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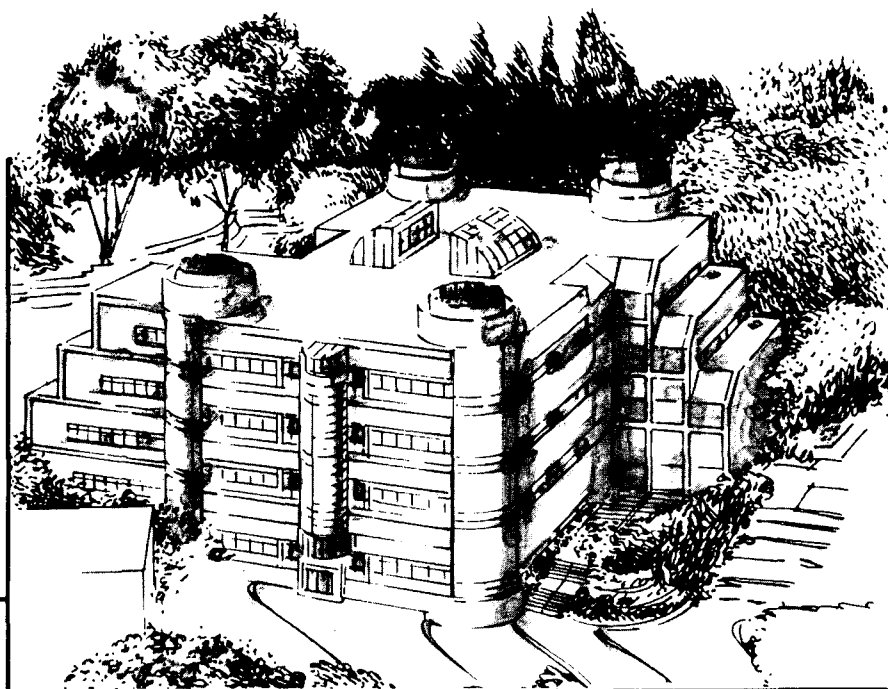
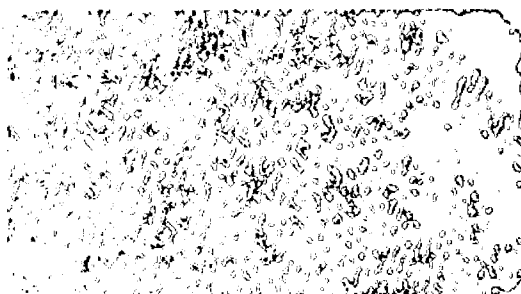
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Exploratory Alloy Development in the System Al-Sc-X

R.R. Sawtell
(Ph.D. Thesis)

December 1988



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Exploratory Alloy Development in the System Al-Sc-X

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Ph.D. Dissertation

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November 1988

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The potential of scandium additions in aluminum-base alloys, while known for many years, has never been fully exploited. One reason for this is the high cost of Sc while another is a lack of basic understanding of the mechanisms by which Sc produces property improvements. The purpose of this research has been to provide a fundamental framework for continued alloy development in the Al-Sc-X system with the ultimate aim of producing a new subclass of Al-based structural materials. Attempts have been made to develop a theoretically based alloy design strategy aimed at improving the precipitation hardening component of strengthening in these alloys. A model is proposed that takes into account the basics of intermetallic compound formation, precipitation from solid solution and strengthening efficiency of precipitates. This model points toward group IIIA rare earth (RE) elements and, more specifically, those in a certain range of atomic diameter, as the most promising candidates for improved strengthening. A series of ternary Al-Sc-(X) alloys incorporating these elements were cast, fabricated and evaluated. Results of these studies showed that peak tensile strength were increased by as much as 25 percent and varied systematically with RE size. Microstructural studies revealed that the RE were incorporated into the L1₂ precipitate phase in a manner that also depends on RE size. These results are interpreted in light of the original alloy design model leading to the conclusion that the modifications in precipitate structure lead to an increase in precipitation strengthening efficiency which dominates an opposing trend in precipitate volume fraction. Recommendations are made for further fundamental studies as well as steps toward commercial development of such alloys.

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II. Introduction

Use of scandium as an alloying addition in Al was first studied and documented by Willey¹ at the Alcoa Research Laboratories in the late 1960's. Willey found that Sc additions increased the strength and thermal stability of almost all aluminum alloys known at that time. Latter investigators showed that, Sc combines with Al to form a stable intermetallic with the stoichiometric composition Al_3Sc and an ordered, L_{12} crystal structure². This phase precipitates from supersaturated solid solution as coherent, spherical particles. Because of the relatively low equilibrium solubility of Sc in Al (0.3 atom pct.) the achievable precipitate volume fraction is small. Nonetheless, Sc additions contribute significantly to alloy strength; in fact, Sc is the most potent strengthener known for Al based systems^{3,4,5}. The Al_3Sc precipitate is also extremely effective in stabilizing the substructure of Al alloys, and hence facilitates the use of strain hardening and stabilization treatments to further augment strength. The combined effects of precipitation, substructure and strain hardening have been used to produce tensile strengths in the range of 250 MPa in Al-Sc alloys. While the strength levels of these binary alloys are too low to be of interest for structural alloys, ternary solid solution strengtheners can be added to raise strength further. For example, Al-Sc-Mg alloys have been produced with very attractive combinations of density, strength, fracture toughness and corrosion resistance⁶. A comparison showing specific (density compensated) tensile properties for two Al-Sc-Mg alloys, AA2090-T81, a new Al-Li alloy and AA7076-T6, is presented in Figure 1. AA7075 is often used in high performance applications and is a good baseline for comparison of new materials. These data show that the specific yield and tensile strengths of the Al-0.5Sc-6Mg alloy are competitive with those of both 2090 and 7075.

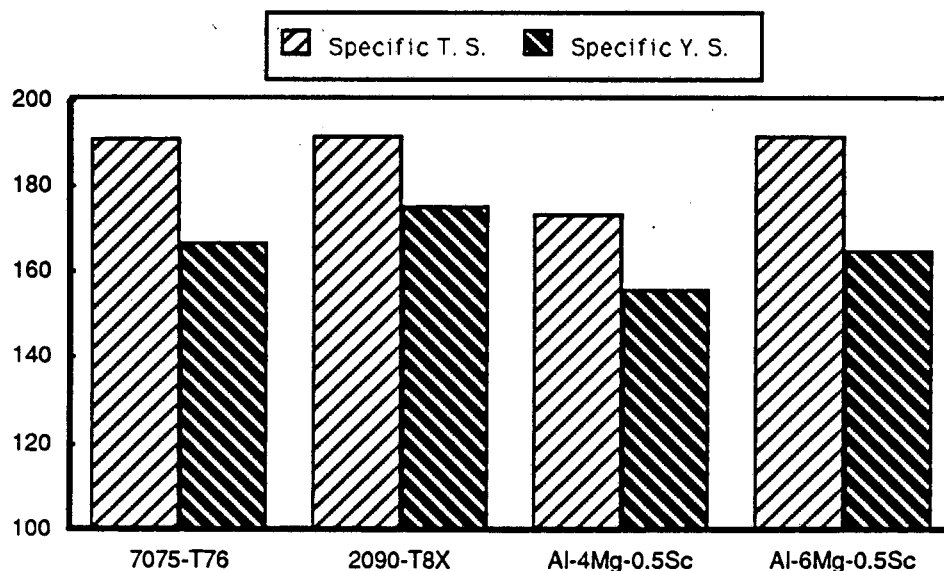


Figure 1. Comparison of the specific yield and tensile strengths of Al-Sc-Mg alloys to those of AA2090-T8X and AA7075-T76.

The exceptional thermal stability of the Al_3Sc precipitate may also prove useful in alloy design. For many years, researchers have sought methods to improve the dismal elevated temperature performance of high performance Al alloys. Recent work^{7,8} has emphasized dispersion hardening because of the inherently high coarsening rates of the common precipitate phases. While promising dispersion hardened alloys have been developed, their usefulness is compromised by the need for powder processing to fabricate usable products, by the relatively high density caused by the high atomic number alloy elements used, and by low fracture toughness, which is due, in part, to the incoherent nature of the dispersions. The Al_3Sc phase precipitates at temperatures well above ($>100^\circ\text{C}$) those characteristic of traditional precipitation strengthening phases in Al and is unusually resistant to coarsening. Hence, there is good reason to expect that Al-Sc alloys can be designed to retain high strength and fracture toughness in a temperature range above that of current aerospace alloys and below the range of dispersion strengthened systems.

The good thermal stability of the Al_3Sc precipitate combined with its effectiveness in limiting grain boundary motion can also be used to impart exceptional superplastic forming properties to Al-base alloys. Al-Sc-Mg alloys have been produced with superplastic forming capability far superior to the currently accepted baseline for SPF Al alloys; AA7475⁶. The ability to superplastically form high performance Al alloys offers potential for performance increases due to more efficient designs and substantial weight saving as total part count is reduced significantly.

Finally, Al-Sc-X alloys might have an important application as tank materials for new launch vehicles. Materials for such tanks must have good strength and high toughness at cryogenic temperatures but must also be weldable. Tear resistance, an indicator of toughness, is plotted versus yield strength for several Al-Sc-(Mg) alloys⁹ in Figure 2; data for 2219-T87, the current baseline for such structures, is included for comparison. These results show that the Sc containing alloys develop combinations of strength and toughness at both room and cryogenic temperatures that are well above those for 2219. In addition, they can be expected to be highly weldable and their lower density (7 pct. lower for Al-6Mg-0.5Sc) could translate into significant weight reductions compared to a 2219 vehicle.

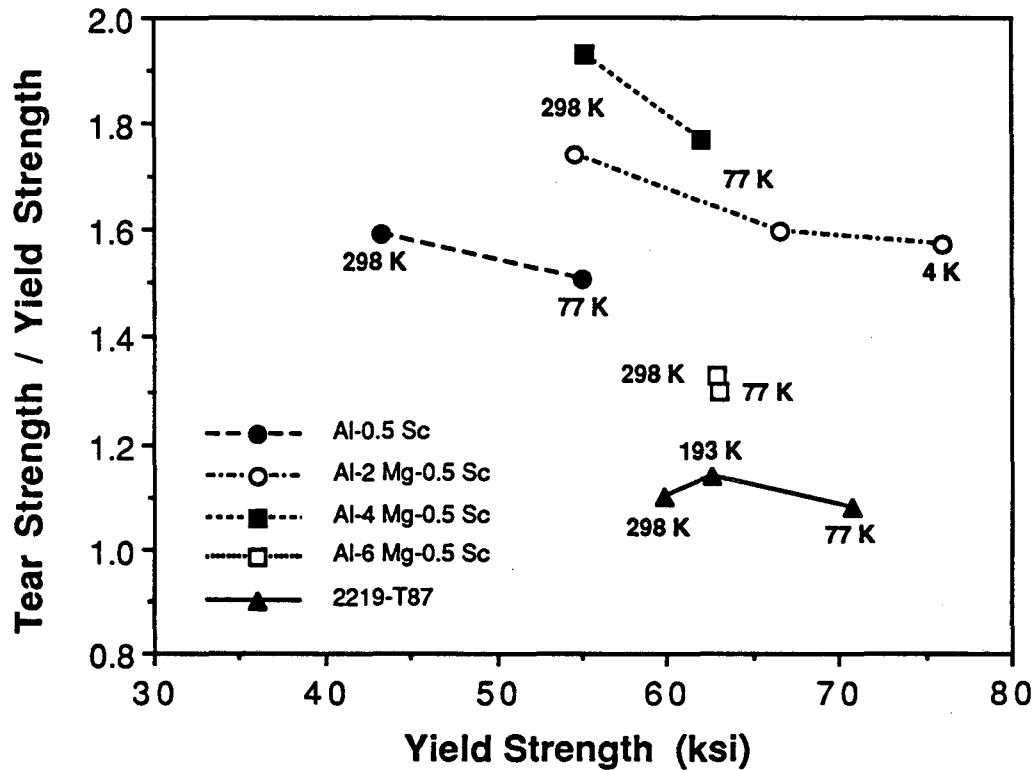


Figure 2. Tear strength plotted versus yield strength for a number of Al-Sc-(Mg) alloys along with AA2219-T87.

With all of the aforementioned benefits the reader will most likely be wondering why Sc is not in widespread use in aluminum alloys. The reasons are straightforward: Sc costs between \$40 and \$80 per gram and because there is little commercial use for it, availability is quite limited. None of the alloys that have been investigated up to now offered sufficient performance improvements to offset this difficulty. Moreover, relatively little fundamental research has been done, which limits the base from which new and potentially more attractive alloy designs could be constructed. The purpose of this work is to attack the latter problem by extending the base of knowledge regarding age hardening in Al-Sc-X alloys and, more specifically, by exploring the potential of ternary additions in augmenting strength in such alloys. If other alloying elements can be found that interact synergistically with the Al_3Sc phase to produce more effective precipitates or larger volume fractions, either performance could be improved in an important way or the amount of Sc required (and cost) could be reduced. Either result could help launch this potentially important new system. Thus, the commercial goal of this research is to identify ternary additions that improve age hardening response, if they exist.

