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirement 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:


Charlie R. Brooks


Thomas T. Meep

Accepted for the Council


Vice Provost
and Dean of the Graduate School

**MORPHOLOGICAL MODIFICATION AND FRACTURE
TOUGHNESS OF THE NIOBIUM ALUMINIDE EUTECTIC**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

P. P. Smith

August 1990

ACKNOWLEDGEMENTS

The author would like to acknowledge and express his genuine gratitude to the many people whom have provided help and guidance during the pursuit of this degree. All of his accomplishments, academic and otherwise, could not have been possible without the support of his parents, Mr. and Mrs. Joe Wayne Smith. Thanks also go to the major advisor of this research, Dr. Ben Oliver, for his guidance throughout its development.

The financial and technical support provided through a research assistantship by NASA, Materials Division of the Lewis Flight Center in Cleveland, Ohio is greatly appreciated. In addition, teaching assistantships provided by the Department of Materials Science and Engineering are gratefully acknowledged.

Thanks are extended to Dr. Charlie Brooks and Dr. William Becker for sharing their wealth of knowledge upon request.

The author wishes to express his appreciation for his fellow graduate students. A word of advice or a friendly conversation is always easily found in the materials department. Specifically, David Johnson, Robert Reviere, Tamara McGill-Taylor, Steve Joslin and Cathy Swindeman were of immeasurable help throughout the course of this research effort.

Thanks are also extended to the secretaries in the Materials Science and Engineering office, and the staffs of the electronics shop, machine shop, and the Chemistry Department glass shop.

A special thanks goes to Lane Utterback, whose moral support greatly aided the author in completion of this work.

ABSTRACT

The processing of alloys of the niobium aluminide system has been investigated to determine their applicability to elevated temperature service. Several alloys have been examined including the eutectic of Nb_2Al and NbAl_3 . This is a degenerate, irregular eutectic whose secondary phase morphology consists of a coarse network of slightly elongated NbAl_3 particles, which appear globular in cross-section. Control procedures have been developed for the directional solidification via levitation zone refining of this eutectic and of the stoichiometric NbAl_3 compound.

Ternary additions of Ni and Ti alter the arc-melted morphology of the eutectic structure. The addition of titanium promotes a semi-lamellar structure around the periphery of the dendritic regions, but does not alter the eutectic regions of the microstructure. Nickel additions refine the structure to a very fine, rod-type morphology. However, the thermal instability of this structure prevents its growth as an "in-situ" composite during levitation zone refining.

The fracture toughness of the binary and Ni-ternary eutectics were determined by a microhardness indentation cracking technique. No change in toughness resulted from the drastic morphology alteration. Elemental analysis, along with the current tentative ternary Nb-Al-Ni phase diagram, indicate that

the Ni addition is taken up almost entirely by the Nb₂Al sigma phase. The morphological modification is most likely due to an alteration of a growth mechanism for this phase during solidification. Possible modes include a change in the triple point interfacial energy balance, and absorption of Ni on certain faceting planes in the sigma structure that inhibits growth in the high velocity directions.

TABLE OF CONTENTS

CHAPTER	PAGE
1 INTRODUCTION	1
2 LITERATURE REVIEW	3
2.1 Intermetallic Compounds	3
2.2 Niobium Aluminides	8
2.3 Unidirectional Solidification	11
2.4 Zone Melting	17
2.5 Levitation Zone Refining	19
2.6 Composite Materials	22
2.7 Eutectic Solidification	24
2.8 Eutectic Morphology Modification	39
2.9 Fracture Toughness Determination from Indentation Microcracking	45
3 MATERIALS AND EXPERIMENTAL PROCEDURE	52
3.1 Materials	53
3.2 Levitation Zone Refining	55
3.3 Metallography	62
3.4 Annealing Studies	62
3.5 Indentation Microcracking	63
3.6 Hardness Testing	64
4 RESULTS AND DISCUSSION	68
4.1 Binary Eutectic Structures	68
4.2 Stoichiometric NbAl ₃ Structure	78
4.3 Ternary Eutectic Microstructures	79
4.4 Nb-Al-Ti Alloys	82
4.5 Nb-Al-Ni Alloys	87
4.6 Transitional Nickel Alloys	92

4.7	Directional Solidification of the Eutectic	98
4.8	Off-Eutectic Ternary Alloys	101
4.9	Microhardness Measurements	107
4.10	Microhardness Indentation Toughness Testing	107
4.11	Elemental Analysis	115
4.12	Annealing Studies	124
5	CONCLUSIONS	126
	LIST OF REFERENCES	130
	APPENDICES	138
	Appendix 1	139
	Appendix 2	144
	Appendix 3	149
	Appendix 4	156
	VITA	161

LIST OF FIGURES

FIGURE	PAGE
1 A superlattice dislocation and the resulting anti-phase boundary in an ordered structure	6
2 Schematic view of a superlattice dislocation, and two antiphase boundaries in a simple cubic structure	7
3 The niobium - aluminum phase diagram	9
4 The unit cell of the complex Nb ₂ Al sigma phase	10
5 The unit cell of NbAl ₃ - a DO ₂₂ structure	12
6 Phase diagrams illustrating the redistribution of solute during equilibrium freezing	14
7 Solute redistribution in solidification with limited liquid diffusion and no convection	15
8 Constitutional supercooling in alloy solidification	18
9 Schematic illustrating the magnetic lifting force during levitation zone refining	20
10 Schematic showing the magnetic field and lifting forces with an eddy current plate	21
11 Proposed mechanism of overlap growth	26
12 Development of aligned growth in eutectic solidification	28

13	Solute concentration in the liquid at the interface during eutectic growth	30
14	Schematic illustrating the instability of lamellae width less than the extremum condition or greater than the upper limit on eutectic spacing	33
15	The coupled zone region in a eutectic phase diagram	37
16	Constitutional supercooling criterion for stability of composites	38
17	The Cd-CdSb eutectic directionally solidified at 1.22 cm/hr	43
18	The Cd-CdSb eutectic directionally solidified at 122 cm/hr	44
19	Two types of microcracking formed around a hardness indentation - dependent upon load	46
20	Microhardness indentation exhibiting crack branching	50
21	Microhardness indentation showing crack deflection	51
22	Levitation zone refiner	60
23	Microhardness indentations in the modified eutectic illustrating microcrack formation	65
24	Microhardness versus indentation load	67
25	As-cast (59.6 a/o Al, 40.4 a/o Nb) eutectic illustrating NbAl ₃ dendrites	69

26	As-cast (40.4 a/o Nb, 59.6 a/o Al) eutectic structure showing globular morphology	70
27	Coarsened eutectic (41.2 a/o Nb, 58.8 a/o Al) microstructure of the directionally solidified binary	73
28	Elongation of the secondary phase in the directionally solidified binary (41.2 a/o Nb, 58.8 a/o Al) eutectic	74
29	Longitudinal view of dendrite growth in the binary eutectic (41.2 a/o Nb, 58.8 a/o Al) during unidirectional solidification	75
30	Transverse sectional view of primary NbAl ₃ at center of the directionally solidified binary eutectic (41.2 a/o Nb, 58.8 a/o Al) bar	76
31	Transverse sectional view of dendrites near the edge of the directionally solidified binary eutectic (41.2 a/o Nb, 58.8 a/o Al) bar	77
32	Single grain of NbAl ₃ (27.0 a/o Nb, 73.0 a/o Al) at 100 x magnification	80
33	Large grains of NbAl ₃ (27.0 a/o Nb, 73.0 a/o Al) directionally solidified by levitation zone melting	81
34	Dendrite structure in the ternary eutectic alloy containing Ti (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti)	83
35	Complex-regular microstructure of the ternary eutectic with titanium (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti)	84

36	Lamellar morphology of the Ti ternary eutectic (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti) surrounding a dendritic region	85
37	Globular morphology of regions removed from dendritic areas in the ternary eutectic containing titanium (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti)	86
38	Arc-melted eutectic structure (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) showing extremely fine rods cut at varying angles to the normal	88
39	Sub-grain structure in the Ni-modified ternary (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) eutectic	89
40	Longitudinal rods in the Ni ternary eutectic (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni)	90
41	Scanning electron microscopy photograph of the Ni-modified structure (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni)	91
42	Scanning electron microscopy photograph of the binary (41.2 a/o Nb, 58.8 a/o Al) eutectic	93
43	Dendrite structure in the arc-melted ternary (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) eutectic containing Ni	94
44	Eutectic morphology of the hyper-eutectic alloy containing Ni (46.7 a/o Nb, 50.0 a/o Al, 3.3 a/o Ni)	95
45	Partially modified eutectic (41.0 a/o Nb, 58.8 a.o Al, 0.14 a/o Ni) showing dramatic decrease in secondary particle size and moderate rod-type formation	96

46	Control binary eutectic alloy (41.1 a/o Nb, 58.9 a/o Al, 0.0 a/o Ni) for comparison with transitional ternary Ni structure	97
47	Transverse sectional view of the directionally solidified ternary eutectic containing Ni (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni)	99
48	Longitudinal view of unidirectionally solidified ternary alloy containing nickel (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni)	100
49	36.1 a/o Nb, 63.9 a/o Al alloy exhibiting a large volume fraction of primary NbAl ₃	102
50	Interdendritic region of binary 36.1 a/o Nb, 63.9 a/o Al alloy	103
51	Interdendritic region of ternary (35.3 a/o Nb, 62.5 a/o Al, 2.1 a/o Ni) alloy	104
52	Three phase microstructure of a Ni-rich (37.1 a/o Nb, 53.3 a/o Al, 9.6 a/o Ni) niobium aluminide	105
53	Ternary Nb-Al-Ni phase diagram	106
54	Average microcrack lengths in unmodified, Ni-modified, and coarsened eutectic alloys	112
55	Indentation microcracking in the binary directionally solidified eutectic (41.2 a/o Nb, 58.8 a/o Al)	113
56	Indentation microcracking in the Ni-altered ternary (45.0 a/o Nb, 53.0 a/o Al, 2.0 a/o Ni) eutectic	114

57	EDS spectrum for a primary NbAl ₃ region in the Ni ternary eutectic	117
58	EDS spectrum for the eutectic region of the Ni-modified ternary alloy	118
59	Region of ternary Ni-niobium aluminide (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni) from which elemental analysis was extracted, illustrating dendritic and eutectic areas	121
60	High magnification view of near-dendritic region in figure 59	122
61	Interaction of the electron beam with the sample during scanning electron microscopy	123
62	Niobium aluminide eutectic (39.7 a/o Nb, 57.5 a/o Al, 2.7 a/o Ni) annealed at 1200 C for 32 hours	125

LIST OF TABLES

TABLE	PAGE
1 Directionally solidified ingots	54
2 Arc-melted binary eutectics	56
3 Arc-melted ternary eutectics	57
4 Additional alloys under investigation	58
5 Microhardness measurements	108
6 Microhardness indentation crack lengths	111
7 Compositions from elemental analysis of 2 a/o Ni alloy	116

CHAPTER 1

INTRODUCTION

The processing of alloys of the niobium aluminide system has been investigated to determine their applicability to elevated temperature service. The purpose of this research effort was to:

1. Develop conditions for the containerless processing of high temperature ordered intermetallics involving niobium.
2. Grow single crystals or oriented in situ composites of these materials where appropriate.
3. Examine the physical metallurgy of deformation of the materials so processed.

Several alloys were examined, including stoichiometric NbAl_3 , the NbAl_3 / Nb_2Al eutectic, and this eutectic with ternary additions. The as-cast binary eutectic structure consists of coarse "globules" of the secondary phase, Nb_2Al , in a NbAl_3 matrix. Directional solidification via levitation zone refining produced a slight elongation of the secondary phase but no well developed alignment. The microstructure was successfully modified through microalloying with nickel to produce an extremely fine rod-type eutectic. Unidirectional solidification of this alloy results in a

digression to the coarse globular structure, thereby indicating the possible instability of the aligned rod eutectic. Incremental additions of very small quantities of Ni show that a gradual transition occurs from the degenerate eutectic to the aligned structure. This supports the idea that the modification in morphology is most likely due to the ternary addition lowering the phase boundary energy. Variations in composition to off-eutectic alloys have shown that the volume fraction of the primary phase is not a determining variable for these structures. Relative fracture toughness values for the unmodified and modified eutectic have been obtained using a microhardness indentation cracking technique. This analysis, which utilizes measurement of microcrack lengths in extremely brittle materials, reveals that the toughness of the niobium aluminide eutectic is not altered by the morphological modification. Additional research efforts included backscattered electron imaging for elemental analysis, and annealing treatments to study the coarsening behavior of the modified structure.

CHAPTER II

LITERATURE REVIEW

This review of the current literature encompasses the areas of intermetallic compounds; the niobium aluminide system; solidification theory, for both basic and for eutectic systems; composite materials; eutectic morphology modifications; and the hardness indentation microcracking fracture toughness technique.

Intermetallic Compounds

An intermetallic compound is an alloy of two or more atomic species which reside in specific sites in the crystal lattice. This site segregation is usually temperature dependent, and these compounds tend to occur at or around simple atomic ratios (AB , AB_3 , A_2B). These materials have traditionally been used for second-phase particle strengthening; however, their significant lack of room temperature ductility has limited their use as structural materials.

A recent resurgence of interest in the use of ordered alloys for high temperature structural applications has been fueled by a variety of motivating factors. These include (1) the possible need

for replacement of primarily imported metals such as cobalt and chromium, and the continuing search for lightweight materials in view of energy conservation needs. In addition, the development of new processing and microanalytical techniques allow further manipulation of mechanical and physical properties and provide the researcher with more powerful tools with which to analyze these properties.

Many of the attractive high temperature aspects of intermetallic compounds have been realized for several decades. These include (2):

- i. low density
- ii. high specific ultimate tensile strength
- iii. high specific modulus
- iv. high strain-hardening rate
- v. slow steady state creep
- vi. high recrystallization temperature
- vii. good oxidation resistance
- viii. variation in mechanical properties with temperature

The inherent brittleness of many ordered alloys, as mentioned previously, is the major obstacle encountered when attempting to take advantage of these high-temperature properties. This problem possibly results from an insufficient number of operational slip systems (primarily in non-cubic alloys), a limited amount of cross slip, and/or intrinsically brittle grain boundaries

(2). The slip system and cross slip concerns are due to the complex nucleation and interaction of superlattice dislocations moving through the ordered structure (see refs. 1,3,4 and figs. 1 & 2). As a result of these limitations, incompatibility of deformation at the grain boundaries of an intermetallic inhibits most plastic deformation for a given state of strain. A further hindrance in the adaptation of a suitable ordered alloy for load-bearing purposes is the dearth of engineering property data presently available for these materials. Additional information concerning the effect of order and ordering kinetics on properties, details of the diffusion process, and an understanding of grain boundary interactions, including impurity segregation, are currently needed.

Since the recent renewal of interest in the intermetallic area, significant strides have been made in improving ambient temperature ductility of several ordered alloys, including the nickel, iron, and titanium aluminides (1,2,5). These include the removal of impurities and second-phase particles, and the use of rapid solidification techniques to produce ribbons of small grained material or powders. Also, alloying with ternary additions has been used successfully to alter a non-cubic to a cubic structure, thereby increasing the possible number of slip systems. Furthermore, microalloying has been utilized to improve grain boundary cohesion, or to decrease the effect of superdislocation movement by slowing the kinetics of the ordering process (1,2).

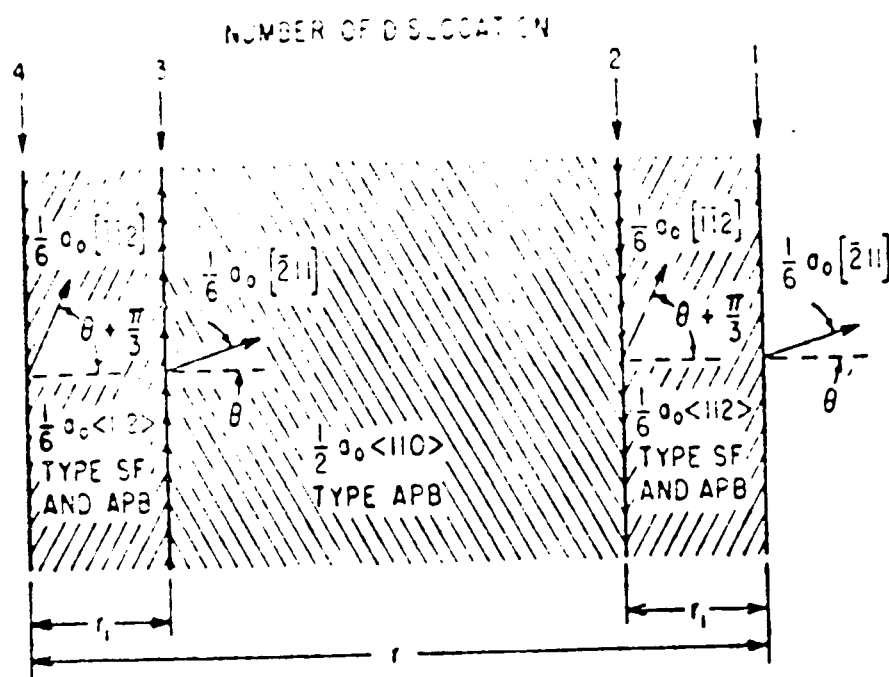


FIGURE 1

A superlattice dislocation and the resulting anti-phase boundary in an ordered structure (ref 3)

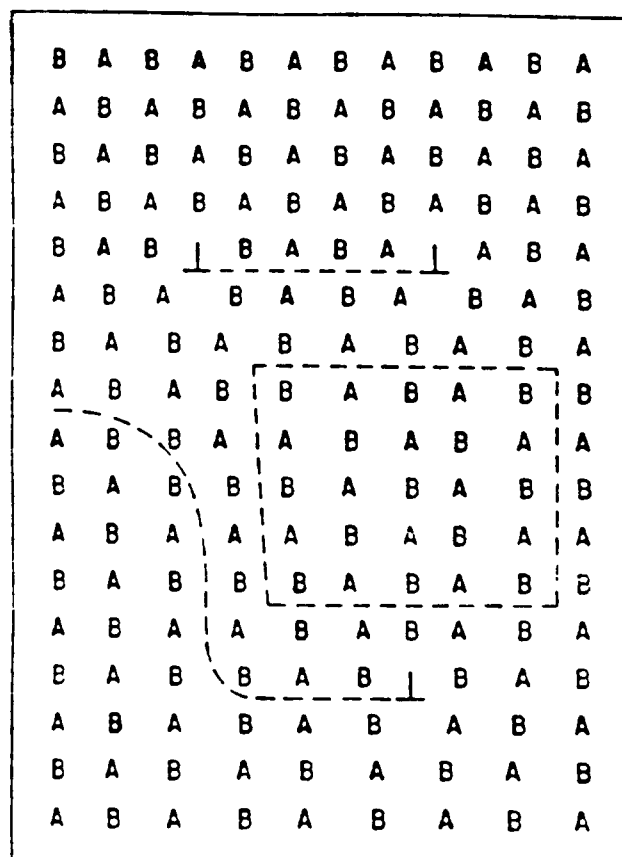


FIGURE 2

Schematic view of a superlattice dislocation, and two antiphase boundaries in a simple cubic structure (ref3)

Niobium Aluminides

The niobium aluminides are a potential material for use at elevated temperatures, due to the many excellent properties as mentioned in the previous section. In addition, Nb-Al based alloys have higher melting points than other aluminides such as Ti-Al, and lower density than iron or nickel-based aluminides. The niobium-aluminum phase diagram (6) is shown in figure 3. It is characterized by the presence of two intermetallic compounds (Nb_2Al & Nb_3Al), each extending several atomic percent off of the stoichiometric compositions, on the niobium-rich end of the diagram; and, a single intermetallic (NbAl_3) on the aluminum-rich side which has no detectable range of non-stoichiometric variation. Nb_2Al melts peritectically at 2143 °K and 66.7 at. % Nb, while NbAl_3 melts congruently at 1878 °K and 25 at. % Nb. There is a wide eutectic composition range between these two phases with a melting temperature of 1823 °K and a eutectic composition of 42.2 at. % Nb.

Nb_2Al is a tetragonal, FeCr-type sigma phase as shown in figure 4. The unit cell contains 30 atoms, which selectively occupy the 5 non-equivalent atomic sites available. It has lattice parameters of $a = 9.94 \text{ \AA}$, $C = 5.17 \text{ \AA}$, $c/a = 1.927$ (9), and is one of

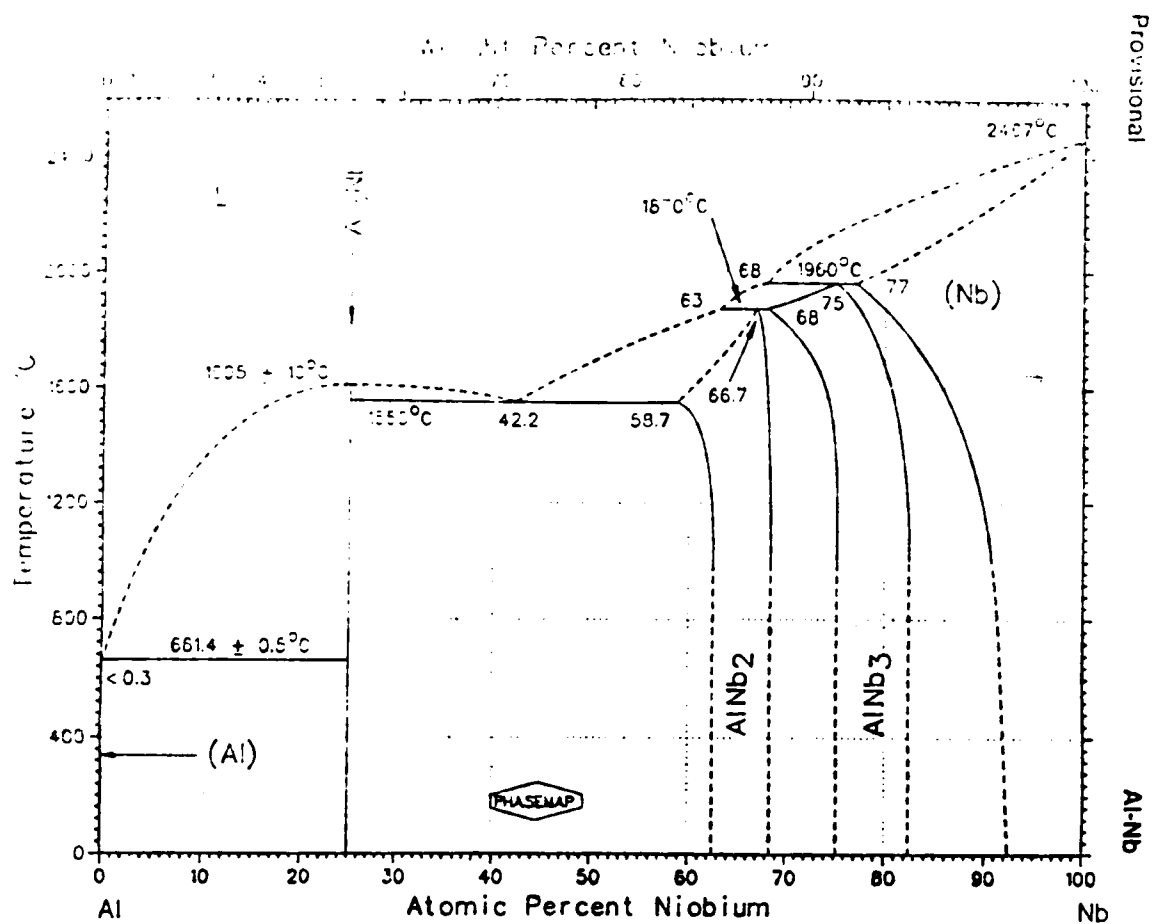


FIGURE 3

The niobium - aluminum phase diagram (ref 6)

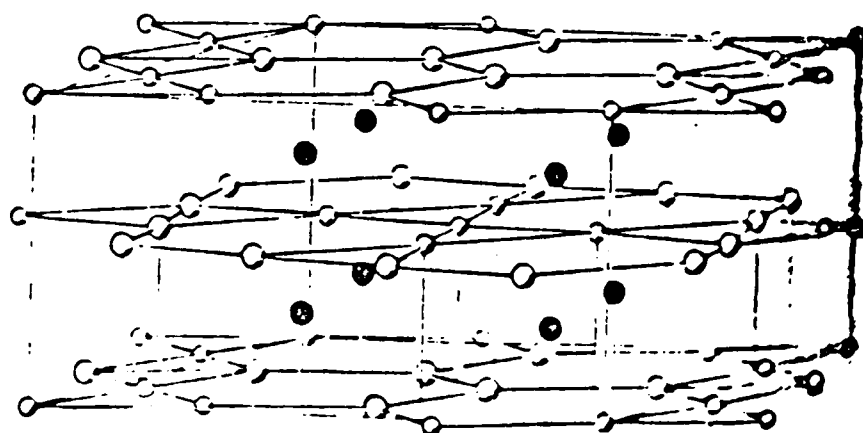


FIGURE 4
The unit cell of the complex Nb₂Al sigma phase (ref 7)

only two (Ta_2Al) binary sigma phase compounds that contain a non-transitional element. (7).

The crystal structure of NbAl_3 is the (DO_{22}) TiAl_3 -type body-centered tetragonal unit cell, with lattice parameters $a=5.438$ Å, $c=8.605$ Å, $c/a=1.582$ (9,11), and containing 2 formula weights per cell as shown in figure 5. This phase has a Vickers hardness of 4900-5100 MN/m^2 (10). Deformation mechanisms operative in this phase have been reported by Schechtman and Jacobson (8).

Unidirectional Solidification

Unidirectional solidification of an alloy utilizing a planar solid-liquid interface is a controlled process used to grow single crystals, to refine impurities, or to homogenize the composition of an ingot. For a pure metal, the liquid-solid transformation is subject only to heat flow constraints; however, for an alloy it is a heat and solute flow problem. The distribution of the solute during freezing is dependent upon the equilibrium partition function k_0 , the velocity of solidification, the degree of mixing in the liquid, the degree of completion of diffusive transport in the solid and in the liquid, and the presence or absence of convection.

Under the condition of an extremely low solidification rate, there is sufficient time for diffusion in the solid to go to completion. As a result of this equilibrium solidification, the

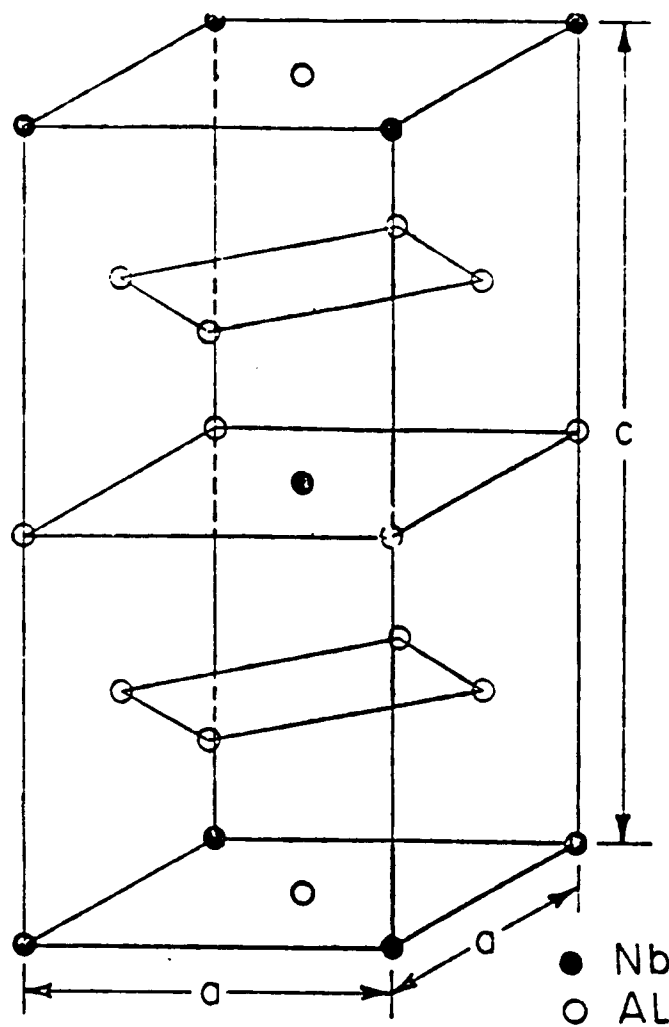


FIGURE 5
The unit cell of NbAl₃ - a DO₂₂ structure (ref 8)

processed bar will have a uniform composition equal to that of the original composition, C_0 . When the freezing velocity is increased, the diffusion in the solid is incomplete. This is the condition of nonequilibrium solidification. In this case, assuming that the liquid is incompletely mixed and that $k_0 < 1$, the initial portion of the bar will freeze with composition $k_0 C_0$ (see Figure 6). Thus, solute must be rejected into the liquid; and, as the solid-liquid interface travels along the length of the bar, the local solid interface composition will follow the solidus curve. Meanwhile, the local liquid interface composition will follow the liquidus curve. When the liquid composition preceding the solid-liquid interface reaches C_0 / k_0 , the solid composition equals the original composition. This is the steady-state condition that will be stable until the end of the bar is reached, at which point the buildup of solute in the liquid will cause the solid to freeze with an increased concentration. The distribution of solute in the liquid ahead of the interface is shown in figure 7. The final solute concentration for this nonequilibrium or normal solidification under the assumption of incomplete mixing is also shown.

