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A COMPARATIVE MICROSTRUCTURAL INVESTIGATION OF RAPIDLY
SOLIDIFIED Al-Fe AND Al-Fe-Ce ALLOYS

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

Bimal K. Kad

December 1985

THIS THESIS IS DEDICATED TO MY PARENTS

Mr. and Mrs. M. L. Kad

ACKNOWLEDGMENTS

The author would like to express deep gratitude to his major professor, Dr. B. F. Oliver, for his unceasing guidance and patience through the entire course of this research.

The financial support provided through research grants and teaching assistantships by the Department of Materials Science and Engineering are gratefully acknowledged.

The author would like to thank Dr. J. O. Stiegler, Dr. D. M. Kroeger of the Metals and Ceramics Division for their kind permission to conduct the initial experiments and melt spinning studies at the Oak Ridge National Laboratory. Thanks are extended to Mr. J. O. Scarborough and Ms Claudette Mckamey for their kind help with the initial studies performed at the Metastable Materials Laboratory at Oak Ridge National Laboratory.

Thanks are extended to Dr. James Bentley and Mr. Jerry Lehman of the REMAG group at Oak Ridge National Laboratory for their kind help and assistance in the use of the electron microscopy facilities.

Thanks are extended to Mr. H. B. Thompson, head of the departmental machine shop and his amiable group, Mr. Raymond Bellamy, Mr. Jack French, Mr. Doug Fielden, for their help in design and fabrication of the splat quenching equipment.

Thanks are extended to Mr. Ted A. Long, head of the departmental electronic shop and his efficient group, Mr. Stephen A. Stiner,

Mr. Michael R. Neal, and Mr. Ronald L. Johnson, in maintaining the electronic and furnace equipment during the course of this study.

Special thanks to Mr. Bob L. McGill for his help with the scanning electron microscope and transmission electron microscope and Mr. Albert W. J. Carter and Mrs. Aileen Cagle for supplying the laboratory materials.

The author is grateful to Mrs. Sancy Hail, Mrs. Phyllis Davis, and Mrs. Betty Frazier for their goodwill, countless loans for coffee, and help with official matters.

The author would like to thank Mr. Vijay Vasudevan for his help in data processing and special assistance in the operation of the transmission electron microscope.

Last but not least, the author would like to thank his fellow graduate students for providing a congenial work atmosphere.

ABSTRACT

Rapidly solidified aluminum alloys are of considerable interest for applications in the aircraft industry. In the current study rapidly solidified Al-8 wt% Fe and Al-8 wt% Fe-3.4 wt% Ce alloys were produced by splat quenching. Microhardness measurements are reported for the two alloys for the different time-temperature aging conditions in the intended service temperature range for these alloys. Microstructural investigations were carried out on the as cast alloys, as quenched splats and after aging for different time temperature aging conditions. Microstructural investigations were made using optical microscopy, SEM, TEM, and AEM. Metastable to stable phase transformations were mapped by x-ray diffraction techniques.

Results indicate that the metastable to stable phase transformation occurs much more slowly in the ternary alloy as compared to the binary alloy. The intermediate metastable precipitate, θ' , is shape modified with a different aspect ratio in comparison to the binary alloy. The dispersed phase coarsening was observed to be slower in the ternary alloy, suggesting that presence of cerium in aluminum plays a role in delaying particle coarsening.

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CHAPTER I

INTRODUCTION

Nonequilibrium materials are of growing metallurgical interest. New controlled microstructures have been obtained in many systems using the rapid solidification approach. The development of new alloys, ultrafine microstructures, new metastable phases, and segregation free structures have shown significant property improvements.

Material property goals with potentially high payoffs are currently being defined for applications in the major new aerospace systems being developed. Benefits of improved range, payload and service life accrue from applications of lower density, higher stiffness and higher strength materials.

Studies include advanced aluminum alloys, titanium alloys and composites. Aluminum alloys are of major interest because of their direct suitability for aerospace application plus the economy of lower cost and component weight advantage.

The current trends in aluminum base alloys in the rapid solidification approach are to make ternary additions of low diffusivity in aluminum to obtain more finely dispersed phases in an attempt to improve material property goals. Additions of cerium, molybdenum and vanadium have shown significant improvements towards that goal.

This study was initiated to investigate the microstructural aspects and improvements in the Al-Fe alloys following a ternary

addition of cerium. Attempts were made to explain the effects of such ternary additions in resulting microstructures.

CHAPTER II

LITERATURE REVIEW

Aspects of Rapid Solidification

Rapid solidification processing (RSP) has evolved a variety of techniques involving direct quenching from the liquid state for improved properties of aluminum alloys. These techniques achieve microstructural modifications using high cooling rates so that a substantial increase in undercooling and corresponding higher solidification velocities can be obtained. This usually implies: (a) improved heat-transfer coefficient at the casting-quenchant interface; and (b) an increase in the surface area to the volume ratio of the casting. The overall effect is the achievement of cooling rates estimated at from 10^2 °K/s to better than 10^6 °K/s. A second guideline in RSP is to obtain enough supercooling prior to nucleation so that the liquid will act as a local sink for the heat of fusion and solidification will proceed in an adiabatic manner.

Microstructures of Rapidly Solidified Aluminum Alloys

Rapid solidification of aluminum alloys commonly results in one or more of the following microstructural effects.

1. microstructural refinement manifested as smaller grain size, dendrite arm spacing (DAS) and eutectic spacings;
2. an extension in terminal solid solubility of alloying elements in the primary α -Al phase and a change in the

segregation patterns leading to the reduction or elimination of second phases;

3. morphological changes of the eutectic or the primary phase;
4. formation of metastable phases;
5. coupled eutectic growth at off-eutectic compositions;
6. vacancy supersaturation.

Although all of these effects have been observed in aluminum alloys, only the first four are important in terms of improving the properties of the final product.

Microstructural Refinement

The fineness of microstructure during dendritic solidification of aluminum alloys can be correlated to the average cooling rate during solidification, ϵ_{avg} , or local solidification time (i.e., time available for coarsening), t_f by:

$$DAS = a\epsilon_{avg}^{-m} = bt_f^m$$

and

$$\epsilon_{avg} = (T_L - T_S)/t_f$$

where $(T_L - T_S)$ is the solidification temperature range, DAS is the dendrite arm spacing. a , b and m are constants [Figure 1 (27)]. The constants in the above equation vary with alloy composition. Studies on the effect of alloy composition on structure at a fixed average cooling rate for aluminum binary alloys with copper, magnesium, silicon or zinc show that increasing the solute content refines the DAS, especially at low solute concentrations (1,2).

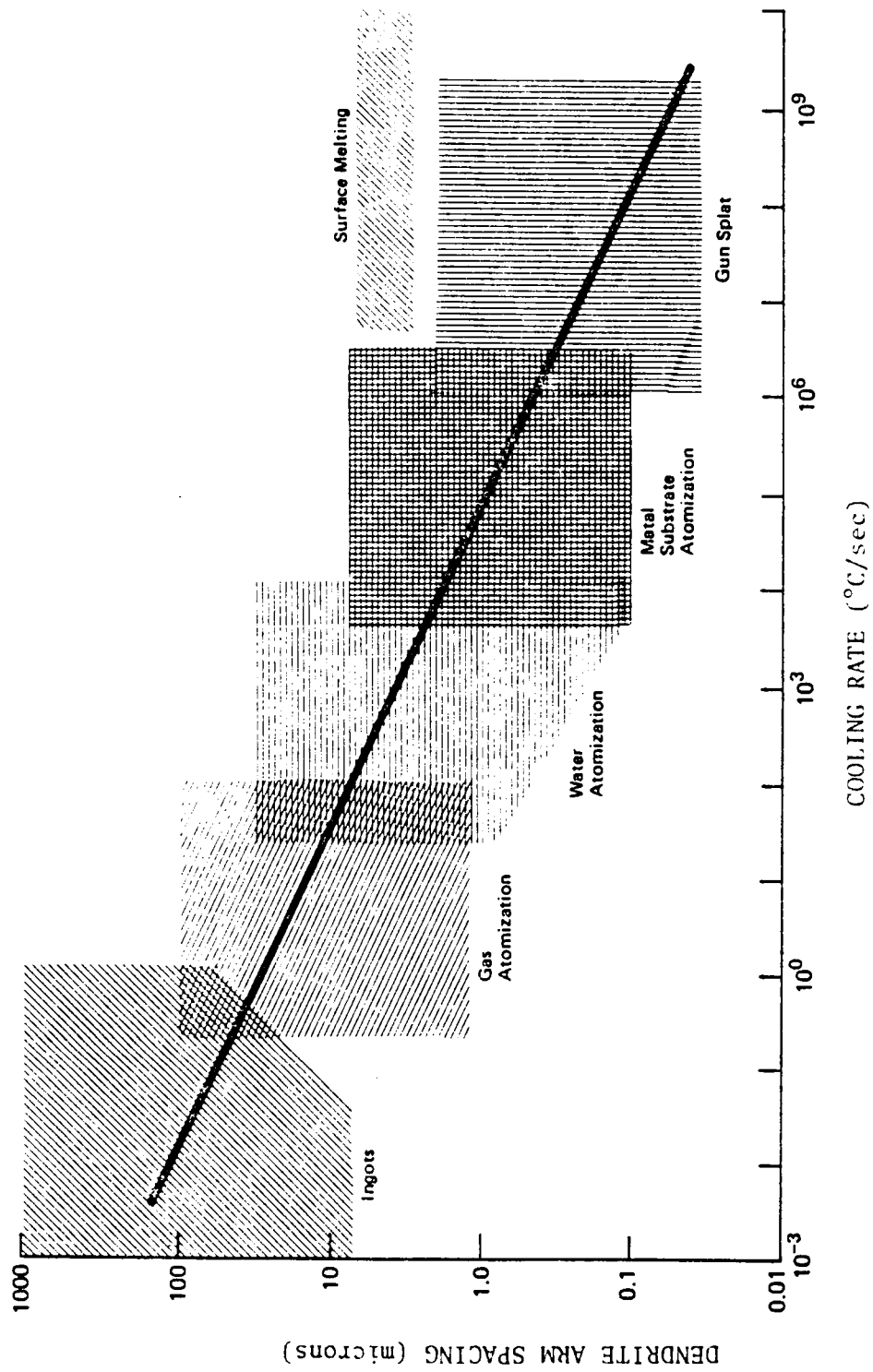


Figure 1. Dendrite arm spacing as a function of cooling rate for aluminum and aluminum alloys.

Refinement of secondary phases including eutectic constituents also occur with increasing cooling rate during solidification. Quantitative analysis of the grain refinement resulting from solidification indicates a good agreement between observed and predicted grain sizes for rapidly quenched aluminum using the above mentioned formulation (3).

Extension in Solid Solubility

With the exception of the aluminum-zinc system (4), terminal solid solubility extension has been obtained at sufficiently high cooling rates in all major aluminum alloys investigated. It is indicated that the range of solid solubility increases with severity of quench (5) and increased initial alloy composition (6) and that they are not necessarily bounded by the eutectic composition. Past work by Jones (5) has shown that additions especially susceptible to solubility extension in binary alloys, e.g., manganese, can be used in ternary alloys to increase the solid solubility limits of less susceptible elements, e.g., iron, cobalt and nickel in aluminum alloys. Table 1 (28) shows the reported maximum solubilities in binary aluminum alloys rapidly quenched from the melt.

Morphological Modifications

Both conventional dendritic (columnar and equiaxed) and modified dendritic morphologies have been reported (7,8). The primary phase in the latter tends to assume a cellular or rod like configuration with progressively faster cooling rates.

Table 1. Extension of Solid Solubility in Binary Aluminum Alloys Quenched from the Melt

Element	Maximum at Equilibrium		Reported Maximum at %
	at %	Temp. (K)	
Cr	0.44	934	5-6
Cu	2.5	821	17-18
Fe	0.025	928	4-6
Mg	18.9	723	36.8-40
Mn	0.7	923	6-9
Ni	0.023	913	1.2-7.7
Si	1.59	850	10-16
Zn	66.5	655	38-?

Source: H. Jones in "Aluminum," Vol. 4, No. 54, 1978, p. 274.

High cooling rates can suppress primary formation of an equilibrium phase from the melt. Jones has reported the formation of α -Al dendrites instead of the equilibrium Al₃Fe phase in hyper-eutectic Al-Fe alloys, both in chill cast (9) and splat cooled specimens (10).

Sufficiently rapid cooling rates can alter the composition range of cooperative eutectic growth, the eutectic constituents and their morphologies. RSP of Al-Fe alloys in the range of 10 °K/s to 10⁴ °K/s has resulted in the eutectic morphology changing from irregular Al-Al₃Fe to regular Al-Al₆Fe as well as coupled eutectic growth at noneutectic compositions (9).

Formation of Metastable Phases

Departure from phase equilibria as indicated by the phase diagrams of aluminum alloys is not as common as the above noted

effects. The few reported cases that have been classified (5) are listed below.

Type 1: phases present at equilibrium but not stable at the temperature and alloy composition at which they were observed.

Type 2: phase not formed from the melt but appearing, normally transiently, or on further heat-treatment or precipitated during quenching through the solid state.

Type 3: phases present in the rapidly quenched sample but not known to exist under equilibrium conditions at any composition within the alloy system.

Table 2 shows a list of nonequilibrium phases as detected in aluminum binary alloys during rapid solidification (29). It has been observed that particular nonequilibrium effects do not happen above a critical thickness in splat cooling (i.e., below a given average cooling rate of the specimen, during solidification).

Problem Statement and Solution Approach

In considering the design of stronger metallic materials, Zackay and Parker (11) concluded that the maximum strength consistent with adequate ductility is given by internal barriers to dislocation movement that are about 50 atomic spacings apart. This barrier spacing and a tensile strength increment of $G/25$ (G - matrix shear modulus) predicted by the Orowan relation, has been established in

ausformed steel ($G/25 = 500,000$ lb/sq.in.) while retaining an elongation to fracture ratio greater than 10%.

Table 2. Nonequilibrium Phases Detected in Aluminum Binary Alloys Under Rapid Solidification

Alloying Element	Concentration Range, at %	Nonequilibrium Phase Detected	Type	Corresponding Eq. Phases	Reference
Cr	1.6 - 3	Al_4Cr	I	$\alpha-Al + Al_7Cr$	Varich and Lyukevich, 1970
Cu	45	Al_3Cu_2 (Trigonal)	III	$O + \eta_2$	Ramachandrarao and Lavidjoni, 1974
Fe	17.3	Noncrystalline	III	$\alpha-Al + O$	Davies and Hull, 1974
	2 - 4	$\gamma, \gamma', \gamma'', O^a$	II	$Al_3Fe + \alpha-Al$	Jacobs et al., 1974
	4	Al_6Fe (Orthorhombic)	II		Jacobs et al., 1974
		Al_6Fe	III		Jones, 1978
Mg	25	$L\delta_2$ superlattice	II	$\alpha-Al + \beta-Al_3Mg_2$	Jones, 1978
	40	($\alpha-Mn$) like structure	III	$\alpha-Al + \beta-Al_3Mg_2$	Jones, 1978
	~10 wt %				
Mn	≤ 6	Al_4Mn	I	$\alpha-Al + Al_6Mn$	Varich and Kolesnichenko, 1961
Ni	7.3 - 10.1	η (Orthorhombic)	III	$\alpha-Al + \beta-Al_3Ni$	Tonejc et al., 1971

^aFormed transiently during aging following a decomposition kinetics similar to the supersaturated Al-Cu solid solutions.

Source: National Materials Advisory Board Report 358 on "Metastable RS Alloys," May 1980.

The highest strength currently obtainable in aluminum alloys is approximately equal to $G/40$ (i.e., 120,000 lb/sq.in.) in atomized powder extrusions. However, the combined levels of precipitation and dispersion hardening seriously impair ductility. Furthermore, the poor strength of aluminum alloys at elevated temperatures limits their application to temperatures below about 300 °C. Reduction in strength near 300 °C and above is caused by the thermal instability of precipitates responsible for the strengthening effect. A microstructure containing a fine dispersion of an insoluble constituent

in the alloy can be the most useful for attaining high strengths and good structural stability at elevated temperatures.

Two general approaches for preparing dispersion hardened alloys with improved elevated temperature stability have been established. The first approach depends on the external introduction of oxide, either by preoxidation of aluminum powder (12), or by blending aluminum and alumina powders (13). The sintered aluminum powder products (SAP) retain strengths up to their melting temperature, but have limited room temperature strength. This arises from an insufficiently small oxide barrier spacing. The reduced ductility at high temperatures is due to the opening of pores at the oxide-aluminum interfaces (14). The second approach involves the internal introduction of hard and stable intermetallic compounds by atomization of liquid aluminum alloys containing transition metal solutes.

Various studies have been conducted with transition metal additives. The most notable elements are iron and chromium. These alloying elements have in common (15):

- (a) a high solubility in molten aluminum;
- (b) a low solid solubility in solid aluminum;
- (c) a low diffusion rate in aluminum; and
- (d) a tendency to form stable precipitates at elevated temperatures.

These solute properties act to retain the microstructural stability at service temperatures due to their fine dispersion of hard and stable intermetallics. The inherent low solid solubility of such

dispersion forming elements prevents their introduction in the desired amounts by traditional metallurgical techniques. Rapid solidification can attain a higher degree of supersaturation, and may offer some solution to the problem. Table 1 shows the solubility extensions obtained by RST for various elemental solutes in aluminum binary alloys. The development of RST is expected to result in the improved performance of aluminum alloys at elevated temperatures.

In addition to iron and chromium, titanium, zirconium, manganese, nickel, vanadium and tellurium meet the requirements listed above. Furthermore, the intermetallic compounds they form are of low density. Thus, appreciable amounts of these alloying elements may be added without a prohibitive increase in the density of the final product (16). Precipitation processes and some of the mechanical properties of aluminum base alloys have been investigated in the past (16-19), the most encouraging results being the high tensile and yield strengths and the retention of strength after exposure to relatively high temperatures. Extrusions of atomized powder of Al-8%Fe alloys show strength characteristics similar to SAP at temperatures up to 670 °C and with an improved ductility at these high temperatures (15). Strength was limited by the intermetallic barrier spacing of about half a micron. That was obtained from DAS measurements within individual atomized droplets. Further strength increase and possibly increased ductility would be expected if the dendrite and dendrite arms spacing can be reduced by obtaining higher freezing rates. The two main techniques employed to this desired end are splat quenching and atomization.

Atomization depends on forced convection to achieve the higher cooling rates. These rates are estimated from DAS measurements to be approximately 10^4 °K/sec for 100 micron droplet sizes. Higher cooling rates can be obtained by splat quenching techniques. Here the molten alloy is spread directly into foil on a cold substrate through which heat is abstracted by conduction. This can yield enhanced solid solubility, new metastable phases and even amorphous structures. Methods which involve spraying molten droplets against a copper substrate seem to offer the most promise for future development.

Current Literature for Al-Fe Alloys

A significant amount of work has been accomplished on the aluminum rich Al-Fe alloys for compositions ranging from Al-0.05 wt% to Al-34 wt% Fe. Several review papers summarize the information available on rapidly solidified Al-Fe alloys (10,31,32). In the region up to 40 wt% Fe, current phase diagrams indicate the presence of two stable phases, namely Al_3Fe and $\alpha\text{-Al}$ with a minute amount of iron (0.5 wt% max.) in solid solution.

Rapid solidification of Al-Fe alloys within the composition range of these two phases yields a number of metastable phases, accompanying the FCC aluminum phase. Different phases, namely Al_6Fe (33,34), Al_9Fe_2 (35), Al_mFe (36) and Al_5Fe (37), have been reported earlier. Shechtman et al. (38) have reported new metastable effects characterized as a "globular 5" phase and a "flower" like phase in melt spun Al-Fe alloys. Recently Skinner et al. (46) have reported a

new metastable phase in the "Zone A" microstructure of melt spun Al-Fe-V, Al-Fe-Zr and Al-Fe-Zr-V alloys. Preliminary electron diffraction on the 50 nm diameter spherical "0" phase shows the crystal structure to be tetragonal with $a = 2.4$ nm and $c = 3.5$ nm. Table 3 lists the reported metastable Al-Fe phases along with the available structural information. The formation of such metastable phases, however, is dependent on the alloy composition and the effective solidification rates achieved. Young and Cline (37) have categorized the various metastable phases occurring in Al-Fe alloys with iron less than 1.5 wt% Fe in the following order of increasing cooling rate: Al_3Fe , Al_5Fe , Al_6Fe , Al_9Fe_2 , Al_mFe .

One of the earliest studies in rapidly solidified alloys was done by Jones (10). Hyper eutectic alloys were rapidly solidified by splat cooling and surface pool freezing. He characterized two zones based on their response to etching. "Zone A," a hardened region with a limited response to etching and "Zone B" soft and dark etching. The microstructure observed by TEM showed Zone A to have a cellular or dendritic like structure with dendrite arm spacing of 30 nm in colonies of one micron diameter. Jacobs et al. (20) extended the study of Jones. Two new metastable phases were observed and their unit cells were reported in their investigation. The Zone A regions contained highly supersaturated cells of α -Al separated by a fine network of a second phase. This was identified as a cubic phase with a lattice parameter of 0.360 nm. A few minutes of annealing at 380 °C led to the decomposition of the supersaturated α -Al. Spheroidal zones, 10 nm

Table 3. Structural Information for Metastable Al-Fe Phases

Phase	Structural Information	Reference
Network Phase of "Zone A"	cubic a = 0.360 nm	20
Spheroidal Zones	diamond cubic a = 0.585 nm	20
Al ₆ Fe	orthorhombic a = 0.6446 nm b = 0.7440 nm c = 0.8779 nm	34
Al ₉ Fe ₂	monoclinic a = 0.869 nm b = 0.635 nm c = 0.632 nm β = 93.4°	35
Al ₅ Fe	monoclinic a = 2.16 nm b = 0.93 nm c = 0.905 nm β = 94°	37
Al _m Fe	not available	36
"S" Phase	not available	68
"O" Phase	tetragonal a = 2.4 nm c = 3.5 nm	46

in diameter, precipitated. Electron diffraction of this precipitate suggested a diamond cubic structure with a lattice parameter of $0.585 \text{ nm} + 0.005 \text{ nm}$. The zones were oriented with respect to the matrix:

(111)precipitate // (001)matrix

[110]precipitate // [010]matrix

After fifteen minutes at 380°C , the zones decomposed to Al_3Fe needles. The fine network structure decomposed to Al_3Fe needles, as well. There are two equivalent orientations with respect to the matrix:

(010)needles // (100)matrix

[100]needles // [010]matrix and

(010)needles // (100 matrix

[100]needles // [001]matrix

Furrer et al. (39), and Blank (40) have also investigated the decomposition behavior of supersaturated Al-Fe alloys in compositions ranging from .032 wt% to 10 wt% iron. Furrer et al. (39) suggest the following precipitation sequence for splat quenched foils:

Supersaturated solid solution GP1 -- θ'' -- θ' -- Al_3Fe

However, no structural information was given for these metastable phases. Blank (40) reports the decomposition process in Al-Fe alloys with iron content ranging from 0.8 wt% to 3.3 wt%, as similar to the

Al-Cu, alloys. Tonjec (42) has reported x-ray studies on the decomposition of metastable Al-rich Al-Fe solid solutions.

Microhardness measurements have been reported for a number of compositions for the binary alloy and with ternary additions. Jones reports increasing hardness values in as splat Al-Fe alloys as a function of increasing iron content for the splat cooling and surface pool freezing processes. He reports a hardness of 25 Kg/sq:mm for Al-11 wt% Fe alloys produced by splat quenching. Blank (40), in contradiction, suggests that microhardness of as quenched splats increases more rapidly with iron concentration than expected from solid solution hardening. He interprets this as an additional superposition of defect hardening leading to a high microhardness. Blank (40) has also reported a small increase in hardness on annealing his Al-Fe splat foils at 350 °C for 10 to 15 hours. Thursfield et al. (18,20) have reported microhardness data on Al-8% Fe alloys with ternary additions of manganese, chromium, zirconium, nickel, etc. Most notable was the Al-8 wt% Fe-3 wt% Mn alloy splat which shows an 80 Kg/sq:mm increase in hardness on annealing at about 225 °C for one hour. All previously reported data indicate a rapid drop in microhardness values on annealing at temperatures beyond 300 °C for times as short as 1 hour.

Low et al. (19) and others have shown that the most significant elements influencing the toughness of aluminum alloys are Fe and Si. Until recently efforts were directed towards improved alloys having the same nominal chemistry, but with Fe and Si contents reduced to minimum levels (.05-.08 wt:%) for improved toughness. RSP of Al-Fe

alloys yielding solubility extensions of iron in aluminum up to 10 wt% has resulted in a very fine dispersion of stable Al_3Fe particles, a favorable condition for high temperature alloys. To further improve the high temperature properties, current efforts are towards ternary additions to the Al-Fe alloys. Sanders (30) reports an extensive study on the mechanical properties data compiled on a series of Al-Fe alloys with transition metal and rare earth additions. Table 4 shows reported mechanical properties for such compositions. Adam et al. (41) have reported similar data for Al-9 wt% Fe-2 wt% Mo. Such data have been obtained on rapidly solidified powders which were compacted and extruded.

Continued efforts to produce suitable high temperature alloys have brought about encouraging work on Al-Fe-Co and Al-Fe-Ce alloys. Previous work (10,18,20) indicates improved strength and other properties at temperatures as high as 340 C. Table 4 (30) shows the reported outstanding mechanical property improvements for two such experimental RS alloys, Al-8 wt% Fe-3.4 wt% Ce and Al-5.7 wt% Fe-6.3 wt% Co. Microstructural investigation of these RS alloys is largely lacking and few published reports of such work are currently available. One such study by Yearim et al. (43) has reported the stability of Al_6Fe by chromium additions to Al-7 wt% Fe alloys. These alloys were prepared by compacting and extruding the rapidly solidified powders, and the reported data were obtained by annealing specimens at 482 C for 100 hours. It is the aim of this study to investigate the microstructural characteristics and their response

Table 4. Room and Elevated-Temperature Properties of Experimental RS Alloys

Alloy ^b	Room Temperature				450 °F ^a				650 °F ^a			
	TS		YS		TS		YS		TS		YS	
	(ksi)	(ksi)	%El	%RA	(ksi)	(ksi)	(ksi)	%RA	(ksi)	(ksi)	(ksi)	%RA
Al-3Mn-6.5Co	67.7	55.0	4	4	44.1	38.3	9	12	24.5	21.2	4	8
-8Mn-1.6Co	60.3	45.9	6	8	35.7	32.2	7	12	22.5	18.0	3	5
-3.8Mn-4Co	58.5	44.9	11	17	35.6	32.1	5	10	20.5	16.2	12	17
-5.6Mn-6.2Co	75.3	59.6	3	2	48.2	43.7	2	2	25.8	19.4	9	7
Al-3.4Fe-7Co	74.3	59.6	5	6	46.2	41.1	5	5	25.2	18.8	7	9
-8.2Fe-1.8Co	72.9	54.4	6	9	49.2	40.2	8	11	26.6	19.6	13	13
-4.2Fe-4.4Co	67.7	53.1	9	20	44.8	41.0	10	12	22.5	15.5	9	12
-5.7Fe-6.3Co	78.5	63.5	5	7	49.5	44.6	5	6	25.2	19.5	8	8
Al-3Mn-6.7Ni	63.7	45.2	7	9	36.2	31.5	19	25	18.0	12.2	10	12
-7.7Mn-1.6Ni	66.8	48.1	8	13	36.2	27.6	11	15	22.3	15.0	8	8
-3.8Mn-4.1Ni	56.2	39.4	13	27	32.5	27.3	19	28	16.8	12.1	14	15
-5.5Mn-6.1Ni	73.8	57.1	2	2	46.0	38.3	10	12	23.6	17.3	10	9
Al-8Fe-3.4Ce	83.5	73.7	6	14	59.3	55.6	6	8	25.5	22.0	7	11
Al-8.5Fe-1.5Cr	72.5	67.1	1	2	47.7	54.3	3	4	26.7	23.6	7	7

^aElevated-temperature tests conducted after 1000 hours exposure at test temperature.

^bSpecimens obtained from upset disk forgings fabricated at 700 °F.

Source: National Materials Advisory Board Report 358 on "Metastable RS Alloys," May 1980.

to annealing treatments for these commercially viable alloy compositions.

The Al-Fe and Al-Ce Systems

Cerium additions to aluminum alloys counter the loss of toughness due to Fe and Si (21), increase strength without loss of electrical conductivity (22,23), refine grain size (24), and improve machinability. Additions of cerium to aluminum alloys with high iron content (>0.7 wt% Fe) reduce the embrittlement due to iron, by transforming the acicular Al_3Fe into a more rounded ternary compound (21, 25). Additions of 3-4 wt% ferrocium 25:75 to 99.5% pure aluminum increases the ultimate tensile strength and elongation by some 10% each (23). Cerium has been added to the Al-Fe binary alloy under the supposition that its low diffusivity in aluminum would limit the coarsening kinetics of the dispersed phases. Table 5 lists the solid state diffusivity for selected elements in aluminum. Cerium shows the lowest rate of diffusion among the elements listed. Both Fe and Ce are reported to have limited solid solubilities in the binary Al-Fe and Al-Ce systems. Figure 2 shows reported data on solid solubilities of these elements as a function of temperature. Table 6 lists several reported binary phases present in the aluminum rich ends of the Al-Fe and Al-Ce systems along with the structural information. Figures 3 and 4 show the current binary phase diagrams for the Al-Fe and Al-Ce systems, respectively. Al_3Fe and Al_4Ce are the phases in equilibrium with Al in the Al-Fe and Al-Ce binary systems, respectively.

Table 5. Solid State Diffusion Data for Selected Elements in Aluminum

Element	Temperature Range (°C)	D_0 (cm ² /s)	Q (kJ/mole)	D(450°C) (cm ² /s)	Ref.
Fe	20-642	0.12×10^0	134.8	2.2×10^{-11}	47
Ce	450-630	1.9×10^{-6}	111.3	1.7×10^{-14}	48
Mo	400-630	1.04×10^{-9}	54.8	1.0×10^{-13}	49
V	400-630	6.0×10^{-8}	82.0	7.1×10^{-14}	50
Cu	300-500	3.8×10^0	146.5	1.0×10^{-10}	51
Zn	300-500	4.6×10^{-3}	100.5	2.5×10^{-10}	51
Mg	300-500	3.5×10^{-2}	113.0	4.9×10^{-10}	51

Note: D(450 C) was calculated using the expression $D = D_0 \exp(-Q/RT)$ where R is the gas constant and R is the absolute temperature.

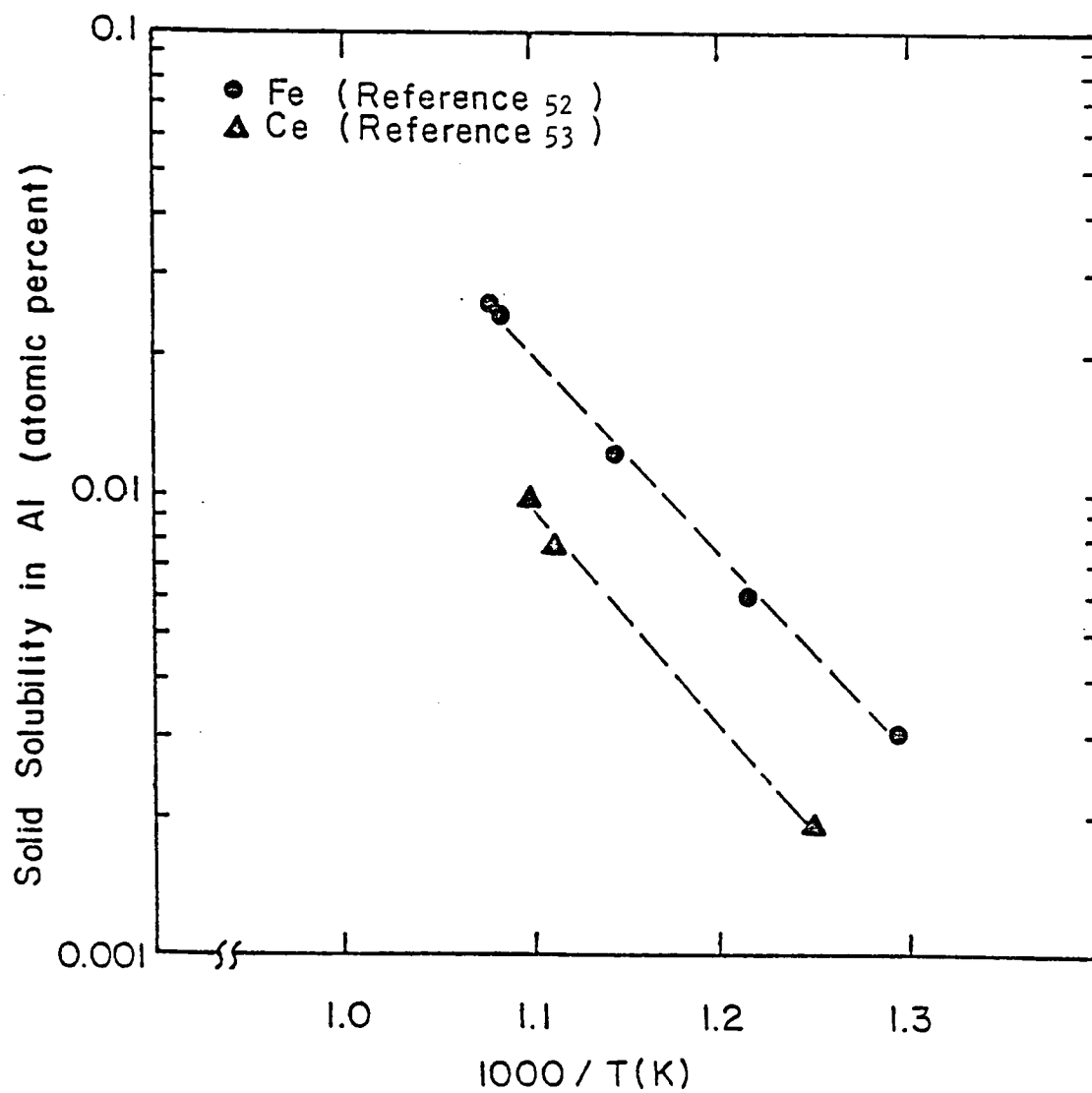


Figure 2. Plot of equilibrium solid solubility limits of Fe and Ce in Al versus $1/T$ in the binary alloys.