III. Background and Theory

In principle, a search for element exhibiting favorable ternary interaction with Al_3Sc could be done in a purely empirical way. However, a more efficient approach would be one guided by existing metallurgical theory. Indeed, it is an additional goal of this research to develop a theoretically based alloy design methodology for this system. This task would be simplified significantly if the relevant equilibrium and nonequilibrium phase relationships were known for various Al-Sc-X systems. Unfortunately, such information is not generally available and we must rely on a more basic approach. The challenge is to predict which elements or combinations of elements interact synergistically with Sc to produce similar distributions of coherent precipitates. This requires considering at least three different phenomena: (1) the formation of intermetallic compounds that resemble Al_3Sc , (2) the precipitation of such compounds from solid solution in Al, and (3) the influence of the precipitates on alloy strength, both directly and indirectly. Fortunately, these subjects have been well studied the general sense and application of relevant theories to the task of developing an alloy design approach will be the subject of the next sections.

A. Intermetallic Compounds

The obvious first step in a search for elements that behave like Sc is to consider the other elements that share its grouping in the periodic table. Scandium, a group IIIA element, should be similar to Y and the Lanthanide or rare earth elements (RE). To begin an assessment of the potential for interactions of these elements in the Al_3Sc phase, available simple theories of intermetallic formation are useful. These are based on two key considerations: chemical interactions, which can often be associated with differences in electronic structure and electronegativity, and elastic interactions, which are due to difference in atom size. Table I presents the radii and electronegativities of the group IIIA elements.

Table I: Radii and Electronegativity for Various Group III Elements

Element	Atomic Number	Ionic Radius (nm)	Metallic Radius (nm)	Electronegativity
Al	13	0.0570	0.1430	1.61
Sc	21	0.0730	0.1620	1.36
Y	39	0.0905	0.1801	1.22
Ce	58	0.1034	0.1820	1.12
Pr	59	0.1013	0.1820	1.13
Nd	60	0.0995	0.1820	1.14
Pm	61			1.13
Sm	62	0.0964	0.1820	1.17
Eu	63			1.20
Gd	64	0.0938	0.1801	1.20
Tb	65	0.0923	0.1782	1.20
Dy	66	0.0900	0.1773	1.22
Ho	67	0.0894	0.1765	1.23
Er	68	0.0881	0.1757	1.24
Tm	69	0.0869	0.1720	1.25
Yb	70	0.0858	0.1790	1.10

The electronic configurations of Sc, Y and RE elements are all quite similar with one d and two s electrons contributing to bonding. The electronegativity difference between Al and Sc is small, which suggests that the bonding between the two is predominantly metallic. Most of the rare earth elements have electronegativity values very similar to Sc, with Y and the series Gd through Tm being the closest. Thus, we can expect that these elements should strongly resemble Sc in their chemical interaction with Al.

In contrast to the electronegativity values, there is a substantial difference between the metallic radii of Al and Sc (12%). In addition, Y and the other rare earth elements are all significantly larger than Sc. It is, hence, likely that differences in the behavior of the IIIA alloying additions in Al will be dominated by size effects. The rare earth elements that are closest to Sc in size are Y and the series Gd through Tm. Thus, the first challenge is to assess the nature of size factor effects in Al-RE intermetallic compounds.

There is a reasonable body of experimental information on the intermetallic compounds that form between aluminum and the rare earth elements of interest¹⁰. A review of this work reveals that the observed intermetallic structures can be divided into three types: (1) Al₃X compounds, (2) cubic Mg₂Cu-type Laves phases and (3) orthorhombic AlDy-type structures. Consistent with the discussion above, these are all recognized to be so-called "size factor" compounds. We are primarily interested in the Al-rich phases with Al₃X

stoichiometry. This category includes a variety of related crystal structures that are based on different stacking sequences of ordered $\{111\}$ planes with triangular symmetry^{11,12,13}. In all cases, the stable structure is the one that minimizes crystal volume and, to first order¹⁴, the structure of the binary intermetallic is determined by the size mismatch between Al and the rare earth element in question. The structural trend is shown in Figure 3, in which the cube root of the cell volume (a') is plotted against the rare earth metallic radius for all of the binary Al_3X structures. Such plots are usually constructed using ionic radius but in this case use of metallic radius is more instructive and justifiable because of the aforementioned chemical similarities among these elements. The Cu_3Au -type, L_{12} crystal structure, which is typified by Al_3Sc , is favored when the size difference is small; the smallest rare earth elements (Er, Tm, Yb) form stable L_{12} structures and the next largest (Ho, Tb) can be induced into this structure by raising the external pressure¹⁵. The upper limit on the rare earth metallic radius for formation of an L_{12} -type Al_3X structure lies at about 0.176 nm at atmospheric pressure and about 0.178 nm at high pressure.

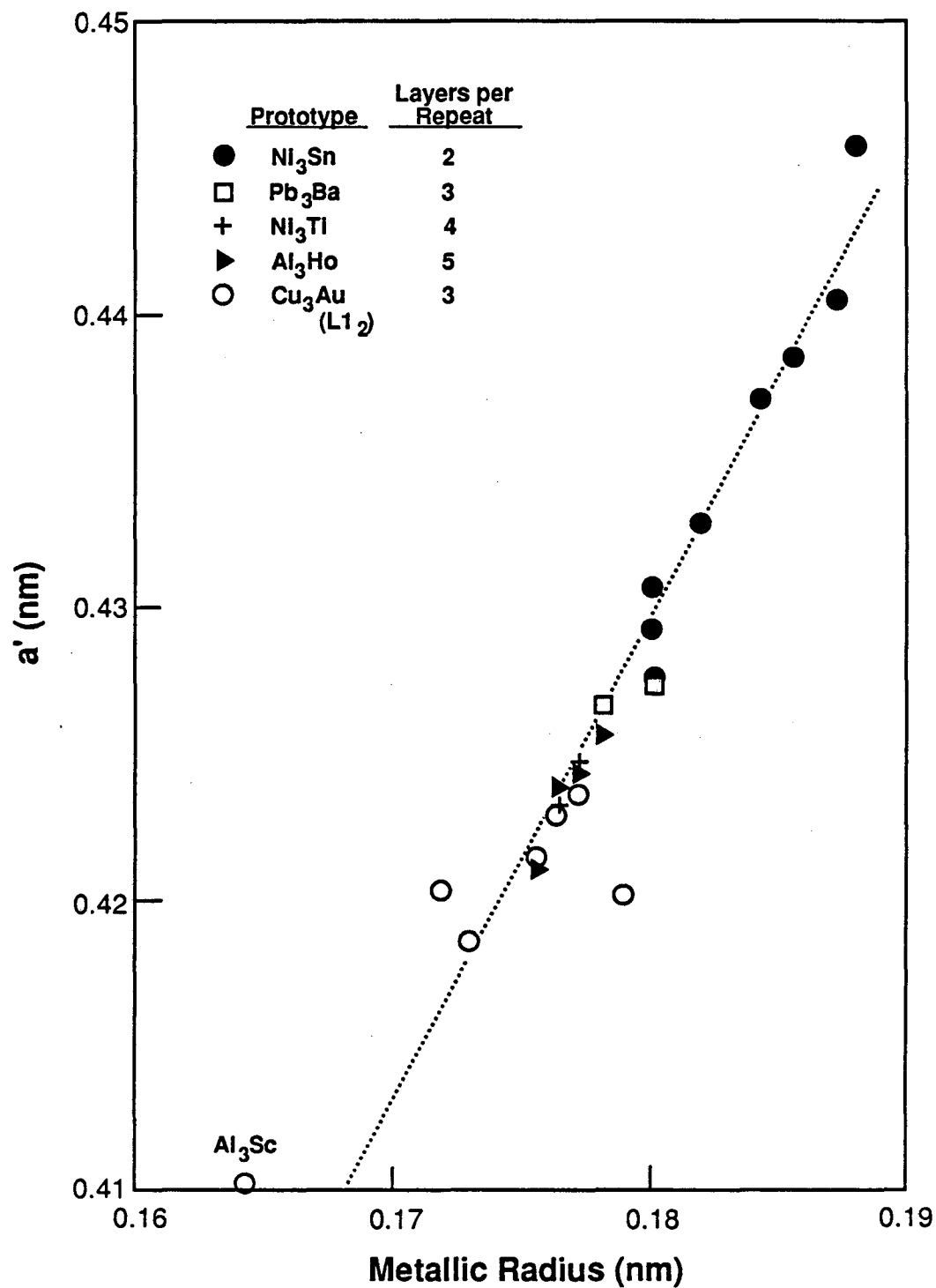


Figure 3. Cube root of the cell volume (a') plotted against rare earth atom size for binary Al_3X structures. Multiple configurations are observed for some RE and L_{12} structures like Al_3Sc are favored for lower values of radius.

As size difference increases a trend from ABC-type, FCC stacking with 3 layer per repeat period toward hexagonal or AB stacking with 2 layers per repeat period is observed. This trend is interpreted in terms of reorganization of the close packed planes to minimize interatomic potential energy¹⁴. *Restricting our attention to structures made up of ordered close-packed planes of triangular symmetry*, a greater fraction of space is filled by increasingly hexagonal stacking of the planes when the size difference among atomic constituents becomes large. There is, of course, a diminishing difference in space-filling between cubic and hexagonal stacking when the size difference is small and under these circumstances the higher symmetry of cubic structures is preferred.

The pressure effect and, specifically, the behavior of Al_3Y compounds appear to be based on second order effects associated with compressibility or the gradient in interatomic repulsive force with respect to distance¹⁶. There is a large difference in compressibility between the RE elements and Al which leads to a decrease in the effective radius ratio as pressure is increased. Thus, there is a transition to structures observed for lower radius ratio as pressure is increased. Yttrium, on the other hand, does not differ much from Al and shows no pressure effect.

Although the trends observed in binary trialuminides is important in developing a basic understanding, ternary interaction are the main focus of this work. The relation between structure and atomic size in the binary aluminum rare earth compounds suggests the existence of ternary compounds with the L1_2 structure and the stoichiometric formula $\text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$. The L1_2 structure should be favored for combinations of scandium and rare earth elements that produce an effective size, $r_{\text{eff}} = (1-x)r_{\text{Sc}} + (x)r_{\text{RE}}$, less than about 0.176 nm. We would, thus, anticipate an inverse relationship between the size of a rare earth element and its maximum solubility in the L1_2 structure. A number of such ternary intermetallic compounds have been observed experimentally^{17,18}. A representative list is given in Table II which also includes the reported solubility limit (X), the lattice constant at the solubility limit and the value of the effective radius (r_{eff}) at the solubility limit. When effective size is considered, these intermetallics follow the same structural trends as the binary trialuminides (Figure 3). As expected, the maximum reported solubility generally decreases as the rare earth size increases except for the notable exception of Y which differs somewhat as described above. However, the reduction in solubility is larger than expected and none of these compounds achieves an effective radius near the limit found for the binary intermetallics (0.176 nm). In addition, the effective radius at maximum solubility decreases with increasing rare earth size. This effect may be a simple consequence of the distortion of the Sc-RE sublattice of the L1_2 structure caused by increasing size difference between Sc and the RE.

Table II. Ternary $\text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$ Intermetallics

RE Addition	Ternary RE Radius (nm)	Maximum RE Solubility	Lattice* Parameter (nm)	Effective Radius (nm)
Er	0.1757	0.90	0.4160	0.1745
Ho	0.1765	0.72	0.4199	0.1730
Dy	0.1773	0.40	0.4190	0.1720
Tb	0.1782	0.57	0.4196	0.1701
Gd	0.1801	0.15	0.4118	0.1664
Y	0.1802	0.60	0.4168	0.1705

*At the reported maximum solubility

B. Precipitation

In the previous section we considered the stable intermetallic configurations in the Al-Sc-RE system and found that interactions do exist that are a function of RE size. As a next step we consider the precipitation of these compounds from an Al solid solution. The thermodynamic driving force for precipitation at given temperature and volume, ΔF , is

$$\Delta F = V_\beta(\Delta f_c + \Delta f_e) + A_\beta(\gamma_{\alpha\beta}) \quad (1)$$

where V_β is the precipitate volume, Δf_c and Δf_e are, respectively, the chemical and elastic free energy changes per unit volume of precipitate phase, A_β is the interfacial area of the precipitate and $\gamma_{\alpha\beta}$ is the interfacial tension. If we consider *differences* in ΔF between L1_2 Al_3RE precipitates we can neglect both the Δf_c and $\gamma_{\alpha\beta}$ terms because of the strong chemical similarities among the RE discussed above. Thus, the differences in the driving force for nucleation for the various compositions is determined by differences in the elastic energy, Δf_e .