The initial transient and the steady state distributions of the solvent in the solid have been described mathematically by Tiller et al. (19):

$$C_s = C_0 [1 + (1 - k_e)(\exp(-Rx/D))] ;$$

where,

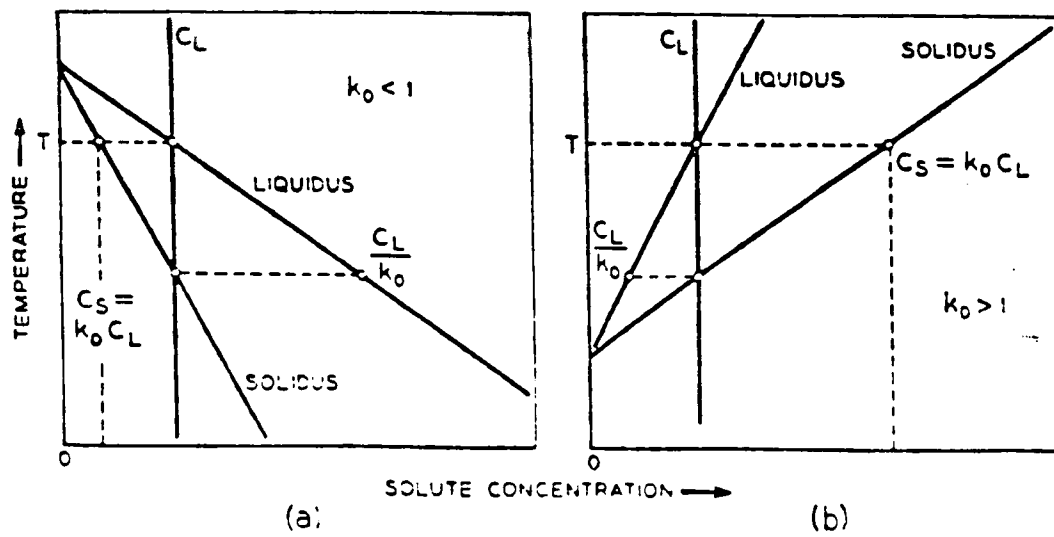


FIGURE 6

Phase diagrams illustrating the redistribution of solute during equilibrium freezing (ref 16)

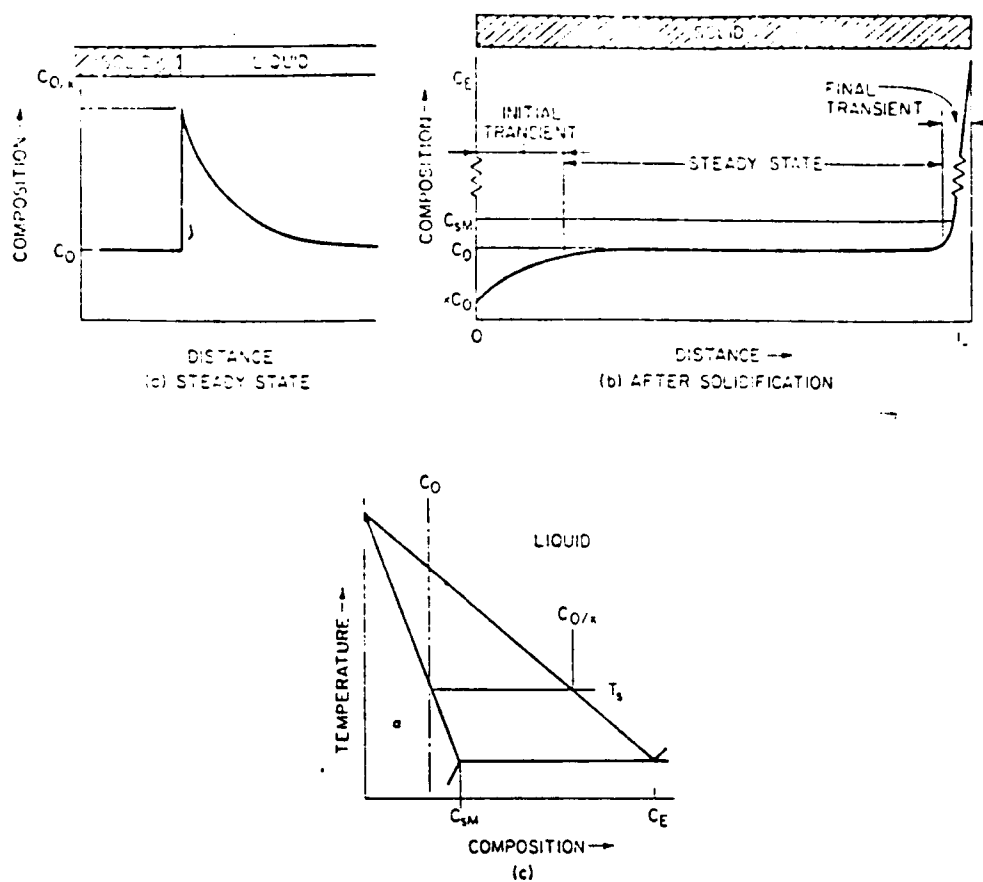


FIGURE 7

Solute redistribution in solidification with limited liquid diffusion and no convection. (a) - Composition profile during steady-state solidification; (b) - composition profile after solidification; (c) - phase diagram (ref 28).

C_s = concentration in the solid

C_0 = initial ingot concentration

k_e = effective segregation coefficient

R = interface velocity

x = distance traversed along bar by molten zone

D = diffusion coefficient of solute in the melt

The effective segregation coefficient arises from the fact that kinetic factors alter the segregation ratio at the freezing interface.

Burton, Prim, and Slichter(20) have defined it as:

$$k_e = k_0 / \{k_0 + (1 - k_0)(\exp(-fd/D))\} ;$$

where,

k_0 = equilibrium distribution coefficient

(obtained from the phase diagram)

f = freezing rate

d = boundary layer thickness

(depth of liquid near the interface in which
solute transport is by diffusion only (29))

As can be seen in figure 6a for an alloy with k less than unity, when the distribution of solute is built up in the liquid preceding the interface, the equilibrium liquidus temperature will

be decreased. If this effect is significant enough such that the local equilibrium liquidus temperature is below the actual temperature, the planar solid-liquid interface will no longer be stable as the region ahead of said interface becomes constitutionally supercooled (see Figure 8). As a result, instabilities which arise on the planar front can grow ahead into this supercooled region, and a cellular or dendritic morphology will be produced (18). The criterion for planar stability is (19):

$$\frac{G_L}{R} > \frac{-m_L C_0 (1-k)}{k_0 D_L} ;$$

where,

G_L = temperature gradient in the liquid

R = freezing velocity

m_L = liquidus slope

C_0 = ingot composition

D_L = diffusion coefficient of solute in the liquid

Zone Melting

A special case of unidirectional solidification is the process of zone melting, where, in contrast to normal freezing, only a small portion of the bar is liquid at any time. This liquid zone is passed at a controlled velocity with a given temperature gradient along

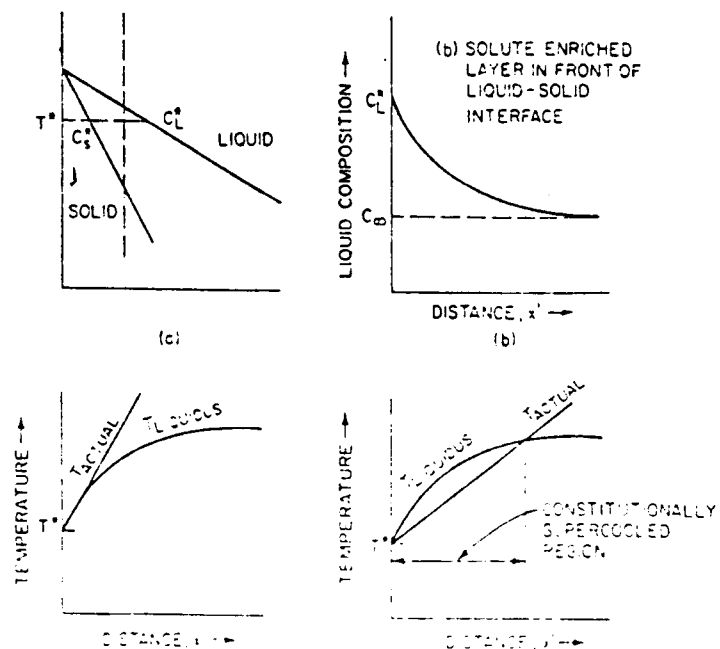


FIGURE 8
 Constitutional supercooling in alloy solidification. (a) - Phase diagram; (b) - solute enriched layer in front of interface; (c) - stable interface; (d) - unstable interface (ref 28).

the length of the bar. This technique is highly purifying in nature and is unique in that consecutive passes of the zone along the length of the bar will result in a more extended and more pure region near the front of the bar with each successive pass.

Levitation Zone Refining

One of the advantages of this zone melting process is that it can be employed without the use of a container; therefore, the possibility of alloy contamination is minimized. This technique, when utilized with an induction coil heater which electromagnetically melts, levitates and shapes the liquid zone in an inert atmosphere or vacuum, is referred to as levitation zone refining. The lifting forces that stabilize the liquid zone between the solid end pieces are created by the interaction of induced currents in the melt with the inducing magnetic field. The cross product of this field with the induced current is a distributive body force that is directed into the melt (see Figure 9). An eddy current plate is placed below the induction coil(s) such that a great majority of the magnetic field is contained above the coil(s) (see Figure 10). Therefore, the resultant body force acts to oppose the gravitational force and support the melt (29,30). This method results in a vigorously stirred melt due to the liquid flow forced by

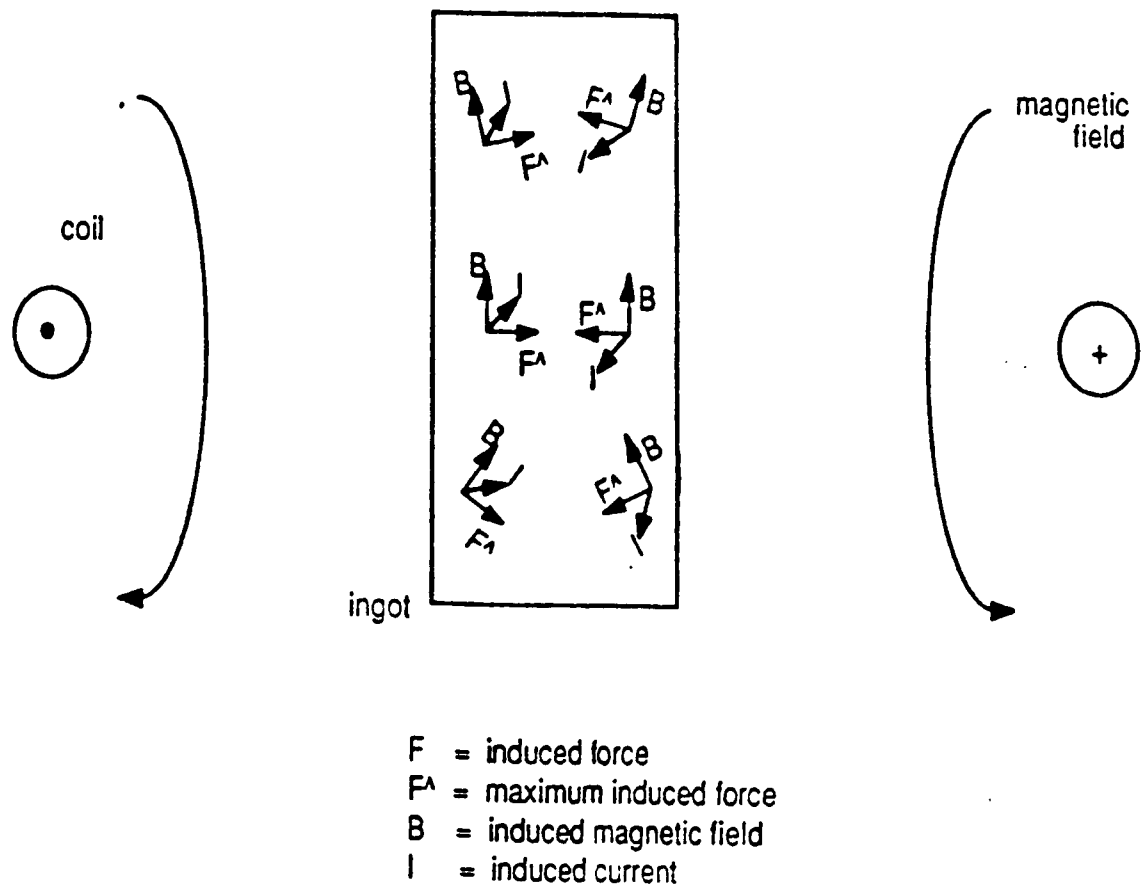
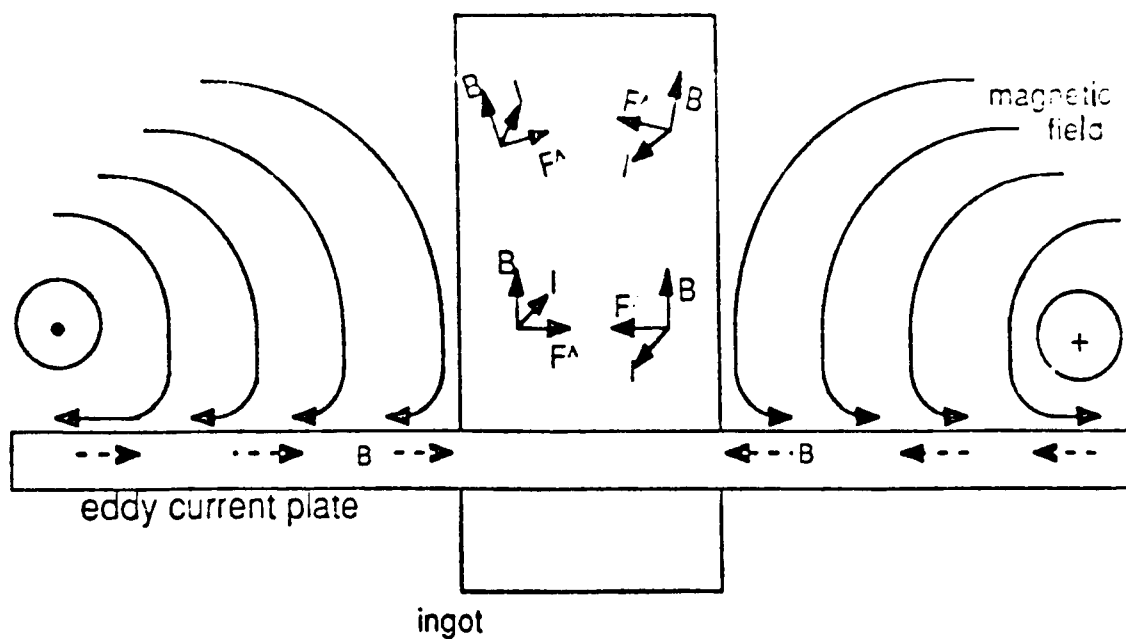


FIGURE 9
Schematic illustrating the magnetic lifting force during
levitation zone refining (ref 29)



- F = induced force vector
- $F^\wedge$ = maximum induced force vector
- B = induced magnetic field vector
- I = induced current vector

FIGURE 10

Schematic showing the magnetic field and lifting forces with an eddy current plate (ref 29)

the induced current and to the mechanical rotation of the solidifying interface.

Composite Materials

A composite is a multiphase material whose physical and mechanical properties are governed by the principle of combined action. It is designed to combine the individual superior properties of each phase, thereby creating a finished product with a combination of properties beyond the scope of each constituent phase. For example, a weak yet ductile matrix can be reinforced by the inclusion of strong, high modulus fibers or particles, with the result being a relatively stronger material that retains most of its ductility. Other properties of a composite are governed by the law of mixtures; whereby, for example, a fiber-reinforced material's elastic modulus in the longitudinal direction of the fibers is dependent upon the elastic moduli of each phase and their volume fractions (13):

$$E_c = E_m V_m + E_f V_f$$

where,

E = elastic modulus

V = volume fraction

m = matrix phase (continuous)

f = fibrous phase (discontinuous)

Among the more essential considerations when designing a composite for structural usage are the degree of contact and the cohesive forces at the interface between the two phases. In fiber-reinforced composites of interest for mechanical properties, the matrix is normally the weaker phase and the fibers the stronger phase. The strength of the composite will depend greatly upon the bonding strength between the two phases, since this is necessary for transferral of the load from the weak matrix to the strong fibers (14). One method of avoiding this problem is to manufacture the material so that the two phases are formed naturally, such as in the case of metal-metal composites grown from the melt. This process, called in-situ growth, requires the solidification at a controlled rate of a eutectic melt with a temperature gradient perpendicular to the solid-liquid interface. By making use of zone melting techniques, an in-situ composite can be grown from the melt such that the rods or sheets of the discontinuous second phase material grow perpendicularly to the interface. Bibring (69) analyzed the various material parameters that must be considered

when attempting to determine the potential of a multiphase material as an in-situ composite. Several characteristics of the secondary, reinforcing phase are of importance, including the morphology, aspect ratio, crystalline perfection, distribution of crystalline defects, interfiber spacing, brittleness, and volume fraction. In addition, the fibers or lamellae should be stronger and of greater modulus than the matrix phase, and should be unidirectionally aligned.

Eutectic Solidification

The unidirectional solidification processing variables described previously are also operative for alloys which solidify into more than one phase. A stable, essentially isothermal plane-front interface must be maintained, and a complicating factor arises due to the presence of diffusion gradients transverse to the solid-liquid interface. In addition, the morphology of the individual phases may take one of several forms, dependent upon the alloy system and the growth conditions. The microstructure of a polyphase material such as a eutectic can many times be altered by changing the process variables.

The freezing process for a eutectic alloy is initiated by the nucleation of one of the solid phases in the supercooled liquid. The

melt surrounding this nucleus is then enriched in solute and a "sympathetic nucleation" (27) of the other phase occurs. Growth of the phases proceeds by a coupled growth process, whereby the primary phase particle forms edgewise into a plate or rod, so as to minimize the supercooling created. The liquid solute buildup or depletion that results will prompt the nucleation of the second phase on the face of the primary phase. This secondary phase particle will also begin to grow in an edgewise fashion. As shown in figure 11, new layers of these alternating phases can be formed by overlap growth of one phase at the edge of the other. This process is more stable at higher interface temperatures than is repeated nucleation, and therefore, will be the mechanism for growth of the multilayered polyphase structure (24). The rate of advance of the interface is dependent upon the local solidification temperature, which is, in turn, a function of the heat flow due to the thermal gradient and the heat evolved due to the change of state. The freezing rate is increased by a high value of thermal conductivity and decreased by a large latent heat of fusion.

The nucleation of the secondary phase will occur for the smallest amount of undercooling when the interfacial energy between the two phases is minimized. A portion of this energy is determined by the lattice strain imposed by the mismatch in crystallography and interatomic distances for each phase at the

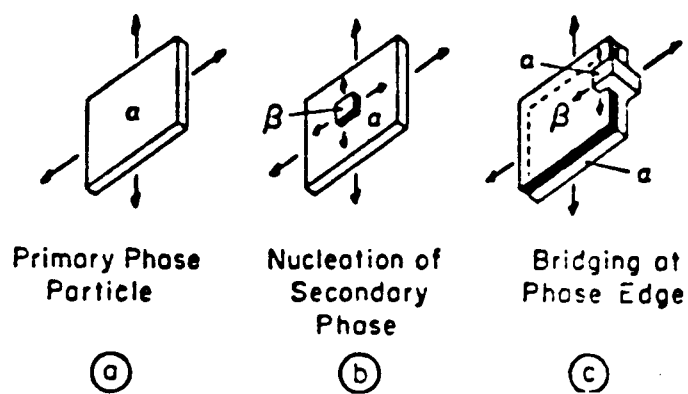


FIGURE 11
Proposed mechanism of overlap growth (ref 24)

plane of contact. Previous research has shown that, for most binary eutectic alloys, an epitaxial relationship exists such that the lattice strain and, consequently, the interfacial energy is minimized. Therefore, the initial lamellae will usually form with a definite orientation relationship between the two phases.

A competitive growth process between eutectic grains in the ingot will lead to a preferred orientation of the secondary phase. For the case of a simple bicrystal growing at some velocity R , such as that shown in figure 12, the right hand grain is oriented with the lamellae or rods perpendicular to the solid-liquid interface. The growth of the complimentary grain occurs with the alpha-beta boundary planes at some angle ϕ to the axis of growth. The effective rate of freezing for this grain is

$$R' = R \cos \phi$$

This greater freezing velocity results in an increased undercooling and an interface step will form as seen in figure 12. Therefore, the perpendicularly aligned grain will encroach on the other and eliminate it from the specimen. However, the optimum condition for decreasing the undercooling is not exclusive to such perpendicular growth. If the α - β interfacial energy is greater for this orientation than for one at an angle j , and this energy increase outstrips the decrease due to minimizing the growth rate, the phase boundaries will form at a non-normal angle to the solidifying interface.

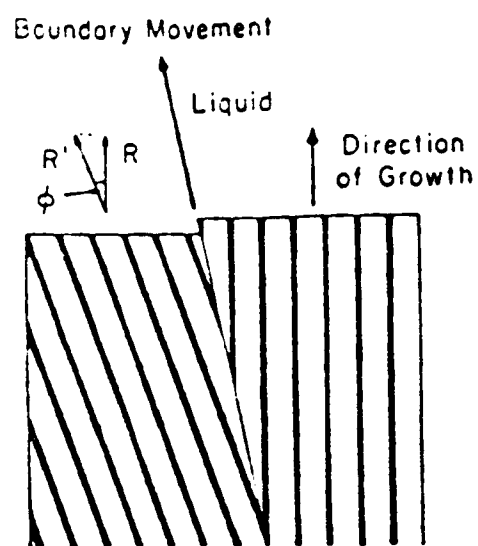


FIGURE 12
Development of aligned growth in eutectic solidification
(ref 24)

A significant number of eutectic systems are characterized by a lamellar or rod morphology. These two types of microstructures are significant in that the second phase has a large contact area with the primary phase and are very ordered in their distribution. These qualities indicate that lamellar and rod eutectics are most suitable for in-situ composite growth.

During the growth of these so-called "normal" structures (the lamellar structure will be assumed for discussion purposes here although the arguments apply equally to rod-type growth), the α and β phases solidify cooperatively through the diffusion of A and B atoms across the face of the solid-liquid boundary. The alpha phase rejects B atoms into the liquid preceding it and the beta phase rejects A atoms. This results in a composition profile of solute atoms as shown in figure 13. This variation is present in the melt only to a distance from the interface of approximately one-half of the interlamellar spacing. A balance between the diffusion requirements in the melt, the α - β surface energy considerations, and the equilibrium volume fractions of the phases dictate the size of the lamellae that will form. This interlamellar distance, along with the volume fraction, is an important variable in controlling the ultimate properties of the material (46). Experimental and theoretical work has shown (24, 26, 31, 32, 33) that for the extremum condition of minimum undercooling for a given growth rate:

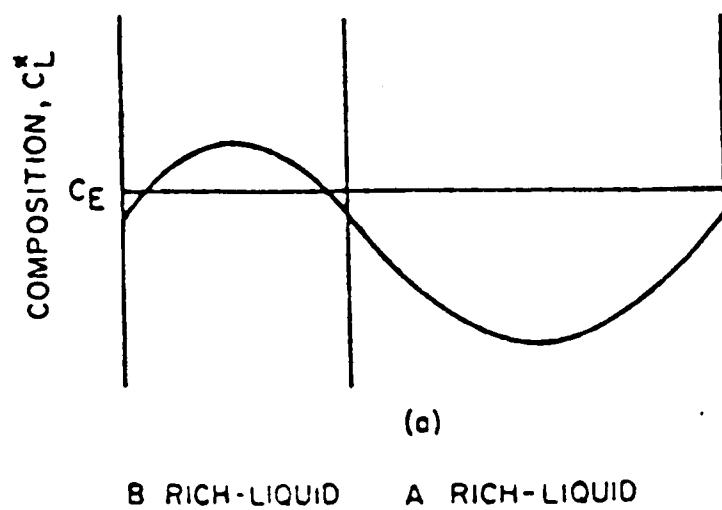


FIGURE 13
Solute concentration in the liquid at the interface during eutectic growth (ref 28).

$$\lambda^2 R = B/A,$$

and,

$$\Delta T^2/R = 4AB;$$

where,

λ = interlamellar spacing

R = growth rate

ΔT = undercooling

A, B = material constants

Therefore, under the extremum condition for a given eutectic alloy system, the lamellar spacing is dependent upon the amount of undercooling present and on the growth velocity. This is the minimum allowable interlamellar spacing. When the alloy system does not operate under minimum undercooling conditions, these spacings are greater than that predicted from the solidification velocity, and are given by

$$\Delta T / C = R\lambda A + B / \lambda$$

where,

C = material constant

However, if these spacings are increased by a factor of two or more, the interface curvature cannot maintain its isothermal nature, and a pocket will develop on the interface in which the secondary phase will nucleate. This will decrease the interlamellar

spacing; therefore, an upper limit on the width of these spacings also exists (see figure 14).

The governing variables that differentiate a rod-type microstructure from the lamellar type are the volume fraction of the second phase and the isotropy of the relevant surface energies (24). If the volume fraction is $1 / \Pi$, then the lamellar and rod morphologies would have equal amounts of surface area; and consequently, their surface free energies would be equal. The rod-type structure results in a lower second phase surface area for the case of a volume fraction less than $1/\Pi$; therefore, it is the more stable morphology, assuming that the surface energies are isotropic. Correspondingly, lamellae are stable at fractions greater than this value. Anisotropy of the surface energies will alter the $1 / \Pi$ ratio to favor the lamellae at even lower volume fractions. In addition, some lamellar microstructures will break down into rods or a degenerate structure at certain growth rates.

The arrangement of the two phases during the solidification process is often not of the simple rod or plate types. Eutectic microstructures can be classified into three distinct groups based upon the faceting nature of the two phases during growth. These are the non-faceted:non-faceted eutectics, the non-faceted:faceted combination, and the mixture of two faceting phases. The faceting nature of a material can be determined from its entropy of fusion; however, since thermodynamic data is non-existent for most

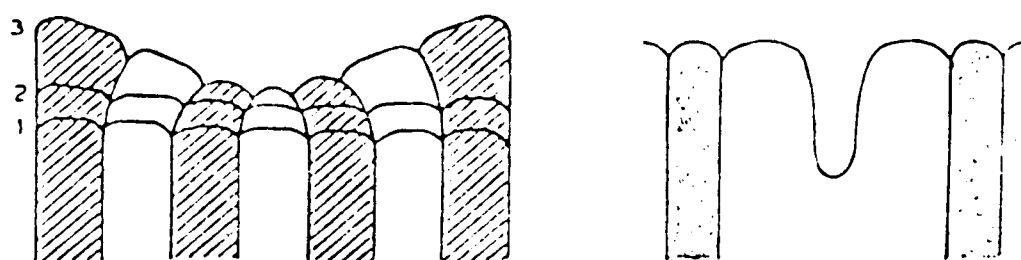


FIGURE 14

Schematic illustrating the instability of lamellae of width less than the extremum condition or greater than the upper limit on eutectic spacing

intermetallic compounds, metallography must be used to determine the preferred growth morphology. A phase will solidify in a faceting nature when the solid-liquid interface is atomistically smooth and additions are made to the surface by layer or lateral growth (27). This process results in the formation of crystal faces on the solidifying phase particle. When the interface is atomistically rough, solidification will occur by continuous growth and the process kinetics are primarily determined by the rate of solute diffusion in the liquid, which is dependent upon the temperature gradient at the interface. However, the kinetics of molecular attachment at the solid-liquid interface greatly influences the overall solidification kinetics during the growth of a faceting phase (59). Jackson (23) postulated a nearest-neighbor bond model for the solid-liquid interface and obtained the following relationship for the change in Gibbs' free energy when N_A atoms are attached to N possible growth sites:

$$\Delta G / NkT_e = \alpha N_A (N - N_A/N^2) - \ln (N/N - N_A) - N_A / N \ln (N - N_A/N_A);$$

where,

$$\alpha = (L / kT_e)$$

k = Boltzmann's constant

T_e = equilibrium melting temperature

L = heat of fusion

When $\alpha < 2$, the solidifying surface is rough, and growth is, in general, non-faceted.