Table 6. Structural Information for Stable Binary Phases Present at the Aluminum Rich End of the Al-Fe and Al-Ce Systems

Phase	Structural Information	Reference
Al_3Fe ($\text{Al}_{13}\text{Fe}_4$)	monoclinic $\text{Al}_{13}\text{Fe}_4$ -type $a = 1.5489 \text{ nm}$ $b = 0.8083 \text{ nm}$ $c = 1.2476 \text{ nm}$ $\beta = 107^\circ 43' \pm 1^\circ$	54
Al_5Fe_2	orthorhombic Al_5Co_2 -type $a = 0.767 \text{ nm}$ $b = 0.640 \text{ nm}$ $c = 0.420 \text{ nm}$	55
Al_4Ce	body centered tetragonal Al_4Ba -type (D_{13}) $a = 0.4374 \text{ nm}$ $c = 1.012 \text{ nm}$ $c/a = 2.314$	56
Al_3Ce	hexagonal Ni_3Sn -type (D_{019}) $a = 0.7043 \text{ nm}$ $c = 0.5451 \text{ nm}$ $c/a = 0.774$	57
Al_2Ce	face centered cubic Cu_2Mg -type (C_{15}) $a = 0.811 \text{ nm}$	56

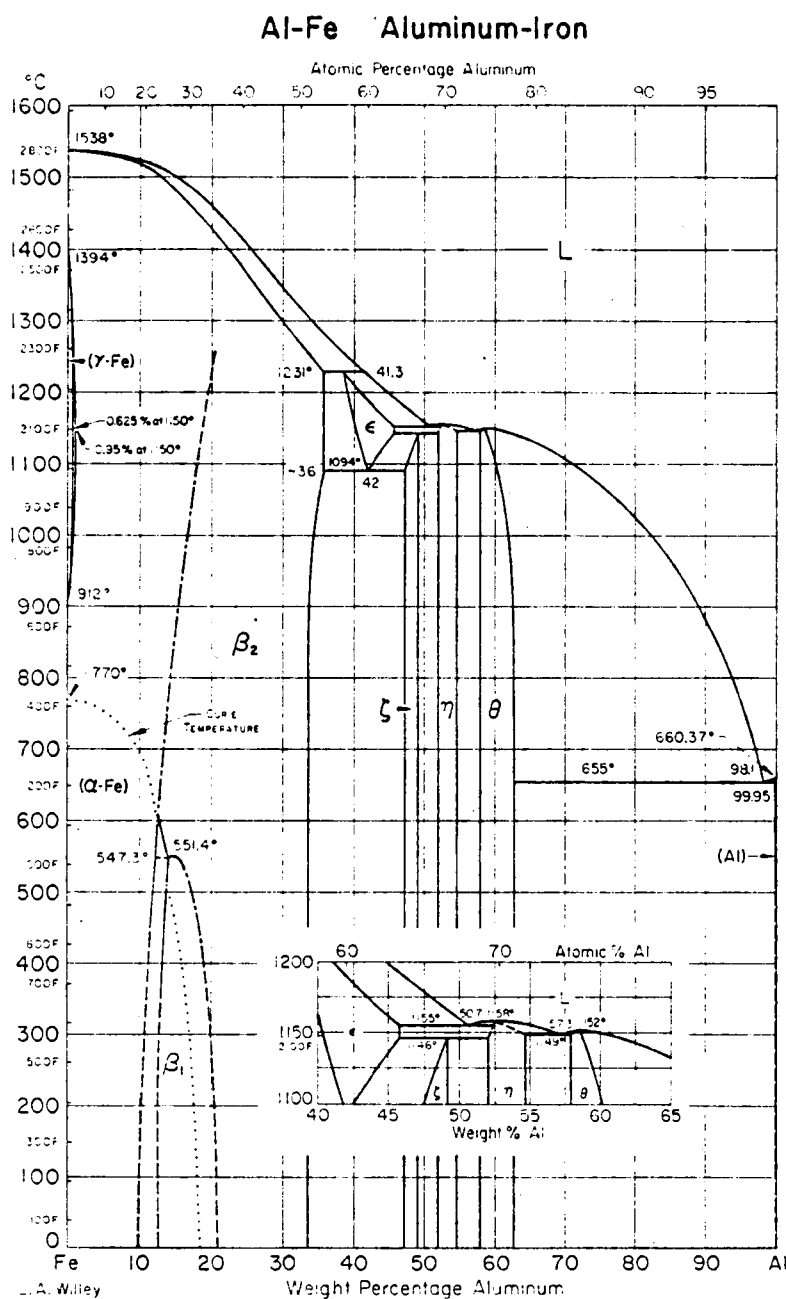


Figure 3. Equilibrium phase diagram for Al-Fe alloy.

Source: Metals Handbook, Vol. 8. ASM, September 1973, p. 260.

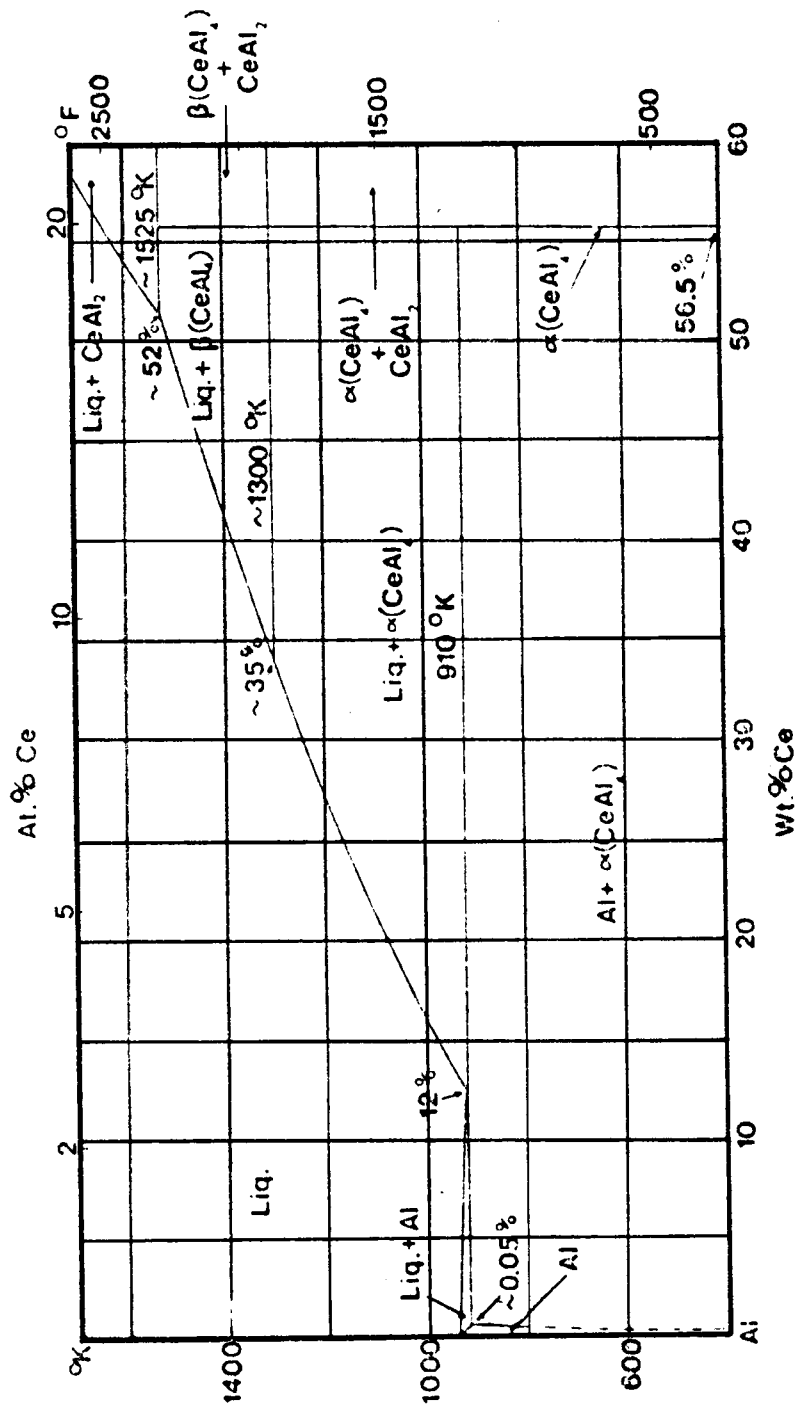


Figure 4. Equilibrium phase diagram for Al-Ce alloy.

Source: L. F. Mondolfo, Aluminum Alloys: Structure and Properties. Butterworth Publishers, Boston, 1976, p. 243.

The Al-Fe-Ce System

Zarechnyuk et al. (58) have reported a 500 °C isotherm of the Al-Fe-Ce equilibrium diagram as shown in Figure 5. The only ternary phase in equilibrium with aluminum is $\text{Al}_{10}\text{Fe}_2\text{Ce}$. Table 7 lists all reported ternary phases along with the available structural information.

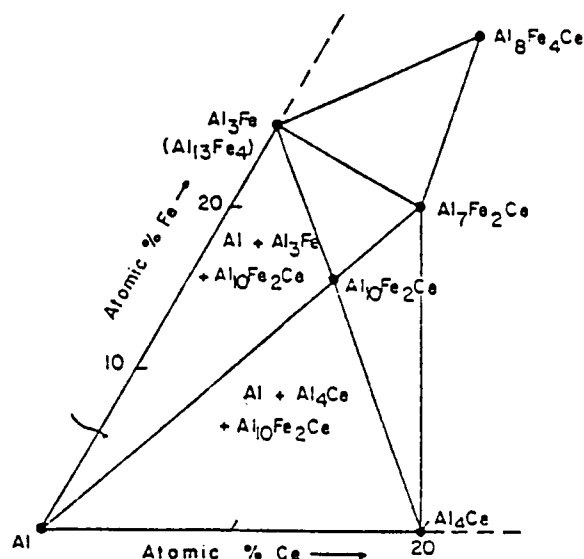


Figure 5. A reproduction of the 500 °C isotherm of the Al rich end of the Al-Fe-Ce phase diagram reported by Zarechnyuk et al. (58).

Table 7. Structural Information for Ternary Phases Reported in the Al-Fe-Ce System

Phase	Structural Information	Reference
ϕ : Al Fe ₄ Ce	body centered tetragonal ThMn ₁₂ -type (D2b) a = 0.886 nm c = 0.508 nm c/a = 0.573	58
ϕ : Al ₁ Fe ₂ Ce	orthorhombic a = 0.894 nm b = 1.022 nm c = 0.906 nm	65
ζ_2 : (Fe,Al) ₁₇ Ce ₂ (Solid solution up to 60 at.% Al)	body centered tetragonal Th ₂ Zn ₁₇ -type a = 0.8512-0.8998 nm c = 1.245-1.297 nm c/a = 1.463-1.442 nm	58
N ₁ : Al ₇ Fe ₂ Ce	not available	58
N ₂ : Al _{1-0.0} Fe _{1-1.4} Ce	not available	58

CHAPTER III

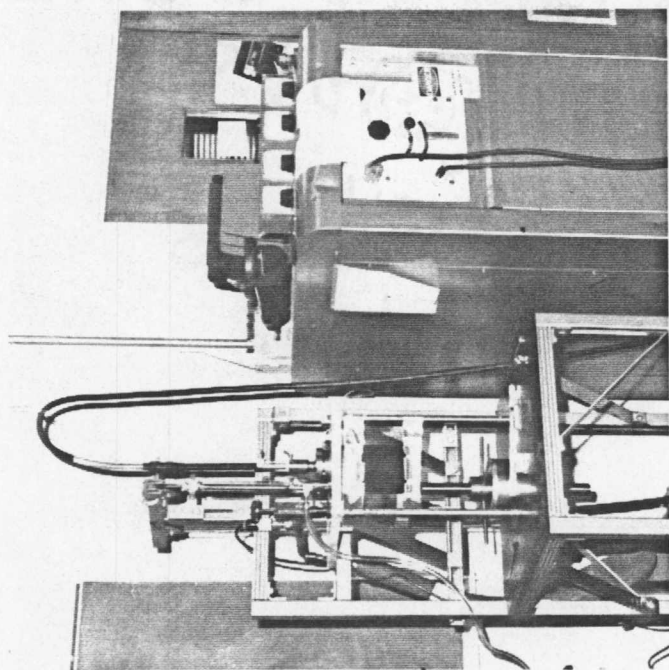
EXPERIMENTAL PROCEDURE

Alloy Preparation

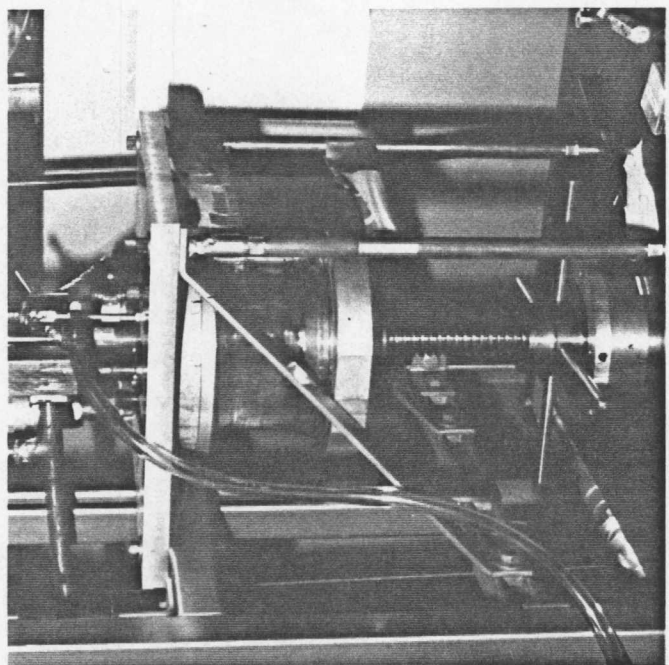
The alloys for this study were prepared in a Balzer's vacuum induction melting and casting unit. High purity metals were weighed on a Philips electronic balance to arrive at the nominal compositions of Al-16% Fe and Al-6.8% Ce. Equal weights of these alloys were used to arrive at the final composition of Al-8% Fe-3.4% Ce. Equal weights of aluminum and Al-16% Fe were used to arrive at the final composition of Al-8% Fe. In addition a third alloy was prepared by directly adding the individual constituents to arrive at a nominal composition of Al-8% Fe-6.2% Co. The alloy batches were melted in a graphite crucible and cast in a carbon coated copper mold, water cooled from the base. Prior to melting, the furnace was evacuated and backfilled with argon to a vacuum of 40 mm mercury. The actual composition obtained, and the impurity analyses, are given in Appendix A.

Splat Quenching

The cast alloys were cold rolled to fragment them into small pieces. These pieces were thoroughly cleaned in an acid solution of phosphoric and nitric acids mixed in the ratio of 94:6 by volume. Sample weights less than 100 milligrams were melted in an arc melting unit similar to one described by Pietrokowsky (44). Figure 6a,b shows



A



B

Figure 6. View of experimental sputat quenching equipment used in this study (A) and (B); calibration plot for the microhardness tester (C).

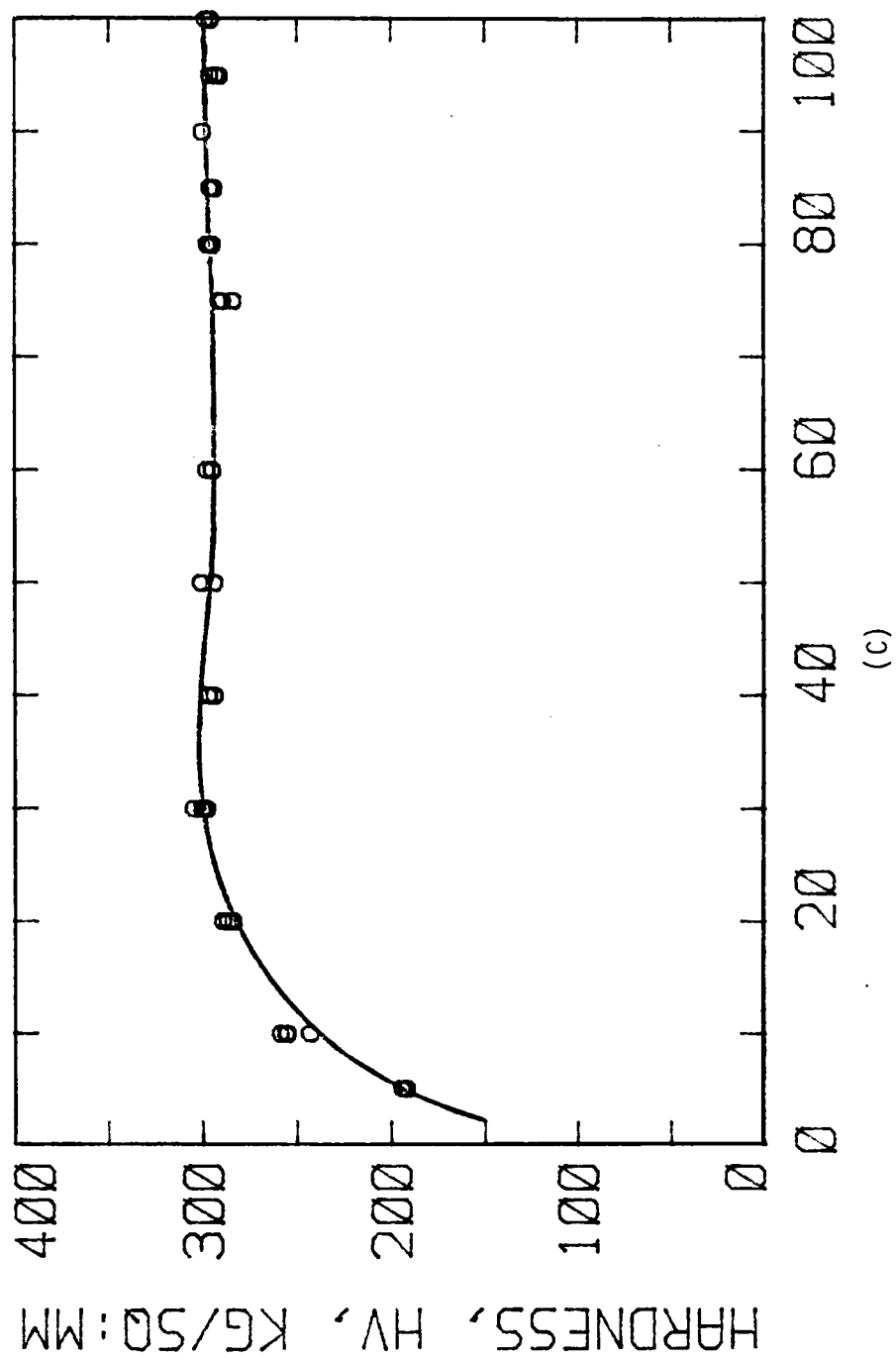


Figure 6 (continued).

the experimental setup in great detail. The process involves melting the sample on a massive copper anvil followed by rapid quenching under impact from a parallel copper hammer, gold coated for increased thermal conduction. The sample is placed on the anvil inside the chamber which is evacuated and back filled with argon. After striking an arc on a tungsten butt, a zirconium button is melted to getter the system of residual oxygen, before melting the sample. A dimple 3 mm in diameter and 4 mils deep was machined in the center of the anvils to prevent the arc pressure from sweeping the molten droplet off the anvil. Despite the superheat of the molten droplet, nucleation invariably begins at the bottom surface in contact with the substrate. Since growth of this region would prevent the splat from attaining finer thicknesses, it was desired to contain this solid skull within the dimple, so that only the remaining molten metal is splatted. The center portion of each splat was then discarded. The average thickness of the peripheral regions of the splats was 30 to 40 microns. In addition, a copper ring was placed concentric around the anvil to collect sprayed molten metal droplets which are propelled radially outwards upon the hammer impact. A detailed calculation of the hammer impact velocity is given in Appendix B. An attempt was made to closely maintain all experimental variables during sample preparation. Approximately the same sample weights were used to obtain splats of similar characteristics.

Annealing Studies

The splat samples were cut into smaller pieces and sealed in pyrex glass tubes under a vacuum of about 10^{-6} torr. The encapsulated samples were annealed in resistance heated air furnaces at temperatures of 300, 325, 350, 400 °C for different lengths of time ranging from 6 minutes to 100 hours. The furnaces were controlled to within 5 °C of the indicated temperature.

Microhardness Measurements

Hardness measurements were made on a Kentron microhardness tester using a 50 gram load. Figure 6c shows a calibration plot for the instrument. Microhardness measurements show a marked load dependency in the lower load ranges (45). Hence the same 50 gm load was used to make all microhardness measurements for annealed as well as quenched specimens. Extremely low hardness values occasionally measured on the splats were attributed to subsurface voids and casting defects. These values were deleted from the calculated mean. On average, 10 readings were taken on any one splat and then averaged. It was noted that the deviation of any one measurement was less than 20 DPH points from the calculated mean. The range of indentation diagonals using the diamond pyramid indenter was 16 to 36 microns for the entire range of aging treatments. From the indenter geometry, included angle = 136 degrees, the depth of the indentation was calculated to be less than 1/5th the average thickness of the splats.

X-Ray Studies

X-ray studies on the splats were performed on a Rigaku diffractometer. The splat powder obtained from the copper ring concentric to the anvil was ground in a mortar under alcohol to reduce oxidation. This powder was used in a Debye-Scherrer camera to obtain x-ray diffraction patterns. The sample needles were prepared by pouring a small quantity of powder in a thin 0.5 mm diameter capillary tube. These needle assemblies were annealed in steps to obtain patterns at different stages. The standard procedure was a one-hour anneal at 300, 350, 400, 475 °C, followed by a final treatment for 100 hours at 475 °C. The operating conditions for the Philip's x-ray unit were 30 Kv, 20 milliamps using CuK radiation. The objective of this experiment was to map any metastable to stable transformations which can be deduced by the appearance of any new lines on the Debye-Scherrer pattern over higher annealing temperatures. In comparing the binary alloy to the ternary one, the binary alloy x-ray pattern was subtracted from the ternary alloy to help identify any new phases forming.

Optical Microscopy

The as cast ingots and a few random splat samples were mounted and polished to 0.6 microns and were etched using HF, Keller's reagent and NaOH etch.

Transmission Microscopy

TEM studies were performed on the Philips EM300 at 100 KV. Some samples were also observed on a Philips EM400T FEG with EDAX 9100 microanalysis system, courtesy of the REMAG group at Oak Ridge National Laboratory. Samples were prepared by electropolishing them using standard solutions of perchloric acid, glycerin and ethyl alcohol mixed in the ratio of 1:2:7. Acetic acid, phosphoric acid, nitric acid and water mixed in the ratio of 4:3:2:1 was also used. The aim of microscopy was to metallographically follow the annealing sequence of samples and map out the precipitation process. It was intended to observe the different precipitation sequences, and to characterize the precipitation events. A few samples were also annealed with a hot stage in-situ in the TEM to obtain an idea of the rate of precipitation and to gain an insight into the nucleation phenomenon. Microanalysis studies using a 1 nm probe were performed on quenched and aged specimens to characterize the different precipitates, courtesy Oak Ridge National Laboratory. This analysis was aimed at determining compositions of precipitates at the grain boundaries as well as mapping the diffusion effects of the alloying elements in specimens aged for long times in the higher temperature ranges.

CHAPTER IV

RESULTS AND DISCUSSION

Detailed results for the microhardness measurements, x-ray and transmission studies are presented in the form of plots, charts and micrographs with selected diffraction patterns. The discussion for these segments involves cross referencing between these sections and is presented with the data.

As Cast Master Alloys

Optical micrographs for Al-8% Fe, Al-8% Fe-3.4% Ce and Al-8% Fe-6% Co are shown in Figures 7-12. The binary alloy consists of massive primary dendrites of Al_3Fe and an alpha Al- Al_3Fe eutectic phase. The solidification sequence was identified as the formation of primary Al_3Fe dendrites from the liquid phase followed by the irregular Al- Al_3Fe eutectic phase. The primary dendrites were flower shaped, and a definite order within a colony of dendrites indicated the sustained formation of secondary dendrite arms. In comparison, the as cast Al-8% Fe-3.4% Ce alloy shows the presence of at least four different microconstituents, as in Figures 13 and 14. These were identified as the primary Al_3Fe dendrites, alpha-Al and two ternary phases. The solidification sequence in this case is identified as the primary formation of Al_3Fe dendrites from the melt followed by dendritic solidification of the alpha-Al phase followed by the interdendritic solidification of the low melting ternary phases. One phase,

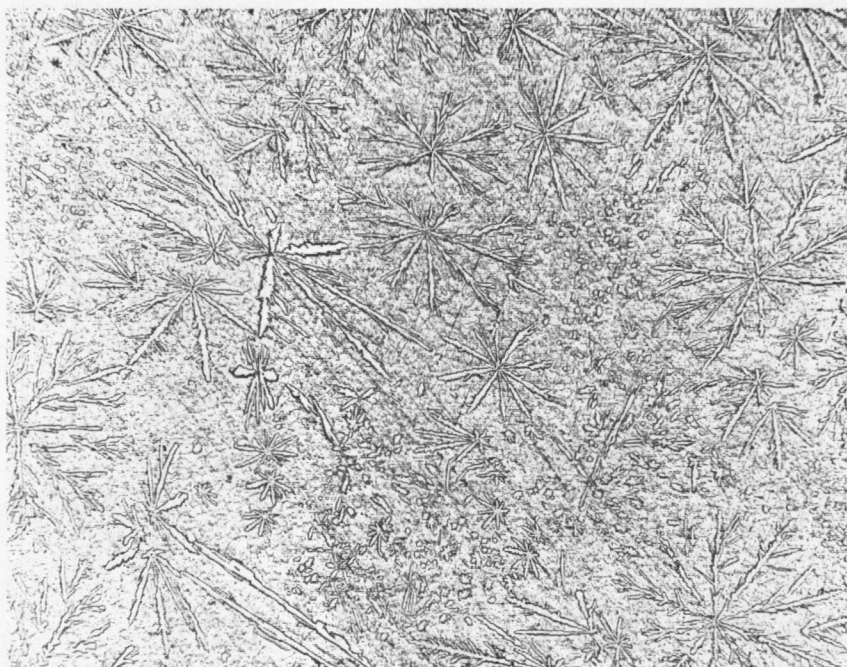


Figure 7. Al-8 wt% Fe, cast master alloy, unetched, 136X.

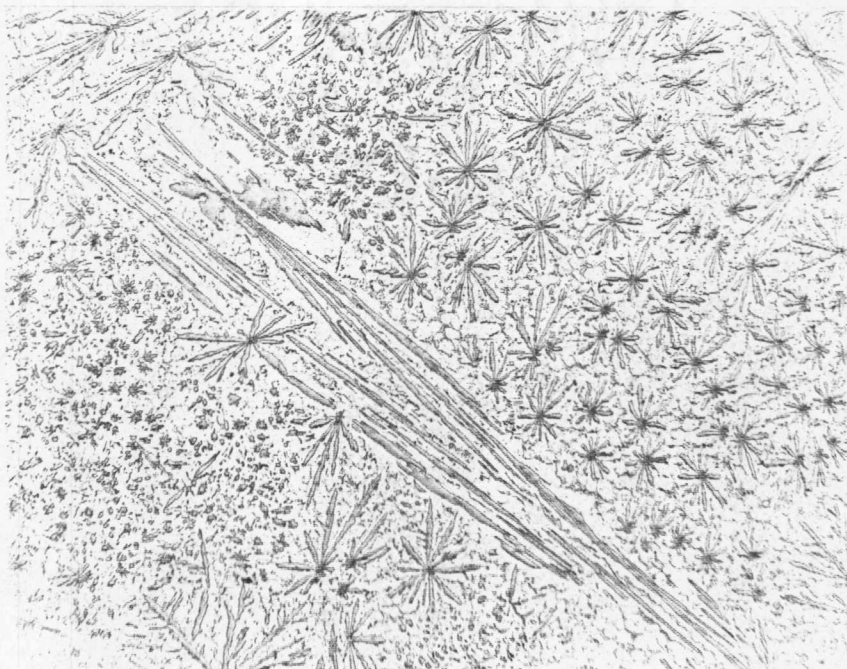


Figure 8. Al-8 wt% Fe, cast master alloy, HF etch, 136X.

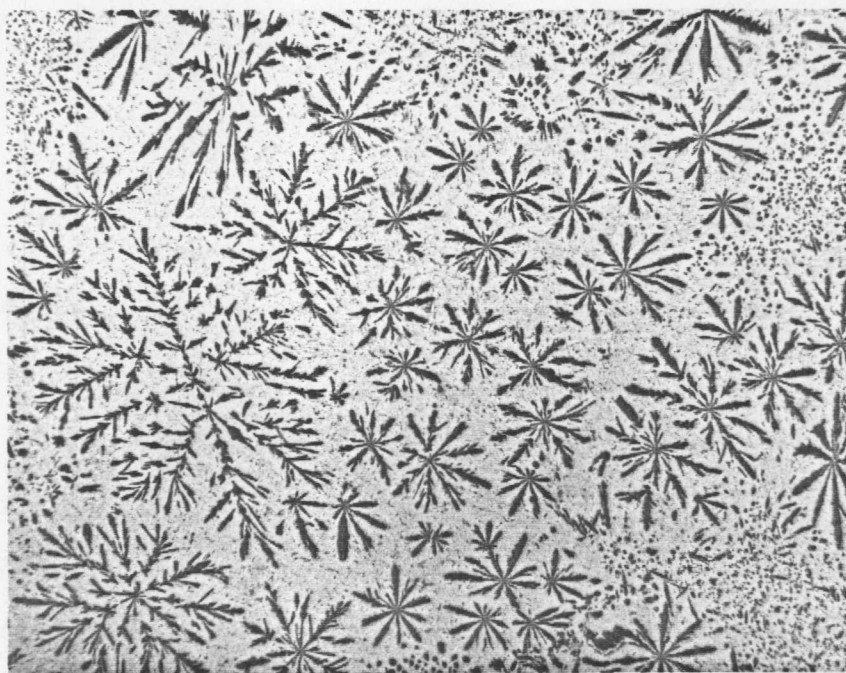


Figure 9. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, unetched, 136X.

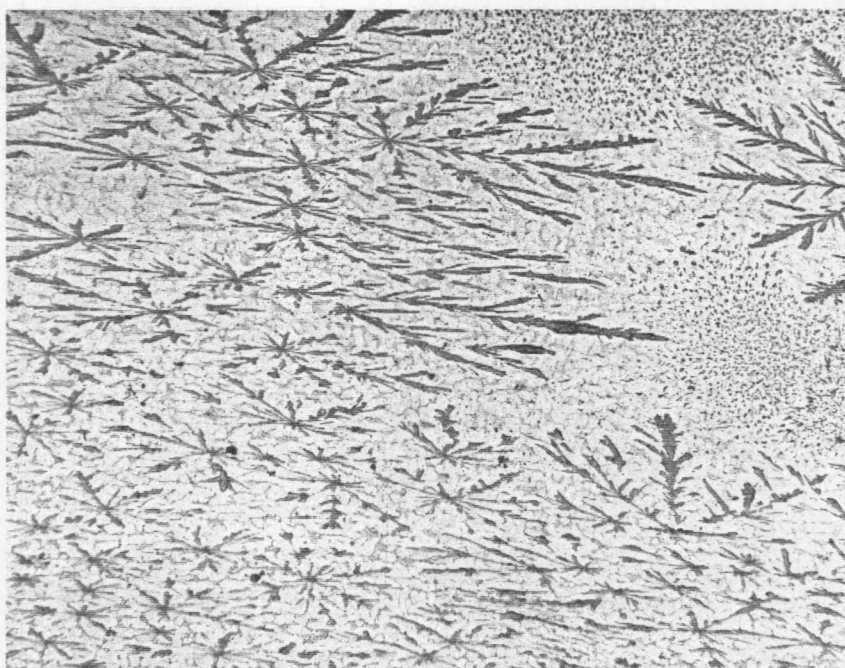


Figure 10. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 136X.

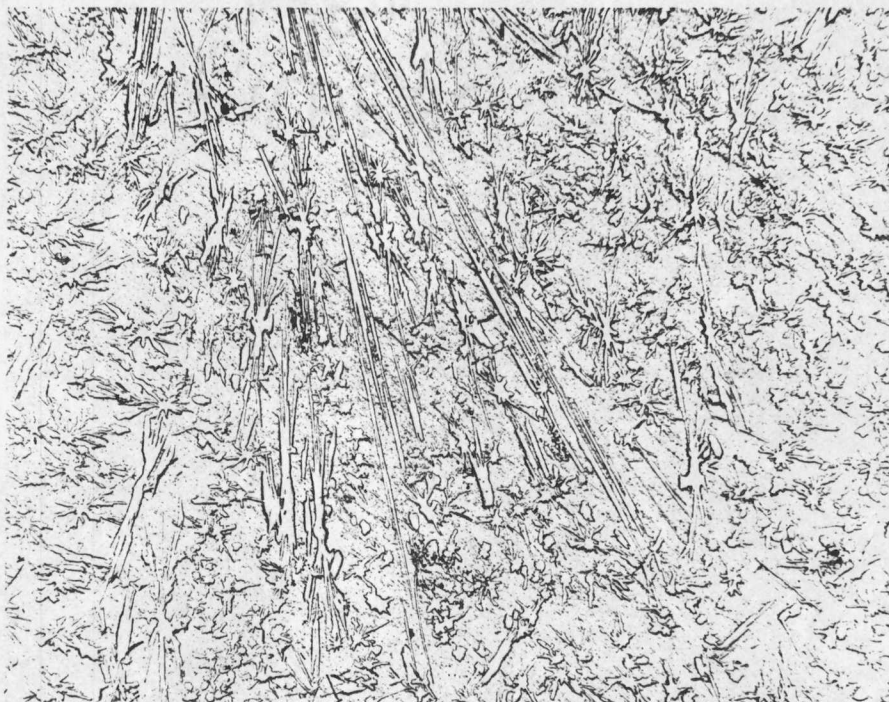


Figure 11. Al-8 wt% Fe-6 wt% Co, cast master alloy, unetched, 136X.

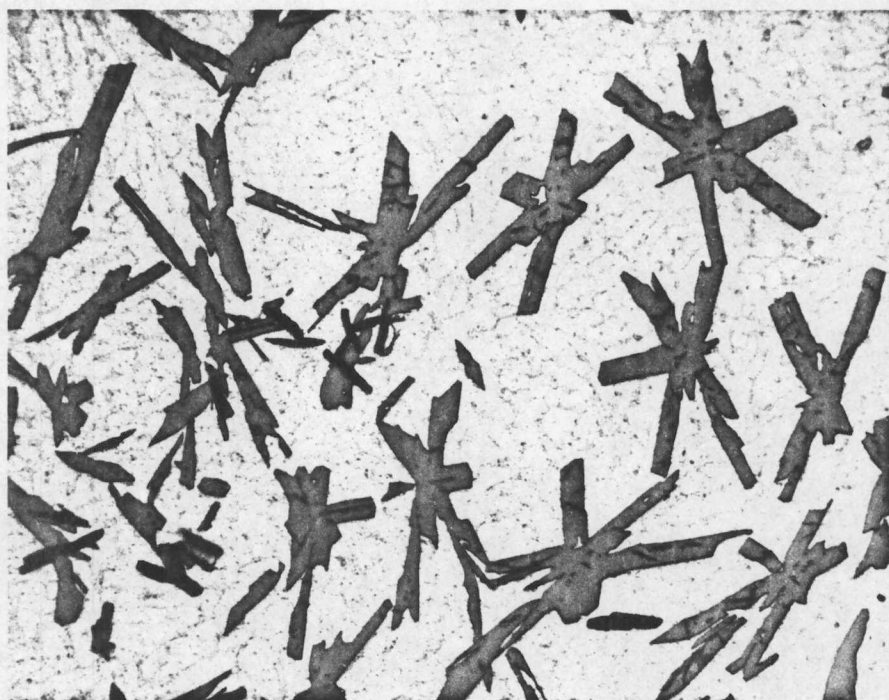


Figure 12. Al-8 wt% Fe-6 wt% Co, cast master alloy, HF etch, 680X.

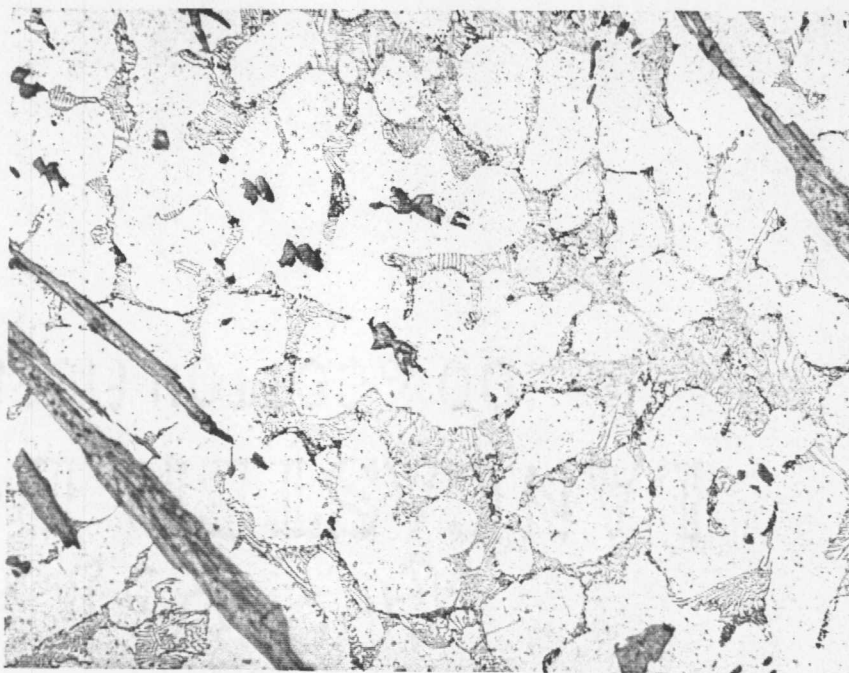


Figure 13. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 680X.