The total change in elastic free energy on forming a precipitate is

$$\Delta^T F_e = N[f_p - f_s] \quad (2)$$

where N is the number of solute atoms in the precipitate, f_p is the elastic free energy of the precipitate per solute atom and f_s is the elastic free energy per solute atom in the solution. The general expression for the elastic free energy change associated with the introduction of an inclusion (solute or precipitate) is

$$\Delta F_e = \int_V \left\{ \int_0^{\epsilon_{ij}} \sigma_{ij} d\epsilon_{ij} \right\} dV \quad (3)$$

where σ_{ij} is the media stress function and ϵ_{ij} is the strain. Evaluation of this expression has been the subject of a great deal of fundamental research over the years and is most easily visualized through reference to the Eshelby cycle^{19,20} (Figure 4). Five steps are involved:

1. Remove a volume of α from the matrix ($\gamma_{\alpha\alpha}$)
2. Transform this volume to β under stress-free conditions (ΔF_e)
3. Apply external tractions to reproduce the original α ' geometry (ΔF_e°)
4. Place the strained β inclusion back into the matrix ($\gamma_{\alpha\beta}$)
5. Allow the β to relax (ΔF_r)

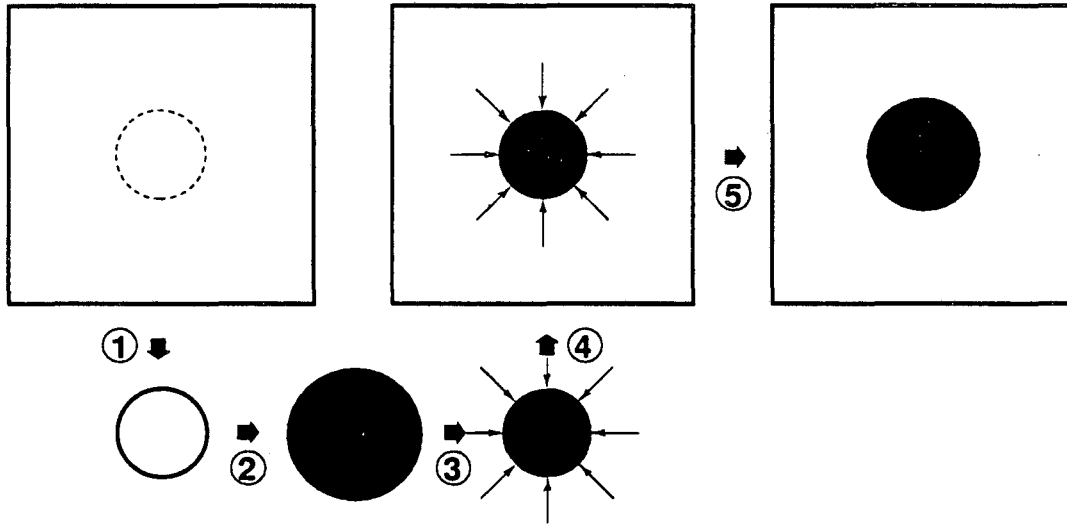


Figure 4. Diagram showing steps involved in the original Eshelby analysis of elastic strain energy.

For the purpose of calculating differences in the elastic free energy contributions, only steps 3 and 5 which represent the inclusion self energy and its relaxation energy, respectively, are relevant.

$$\Delta F_e = \Delta F_e^\circ + \Delta F_r \quad (4)$$

The self energy is due to elastic constraint of the stress free transformation strain while the relaxation energy accounts for partial relaxation of this strain when the artificial constraint is removed. The self and relaxation energies can be written as

$$\Delta F_e^\circ = \frac{1}{2} \int_V \sigma_{ij}^\circ \epsilon_{ij}^\circ dV_p \quad (5)$$

$$\Delta F_r = \frac{1}{2} \int_V \sigma_{ij}^o \epsilon_{ij} dV_p \quad (6)$$

Evaluation of the relaxation energy for a completely general solid is complex²¹. However, the L1₂ precipitate (or a solute atom) represents a simple dilatation in an FCC matrix and Al is quite isotropic with respect to its elastic constants. If, in addition, we assume that the elastic constants are homogeneous, considerable additional simplification of the components of (5) and (6) is possible²².

$$\epsilon_{ij}^o = \text{transformation strain} = \left(\frac{\epsilon^o}{3}\right) \delta_{ij} \quad (7)$$

$$\epsilon_{ij} = \text{relaxation strain} = \left(\frac{1}{3}\right) \left(\frac{1+\nu}{1-\nu}\right) \left(\frac{\epsilon^o}{3}\right) \delta_{ij} \quad (\text{in precipitate}) \quad (8)$$

$$\sigma_{ij}^o = \text{transformation stress} = \lambda_{ijkl} \epsilon_{kl}^o = (2G) \left(\frac{1+\nu}{1-2\nu}\right) \left(\frac{\epsilon^o}{3}\right) \delta_{ij} \quad (9)$$

where G and ν are, respectively, the shear modulus and Poisson's ratio of the elastic medium and ϵ_o is the stress-free strain of the inclusion (unconstrained misfit) and λ_{ijkl} the matrix of elastic constants. Rearrangement of these expressions leads to the equation

$$\Delta F_e = V_p \left(\frac{2}{9}\right) G \left[\frac{1+\nu}{1-\nu}\right] \epsilon_o^2 \quad (10)$$

Application of this relation to precipitation from solid solution requires values for the stress-free strain, ϵ_o , of the precipitate and the solute atom in solution. For the solution,

$$\epsilon_o \cong 3(\delta r/r) \quad (11)$$

where r is the radius of and aluminum matrix atom and $\delta r = r_{\text{eff}} - r$, where r_{eff} is the effective radius of the solute. Strictly, we should compute the effective radius in solution from the Vegard's Law constants of the solute species. Since these data are unavailable, we use the metallic radii of the atoms. For the precipitate,

$$\epsilon_o \cong 3(\delta a/a) \quad (12)$$

where a is the lattice parameter of the FCC unit cell, $\delta a = a' - a$ where a' is the lattice parameter of the L1₂ cell of the precipitate, and we have assumed complete precipitation of the available solute. Applying (10) to both an isolated solute atom and a precipitate using (11) and (12) allows calculation of the total elastic energy effect of the solute atom leaving the solid solution and entering the precipitate

$$f_s = 2G \left[\frac{1+\nu}{1-\nu}\right] \left\{ \Omega_s \left(\frac{dr}{r}\right)^2 \right\} \quad (13)$$

$$f_p = 2G \left[\frac{1+v}{1-v} \right] \left\{ v_s \left(\frac{da}{a} \right)^2 \right\} \quad (14)$$

$$\Delta F_e^T = 2(N)G \left[\frac{1+v}{1-v} \right] \left\{ v_s \left(\frac{da}{a} \right)^2 - \Omega_s \left(\frac{dr}{r} \right)^2 \right\} \quad (15)$$

where v_s is the volume of precipitate per atom of solute and Ω_s is the volume per atom in the solid solution. While v_s is four times Ω_s , the solute strain (dr/r) is always much greater than the precipitate strain (da/a), with the consequence that the *elastic energy term is always negative and promotes precipitation*. The magnitude of the effect increases with the atomic size and atom fraction of the ternary rare earth addition. A semiquantitative picture of this effect is drawn in Figure 5, which shows the energy change versus effective RE size for binary and equiatomic (equal amounts of Sc and RE) ternary precipitates. The binary curve shows what the elastic energy effect would be if the $L1_2$ configuration were structurally stable (which is not the case for the larger RE). The upper ternary curve considers only elastic effects for formation of a ternary $L1_2$ precipitate while the lower one shows the additional contribution of entropy changes in a qualitative way. This additional lowering of the free energy of the system is due to the fact that there are now two distinct configurations on the Sc-RE sublattice which increases total entropy.

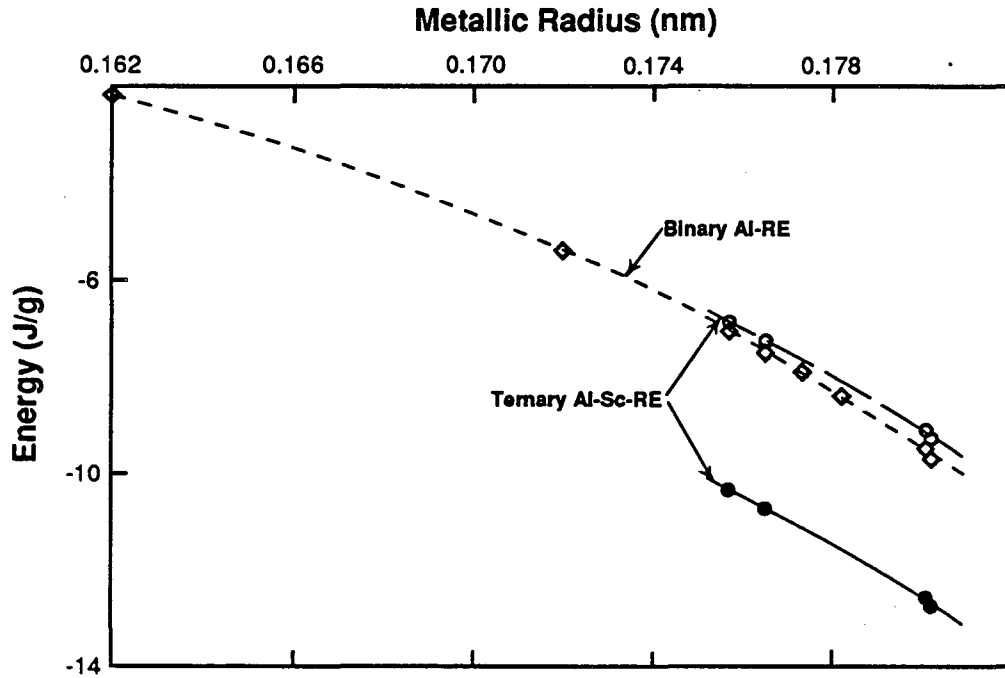


Figure 5. Calculated elastic free energy change for formation of binary and ternary Al_3RE precipitates in an aluminum matrix. Lower curve includes entropic effects.

Thus, it has been shown that the thermodynamic driving forces favor decomposition of an Al-Sc-RE solid solution to form $L1_2$ precipitates and that the driving forces increase with increasing RE size. To the extent that the RE can be structurally accommodated in the $L1_2$ phase this should result in increased precipitate volume fractions and greater phase stability. The ternary addition should be decidedly beneficial provided that it does not diminish the strengthening effect of the precipitate phase.

C. Strengthening

In the previous sections it was determined that ternary interaction should occur and result in greater amounts of more stable precipitates. We now consider the effect these changes will have on strengthening efficiency of the precipitates. This general subject has been reviewed several times^{23,24,25} and these reviews act as the basis for the following discussion. The influence of an array of precipitates on alloy strength is determined by its effect on the critical resolved shear stress for dislocation glide (τ_c), which is related to the tensile yield strength by the Taylor factor. The critical resolved shear stress for the regime where the precipitates are sheared is described by

$$\tau_c = \left[\left(\frac{6\Gamma^2}{\pi b^2} \right)^{1/2} \right] \frac{f^{1/2} Q \beta_c^n}{\langle r \rangle} \quad (16)$$

or

$$\tau_c = \Omega \left(\frac{f^{1/2} \beta_c^n}{\langle r \rangle} \right) \quad (17)$$

where b is the magnitude of the Burger's vector, Γ the dislocation line tension, $\langle r \rangle$ is the average particle radius and β_c is the effective obstacle strength. Q and n are positive constants that depend on the specific theoretical approach used. A value of 3/2 is the most appropriate value of n for relatively "weak" obstacles ($\beta_c < 0.6$) while 1 is the accepted value for "strong" obstacles. In the limit of Orowan looping equation (17) can be used if β_c is set equal to unity.

The strength (β_c), size ($\langle r \rangle$) and volume fraction (f) of the obstacles are the key parameters from the point of view of this work. The physical meaning of parameters like the average size and volume fraction are intuitively clear and although obstacle strength is easy to grasp as a general concept, a great many factors can be superimposed in determining its value. Typically, chemical, modulus, stacking fault, coherency and order strengthening effects must all be considered.

Ultimately, it is the maximum value of τ_c that is of interest in predicting alloy performance. Expressions have been developed for the maximum value of τ_c depending on the dominant hardening mechanism. In an alloy strengthened by ordered, $L1_2$ precipitates, strengthening will be dominated by coherency, order or modulus hardening. The expression for maximum strength when coherency hardening dominates is

$$\tau_{c,\max}^e = 1.84 G \epsilon f^{1/2} \quad (18)$$

where G is the shear modulus, ϵ the precipitate / matrix strain and f the volume fraction. For order hardening the expression is

$$\tau_{c,\max}^0 = \left(\frac{\gamma_{apb}}{2b} \right) \left(\frac{3\pi f}{8} \right)^{1/2} \quad (19)$$

where γ_{apb} is the antiphase boundary energy and b is the magnitude of the Burger's vector.

Modulus hardening is a more complex case and no closed form solutions for the maximum CRSS are available. However, the expected increment in τ_c is proportional to the difference in moduli between the obstacle and matrix taken to the 3/2 power.

In order to gauge the effects of varying RE on strengthening efficiency in light of the equations presented above, we consider variations in volume fraction, precipitate/matrix misfit and γ_{apb} . Maximum strength increases with increased volume fraction regardless of the dominant mechanism. This effect would increase strength as degree of substitution of the RE increases which is predicted to vary as the inverse of RE size. If coherency strengthening dominates, strength will increase with increasing precipitate misfit (ϵ) which increases with increasing RE size (at a given volume fraction). In the case of dominance by order hardening, peak strength will increase with increasing antiphase boundary energy. The antiphase boundary energy is a more subtle property, but to a first approximation, it increases with the stability of the precipitate phase relative to the disordered solution^{26,27}. It should, therefore, increase with the difference between the elastic energy of the precipitate and that of the solution and thus RE size. An additional effect is anticipated that results from the size differences among atomic constituents. As the size difference between Sc and RE atom occupying the Sc sublattice increases, the structure will become more effectively "locked" or pinned by the RE atoms which extend into the spaces in alternate ordered layers occupied by the smaller Al atoms. In essence, the precipitate is solid solution strengthened by the RE on the Sc sublattice. This effect should also tend to increase the APB energy of the phase and, hence, increase its effectiveness as an obstacle. Finally, for modulus hardening the most important factor is the internal chemical configuration of the precipitates and its effect on basic elastic properties. In previous sections, it was assumed that such interactions would not vary much among the RE so this effect should be relatively small.