A eutectic that is composed of two non-faceting phases tends to form a regular rod or plate morphology. The solidification of a mixture of two faceting phases is not well understood; however, the non-faceted:faceted eutectics, which normally occur for alloys containing elements of highly different melting points, have been studied extensively. The microstructures formed upon solidification of these alloys are irregular in that they have a very low degree of uniformity, large phase spacings, and no preferred orientation. Kurz and Fisher (37,38) theorized that non-faceted:faceted eutectics experience non-optimum growth due to anisotropic growth kinetics. Therefore, the optimum spacings at minimum supercooling conditions are not possible.

The formation and growth of these irregular, or degenerate, structures are influenced by the volume fraction of the secondary phase, the growth velocity, the temperature gradient, the composition and the presence or absence of impurities. Additionally, anisotropy of physical properties such as the alpha-beta surface energy or thermal conductivity can have a profound effect on the regularity of the eutectic morphology (42).

An alloy of non-eutectic composition will normally freeze by the growth of primary dendrites, followed by eutectic solidification of the remaining liquid. However, there is a coupled zone region

extending over a range of composition on the eutectic phase diagram in which it is possible to grow a completely eutectic structure utilizing a stable planar quasi-isothermal interface (figure 15). This coupled zone is stabilized under solidification conditions of a high G / R ratio (39) or at very high growth rates, and allows variance of the average composition while maintaining a normal eutectic structure. This is critically important from an engineering design flexibility point of view since the mechanical properties of aligned eutectic composites depend greatly on the volume fraction of the two phases present. Stability of the eutectic structure is destroyed when the growing solid-liquid interface is not stable, and is governed by a simple constitutional supercooling criterion. This may derive from nucleation requirements (40) or from the disparity in growth rates between the two phases. (42).

During unidirectional solidification of a polyphase alloy, the solute distribution normal to the freezing interface is similar to the case of single-phase solidification several structural wavelengths from the interface. As seen from figure 16, the solute buildup ahead of the interface will peak at the eutectic composition during steady state growth, and the plane front will be stable if (16):

$$G_L / R > -m_L (C_E - C_O) / D_L$$

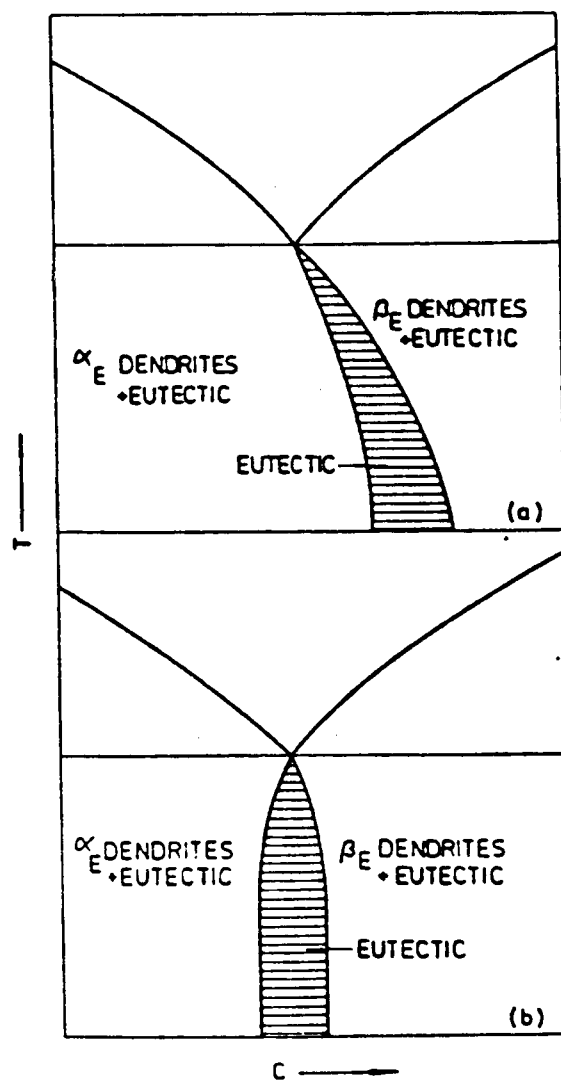


FIGURE 15

The coupled zone region in a eutectic phase diagram (ref 27)

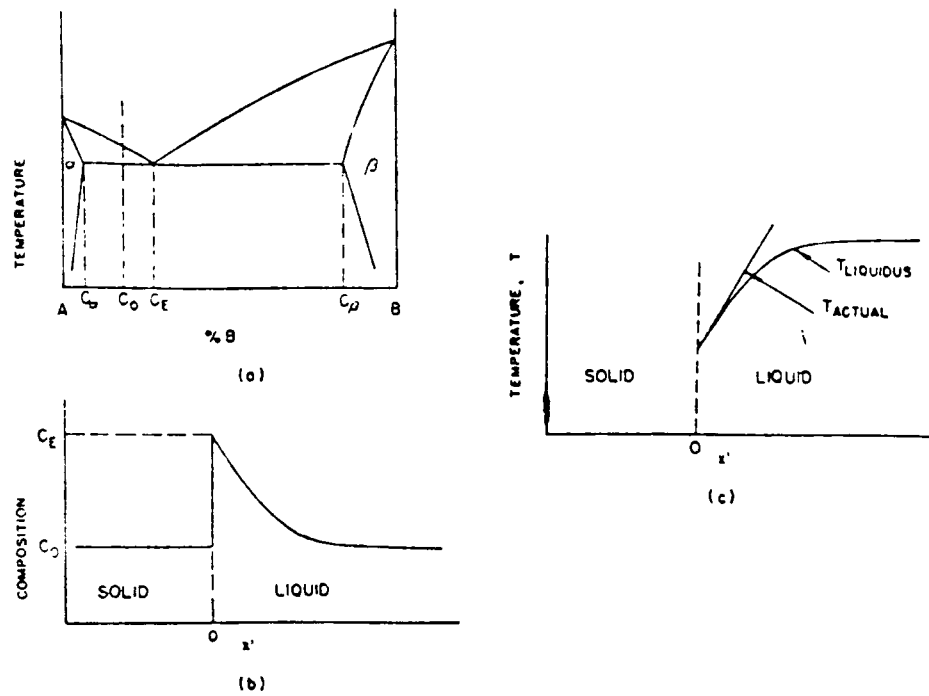


FIGURE 16

Constitutional supercooling criterion for stability of composites. (a) - Phase diagram; (b) - solute distribution at steady state in growth direction; (c) - required condition for stability (ref 28).

which is similar to the stability criterion for single phase alloys. A dendritic or cellular morphology occurs if this limiting value is not exceeded. An alloy which solidifies into cells of the α -phase will many times experience β formation in the intercellular spaces (45). Consequently, a coarse structure of aligned alpha and beta lamellae will form. However, this microstructure will, in general, exhibit inferior mechanical properties in comparison with the fine, aligned eutectic microstructures solidified at higher values of G_L/R .

Eutectic Morphology Modification

The morphology that is normally stable for a degenerate eutectic alloy system can be modified by altering the freezing velocity and/or the temperature gradient. This goal can also be accomplished by changing the composition of the specimen, such as through the addition of a ternary element. An example of the latter is the well researched modifying power of Na upon the aluminum-silicon eutectic. The presence of this third element alters the curved plate microstructure stable under solidification of the binary alloy to a fine fibrous one when a small (0.01 wt %) quantity of Na is added. This morphology is realized due to a change in the solidification behavior. For the binary, growth is uncoupled, and one phase grows into the liquid well in advance of the other. Sodium additions cause the growth process to become

coupled and a nearly planar, isothermal interface is responsible for the growth of the fine, fibrous structure. The stability of coupled growth is governed by a compatibility requirement for the planar solid-liquid interface between the thermodynamic equilibrium of the α - β -liquid triple point surface energies and the constraints imposed by diffusion (59). Therefore, the modifying power of ternary elements must be explained in terms of their effect on this compatibility requirement during steady state coupled eutectic solidification (58). Characteristics of a a ternary modified eutectic structure include (42):

1. Refinement of the microstructure to a rod or fibrous morphology.
2. An increase in the undercooling necessary for growth.
3. Appearance of dendrites of the non-faceting phase.
4. A tendency towards following the Jackson-Hunt model for normal growth at the extremum condition.

The mechanism by which this ternary addition stabilizes eutectic growth has been attributed to each of the following processes (58,60,61,62,70):

- Alteration of the interfacial energy balance at the triple junction, thereby altering the solid-liquid interface curvature in this region.

- Change in the growth mechanism for one phase. For example, increasing the number of habit planes preferred by the phase during solidification.
- Strong absorption of the ternary element on certain faceting planes inhibit growth in the high growth velocity directions.
- Establishment of a large ternary composition gradient in the liquid for elements which segregate strongly in each phase. These gradients would also modify the growth form of one or both eutectic phases.
- "Forced" growth crystallography imposed by highly constrained solute diffusion conditions, such as rapid solidification.

One aspect of eutectic solidification that seemingly is not a significant factor in the formation of a degenerate structure is nucleation. During the freezing process for a faceted:non-faceted eutectic alloy, the secondary phase is continuous (58); and therefore, the ease with which it nucleates is of little importance since repeated nucleation is not occurring substantially. An additional modification commonly seen upon addition of a ternary element to a eutectic system is the formation of a colony structure. This is the product of the ternary diffusion layer causing the solidifying interface to become slightly cellular in nature.

Directionally solidified systems that contain faceting phases exhibit a strong growth rate morphology dependence, with several morphologies possible. The Cd-CdSb eutectic, for example, is globular, as seen in figure 17, when solidified at a relatively slow growth rate of 3.4×10^{-4} cm/second (61) . Upon increasing the solidification velocity by two orders of magnitude, a fibrous microstructure is produced, as seen in figure 18.

A similar example is that of the Al_3Fe -Al eutectic, which is lamellar at high temperature gradients or G/R ratios (62). For high values of G/R, the solidifying interface is subject to stringently controlled thermal and solute fields of diffusion. If solidification occurs with a lower value of this ratio, the aluminum phase develops sufficient curvature instability to destroy the coupling of the diffusion field. The two phases are then free to grow in a semi-independent manner, causing a breakdown of the planar interface.

Ternary additions of lithium to the iron aluminide eutectic decrease the interparticle spacing and increase the fiber symmetry. Adam et. al. (62) attribute this effect to the lithium altering the interfacial energy balance by lowering the energy of the interface between the faceting phase, Al_3Fe , and the melt. This reduction causes the interfacial energies of the two phases to be approximately equal, and leads to a reduction in $\lambda\Delta T$, nearer to the Jackson and Hunt (31) extremum condition. Therefore the lithium addition reduces the interfacial kinetic undercooling required for

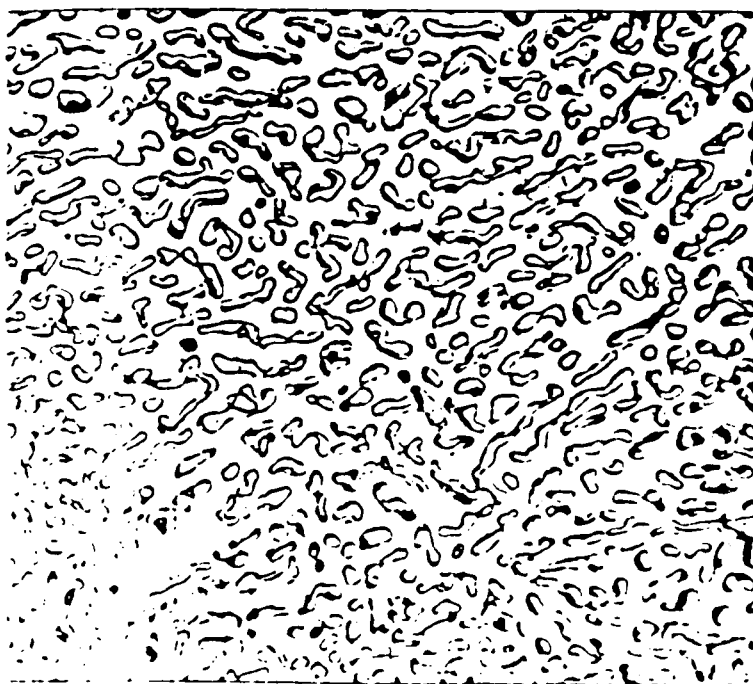


FIGURE 17
The Cd-CdSb eutectic directionally solidified at 1.22
cm/hr. (ref 61)

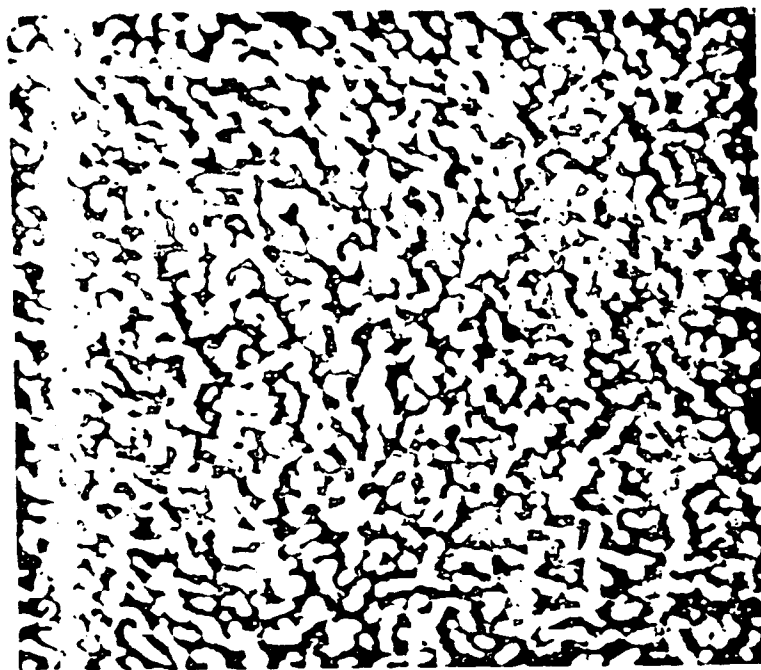


FIGURE 18

The Cd-CdSb eutectic directionally solidified at 122 cm/hr. (ref 61)

growth of the faceted Al_3Fe phase. One consequence of growth near the Jackson and Hunt extremum condition is that of growth isotropy for this phase. Therefore the structure becomes more isotropic and fibrous by suppressing planes of high growth velocity and attaining relative growth velocity isotropy in the Al_3Fe phase.

Fracture Toughness Determination from Indentation Microcracking

The concept that a relationship should exist between the extent of cracking that emanates from a microhardness indentation in a brittle material and that material's fracture toughness was originally put forth by Palmquist (63). A fracture mechanics analysis of the indentation process can be used to establish the exact nature of this relationship (64). If the deformation caused by the indenter cannot be accommodated by plastic flow in the material, cracks will form and propagate from the corners of the indentation. Two types of microcracking can occur around a Vickers indentation, as seen in figure 19. The less pertinent of these is the Palmquist crack, whose depth is approximately on the order of the hardness impression. The length of this form of microcrack is generally significantly less than the diagonal of the indentation. Of more importance to the fracture toughness determination technique is the half-penny, or medial crack. This is a semi-circular crack that forms beneath the indentation and is

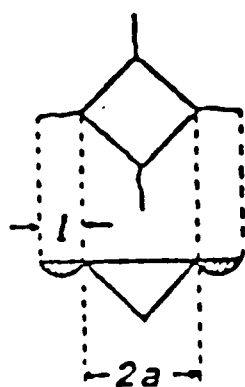
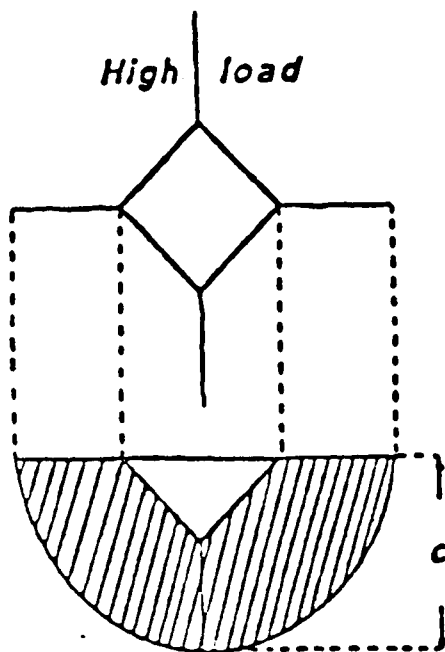
*Palmqvist**Low load**Median**High load*

FIGURE 19

Two types of microcracking formed around a hardness indentation - dependent upon load (ref 65)

greater in length on the polished surface than the diagonal of the impression. Median cracks generally will occur on a specimen at higher test loads than those producing Palmquist cracks.

The formation of the penny-like cracks can be understood by examining the elastic and plastic zones of stress produced by the microhardness indentation and unloading processes (65). Cracks initially form beneath the indentation during loading. A tensile stress is induced due to a mismatch between the elastic deformation of the bulk material and the plastic deformation experienced by the indented area. The elastic compressive stresses present while the indenter is contacting the sample are relieved during unloading. Therefore, the remaining tensile residual stress causes the crack to grow to the specimen surface. This is the driving force for both the Palmquist and median-type cracking.

Multiple equations have been derived in order to best relate the indentation load and resulting crack length to the real fracture toughness of extremely brittle materials. It can be shown through a fracture mechanics approach (see appendix) that, for an indentation exhibiting median cracks, the fracture toughness, K_C , is given by:

$$K_C = \beta (E/H)^{1/2} (P/C_0^{3/2})$$

where,

β = a material-independent constant for Vickers
induced radial cracks

E = Young's modulus

H = material hardness

P = indentation load

C_0 = radial crack length

β has been estimated to be 0.16 ± 0.04 (64).

Another approach (66) utilizes numerical analysis to obtain a relationship for the fracture toughness approach (see appendix) that can be used for both types of indentation microcracking:

$$(K_C \phi / H a^{1/2})(H / E \phi)^{0.4} \alpha = (c/a)^{(c/18a)-1.51}$$

where,

$$\alpha = 14[1-8(4\nu-0.5/1+\nu)^4]$$

where,

ϕ = constraint factor = 3

a = one-half diagonal length of hardness impression

ν = Poisson's ratio

This equation has been shown to be accurate to within 10% when compared to fracture toughness values determined by more traditional means.

Several complicating factors can invalidate the preceding relationships. The crack length seen on a polished surface must be as long or longer than the diagonal of the hardness indentation in order for the simple K_C relationship to be valid. Samples exhibiting chipping contain a more complex crack system and cannot be utilized. Indentations showing crack branching, irregular or

nonlinear cracks, or crack deflection must also be discarded from use in this technique (67). Examples are shown in figures 20 and 21. However, the most important consideration in determining the utility of this procedure for a given system is the effect of the microstructure on the crack propagation. Materials with inhomogeneities, such as inclusions or secondary phases, of the same relative size as the crack length will show a significant fluctuation in crack behavior due to interaction with phase boundaries.

Ekberg et al. (65) have established the applicability of the indentation microcracking test to a SiC-whisker reinforced Al_2O_3 composite. Crack length measurements were found to be reproducible for a multi-phase material only if each crack is larger than several interparticle spacings, i.e. $\lambda_C \gg \lambda_{\text{structure}}$. There are no fundamental assumptions in the indentation fracture toughness theory that prevent the use of this procedure with such materials. Schneibel et. al. (70) have used a similar approach to determine the fracture toughness of NbAl_3 .

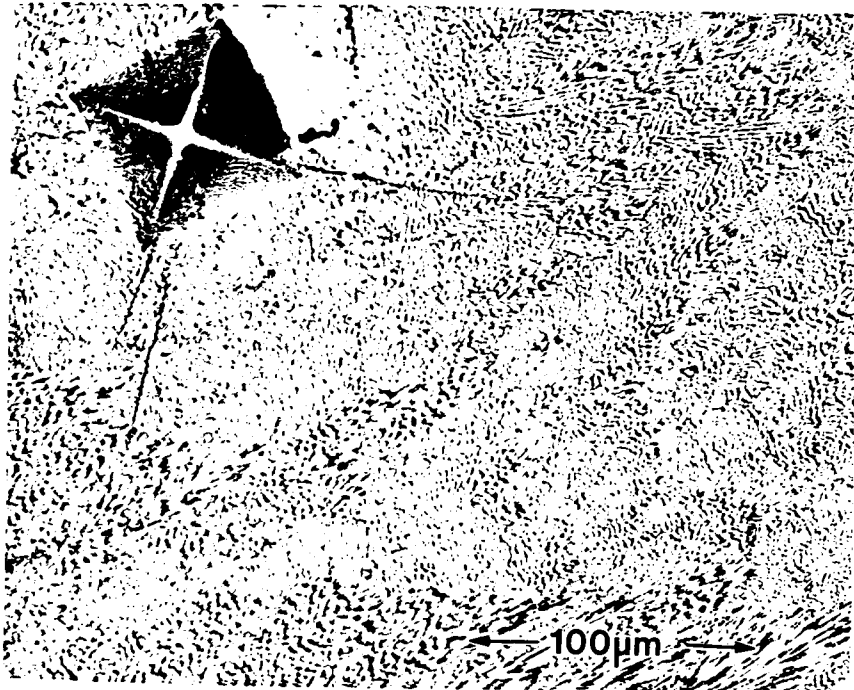


FIGURE 20
Microhardness indentation exhibiting crack branching (400 x)

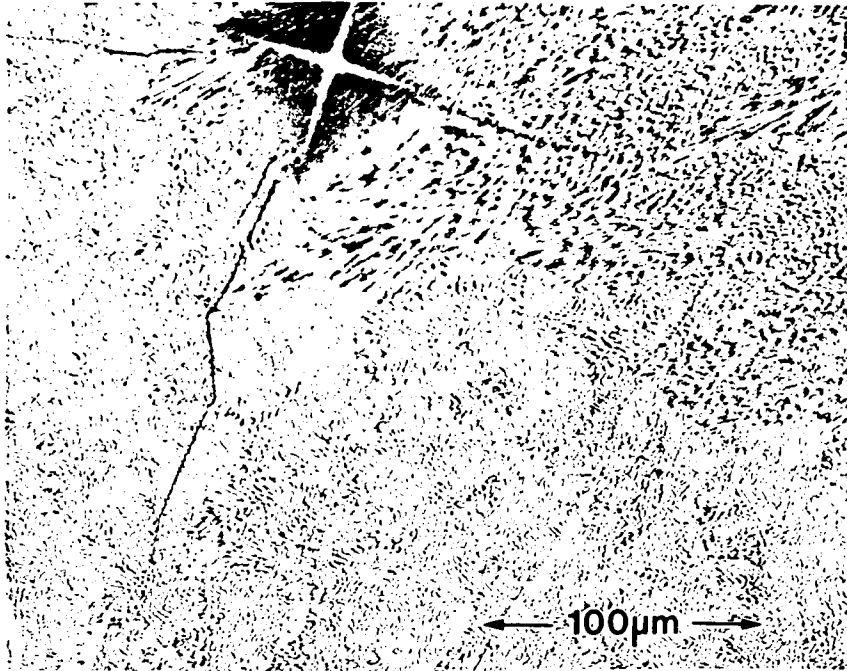


FIGURE 21
Microhardness indentation showing crack deflection (400 x)

CHAPTER III

MATERIALS AND EXPERIMENTAL PROCEDURE

The purpose of this research effort was to investigate the microstructural modifications that result from a variety of alloying and solidification conditions on the niobium aluminide system. Additional work was conducted to determine the effect of the microstructure on the mechanical properties of the resulting alloys. As-cast, arc-melted, and unidirectionally solidified ingots of several compositions were studied. These included the stoichiometric intermetallic compound NbAl_3 , the $\text{NbAl}_3/\text{Nb}_2\text{Al}$ eutectic, and this eutectic with ternary additions. The as-cast binary eutectic has a microstructure of coarse "globules" of the secondary phase, Nb_2Al . Directional solidification via levitation zone refining produced a slight elongation of this phase but no well developed alignment in the structure. The microstructure was successfully modified through microalloying with Ni to produce an extremely fine rod-type eutectic. Unidirectional solidification of this alloy results in a regression to the coarse globular structure; thereby indicating the possible instability of the aligned rod eutectic. Incremental additions of very small amounts of nickel show that a gradual transition occurs from the coarse degenerate

eutectic to the aligned structure. This supports the idea that the modification in morphology is most likely traced to the ternary addition lowering the phase boundary energy. Evaluation of material toughness was accomplished by the adoption of a traditional ceramic microhardness indentation crack length measurement technique. This analysis, which utilizes measurement of microcrack lengths in extremely brittle materials, reveal that the toughness of the niobium aluminide eutectic is not altered by the morphological modification.

Materials

The original binary $\text{NbAl}_3/\text{Nb}_2\text{Al}$ eutectic of composition 60 a/o Al- 40 a/o Nb was produced by conventional casting. Precursor ingots were supplied by NASA, Materials Division of the Lewis Flight Center in Cleveland, Ohio. One-inch diameter bars for levitation zone refining were drop-cast under argon in a preheated graphite crucible. Compositions of the directionally solidified ingots are shown in Table 1. Longitudinal and transverse sections of each bar were obtained before and after levitation zone refining via electro-discharge machining. The growth direction was noted on all longitudinal sections. Metallographic discs were obtained from each end of the refined bars in order to determine segregation and microstructural variations along the length of the ingots.

Table 1
Directionally Solidified Ingots

Sample #	a/o Nb	a/o Al	a/o ternary
25	41.2	58.8	0.0
34	40.3	59.7	0.0
35	27.0	73.0	0.0
39-E	41.1	58.9	0.0
38	41.2	56.8	1.8

Small button melts of 5-10 gram weight of the intermetallics were alloyed using an arc-melting technique. Chemical compositions of the arc-melted binary eutectic buttons are presented in Table 2. Prior to melting, the arc-melter was evacuated to a pressure below 30 microns and backfilled with high purity argon gas. Melting was performed under a system pressure of a positive argon flow of 40 mm of mercury.

Ternary additions were weighed on a Phillips electronic balance and incrementally added to fixed weights of the niobium aluminide to arrive at the working compositions. The ternary additions examined were Ni, Ti, Ga, Mn, and Cr in amounts ranging from 0.1 to 10 wt. %. The nickel and chromium were added in the form of high purity shot, and the titanium in whisker form. The gallium and manganese were cut from high purity block materials. The compositions of the arc-melted ternary Nb-Al-x alloys that were studied are shown in Table 3. The niobium aluminide source material for all ternary melts were obtained by the crushing of one-inch diameter drop-cast bars. Additional alloys of the niobium aluminide system that were produced via arc melting are shown in Table 4.