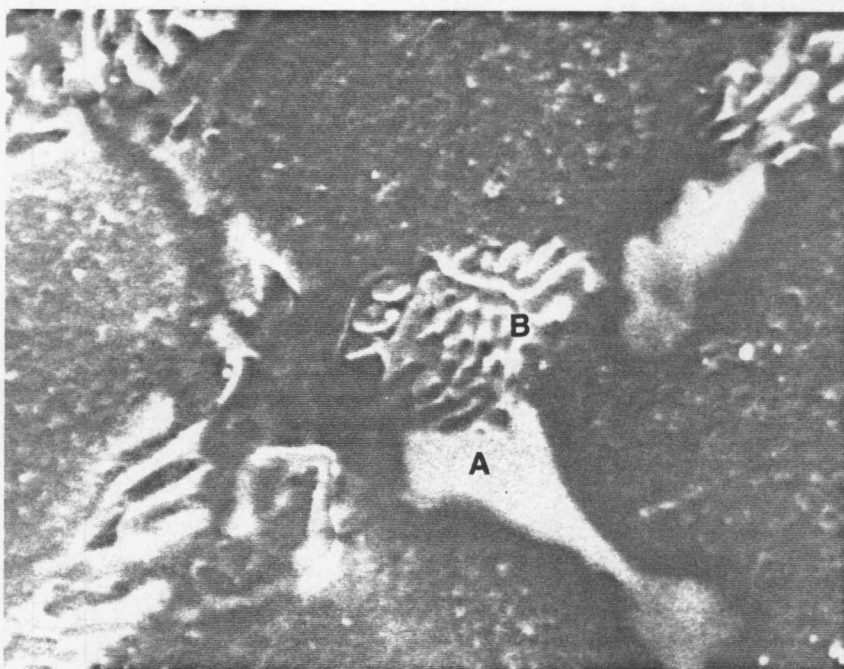


Figure 14. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 20,000X. Two ternary phases: (A) Fe rich phase; (B) Ce rich phase.

containing aluminum, iron and cerium appears as globular shaped in close proximity to the lamellar eutectic, Figures 14 and 15. The second phase, probably the last to solidify is a cerium rich phase with traces of iron present (Figures 14 and 15). The iron rich ternary phase was also found dispersed in the aluminum matrix away from the eutectic in isolated cases as shown in Figure 16. EDAX analyses of the different phases present are shown in Figures 17 and 18. The indicator bars show the position of the $\text{FeK}\alpha$ line with the indicated energy.

Two significant differences were observed in the ternary alloy in comparison to the binary alloy. First a large density of broken, fine primary Al_3Fe particles were observed dispersed in the aluminum matrix as shown in Figures 19 and 20. Though similar effects were observed in the binary alloy, its density of occurrence was much higher in the ternary alloy. Second, the eutectic morphology was different in the two alloys as shown in Figures 21 and 22. In the binary alloy, the $\text{Al-Al}_3\text{Fe}$ eutectic forms irregularly and is coarse. In the ternary alloy, the eutectic is very regular and has a fine, lamellar structure.

The Al-8% Fe-6% Co alloy was very similar to the Al-8% Fe alloy. No fine intermetallics were observed in the Al-8% Fe-6% Co alloy as shown in Figures 19 and 20 for Al-8% Fe-3.4% Ce. Cobalt additions to aluminum alloys beyond 1 wt% (max solubility limit of cobalt in aluminum) form the primary Al_9Co_2 phase on solidification. EDAX analyses of the intermetallics showed Al_3Fe particles as well as

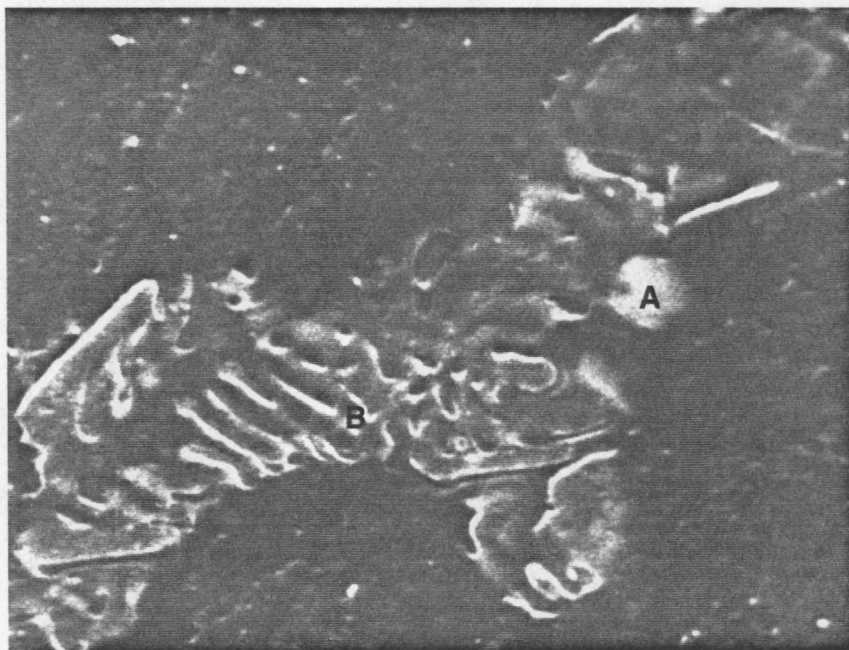


Figure 15. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 20,000X. Morphology of Fe rich (A), Ce rich (B) ternary phases.

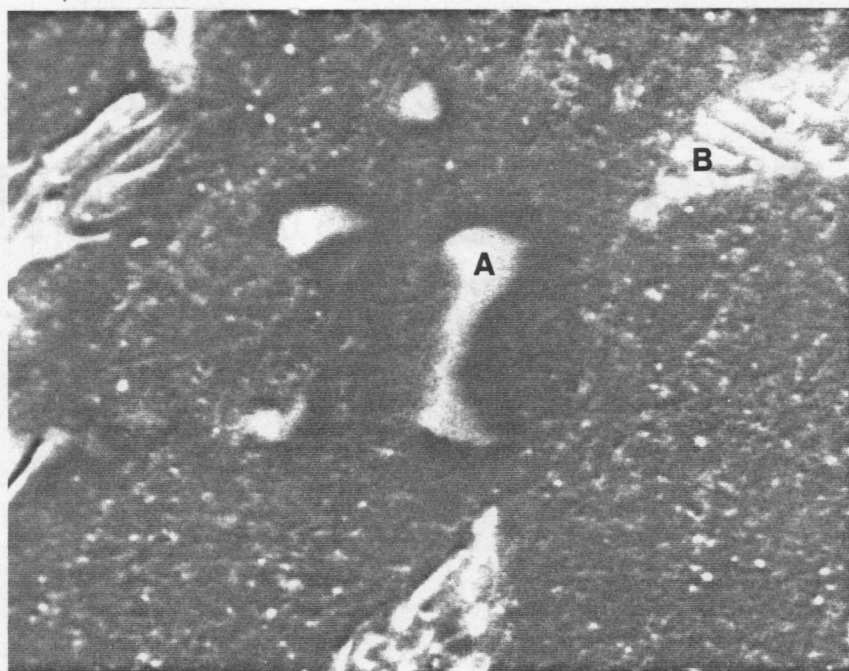


Figure 16. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 20,500X. Morphology of Fe rich (A), Ce rich (B) ternary phases.

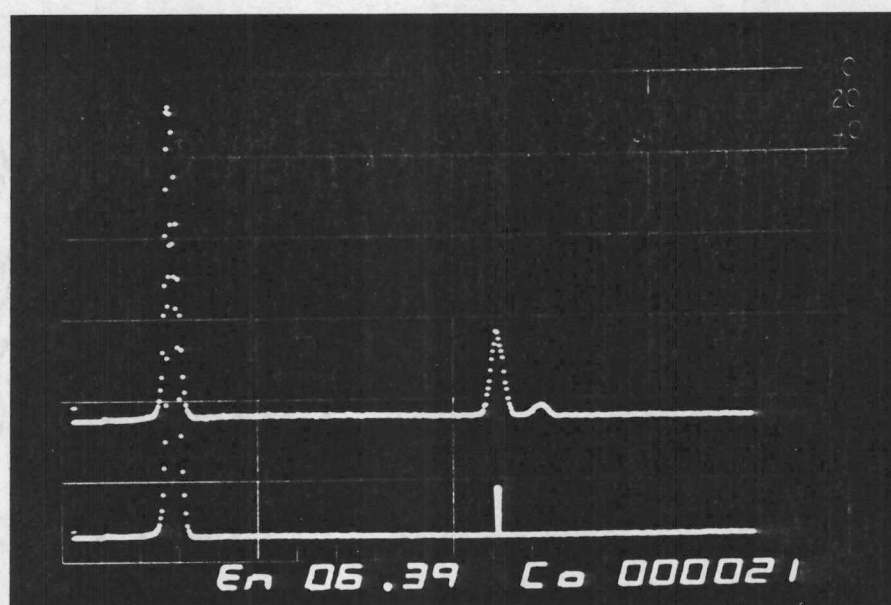


Figure 17. EDAX peaks for primary Al_3Fe phase (top) and the $\alpha\text{-Al}$ matrix (bottom) in the as cast ternary alloy.

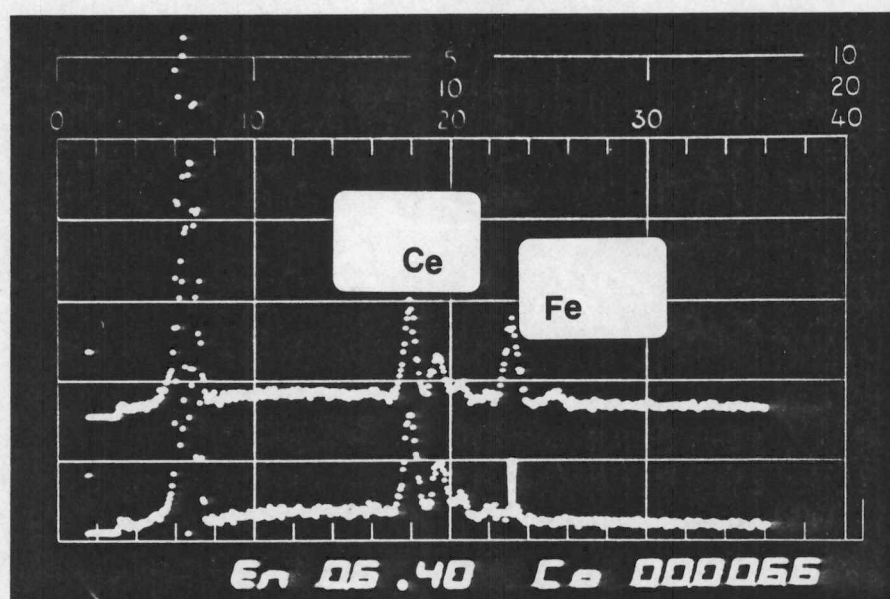


Figure 18. EDAX peaks for the ternary phases, Fe rich (top) and Ce rich (bottom) in the as cast ternary alloy.

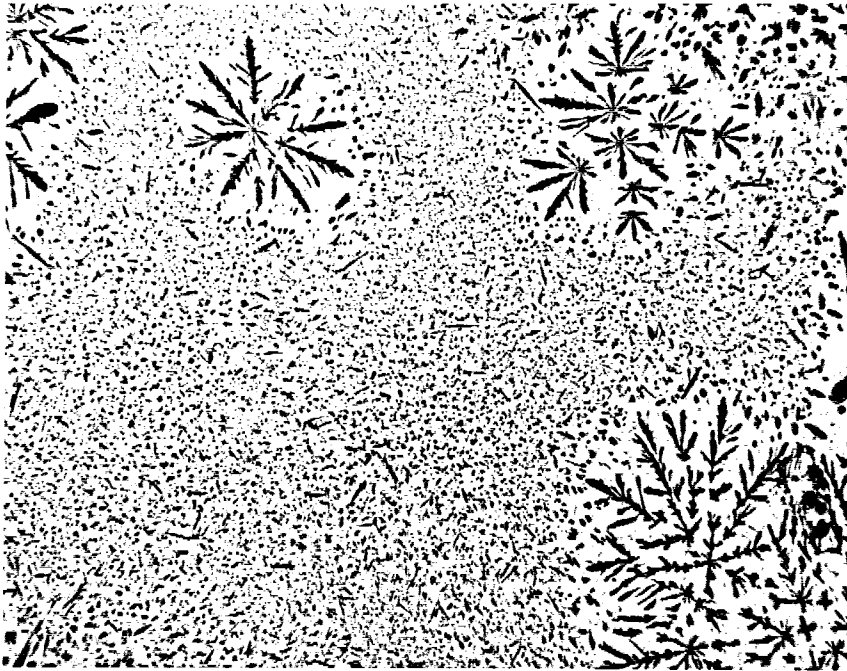


Figure 19. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, unetched, 136X.
Fine dispersion of Al₃Fe intermetallic in the matrix.

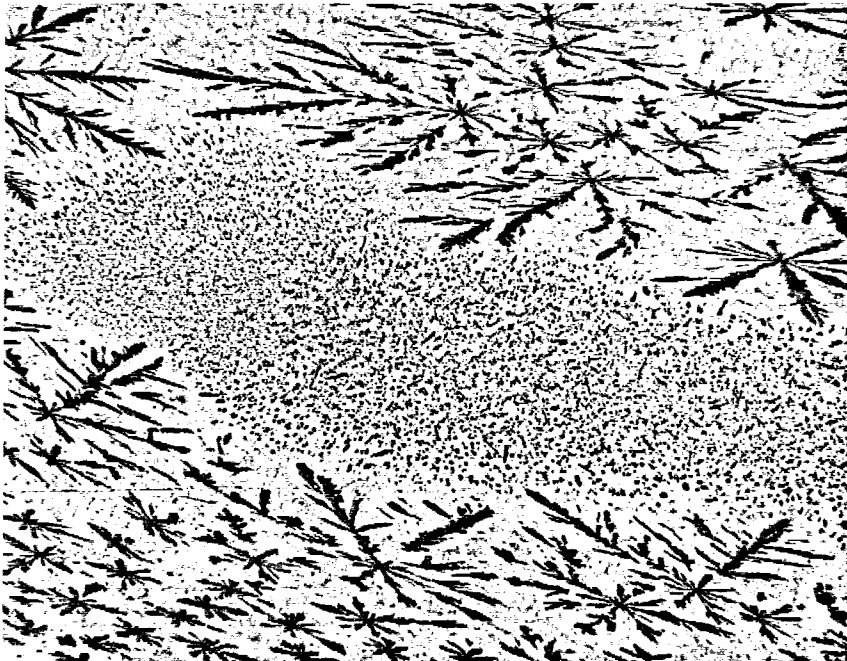


Figure 20. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 136X.
Fine dispersion of Al₃Fe intermetallic in the matrix.



Figure 21. Al-8 wt% Fe, cast master alloy, HF etch, 680X. Figure shows coarse, irregular α -Al-Al₃Fe eutectic.

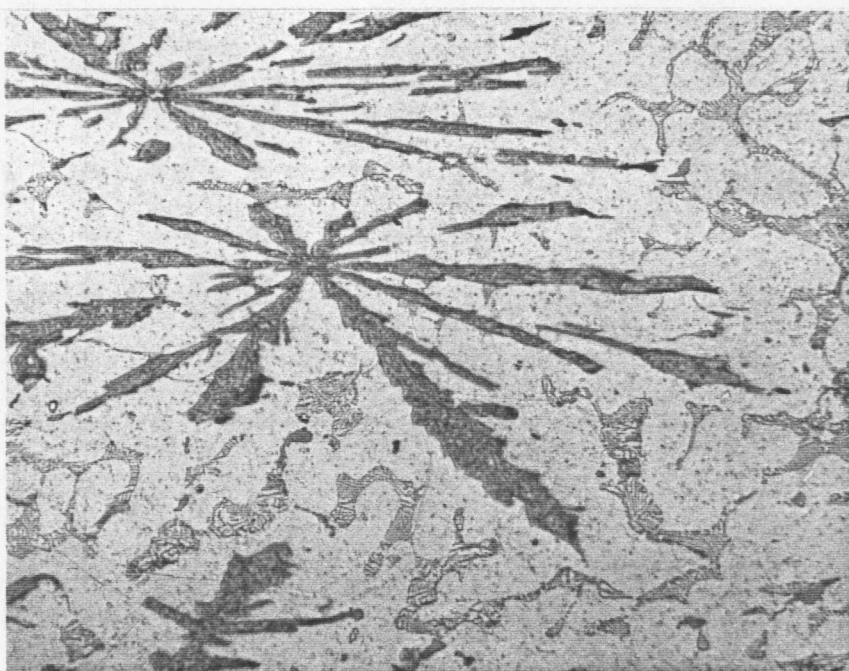


Figure 22. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, HF etch, 680X. Figure shows fine, lamellar α -Al-Al-Fe-Ce eutectic.

Al-Fe-Co particles. This is due to the solution of iron in the Al_9Co_2 phase. Iron substitutes for cobalt in this intermetallic with the chemical composition identified as $(\text{Fe,Co})_2\text{Al}_9$ (61).

Fracture Analysis

Ternary additions to the Al-8% Fe alloys are made to improve the various mechanical properties as discussed earlier in the literature review. It was considered imperative to determine if any of the inherent ductility and fracture toughness properties of the as quenched Al-8% Fe splats were retained following a ternary addition. SEM results of the fracture surfaces produced by bending the splats are shown in Figures 23, 24, and 25. Both Al-8% Fe and Al-8% Fe-3.4% Ce were fairly ductile exhibiting a ductile mode of fracture. The splat films could be readily cut with scissors. In contrast Al-8% Fe-6% Co exhibited a brittle mode of fracture and always fragmented on efforts to cut it with scissors.

Optical Microscopy and X-Ray Analysis of As Quenched Splats

The splat specimens showed a characteristically high intensity for the (111) reflection in all the splat specimens. Figure 26 shows a diffractometer trace for an Al-8% Fe-3.4% Ce specimen with the intensities as obtained. A Hanawalt search on the PDP 11/34 with these data revealed no match for aluminum or any other indexed phases. This indicates the highly preferred orientation in the (111) orientation for splats. Additionally, the diffractometer was unable to

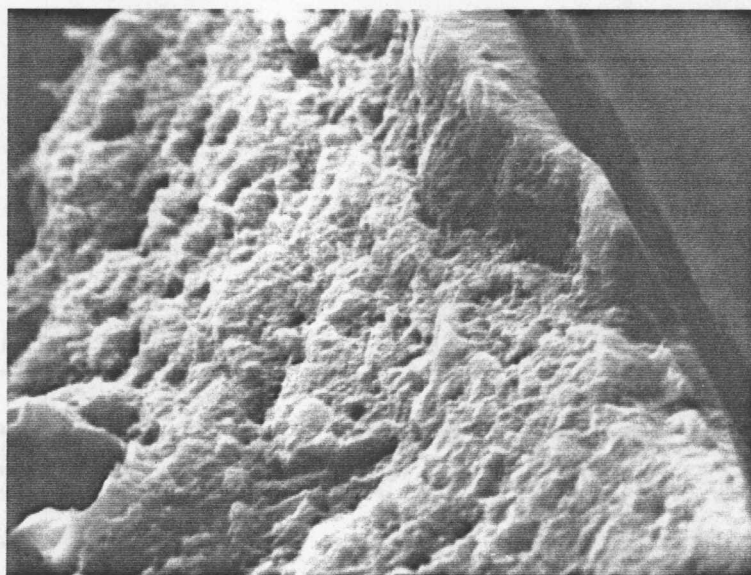


Figure 23. Al-8 wt% Fe, as quenched, SEM, 5000X. Figure shows ductile-brittle mode of fracture.

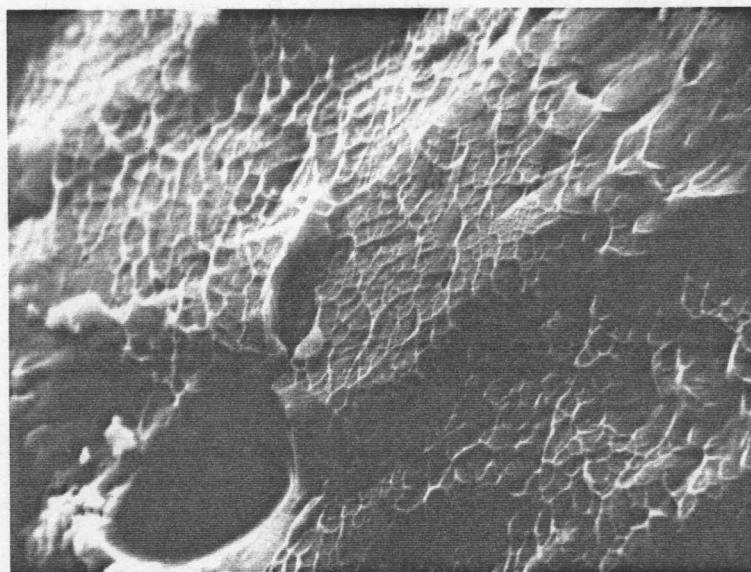


Figure 24. Al-8 wt% Fe-3.4 wt% Ce, as quenched, SEM, 5000X. Figure shows dimple mode of fracture on edge.

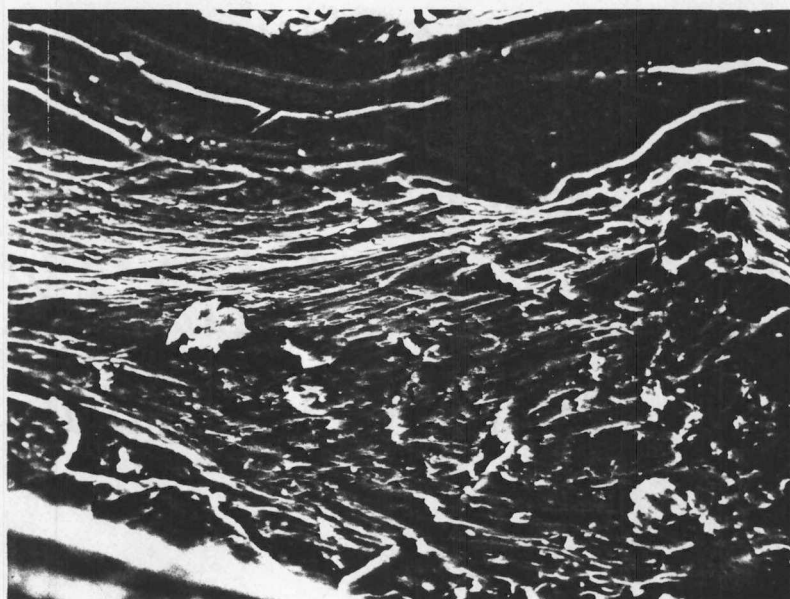


Figure 25. Al-8 wt% Fe-6 wt% Co, as quenched, SEM, 450X. Figure shows brittle mode of fracture on edge.

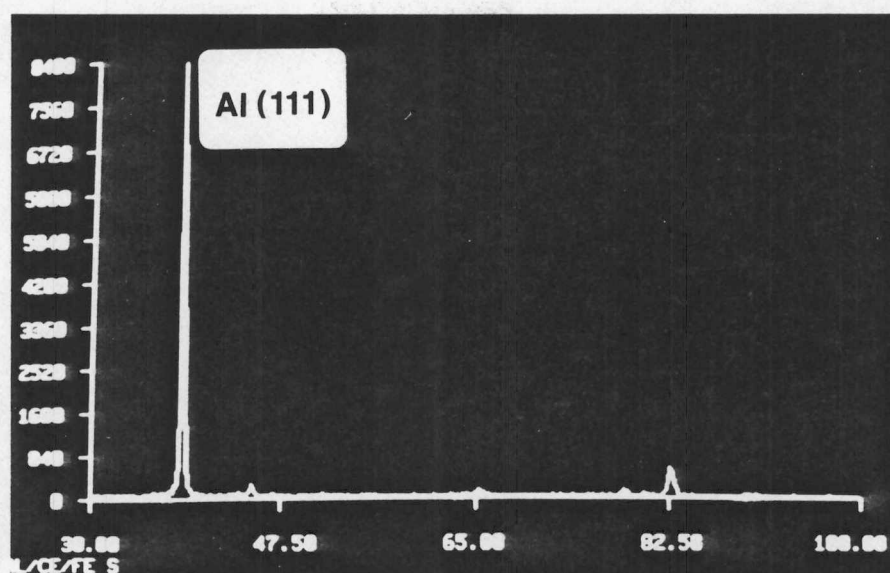


Figure 26. Al-8 wt% Fe-3.4 wt% Ce, as quenched, diffractometer scan showing high intensity for the (111) reflection. No second phase reflections present.

detect one surface from the other, revealing similar traces for the bottom and top surfaces. This was due to the high cooling rates attained on both sides of the splat in the arc quenching process. Optical microscopy showed no second phases in the quenched specimens (Figure 27).

The specimen has limited etching response to Keller's reagent and was identified as Zone A, as described by Jones (10). The thicker rejected center portion of splats showed second phase reflections readily as shown in Figure 28. Optical microscopy shows the presence of second phases, Figure 29, on etching with Keller's reagent. This region was identified as Zone B as described by Jones (10). The diffractometer trace for the bottom surface of the melt spun filament, Figure 30, indicated a similar behavior as the splats. The top surface indicated reflections for a second phase identified as Al_3Fe in addition to the aluminum reflections confirming the earlier observations made in the SEM studies. Mehrabian has reported [111] growth direction in rapidly solidified submicron alloy powders (62). The results are consistent with the fact that (111) planes are termed as fast growth planes in FCC type structures, i.e., atomic attachment on these planes are the most favorable thermodynamically. Under rapid solidification conditions of nonequilibrium solidification this would be expected. TEM studies of a one-sided electropolished splat showed the symmetric (111) orientation most readily at 0 degree tilt. Small variations in orientations were also observed between neighboring



Figure 27. Al-8 wt% Fe-3.4 wt% Ce, as quenched, Keller's etch, 200X. Complete Zone A, no second phase reflections present as shown in the diffractometer scan above.

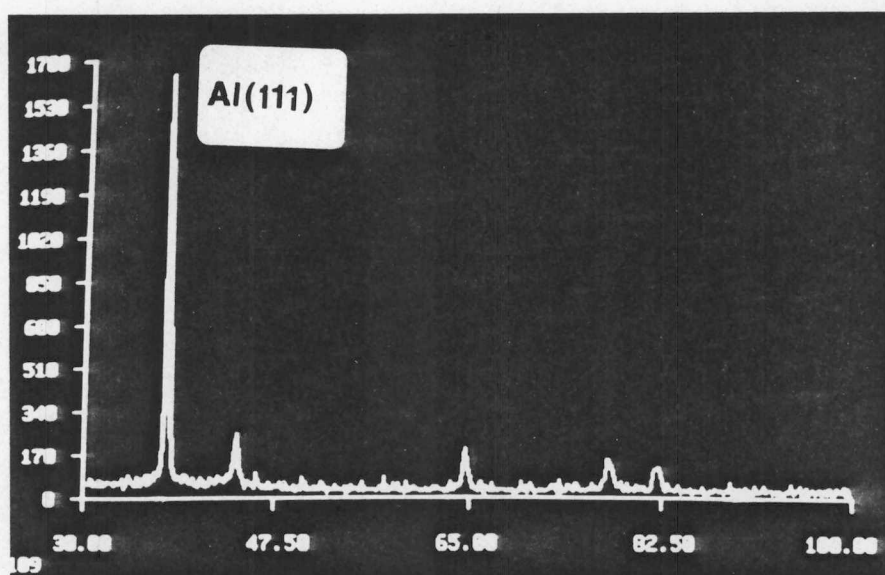


Figure 28. Al-8 wt% Fe-3.4 wt% Ce, as quenched thicker center region diffractometer scan showing second phase reflections.

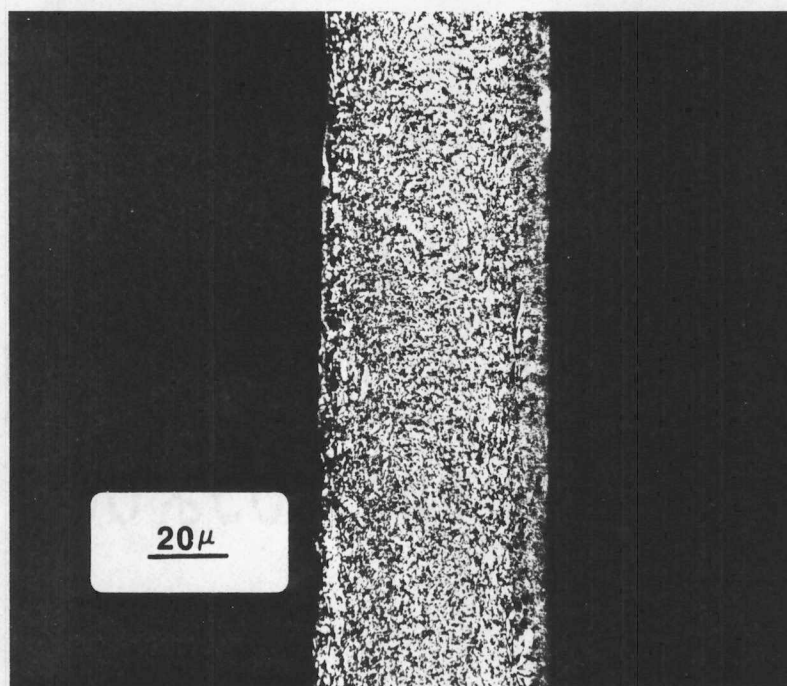


Figure 29. Al-8 wt% Fe-3.4 wt% Ce, as quenched thicker center region Keller's etch, 500X, complete Zone B, second phases present as shown by diffractometer scan above.

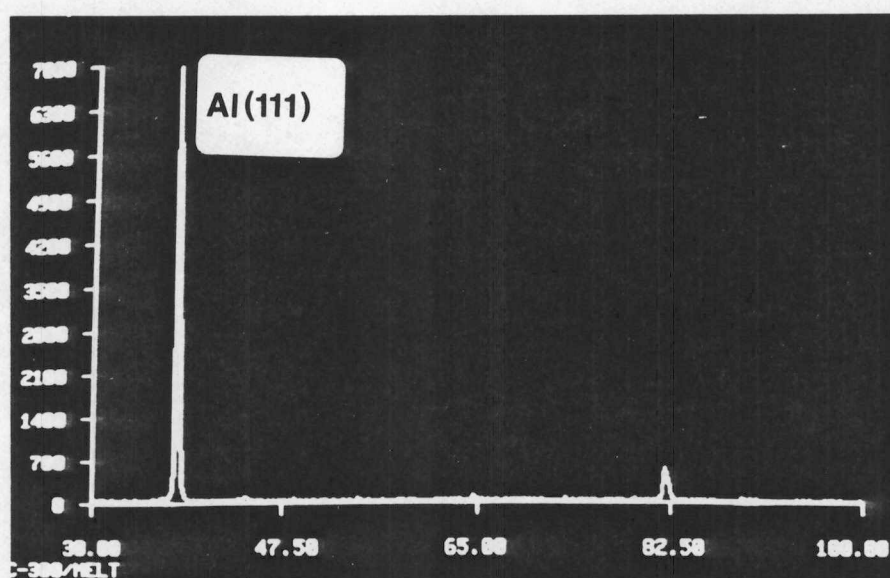


Figure 30. Al-8 wt% Fe-3.4 wt% Ce, meltspun filament, bottom surface. Identical behavior to that of splats, Figure 26, showing no second phase reflections.

pairs of grains. Figure 31 shows the diffractometer trace for the as cast Al-Fe-Ce alloy with aluminum peak intensities for comparison with Figures 26, 28, and 30 indicating preferred orientation. Deeply etched cross sections of the splat revealed a columnar type structure growing inwards with a more equi-axed structure in the middle of the splat specimen as shown in Figure 32. Optical and scanning electron microscopy did not indicate the presence of any second phases in this splat specimen.

Significant line broadening was observed, with the reflections shifting to the higher 2θ angle values, indicating a decrease in the aluminum lattice parameter for both the binary and the ternary alloy. This effect was more pronounced for the binary than in the ternary splat alloys.

Table 8 lists the atomic dimensions for aluminum, iron and cerium. Iron has an atomic radius smaller than both aluminum and cerium whereas cerium has an atomic radius larger than both iron and aluminum. It is possible that the differences tend to change the lattice dimension in opposing directions, the effects tending to cancel each other. Our observations appear to be consistent with this statement.

As Quenched Structures

A variety of structures were identified in the as quenched splat specimens of Al-8 wt% Fe-3.4 wt% Ce alloys. Figures 33-36 show the typical structures observed by transmission electron microscopy.

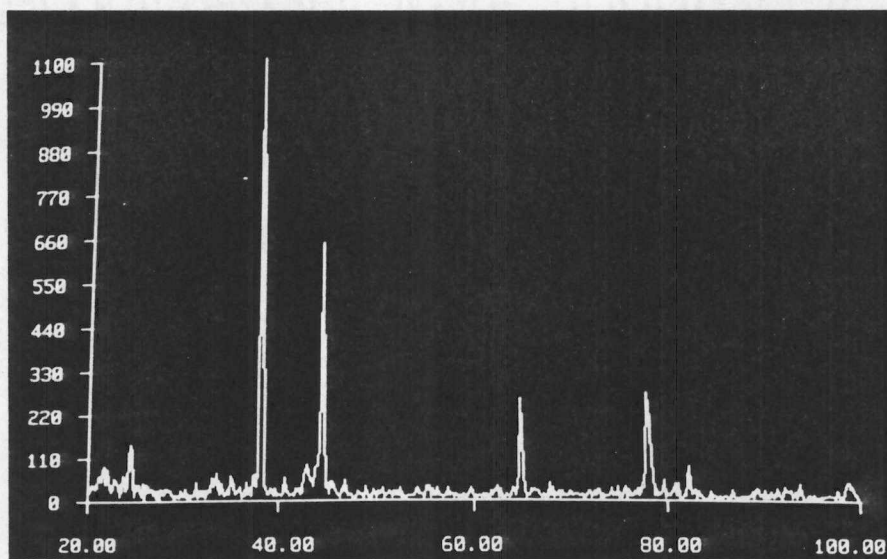


Figure 31. Al-8 wt% Fe-3.4 wt% Ce, cast master alloy, diffractometer scan shows aluminum peak intensities with good match for JCPDS card 4,787 for aluminum. Also shows second phase reflections.

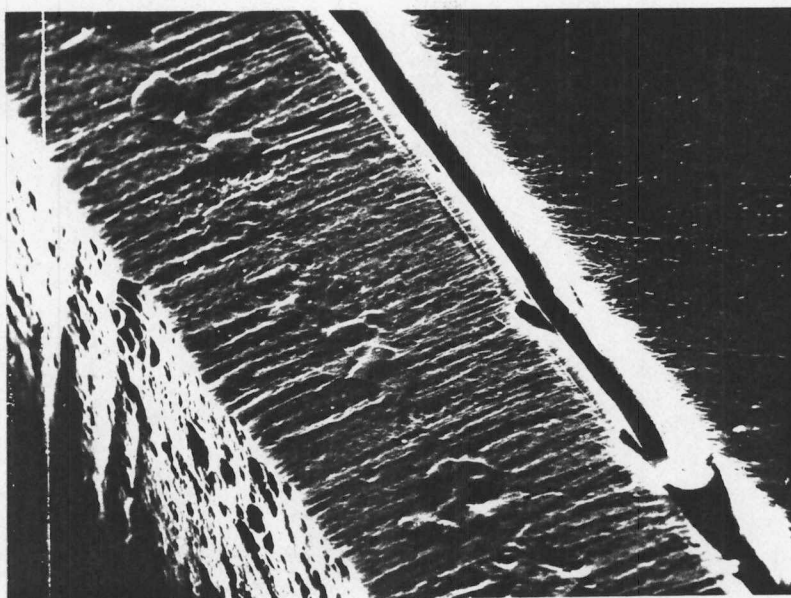


Figure 32. Al-8 wt% Fe-3.4 wt% Ce, as quenched, deep NaOH etch, 900X. SEM micrograph showing columnar growth from the edges to the center region. No second phases observed.

Table 8. Atomic Radii for the Al, Fe and Ce Atoms

Atom	Atomic Radii, nm
Al	0.1432
Fe	0.1278*
Ce	0.1824

*The bcc iron atomic radius was increased by 3% to obtain the fcc atomic radius.