The considerations discussed above suggest that the volume fraction, stability and hardening effect of precipitates in an alloy containing a given amount of scandium will be improved by adding any of the RE elements listed in Table II. Volume fraction of precipitate is expected to vary as the inverse of ternary RE size, while strengthening efficiency and stability are expected to be improved with increasing ternary RE size. It is anticipated that the transformation stress (pressure) of precipitation will allow incorporation of RE that would have little solubility when unconstrained in a manner analogous to that observed in the pure intermetallics and, thus, mitigate the negative effects of increased RE size on volume fraction. The optimal addition will be determined by the relative importance of these various effects. These trade-offs will be discussed in more detail in section IV-A.

In the previous paragraphs we considered the direct effects of variation in ternary RE additions on precipitation hardening in the system Al-Sc-RE. It is also possible for variations in alloying to exert an indirect influence on strength through variations in grain or substructure. Effects of grain and subgrain size on strength have been heavily studied^{28,29,30,31} and follow a general trend described by the equation

$$\sigma = \sigma_0 + k(\bar{L})^m \quad (20)$$

where σ is the 0.2 pct. flow stress, σ_0 the flow stress at infinite grain size, $\bar{L}$ the mean linear intercept. The variables k and m are constants with m being in the range of -0.5 to -1. The value of k is said to depend on the nature of the boundary and its misorientation while m has been observed to vary with the range of grain size considered. Meyers and Ashworth³² have put forth a model that regards the polycrystalline aggregate as a composite material. This model produces a relationship of the type

$$\sigma = \sigma_0 + 8k(\sigma_b - \sigma_0)D^{-1/2} - 16k^2(\sigma_b - \sigma_0)D^{-1} \quad (21)$$

where k is again a constant and σ_b is the flow stress in the vicinity of the grain boundary. D is the grain diameter and is related to the mean intercept length by a constant factor of 1.68³¹. This model addresses the qualitative observation that σ follows a $D^{-1/2}$ trend at relatively larger grain sizes and D^{-1} relationship at smaller sizes. In relatively pure aluminum alloy wire the D^{-1} trend predominates^{30,31} leading to

$$\sigma = 25 + 85(\bar{L})^{-1} \text{ MPa} \quad (22)$$

where $(\bar{L})^{-1}$ is expressed in μm^{-1} . Thus, an alloy of this type with a $1\mu\text{m}$ grain size would be expected to exhibit a yield strength of approximately 110 MPa. Halving the grain size would result in an increase of 85 MPa or 75 pct.

Grain size in aluminum alloys is heavily influenced by the size type and distribution of dispersed phases^{33,34,35}. The drag forces exerted on a grain or subgrain boundary by a coherent precipitate is

$$F = \left(\frac{6(\gamma_{gb})f}{r} \right) \quad (23)$$

where γ_{gb} is the grain energy, f is the particle volume fraction and r the particle radius. Hence, an increase in volume fraction of a dispersed phase will tend to limit boundary mobility and decrease average subgrain size which, in turn, could have a marked effect on alloy strength. In a previous section it was shown that if the limit of RE substitution is reached, substitution of RE and volume of the $L1_2$ precipitate will decrease with increasing RE size. Thus, to the extent that subgrain size increases as a result of this increase in volume of pinning precipitates, alloy strength will decrease also.

Finally, solid solution hardening effects should be considered. To the extent that alloying remains in solution after artificial aging, the strength of the alloy will vary with the amount of material and the misfit³⁶. Thus, either increased amounts of RE in solution or increased RE size should result in greater yield stress.

IV. Materials and Procedures

A. Materials

1. Experimental Design

In the previous sections theoretical knowledge on the formation of $L1_2$ $Al_3(Sc,X)$ intermetallics, their precipitation from an Al solid solution matrix and subsequent influence on alloy strength were all reviewed. Also considered were the anticipated interactions between Sc and the RE elements and the trends expected with respect to systematic variations in RE type or size. It is now possible to integrate this information to form an alloy design strategy for Al-Sc-RE alloys and experiments to test this design. Figure 6 was constructed to assist in summarizing the theoretical trends with regard to the precipitation hardening components. This figure shows that most of the effects are optimized by increasing RE radius. The only negative factor is decreasing ternary solubility in the $L1_2$ phase with increasing RE size. Thus, the key question becomes: will the decrease in potential precipitate volume fraction outstrip the increases in precipitate efficiency? One option is to attempt further refinement of the theoretical aspects in an attempt to resolve the competition between these factors. However, because of the likelihood of complex interactions it was decided to pursue a systematic experimental program instead. A series of Al-Sc-RE alloys were chosen for this purpose and are listed in Table III. RE were selected to provide a systematic variation in size at the limit of binary $L1_2$ stability and varying ternary solubility. Equal atom fractions of Sc and the RE were used and Sc content remained constant. The amount of alloy addition was chosen in the expectation that it would exceed the $L1_2$ solubility limit for the larger ternary additions, but not for the smaller ones, and would hence allow study of the balance between the size effect on the inherent hardening by the precipitate phase and the inverse effect on solubility, which determines the total amount of precipitate that will form.

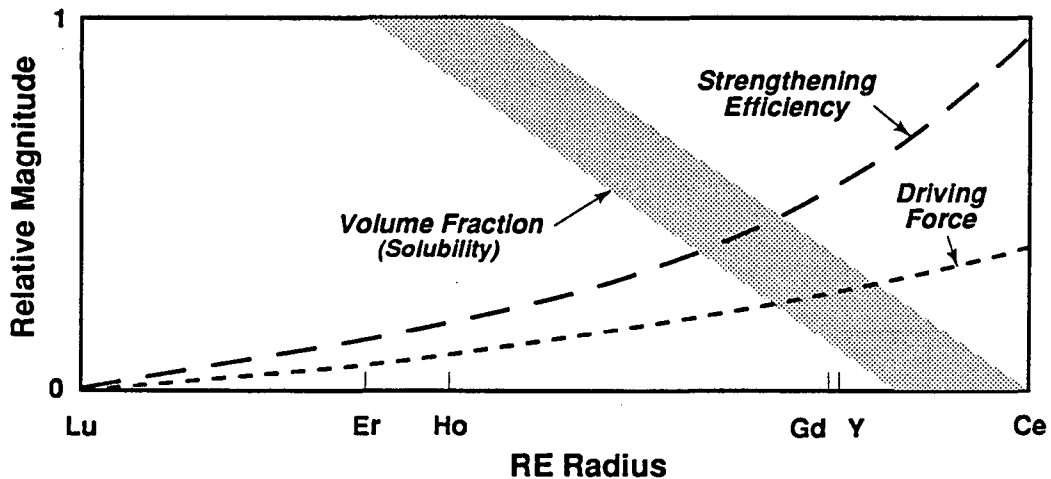


Figure 6. Schematic summary of influence of RE size on factors effecting precipitation hardening in the system Al-Sc-RE.

Table III: Phase I Alloy Compositions

System	RE Radius (nm)	Composition, at. pct. (wt. pct.)				
		Sc	Er	Ho	Gd	Y
Al-Sc	--	0.3 (0.5)				
Al-Sc-Er	0.1757	0.3 (0.5)	0.3 (1.8)			
Al-Sc-Ho	0.1765	0.3 (0.5)		0.3 (1.8)		
Al-Sc-Gd	0.1801	0.3 (0.5)			0.3 (1.7)	
Al-Sc-Y	0.1802	0.3 (0.5)				0.3 (1.0)

Although little phase diagram information is available for Al-Sc-RE alloys, the Al-Sc phase diagram has been investigated and offers some insight into optimum fabrication schemes for these alloys. The Al end of the Al-Sc binary phase diagram, as originally determined by Willey³⁷, is shown in Figure 7. More recent work by Fujikawa et al.³⁸, based on resistivity, agrees well with the solid solubility data presented in this figure but is in some conflict on the eutectic temperature. DSC analysis of the material used in this study yielded a value of 658.6°C, which is in good agreement with Willey's data.

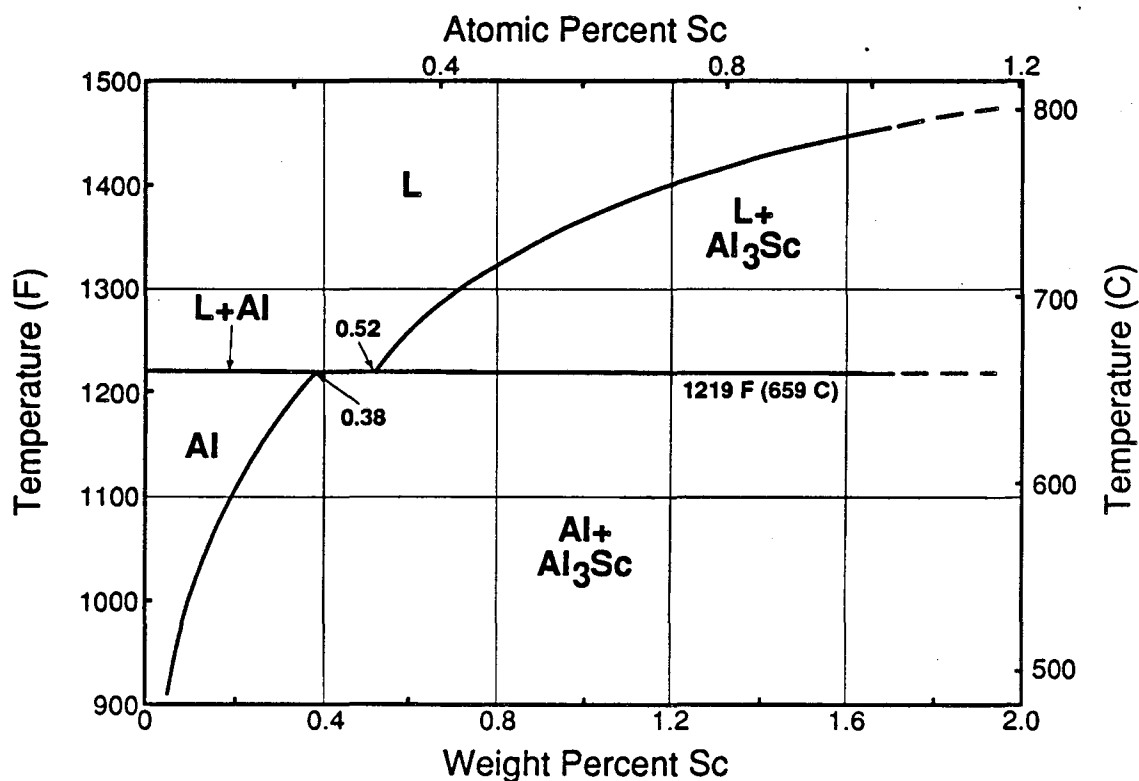


Figure 7. Al-rich end of the Al-Sc phase diagram. Note the shallow Al+L phase field.

As shown in Figure 7, the system is characterized by an extremely shallow α +liquid phase field and, thus, a very narrow hypoeutectic freezing range. It is, therefore, relatively easy to obtain a supersaturated solid solution from the melt for binary alloys with up to about 0.52 weight percent Sc, the composition at which primary Al_3Sc begins to form. This scandium content is above that which could be placed in solution with a solution annealing treatment, since the maximum solid solubility of Sc is about 0.38 percent. Thus, higher precipitate volume fractions are obtained by artificially aging *directly* from the as-cast condition in this system⁶. Unfortunately, the equilibrium solubilities of the proposed ternary alloying elements are significantly lower than that of Sc. Thus, it is important to use rapid solidification to extend the solubility of these components.

2. Melting and Casting

Each of the alloys was melted and alloyed in air employing a MgO crucible in a resistance furnace operating at 775 °C. All of the alloying elements used were 99.999 pct. pure. The aluminum base was 99.99 pct. pure. During melting the crucibles were periodically removed from the furnace and stirred with a graphite rod. When all alloying additions were dissolved, the melt was skimmed using stainless steel mesh and poured into a rectangular Cu mold preheated to approximately 200 °C. The mold design used is shown in Figure 8.