Levitation Zone Refining

The one-inch diameter drop-cast bars of both the

Table 2
Arc-melted Binary Eutectics

Sample #	a/o Nb	a/o Al	a/o ternary
28-H	44.0	56.0	0.0
121	41.2	58.8	0.0
122	44.0	56.0	0.0
44-0	41.1	58.9	0.0

Table 3
Arc-melted Ternary Eutectics

Sample #	a/o Nb	a/o Al	a/o ternary
28-C	40.3	57.6	2.1 Cr
28-N	40.5	57.5	2.0 Ni
28-M	40.1	57.4	2.4 Mn
29-M	40.3	57.5	2.2 Mn
29-G	40.5	57.9	1.6 Ga
29-T	40.3	57.5	2.2 Ti
30-N	40.4	57.6	2.0 Ni
30-H	45.0	53.0	2.0 Ni
31-H	46.7	50.0	3.3 Ni
31-N	40.0	56.1	3.9 Ni
123	46.3	50.8	2.9 Ni
124	48.1	48.9	3.1 Ni
41-M	41.2	56.8	1.8 Ni
41-N	40.3	55.6	4.1 Ni
C-7	39.7	57.5	2.7 Ni

Table 4
Additional Alloys Under Investigation

Sample #	a/o Nb	a/o Al	a/o ternary
23	40.4	59.6	0.0
42-1	31.1	68.9	0.0
42-6	36.1	63.9	0.0
42-9	52.2	47.8	0.0
43-0	31.5	67.1	1.40 Ni
43-5	35.4	62.5	2.10 Ni
43-8	53.3	44.5	2.10 Ni
44-.1	41.0	58.8	0.14 Ni
44-.7	40.8	58.6	0.61 Ni
44-10	37.1	53.3	9.60 Ni
45-.1	41.0	58.9	0.09 Ni

stoichiometric NbAl_3 and the eutectic were processed by levitation zone refining. The refiner contains a stainless steel vacuum chamber, as seen in figure 22. This process volume may have a vacuum, helium, or purified hydrogen environment. Contained within the chamber is a movable C-frame assembly that can be translated vertically to control the solidification velocity and the mass input rate to the zone. The ingot is mounted into place by upper and lower chucks that have been mounted into the C-frame. The upper chuck can be moved relative to the lower one by a stretch/squeeze motor, thereby affecting the shape of the liquid zone. Induction heating and levitation are accomplished through the use of a watercooled copper induction coil and eddy current plate. The operating variables under control are the interface rotation rate, the stretch/squeeze motion, the scanning speed, and the induction power.

The shape of the molten zone in the refining process is an important variable in producing a uniform directionally solidified structure. The zone is shaped via a computer control scheme which is based upon controlling the zone geometry identified by image processing. A feedback control strategy links the process to a DEC, RT-11/23 computer which is interfaced with an infrared pyrometer, an image processing system, the stretch.squeeze motor, the generator coil voltage, and a power meter.

The bar of material to be processed is sectioned into two

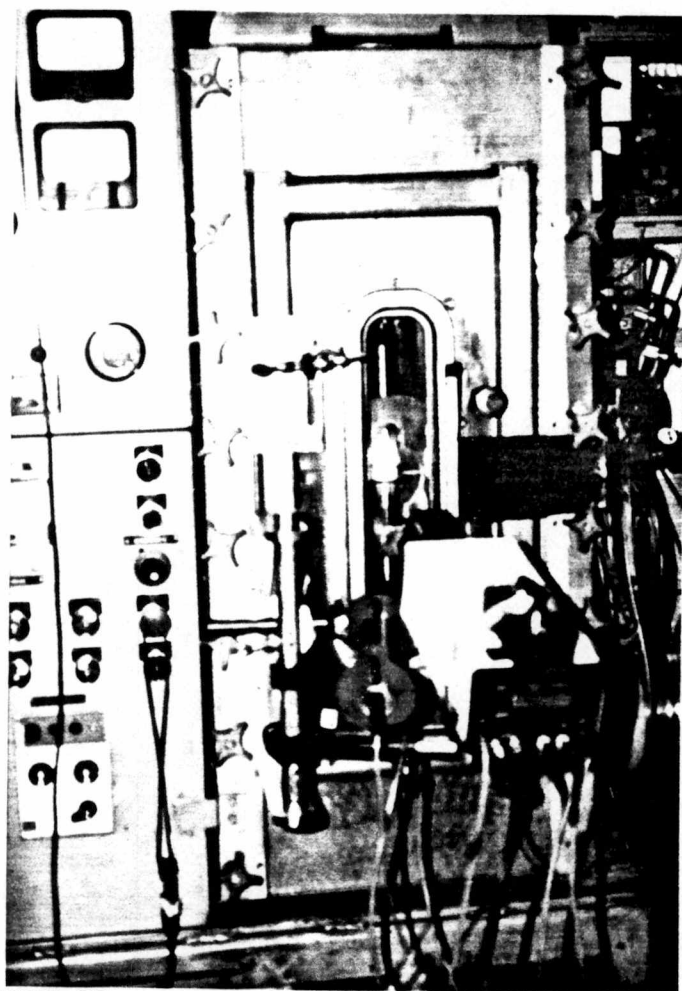


FIGURE 22
Levitation Zone Refiner

pieces and placed into the C-frame assembly such that a small gap is introduced between them. This allows for any volumetric expansion of the material as it changes phase from the solid to the liquid. This gap is positioned slightly above the induction coil; therefore, when the induction power is applied, the uppermost region of the bottom piece becomes molten and is levitated into the upper piece. This liquid region wets the upper bar and the zone is established. It can then be shaped by a small stretch or squeeze of the inter-chuck distance. The solidifying interface is rotated and the liquid is magnetohydrodynamically stirred to produce a nearly turbulent melt. These factors combine to decrease the thickness of the diffusion controlled boundary layer adjacent to the solidifying interface, thereby improving the efficiency of diffusion in the melt. After the thermal gradient is stabilized and grain growth begins in the solid, the C-frame is translated such that the zone is passed through the ingot at a controlled rate.

Drop-cast one inch diameter bars of NbAl_3 , the binary eutectic, and this eutectic with Ni were processed by levitation zone refining utilizing a positive gas flow of purified helium. Metallographic sections were prepared to determine the effect of the refining process on the resulting microstructure.

Metallography

All directionally solidified materials were sectioned for metallography via electro-discharge machining. Disks of approximately 0.5 cm thickness were cut from each processed bar and halved parallel to the growth direction, thereby providing longitudinal and transverse sections for metallographic preparation. Arc-melted alloys were sectioned either by a high-speed water cooled circular saw, or by a low speed, oil lubricated diamond cutoff wheel. It was found that the brittle intermetallics under study here are easily damaged by the high temperatures and pressures present during Bakelite mounting. Therefore, all samples were mounted in epoxy. Brittleness considerations for these materials also limited the amount of coarse grinding used on most samples. All alloys were polished with 9 micron and 1 micron diamond pastes. Fine polishing was done using 0.06 micron alumina powder suspended in distilled water. The etch used was a mixture of 3 parts HF, 1 part H_2SO_4 , 1 part HNO_3 , to 5 parts H_2O . Both optical and scanning electron microscopy were utilized for examining the microstructures.

Annealing Studies

Six ternary eutectic alloys containing 2-4 wt % Ni were

encapsulated in fused silica tubing with an argon atmosphere following evacuation to minimize oxidation. The samples were furnace annealed at 1200 C for 30 minutes, 1 hour, 3 hours, 8 hours, 16 hours, and 32 hours. Metallographic preparation of the resulting microstructures included polishing well below the material surface so as to eliminate any regions affected by oxygen intrusion.

Indentation Microcracking

Attempts to determine the bending strength of the unmodified eutectic of NbAl_3 and Nb_2Al via a four-point bend test were hindered by the very limited room temperature ductility of this intermetallic. A bend test apparatus was designed for adaptation to an Instron tensile frame operated in compression. 1-1/8" by 1/8" by 1/4" specimens were electro-discharge machined from several directionally solidified ingots. However, these samples showed evidence of extensive EDM surface cracking upon polishing with 30 micron diamond paste. This severely limits their applicability to four-point bend testing.

In lieu of this traditional materials property evaluation, a microhardness indentation cracking technique was adopted. Traditionally applied to ceramic materials, the test involves measurement of the lengths of microcracks emanating from a

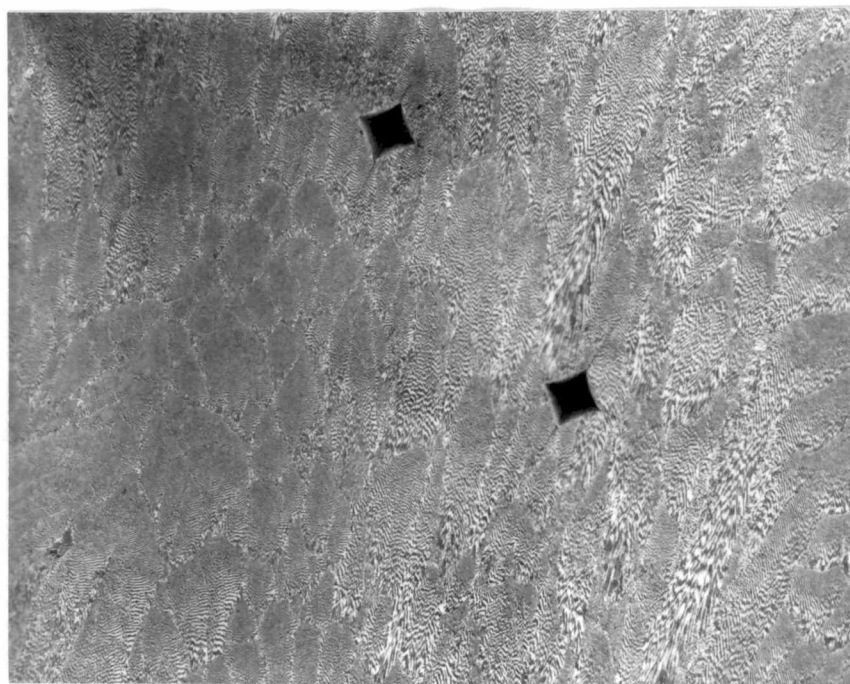
microhardness indentation on extremely brittle samples. A correlation between this crack length and the fracture toughness, K_C , has been developed, as was discussed previously:

$$K_C = \beta (E/H)^{1/2} (P/C^{3/2})$$

Multiple (12-18) areas were indented on each specimen under study using a Kentron microhardness unit. Typical indentations, demonstrating linear microcracking, are shown in figure 23. Loads of 1 and 3 kilograms were used, and light microscopy photographs were taken of each indentation at 400x - 1000x magnification immediately following microhardness testing. Crack lengths were measured from the photographs with a digital micrometer, adjusting for magnification. The length was taken as the distance from the center of the indentation to the blunted end of the crack. Any microcracks showing significant deviation from linearity, branching, or emanation from the side of the indent were disregarded. The samples under study included between 8 and 17 microcracks that were sufficiently well developed so as to be included.

Hardness Testing

Hardness measurements were performed using a LECO M-400 digital microhardness tester. A calibration curve of the measured hardness versus load was established to determine the



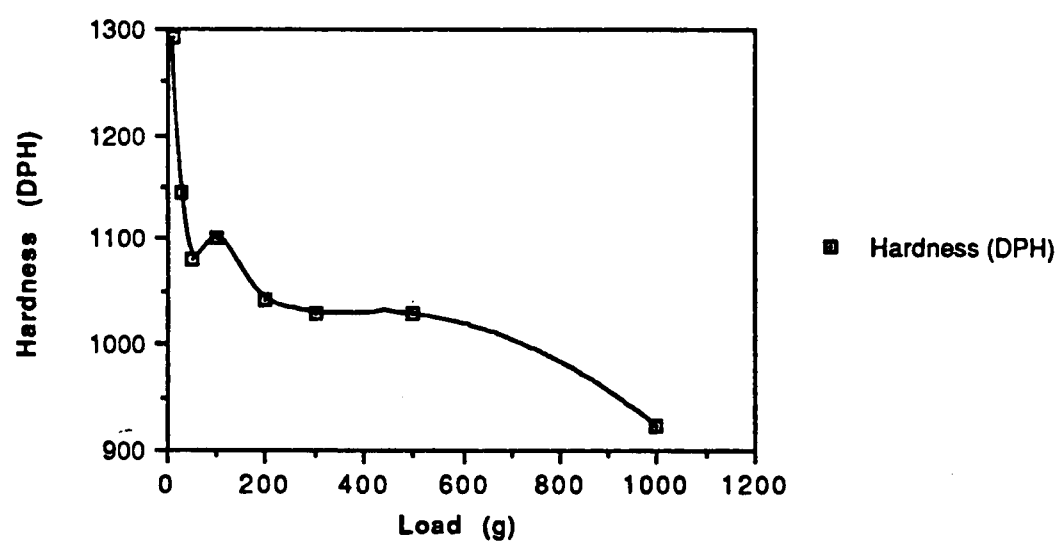
100μm

FIGURE 23

Microhardness indentations in the modified eutectic illustrating microcrack formation (200 x)

load dependency, as seen in figure 24. Loads of 200 and 500 grams were used for testing purposes.

Figure 24 Microhardness versus indentation load



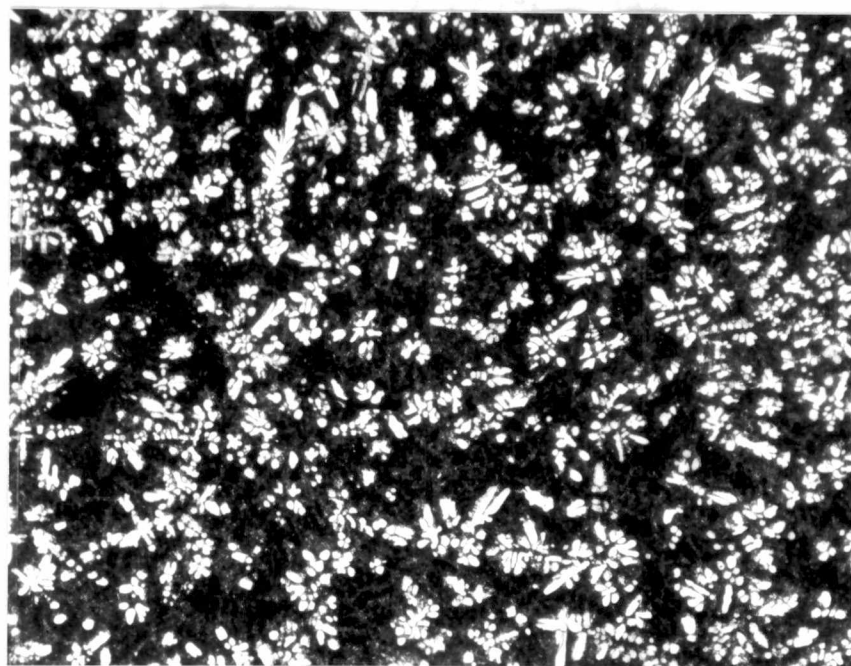
CHAPTER IV

RESULTS AND DISCUSSION

The goal of this research program has been to investigate the metallurgical processing and resulting microstructure of alloys of the niobium aluminide system. The alloys included in the study were stoichiometric NbAl_3 , the Nb_2Al / NbAl_3 eutectic, and this eutectic with ternary additions. These materials are potential elevated temperature structural materials, but are currently limited by their inherent lack of ambient temperature ductility. The development of containerless directional solidification conditions, and thereby, growth of large grained or oriented composites, was also addressed. Furthermore, the effect of modification of the eutectic alloy morphology upon the material toughness was investigated.

Binary Eutectic Structures

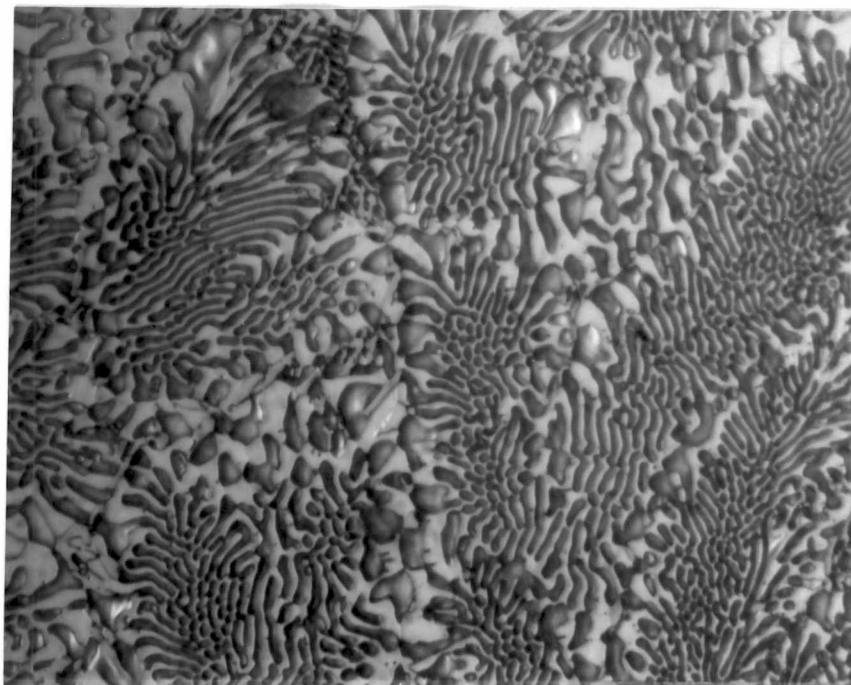
The structure of the original as-cast eutectic alloy is shown in figures 25 and 26. This sample is 60 atomic % aluminum - 40 atomic % niobium and is slightly on the aluminum rich side of the eutectic composition. The primary phase is NbAl_3 . At the lower



100μm

FIGURE 25

As-cast (59.6 a/o Al, 40.4 a/o Nb) eutectic illustrating NbAl₃ dendrites (50 x)



10 μ m

FIGURE 26

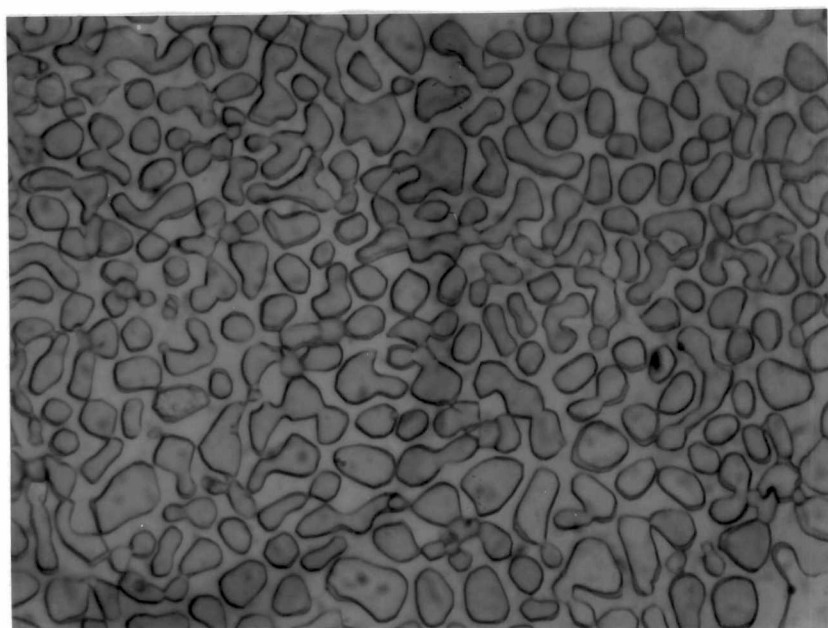
As-cast (40.4 a/o Nb, 59.6 a/o Al) eutectic structure showing globular morphology (1000 x)

magnification, the morphology of the NbAl_3 dendrites can be seen and are surrounded by the eutectic mixture of NbAl_3 and Nb_2Al . Most of the observed dendrites have a small aspect ratio, indicating that they projected only a small distance into the melt during the liquid to solid transformation.

The eutectic morphology of the as-cast specimen is somewhat "globular" in nature. The microstructure shown is indicative of a region in which the secondary phase tends toward elongation to aspect ratios of ten or more. The $\text{Nb}_2\text{Al} / \text{NbAl}_3$ eutectic apparently does not form a "normal" rod or lamellar structure. This irregular morphology that is stable for the binary niobium aluminide eutectic is of the type that has been termed degenerate. A degenerate eutectic forms as a result of one the contained phases solidifying in a faceting manner. Kurz and Fisher (37,38) have theorized that a non-faceted:faceted eutectic mixture experiences non-optimum growth conditions due to anisotropic growth kinetics. Therefore the optimum spacings at the extremum condition for growth described by Jackson and Hunt (31) are not possible, and an irregular, unaligned structure results. In addition, any anisotropy of physical properties, such as the surface energy between the eutectic phases during growth or the thermal conductivity, can promote a degenerate morphology. Rutter (58) has reported that the secondary phase in an irregular eutectic is continuous, indicating that the "globular" microstructure is actually

an interpenetrating network of the two phases.

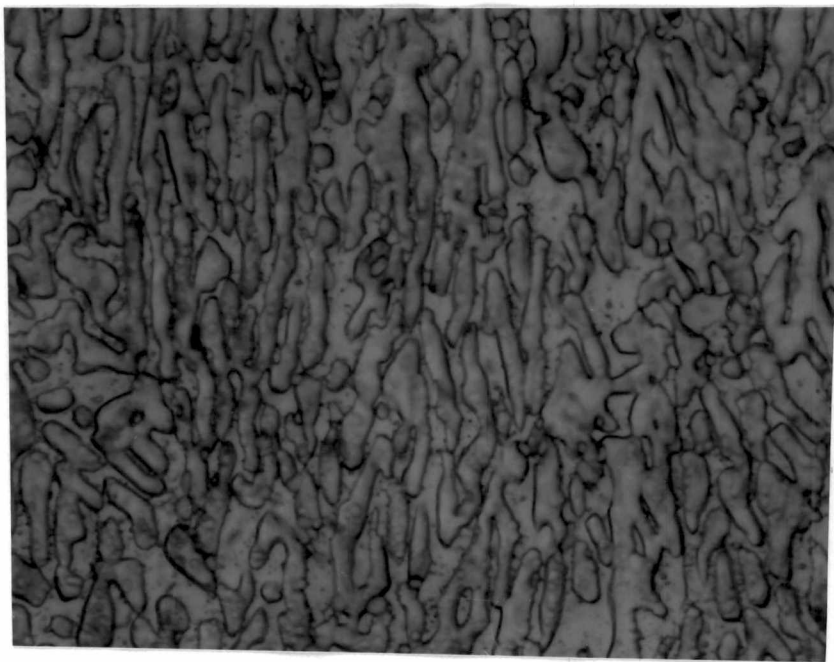
Unidirectional solidification via levitation zone melting of the aluminide eutectic produced the structures shown in figures 27 through 31. The transverse section shown in figure 27 indicates that, as a result of this process, a coarsening of the morphology occurs relative to the as-cast structure. The longitudinal section of the degenerate structure, which is shown in figure 28, shows that the secondary phase particles are elongated in the direction of growth. Figures 29 through 31 show the primary dendrite morphology in the directionally solidified eutectic alloy. The NbAl₃ dendrites grow at a skewed angle with respect to the normal of the solid-liquid interface. This can be seen from figure 29. It can also be seen that the volume fraction of the primary phase is significantly higher at the center of the bar, shown in figure 30, than at the bar's edge (figure 31). Very little dendrite growth occurs near the circumference of the ingot due to the large current density in this region during solidification. The majority of the solidifying interface seen during processing is convex upwards into the melt; however, at the edges of the bar a small region of concave curvature is seen due to the local levitation lifting forces and radiation loss from the surface. This greatly enhances the mixing in the liquid near the circumference of the melt, and a dendrite attempting to grow from this region will not be stable. After formation, the dendrite will be surrounded and remelted by



10 μ m

FIGURE 27

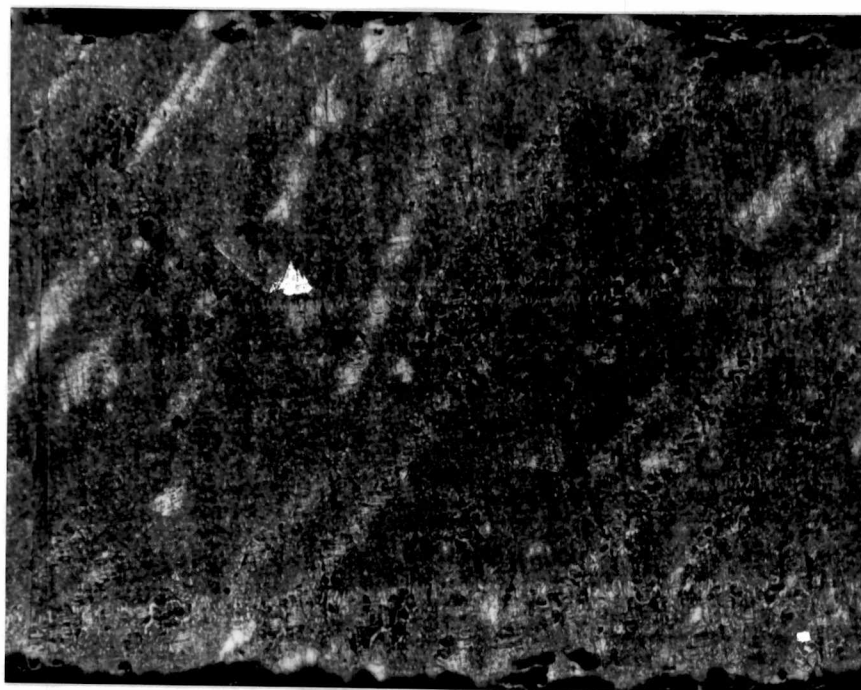
Coarsened eutectic (41.2 a/o Nb, 58.8 a/o Al) microstructure of the directionally solidified binary (1000 x)



10μm

FIGURE 28

Elongation of the secondary phase in the directionally solidified binary (41.2 a/o Nb, 58.8 a/o Al) eutectic (1000 x)



100μm

FIGURE 29

Longitudinal view of dendrite growth in the binary eutectic (41.2 a/o Nb, 58.8 a/o Al) during unidirectional solidification (50 x)

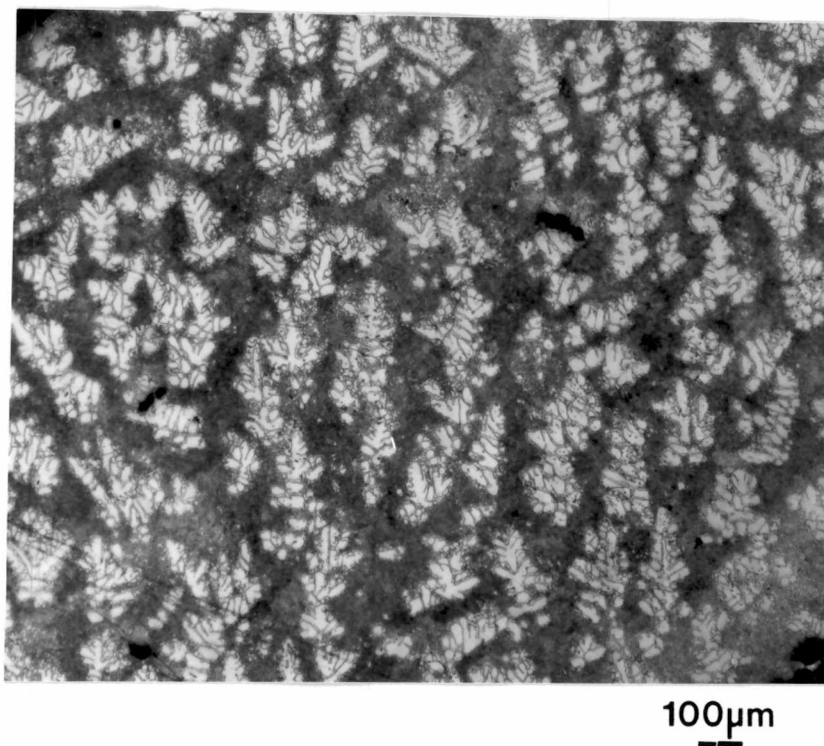


FIGURE 30
Transverse sectional view of primary NbAl_3 at center of the
directionally solidified binary eutectic (41.2 a/o Nb, 58.8 a/o Al)
bar (50 x)

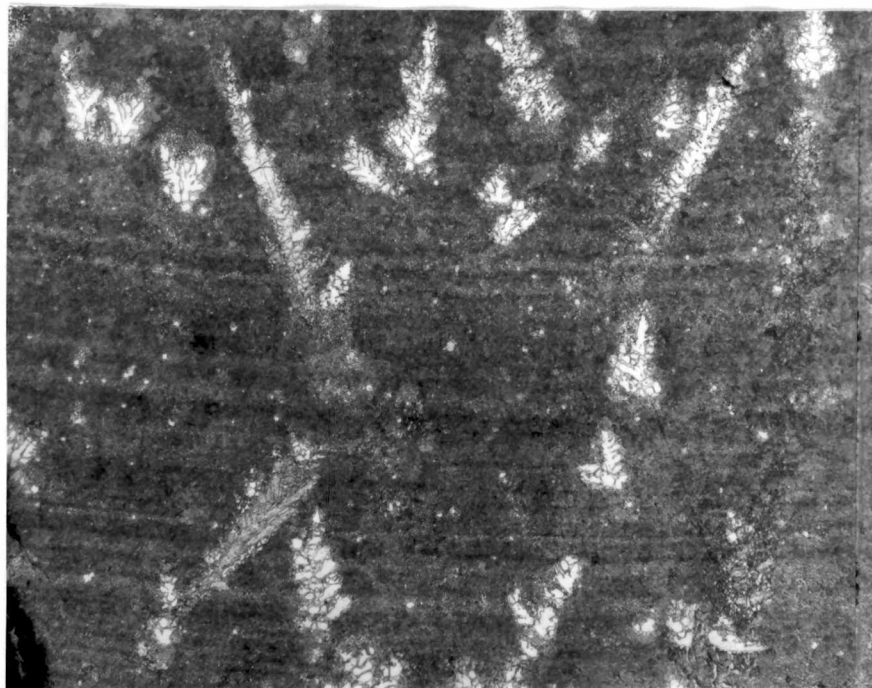


FIGURE 31

Transverse sectional view of dendrites near the edge of the directionally solidified binary eutectic (41.2 a/o Nb, 58.8 a/o Al) bar (50 x)

this highly mixed region. The circumference of the bar thus experiences a radical difference in fluid flow effects from the majority of the ingot, and this effect is seen in the resulting microstructure. Surface grains in the stoichiometric NbAl_3 compound can also be traced to this interface curvature effect. This eutectic was processed in the levitation zone refiner utilizing a multiple turn coil field shaping assembly.