Large featureless regions were most commonly observed in the electropolished specimens in Figures 33 and 34. These regions have apparently undergone an essentially partitionless solidification without redistribution of solute. EDAX scans across these regions show no compositional fluctuations within the limits of experimental error for the EDAX microanalytical apparatus used with the TEM. The diffraction patterns from these regions show the typical FCC reflections of the aluminum matrix. It was noted that the patterns were of a diffuse nature, possibly because of the slight distortion in the aluminum lattice parameter due to the solute in solution. Figure 33 shows such featureless regions in the binary alloy. Electron microscopy of as quenched Al-8% Fe showed a fine grain size of the order of 0.5-1.0 microns. This measurement was suitably made by in situ annealing of the as quenched electropolished specimens in the TEM at about 400 °C for a few minutes. A large volume of precipitates form decorating the grain boundary. Figure 37 shows fine grained structure obtained in these regions. Large variations in grain size, however, were frequently observed in both the as quenched and the annealed specimens. Normally a ring diffraction pattern was obtained, for the large grains, along with the aluminum matrix spots, similar to

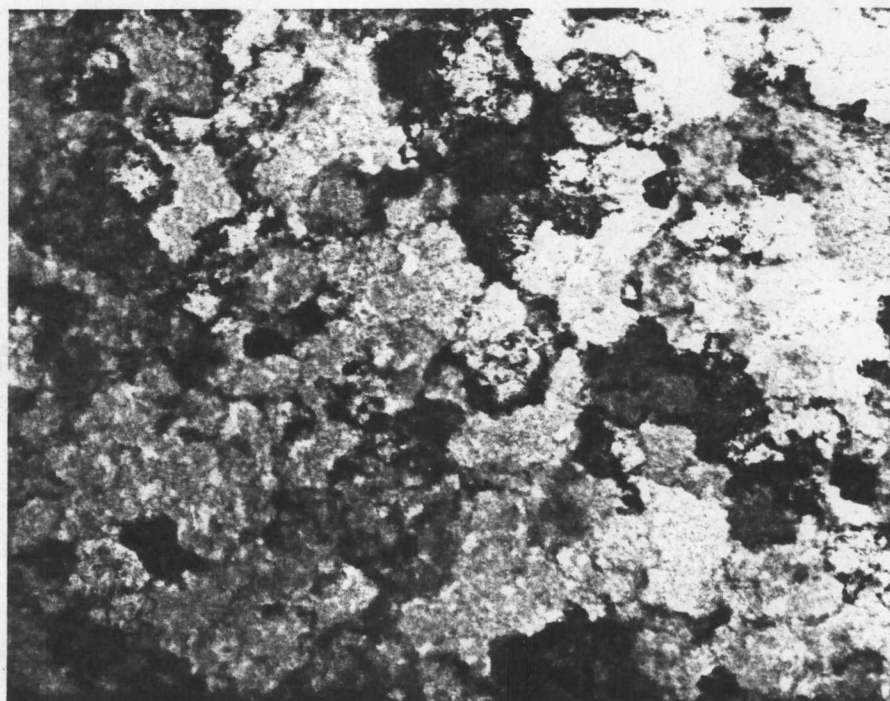


Figure 33. Al-8 wt% Fe, as quenched sample, TEM micrograph, 62,000X. Limited featureless regions of complete solid solution.

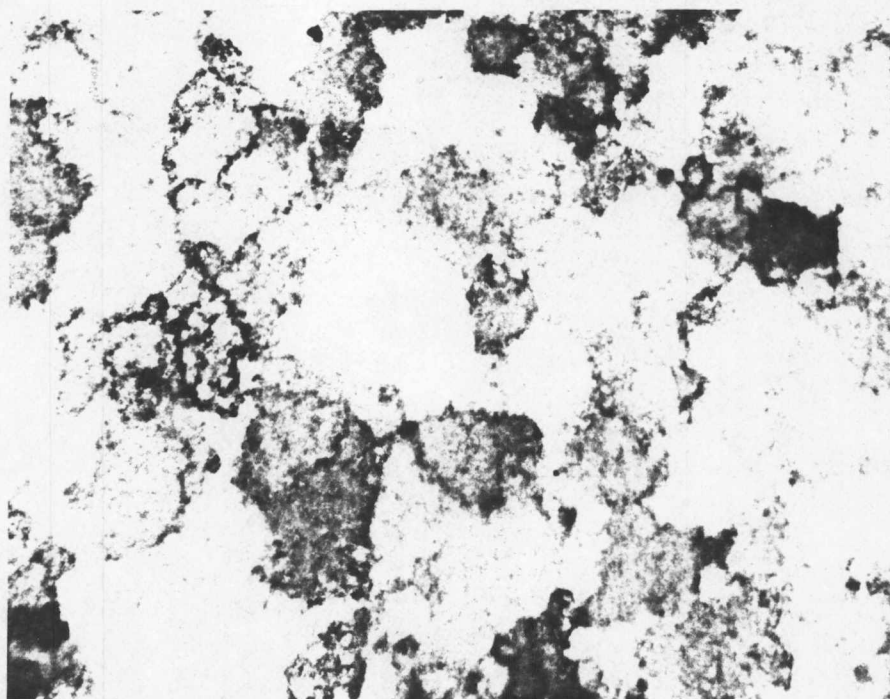


Figure 34. Al-8 wt% Fe-3.4 wt% Ce, as quenched sample, TEM, 62,500X. Featureless regions of complete solid solution.

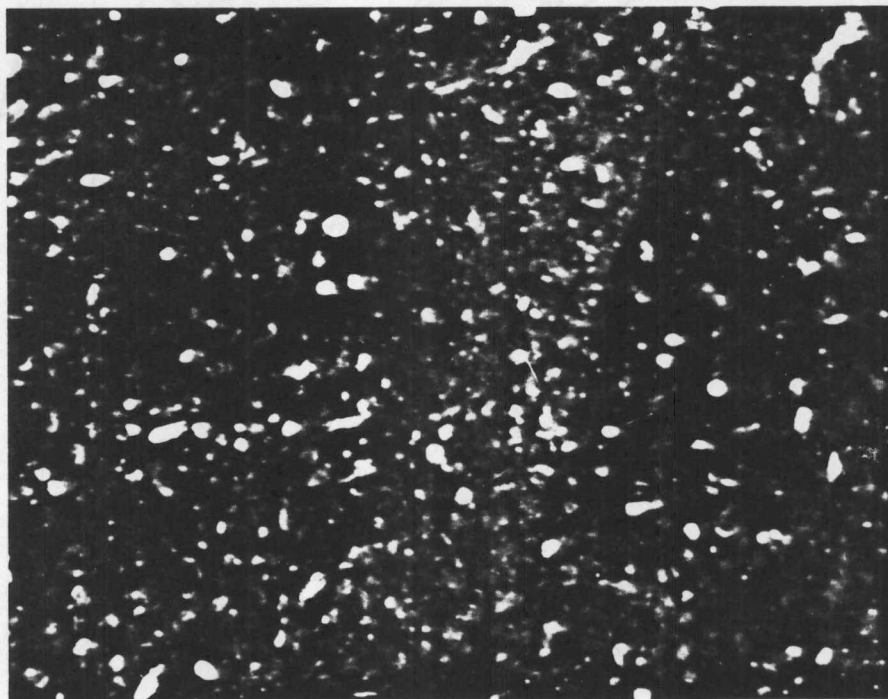


Figure 35. Al-8 wt% Fe-3.4 wt% Ce, as quenched sample, TEM, 250,000X. Dark field micrograph highlighting small crystallites.

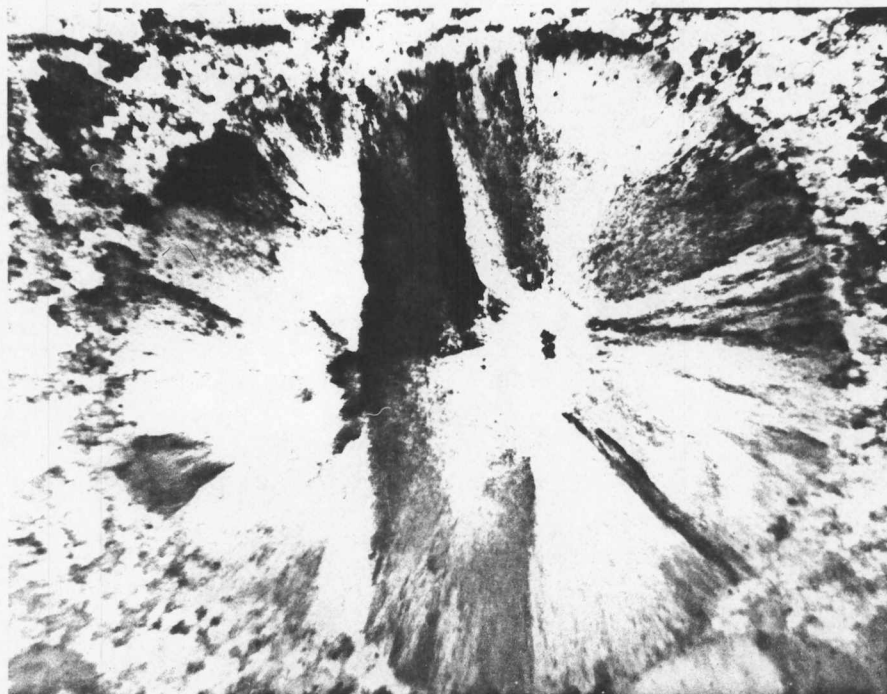


Figure 36. Al-8 wt% Fe-3.4 wt% Ce, as quenched sample, TEM, 62,000X. Heterogeneous nucleation of spherulitic structure around coarse primary intermetallic particle.

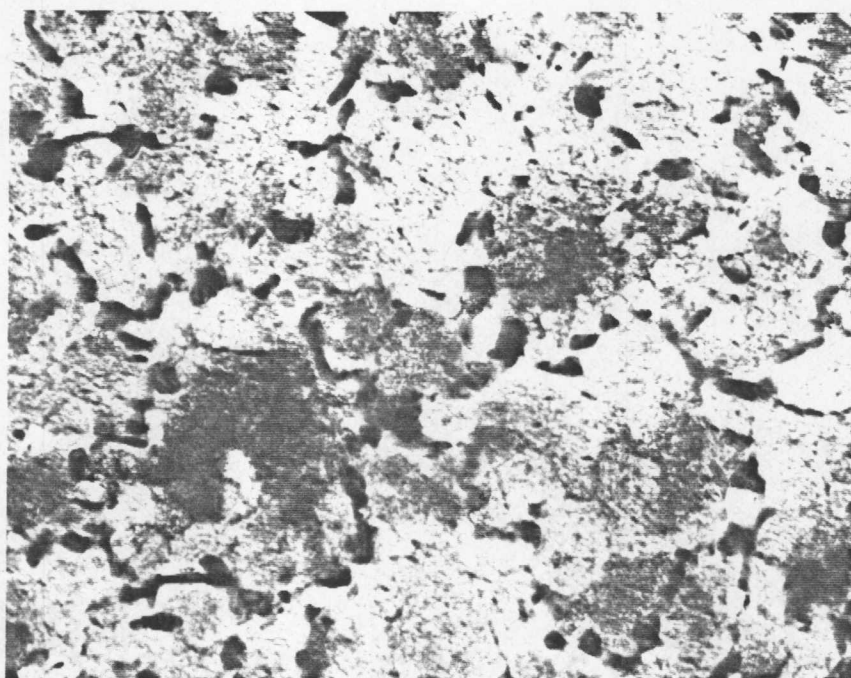


Figure 37. Al-8 wt% Fe-3.4 wt% Ce, aged in-situ at 440 °C/1 hour, TEM, 62,000X, precipitation at the grain boundary gives an estimation of the grain size 0.5-1.0 micron for the featureless regions.

that described by Jones and Jacobs et al. (20). The strongest ring observed had a d-spacing of 0.21 nm and dark field effects highlighted fine particles randomly distributed within the grains (Figure 35). The largest of these particles is less than 10 nm in size and a large density of smaller particles were also present. Satellite rings were often too weak to reveal any significant dark field effects. Limited evidence of a fine cellular structure was observed in as quenched specimens in the dark field mode. The cells are of the order of 20 nm and decorated by a fine second phase network. Spherulitic type structures were observed in both Al-8% Fe and Al-8% Fe-3.4% Ce alloy specimens (Figure 36). The spherulites were observed to be growing radially and were circular in the cross section observed. The spherulites were significantly larger than the normal grain size reported above. Occasionally a fine intermetallic was observed as the nucleating agent for this event (Figure 36). The growth of spherulitic regions appears to form by heterogenous nucleation around these coarse primary particles. It was concluded that variations in cooling conditions favored the formation of primary intermetallic particles from the melt resulting in the spherulitic structure. The Al-8% Fe-6% Co structure was significantly different from both Al-8% Fe and Al-8% Fe-3.4% Ce alloys. Intermetallic particles were observed throughout the specimen (Figures 38 and 39). In the composition range studied, it is unlikely that the intermetallic was not taken in solution during melting. Temperatures under the arc are well above the liquidus temperature for this composition. It is possible that

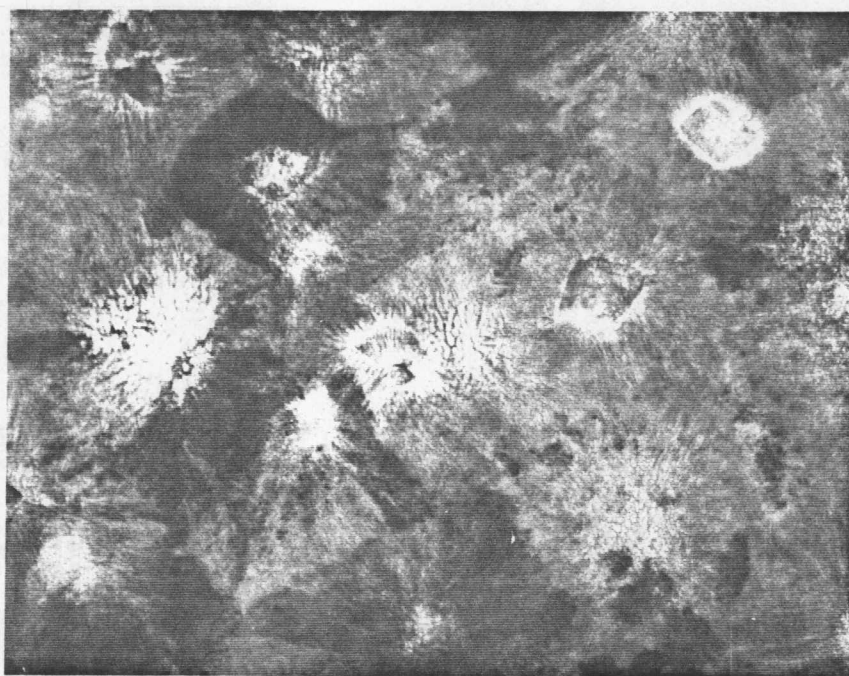


Figure 38. Al-8 wt% Fe-6 wt% Co, as quenched sample, TEM, 62,000X. Coarse intermetallic particles present extensively.

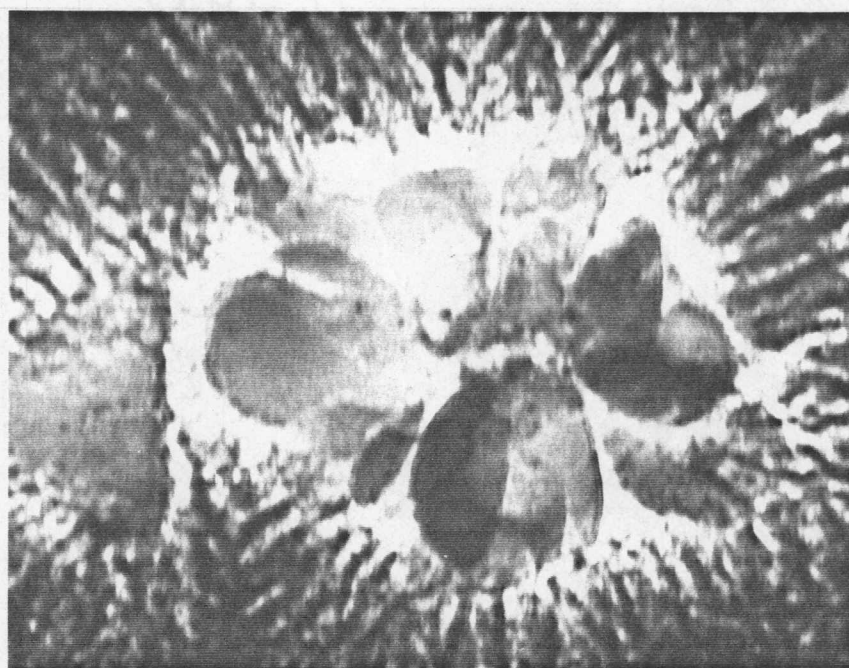


Figure 39. Al-8 wt% Fe-6 wt% Co, as quenched sample, TEM, 400,000X. Intermetallic particle acting as nucleant for growth of fine cellular, lamellar regions around.

under the conditions used in this study for preparing splats, formation of such coarse intermetallics could not be avoided. Garret and Sanders (63) have also reported the formation of coarse intermetallics in rapidly solidified Al-Co alloys.

Melt Spun Structures

Figures 40 and 41 show observed surface microstructures in the etched top surface of a melt spun filament, prepared at the Oak Ridge National Laboratory. The bottom surface in contact with the copper wheel was smooth in appearance as compared to the top surface which was rough. Variations in cooling rates across the thickness resulted in the formation of rod like Al_3Fe particles embedded in the matrix of the top surface. The solidification structure was essentially dendritic (Figure 41). Since the primary objective of this work is to study the annealing behavior of supersaturated Al solid solutions and these were not attainable by melt spinning, this experimental approach was not continued.

Microhardness Measurements

Isochronal annealing curves for the three alloys studied, for 1 hour, 10 hours, 100 hours, are shown in Figures 42, 43, and 44. Earlier reported microhardness data show a much lower hardness than values obtained herein for binary alloys with up to 8 wt% iron (10). Jones' microhardness measurements were made using a 10 gram load, and a mean as quenched hardness of 260 Kg/sq:mm was reported (10). The

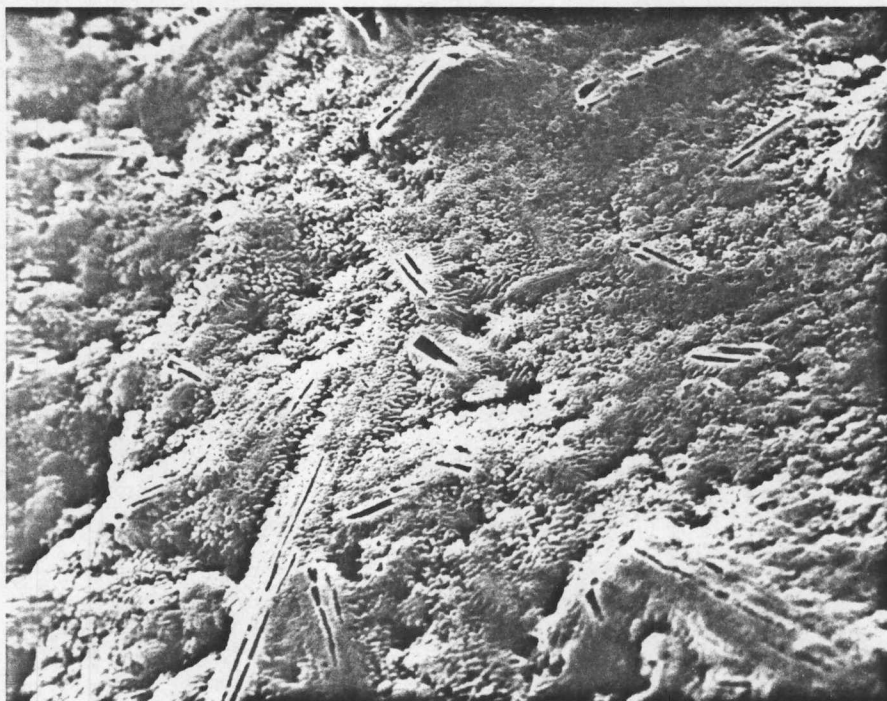


Figure 40. Al-8 wt% Fe-3.4 wt% Ce, melt spun filament, top surface HF etch, 2,700X coarse Al_3Fe rods dispersed at the top surface of the filament.

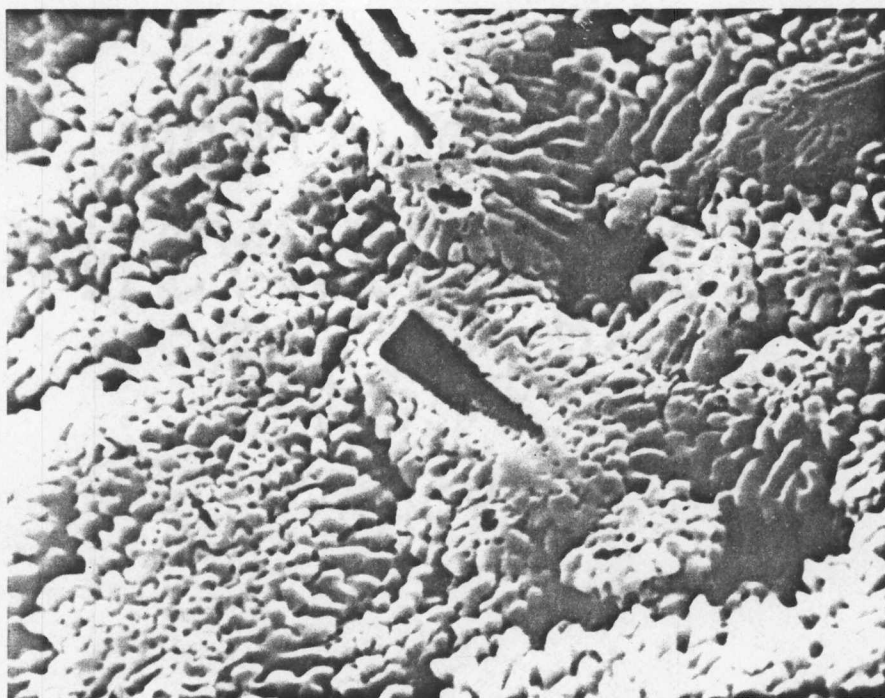
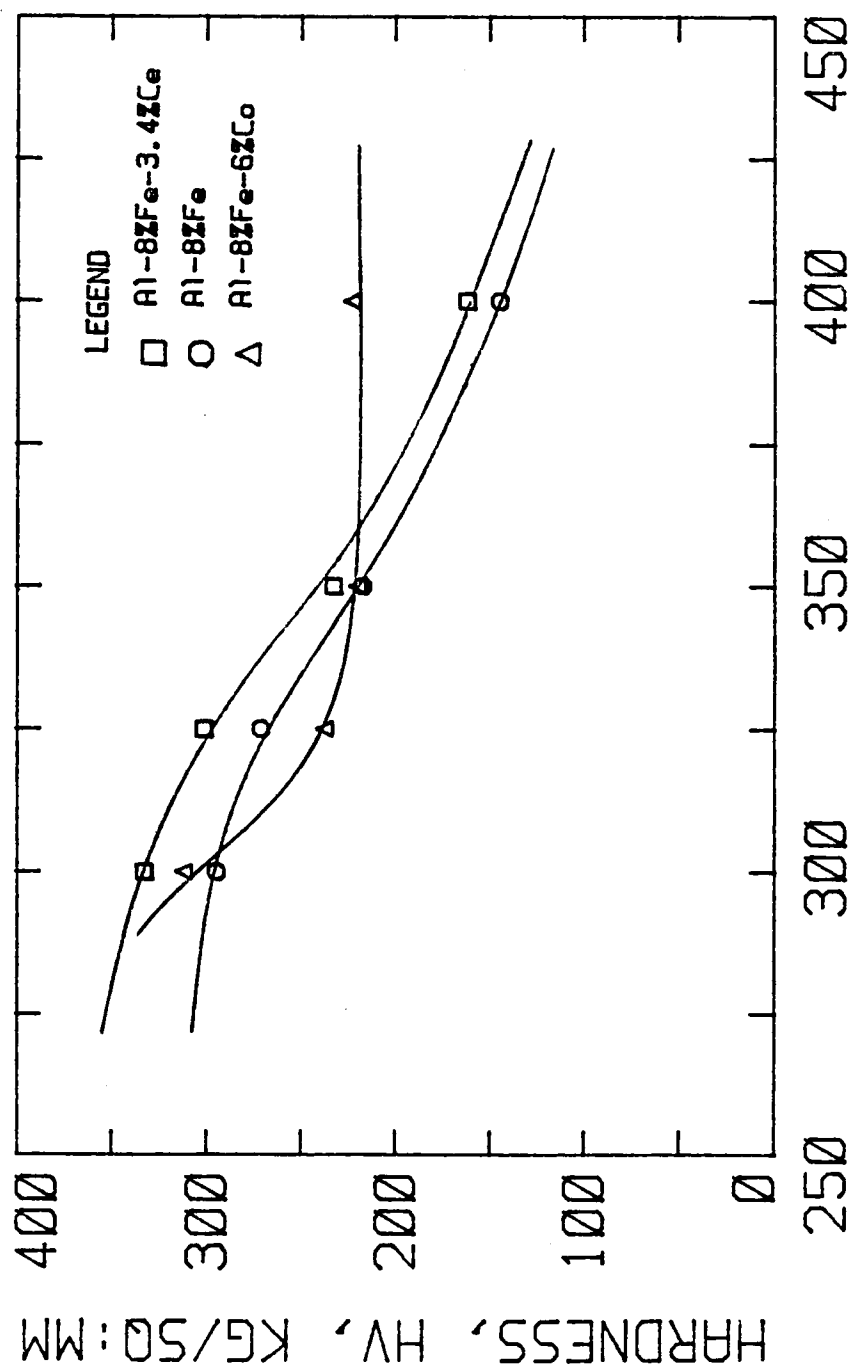


Figure 41. Al-8 wt% Fe-3.4 wt% Ce, melt spun filament, top surface HF etch, 6,800X dendritic solidification around coarse primary intermetallic.



AGING TEMPERATURE, DEGC

Figure 42. Microhardness vs. aging temperature for isochronal aging for 1 hour at 300, 325, 350, 400 °C.

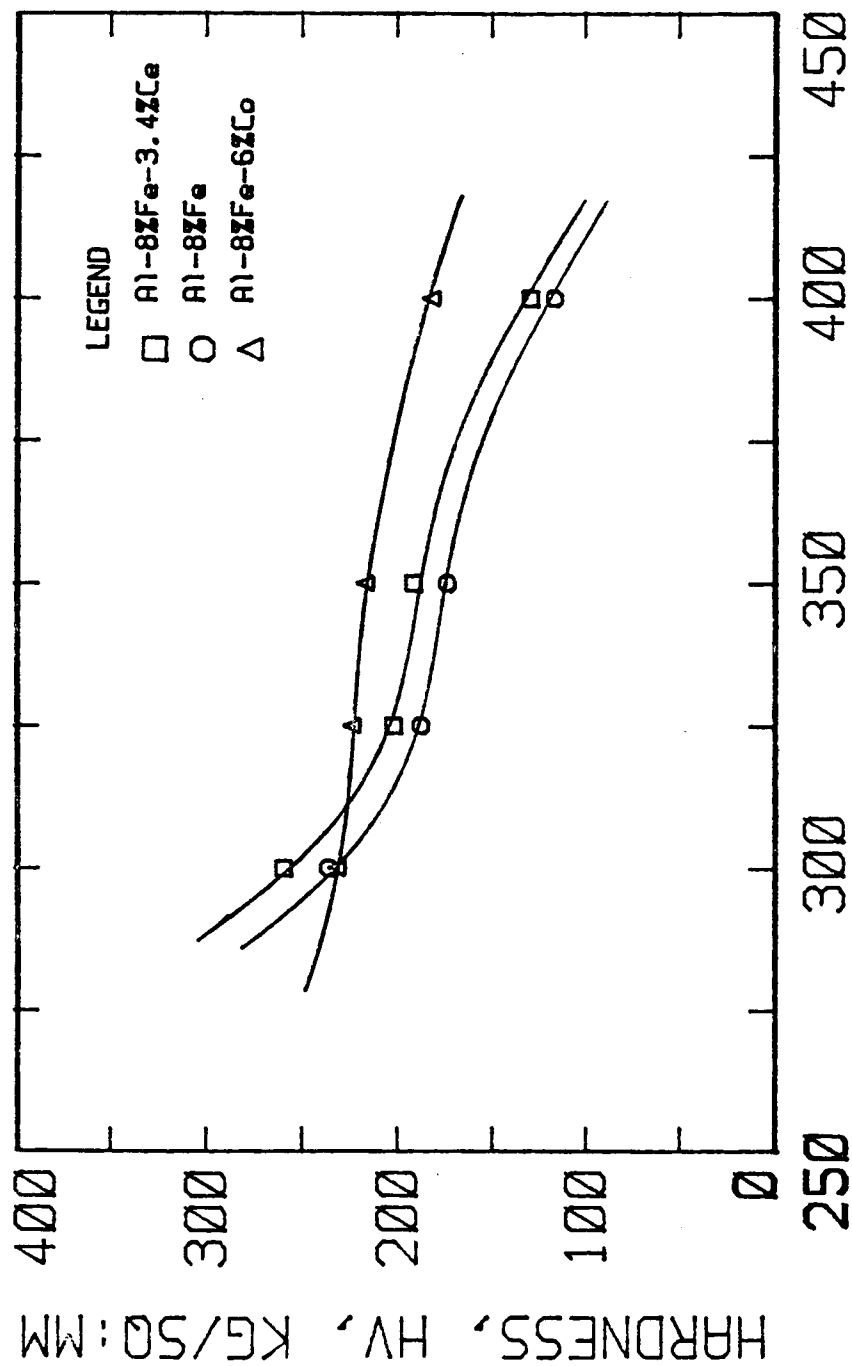


Figure 43. Microhardness vs. aging temperature for 10 hours at 300, 325, 350, 400 °C.

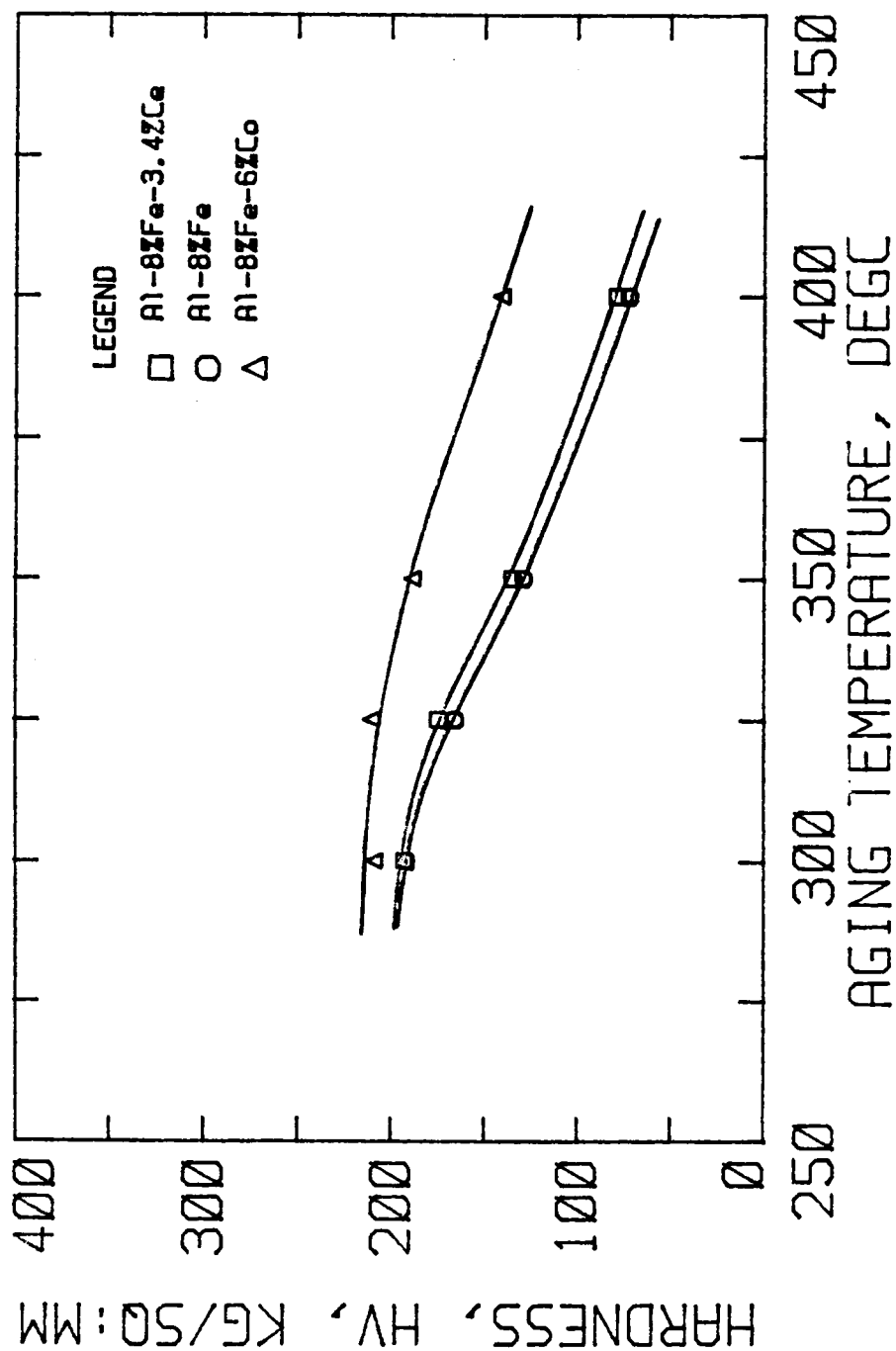


Figure 44. Microhardness vs. aging temperature for isochronal aging for 100 hours at 300, 325, 400 °C.

consistently higher hardness values obtained here can be explained as follows. The question of load dependency of hardness values was mentioned earlier. It was our observation that normal hardness measurements at lower loads are subject to a greater degree of scatter. The calibration plot shows that a measured 250 Kg/sq:mm hardness measured at a 10 gram load would measure about 295 Kg/sq:mm at a 50 gram load (Figure 6c, p. 28). This still does not explain clearly the increased hardness values obtained in this study. Microstructural evidence on our splats show that it was possible to obtain Zone A throughout the thickness of a 35 micron thick splat on quenching (Figure 27, p. 48). Renaut et al. (64) have suggested that the specific conditions of solidification rate and cooling conditions through the solid state would influence the hardness values obtained for Zone A. This is most likely the case for regions where essentially partitionless transformation has occurred yielding high solid solution hardness values. Dispersion strengthening effects of a fine inter-cellular precipitate are also the likely effects contributing to a high hardness (64). Our cellular network of about 20 nm spacing is smaller than that obtained by Jones (10) and could also contribute to higher hardness values. In addition, Blank (40) has indicated that defect hardening is probably responsible for increased hardness values. Annealing out of lattice defects should occur early in the annealing stages resulting in a consequent rapid drop in hardness. This was not observed so, and does not consistently explain the retention of high hardness after one hour of aging at 300 °C for the Al-8 wt%-3.4% Ce alloy.

Apart from the hardness differences in the as quenched condition the measured drop in hardness was identical to that obtained by Jones for isochronal annealing at 1 hour for different temperatures (10).

The smooth curve drawn in Figure 42 for 1 hour shows a gradual drop for Al-8% Fe-3.4% Ce in the earlier stages with the slope of the curve attaining a relatively constant value between 300 °C to 360 °C with the slope decreasing gradually beyond 360 °C. Al-8% Fe alloy shows a larger drop in hardness in the initial stage with the nature of the curve similar to the Al-8% Fe-3.4% Ce at temperatures above 330 °C. Al-8% Fe-6.2% Co alloy shows a gradual drop in hardness up to 325 °C with the curve being essentially flat beyond 325 °C. TEM studies on splats annealed for 1 hour at 300 °C for Al-8% Fe and Al-8% Fe-3.4% Ce showed increased grain boundary precipitation in the former case. TEM results are shown in a later section. The notable retention of hardness in the Al-8% Fe-3.4% Ce alloy is attributed to the cerium in solution. The effect of cerium in this case is twofold. First, solid solution strengthening due to cerium would contribute to hardness. Second, cerium acts as a barrier to the diffusion of iron to the grain boundary thereby slowing the drop in hardness.

The smooth curve drawn in Figure 43 for 10 hours shows a rapid drop for all the alloys up to temperatures of 325 °C followed by a gradual drop in hardness at temperatures beyond 330 °C. Of special interest is the Al-8% Fe-6% Co alloy. The hardness at 300 °C was comparable to Al-8% Fe but lower than Al-8% Fe-3.4% Ce. However, at temperatures beyond 325 °C the hardness for this alloy was higher than

both Al-8% Fe and Al-8% Fe-3.4% Ce. This indicates that after an initial softening of the matrix the precipitates are very stable up to 400 °C. Unfortunately, due to the severe brittle behavior of this alloy, extensive TEM work was not carried out. For the Al-8% Fe and Al-8% Ce alloy little difference in hardness values was observed at 400 °C. Thus the beneficial effects of cerium are largely lost after annealing for 10 hours at 400 °C. Microstructural evidence, however, shows that cerium does play an important role in the transformation process of metastable to stable phase formation. These results are presented in the section of TEM results.