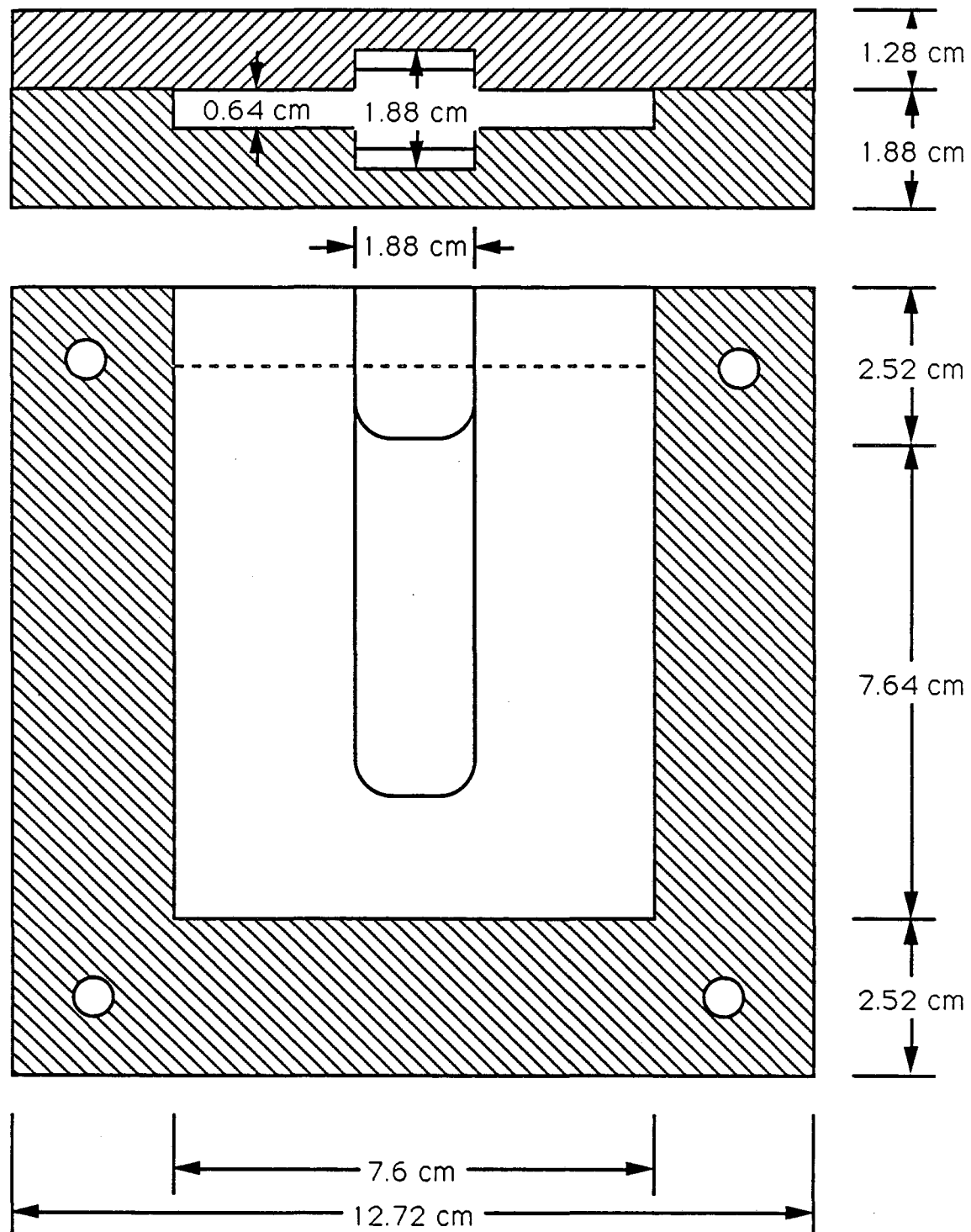


Figure 8. Drawing showing the mold configuration for casting Al-Sc-(RE) alloys.

Actual compositions of the alloys as determined by atomic absorption spectrometry are shown in Table IV. Spectrographic analysis was also performed and confirmed that trace element concentrations were all below 0.02 wt. pct..

Table IV: Chemical Analyses for Al-Sc-(RE) Alloys

System	Sample Identification	Composition (wt. pct.)				
		Sc	Er	Ho	Gd	Y
Al-Sc	609975	0.52				
Al-Sc-Er	609982	0.51	1.75			
Al-Sc-Ho	609981	0.51		1.91		
Al-Sc-Gd	609980	0.50			1.72	
Al-Sc-Y	609979	0.52				0.96

For simplicity, these alloys will be referred to throughout the remainder of this work by listing the intended additions rather than their specific composition (i.e. Al-Sc-Gd versus Al-0.50Sc-1.72Gd).

3. Fabrication

After casting, the ingots were trimmed of solidification defects and the riser removed. Sections were machined from the ingots as depicted in Figure 9. The sections destined for mechanical and physical property evaluation were turned to a cylindrical cross section and cold swaged to approximately 1.5 mm. They were then cold drawn to 0.44 mm wire. The material intended for microstructural characterization was cold rolled to either 1 or 0.25 mm sheet. All thermal treatments were carried out in circulating air furnaces maintained within ± 2 °C of set point. In all cases, samples were placed into a furnace that had been stabilized at the nominal process temperature.

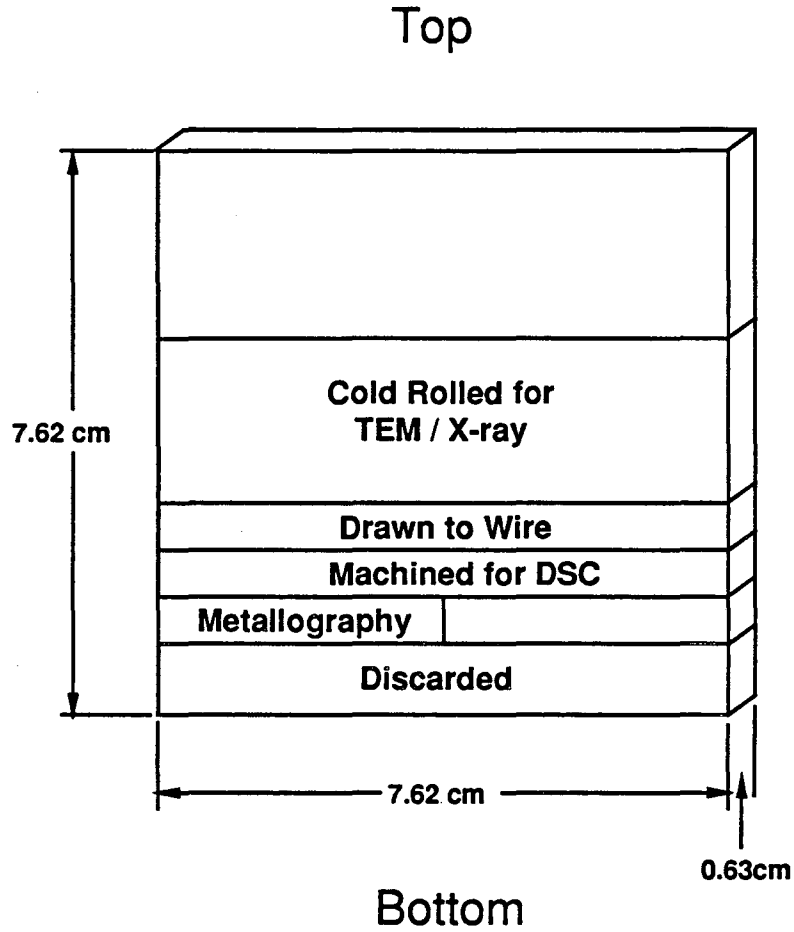


Figure 9. Drawing showing sample locations in the original Al-Sc-(RE) alloy ingots.

B. Procedures

1. Physical Properties

Both electrical resistivity and tensile properties were used to monitor artificial aging trends in the 5 alloys studied. Electrical resistance was determined using a standard 4 point probe configuration employing a Kelvin bridge for measurement. The contact assembly constructed for this purpose is shown in Figure 10. The upper probe was spring-loaded to maintain a constant pressure on the wire sample and the electrical leads were connected directly to the body of each of the lower probes. The sample and the probe contacts were immersed in an oil bath maintained at 21 ± 1 °C during measurement. Resistance, which is geometry dependent, was converted to resistivity using the simple formula

$$\rho = \left(\frac{A}{L} \right) R \quad (24)$$

where ρ is resistivity, A cross sectional area, l length and R resistance. For the particular geometry used here $\left(\frac{A}{l}\right)$ was equal to 2.951×10^{-4} cm.

Because of the wire configuration chosen to evaluate artificial aging behavior, a dedicated testing machine was required to determine tensile properties. Such a machine was designed and constructed based on concepts used by Fultz³⁹. A drawing showing the key components schematically is presented in Figure 11 while a photograph of the actual apparatus is shown in Figure 12.

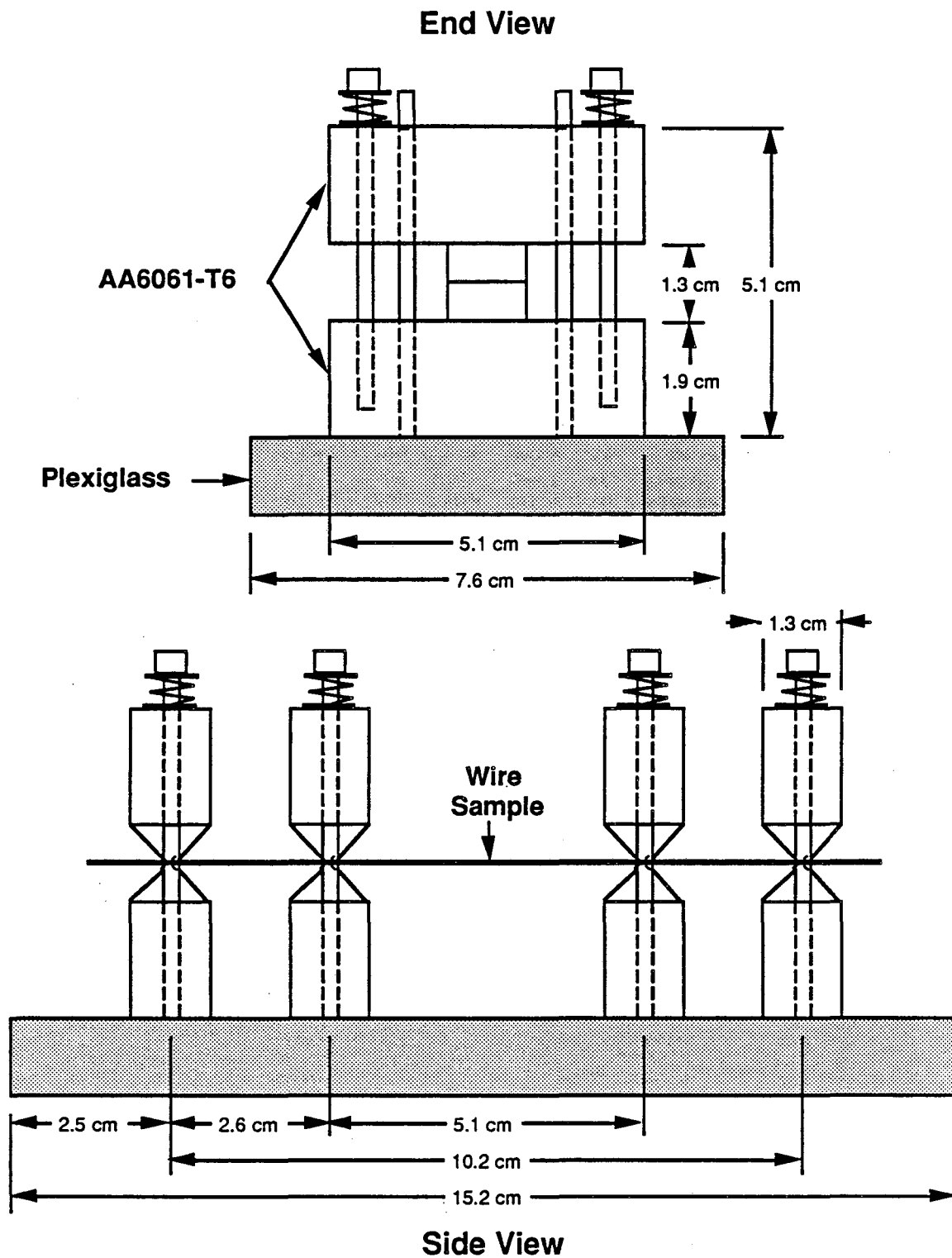


Figure 10. Drawing showing the contact configuration and materials used for measuring resistivity of the Al-Sc-(RE) alloy wires.