Stoichiometric NbAl_3 Structure

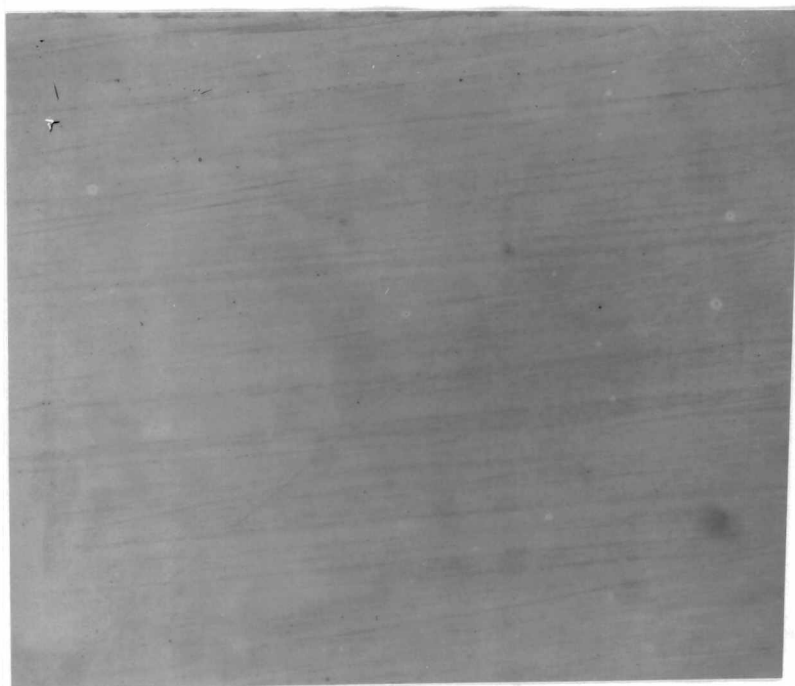
A one inch diameter bar of the compound NbAl_3 was directionally processed using the multiple turn coil arrangement. An initial attempt at processing an ingot of a composition on the aluminum-rich side of stoichiometry was unsuccessful due to an operational control problem. This was associated with the steep composition-temperature variation of the liquidus and the associated high activity (high vapor pressure) of aluminum in the melt. A second attempt utilized a composition of 27 atomic % Nb, which is slightly on the eutectic (niobium) side of the stoichiometric composition. This directional solidification attempt succeeded. This confirmed the drop in the thermodynamic activity of Al in the melt on the niobium side of stoichiometry, as evidenced by the large drop in the vapor pressure of Al. The melting behavior indicated that the transition temperature for

NbAl_3 is higher than the 1605 ± 10 C indicated on the current tentative phase diagram. This observation was substantiated by differential thermal analysis. As shown in Appendix 4, DTA scans indicate that the true melting point of NbAl_3 is in the 1650 -1690 C range. In addition, from the melt behavior, it was noted that NbAl_3 has a rather high thermal conductivity.

An extremely pure, large grained NbAl_3 structure resulted from the refining procedure. Figure 32 shows a structure relatively free of second phases. It also illustrates, along with figure 33, the large size of the resultant grains. The NbAl_3 grain boundaries show no secondary phase or impurity segregation. The processed alloy was extremely brittle and was severely damaged by all attempts to cut metallographic or mechanical property specimens by electro-discharge machining. In addition, coarse metallographic grinding caused significant crack formation in the large grained stoichiometric microstructure.

Ternary Eutectic Microstructures

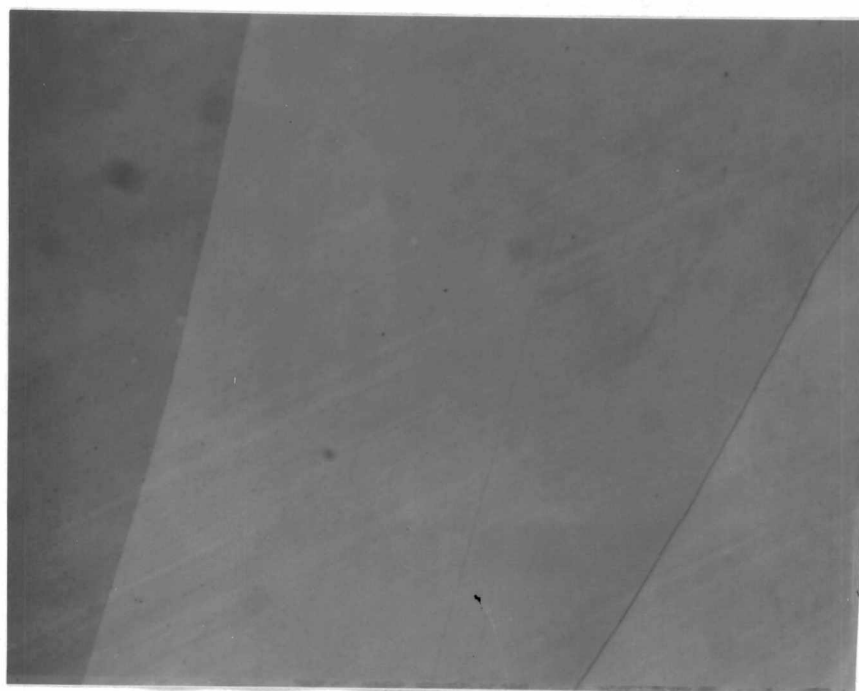
An investigation into modifying the degenerate eutectic $\text{NbAl}_3/\text{Nb}_2\text{Al}$ morphology was begun by attempting to alter the surface tension of the respective inter-phase boundaries during solidification. Ternary elements were added as shown in Table 3.



100μm

FIGURE 32

Single grain of NbAl₃ (27.0 a/o Nb, 73.0 a/o Al) at 100 x magnification



100μm

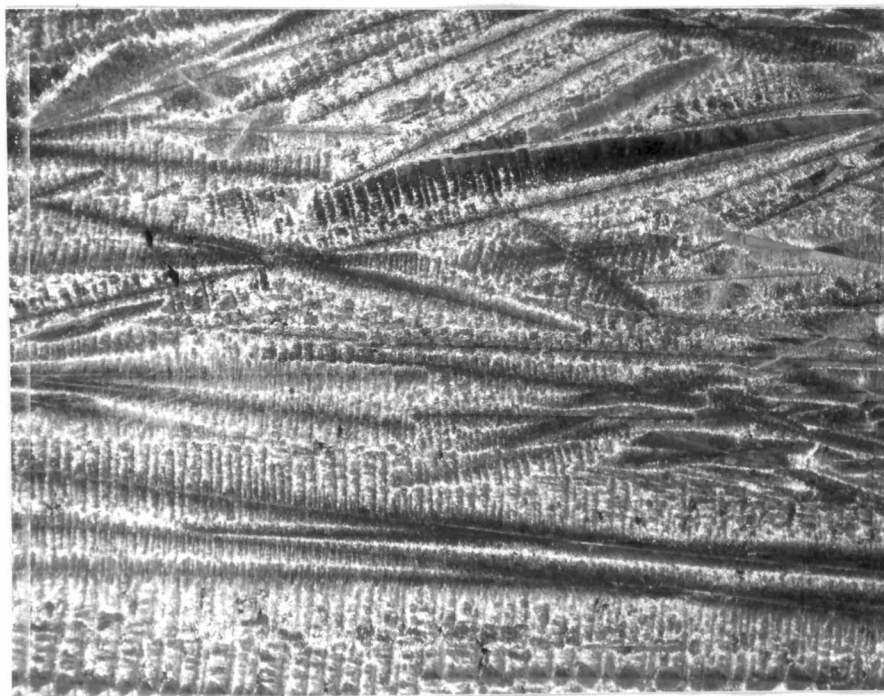
FIGURE 33

Large grains of NbAl₃ (27.0 a/o Nb, 73.0 a/o Al) directionally solidified by levitation zone melting (100 x)

The stoichiometric nature of NbAl_3 and the wide range of solubility of Nb_2Al suggest that an alloying addition should preferentially segregate into the sigma phase. Any composition change in Nb_2Al could result in an alteration of the interfacial surface tension forces present during solidification, and thereby, alter the morphology of the resulting structure. The base material for all additions was a slightly hypo-eutectic alloy of 58.8 atomic % aluminum - 41.2 atomic % niobium. The gallium, manganese, and chromium ternary alloys showed no significant change in morphology from the binary.

Nb-Al-Ti Alloys

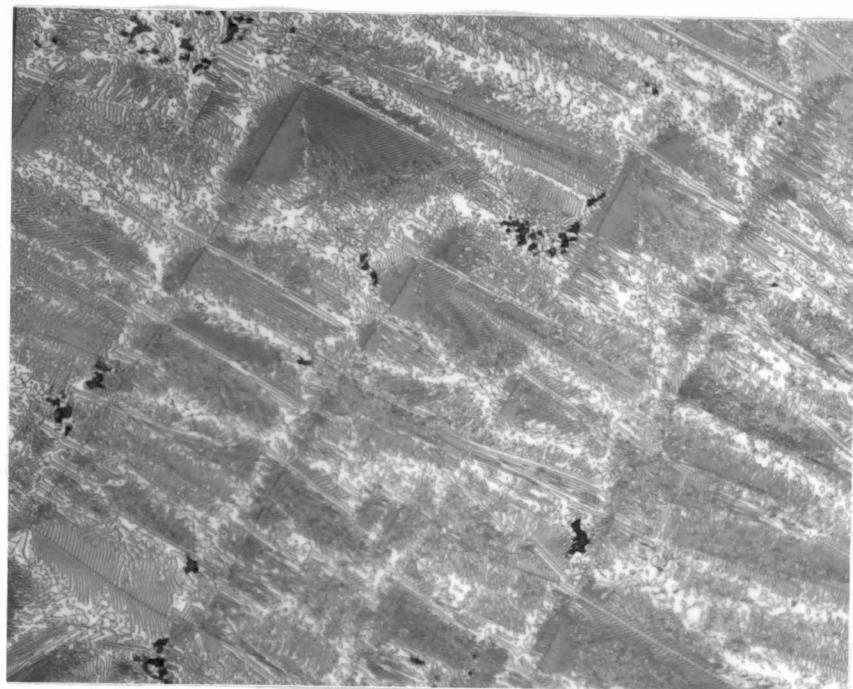
The morphological change resulting from the microalloying addition of titanium is shown in figures 34 through 37. Figure 34 shows the acicular, extended dendrites that form in this arc-cast alloy. Further arc-melting studies show that this dendrite structure is the result of the relatively rapid solidification velocity and large undercoolings associated with this process, and are not related to the alloying addition. However, figures 35 and 36 illustrate the semi-lamellar structure surrounding the dendrites, indicative of a complex-regular eutectic microstructure. When the eutectic area of the Nb-Al-Ti structure that is removed from any dendritic region (figure 37) is compared to the unmodified binary morphology, it



100μm

FIGURE 34

Dendrite structure in the ternary eutectic alloy containing Ti (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti) (100 x)



← 100μm →

FIGURE 35

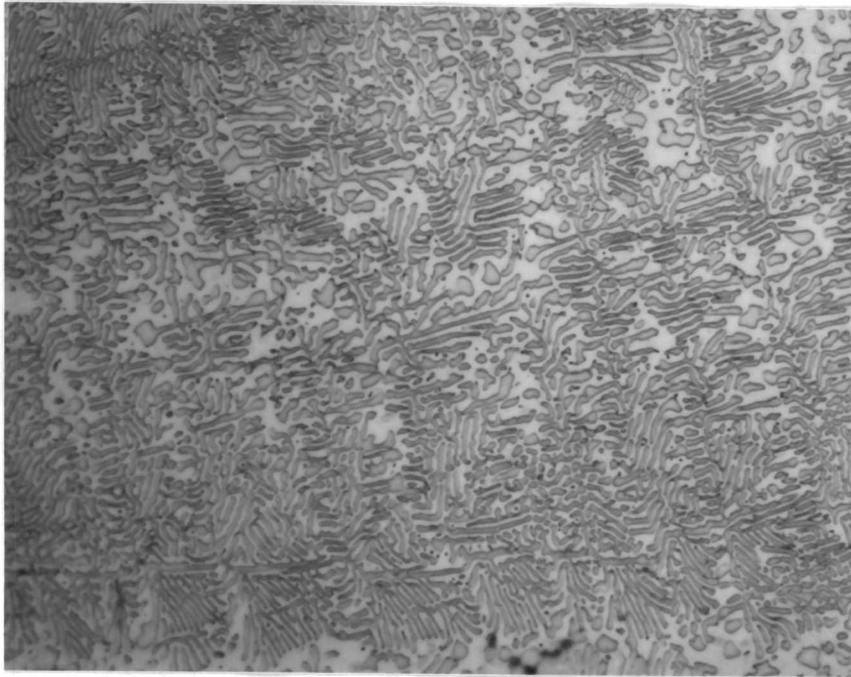
Complex-regular microstructure of the ternary eutectic with titanium (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti) (400 x)



10μm

FIGURE 36

Lamellar morphology of the Ti ternary eutectic (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti) surrounding a dendritic region (1000 x)



10μm

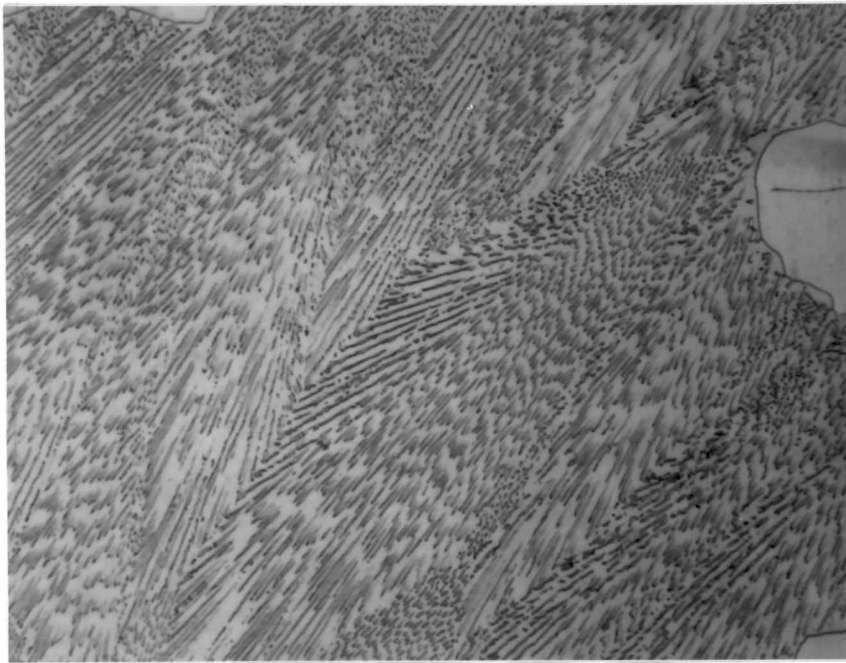
FIGURE 37

Globular morphology of regions removed from dendritic areas in the ternary eutectic containing titanium (40.3 a/o Nb, 57.5 a/o Al, 2.2 a/o Ti) (1000 x)

can be seen that no significant change in microstructure has occurred. Therefore, the effect of the titanium addition is to alter the morphology of the dendrites growing into the melt.

Nb-Al-Ni Alloys

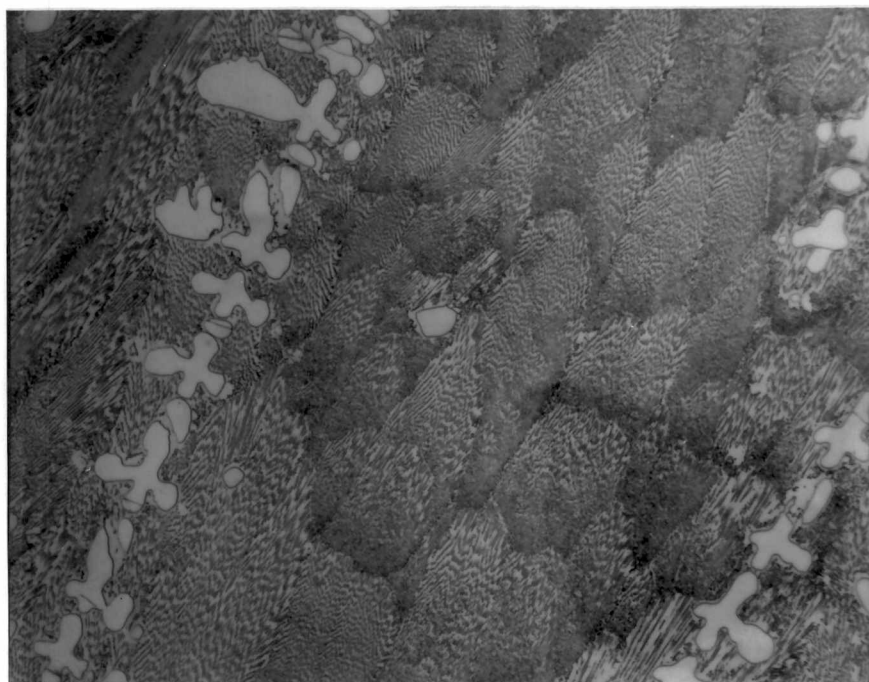
A more dramatic modification of the arc-melted Nb_2Al / NbAl_3 morphology occurs upon alloying with 2 wt. % Ni. The microstructure has been altered to one of extremely fine rods of NbAl_3 in an Nb_2Al matrix. This structure is shown in figure 38. The average rod length is difficult to determine in the arc-melted samples since any metallographic slice through the alloy will normally have a nearly circular intersection area with any particular rod. The angle between the rod growth direction and the metallographic cut must be very small for resolution of the true rod length. This distance is most likely limited by and equal to the colony size as seen in figure 39. The rod-type eutectic region repeatedly nucleates, causing "packets" of aligned rods to form. Each colony has an independent orientation as seen by the variety of rod cross sections. Several colonies with orientations such that a longitudinal cut of the rods has occurred can be seen in figure 40. Shown in figure 41 is an SEM photograph of the Ni-modified structure. The eutectic matrix surrounds the primary dendrites and the etch has attacked both the dendrites and the rods in the



10μm

FIGURE 38

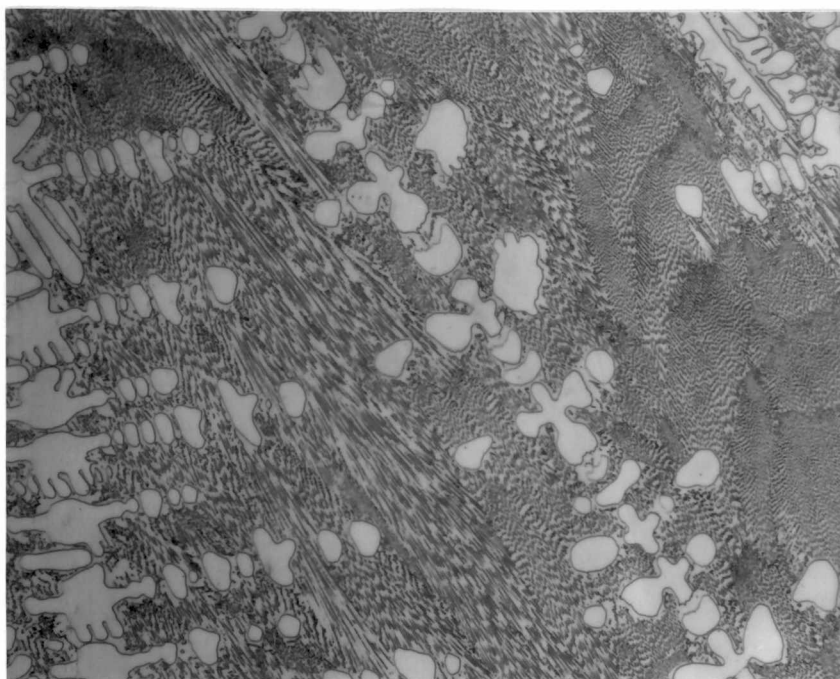
Arc-melted eutectic structure (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) showing extremely fine rods cut at varying angles to the normal (1000 x)



← 100μm →

FIGURE 39

Sub-grain structure in the Ni-modified ternary (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) eutectic (400 x)



← 100μm →

FIGURE 40

Longitudinal rods in the Ni ternary eutectic (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) (400 x)

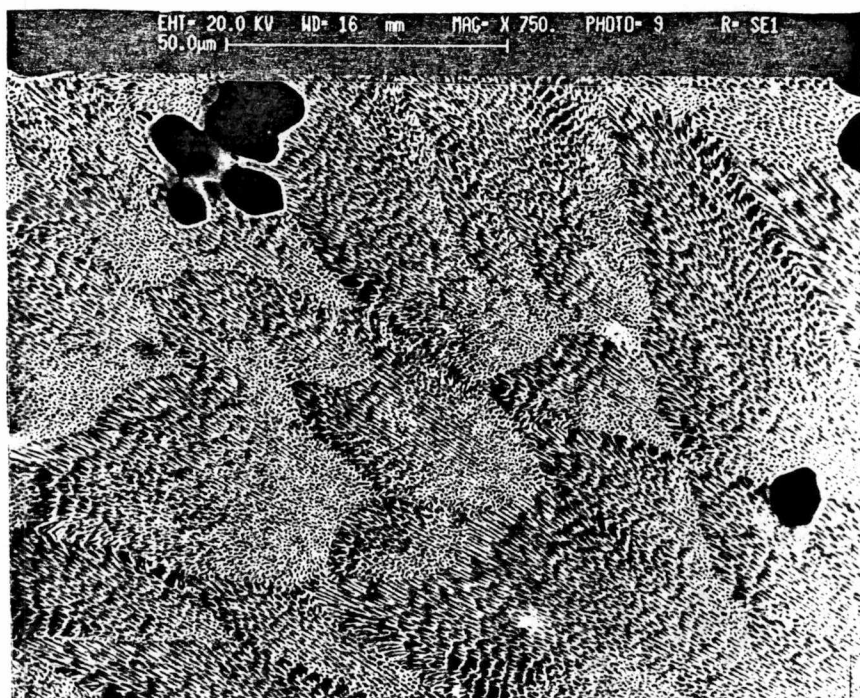


FIGURE 41

Scanning electron microscopy photograph of the Ni-modified structure (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) (750 x)

eutectic colonys. The primary phase is NbAl_3 , since the alloy is slightly hypo-eutectic. Therefore, we can surmise that the altered eutectic consists of rods of NbAl_3 in an Nb_2Al matrix. An SEM photograph of the modified microstructure can be compared with one of the unmodified binary in figure 42.

The dendrites in this alloy containing Ni are greatly extended as in all of the arc-melted alloys studied. However, the primary phase modification noted in the titanium-altered structure is not seen in the Ni ternary. The dendrite structure is shown in figure 43. Hyper-eutectic alloys of the Ni-modified niobium aluminide structure also demonstrate the rod morphology, as can be seen in figure 44. This alloy supports the assumption of the rod phase as being NbAl_3 . The primary dendrite, Nb_2Al , leads continuously into the eutectic matrix with no discernable phase boundary.

Transitional Nickel Alloys

An $\text{Nb}_2\text{Al} / \text{NbAl}_3$ alloy containing only 0.14 a/o Ni is shown in figure 45, along with the binary at the same magnification in figure 46. This minute addition of the ternary greatly decreases the average width and spacing of the secondary phase. In addition, the NbAl_3 "particles" are slightly elongated and a tendency towards colony formation can be seen. Therefore, this alloy shows

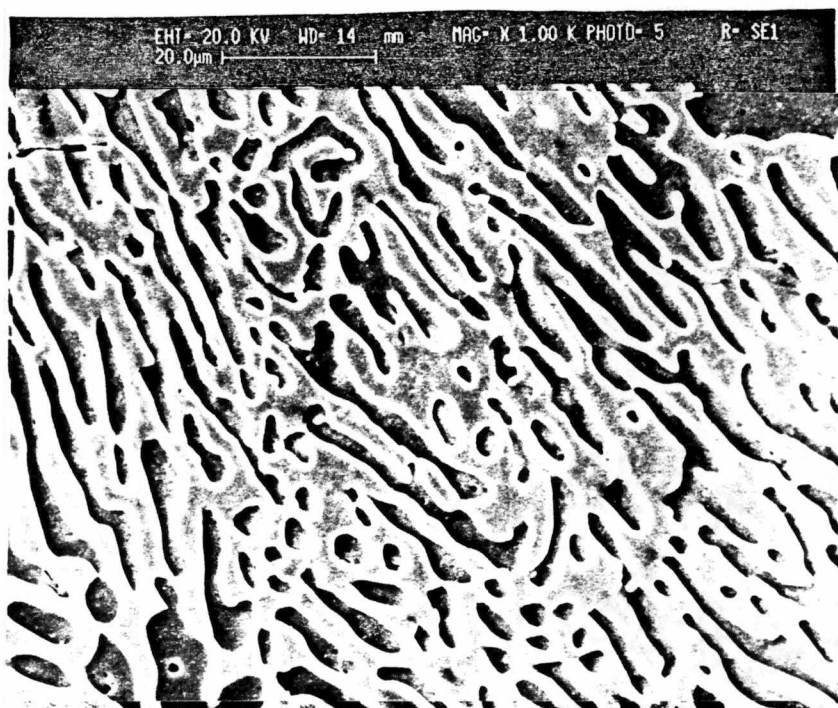
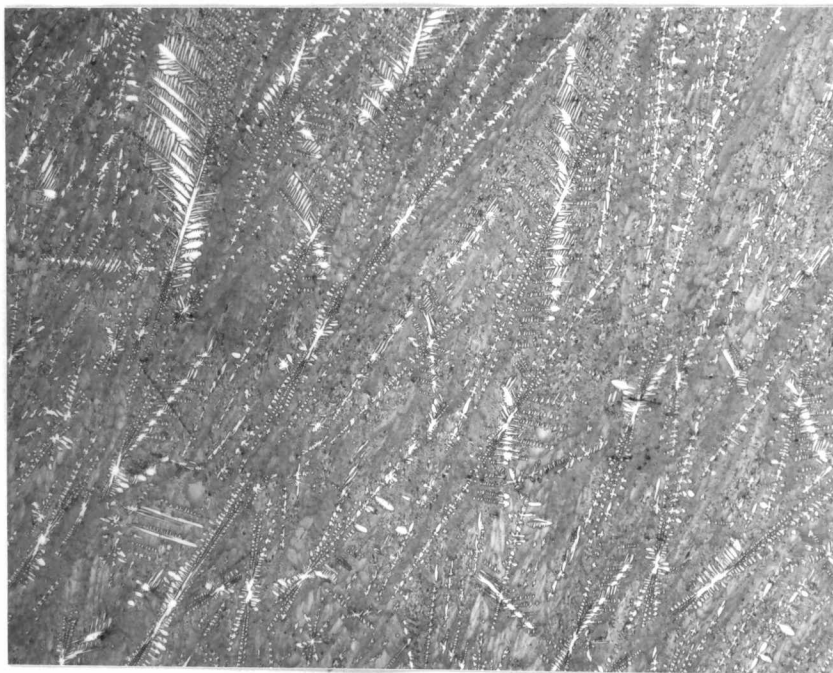