The smooth curves drawn in Figure 44 for 100 hours show higher hardness values for Al-8% Fe-6.2% Co at all temperatures indicated in this study. The difference in hardness increasing with increasing temperature up to 400 °C. For Al-8% Fe and Al-8% Fe-3.4% Ce no difference in hardness values was observed. This, then, suggests that cerium contributes no effects at 400 °C and beyond. The effect of cerium in hardness retention is evident only for the shorter aging times and at lower temperatures (Figure 42). With increasing aging times the hardness of the ternary alloy approaches that of the binary alloy at all temperatures (Figures 43 and 44). That cerium does show better hardness values for the lower temperatures and shorter times is probably due to its increased solid solubility on rapid solidification. Additionally, presence of cerium (its large atomic dimensions compared to aluminum or iron) probably slows down the diffusion of iron to the grain boundary.

Isothermal annealing curves for the ternary alloys in comparison to the binary Al-8% Fe alloy for different time temperature combinations are shown in Figures 45 and 46. Figure 46 shows that Al-8% Fe-6% Co has comparable hardnesses at 300 °C for samples annealed for 10 to 100 hours. Beyond 325 °C the ternary Al-8% Fe-6% Co shows high hardness values at 100 hours in comparison to the binary Al-8% Fe alloy at all temperatures up to 400 °C. The difference in hardness values after 100 hours of aging increases with increasing temperatures up to 400 °C.

Transmission Microscopy Studies

Extensive transmission work was done on the Al-8% Fe-3-4% Ce alloys for samples annealed for 1 hour, 10 hours and 100 hours at aging temperatures of 300, 325, 350, and 400 °C. For comparison, selected samples of the Al-8% Fe alloys were observed in the TEM.

Aging Studies at 300 °C

Micrographs of the as quenched specimens were shown in an earlier section. TEM micrographs and plots of all samples aged at 300 °C are shown in Figures 47-55. For samples annealed at 300 °C for 1 hour, a very fine precipitate was observed in the grain. Small, discontinuous globular particles were observed at the grain boundary. This effect was observed in both the binary and the ternary alloy (Figures 47, 50). The higher incidence of these globular particles in the binary alloy was discussed earlier in conjunction with hardness

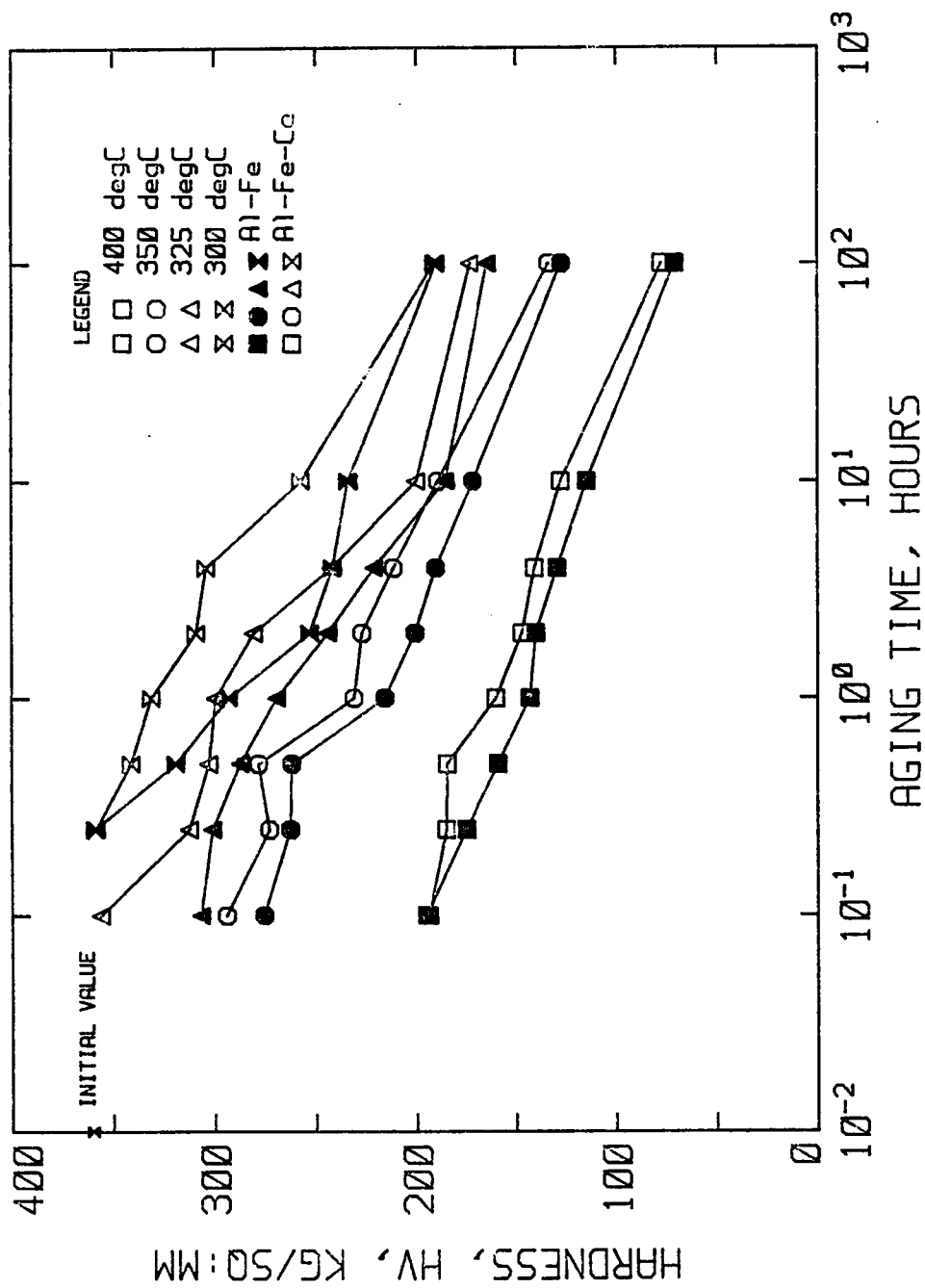


Figure 45. Microhardness vs. aging time plot for the Al-8 Fe and Al-8 Fe-3.4 Ce alloys at 300, 325, 350, and 400 °C.

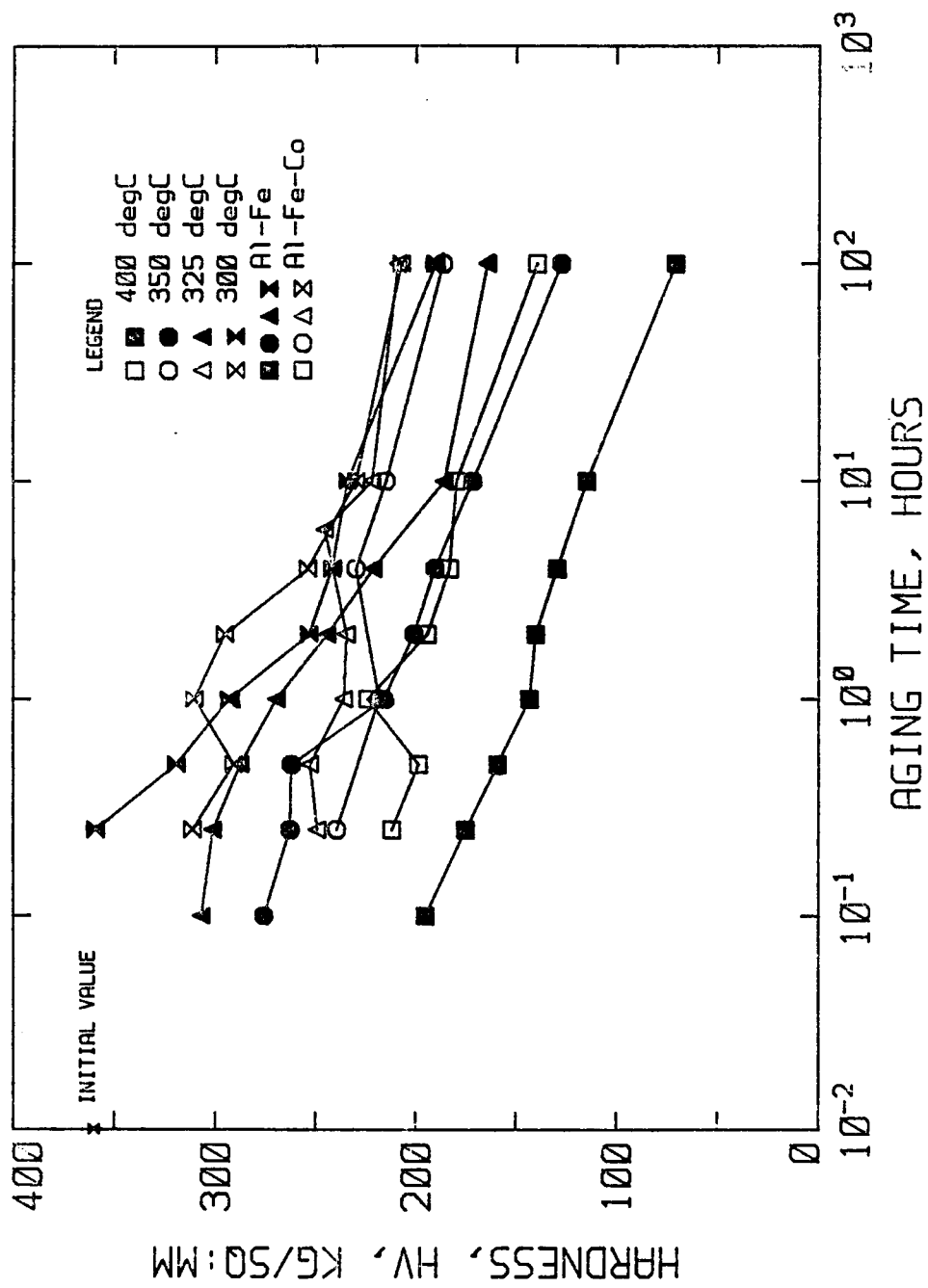


Figure 46. Microhardness vs. aging time plot for the Al-8 Fe and Al-8 Fe-6 Co alloys at 300, 325, and 400 °C.

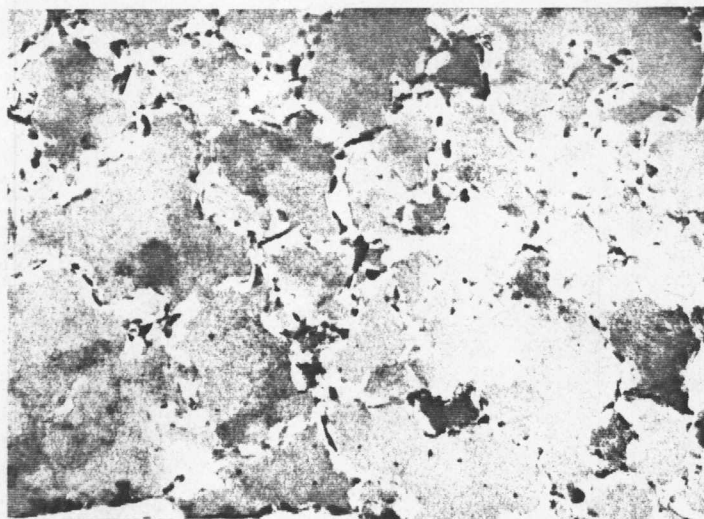
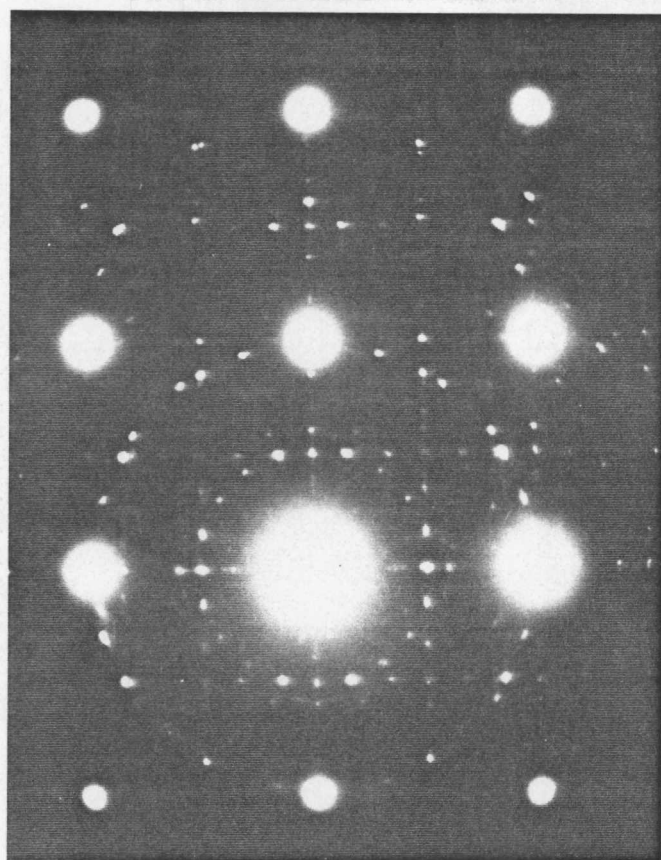
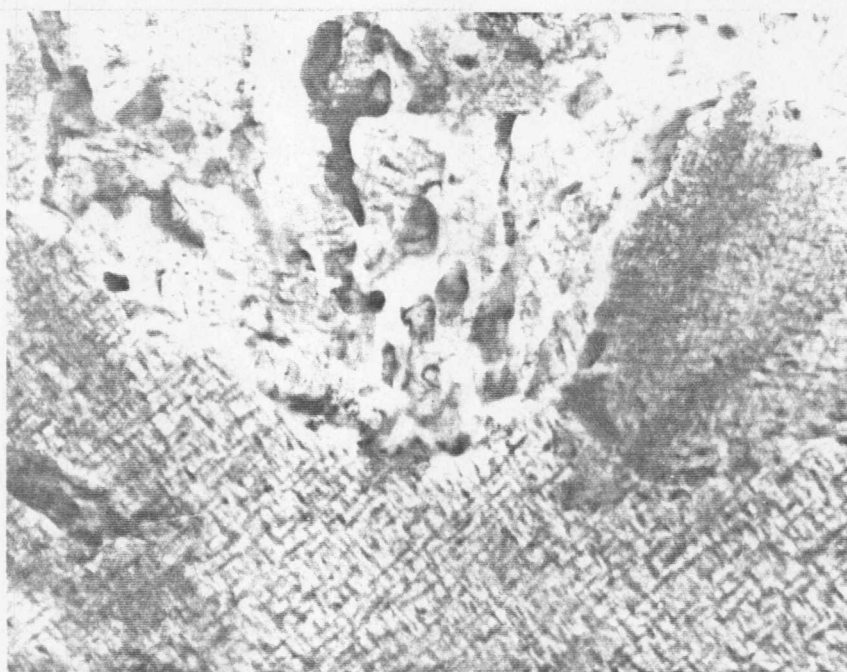


Figure 47. Al-8 wt% Fe aged at 300 °C for 1 hour, TEM, 62,000X. Large incidence of grain boundary precipitation.



Figure 48. Al-8 wt% Fe aged at 300 °C for 100 hours, TEM, 62,000X. Complete transformation to oriented needles of Al₃Fe, θ', in the grains. The grain boundary phase is still Al₆Fe.



● 020	● 220
x ₀₀₅	x ₀₂₅ x
x ₀₀₄	x ₀₂₄ x
x ₀₀₃ . .	x ₀₂₃ . . . x
x ₀₀₂	x ₀₂₂ x
x ₀₀₁	x ₀₂₁ x
● 000 . .	x ₀₂₀ . . . ● 200

● α-Al matrix

x FeAl₃ needle along [100]
α-Al

• FeAl₃ needle along [010]
α-Al

Figure 49. Al-8 wt% Fe aged at 300 °C for 100 hours, TEM, 62,000X. Diffraction pattern plus explanatory diagram obtained from the oriented needles of Al₃Fe, θ', phase.



Figure 50. Al-8 wt% Fe-3.4 wt% Ce aged at 300 °C for 1 hour, TEM, 62,000X. Formation of fine spheroidal zones, θ'' , in the grain. Fine precipitation at the grain boundary.



Figure 51. Al-8 wt% Fe-3.4 wt% Ce aged at 300 °C for 10 hours, TEM, 62,000X. Enhanced precipitation in the grain as well as at the grain boundary.

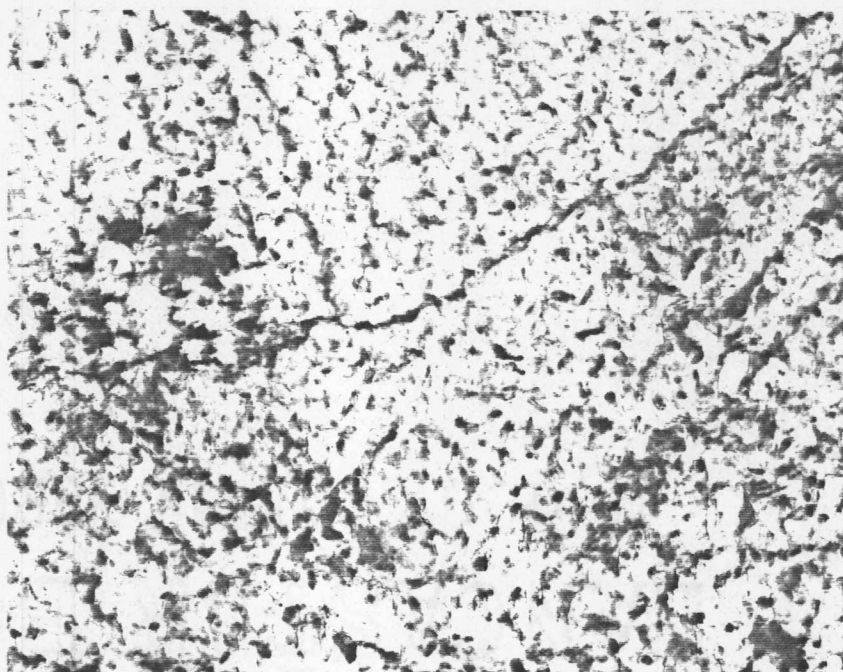


Figure 52. Al-8 wt% Fe-3.4 wt% Ce aged at 300 °C for 10 hours, TEM, bright field, 180,000X. Fine cellular structure.

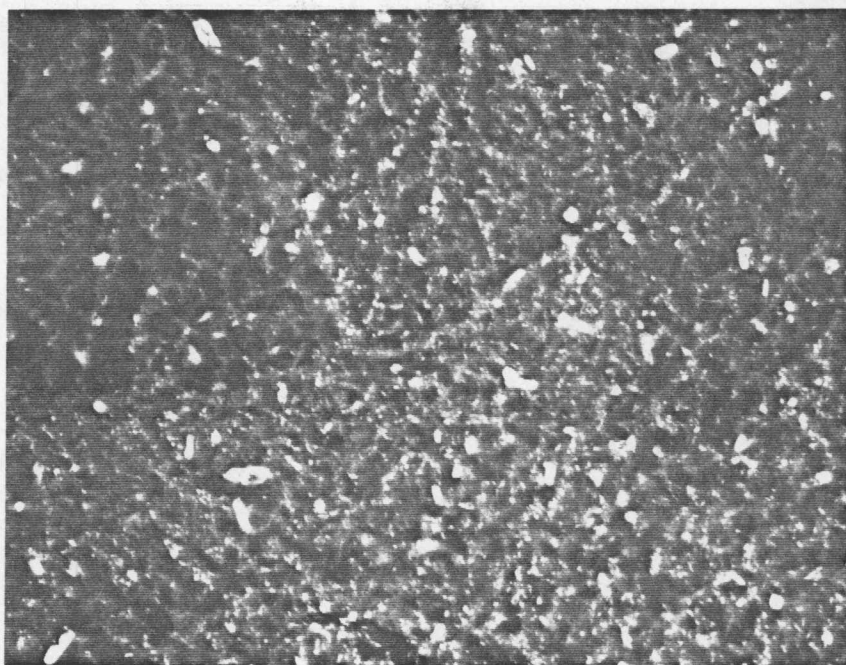


Figure 53. Al-8 wt% Fe-3.4 wt% Ce aged at 300 °C for 10 hours, TEM, dark field, 180,000X. Fine cellular structure.

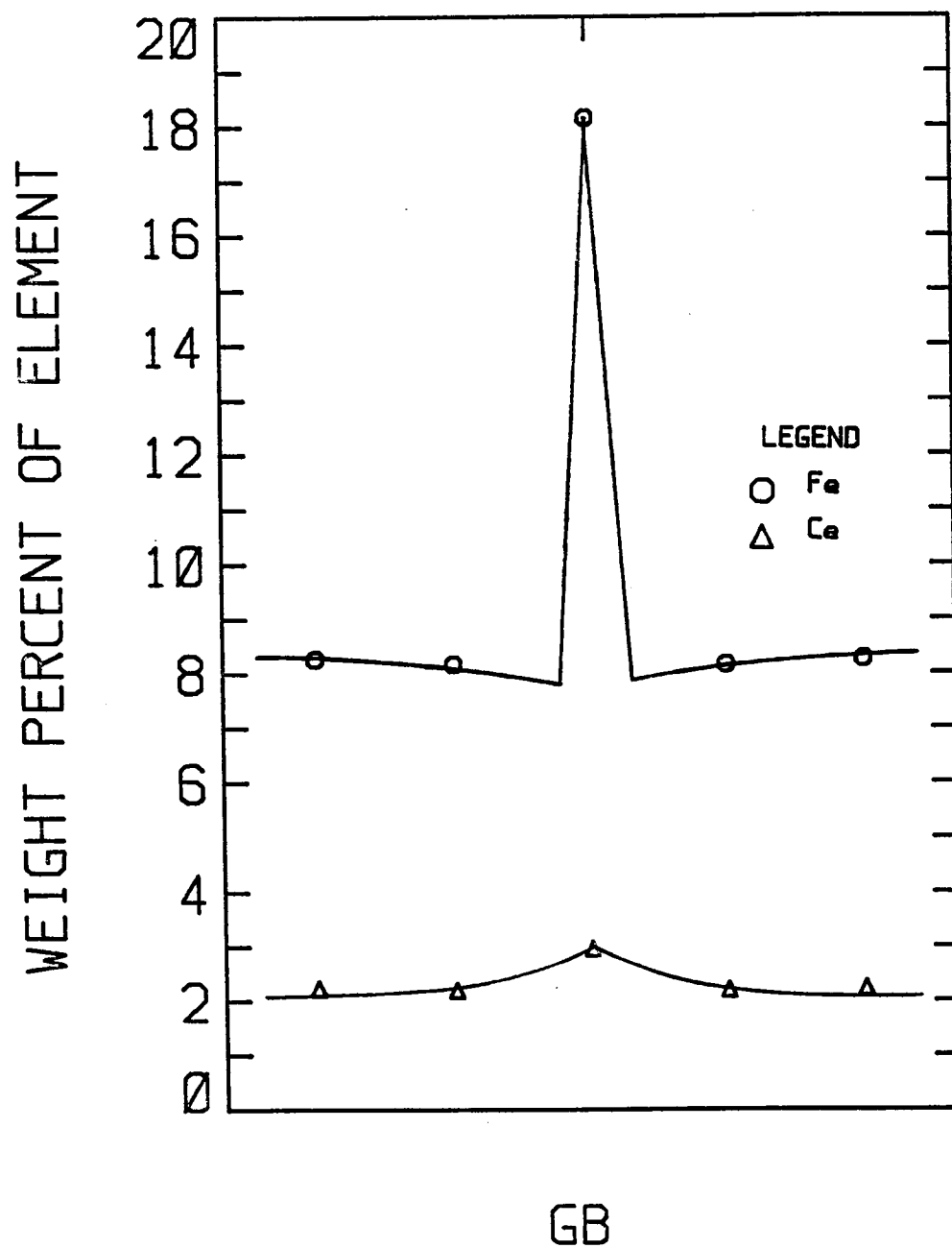


Figure 54. EDAX microanalysis across the grain boundary precipitate for Al-8 wt% Fe-3.4 wt% Ce alloy aged at 300 °C/10 hours.



Figure 55. Al-8 wt% Fe-3.4 wt% Ce aged at 300 °C for 100 hours, TEM, 253,000X. Coarse spheroidal, θ'' , precipitate in the grain. Large globular and angular shape precipitated at the grain boundary.

values. Earlier researchers (20) have shown that this globular phase is metastable Al_6Fe . Identification of this metastable phase was made based on this earlier observation and subsequently confirmed with an EDAX microanalysis and electron diffraction. For samples annealed at 10 hours, growth of this grain boundary phase was observed (Figure 51). A fine precipitate was observed to form in the grain. This precipitate gives extra reflections in the diffraction pattern apart from the ring pattern seldom observed in the as quenched specimens. Limited evidence of second phase at the cell walls was observed which is highlighted in the dark field mode with the objective aperture placed around the strongest ring in the diffraction pattern (Figures 52, 53).

EDAX analysis of the sample annealed at 300 °C for 10 hours showed a variation in the iron concentration across the grain boundary as shown in Figure 54. A narrow region near the grain boundary is depleted of iron with the grain boundary iron concentration observed at 18 wt% in the small volume irradiated. A slight increase in cerium content at the grain boundary was also noted. For samples annealed at 300 °C for 100 hours significant microstructural differences were observed for the Al-8 wt% Fe and Al-8 wt% Fe-3.4 wt% Ce (Figures 48 and 55). The metastable phase (diamond cubic) observed for Al-Fe alloys for samples annealed at 300 °C for 10 hours transforms to well-oriented needles of Al_3Fe (θ'). The Al_3Fe needles have an orientation relationship with the aluminum matrix as explained in Figure 49. While the transformation in the grain is seemingly complete, the phase at the grain boundary is still metastable Al_6Fe . The exact reason for

this behavior could not be determined. Jones (67) has suggested the possibility that nonequilibrium segregation of iron to the grain boundary is sufficient to nucleate Al_6Fe but not Al_3Fe . It should be noted, however, that no such transformation was observed in the ternary alloy annealed under the same conditions. Figure 55 shows the coarsening of the spheroidal precipitates, as well as large precipitate phases at the grain boundary and triple junctions. The precipitates are globular and angular shaped. This effect is thus attributed to the presence of cerium in the ternary alloy. This effect was corroborated for a number of specimens for this annealing treatment as well as at higher temperatures.

Aging Studies at 325 °C

TEM micrographs of all samples aged at 325 °C are shown in Figures 56-60. Annealing studies for specimens annealed at 1 and 10 hours for the Al-8 wt% Fe-3.4 wt% Ce and Al-8 wt% Fe showed a similar precipitation process as reported above for 300 °C (Figures 56, 57, 58). The grain boundary phase, identified as Al_6Fe was more readily observed in specimens annealed for 1 hour, due to increased diffusion of the atomic species aided by the slightly higher temperature. Figures 58 and 59 show no significant change in the precipitate morphology in the grain for samples annealed for 10 hours. Furrer identified a metastable precipitate, later identified as monoclinic FeAl_3 (θ'), and has presented a series of diffraction patterns. Our diffraction evidence suggests the formation of θ' phase, Figure 60,

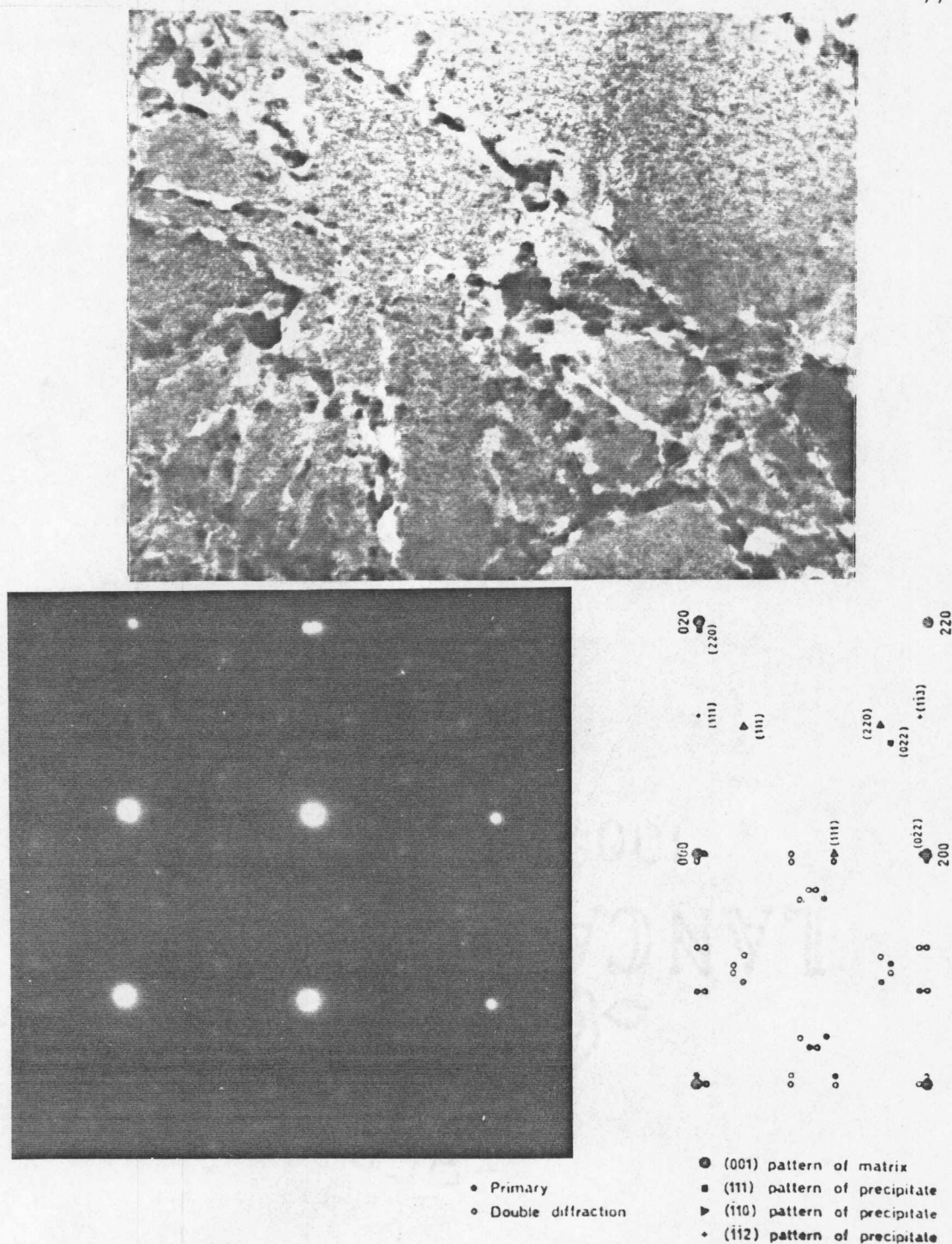


Figure 56. (a) Al-8 wt% Fe aged at 325 °C for 10 hours, TEM, 62,000X; (b) diffraction pattern for θ'' precipitates plus reference diagram.

Source: Jacobs et al., J. Mat. Sci. 9 (1974), p. 1638.

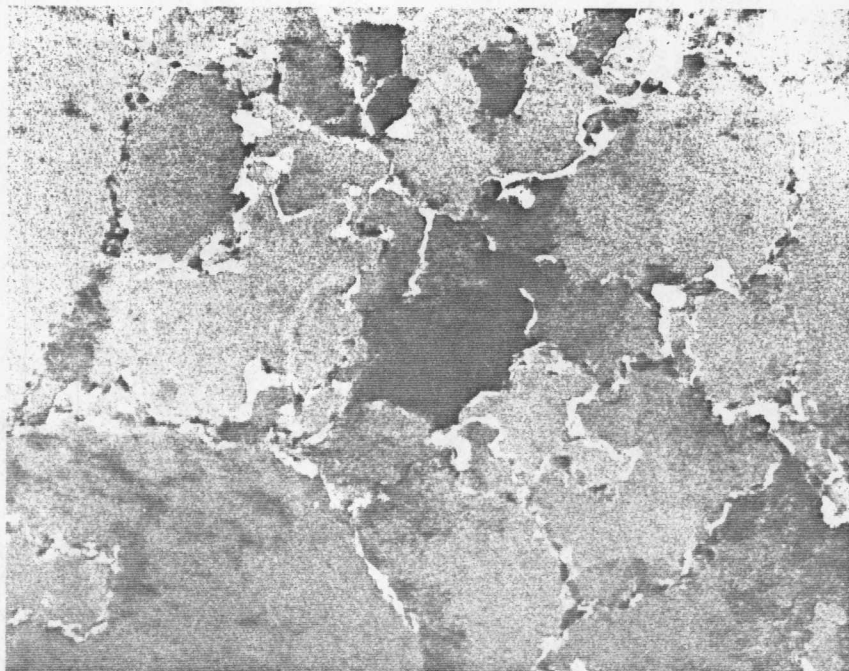


Figure 57. Al-8 wt% Fe-3.4 wt% Ce aged at 325 °C for 1 hour, TEM, 62,000X. Precipitation of spheroidal zones, θ'' , in the grain. Precipitation of metastable Al_6Fe at the grain boundary.

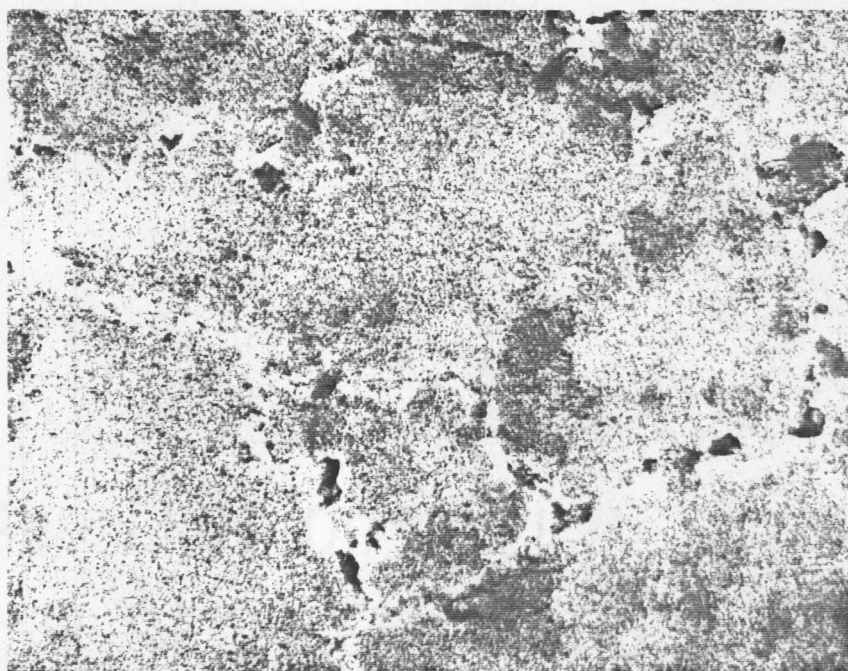


Figure 58. Al-8 wt% Fe-3.4 wt% Ce aged at 325 °C for 10 hours, TEM, 62,000X.

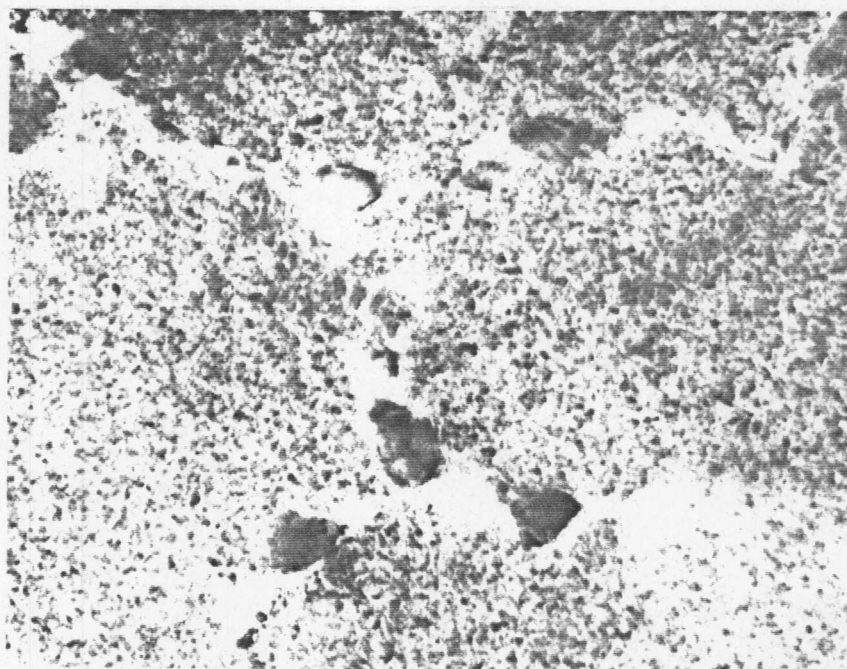


Figure 59. Al-8 wt% Fe-3.4 wt% Ce aged at 325 °C for 10 hours, TEM, 165,000X.