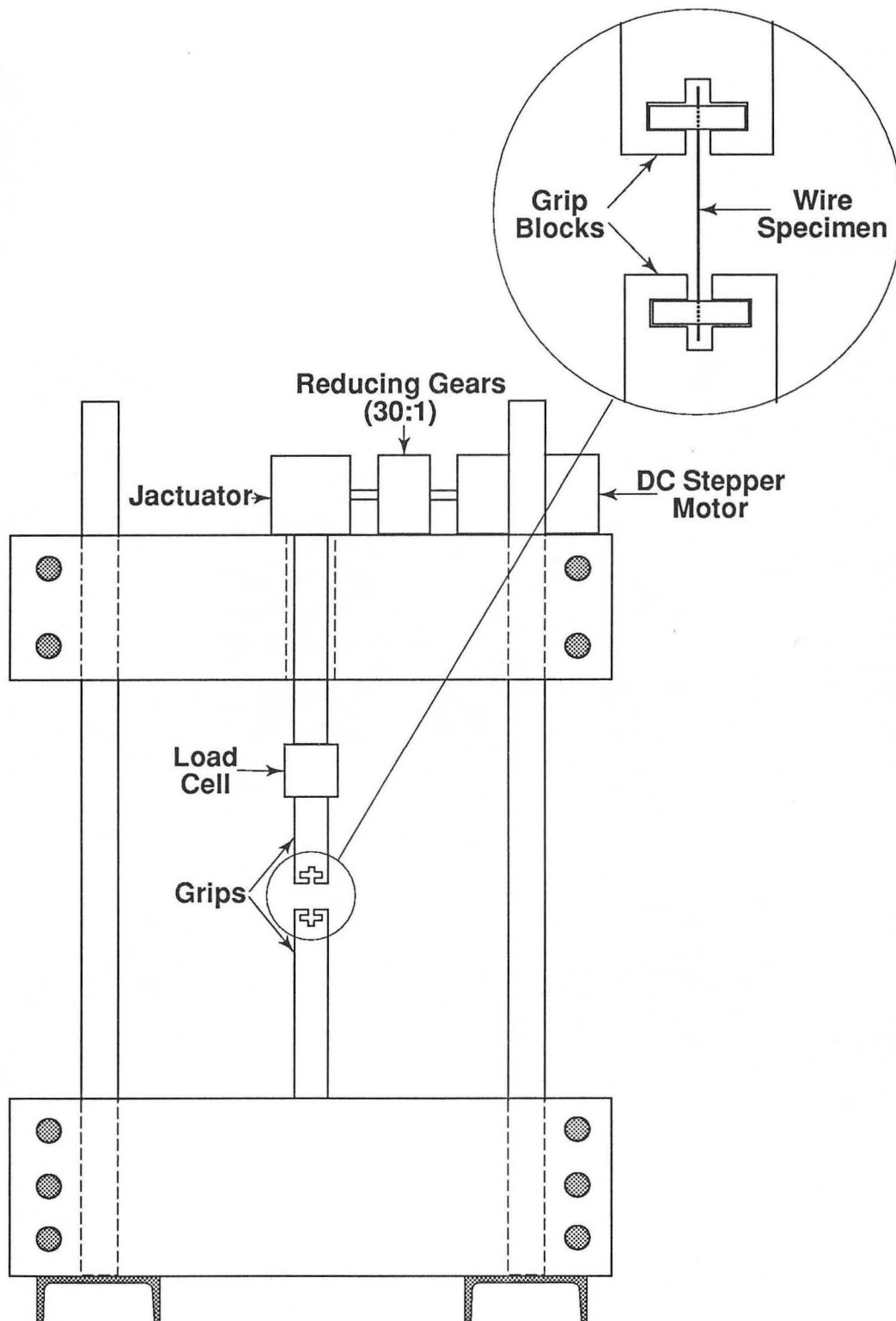
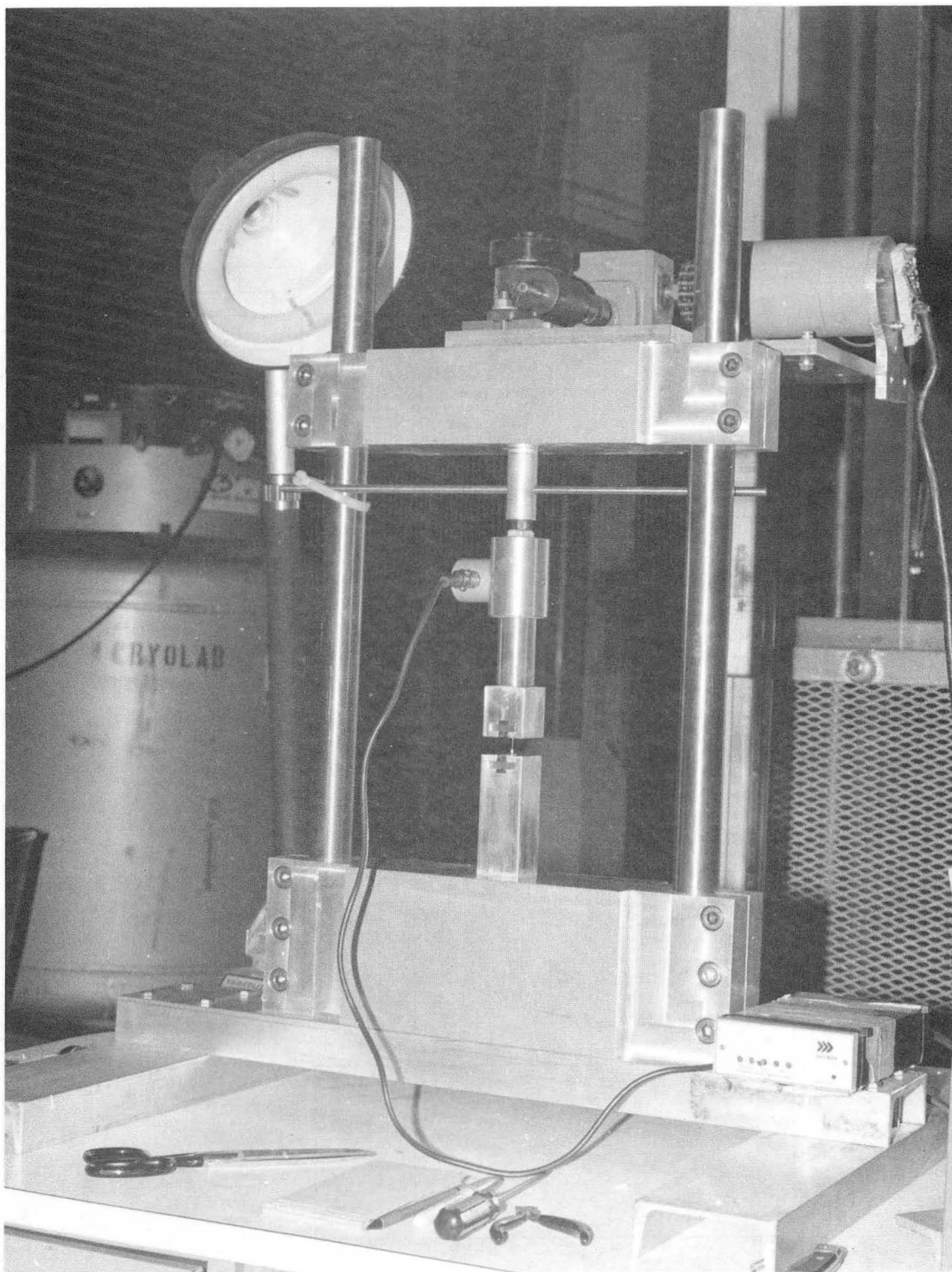


Figure 11. Schematic drawing showing the key components of a digital load frame constructed for tensile properties.



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Figure 12. Photograph of the digital load frame used for obtaining tensile properties.

Tests were run at constant applied stroke rate which, due to the high relative stiffness of the load frame, closely approximated strain rate in the wire specimen. A special jig was used to mount (via epoxy) the wires to the gripping blocks to ensure a constant 2.54 cm gauge length. A strain rate of 1 percent per min. was used for all testing and was achieved by running the DC stepper motor at 1000 steps per second or 300 RPM. Translated through the reducing gear, this produced 10 RPM at the jactuator for the required 0.0254 cm per minute of axial translation. Load cell output was captured on a strip-chart recorder operated at constant speed. Because of the unusual sample configuration, no attempt was made to strain gauge the samples. Thus, analysis of the data was restricted to determining ultimate tensile strength from peak load. Typical breaking loads were on the order of 45 Newtons.

2. Characterization

Characterization of precipitation reactions was carried out using differential scanning calorimetry (DSC). The apparatus used was a Model DSC-7 manufactured by the Perkin-Elmer Corp. All DSC runs were made using aluminum sample pans in a dynamic Ar atmosphere. Scan rates were varied from 10 to 80 °C/min. Both the magnitude of the L1₂ phase precipitation reaction and the temperature at maximum reaction rate were typically recorded.

If we assume first order kinetics, we can use this information to determine activation energy and frequency factor for the precipitation reaction^{40,41,42}. Because this is a little used technique in Materials Science, the analysis is outlined below.

For first order reactions we write

$$\frac{dF}{dt} = k(1-F)^n \quad (25)$$

where F is the fraction transformed, t is time, n is the reaction order (=1) and k the rate constant. The rate constant, k is written

$$k = Ze^{-(E/RT)} \quad (26)$$

where Z is the frequency factor, E the activation energy, R the universal gas constant and T is absolute temperature.

The activation energy is obtained by determining the change in peak position with scan rate;

$$\frac{\partial(\ln\beta)}{\partial(1/T_p)} = P(x) \left(\frac{E}{R} \right) \quad (27)$$

where β is the scan rate (i.e. 20 °C/min.), T_p is the temperature for maximum reaction rate and $P(x)$ is a function of the activation energy and temperature;

$$P(x) = -\left(\frac{e^x}{x}\right) \int_{-\infty}^x \left(\frac{e^x}{x}\right) dx \quad (28)$$

$$x = \left(\frac{E}{RT}\right)$$

An approximate expression for $P(x)$ which can easily be solved numerically is:

$$P(x) \cong \left(\frac{1}{(x+3)} - \frac{1}{x} - \frac{1}{(x+1)} - \frac{1}{(x+4)} - 1 \right) \quad (29)$$

After the activation energy has been determined, the frequency factor is calculated using

$$Z_i = \frac{\beta_i E e^{(E/RT)}}{RT_i^2} \quad (30)$$

$$Z = \frac{\left(\sum_0^i Z_i \right)}{i} \quad (31)$$

where the summation is carried over the number of different β employed.

Extensive microstructural characterization studies were performed during the course of this work involving X-ray methods, optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

X-ray analysis were conducted to determine the identity of phases formed during solidification. Samples were prepared by chemical thinning to ~0.1 mm using a solution of concentrated HCl and water with an NiSO_4 catalyst. Analyses were made with a Guinier-deWolfe camera in the transmission configuration and employing monochromated Cu radiation. Diffraction patterns were recorded on film. Line positions were then digitized and lattice spacing calculated using a calibration function for this radiation type and geometry.

Optical metallography was used to obtain a broad perspective of the general microstructure of both the as-cast and fabricated materials. Standard sample preparation and analysis techniques were used.

SEM was used to obtain information on the grain and subgrain structure of the fabricated wires as well as their crystallographic texture. The method used for analyzing substructure was somewhat unusual and relies on channeling enhanced contrast in the

backscattered mode⁴³. The microscope used was a JEOL JSM 840A operating at 7KV. Samples were prepared by electropolishing using an electrolyte contained 23 pct. concentrated nitric acid in methanol maintained at -30°C. Samples were electropolished for 1.5 min. at 8 volts. Mean grain intercept length was determined by digitizing boundary intersections along a series of randomly oriented lines. Texture was determined using the same instrument employing electron backscattering patterns (EBSP). This technique⁴⁴ involved using backscatter Kikuchi diffraction at high incident angle to give very localized information on crystallographic orientation. An accelerating voltage of 14kV was used for the EBSP work.

TEM was used extensively to determine configuration and composition of the strengthening precipitates. A variety of specialized techniques and microscopes were used during the investigation including Philips EM301, EM400T and EM420T machines as well as the Atomic Resolution Microscope (ARM) at the National Center for Electron Microscopy (NCEM). The EM301 was operated at 100 kV and used for general examinations while the EM400 and EM420T were operated at 120 kV and used primarily for analytical electron microscopy. KEVEX and EDAX energy dispersive x-ray spectrometers were installed on these instruments. Theoretical K-factors were used in both cases. Absorption effects were considered but found to be insignificant. The ARM was used for high resolution studies of precipitates in the peak aged condition. This instrument was operated at 800 kV. HREM simulations and optical diffraction analyses were also carried out at NCEM. Simulations were constructed using the NCEMSS package⁴⁵ employing parameters appropriate for the ARM.

Standard electrochemical techniques were used for sample preparation in all cases. An electrolyte containing 23 pct. HNO₃ in methanol at -30 °C was used in a Struers Tenupol 2 electropolishing unit with an average sample potential of 18 volts. These condition produce an average current density of about 3 A/cm².

V. Results

A. Precipitation Reactions

1. Degree of Precipitation

Differential scanning calorimetry (DSC) runs were made for each of the alloys at heating rates of 10, 20, 40 and 80 °C/min., and a typical curve is shown in Figure 13. The exothermic peak observed is a result of the thermal effects associated with precipitation of the L_{12} , $Al_3(Sc,RE)$ phase and its magnitude is a measure of the specific energy of reaction. Specific energy of precipitation for each alloy in the as-cast condition is shown in Table V along with ternary RE radius. These data are plotted in Figure 14 showing a strong trend toward greater energy of precipitation with greater RE radius.

All values for the ternary alloys are greater than that observed for the Al-Sc binary alloy. This indicates that the RE elements are interacting in the L_{12} phase and that the interaction increases with RE radius. If there were no interaction and the RE remained in solid solution the heats of precipitation would be expected to remain constant. Unfortunately, these data do not indicate whether the interaction is in the form of greater specific energy of reaction or an increased volume of the L_{12} phase. The former effect could result if an Al_3Sc phase is precipitated that is more stable with respect to the strained solid solution matrix containing the RE; a result anticipated earlier.