FIGURE 42

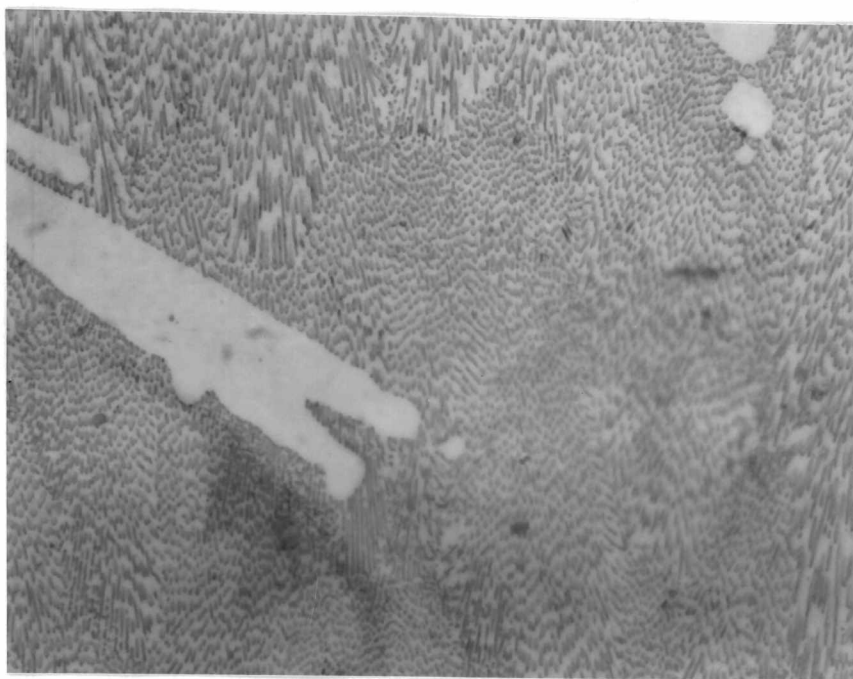
Scanning electron microscopy photograph of the binary (41.2 a/o Nb, 58.8 a/o Al) eutectic (1000 x)



100μm

FIGURE 43

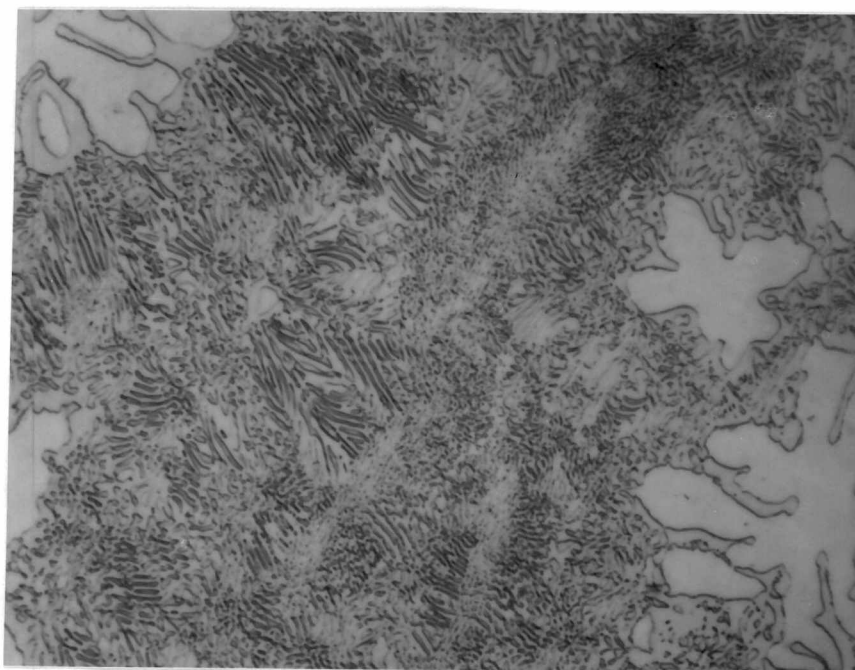
Dendrite structure in the arc-melted ternary (40.5 a/o Nb, 57.5 a/o Al, 2.0 a/o Ni) eutectic containing Ni (50 x)



10μm

FIGURE 44

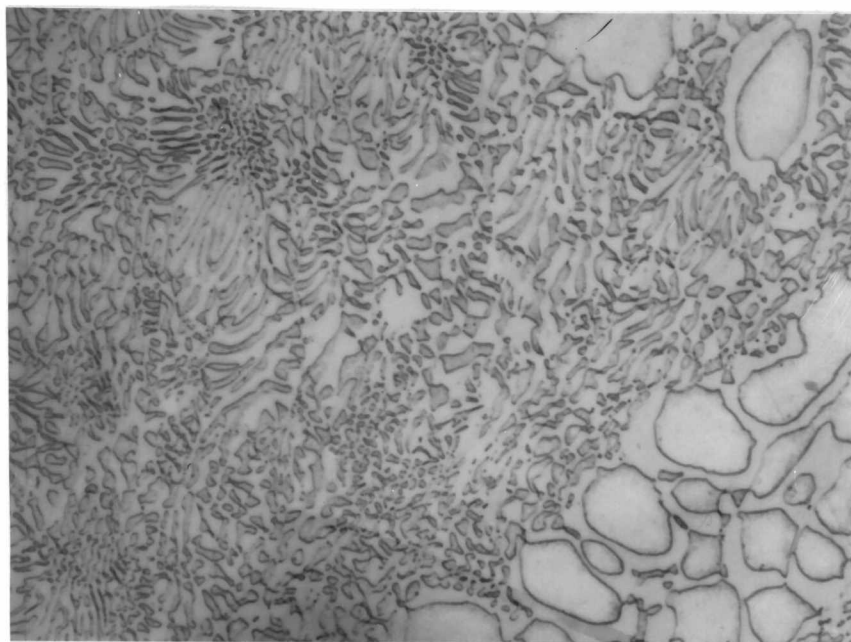
Eutectic morphology of the hyper-eutectic alloy containing Ni (46.7 a/o Nb, 50.0 a/o Al, 3.3 a/o Ni) (1000 x)



10μm

FIGURE 45

Partially modified eutectic (41.0 a/o Nb, 58.8 a.o Al, 0.14 a/o Ni) showing dramatic decrease in secondary particle size and moderate rod-type formation (1000 x)



10 μ m

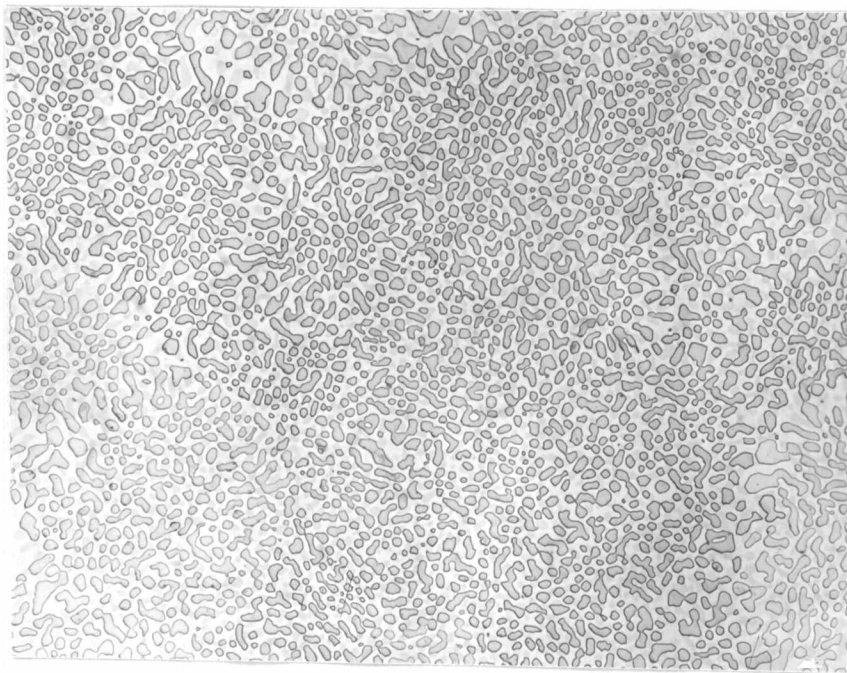
FIGURE 46

Control binary eutectic alloy (41.1 a/o Nb, 58.9 a/o Al, 0.0 a/o Ni)
for comparison with transitional ternary Ni structure (1000 x)

a transition microstructure between the binary and the Ni-modified eutectic. This lends credence to the idea that the Ni alters some mechanism of growth during solidification. The method by which the ternary addition stabilizes the eutectic growth has been attributed (58,60,61,62,70) to several processes. They include: alteration of the interfacial energy balance at the triple junction of the solid-liquid interface, a change in the growth mechanism of one phase, strong absorption of the ternary element on certain faceting planes, and establishment of a large ternary composition gradient in the liquid for elements that segregate strongly in each phase.

Directional Solidification of the Eutectic

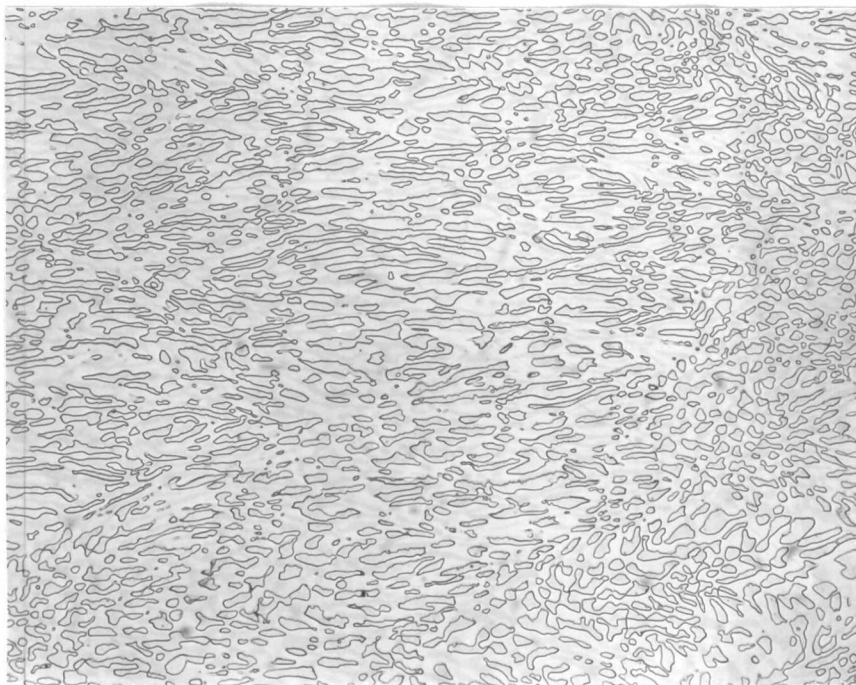
Unidirectional solidification by levitation zone refining of a ternary alloy containing nickel produced the structure shown in figures 47 and 48. Both the longitudinal and transverse cross-sections are represented. The directionally solidified alloy shows a digression in microstructure to the coarse "globular" morphology present in the binary. Therefore, the morphological modification that occurs upon addition of Ni to the niobium aluminide eutectic in the arc-melted condition is negated by this process. This result is an indication of the relative thermal instability of the rod-type microstructure.



← 100μm →

FIGURE 47

Transverse sectional view of the directionally solidified ternary eutectic containing Ni (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni) (400 x)



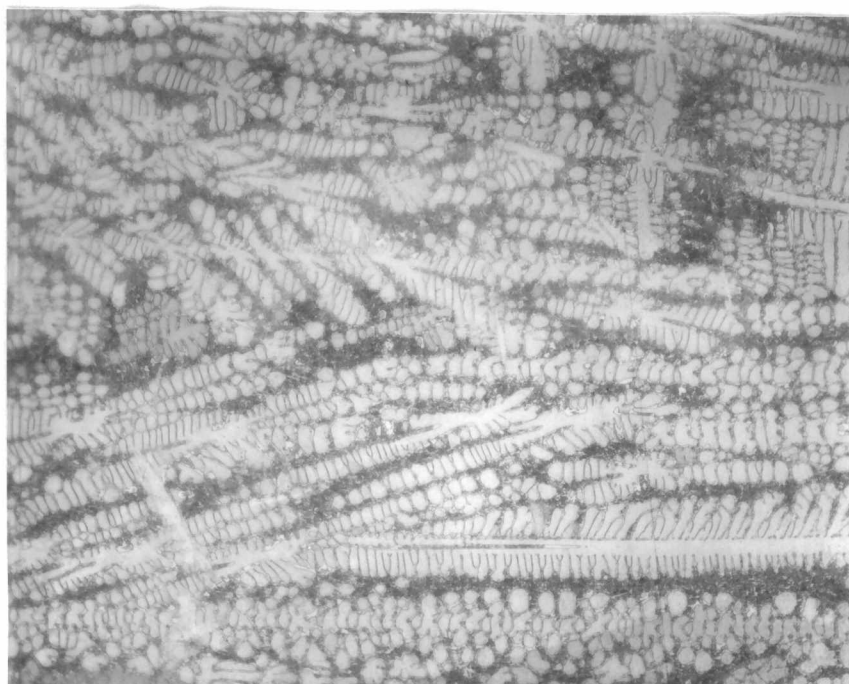
← 100μm →

FIGURE 48

Longitudinal view of unidirectionally solidified ternary alloy containing nickel (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni) (400 x)

Off-Eutectic Ternary Alloys

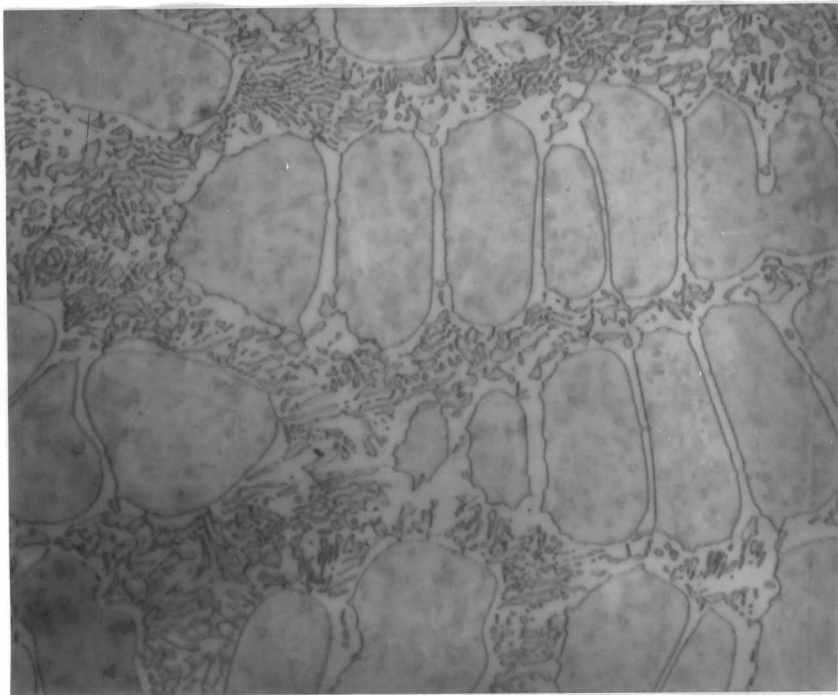
The eutectic morphology of the arc-melted alloys of both the binary and ternary compositions are not appreciably affected by the volume fraction of the primary phase. Figures 49 through 51 illustrate that the rod or globular structures are stable in alloys whose compositions vary greatly from that of the eutectic point. An alloy of 36 atomic % Nb contains an extensive amount of primary NbAl_3 , as evidenced by figure 49. The interdendritic eutectic regions in the binary sample of this composition are globular (figure 50). However, as seen in figure 51, the rod morphology is stable for an alloy of comparable composition containing nickel. Although the eutectic structures are preserved as the Nb and Al contents are varied, more significant additions of Ni produce a microstructure such as shown in figure 52. This 9.60 a/o Ni alloy has only a small volume fraction of the eutectic, and shows strong evidence of containing three phases. This is supported by the tentative ternary phase diagram (71) for Nb-Al-Ni as shown in figure 53. It indicates that, at 1140 C, a 10 a/o addition of nickel to the Nb_2Al / NbAl_3 eutectic would push the alloy into the 3-phase region. According to this diagram, the maximum solubility of Ni in this alloy would be approximately 5 atomic %.



100μm

FIGURE 49

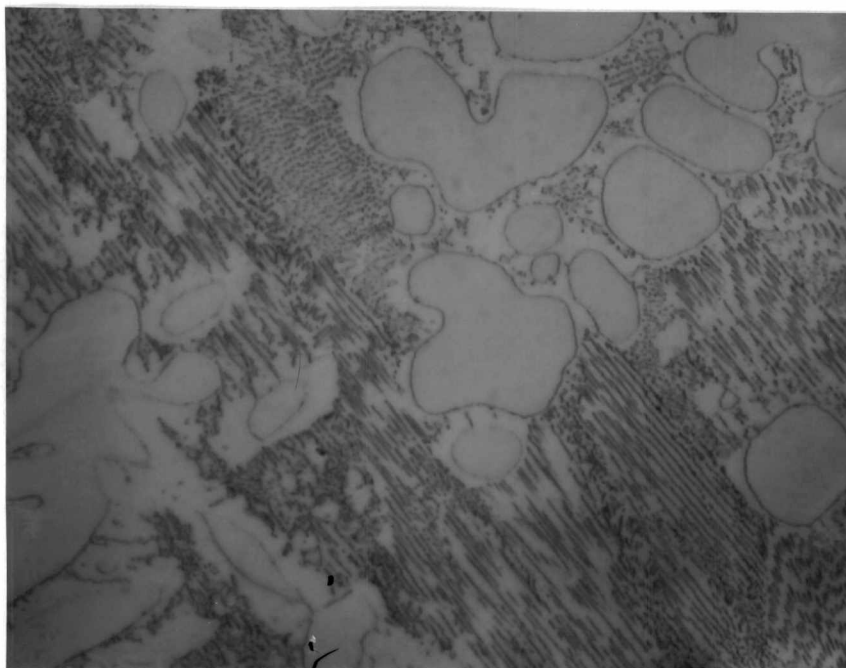
36.1 a/o Nb, 63.9 a/o Al alloy exhibiting a large volume fraction of primary NbAl₃ (100 x)



100μm

FIGURE 50

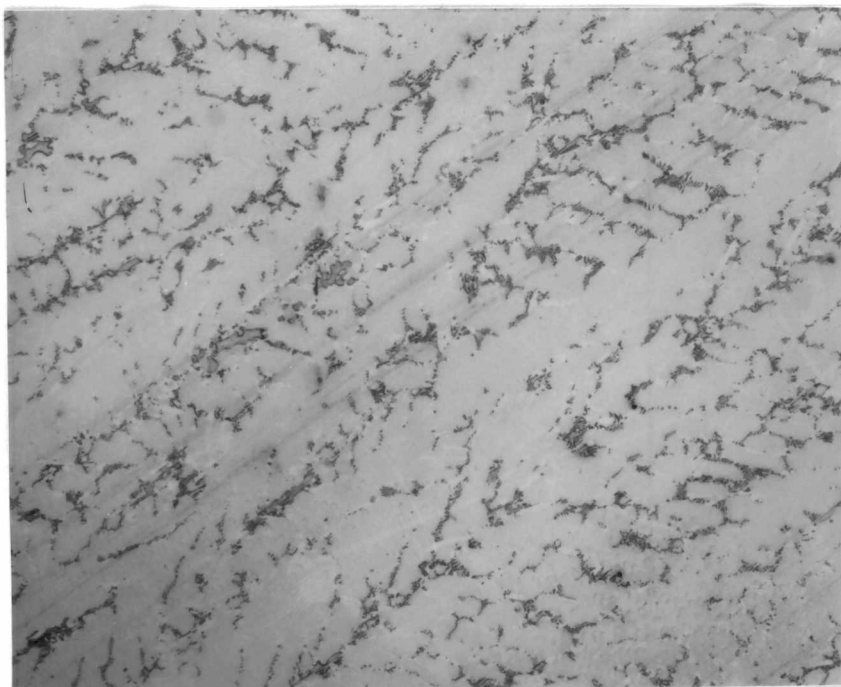
Interdendritic region of binary 36.1 a/o Nb, 63.9 a/o Al alloy
(1000 x)



10μm

FIGURE 51

Interdendritic region of ternary (35.3 a/o Nb, 62.5 a/o Al, 2.1 a/o Ni) alloy (1000 x)



← 100μm →

FIGURE 52

Three phase microstructure of a Ni-rich(37.1 a/o Nb, 53.3 a/o Al, 9.6 a/o Ni) niobium aluminide (400 x)

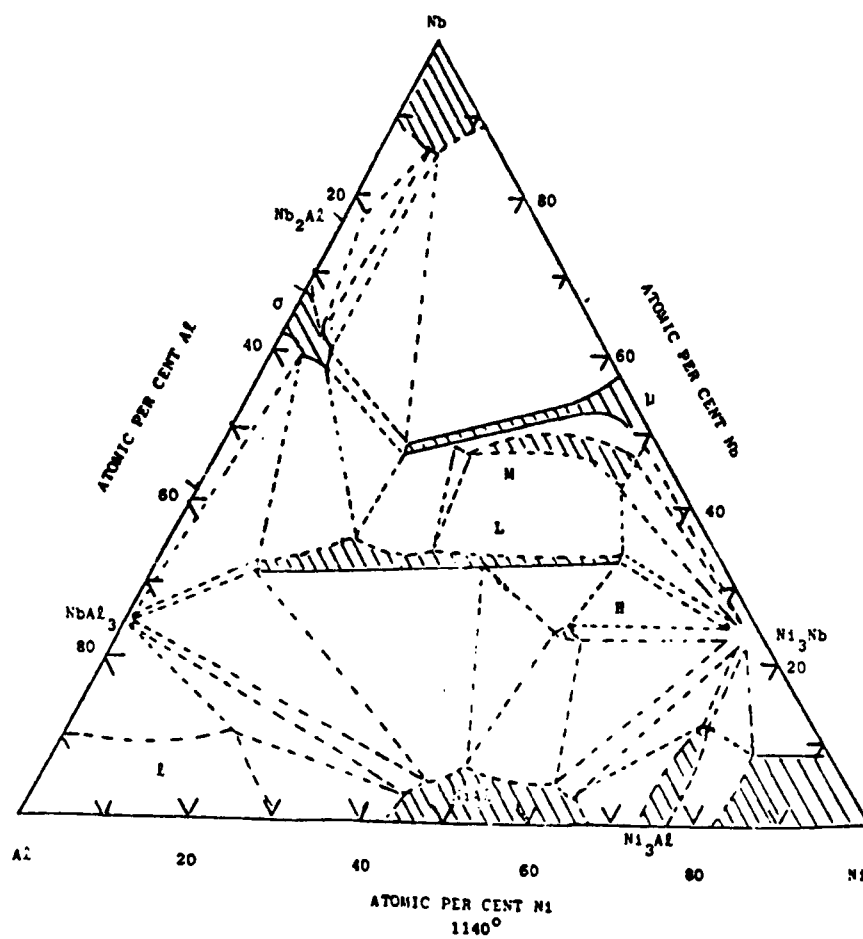


FIGURE 53
Ternary Nb-Al-Ni phase diagram

Microhardness Measurements

The niobium aluminide eutectic is an extremely hard and brittle alloy at ambient temperatures. Hardness measurements for the alloyed and unmodified eutectics are shown in Table 5, along with those for the stoichiometric NbAl_3 . The ternary alloy containing nickel shows little or no change in hardness for the arc-melted alloys. Inconsistencies in the microhardness readings arose from measurement difficulties due to the small indentations sizes and the two phase structure of the eutectic.

Microhardness Indentation Toughness Testing

The more promising of the two eutectic microstructural modifications is the Nb-Al-Ni ternary. Although our initial attempts at aligning a stable rod morphology through directional solidification have been unsuccessful due to the high temperature structural instability, future efforts may be more promising and mechanical properties measurements are desired. A relative measurement of the fracture toughness of the modified ternary alloy with respect to the binary has been obtained via the microhardness indentation fracture toughness technique. The

Table 5

Microhardness Measurements
(see appendix 3 for data summary and compositions)
Load = 200 g

Primary NbAl ₃	622 DPH
Unmodified Eutectic	927 DPH
Modified Eutectic	923 DPH
Coarsened Eutectic	988 DPH

fracture toughness of a very brittle material, as mentioned previously, can be described by:

$$K_C = \beta (E/H)^{1/2} P/C^{3/2}$$

The utilization of this relationship is limited to materials which obey the assumptions in the fracture mechanics derivation. Any inhomogeneities in structure, such as eutectic secondary phases, must be on much smaller scale than the microcrack lengths ($l_{\text{structure}} \ll l_c$). The indentation load must be sufficient to cause median cracks which are larger than the indentation diameter. However, the load cannot be so large as to cause chipping around the circumference of the indent. Lateral crack growth, which is the source of the chipping problem at high load values, is incorporated into the derivation for the normal loading conditions in the form of a complex geometrical factor. This is normally determined by experimental calibration. All of the preceding assumptions are valid for the niobium aluminides tested by hardness indentation microcracking .

In this equation β is constant for all tests. All measurements have been conducted at a constant load of 3 kg. If it is assumed that two materials have equivalent elastic moduli and hardnesses, relative values for fracture toughness may be determined directly

from crack length measurements. This assumption should be approximately valid for niobium aluminide eutectic structures. As mentioned previously, microhardness measurements on the binary and ternary alloys have shown that the nickel addition does not alter the hardness of the eutectic. The elastic moduli should also be nearly equivalent. The rule of mixtures for a composite material states that the modulus of a composite material is given by:

$$E_C = E_m V_m + E_f V_f$$

Therefore, the elastic modulus of the eutectic structure is a function of the elastic moduli of the individual phases and their respective volume fractions. Both the volume fractions and the individual phase moduli should be approximately equivalent in the ternary and the binary structures. Therefore, the elastic moduli of the two alloys should be equivalent.