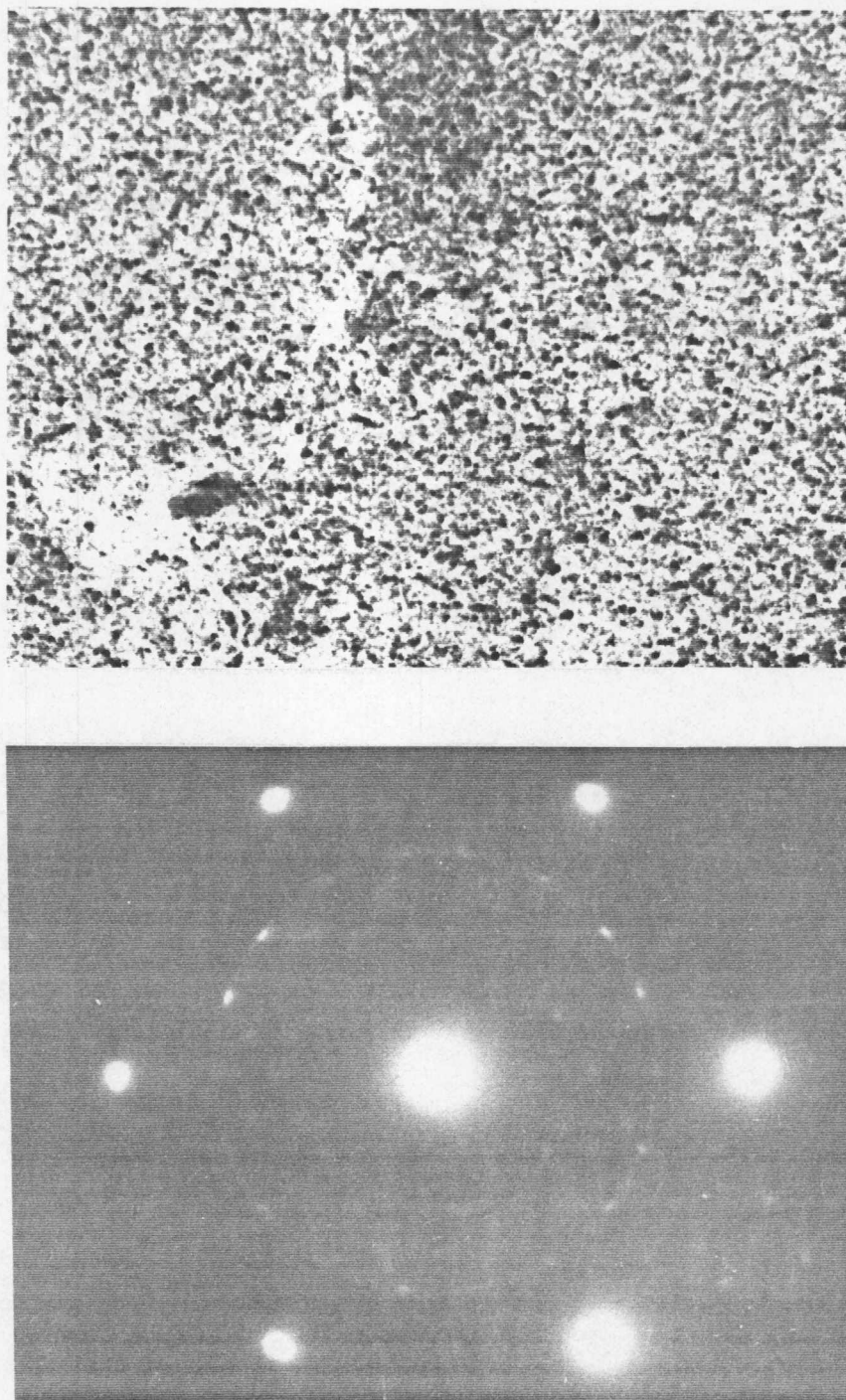


Figure 60. (a) Al-8 wt% Fe-3.4 wt% Ce aged at 325 °C for 10 hours, TEM, 165,000X; (b) diffraction pattern shows spots for spheroidal zones, θ'' , and Al_3Fe , θ' precipitates.

however, fine needles as reported by Furrer (39) are not observed at any of these treatments. It is likely that the precipitate is cerium modified initially nucleating as very fine particles that cannot be readily distinguished in the bright field or the dark field mode in the TEM. However, at higher temperatures this needle shape phase does form though the transformation is much slower in the ternary alloy.

Aging Studies at 350 °C

TEM micrographs of all samples aged at 350 °C are shown in Figures 61-66. Microhardness data showed a significant drop in hardness over time with the largest drop occurring in the first hour of annealing. Figure 63 shows large incidence of grain boundary precipitation for times as short as 30 minutes. In the later stages this drop slows down with the dominant process, probably being the slow diffusion of the alloying elements from the grain center to the grain edges. This is due to the concentration gradient set up because of the local depletion of the thin region adjacent to the grain boundary. It was noted that precipitates were larger and more numerous around the smaller grains possibly due to the shorter diffusion distances involved (Figure 64). Al-8 wt% Fe-3.4 wt% Ce alloy shows no visible evidence of transformation to oriented needles for specimens annealed for one hour. Figures 61 and 65 show micrographs for Al-8 wt% Fe and Al-8 wt% Fe-3.4 wt% Ce annealed for 10 hours. Partial transformation to oriented needles of monoclinic Al_3Fe has occurred in the ternary

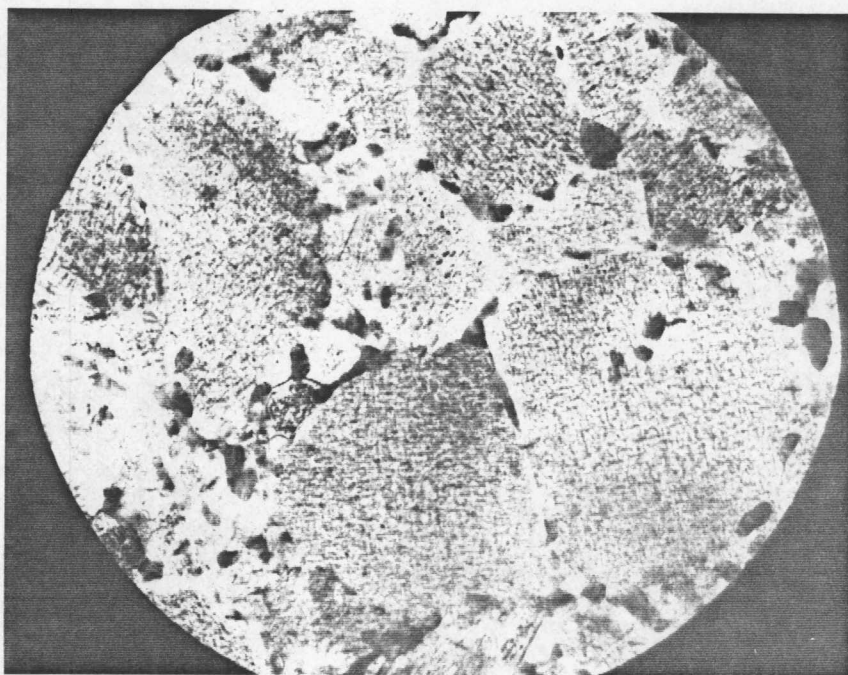


Figure 61. Al-8 wt% Fe aged at 350 °C for 10 hours, TEM, 62,000X. Well-developed Al₃Fe, θ', needles in the grain.

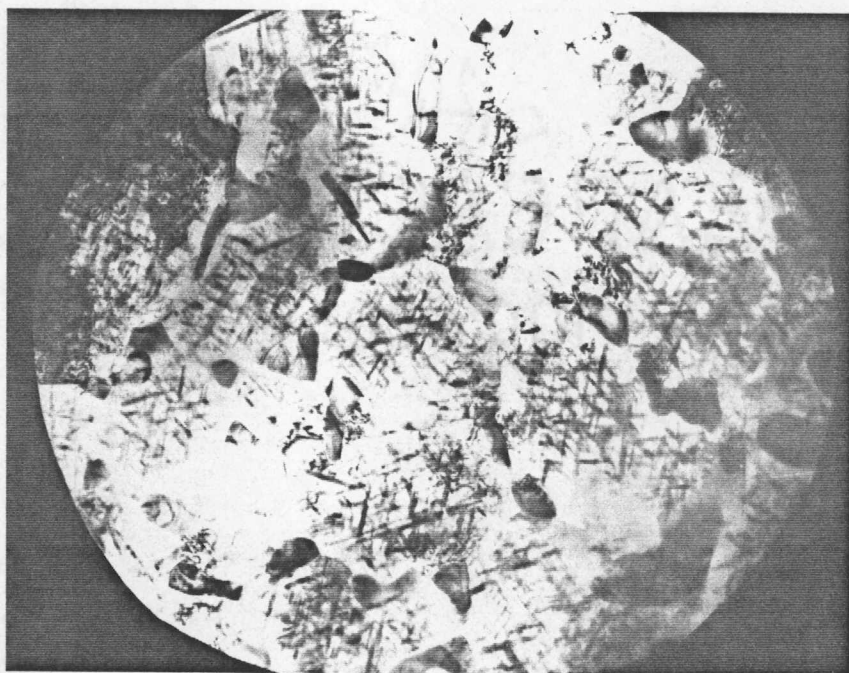


Figure 62. (a) Al-8 wt% Fe aged at 350 °C for 100 hours, TEM, 62,000X. Precipitate coarsening in the grains.
(b) Al-8 wt% Fe aged at 350 °C for 100 hours, TEM, 62,000X. Diffraction pattern plus explanatory diagram of Al_3Fe precipitate at the grain boundary.

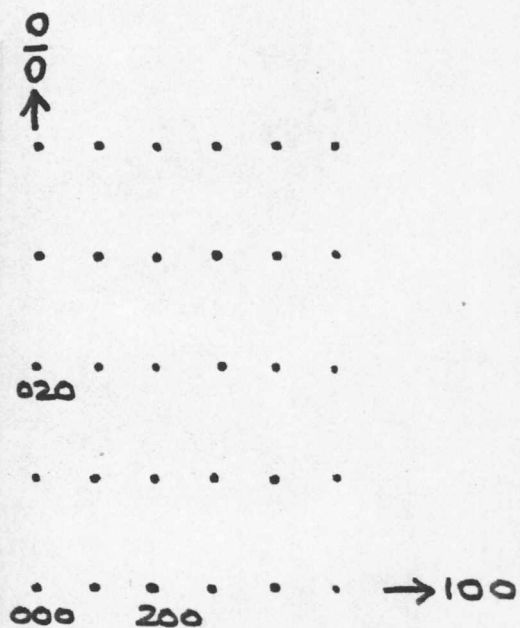
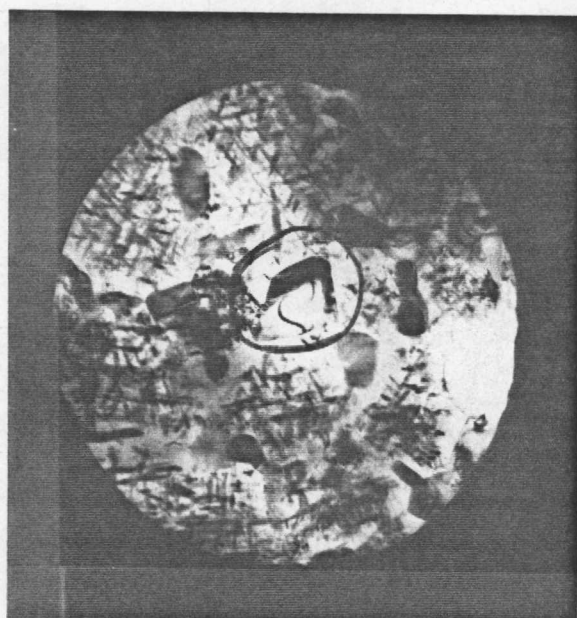
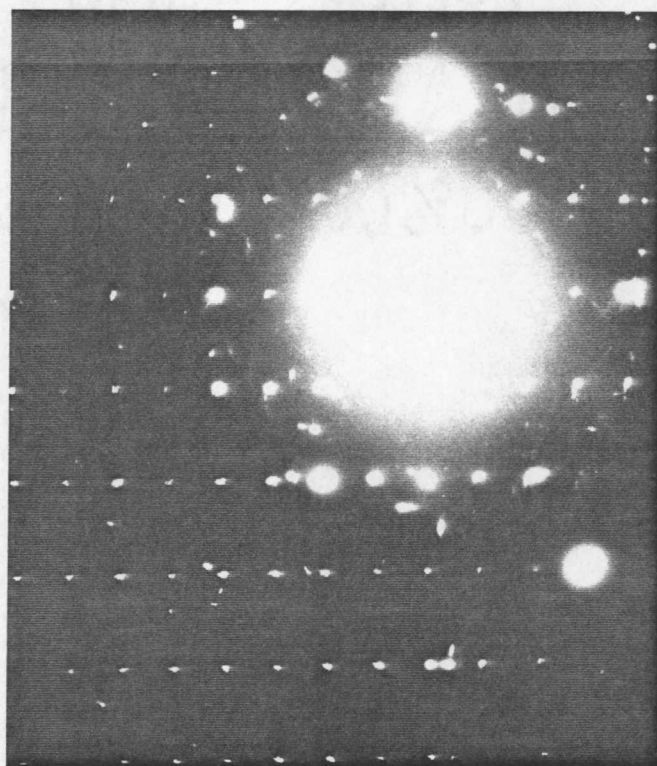


Figure 62 (continued)

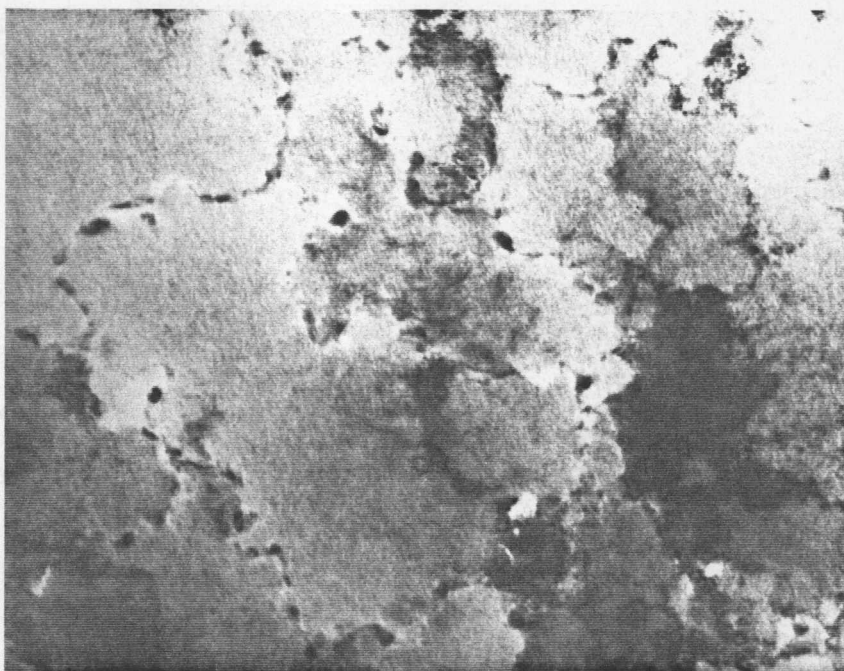


Figure 63. Al-8 wt% Fe-3.4 wt% Ce aged at 350 °C for 30 minutes, TEM, 62,000X. Shows evidence of grain boundary precipitation.

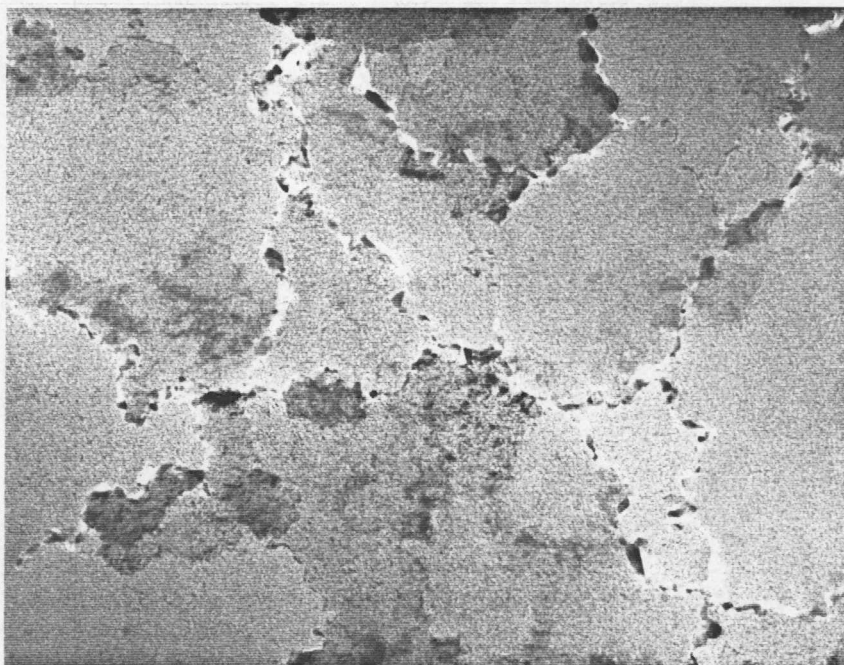


Figure 64. Al-8 wt% Fe-3.4 wt% Ce aged at 350 °C for 1 hour, TEM, 62,000X. Formation of spheroidal zones in the grains.

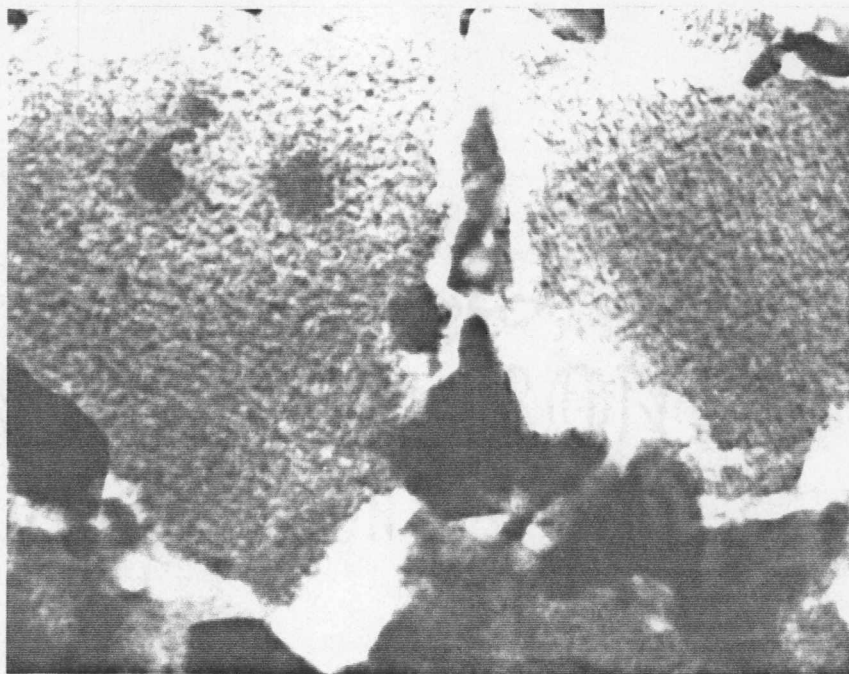


Figure 65. Al-8 wt% Fe-3.4 wt% Ce aged at 350 °C for 10 hours, TEM, 165,000X. Microstructure shows a mix of spheroidal, θ'' , zones and Al_3Fe , θ' , needles in the grain.

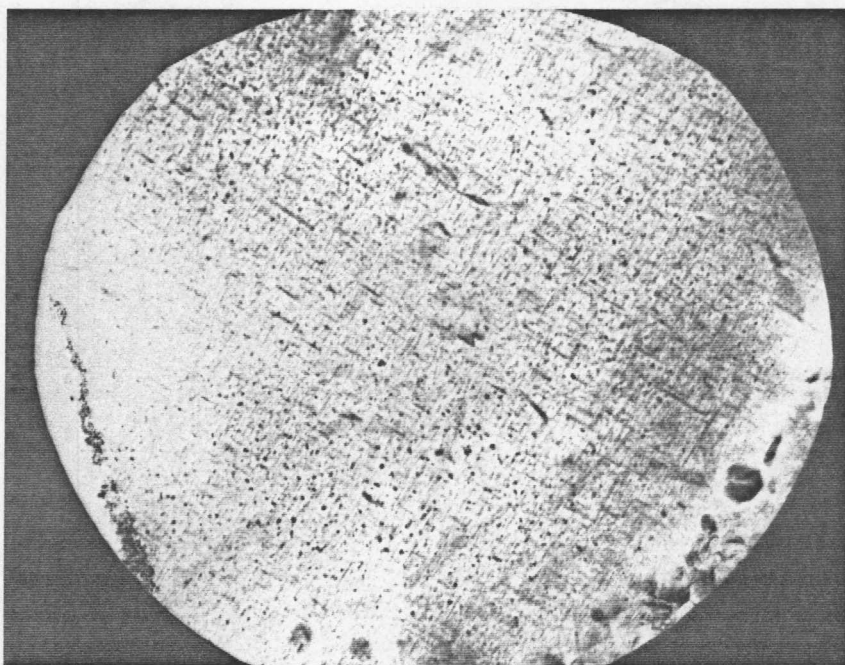


Figure 66. Al-8 wt% Fe-3.4 wt% Ce aged at 350 °C for 100 hours, TEM, 62,000X. Complete transformation to Al_3Fe needles in the spherulitic grain. Note the large grain size.

alloy. These needles have the growth direction as $[010]$ and its b axis provides a good match with the aluminum matrix (b axis for Al_3Fe = .8083 nm is about twice that for aluminum = .4049 nm). These needles of Al_3Fe have grown to about 20 nm in the ternary alloy. Figure 61 shows that the transformation for the binary alloy is almost complete with the oriented needles growing to a length of about 35 to 40 nm, almost twice in size compared to the binary alloy. The precise role of cerium in this transformation is not yet clear. For example, it could not be determined whether cerium is present in the precipitate itself, or if it is just a surface effect. EDAX microanalysis studies of regions in the grains show significant amounts of cerium. It is likely that cerium has some effect in the nucleation process, and it is altering the conditions thus slowing down the formation of these needles. Figures 62 and 66 show the micrographs for the binary and ternary alloys aged for 100 hours. Precipitate coarsening is readily visible in the binary alloy. The metastable phase, Al_6Fe , at the grain boundary was observed to partially transform to the stable Al_3Fe phase. Figure 62b shows diffraction evidence of the Al_3Fe phase formation at the grain boundary for the binary alloy aged at 350 °C for 100 hours. For the ternary alloy the transformation, in the grain, to oriented needles of Al_3Fe appears to be complete. Little precipitate coarsening was observed for the ternary alloy at this treatment.

Aging Studies at 400 °C

Microhardness data showed a rapid drop in hardness to half its as quenched value in about 15 minutes. For the binary alloy annealed for 1 hour, Figure 67 shows that the transformation to oriented needles is complete. For the ternary alloy, Figures 68 and 69 show that such transformation has begun and the microstructure is a mix of spheroidal metastable phase and the needle phase. Figure 70 shows a large spherulitic type of grain with a significantly larger dimension than the neighboring grains. Figure 71 shows the diffraction pattern obtained from this grain showing θ'' and θ' precipitate reflections. For samples annealed for 10 hours the binary alloy shows coarsening of the needle phase (Figures 72 and 73). For the ternary alloy this transformation appears to be complete (Figures 74 and 75). Correlation with microhardness data show that the hardness drop was very slow during the initial nucleation and growth of this θ' phase. Comparing Figures 74 and 61 shows that the precipitation for the ternary alloy at 400 °C is almost similar to that for binary alloy at 350 °C, both samples being aged for 10 hours. Cerium thus introduces a roughly 50 °C differential in the annealing treatments giving similar results. It appears that cerium stabilizes the diamond cubic, θ'' , phase. The θ'' phase was observed to exist in minor traces even after aging at 400 °C for 10 hours. No evidence of θ'' phase was observed in the binary alloy at the same treatment.

Figure 76 shows the microanalysis plot of the alloying element concentrations close to the grain boundary. While the average

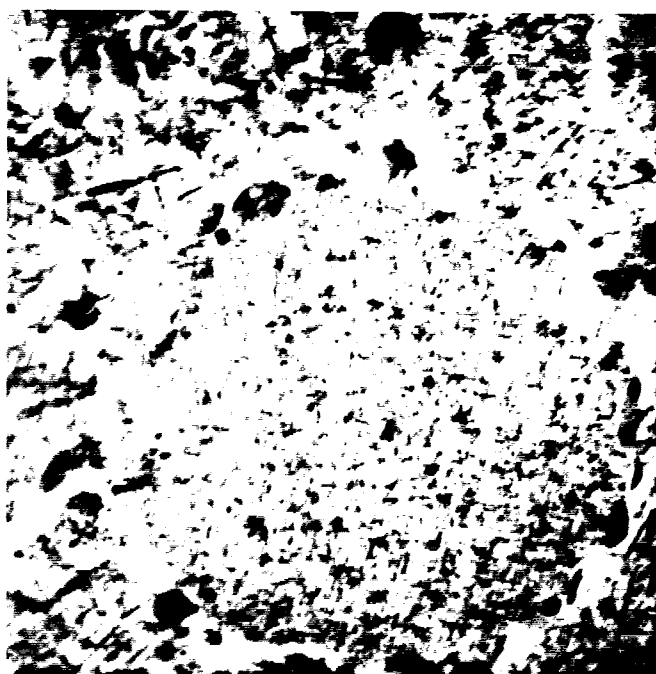


Figure 67. Al-8 wt% Fe aged at 400 °C for 1 hour, TEM, 62,000X. Oriented needles of Al₃Fe in the grain.

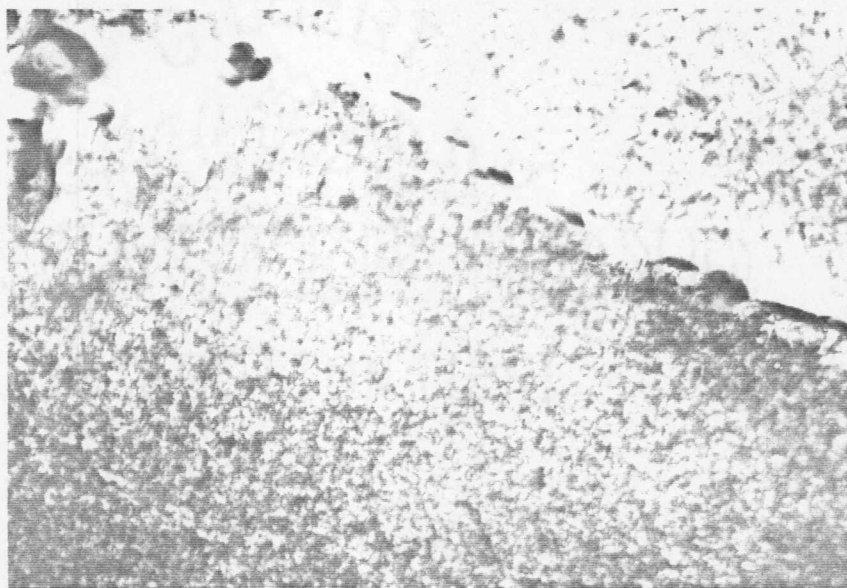


Figure 68. Al-8 wt% Fe-3.4 wt% Ce aged at 400 °C for 1 hour, TEM, 62,500X. Microstructure shows a mix of θ'' and θ' precipitates.

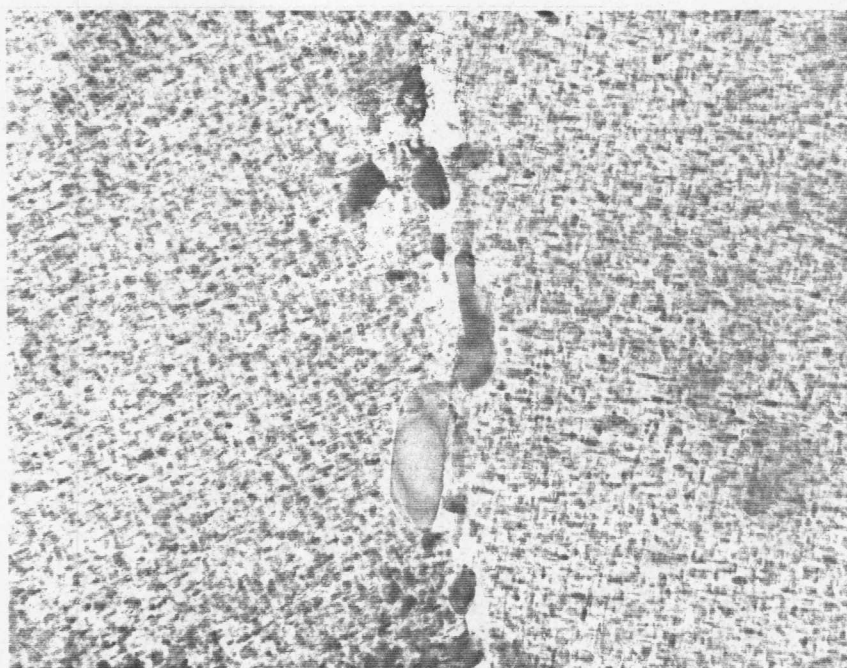


Figure 69. Al-8 wt% Fe-3.4 wt% Ce aged at 400 °C for 1 hour, TEM, 193,000X. Partial transformation to oriented needles of Al_3Fe phase in the grain.

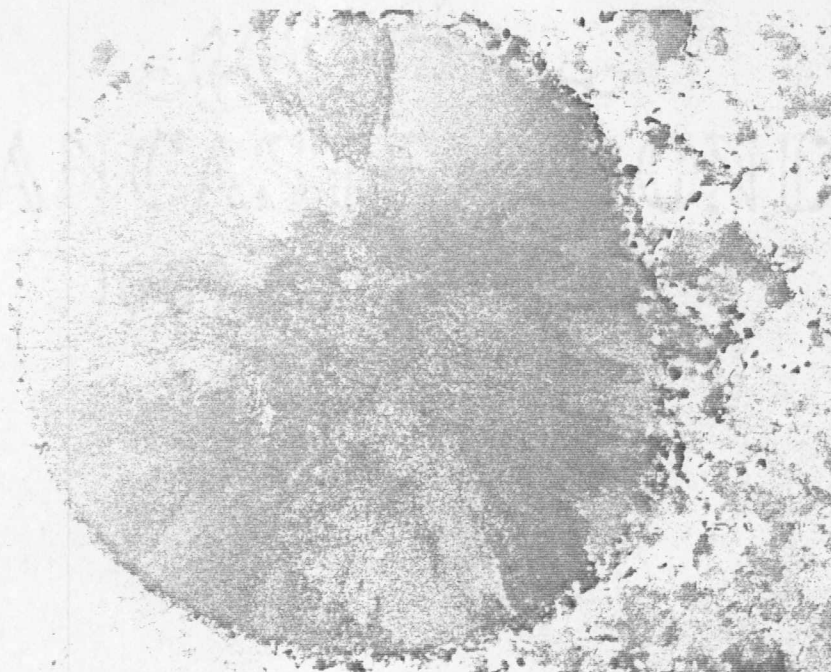


Figure 70. Al-8 wt% Fe-3.4 wt% Ce aged at 400 °C for 1 hour, TEM, 62,000X. View of circular grain for diffraction pattern. Note no coarse particles present as in Figure 36 (p. 54).

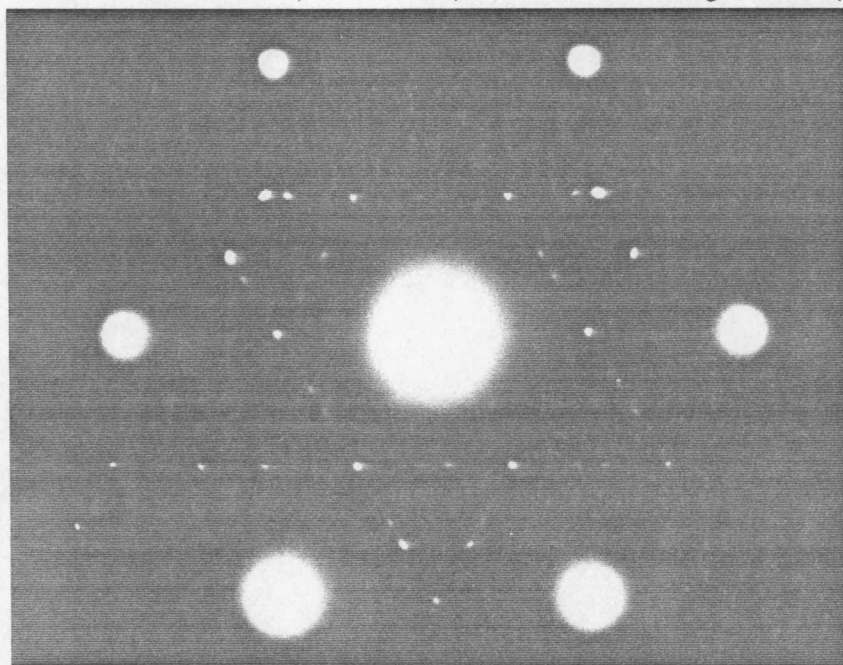


Figure 71. Diffraction pattern of the grain, (111) beam direction. Shows θ'' and θ' precipitate spots in the pattern.



Figure 72. Al-8 wt% Fe aged at 400 °C for 10 hours, TEM, 150,000X. Precipitate coarsening at the grain boundary.



Figure 73. Al-8 wt% Fe aged at 400 °C for 10 hours, TEM, 150,000X. Remnants of regions with oriented Al_3Fe needles.

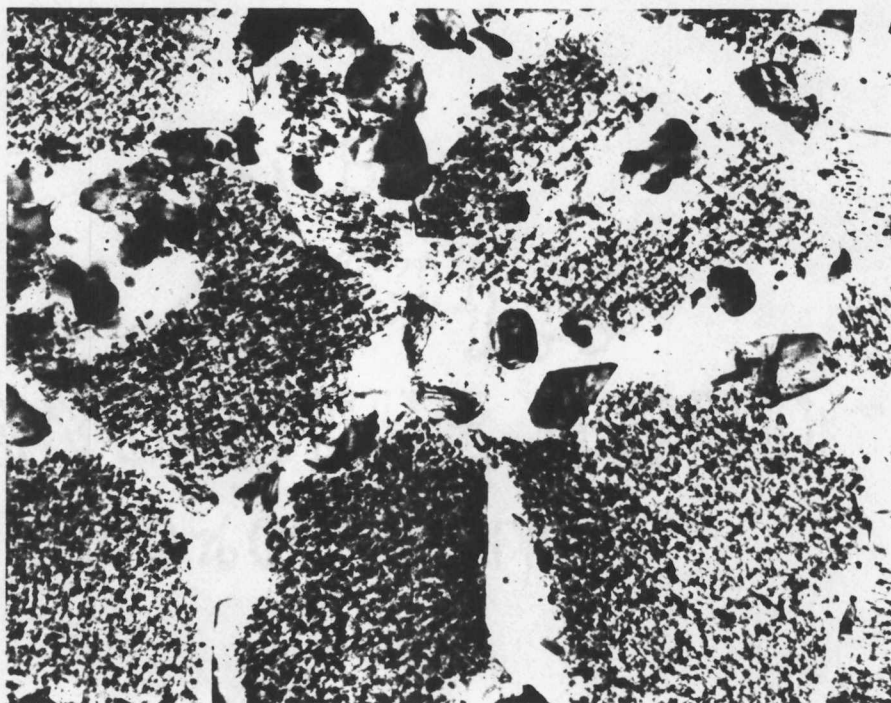


Figure 74. Al-8 wt% Fe-3.4 wt% Ce aged at 400 °C for 10 hours, TEM, 62,000X. Fine precipitation of Al₃Fe needles.