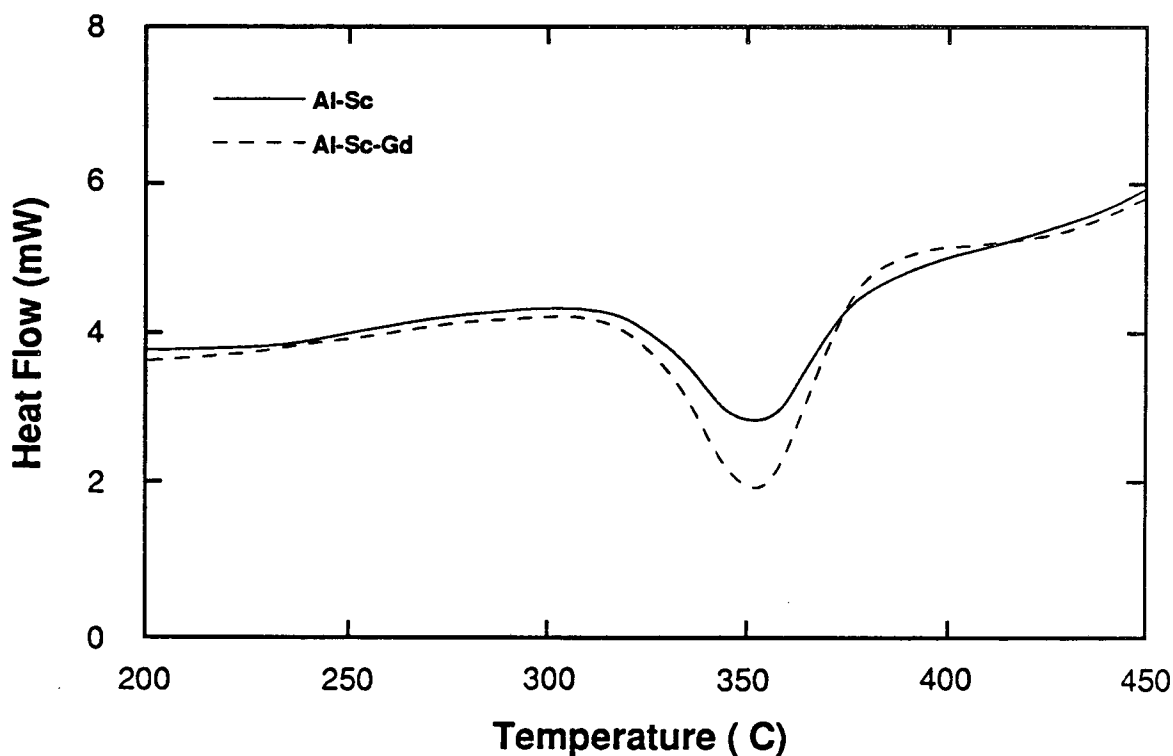


Figure 13. Plot of heat flow versus temperature for as-cast Al-Sc and Al-Sc-Gd alloys obtained using a heating rate of 40 °C/min. Note exothermic reaction peaks.

Table V: Specific Heat of Precipitation for Al-Sc-(RE) Alloys

Alloy	Heat of Precipitation (J/g)	Ternary RE Radius (nm)
Al-Sc	2.39	--
Al-Sc-Er	2.74	0.1757
Al-Sc-Ho	2.97	0.1765
Al-Sc-Y	3.35	0.1800
Al-Sc-Gd	3.32	0.1801

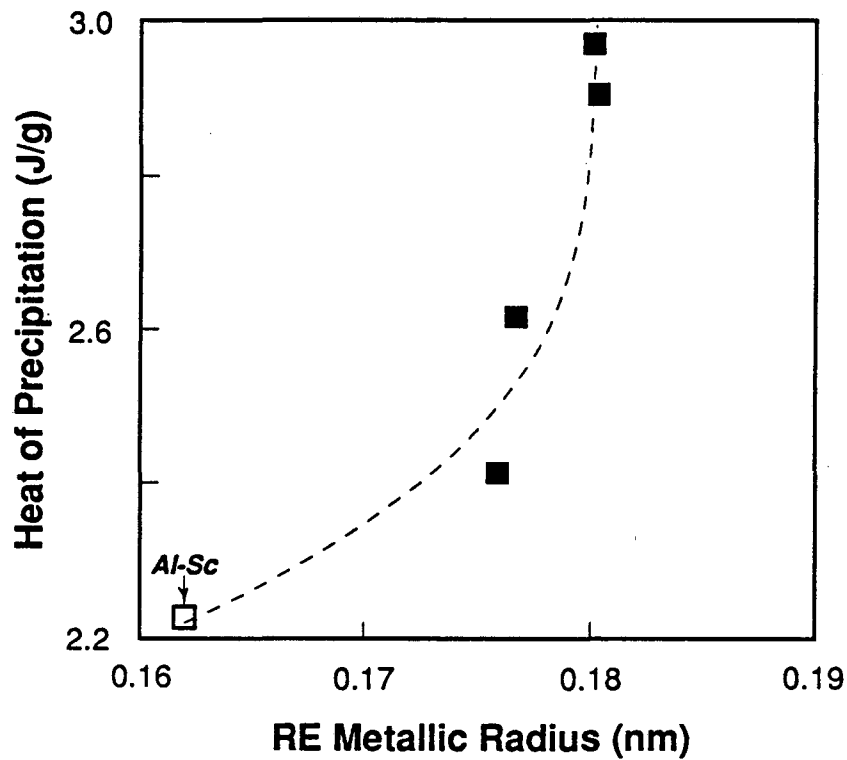


Figure 14. Specific heat of precipitation versus ternary RE radius for Al-Sc-RE alloys. Al-Sc data is shown for comparison.

2. Kinetics

The temperatures for maximum dynamic reaction rate as a function of heating rate are listed in Table VI. These data include values for both as-cast and cold rolled samples.

They were analyzed using the methods described in Section IV-B-2 to determine E and Z for the precipitation reaction which are presented in Table VII. The differences among alloys were small and appear uncorrelated. There is a consistent trend toward lower activation energy for the cold rolled material but the differences were, again, quite small. As a more tangible indication of the precipitation kinetics, the calculated fraction transformed (precipitated) as a function of temperature and time is shown for the Al-Sc alloy in Figure 15. These calculations were made using equations 25 and 26 presented in section IV-B-2. The reader is asked to note that full reaction occurs in less than 1 hour at temperatures above 260 °C.

Table VI: Temperature at Maximum Transformation Rate for Al-Sc-(RE) Alloys

Alloy	Condition	Temperature at Maximum Reaction Rate			
		10°C/min.	20°C/min.	40°C/min.	80°C/min.
Al-Sc	as-cast	316.5	331.4	353.2	374.9
	cold rolled	315.6	332.0	353.2	377.1
Al-Sc-Er	as-cast	316.3	334.6	355.2	379.8
	cold rolled	316.3	333.7	356.3	382.8
Al-Sc-Ho	as-cast	316.3	332.0	352.8	376.7
	cold rolled	317.1	332.5	355.2	379.4
Al-Sc-Y	as-cast	318.5	336.9	357.8	383.2
	cold rolled	317.8	337.4	359.9	387.2
Al-Sc-Gd	as-cast	319.5	336.0	357.2	381.8
	cold rolled	319.0	339.5	359.1	385.8

Table VII: Kinetic Parameters for Al-Sc-(RE) Alloys

Alloy	As-Cast		Cold Rolled	
	E (J/g)	Z (1/sec.)	E (J/g)	Z (1/sec.)
Al-Sc	24153	3.57E+08	23105	1.43E+08
Al-Sc-Y	22762	9.95E+07	21557	3.45E+07
Al-Sc-Gd	23697	2.38E+08	22646	9.14E+07
Al-Sc-Ho	22457	7.03E+07	20776	1.59E+07
Al-Sc-Er	23129	1.27E+08	21918	4.19E+07

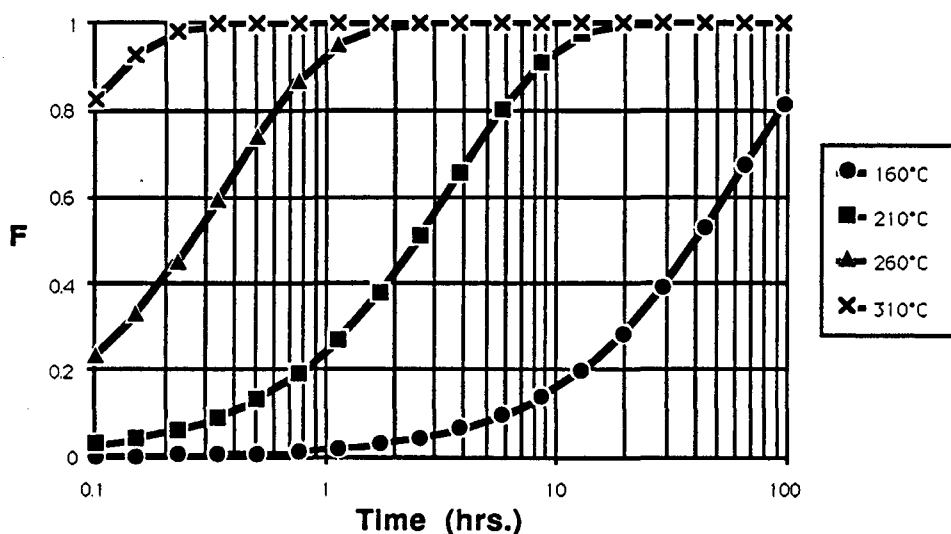


Figure 15. Calculated fraction precipitated (F) versus time for cold worked Al-Sc at a variety of temperatures.

B. Artificial Aging Behavior

1. Resistivity

Resistivity is plotted as a function of artificial aging temperature and time for Al-Sc, Al-Sc-Y, Al-Sc-Gd, Al-Sc-Ho and Al-Sc-Er in Figures 16 thru 20, respectively. In all cases, the resistivity decreases monotonically with increasing aging time or temperature. At higher temperatures like 335°C, resistivity approaches that observed for pure aluminum (2.8 $\mu\text{ohm-cm}$). In light of the DSC results which indicate that precipitation is complete after very short times in this temperature range, it is likely that these trends are the result of changes in precipitate size rather than alloying in solid solution. It is known that fine precipitates can have a marked effect on resistivity⁴⁶, a trend which is interpreted in terms of electron scattering⁴⁷. If the observed changes are dominated by precipitate size, resistivity could be an excellent way of monitoring precipitate evolution during aging. Indeed, this phenomena will be used in the next section as a means of normalizing tensile properties obtained after aging at different temperatures.

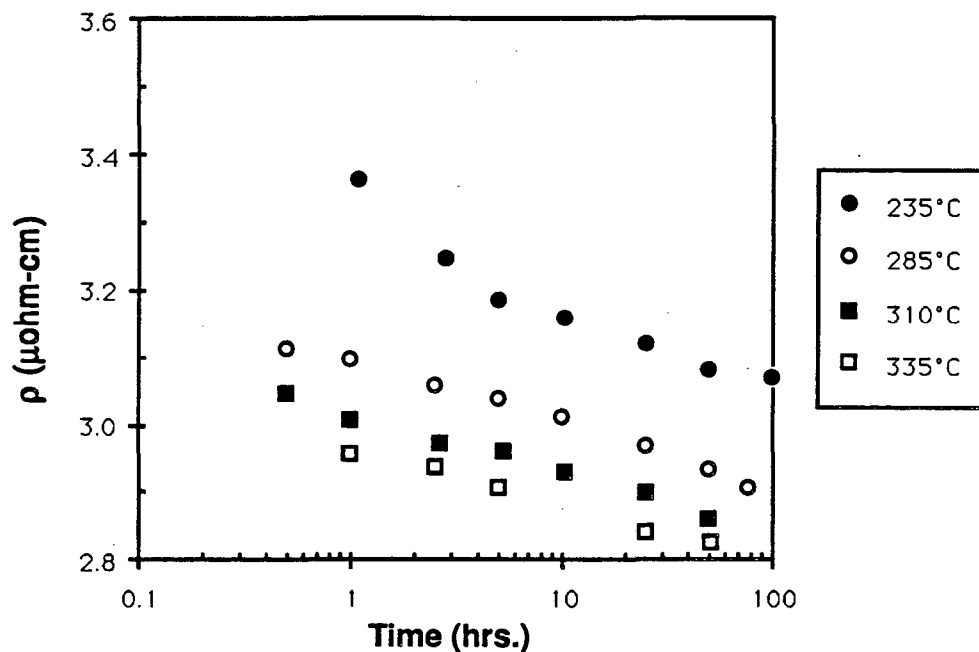


Figure 16. Resistivity (ρ) of an Al-Sc alloy shown as a function of artificial aging time and temperature.