Microcrack measurement results for several modified and unmodified samples are shown in Table 6 and presented in bar graph form for comparison purposes in figure 54. Typical photographs from which microcrack lengths were measured are shown for the unmodified and modified alloys in figures 55 and 56. The average crack length for the modified structure is 113 microns, and the average value for the binary alloys is 115

Table 6

Microhardness Indentation Crack Lengths
(see appendix 3 for data summary and compositions)
Load = 3 Kg

Sample	Average Microcrack Length
25T(Binary)	118 microns
25L(Binary)	110 microns
41M(Ternary)	107 microns
30H(Ternary)	117 microns
38T(Coarsened)	107 microns
C7(Coarsened)	115 microns

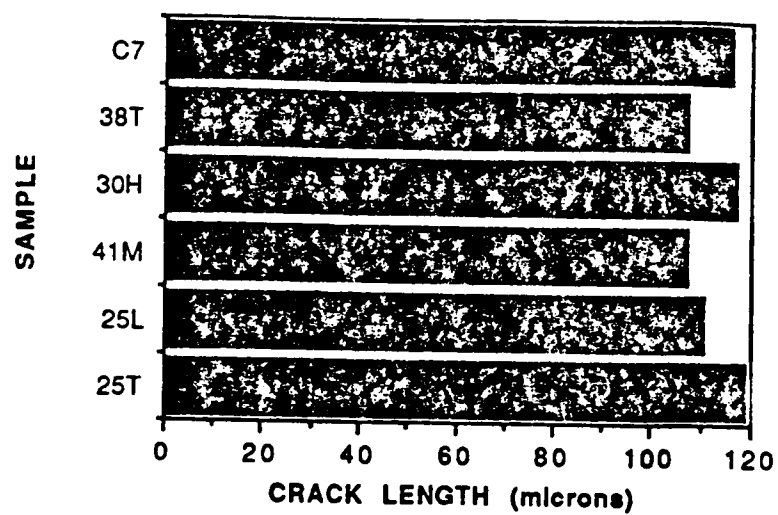


FIGURE 54

Average microcrack lengths in unmodified, Ni-modified, and coarsened eutectic alloys

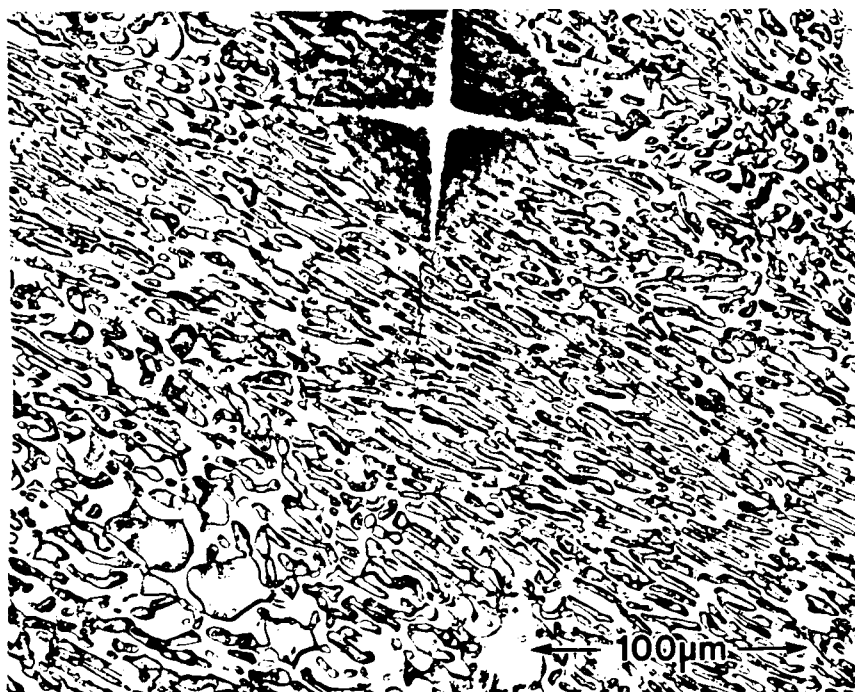


FIGURE 55

Indentation microcracking in the binary directionally solidified eutectic (41.2 a/o Nb, 58.8 a/o Al) (400 x)

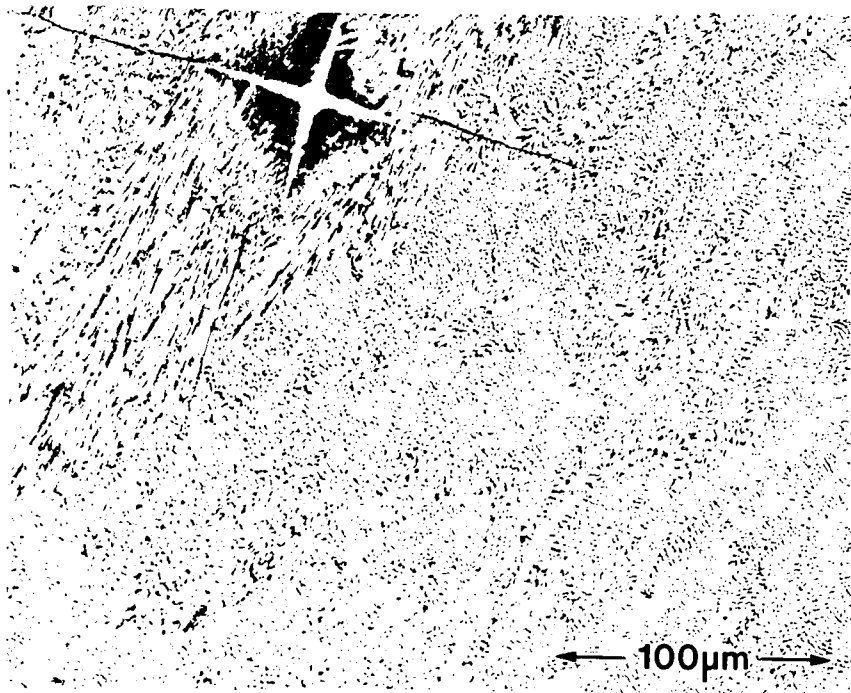


FIGURE 56

Indentation microcracking in the Ni-altered ternary (45.0 a/o Nb, 53.0 a/o Al, 2.0 a/o Ni) eutectic (400 x)

microns. Therefore, according to this technique, the fracture toughnesses of the binary and ternary alloys are approximately equal with the above assumptions; and the microstructural modification that results upon addition of nickel does not appreciably alter the toughness of this intermetallic. This is somewhat surprising upon initial examination in light of the dramatic change in morphology produced by the ternary addition. However, since both phases are extremely brittle intermetallics of comparable hardnesses, load transfer is of little importance; and the effect of the shape of the secondary phase on the material toughness is minimized.

Elemental Analysis

Analysis of the elemental distribution of Ni, Nb, and Al was performed on the modified eutectic structure using energy dispersive spectroscopy in a Cambridge 360 scanning electron microscope. The average compositions of the primary NbAl_3 dendrites and of the eutectic region are shown in Table 7. Typical EDS spectrums for these regions are shown in figures 57 and 58. The average composition of the eutectic region is 2.5 a/o nickel, 52.2 a/o aluminum, and 45.3 a/o niobium; and the dendritic region is indicated to be 0.5 a/o nickel, 71.6 a/o aluminum, and 27.9 a/o niobium. This data suggests that the nickel has segregated to the

Table 7

Compositions From SEM Elemental Analysis of 2 a/o Ni alloy
(see figure 59)

Region	Element	wt. %	a/o
Eutectic	Ni	3	3
	Al	24	52
	Nb	73	45
NbAl ₃ Dendrite	Ni	<1	<1
	Al	42	72
	Nb	57	28

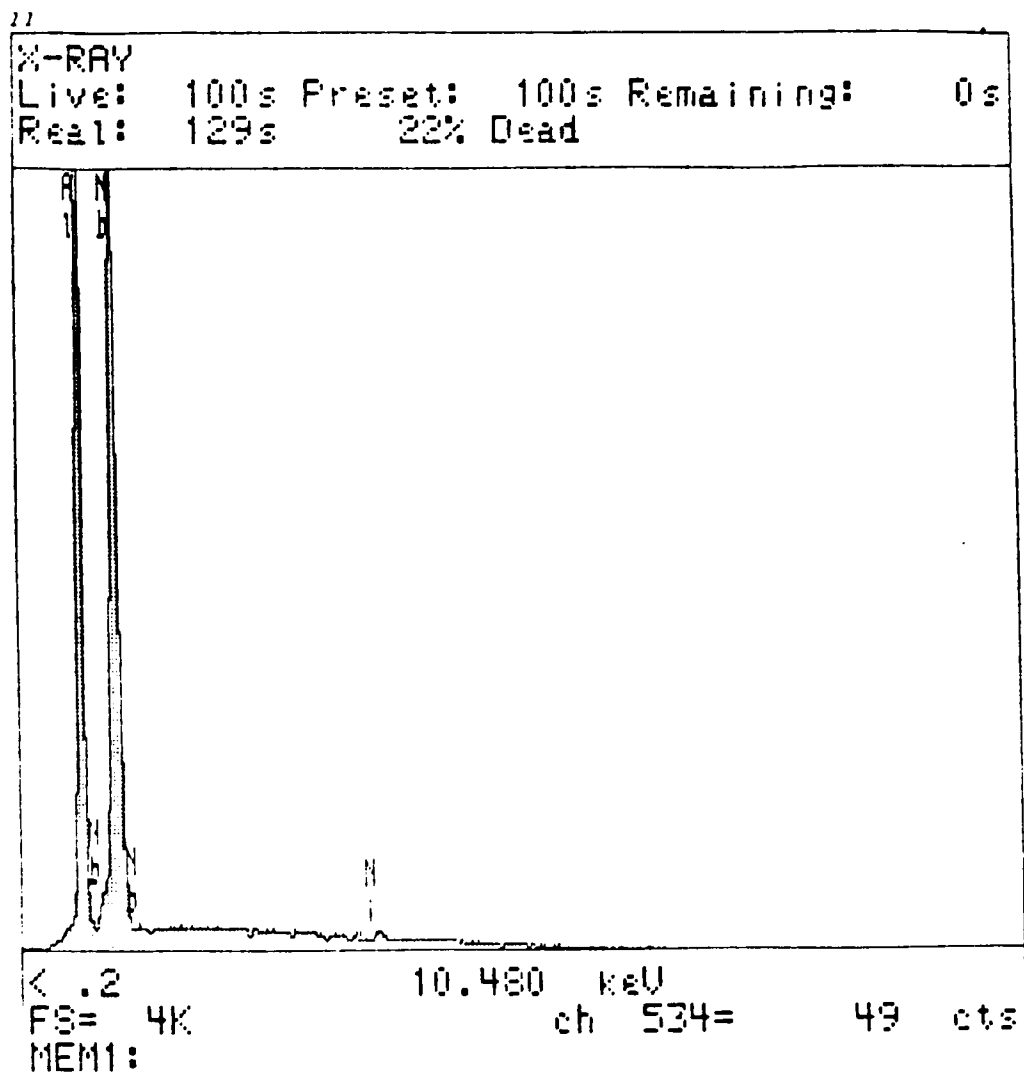


FIGURE 57

EDS spectrum for a primary NbAl₃ region in
the Ni ternary eutectic

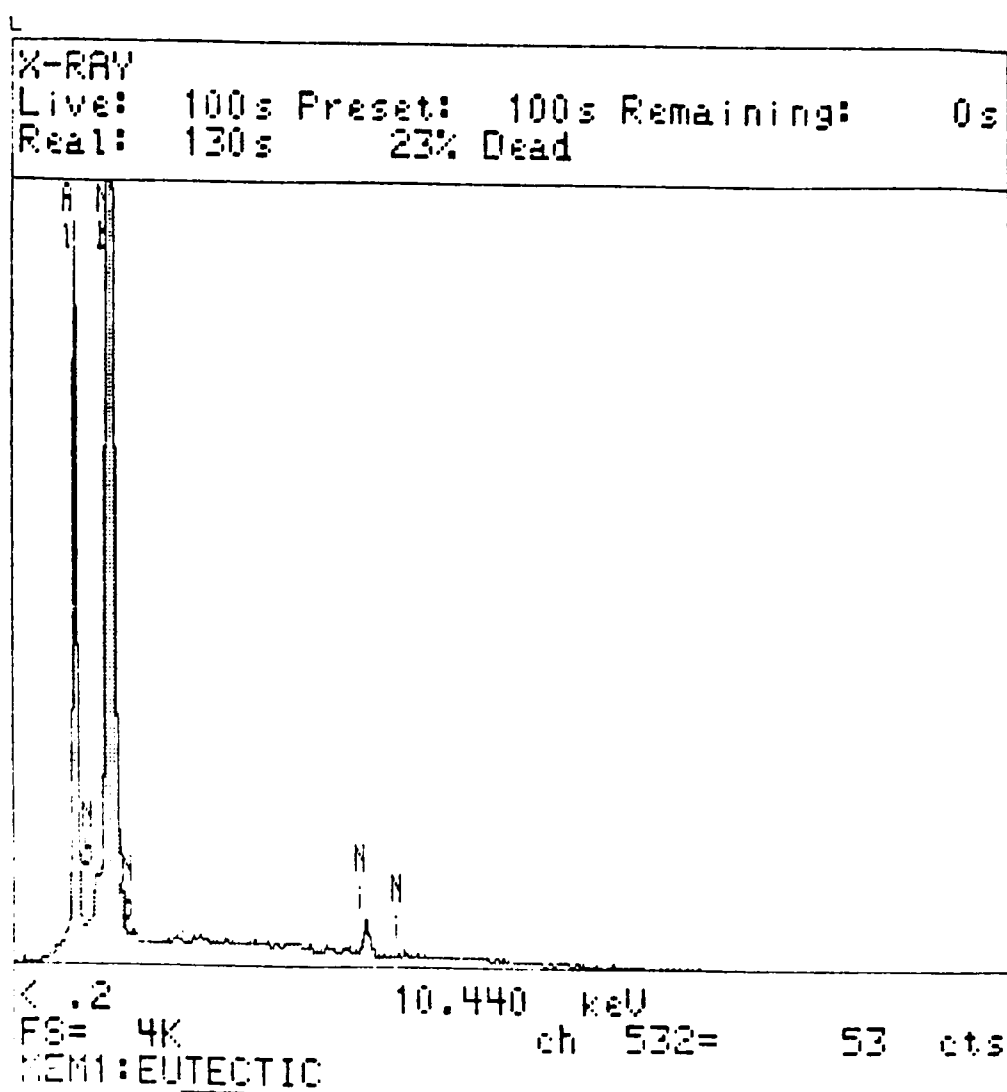


FIGURE 58

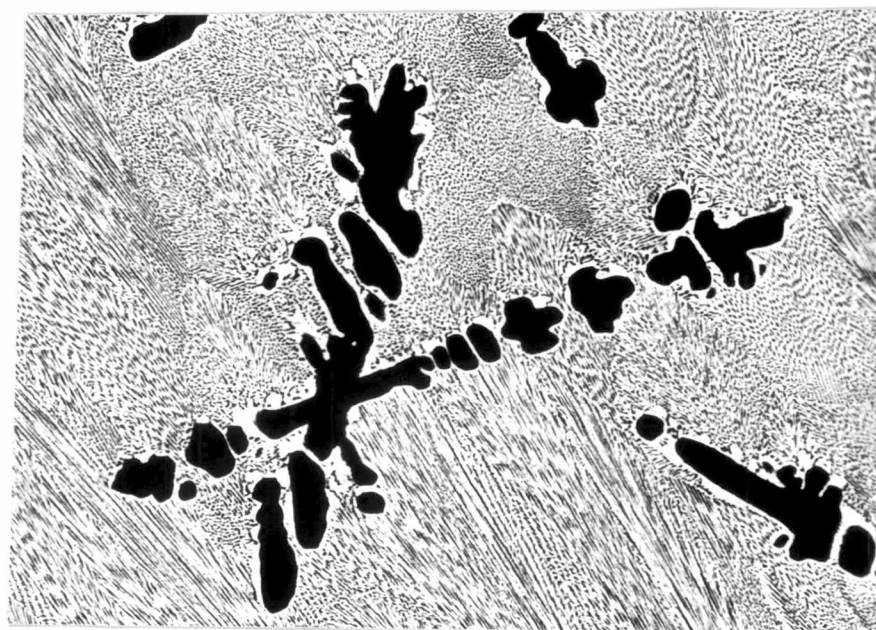
EDS spectrum for the eutectic region of the
Ni-modified ternary alloy

eutectic regions of the specimen. As can be seen from the ternary Nb-Al-Ni phase diagram in figure 53, Ni has very little solubility in the stoichiometric NbAl_3 compound. It does, however, have a wide range of solubility in the Nb_2Al sigma phase. Therefore, the Ni addition moves preferentially into the Nb_2Al matrix during solidification. This would appreciably alter the composition of the phase to include 5-10 atomic % Ni. This lends support to the proposition that the morphology change occurs due to an alteration of a mechanism of growth of the Nb_2Al . Possible modes are a change in the triple point interfacial energy balance, and adsorption of Ni on certain faceting planes in the sigma phase structure which inhibits growth in the high velocity directions. The former seems a very likely source for this eutectic system. The NbAl_3 phase has the DO_{22} structure, and the Nb_2Al has a sigma-type structure. Both of these lattice classes are extremely complex and a boundary between them will have a relatively high surface energy. Therefore, it is possible that the preferential Ni substitution into the Nb_2Al phase lowers the surface energy between the two phases during solidification.

The elemental analysis of the eutectic region indicates that the aluminum content is significantly less than that indicated by the eutectic point of the binary phase diagram. This suggests that the ternary addition has shifted the eutectic point relative to binary Nb-Al value. This shift is supported by microstructural

examination of the primary NbAl_3 volume fraction of the eutectic region in alloys containing Ni. The eutectic point in these alloys is approximately 45.0 a/o Nb, as opposed to the 42.5 a/o Nb value of the binary.

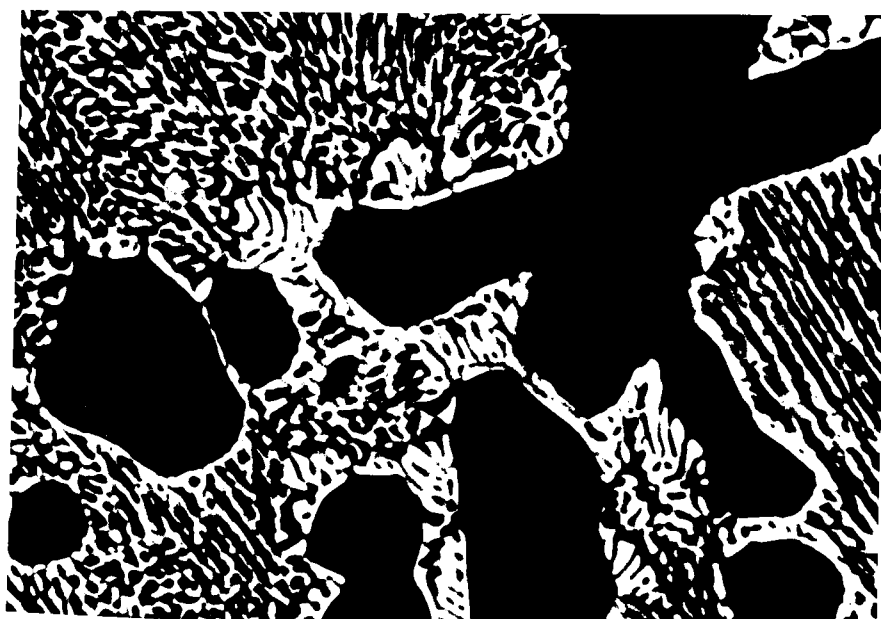
Although no solubility for Ni in the DO_{22} NbAl_3 structure is predicted by the phase diagram, the EDS analysis indicates the presence of 0.5 a/o Ni in the dendritic regions. In addition, the aluminum content of 71.6 a/o is much less than would be predicted. These analytical results relate to the nature of the interaction of the electron beam with the specimen during spectroscopic analysis (72,73). As shown in figure 61-a, a volume of primary excitation is created when the scanning electron beam is applied to the surface of the sample. Within this region, elastically scattered electrons can be emitted back from the specimen surface. It is these backscattered electrons, along with secondary electrons created only by interactions near the surface of (figure 61-b), that are collected to form the EDS spectrum. Therefore, the structure below the surface of an alloy greatly influences the resulting elemental analysis. The region of the ternary eutectic from which the elemental analysis was taken is shown in figures 59 and 60. The spectra obtained in the dendritic regions were undoubtedly influenced to some degree by the surrounding eutectic material due to the size of the primary excitation volume. It follows that a small amount of the Nb_2Al was



10 μ m
—

FIGURE 59

Region of ternary Ni-niobium aluminide (41.2 a/o Nb, 56.8 a/o Al,, 1.8 a/o Ni) from which elemental analysis was extracted, illustrating dendritic and eutectic areas (500 x)



10μm

FIGURE 60

High magnification view of near-dendritic region in figure 59
(2000 x)

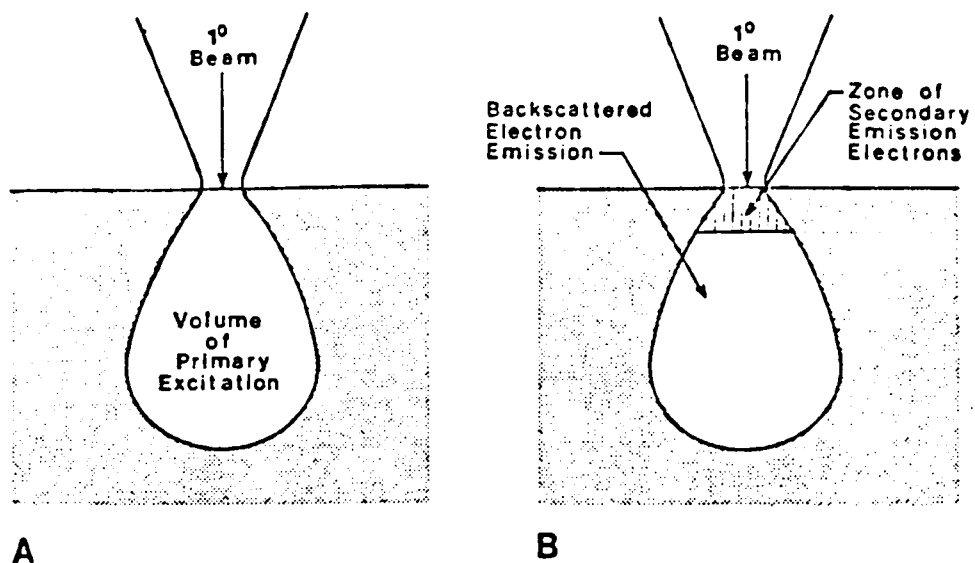
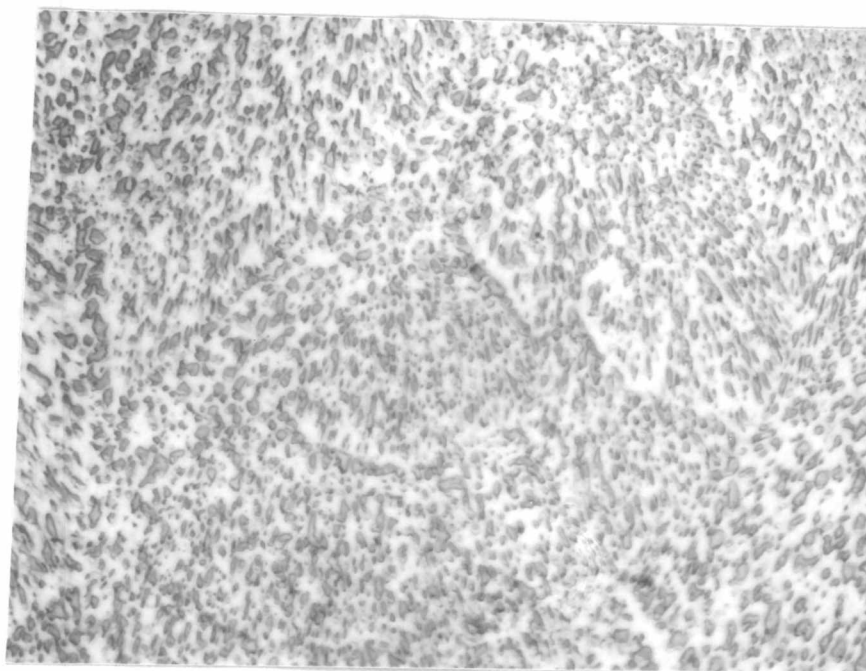


FIGURE 61
Interaction of the electron beam with the sample during scanning electron microscopy (ref 72)

sampled, thereby creating measured niobium and nickel contents in excess of those expected. This is substantiated by the experimental results, and provides evidence that the primary phase contains only negligible traces of the Ni addition.

Annealing Studies

The Ni-modified $\text{NbAl}_3\text{-Nb}_2\text{Al}$ eutectic was furnace annealed at 1200 C for 32 hours to determine the thermal stability of the rod structure. The resulting microstructure is shown in figure 62. After 32 hours at temperature, the microstructure has coarsened greatly, resulting in a uniform distribution of only slightly elongated secondary particles. This result indicates that the "globular" morphology present in the directionally solidified ternary nickel eutectic can possibly be associated with the thermal instability of the rod structure. Coarsening of the rod eutectic occurs behind the solidifying interface during levitation zone refining due to the high thermal conductivity of this alloy and the slow rate of growth of the specimen. The toughness of the annealed ternary alloy is approximately equivalent to the toughnesses of the rod and original binary structures (see table 6). This again emphasizes that the shape of the secondary NbAl_3 phase does not affect the toughness of the material.



10μm

FIGURE 62

Niobium aluminide eutectic (39.7 a/o Nb, 57.5 a/o Al, 2.7 a/o Ni) annealed at 1200 C for 32 hours.

CHAPTER V

CONCLUSIONS

1. The eutectic at 71.5 a/o aluminum, 1550 C in the niobium aluminide system consists of an degenerate, irregular structure of NbAl_3 in an Nb_2Al matrix. The morphology of the secondary phase consists of a coarse network of slightly elongated NbAl_3 particles, which appears globular in cross-section.
2. A control procedure for the directional solidification of this eutectic and for stoichiometric NbAl_3 has been developed. A large grained, extremely pure NbAl_3 structure has been processed by containerless directional solidification.
3. Containerless directional solidification of this eutectic structure coarsens the morphology of the secondary phase, and elongates the NbAl_3 in the direction of growth. However, an aligned "in-situ" composite structure is not formed.

4. A ternary addition of 2 wt. % Ti to the eutectic alters the morphology to a semi-lamellar structure stable under arc-melting conditions. This is termed a complex-regular microstructure. The semi-lamellar structure surrounds the dendritic region in this alloy. The titanium addition alters the growth morphology of the dendrites but not of the eutectic regions of the structure.
5. A ternary addition of 2 wt. % Ni to the binary eutectic alters the morphology under arc-melting conditions to a fine rod-type structure. This microstructure alteration is not dependent upon the presence or volume fraction of the primary dendrites.
6. Microalloying additions of less than 0.2 wt. % Ni to the eutectic produces a microstructure of reduced secondary particle widths and spacings compared to the binary. In addition, the NbAl_3 phase is elongated and shows a tendency towards colony formation, similar to the rod-type ternary morphology. This structure lends support to the idea that the nickel alters some mechanism of growth during moderately rapid solidification.

7. Unidirectional solidification of the ternary eutectic containing nickel shows a regression in structure to the coarse degenerate structure present in the binary. However, the structure has been refined by a reduction of secondary phase particle size. This result is an indication of the relative thermal instability of the rod-type microstructure.
8. The addition of nickel to the eutectic structure does not alter the hardness of the material in the arc-melted condition.
9. The fracture toughness of the ternary eutectic, as measured by a microhardness indentation cracking technique, is equivalent to that of the binary, despite the dramatic change in morphology. Since both phases are extremely brittle intermetallics, load transfer is of little importance; and the effect of the shape of the secondary phase on the toughness is minimized.
10. Elemental analysis, along with the current tentative ternary Nb-Al-Ni phase diagram, indicate that the nickel addition is accommodated almost entirely into the

Nb₂Al sigma phase. The resulting morphological modification is likely due to an alteration of a growth mechanism of Nb₂Al during the liquid-solid transition. A possible mode is an alteration of the interfacial energy balance during solidification.

11. The Nb-Al eutectic point is shifted towards a higher concentration of niobium in the ternary alloys containing nickel. The eutectic point is near 45.0 a/o Nb for Nb-Al - 2 a/o Ni alloys.
12. The regression in structure of the ternary eutectic alloy containing Ni to the "globular" morphology during directional solidification is possibly associated with coarsening of the rod eutectic. Coarsening of the structure during annealing illustrates its thermal instability. The fracture toughness of the coarsened ternary eutectic is equivalent to that of the rod and original binary structures.

LIST OF REFERENCES

LIST OF REFERENCES

1. Stoloff, N. S., International Metals Reviews, Vol. 29, 3 (1984) 123-135.
2. National Materials Advisory Board, Structural Uses for Ductile Ordered Alloys; (1984, Washington, D.C., National Academy Press).
3. Stoloff, N. S., and Davies, R. G., Progress in Materials Science, Vol.13 (1966) 1-84.
4. Haasen, P. in Physical Metallurgy, 3rd ed., Cahn, R. W. and Haasen, P. eds.; (1983, New York, North Holland Physics Publishing).
5. Kad, B., Doctoral Dissertation, University of Tennessee, 1990.
6. 1981 Bulletin of Alloy Phase Diagrams.ASM, Metals Park,1981.
7. Brown, P. W., and Worzala, F. J., Resistivity and Lattice Parameter Variations in Nb₂Al Type Sigma Phases, Journal of Materials Science. 11, p. 760,1976.
8. Schectman, D., and Jacobsen, L.A., Deformation Modes in NbAl₃, Metallurgical Transactions A. 6A, p. 1325, 1975.
9. Elliot, R.P. Constitution of Binary Alloys, First Supplement. (1965, McGraw-Hill, New York).
10. Mondolfo, L.F., Aluminum Alloys: Structure and Properties. (1976, Butterworths, London).

11. Hansen, M. Constitution of Binary Alloys. (1958, McGraw-Hill, New York).
12. Shunk, Constitution of Binary Alloys: Second Supplement. (McGraw-Hill, New York).
13. Callister, W. D., Materials Science and Engineering. (1985, John Wiley and Sons, New York).
14. Ashbee, K. H. G., Fundamental Principles of Fiber Reinforced Composites. (Technomic, Lancaster, PA., 1989).
15. Frommeyer, G., "Metallic Composite Materials" in Physical Metallurgy, 3rd ed., Cahn, R.W. and Haasen, P. eds.; (1983, New York, North Holland Physics Publishing).
16. Pfann, W., Zone Melting, 2nd ed., (1966, New York, John Wiley & Sons).
17. Smith, V. G. et. al., A Mathematical Analysis of Solute Distribution, Canadian Journal of Physics, 33, p.723, 1955.
18. Rutter, J. W., and Chalmers, B., A Prismatic Substructure Formed During Solidification of Metals, Canadian Journal of Physics, 31, 15, 1953.
19. Tiller, W. A. et. al., Acta Metallurgica, 1, 428, 1953.
20. Burton, J. W., et. al., Journal of Chemical Physics, 21, 1987, 1953.
21. Oliver, B. F., and Haworth, C. W., Solidification Structures in Directionally Frozen Ingots, AIME, 239, 1129, 1967.
22. Mullins, W. W., and Serkaka, R. F., Stability of a Planar Interface During Solidification of a Dilute Binary Alloy, Journal of Applied Physics. 35, p.444, 1964.