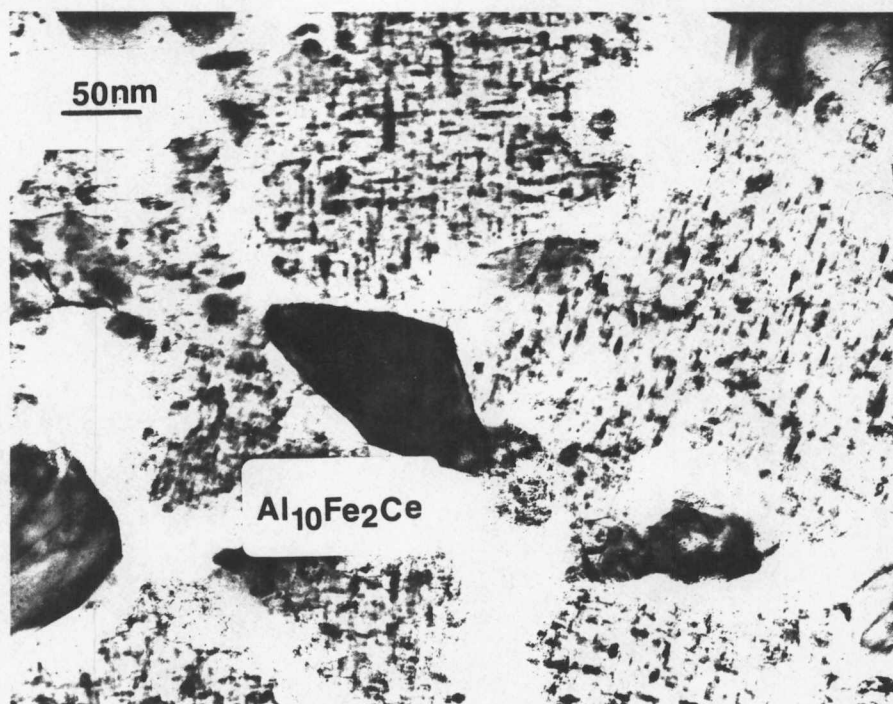


Figure 75. Al-8 wt% Fe-3.4 wt% Ce aged at 400 °C for 10 hours, TEM. Preferential formation of the stable ternary phase at the grain junction.

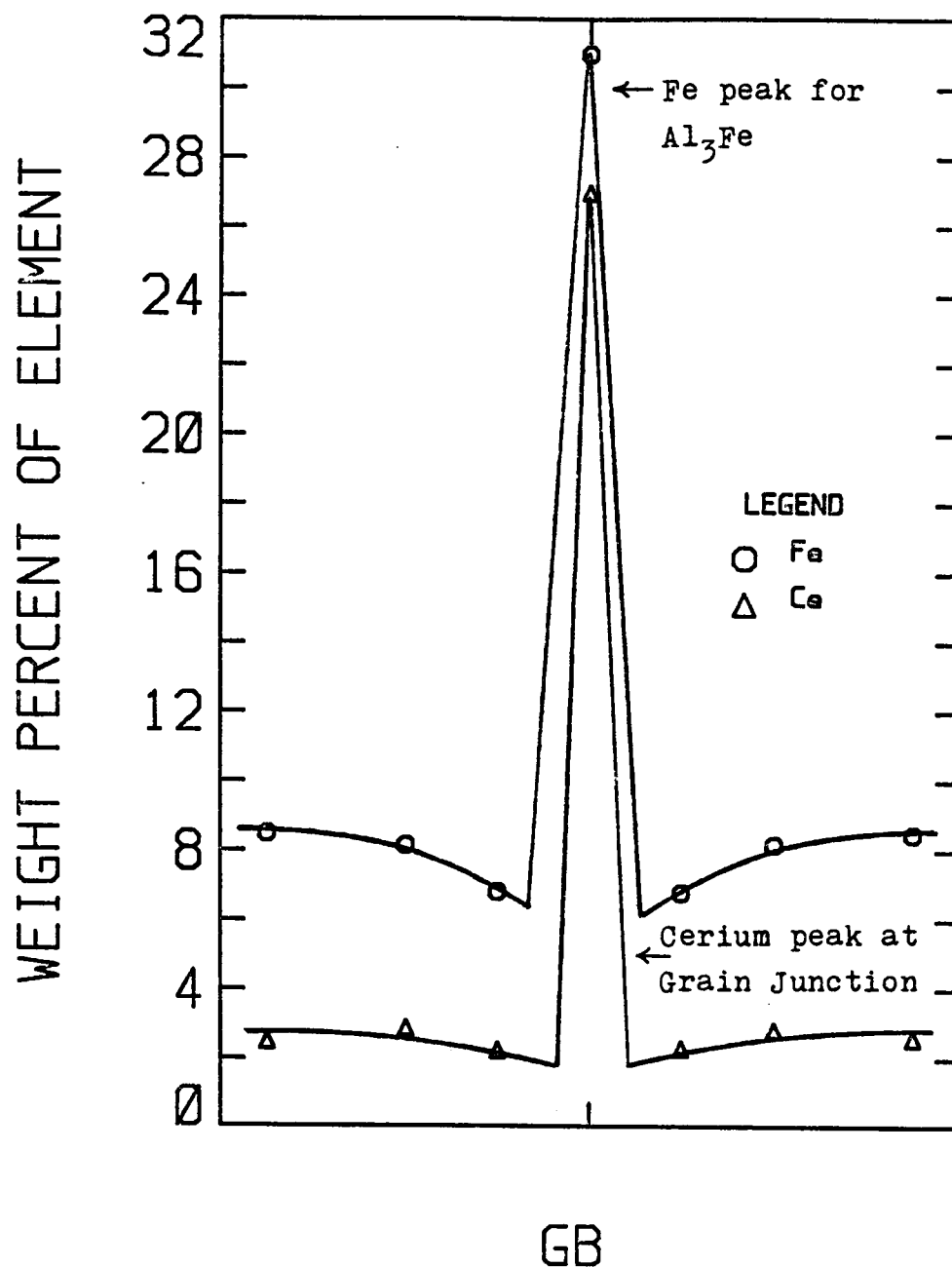


Figure 76. EDAX microanalysis across the grain boundary and grain junction precipitates in Al-8 wt% Fe-3.4 wt% Ce alloy aged at 400 °C for 10 hours.

concentrations of cerium at the grain boundary was less than 1 wt%, it shows a significantly large concentration at the grain junctions. Though this effect was not observed at each and every grain junction, this observation was corroborated for a large number of grain junctions on microanalysis. This effect is dealt with in greater detail in the section for microanalytical studies.

Figures 77, 78, and 79 show the microstructure of the binary and ternary alloys aged at 400 °C for 100 hours. Coarsening of the needles is observed in both the alloys. At this treatment, formation of incoherent Al_3Fe is observed in both alloys, and no orientation relationships were observed in either alloy. For the binary alloy some grains are almost transparent to the electron beam indicating that iron has diffused to the grain boundary (Figure 77). The same trend was observed in the ternary alloy but to a lesser extent. Note that hardness data showed no difference between the binary and the ternary alloy for samples annealed at 400 °C for 10 hours. In addition, it showed little difference for samples annealed at 300 °C for 100 hours while the microstructures were completely different. It is concluded that formation of these needles by itself does not significantly reduce hardness, as was the case for samples aged at 300 °C for 100 hours. Further support for this argument is available from microstructural evidence of the binary alloy aged for 10 hours at 325 °C and 350 °C, respectively (Figures 56 and 61, pp. 77 and 82). Figure 56 shows the grain interior to consist of a dense distribution of θ'' particles, as confirmed by diffraction evidence (Figure 56b).

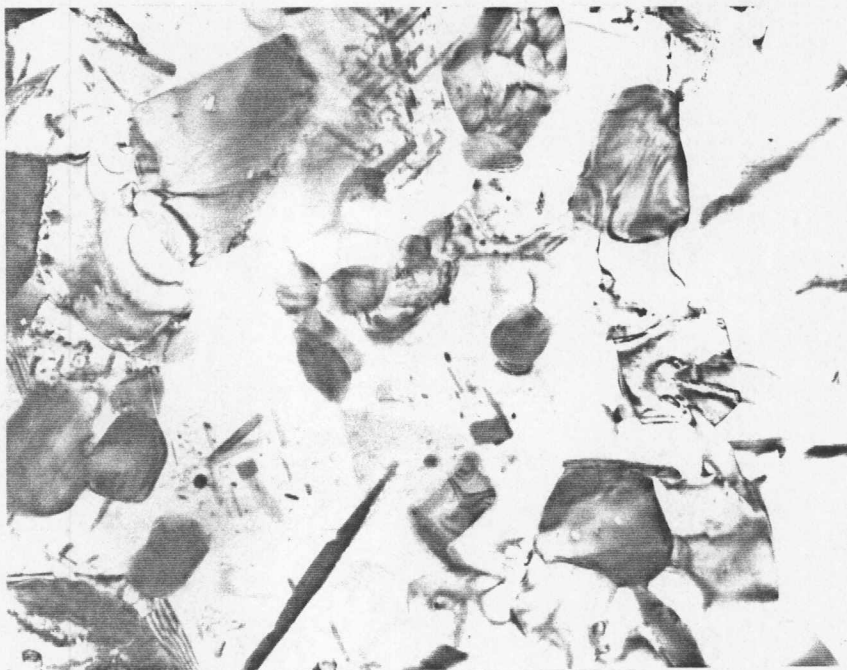


Figure 77. Al-8 wt% Fe aged at 400 °C for 100 hours, TEM, 62,000X. Clear regions visible in the grains.

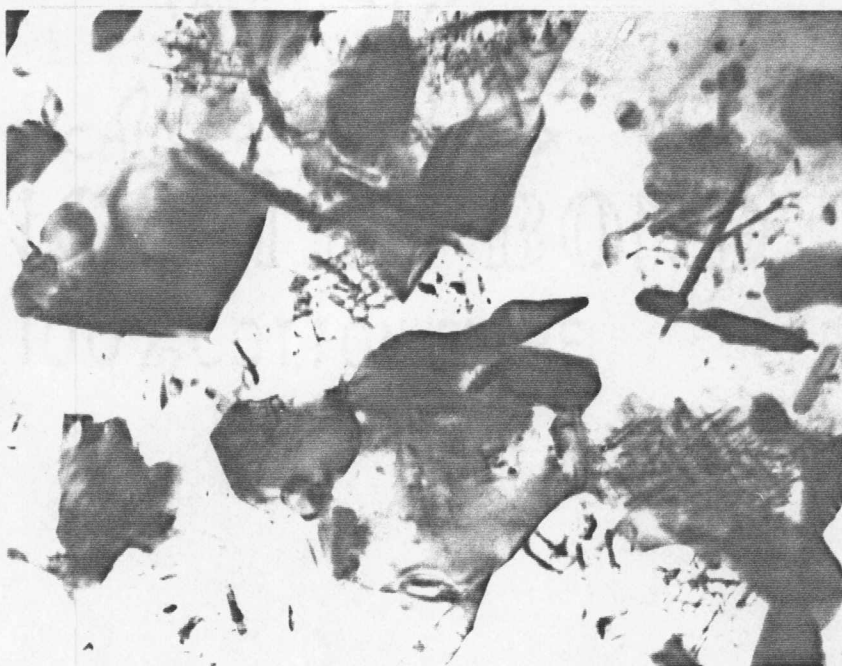


Figure 78. Al-8 wt% Fe aged at 400 °C for 100 hours, TEM, 62,000X. Extensive precipitate coarsening and growth of spherodized Al_3Fe up to 0.5 micron size.

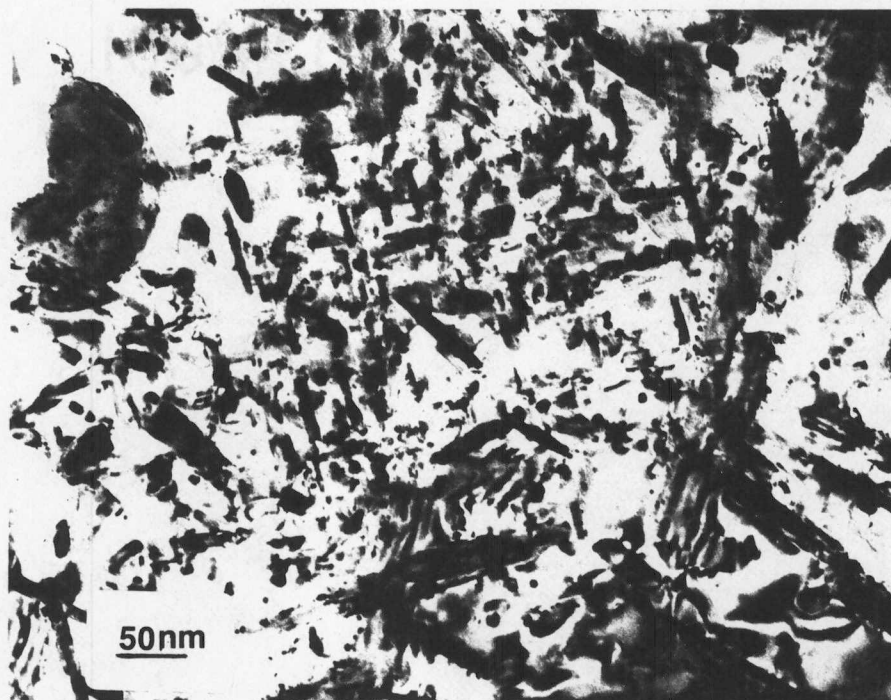


Figure 79. Al-8 wt% Fe-3.4 wt% Ce aged at 400 °C for 100 hours, TEM. Large needles of Al_3Fe at random orientations.

In comparison, Figure 61 (p. 82) shows that the transformation to θ' particles is almost complete. However, at this stage the difference in hardness values was a minor 15 kg/sq:mm. The initial drop in hardness can be better explained by the formation of the grain boundary phase. Slower rate of formation and growth at lower temperatures results in slower drops in hardness values. Large massive grain boundary precipitation at high temperatures would then account for the large drops in hardnesses observed at higher temperatures for times as short as 15 minutes. The average indentation being about 20 microns at 300 °C the hardness measurements are essentially of the bulk phase (matrix) which is being denuded of its solid solution hardening. During the later stages of aging, formation of incoherent Al_3Fe and its subsequent coarsening would result in further drops in hardness. It is our contention that microhardness may be a misleading criteria to ascertain the beneficial effects of cerium. Comparing shape effects of the spheroidal precipitates to the needle shape, it is possible that mechanical properties would be different. However, at this moment no published data are available to the author.

In Situ Aging Studies

A few samples were annealed in the microscope to observe the precipitation and coarsening process in both alloys at 440 °C. For the binary alloy the transformation occurs very fast. After about 3 minutes time grain boundary precipitation occurs. This phase was identified as metastable Al_6Fe . Heterogenous nucleation of metastable

Al_6Fe was also observed to occur on the free surface of the thin foil. Thus nucleation process has an orientation relationship with the matrix as explained in Figure 80. After about 6 minutes the needle phase appears in the grains, with an orientation relationship with the matrix as explained earlier in Figure 49 (p. 70). Figure 80 shows the diffraction pattern obtained after aging 7 minutes at 440 °C. Note that the diffraction pattern shows spots for both Al_6Fe and Al_3Fe phases with specific orientation with respect to the matrix. After 15 minutes the transformation to Al_3Fe needles was complete with some coarsening apparent. At this point no Al_6Fe spots were observed in the diffraction pattern for the grain, indicating that the metastable phase had transformed to the stable phase. Figure 81 shows the microstructure of the sample after aging for 1 hour. Coarsening and incoherent formation of Al_3Fe phase is readily evident. Note that the Al_3Fe , θ' , phase started forming after about 6 minutes. Hence the metastable phase, θ'' , is definitely not stable at this temperature for the binary alloy. Due to the rapid transformation of the solid solution matrix, attempts to observe the formation of the θ'' phase were not successful. Hence it cannot be conclusively determined if the metastable phase, θ'' , forms at all. It is possible that at this high temperature of aging the transformation to the θ' phase occurs directly from the solid solution matrix.

A sample of the ternary alloy was similarly aged in situ at 330 °C. In this case the formation of the spheroidal zones, θ'' , was observed preceding the Al_3Fe , θ' , phase. The Al_3Fe phase starts

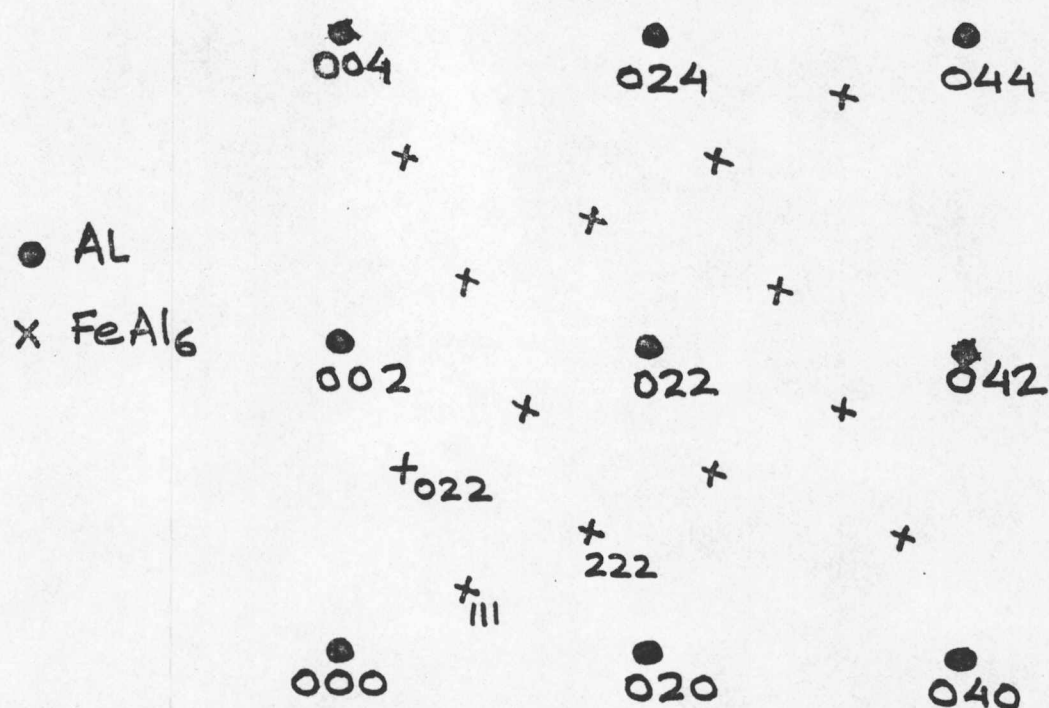
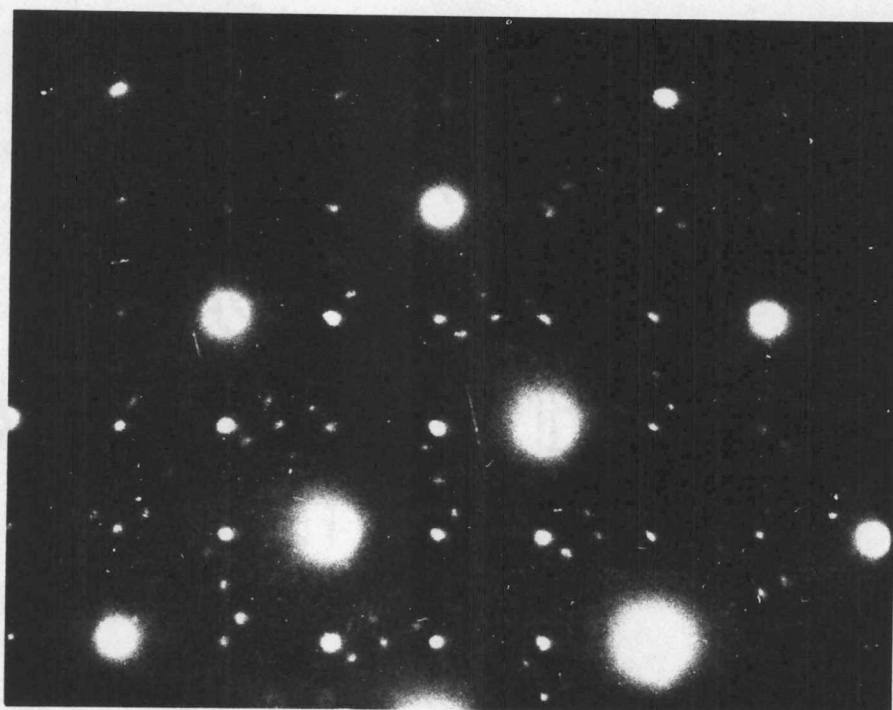


Figure 80. Al-8 wt% Fe-3.4 wt% Ce aged in situ at 440 °C/6 minutes. Diffraction pattern shows orientation relationship of heterogenously nucleated Al₆Fe with the aluminum matrix. $[111] \text{ Al}_6\text{Fe} // (042) \text{ Al}$ and $[011] \text{ Al}_6\text{Fe} // [100] \text{ Al}$.

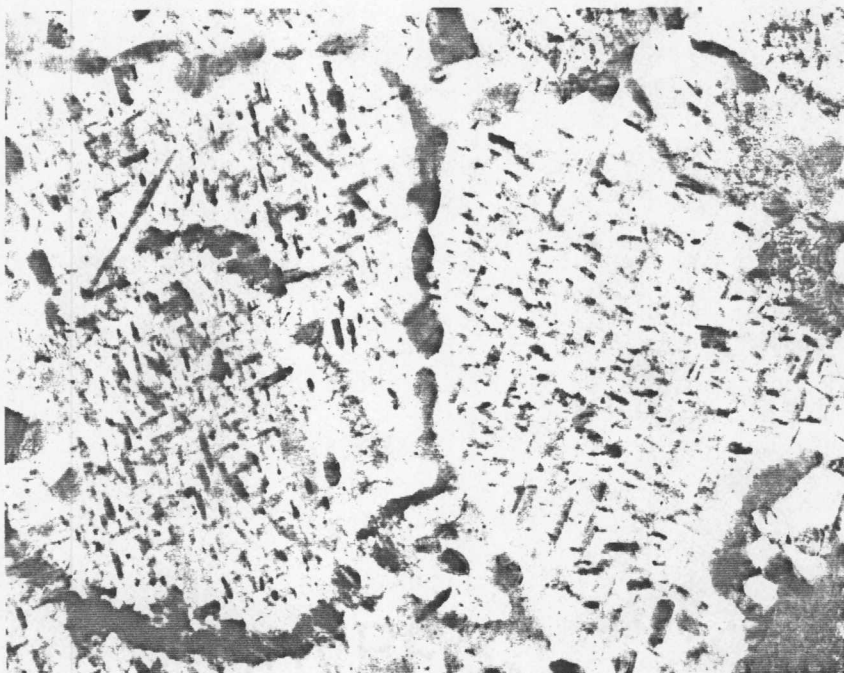


Figure 81. Al-8 wt% Fe aged in situ at 440 °C for 1 hour, TEM, 62,000X. Coarse needle precipitates in the grain.

appearing after about 30 minutes and continues to grow. This phase appears as rod-shaped compared to the needles in the binary alloy. The aspect ratio of this phase is different, 2 to 3 in the ternary alloy compared to 5 to 6 for the binary alloy. Cerium modification of this phase is readily evident in the ternary alloy (Figure 82). After 1 hour the metastable phase, θ'' , still persists though much coarser. Figure 83 shows the coarse θ'' precipitates in the dark field mode obtained with the objective aperture placed around the (202) precipitate spot. Comparing Figures 83 and 84 shows the coarsening behavior of the, θ'' , phase, both figures obtained in the dark field mode with the objective aperture placed around the (202) precipitate spot. This observation suggests that the metastable phase is relatively more stable in the ternary alloy occurring simultaneously with the θ' phase over a wide range of aging treatments.

EDAX Microanalyses Studies

EDAX microanalysis studies were done on selected samples of the ternary alloy aged at 300 °C for 1 hour and 400 °C at 1 and 10 hours. The data presented in this section were obtained exclusively from the grain boundary precipitates. All measurements were made on precipitates at or close to the edge of the thin area of the TEM specimen to obtain an accurate composition analysis. Since the precipitates are either embedded in the matrix or coated with the matrix phase, the obtained intensities data are representative of the volume of the thin film excited by the electron beam. Separating the matrix effect from



Figure 82. Al-8 wt% Fe-3.4 wt% Ce aged in situ at 440 °C, 1 hour, TEM, 535,000X. Disc-shaped precipitates with aspect ratio different from the Al-Fe alloy precipitates in the similarly aged specimen.

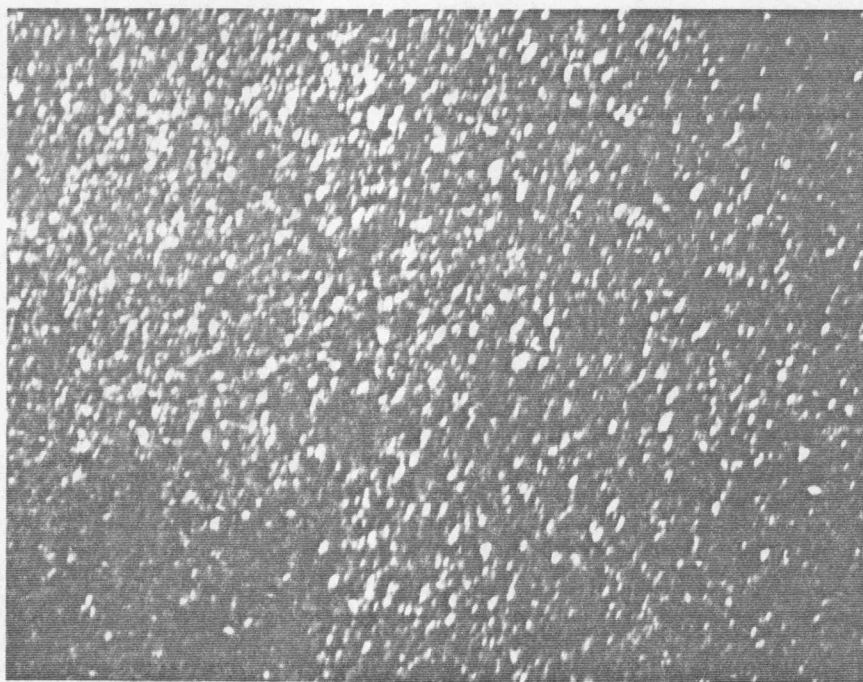


Figure 83. Al-8 wt% Fe-3.4 wt% Ce aged at 440 °C for 10 hours, TEM, 165,000X. Dark field of limited regions of spheroidal zones, θ'' , obtained with the (202) precipitate spot.

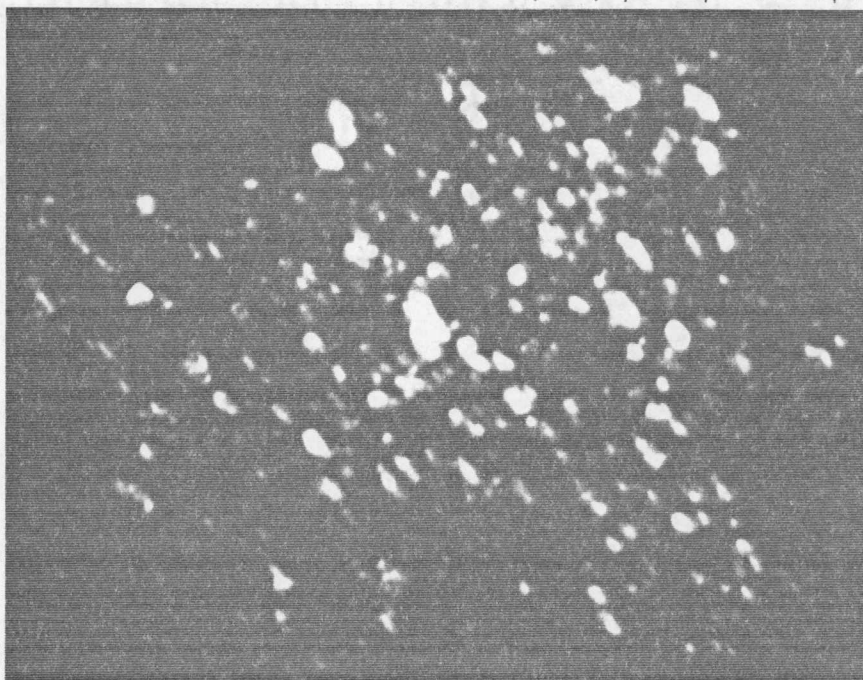


Figure 84. Al-8 wt% Fe-3.4 wt% Ce aged at 325 °C for 10 hours, TEM, 330,000X. Dark field of spheroidal zones, θ'' , obtained with the (202) precipitate spot.

the precipitate phase is a nontrivial matter. The results presented here should then be used only as a semi-quantitative analyses.

For the sample annealed at 300 °C for 10 hours only the metastable phase, Al_6Fe was observed to be present at the grain boundary. Figure 85 shows the composition analysis as obtained along with confirmatory diffraction evidence for the Al_6Fe phase (Figure 86). For the sample aged at 400 °C for 1 hour, Al_6Fe , Al_3Fe and $\text{Al}_{10}\text{Fe}_2\text{Ce}$ precipitates were observed to be present. Both Al_6Fe and Al_3Fe have a minute amount of cerium present as evident from the analyses. Ternary particles with composition close to that of $\text{Al}_{10}\text{Fe}_2\text{Ce}$ were observed most readily at grain junctions. For the sample aged at 400 °C for 10 hours, both Al_3Fe and $\text{Al}_{10}\text{Fe}_2\text{Ce}$ particles were present. Figures 87 and 88 show the result of analyses performed on the samples. Scattered particles of Al_6Fe were also present, indicating that the transformation of metastable Al_6Fe to stable Al_3Fe is still not complete. At this treatment only one stable ternary phase was observed, with composition close to that of $\text{Al}_{10}\text{Fe}_2\text{Ce}$. This precipitate was found to be preferentially present at or very close to the grain junction. Figure 75 shows one such particle embedded in the matrix at the grain junction. The exact reason for this behavior is not well understood at this moment. It is possible that the misfit parameter for the precipitate-matrix orientation is the least at the grain junction. Angers (65) in a recent study on the Al-Fe-Ce system has identified at least two metastable ternary precipitates "Al-Fe-Ce-1" and "Al-Fe-Ce-2" apart from the stable $\text{Al}_{10}\text{Fe}_2\text{Ce}$ phase. Angers

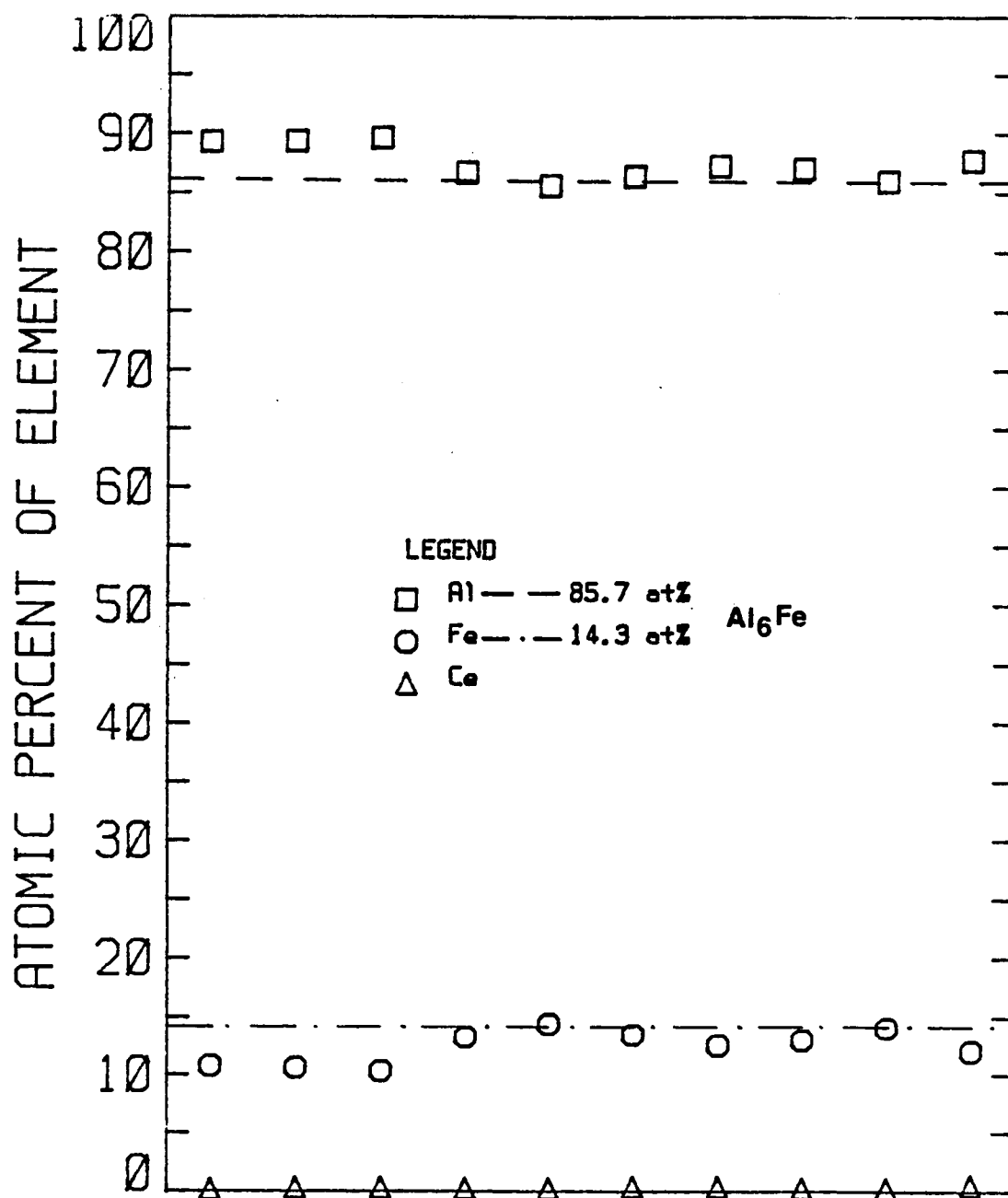


Figure 85. EDAX microanalysis for Al-8 wt% Fe-3.4 wt% Ce alloy aged at 300 °C for 10 hours. Metastable Al_6Fe was the only phase detected at the grain boundary.

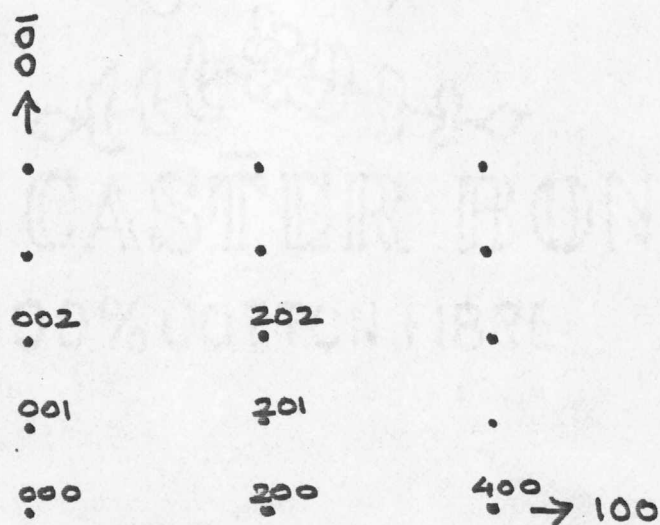
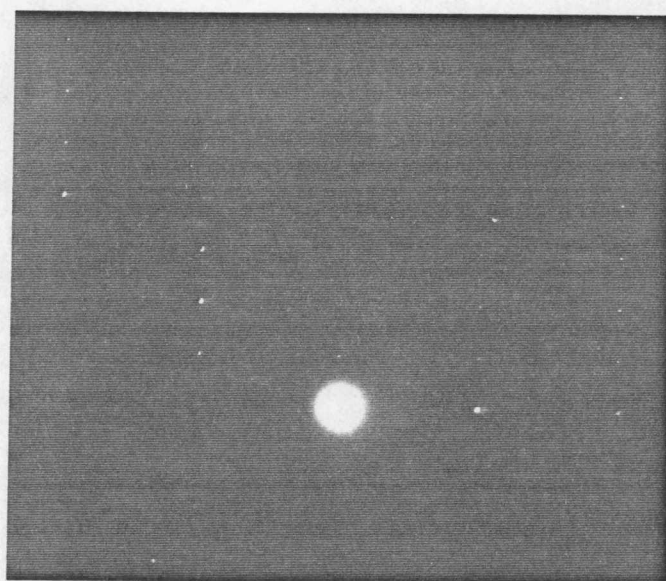


Figure 86. Diffraction pattern of Al_6Fe plus explanatory diagram.