23. Jackson, K.A., Mechanisms of Growth, Liquid Metals and Solidification. (1958. ASM) p.174.
24. Tiller, Polyphase Solidification, Liquid Metals and Solidification. (1958. ASM).
25. Sundquist, B.E., and Mondolfo, L.F., Heterogenous Nucleation in the Liquid to Solid Transformation in Alloys, Transactions AIME. 221,p.157,1961.
26. Lemkey, F.D. et. al., Trans. AIME. 233,1965,,334.
27. Bolini, H., "Solidification," in Physical Metallurgy, Cahn, R.W. and Haasen, P. eds. (1983, North Holland Publishing, Amsterdam).
28. Flemings, Merton C., Solidification Processing. (McGraw Hill, New York, 1974).
29. Reviere, R.D., Master's Dissertation, University of Tennessee, 1988.
30. Reviere, R.D., Oliver, B.F., and Bruns, D.D., "Computer Controlled Containerless Processing of High Temperature Intermetallic Compounds," Materials and Manufacturing Processes. (4, 1989,103.
31. Jackson, K.A. and Hunt,J.D., Lamellar and Rod Eutectic Growth, Transactions AIME.236,p.1129, 1966.
32. Chadwick, G.A., Interlamellar Spacing Measurements in Certain Binary Eutectic Systems, Journal of the Institute of Metals. 92, p. 18, 1963.
33. Hunt, J. P. and Chilton, J. P., Experimental Undercooling at the Solid-Liquid Interface of the Pb-Sn Eutectic. Z Physik Chem. 47, p. 21,1904.
34. Cahn. J.W. Acta Metallurgica. 8, 1960, 554.

35. Cahn et. al., Molecular Mechanisms of Solidification, Acta Metallurgica. 12, 1421,1964.
36. Jackson, K.A., Journal of Crystal Growth. 24/25,1974,130.
37. Fisher, D.J., and Kurz, W. in Solidification and Casting of Metals (1979,TMS, London) p. 57.
38. Kurz, W., and Fisher, D.J., Inter. Met. Review. 24,1979,177.
39. Mollard, F. and Flemings, M.C., Trans. Met. Soc. AIME. 239,1967,1534.
40. Cline, H.E., Trans. AIME. 1967.
41. Flemings, M.C., "Directional Solidification and Composite Structures." in Surfaces and Interfaces II.
42. Elliot, R., Eutectic Solidification Processing. (1983, Butterworths, London).
43. Chadwick, G. A., Eutectic Alloy Solidification. (Permagon Press, Oxford, 1963).
44. Zener, C., Trans. AIME,167,1946,550.
45. Boettinger, W.J., "The Structure of Directionally Solidified Two-Phase Sn-Cd Peritectic Alloys", Met. Trans. 5, 1974,2023.
46. Trivedi, R., and Kurz, W., "Microstructure Selection in Eutectic Alloy Systems," in Solidification Processing of Eutectic Alloys. (1988, TMS).
47. Proceedings of the Conference on In-Situ Composites I, Vols. 1 & 2. NMAB, 1973.
48. Proceedings of the Conference on In-Situ Composites II. Xerox Publishing, 1976.

49. Proceedings of the Conference on In-Situ Composites III. Ginn Custom Publishing, 1979.
50. Adam, C.M. and Logan, L.M., "Crystallography of the Al-Al₃Fe Eutectic" Acta Metallurgica. 23, 1975, 345.
51. Proceedings of the Conference on In-Situ Composites IV. (North Holland, New York, 1982).
52. Hondros, E. D., and Seah, M.P., "Interfacial and Surface Microscopy" in Physical Metallurgy, Cahn, R.W. and Haasen, P. eds. (1983, North Holland Publishing, Amsterdam).
53. Evans, A.G., "Fracture Toughness: The Role of Indentation Techniques," Fracture Mechanics Applied to Brittle Materials. ASTM STP 678, ASTM, 1979, 112.
54. Lupis, C.H.P., Chemical Thermodynamics of Materials. (1983, North Holland, New York).
55. Verhoeven, J.D., Fundamentals of Physical Metallurgy. (John Wiley and Sons, New York, 1975).
56. Pugachevich in The Role of Surface Phenomenon in Metallurgical Processes.
57. Carlberg, T. and Fredricksson, H., "On the Mechanism of Lamellar Spacing Adjustment in Eutectic Alloys," Journal of Crystal Growth. 42, 1977, 526.
58. Rutter, J.W., "Modification of Eutectic Morphology:", in Journal of Crystal Growth. 42, 1977, 515.
59. Nash, G.E., and Glicksman, M.E., in Proceedings of the Conference on In-Situ Composites II. (1976, Xerox Publishing) p.341.

60. Baragar, D.L. et. al., "The Structural Modification of the Complex Regular Eutectics of Bismuth-Lead, Bismuth-Tin and Bismuth-Thallium." in Journal of Crystal Growth. 41,1977,278.
61. Sahoo, M., and Smith, R.W. "Structure and Mechanical Properties of Modified Eutectics." Can. Met. Quarterly. 15,1976,1.
62. Adam, C., et. al., "Structural Modification of Al-Al₃Fe Alloys." Journal of Crystal Growth. 51, 1981, 525.
63. Palmquist, S. in Arch. Eisenhutenwes. 33,1962, 629.
64. Antis, G.R. et. al., " A Critical Evaluation of Indentation Techniques for Measuring Fracture Toughness."
65. Ekberg, I., et. al., "Indentation Testing of SiC-Whisker Reinforced Al₂O₃ Composites." 1988.
66. Orange, G., et. al., "Crack Resistance and Fracture Toughness of Alumina and Zirconia Ceramics: Comparison of Notched Beam and Indentation Techniques." Science of Ceramics. 1988, 14, 709.
67. Dorward, R.C., "Indentation Fracture of Titanium Diboride." Journal of Materials Science Letters. 1985, 4, 694.
68. Bibring, H. in Proceedings of the Conference on In-Situ Composites II. Xerox Publishing, 1976, p.1.
69. Kim, C.B., and Heine, R.W., Journal of the Institute of Metals. 92,1963-64,367.
70. Schneibel et. al., "Microstructure and Fracture Toughness of Powder-processed Al₃Nb," Journal of Materials Research. 3, 1988, 1272.

71. Stuart, H., ed., Niobium: Proceedings of the International Symposium. (AIME, New York, 1984).
72. Postek, M.T., et. al., Scanning Electron Microscopy. (Ladd Research Industries, 1980).
73. Goldstein, J.I., and Yakowitz, H., eds., Practical Scanning Electron Microscopy. (Plenum Press, New York, 1975).
74. Marion, R.H., "Use of Indentation Fracture to Determine Fracture Toughness," Fracture Mechanics Applied to Brittle Materials. ASTM STP 678, ASTM, 1979, 103.
75. Lawn, B.R., and Fuller, E.R., "Equilibrium Penny-like Cracks in Indentation Fracture," Journal of Materials Science. 10, 2016, 1975.
76. Lawn, B.R., and Wilshaw, R., "Indentation Fracture: Principles and Applications," Journal of Materials Science. 10, 1049, 1975.
77. Lawn, B.R., and Evans, A.G., "A Model for Crack Initiation in Elastic / Plastic Indentation Fields," Journal of Materials Science. 12, 2195, 1977.
78. Marshall, D.B., and Lawn, B.R., "Residual Stress Effects in Sharp Contact Cracking," Journal of Materials Science. 14, 2001, 1979.

APPENDICES

APPENDIX 1

The following summary of the fracture mechanics approach to the derivation of a brittle material indentation microcracking - fracture toughness correlation is taken from the references by Antis, Chantikul, Lawn, and Marshall; Marshall and Lawn; Lawn and Fuller; Evans; and Orange, Liang, and Fantozzi.

A microhardness indentation on an extremely brittle material which causes median microcracking takes the form shown in figure 19. Dimensional analysis demonstrates that the material hardness is directly related to the load and indentation impression dimensions by:

$$H = P / \alpha_0 a^2$$

where,

H = material hardness

P = indentation load

α_0 = numerical constant

a = one-half the diagonal length of a Vicker's
hardness indentation

A similar relationship can be derived for the fracture toughness of a brittle material in terms of microcrack lengths and the applied load. From the following relationships, a surface energy

balance shows that the fracture surface energy is proportional to P^2 / c^3 , where c is the crack length measured from the center of the indentation:

- i. The intensity of the indentation stress field will be determined by the point load divided by a characteristic area (proportional to P / c^2)
- ii. The strain energy density is given by the square of the stress divided by the elastic modulus (proportional to $P^2 / c^4 E$).
- iii. The volume of the stressed material associated with the field of the crack will scale with the cube of the crack dimension (proportional to c^3).

From the fact that the fracture toughness is proportional to the square root of the fracture surface energy, it can be seen that

$$K = XP / c^{3/2}$$

X in this equation corresponds to a complex geometrical factor for median crack systems, incorporating interaction effects due to the specimen free surface and the multiple plane crack configuration. It is normally determined by experimental calibration. This factor must also take into account interactions of the lateral cracks

(which, if large enough, result in chipping around the circumference of the indent) with the median crack system.

X can be determined from the manner in which the volume of the plastic impression is accommodated by the surrounding elastic matrix. From the mathematical theory of plasticity:

$$H / E = (2/9) [1 + \ln (b/a)^3] / [(1-\nu)(b-a)^3 - 2(1-2\nu) / 3]$$

where,

b = radius of the plastic zone surrounding the
indentation

ν = Poisson's ratio

E = elastic modulus

This function is nearly linear in logarithmic coordinates over a wide range of b/a, so that a power law relation applies:

$$b/a = (E/H)^{1/2}$$

Therefore,

$$X = \beta_0 (E/H)^{1/2}$$

where,

β_0 = a material-independent constant for
Vicker's-produced radial cracks

If the crack system is subject to conditions of mechanical equilibrium both during and after the contact event, the radial cracks remain stable, and $K = K_C$. We then obtain:

$$K_C = \beta_0 (E/H)^{1/2} (P/c^{3/2})$$

An experimental calibration for β_0 has been obtained by averaging data for well-behaved brittle materials:

$$\beta_0 = 0.016 \pm 0.004$$

This formulation was derived under the assumption of median microcrack formation during indentation. The derivation is not valid for materials which experience Palmquist cracking as is shown in figure 19. A modified analysis based simply on curve fitting has been proposed that takes into account the two modes of microcrack formation; and can therefore be utilized with a wide range of indentation loads.

An alternative version of the median-type cracking equation indicates that c / a is proportional to:

$$(K_C \phi / H a^{1/2}) (H / E \phi)^{0.4}$$

A plot of c / a versus this value for many different brittle materials indicates that a slope can be fit to the relationship as a function of the crack length and impression dimensions. This slope is estimated to be:

$$(c / 18a) - 1.51$$

Orange et. al. showed that this curve can then be fit collinearly for all materials by including a function related to specific properties of the materials studied, such as their yield stress or Poisson's ratio. They found that a best fit is described by an α factor of:

$$\alpha = 14[1 - 8(4\nu - 0.5 / 1 + \nu)^4]$$

Therefore, the resulting best fit relationship, which establishes K_C to within 10% accuracy for both types of microcracking, is:

$$(K_C \phi / H a^{1/2}) (H / E \phi)^{0.4} \alpha = (c / a)^{(c / 18a) - 1.51}$$

APPENDIX 2

EDS data for primary dendrite (PRI) and eutectic (EUT) regions of a 2 a/o Ni alloy of the niobium aluminide eutectic.

EUTECTIC
 ENERGY RES AREA
 2.8 94.21 64015
 TOTAL AREA= 168555

LIVETIME (sec.) = 100

.....

FIT INDEX= 1.58

ELMT	APP.CONC	ERROR(WT%)
NiK : 0	2.716	.176
AlK : 0	12.951	.127
NbL : 0	37.944	.353

....[3 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: EUTECTIC

All elmts analysed, NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NiK : 0	1.004	4.128	4.056
AlK : 0	.820	24.146	51.514
NbL : 0	.809	71.717	44.430
TOTAL		100.000	100.000

EUT2 LIVETIME (spec.) = 100

ENERGY RES AREA
3.2 94.88 64291
TOTAL AREA= 166959

.....

Peak at .48 keV omitted?
FIT INDEX= 1.75

ELMT	APP.CONC	ERROR(WT%)
NiK : 0	1.743	.159
AlK : 0	12.370	.124
NbL : 0	38.831	.356

...[3 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: EUT2

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NiK : 0	1.007	2.705	2.702
AlK : 0	.831	23.270	50.577
NbL : 0	.820	74.025	46.722
TOTAL		100.000	100.000

EUT3 LIVETIME (spec.) = 100

ENERGY RES AREA
3.2 95.25 64394
TOTAL AREA= 169022

.....

Peak at .48 keV omitted?
FIT INDEX= 2.15

ELMT	APP.CONC	ERROR(WT%)
NiK : 0	1.359	.155
AlK : 0	12.506	.125
NbL : 0	38.879	.356

...[3 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: EUT3

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NiK : 0	1.007	2.719	2.717
AlK : 0	.836	23.490	50.580
NbL : 0	.820	74.391	46.697
TOTAL		100.000	100.000

EUT4
 ENERGY RES AREA
 3.0 94.78 64165
 TOTAL AREA= 165149

 Peak at .49 keV omitted?
 FIT INDEX= 2.07

ELMT	APP.CONC	ERROR(WT%)
NiK : 0	1.981	.164
AlK : 0	13.646	.128
NbL : 0	36.505	.343

...[3 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: EUT4

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NiK : 0	1.000	3.103	2.982
AlK : 0	.831	25.724	53.795
NbL : 0	.803	71.175	43.223
TOTAL		100.001	100.000

EUT5
 ENERGY RES AREA
 3.3 94.24 63964
 TOTAL AREA= 165923

 Peak at .46 keV omitted?
 FIT INDEX= 2.33

ELMT	APP.CONC	ERROR(WT%)
NiK : 0	1.423	.151
AlK : 0	13.460	.129
NbL : 0	37.297	.349

...[3 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: EUT5

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NiK : 0	1.000	2.234	2.168
AlK : 0	.833	25.277	53.300
NbL : 0	.867	72.489	44.532
TOTAL		100.000	100.000

FRI1
 ENERGY RES AREA
 3.3 95.43 64151
 TOTAL AREA= 158235

 FIT INDEX= 1.87

ELMT	APP.CONC	ERROR(WT%)
NIK : 0	.397	.126
AIK : 0	24.139	.163
NBL : 0	25.749	.295

...[3 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: FRI1

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NIK : 0	.960	.651	.502
AIK : 0	.886	42.823	71.927
NBL : 0	.716	56.526	27.571
TOTAL		100.000	100.000

FRI2
 ENERGY RES AREA
 3.3 94.39 64090
 TOTAL AREA= 157179

 Peak at .48 keV omitted?
 FIT INDEX= 1.54

ELMT	APP.CONC	ERROR(WT%)
NIK : 0	.386	.124
AIK : 0	23.485	.162
NBL : 0	26.382	.296

...[2 ZAF'S]

20.00 kV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: FRI2

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NIK : 0	.960	.651	.502
AIK : 0	.886	42.823	71.927
NBL : 0	.716	56.526	27.571
TOTAL		100.000	100.000

PRI3 LIVETIME(spec.)= 100

ENERGY RES AREA
3.3 94.59 64193
TOTAL AREA= 158023

.....
FIT INDEX= 2.17

ELMT	APP.CONC	ERROR(WT%)
NIK : 0	.321	.124
AlK : 0	23.858	.163
NbL : 0	26.357	.295
...[2 ZAF'S]		

20.00 KV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: PRI3

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NIK : 0	.962	.522	.406
AlK : 0	.886	42.162	71.408
NbL : 0	.720	57.308	28.185
TOTAL		99.993	100.000

PRI4 LIVETIME(spec.)= 100

ENERGY RES AREA
3.1 95.07 64242
TOTAL AREA= 156883

.....
FIT INDEX= 1.25

ELMT	APP.CONC	ERROR(WT%)
NIK : 0	.402	.125
AlK : 0	23.984	.163
NbL : 0	25.664	.294
...[3 ZAF'S]		

20.00 KV TILT= .00 ELEV=35.00 AZIM= .00 COSINE=1.000

Spectrum: PRI4

All elmts analysed,NORMALISED

ELMT	ZAF	%ELMT	ATOM.%
NIK : 0	.960	.662	.511
AlK : 0	.886	42.759	71.872
NbL : 0	.717	56.579	27.616
TOTAL		100.000	100.000

APPENDIX 3

The following is a hardness data and microcrack length measurement summary for arc-melted binary eutectic and Ni-altered eutectic alloys, along with the directionally solidified NbAl₃ structure.

Sample 41M (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni)

Hardness measurements (DPH)

891	
970	
951	
1001	
980	
951	
965	
980	Load = 200 g
1016	
965	AVG = 967 DPH

Sample 30H (45.0 a/o Nb, 53.0 a/o Al, 2.0 a/o Ni)

Hardness Measurements (DPH)

882	
900	
813	
891	
891	
810	
882	
913	Load = 200 g
904	
895	AVG = 878 DPH

(AVG for 41M and 30H) = 923 DPH

Sample 44-0 (41.1 a/o Nb, 58.9 a/o Al)

Hardness Measurements (DPH)

831

911

883

980

971

974

889

962

Load = 500 g

940

928

AVG = 927 DPH

Sample 35 (27.0 a/o Nb, 73.0 a/o Al)

Hardness Measurements (DPH)

610

605

633

600

600

649

641

646

Load = 200 g

636

598

AVG = 622 DPH

Sample C7 (39.7 a/o Nb, 57.5 a/o Al, 2.7 a/o Ni)

Hardness Measurements (DPH)

974

977

965

1000

990

1010

1016

955

Load = 200 g

962

1033

AVG = 988 DPH

Sample 25L (41.2 a/o Nb, 58.8 a/o Al)

Indentation Crack Lengths (microns)

125.6

95.1

84.1

87.5

116.4

119.1

112.7

112.3

91.1

114.9

188.8

Load = 3 Kg

78.9

110.8

AVG = 110.6 μm

Sample 25T (41.2 a/o Nb, 58.8 a/o Al)

Indentation Crack Lengths (microns)

100.3

90.3

85.5

181.5

106.2

101.1

128.8

107.1

124.8

106.6

168.1

118.3

Load = 3 Kg

114.0

134.3

AVG = 118.9 μm

Sample 41M (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni)

Indentation Crack Lengths (microns)

144.8

100.6

121.3

113.4

88.3

84.7

Load = 3 Kg

93.5

114.4

AVG = 107.6 μm

Sample 30H (45.0 Nb, 53.0 Al, 2.0 Ni)

Indentation Crack Lengths (microns)

94.0

152.0

103.4

100.2

117.3

119.8

Load = 3 Kg

114.5

168.3

AVG = 117.5 μm

Sample 38 (41.2 a/o Nb, 56.8 a/o Al, 1.8 a/o Ni)

Indentation Crack Lengths (microns)

100.1
110.0
130.1
83.2
94.3
126.2
108.3
101.2
116.6
118.1
125.4
107.8
109.8
90.5
92.5
107.2

Load = 3 Kg

AVG = 107.6 μm

Sample C7 (39.7 a/o Nb, 57.5 a/o Al, 2.7 a/o Ni)

Indentation Crack Lengths (microns)

89.1
111.9
105.3
141.9
104.1
118.2
94.1
105.3
138.7
116.6
97.4
96.2
113.2
151.1
163.0
112.0
104.2
102.9
112.4
147.1
102.0
122.8

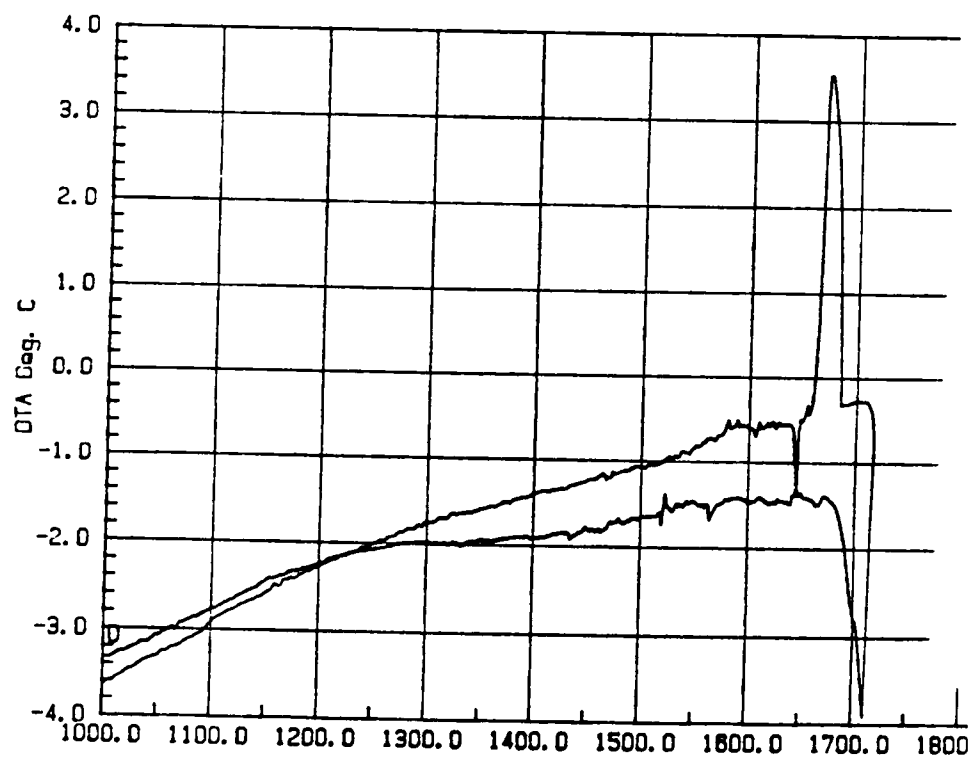
Load = 3 Kg

AVG = 115.9 μm

APPENDIX 4

The following is the result of the differential thermal analysis of NbAl_3 as performed at NASA, the Materials Division of the Lewis Flight Center in Cleveland, Ohio.

OPERATOR: J. WAGNER	NETZSCH STA 429/409	ATM. HELIUM
DATE: 7/28/89	REFERENCE: CRUC.	FLOW = 30 cc/min
RUN No. R. N. NIAL-1	CRUCIBLE: AL2O3	HEAT RATE = 10 C/min
TG Setting: 0mg	FILE NAME: NB NbAl3	SAMPLE WT. = 341.1 mg
DTA Setting: .2mV	MATERIAL: NbAl3	REF WEIGHT = 0 mg

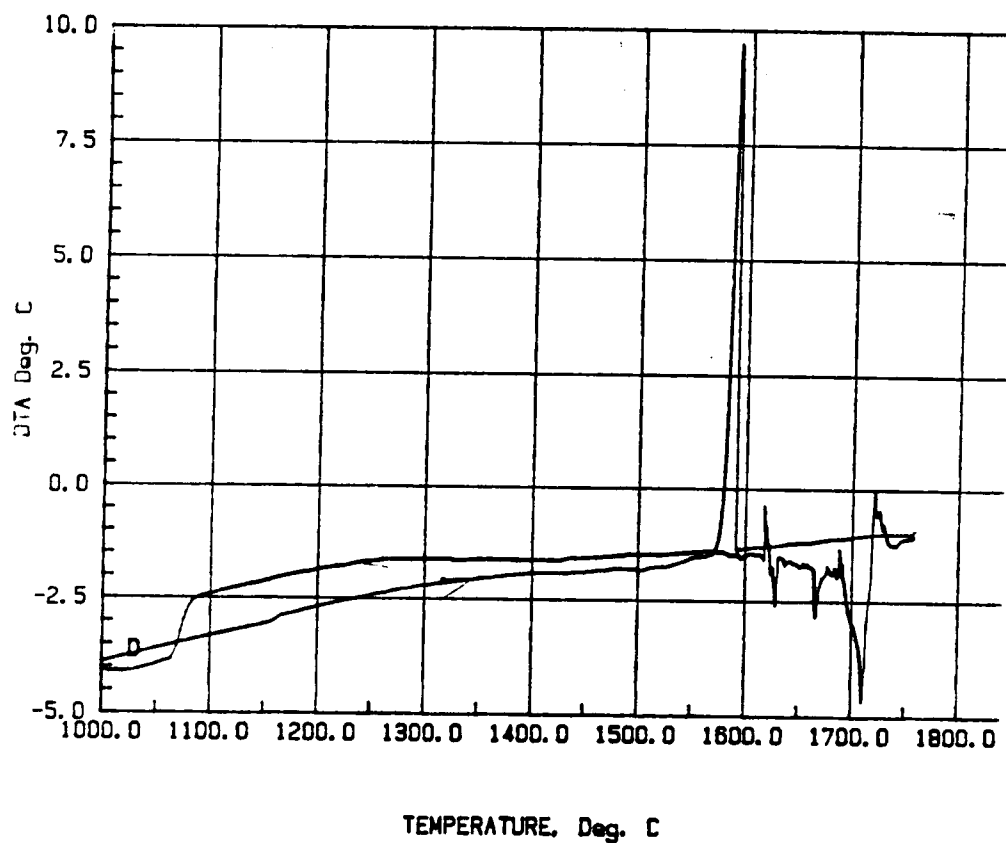


OPERATOR :	J. WAGNER	DATE :	7/28/89
RUN No.	R. N. NIAL-1	TG Setting	0mg
MATERIAL :	NbAL3	DTA Setting	.2mV
REFERENCE :	CRUC.	CRUCIBLE :	AL203
ATMOSPHERE :	HELIUM	GAS FLOW -	30 cc/min
HEAT RATE -	10 C/min	FILE NAME :	NB NbAl3
SAMPLE WGT -	341.1 mg	REF WEIGHT -	0 mg

DTA PEAK RESULT TABLEMP. BASE

PEAK No.	1	2
CURVE	UP	DOWN
BOUNDARY#1	1650	1650
BOUNDARY#2	1717.5	1700
PEAK TEMP.	1712.1	1670.3
ONSET TEMP.	1692.1	1687
OUTSET TEMP.	1717	1661.8
PEAK AREA	55.2	66

OPERATOR: J. WAGNER	NETZSCH STA 429/409	ATM. HELIUM
DATE: 7/31/89	REFERENCE: CRUC.	FLOW = 30 cc/min
RUN No. R. N NBAL-2	CRUCIBLE: AL2O3	HEAT RATE = 10 C/min
TG Setting: 0mg	FILE NAME: NBAL-2	SAMPLE WT. = 387 mg
DTA Setting: .2mV	MATERIAL: NBAL3	REF WEIGHT = 0 mg



NETZSCH THERMAL ANALYSIS

OPERATOR :	J. WAGNER	DATE :	7/31/89
RUN No.	R. N NBAL-2	TC Setting	0mg
MATERIAL :	NbAL3	DTA Setting	.2mV
REFERENCE :	CRUC.	CRUCIBLE :	AL2O3
ATMOSPHERE :	HELIUM	GAS FLOW =	30 cc/min
HEAT RATE =	10 C/min	FILE NAME :	NBAL-2
SAMPLE WGT =	387 mg	REF WEIGHT =	0 mg

DTA PEAK RESULT TABLEMP. BASE

PEAK No.	1	2
CURVE	UP	DOWN
BOUNDARY#1	1675	1550
BOUNDARY#2	1750	1600
PEAK TEMP.	1710.9	1589.7
ONSET TEMP.	1699.9	1591.6
OUTSET TEMP.	1716.4	1579.5
PEAK AREA	28.3	74.6

VITA

Preston P. Smith was born in Memphis, Tennessee on May 19, 1965. He attended Christian Brothers High School in Memphis, graduating in 1983. In September of that year, he was enrolled at the University of Tennessee at Knoxville in the Department of Chemical Engineering. After working at the Memphis plant of Kimberly Clark Inc. as a cooperative Education Intern, he changed his major to Engineering Science and Mechanics. After an internship at Richards Medical Company in Memphis, he graduated with a Bachelor of Science in December of 1987, with a concentration in biomedical engineering. Study towards a Master of Science in Metallurgical Engineering commenced in January of 1988. This degree was awarded in May of 1990. Upon completion of the M. S. degree, the author began work as a consultant for Arthur Anderson Consulting in Nashville, Tennessee in June of that year.

The author is a member of Tau Beta Pi, the American Society for Materials International, The Minerals, Metals and Materials Society, and the Materials Research Society.