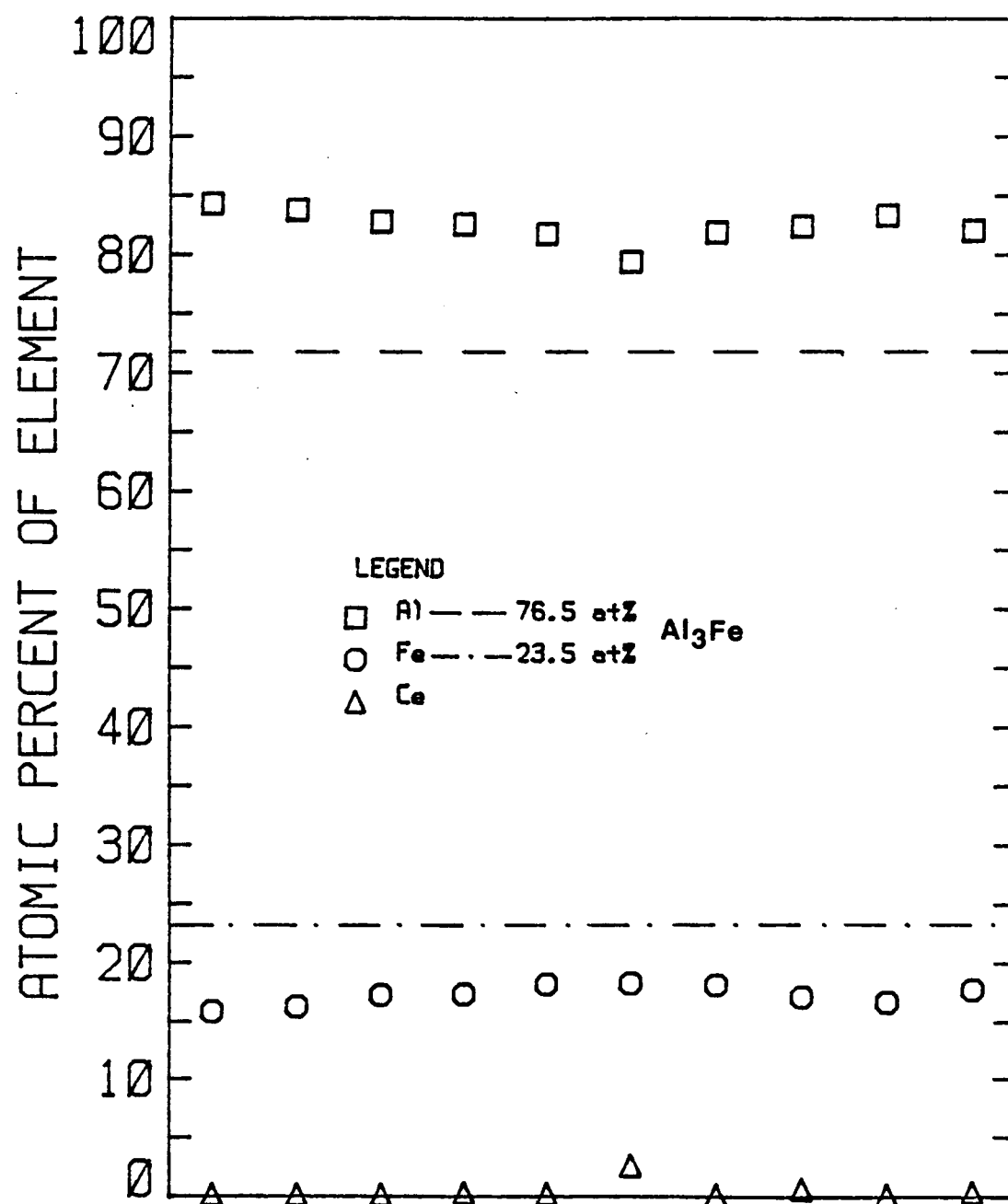


Figure 87. EDAX microanalysis for Al-8 wt% Fe-3.4 wt% Ce alloy aged at 400 °C for 10 hours for Al_3Fe precipitates.

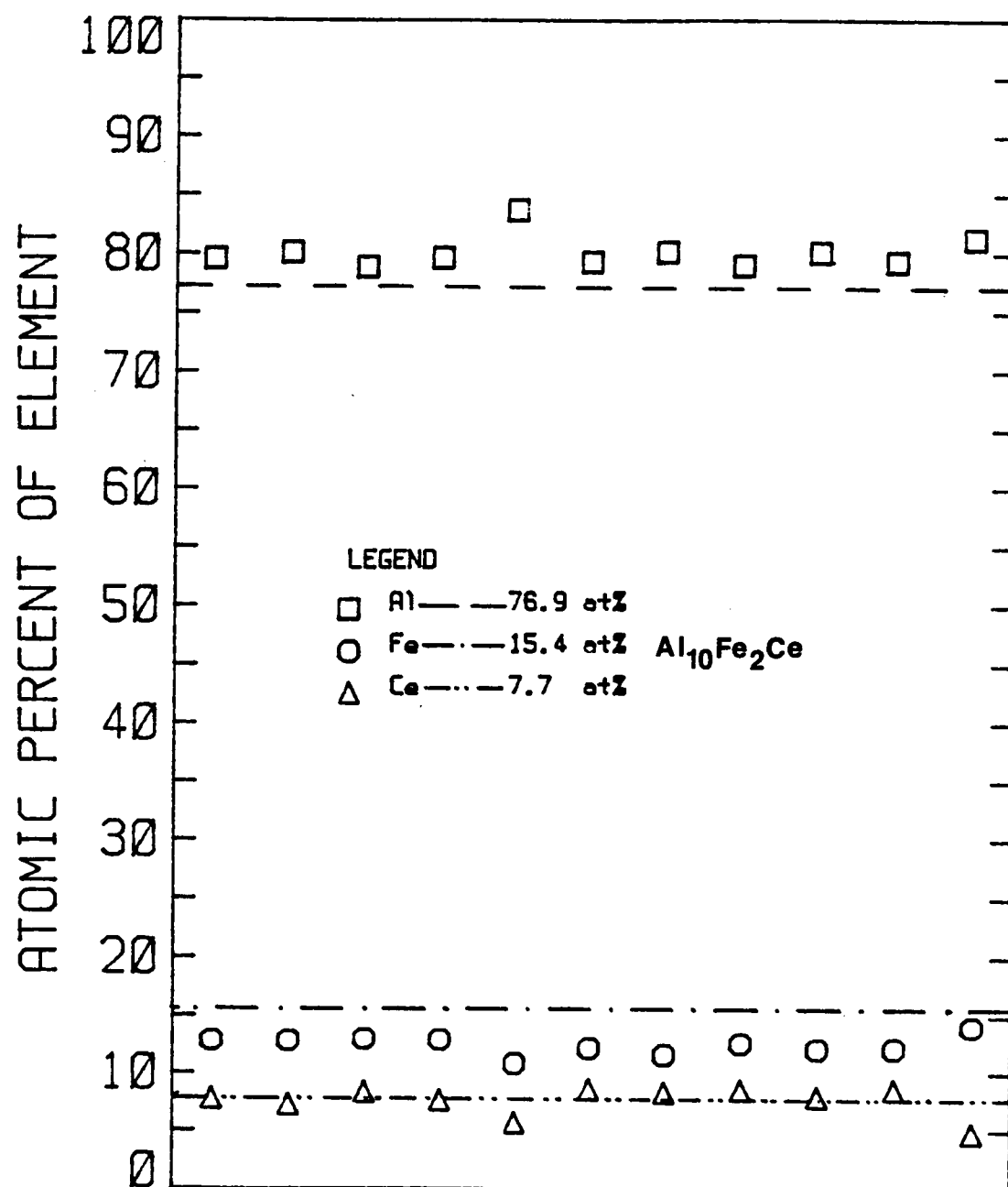


Figure 88. EDAX microanalysis for Al-8 wt% Fe-3.4 wt% Ce alloy aged at 400 °C for 10 hours for $\text{Al}_{10}\text{Fe}_2\text{Ce}$ precipitates.

reports that "since Al-Fe-Ce-1 and Al-Fe-Ce-2 phases nucleate in preference to the $\text{Al}_{10}\text{Fe}_2\text{Ce}$ phase, these phases are expected to have lower particle-matrix interfacial energies." By implication this suggests that $\text{Al}_{10}\text{Fe}_2\text{Ce}$ has a higher particle-matrix interface energy and the preferential formation at the grain junction would be a thermodynamically favorable condition. Fine has suggested that better matching of particle lattice parameters to the matrix lattice parameters will result in a reduction of the particle-matrix interfacial energy (66). The following formula has been suggested to describe a measure of the lattice parameter mismatch, D:

$$D = (A_p - A_m) / A_m$$

where A_p and A_m are the lattice parameters of the particle and the matrix, respectively. For particles having noncubic structures a value for the lattice parameter mismatch in each direction can be defined. The above equation has been rewritten to allow for the lattice matching over an integral number of lattice spacings in any of the three directions.

$$D_i = (mA_{p,i} - nA_{m,i}) / (nA_{m,i})$$

where m, n are integers. Table 9 shows the lattice parameter mismatch in each of the three directions for both the Al-Fe-Ce-2 and $\text{Al}_{10}\text{Fe}_2\text{Ce}$ phases. An average lattice mismatch, D_{avg} , defined as one-third of the sum of the values of mismatch in either direction is also included in the table.

Table 9. Values of Lattice Parameter Mismatch for the Al-Fe-Ce-2 and the $\text{Al}_{10}\text{Fe}_2\text{Ce}$ Phases in the Al-Fe-Ce Alloy

Phase	D_x	D_y	D_z	D_{avg}
Al-Fe-Ce-2	0.007 (m=2,n=5)	0.0 (m=1,n=4)	0.037 (m=1,n=1)	0.015
$\text{Al}_{10}\text{Fe}_2\text{Ce}$	0.0104 (m=1,n=2)	0.009 (m=2,n=5)	0.119 (m=1,n=2)	0.077

Source: Lynette Angers, Ph.D. thesis, Northwestern University, Evanston, IL, August 1985.

An overall lattice mismatch of 1.5% for the Al-Fe-Ce-2 phase compared to 8% for the $\text{Al}_{10}\text{Fe}_2\text{Ce}$ phase is consistent with the idea that the improved lattice matching and lower particle-matrix interfacial energies are related. Formation of $\text{Al}_{10}\text{Fe}_2\text{Ce}$, then is more probable at the grain junction from the standpoint of interfacial energies. In addition the possibility of enhanced volume diffusion at the grain junction cannot be ruled out. Note that during the course of this study little evidence of ternary metastable phases was obtained. X-ray data may reveal such information. However, due to the difficulties associated with finding sharp peaks attributable to only one phase, the x-ray diffraction procedure used in this study was not suitable for obtaining this kind of information with certainty. One cerium rich ternary phase was observed with its microanalysis subsequently different from the $\text{Al}_{10}\text{Fe}_2\text{Ce}$ phase. This phase was needle shaped occurring at the grain boundary with striations in the long direction (Figure 89). It must be mentioned that this phase was observed only once in a sample during this entire study.

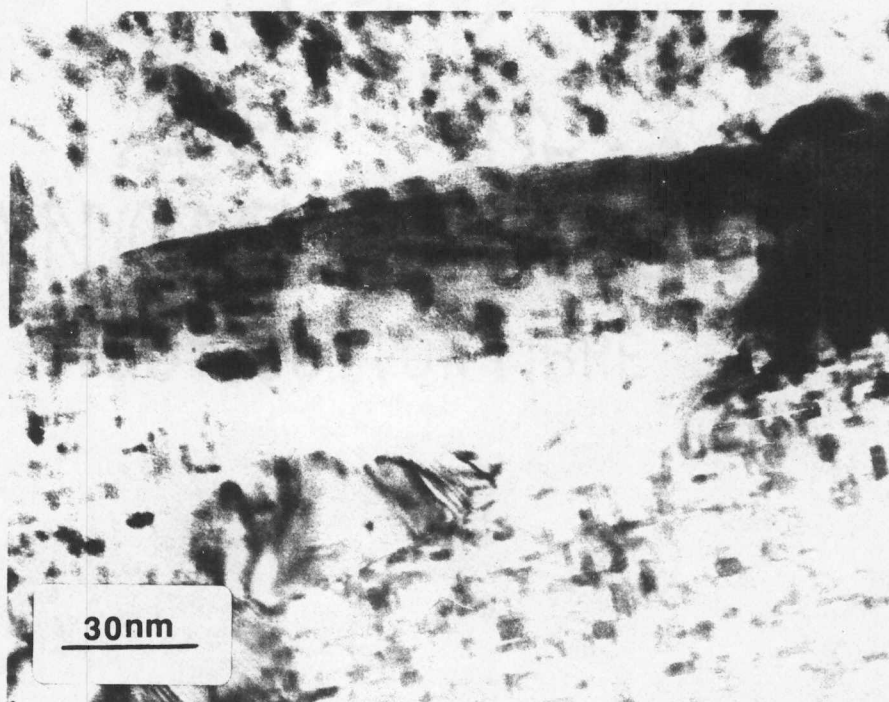


Figure 89. Al-8 wt% Fe-3.4 wt% Ce aged in situ at 440 °C for 1 hour. Nucleation and growth of an Al-Fe-Ce particle at the grain boundary. Note striations in the long direction.

X-Ray Analyses

X-ray studies were performed on powder specimens in the step annealing sequence to identify the different metastable and stable phases. It was also desired to map the metastable to stable phase transformations. Figure 90 gives the composite information on the d-spaces obtained during the annealing sequence for the binary and ternary alloys at each step. A listing of all the d-spaces at each step is listed in Appendix C for reference. During the grinding operation to obtain powder from the splats, some oxide formation (Al_2O_3) occurred. The x-ray patterns also show the presence of oxide lines. To aid interpretation these oxide lines have been deleted from all the information listed herein. The reference plot was generated by converting the d-space data to 2θ angle values using $\text{CuK}\alpha$ radiation of 0.154 nm. Information for Al_6Fe phase was calculated using the structural information and lattice parameter reported by Walford (34). The intensity information for this phase was obtained from JCPDS card 6-669 for Al_6Mn of the same structure. Information for the $\text{Al}_{10}\text{Fe}_2\text{Ce}$ was recently made available by Anders (65) in the form of structural and d-space data. For ease of reference all pertinent information for these phases is listed in Appendix C.

For the binary alloy the transformation was identified as metastable Al_6Fe to stable Al_3Fe phase. For the ternary alloy the same mode of transformation was observed. The obtained data gives no conclusive evidence of any metastable ternary phases. It must be mentioned, however, that extra lines were obtained for the ternary

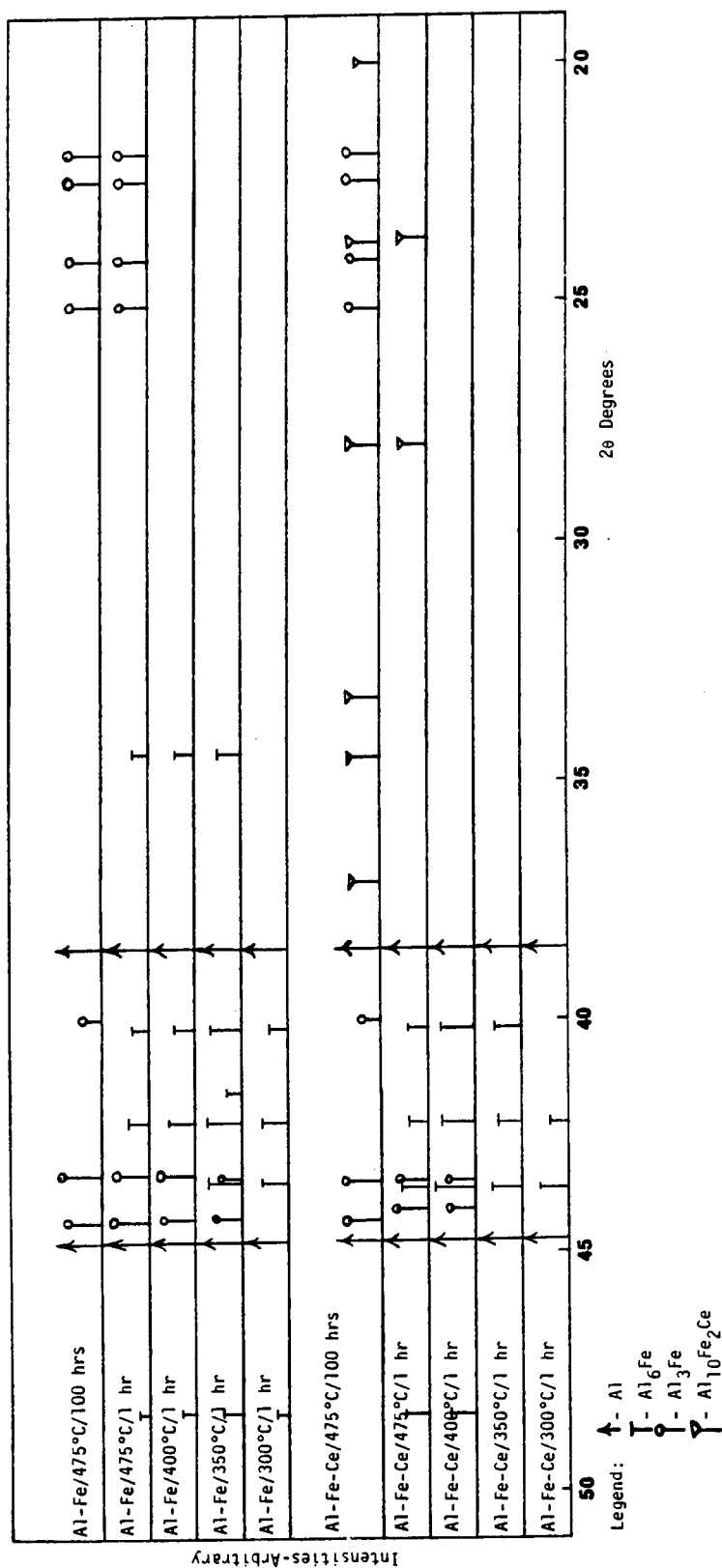


Figure 90. Composite plot for the x-ray analyses for the binary and ternary alloys, after different aging treatments.

alloy which could not be attributed to any of the above mentioned phases. A stable phase $\text{Al}_{10}\text{Fe}_2\text{Ce}$ was identified from the x-ray data. This identification was concluded by subtracting the binary x-ray pattern from the ternary x-ray pattern, after aging for 100 hours at 475 °C. For the binary alloy, maximum intensity and large number of lines were observed for the metastable Al_6Fe phase at 350 °C/1 hour. Since Al_6Fe forms by precipitation from the supersaturated solid solution, it indicates that the formation of Al_6Fe is most rapid in this temperature range. This observation is further supported by the fact that the volume of Al_6Fe is large enough to diffract the weaker reflections ($\approx 20\%$ I/I_0) of Al_6Fe . For the ternary alloy, maximum intensity of Al_6Fe lines was observed at 500 °C/1 hour.

After aging for 100 hours at 475 °C only the stable phases were identified in both the binary and the ternary alloy specimens. Tables 10 and 11 list the d-spaces obtained along with the indexed reflections.

Table 10. D-Space Listing for Al-8 wt% Fe Alloy Aged for 100 Hours
at 475 °C

D-Space, nm	Phase / hkl
0.405	Al ₃ Fe,020
0.395	Al ₃ Fe,003
0.368-0.369	Al ₃ Fe,400,40-2,311
0.354	Al ₃ Fe,220,22-1
0.325-0.326	
0.287	
0.234	Al,111
0.225-0.226	Al ₃ Fe,60-4,13-3
0.209	Al ₃ Fe,62-3,332
0.204-0.205	Al ₃ Fe
0.202	Al ₃ Fe,040,Al,200
0.193	
0.145	
0.143	Al,220
0.122	Al,311
0.117	Al,222

Table 11. D-Space Listing for Al-8 wt% Fe-3.4 wt% Ce Alloy Aged for 100 Hours at 475 °C

D-Space, nm	Phase / hkl
0.690	
0.487-0.489	
0.445	$\text{Al}_{10}\text{Fe}_3\text{Ce}, 021$
0.405	$\text{Al}_3\text{Fe}, 020$
0.395	$\text{Al}_3\text{Fe}, 003$
0.372-0.375	$\text{Al}_{10}\text{Fe Ce}, 112$
0.367-0.369	$\text{Al}_3\text{Fe}, 400, 40-2-2, 311$
0.352-0.354	$\text{Al}_3\text{Fe}, 220, 22-1$
0.318-0.319	$\text{Al}_{10}\text{Fe}_2\text{Ce}, 130, 202$
0.288-0.290	
0.268-0.269	$\text{Al}_{10}\text{Fe}_2\text{Ce}, 222$
0.260	$\text{Al}_{10}\text{Fe}_2\text{Ce}, 023$
0.240-0.242	$\text{Al}_{10}\text{Fe}_2\text{Ce}, 312$
0.234	$\text{Al}, 111$
0.225-0.226	$\text{Al}_3\text{Fe}, 60-4, 13-3$
0.208-0.209	Al_3Fe
0.204	Al_3Fe
0.202	$\text{Al}_3\text{Fe}, 040, \text{Al200}$
0.143	$\text{Al}, 220$
0.122	$\text{Al}, 311$
0.117	$\text{Al}, 222$

CHAPTER VI

CONCLUSIONS

As Cast Alloys

1. Cerium promotes the breakdown of primary Al_3Fe intermetallic particles. These finer particles are dispersed in the aluminum matrix.
2. The eutectic morphology is fine and lamellar in the ternary alloy as compared to coarse and irregular in the binary alloy.
3. At least two different ternary compounds are present in the ternary alloy. These phases are apparently the last to solidify and appear in close proximity to each other.

As Quenched Splats

4. Splat quenching produces a high cooling rate on both sides of the splats in comparison to the melt spun alloys.
5. The splats have a high degree of preferred orientation with the (111) planes oriented as parallel to splat surface.
6. By careful treatment and preparation of the quenching surfaces, gold coated in this study, it is possible to obtain complete regions of zone A structures in splat thicknesses of up to 35 microns.

Microhardness Measurements

7. Better quenching techniques yield higher as quenched hardness values, due to the formation of large regions of zone A.

8. The initial drops in hardness values at short aging times can be explained by the formation of the grain boundary phase as a result of depletion of solutes from a thin region adjacent to the grain boundary. Slower rates of diffusion at the lower temperatures yields slower drops in hardness values. At the higher temperatures, enhanced diffusion promotes rapid, massive precipitation yielding large drops in hardness values.

9. The retention of hardness values at the lower temperatures in the ternary alloys, initially at short aging times, is due to cerium delaying the diffusion of alloying species.

10. Formation of the needle phase does not significantly reduce hardness.

11. Hardness is a misleading criterion in attempting to explain the differences in microstructures of the binary and ternary alloys at equivalent hardness values.

Electron Microscopy

12. Cerium inhibits the metastable θ'' to θ' transformation at 300 °C up to 100 hours.

13. Metastable θ'' to θ' transformation occurs much slower in the ternary alloy. The metastable θ'' and θ' phases coexist over a wide range of aging treatments.

14. The shape effects of the θ'' phase are significantly different in the two alloys. The aspect ratio is 2-3 in the ternary as compared to 5-6 in the binary alloy.

15. Cerium introduces a 50 °C increase in aging temperature in the ternary alloy yielding similar microstructures to Al-8% Fe aged at 350 °C for 10 hours.

16. Slower coarsening rates of the dispersed phases in the ternary alloy suggest that the presence of cerium plays a role in delaying particle coarsening.

17. The only stable phase observed in the binary alloy is Al_3Fe . In the ternary alloy the stable phases observed are $\text{Al}_{10}\text{Fe}_2\text{Ce}$ and Al_3Fe .

18. The ternary precipitate $\text{Al}_{10}\text{Fe}_2\text{Ce}$ forms preferentially at the triple grain junctions. Particle-matrix interfacial energy criteria offers some explanation for this behavior.

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APPENDICES

APPENDIX A

IMPURITY ANALYSES FOR THE THREE ALLOYS

Table A.1. Impurity Analyses for the Three Alloys, Al-8 wt% Fe, Al-8 wt% Fe-3.4 wt% Ce, and Al-8 wt% Fe-6 wt% Co Used in This Study

Element	Al-Fe	Al-Fe-Ce	Al-Fe-Co
La	<1	10	<1
As	1	0.1	0.3
Zn	2	4	3
Cu	8	10	6
Co	1	<0.5	6 wt% (m)
Fe	8.6 wt% (m)	6.9 wt% (m)	8 wt% (m)
Mn	4	4	8
Cr	3	2	1
Ca	1	3	2
K	0.1	0.2	0.5
Cl	6	30	2
S	5	<0.5	5
P	110	5	5
Si	8	15	3
Al	92 wt% (m)	93 wt% (m)	87 wt% (m)
Mg	4	10	5
Na	0.4	0.2	0.2
Ce	20	2.43 wt% (m)	30

All concentrations for impurity elements are in parts per million. Major constituents, m, listed in wt% $\pm$ 1 wt%.

Chemical analyses obtained courtesy of Oak Ridge National Laboratory.

APPENDIX B

CALCULATION FOR HAMMER VELOCITY

The actual hammer impact velocity was theoretically calculated using the undermentioned formulation. For the purpose of this calculation, the effect of friction has been neglected.

$$V = X (K/M)^{1/2}$$

where V = velocity of impact, X = spring extension, K = spring constant and M = mass of the hammer. The following particulars for a set of springs used in this study were obtained from "Lee Springs 1970 Catalog 112."

Extension Spring LE-036E-R, page 23

1/2" outside diameter

5.0" free length

19 lb max load

K = 2.07 lb/in or 362.5 N/meters

M = 0.5 KG

Maximum extension in length = 191 lb/in/2.071b/in

Hence, X = 9.178 inches or 0.233 meters.

By substituting these values in the equation we get a maximum obtainable velocity of about 6 meters/second. Hence, using two springs, the maximum velocity attainable, neglecting friction, = 8.414 meters/second. The actual hammer velocity was measured using a pulse timer arrangement which gives readings in the range of 8-10 meters/second.

APPENDIX C

D-SPACE LISTINGS FOR BINARY AND TERNARY ALLOYS

The d-space data obtained at each step in the annealing sequence for both the binary and the ternary alloy are presented here for reference.

Table C.1. D-Space Listing for Al-8 wt% Fe-3.4 wt% Ce Alloy

D-Space	Phase / hkl
Annealing treatment: aged at 300 °C for 1 hour	
0.242	
0.234	Al
0.214	Al ₆ Fe,222
0.207-0.208	Al ₆ Fe,310
0.202	Al
0.143	Al
0.122	Al
0.117	Al
Annealing treatment: aged at 350 °C for 1 hour	
0.485-0.490	
0.430	
0.410	
0.325-0.327	
0.234	Al
0.224	Al ₆ Fe,131
0.214	Al ₆ Fe,222
0.207	Al ₆ Fe,310
0.202	Al
0.143	Al
0.122	Al
0.117	Al

Table C.1 (continued)

D-Space	Phase / hkl
Annealing treatment: aged at 400 °C for 1 hour	
0.490	
0.430	
0.405	
0.375	
0.325-0.326	
0.295	
0.285-0.290	
0.247	
0.242	
0.234	Al
0.225	Al ₆ Fe,131
0.214	Al ₆ Fe,222
0.207-0.208	Al ₆ Fe,Al ₃ Fe
0.205	Al ₃ Fe
0.202	Al
0.186	Al ₆ Fe
0.143	Al
0.122	Al
Annealing treatment: aged at 475 °C for 1 hour	
0.690	
0.490	
0.470	
0.427-0.430	
0.410	
0.375	
0.318	
0.295-0.297	
0.234	Al
0.224-0.225	Al ₆ Fe,131

Table C.1 (continued)

D-Space	Phase / hkl
0.214	Al ₆ Fe, 222
0.208	Al ₃ Fe
0.205	Al ₃ Fe
0.202	Al
0.186	Al ₆ Fe
0.143	Al
0.122	Al
0.117	Al

Table C.2. D-Space Listing for Al-8 wt% Fe Alloys

D-Space	Phase / hkl
Annealing treatment: aged at 300 °C for 1 hour	
0.490	
0.324-0.325	
0.283-0.284	
0.242	
0.238	
0.234	Al
0.224	Al ₆ Fe,131
0.214	Al ₆ Fe,222
0.207-0.208	Al ₆ Fe,310
0.202	Al
0.186-0.188	Al ₆ Fe,040
0.143	Al
0.122	Al
0.117	Al
Annealing treatment: aged at 350 °C for 1 hour	
0.488-0.490	
0.470	
0.440	
0.430	
0.325-0.326	
0.283-0.284	
0.260	Al ₆ Fe,202
0.234	Al
0.227	
0.224	Al ₆ Fe,131
0.217-0.218	Al ₆ Fe,203
0.214	Al ₆ Fe,222
0.208	Al ₃ Fe
0.207	Al ₆ Fe

Table C.2 (continued)

D-Space	Phase / hkl
0.204	Al_3Fe
0.202	Al
0.186	Al_6Fe
0.143	Al
0.122	Al
0.117	Al
Annealing treatment: aged at 400 °C for 1 hour	
0.488-0.490	
0.470	
0.437	
0.427	
0.370	
0.325	
0.260	Al_6Fe
0.242	
0.234	Al
0.224	$\text{Al}_6\text{Fe}, 131$
0.214	$\text{Al}_6\text{Fe}, 222$
0.208-0.209	Al_3Fe
0.204	Al_3Fe
0.202	Al
0.186	Al_6Fe
0.143	Al
0.122	Al
0.117	Al
Annealing treatment: aged at 475 °C for 1 hour	
0.490	
0.470	
0.430-0.435	
0.405	Al_3Fe

Table C.2 (continued)

D-Space	Phase / hkl
0.395	Al ₃ Fe
0.372-0.373	
0.368	
0.353-0.354	Al ₃ Fe,220,22-1
0.326	Al ₃ Fe,221
0.287-0.288	
0.260	Al ₆ Fe
0.243	
0.238	
0.234	Al
0.224	Al ₆ Fe,131
0.218	Al ₆ Fe,203
0.214	Al ₆ Fe,222
0.209	Al ₃ Fe
0.204	Al ₃ Fe
0.202	Al
0.186	Al ₆ Fe
0.143	Al
0.122	Al
0.117	Al

Table C.3. Interplanar Spacings with Relative Intensities for the $\text{Al}_{13}\text{Fe}_4$ Phase

Interplanar Spacing (nm)	Reflection (hkl)	Intensity (I/I_0)
0.7378	2 0 0	2
0.7089	1 1 0	16
0.6523	1 1 -1	22
0.5943	0 0 2 , 0 0 -2	4
0.5731	1 1 1	6
0.4258	1 1 2	3
0.4064	2 0 2	29
0.4040	0 2 0	35
0.3962	0 0 3 , 0 0 -3	40
0.3872	4 0 -1	8
0.3826	0 2 1	3
0.3689	4 0 0	28
0.3674	4 0 -2 , 3 1 1	32
0.3545	2 2 0 , 2 2 -1	53
0.3342	0 2 2 , 0 2 -2	28
0.3268	2 2 1	30
0.3234	4 0 -3	7
0.3118	2 0 3	3
0.3102	2 0 -4	4
0.2971	0 0 4 , 0 0 -4	3
0.2842	5 1 -2	2
0.2725	4 2 0	2
0.2655	5 1 -3	2
0.2565	6 0 -2	3
0.2557	1 3 1	3
0.2535	4 2 1	3
0.2525	4 2 -3	4
0.2469	2 2 3	2
0.2461	2 2 -4	3
0.2394	0 2 4	2
0.2373	1 3 2	6
0.2363	3 3 0	5
0.2315	3 3 -2	6
0.2276	5 1 2	3
0.2261	6 0 -4 , 1 3 -3	17
0.2174	3 3 -3	3
0.2161	1 1 5	10
0.2130	5 1 -5	10
0.2101	6 2 0	75
0.2095	6 2 -3 , 3 3 2	100
0.2078	7 1 -3 , 2 0 -6	38
0.2062	6 0 2	26
0.2049	0 2 5 , 0 2 -5	85
	6 0 -5	

Table C.3 (continued)

Interplanar Spacing (nm)	Reflection (hkl)	Intensity (I/I_0)
0.2041	4 2 3 , 7 1 0	83
0.2031	4 2 -5 , 5 3 1	62
0.2021	0 4 0	62
0.2015	5 3 -2	46
0.2004	3 1 -6	7

C.4. Interplanar Spacings with Relative Intensities for the Al_6Fe Phase

Interplanar Spacings (nm)	Reflection (hkl)	Intensity (I/I_0)
0.4872	110	20
0.4389	002	10
0.4260	111	10
0.3720	020	10
0.3261	112	10
0.3223	200	10
0.3026	201	6
0.2838	022	6
0.2598	202	20
0.2509	113	20
0.2436	220	6
0.2347	221	6
0.2315	130	10
0.2238	131	50
0.2195	004	20
0.2167	203	20
0.2130	222	50
0.2064	310	100
0.2010	311	50
0.1890	024	10
0.1872, 0.1860, 0.1868	223, 040, 312	30
0.1815, 0.1814	133, 204	10
0.1713	042	10
0.1687, 0.1652	313, 115	6
0.1630, 0.1624	224, 330	10
0.1612	400	6
0.1597, 0.1593	331, 134	2
0.1584, 0.1585	241, 401	2
0.1542	205	6
0.1523	332	2
0.1512	242	20
0.1513, 0.1504	402, 314	2
0.1479	420	16
0.1463, 0.1458, 0.1450	006, 421, 150	30
0.1424, 0.1419, 0.1420	225, 044, 333	4
0.1411, 0.1187	243, 405	16

Table C.5. Interplanar Spacings for the $\text{Al}_{10}\text{Fe}_2\text{Ce}$ Phase

Interplanar Spacings (nm)	Reflection (hkl)
1.022	010 (f)
0.906	001 (f)
0.894	100 (f)
0.678	011 (f)
0.673	110
0.636	101 (f)
0.540	111
0.511	020
0.453	002
0.447	200
0.445	021
0.444	120 (f)
0.414	012 (f)
0.4095	210 (f)
0.404	102 (f)
0.401	201
0.398	121 (f)
0.376	112
0.373	211 (f)
0.341	030 (f)
0.339	022
0.336	220
0.319	031 (f)
0.318	130
0.318	202
0.317	122 (f)
0.315	221
0.304	212 (f)
0.302	003 (f)
0.300	131
0.298	300 (f)
0.290	013 (f)
0.286	103 (f)
0.286	310
0.283	301 (f)
0.2755	113
0.273	311
0.272	032 (f)
0.271	230 (f)
0.270	222
0.2605	132
0.260	023
0.257	320 (f)
0.2555	040
0.250	203 (f)

Table C.5 (continued)

Interplanar Spacings (nm)	Reflection (hkl)
0.250	123 (f)
0.249	302 (f)
0.248	321 (f)
0.246	041
0.246	140 (f)
0.243	213 (f)
0.242	312
0.237	141 (f)
0.232	232 (f)
0.226	004
0.226	033 (f)
0.225	223
0.224	330 (f)
0.224	322 (f)
0.2235	400
0.2225	042
0.222	240
0.221	014 (f)
0.220	104 (f)
0.219	131
0.218	410 (f)
0.218	331
0.217	401 (f)
0.216	142 (f)
0.2155	241
0.215	114
0.212	411 (f)
0.212	303 (f)
0.208	313
0.207	024
0.205	420
0.202	204
0.202	124 (f)
0.202	233 (f)
0.201	332
0.200	402
0.200	421
0.199	242
0.198	214 (f)
0.197	412 (f)
0.196	323 (f)
0.195	043
0.194	340 (f)
0.191	143 (f)
0.190	341 (f)

Table C.5 (continued)

Interplanar Spacings (nm)	Reflection (hkl)
0.189	034 (f)
0.188	224
0.187	430 (f)
0.187	422
0.185	134
0.183	431 (f)
0.180	304 (f)
0.180	333
0.180	403
0.179	243
0.178	342 (f)
0.178	314
0.177	413 (f)
0.174	234 (f)
0.173	432 (f)
0.170	324 (f)
0.1695	044
0.168	440
0.1665	144 (f)
0.165	441
0.163	343 (f)
0.159	334
0.159	404
0.159	433 (f)
0.1585	244
0.158	442
0.157	414 (f)
0.152	424
0.147	344 (f)

Source: Lynette Angers, Ph.D. thesis, Northwestern University, Evanston, Illinois, August 1985.

VITA

Bimal K. Kad was born in Punjab, India, on June 13, 1959. He attended high school in Patna, India, and graduated from St. Michael's High School in March 1976. He earned his B. Tech. degree in metallurgical engineering from the Indian Institute of Technology, Kharagpur, India, in May 1981. After graduation he was associated with Mukand Iron and Steel Works, Bombay, India, as a production engineer in the steel melting shop until November 1981. He was then associated with ABC Metallurgicals Pvt. Ltd as a product development engineer in the Foundry and Casting Division until August 1982. In the Fall of 1982 he came to The University of Tennessee, Knoxville, on a teaching assistantship and started working toward a M.S. degree in metallurgical engineering. This degree will be awarded in December 1985. He plans on continuing his education toward a Ph.D. there.

The author is a member of the American Society for Metals and the Metallurgical Society of AIME. He has avid interests in video and still photography.