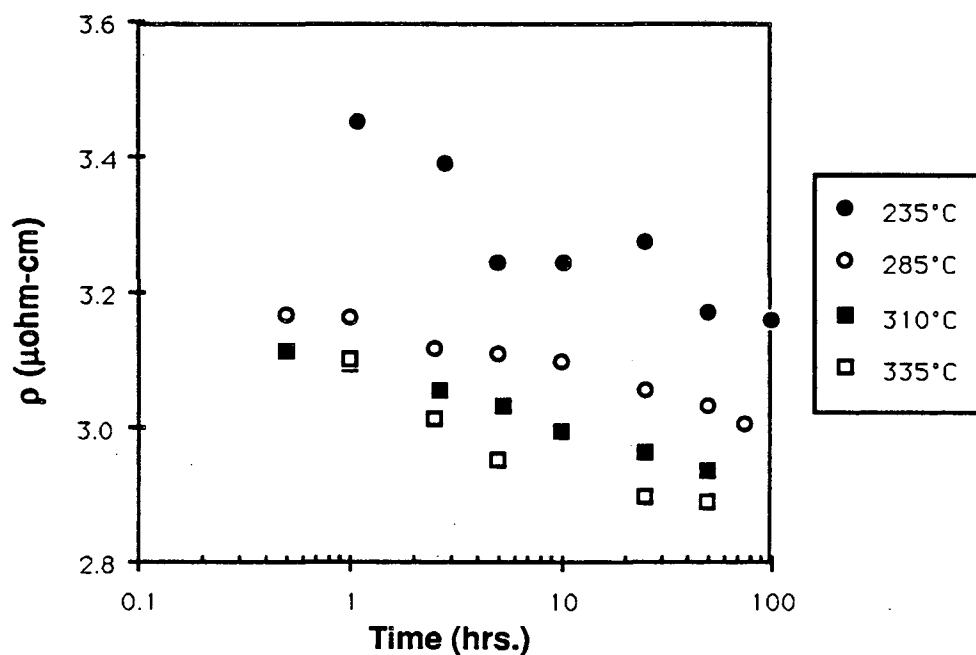


Figure 17. Resistivity (ρ) of an Al-Sc-Y alloy shown as a function of artificial aging time and temperature.

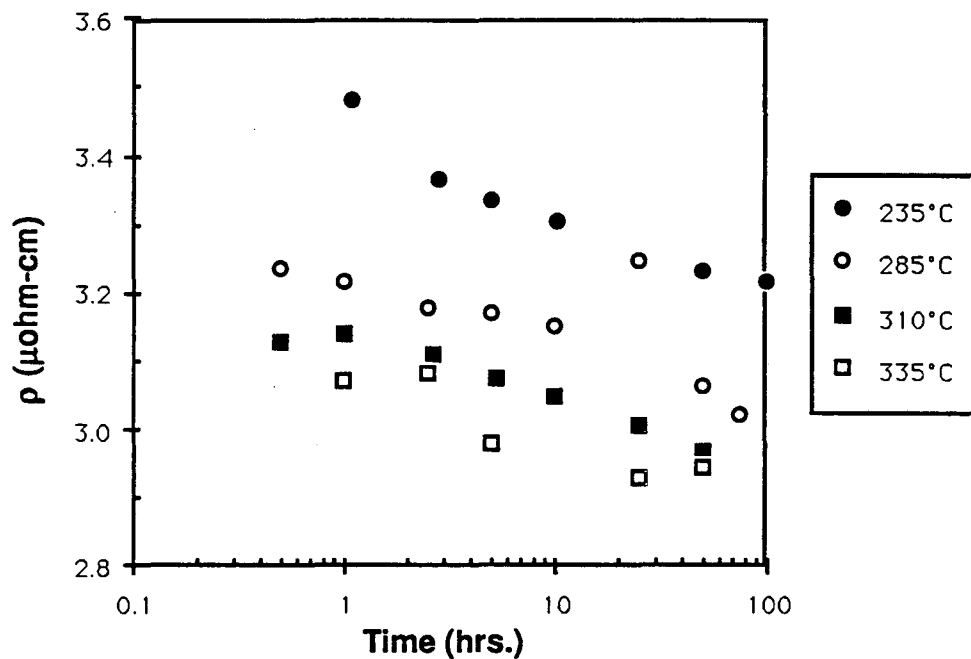


Figure 18. Resistivity (ρ) of an Al-Sc-Gd alloy shown as a function of artificial aging time and temperature.

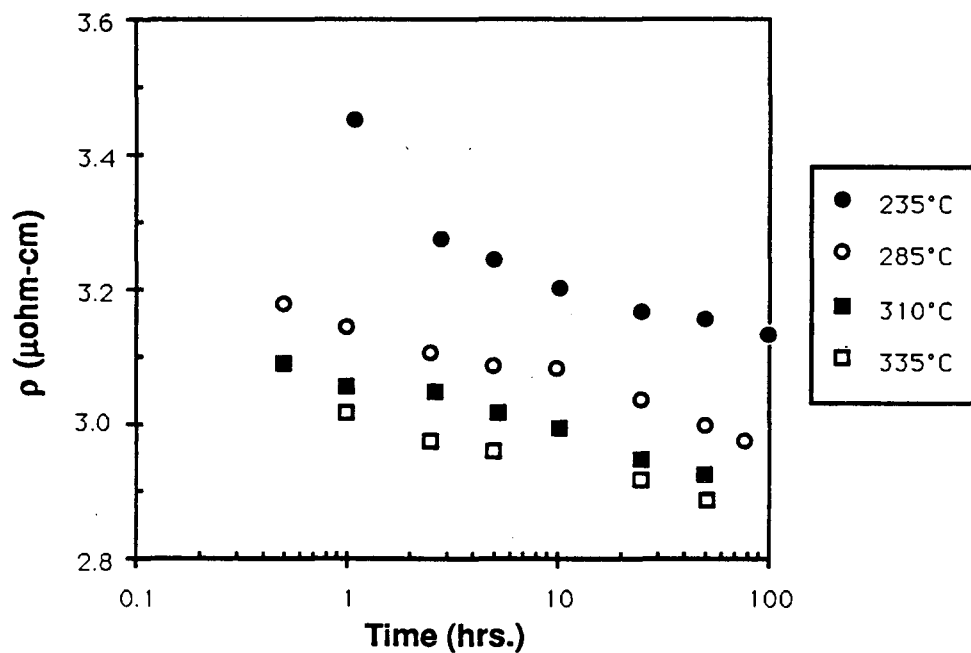


Figure 19. Resistivity (ρ) of an Al-Sc-Ho alloy shown as a function of artificial aging time and temperature.

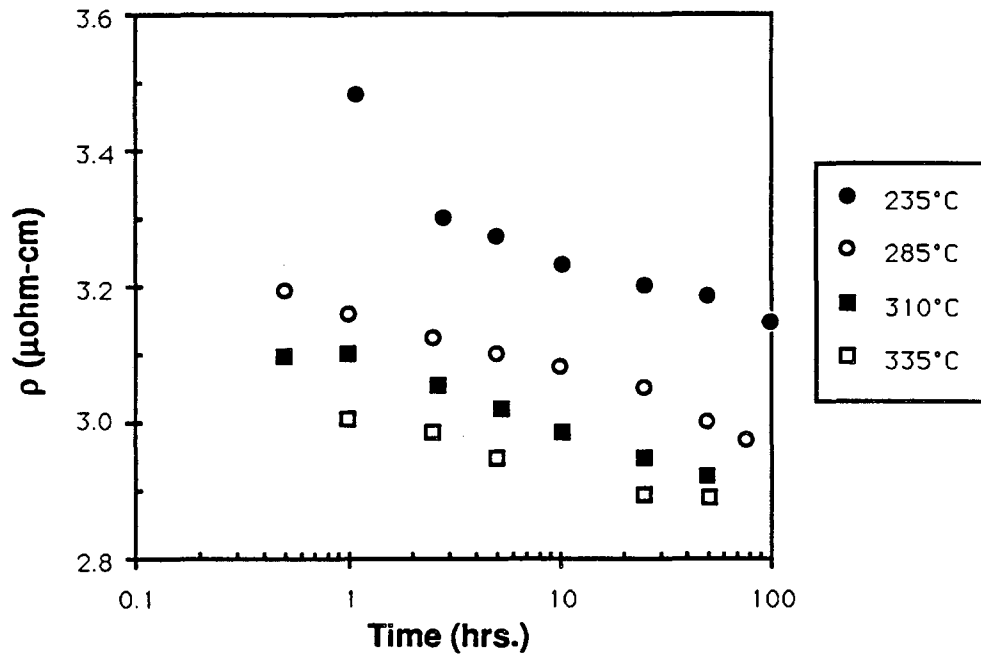


Figure 20. Resistivity (ρ) of an Al-Sc-Er alloy shown as a function of artificial aging time and temperature.

2. Tensile Properties

Tensile properties were determined for a restricted subset of the artificial aging conditions investigated using resistivity. The conditions examined and the measured ultimate tensile strengths are listed in Table VIII thru XII. Resistivities of the alloys are also shown in these tables and tensile strength is plotted versus resistivity in Figures 21 through 25 for Al-Sc, Al-Sc-Y, Al-Sc-Gd, Al-Sc-Ho and Al-Sc-Er, respectively. Resistivity decreases with increasing aging so effective aging time increases to the left in these figures. When compared in this way, data for the 3 different aging temperatures appear to follow similar trends, as anticipated in the previous section. Normal artificial aging behavior is observed with an initial increase in strength to a peak value followed by a decrease. Peak strength and the resistivity at peak strength for each alloy are shown in Table XIII along with ternary RE radius. These values were obtained by fitting a third degree polynomial to the experimental data and then employing standard mathematical analysis to determine the maximum.

When examining these data it should first be noted that the maximum strength of each of the ternary alloys is greater than that for the Al-Sc control. In the case of Al-Sc-Gd, the increase is 25 percent. In one sense this is not surprising since the ternary alloys contain twice as much solute. However, all of the alloys have the same Sc content and if Sc alone were determining strength the values should all be the same. A strong trend toward higher peak strength and higher resistivity at peak strength with increasing RE radius is also observed as shown in Figure 26. This is an indication that RE radius may have a significant effect on the physical evolution of the precipitate array during artificial aging.

Resistivity at peak strength and its variation with alloy has a variety of interesting implications. As a practical matter, the values for resistivity at peak strength can be used, in concert with the plots of resistivity versus time and temperature presented in Figures 16 thru 20, to determine aging time for peak strength over a wide range of temperatures. From the more fundamental point of these variations indicate a great deal about the precipitates and precipitate aging kinetics. The increase in resistivity at peak strength indicates that the peak occurs at smaller precipitate size as RE radius increases. This trend will be discussed further, in light of strengthening theory, in latter sections. When the time to reach peak strength is considered another interesting trend becomes apparent. Time required to reach peak strength increases with increasing RE radius from ~6 hours for Al-Sc-Er to ~10 hours for the Al-Sc-Y and Al-Sc-Gd alloys. As a point of comparison, the peak is attained after 5 hours in the case of the binary Al-Sc alloy. The implications of this trend will also be treated in latter discussions.

Table VIII: Artificial Aging Data for Cold Rolled Al-Sc

Al-Sc			
Aging		Resistivity ($\mu\text{ohm-cm}$)	Tensile Strength (MPa)
Temperature ($^{\circ}\text{C}$)	Time (hrs.)		
235	1	3.364	196.5
	10	3.157	231.7
	100	3.069	242.7
285	1	3.095	256.5
	5	3.039	254.4
	10	3.013	251.7
	25	2.969	236.5
310	1	3.007	255.8
	10	2.930	236.5
	50	2.859	205.5

Table IX: Artificial Aging Data for Cold Rolled Al-Sc-Y

Al-Sc-Y			
Aging		Resistivity ($\mu\text{ohm-cm}$)	Tensile Strength (MPa)
Temperature ($^{\circ}\text{C}$)	Time (hrs.)		
235	1	3.453	199.3
	10	3.246	246.1
	100	3.160	284.8
285	1	3.163	284.1
	5	3.110	289.6
	10	3.098	289.6
	25	3.057	282.7
310	1	3.095	291.0
	10	2.995	272.3
	50	2.936	243.4

Table X: Artificial Aging Data for Cold Rolled Al-Sc-Gd

Al-Sc-Gd			
Aging		Resistivity ($\mu\text{ohm-cm}$)	Tensile Strength (MPa)
Temperature ($^{\circ}\text{C}$)	Time (hrs.)		
235	1	3.482	236.5
	10	3.305	273.0
	100	3.216	299.9
285	1	3.216	296.5
	5	3.169	304.1
	10	3.152	315.1
	25	3.246	302.7
310	1	3.140	308.2
	10	3.048	293.0
	50	2.969	264.1

Table XI: Artificial Aging Data for Cold Rolled Al-Sc-Ho

Al-Sc-Ho			
Aging		Resistivity ($\mu\text{ohm-cm}$)	Tensile Strength (MPa)
Temperature ($^{\circ}\text{C}$)	Time (hrs.)		
235	1	3.453	196.5
	10	3.205	241.3
	100	3.134	255.8
285	1	3.146	261.3
	5	3.087	259.2
	10	3.084	266.8
	25	3.039	253.7
310	1	3.057	266.8
	10	2.995	249.6
	50	2.927	231.7

Table XII: Artificial Aging Data for Cold Rolled Al-Sc-Er

Al-Sc-Er			
Aging		Resistivity ($\mu\text{ohm-cm}$)	Tensile Strength (MPa)
Temperature ($^{\circ}\text{C}$)	Time (hrs.)		
235	1	3.482	207.5
	10	3.234	255.1
	100	3.149	273.0
285	1	3.160	278.5
	5	3.104	279.2
	10	3.084	275.1
	25	3.054	271.0
310	1	3.104	280.6
	10	2.986	257.9
	50	2.921	233.7

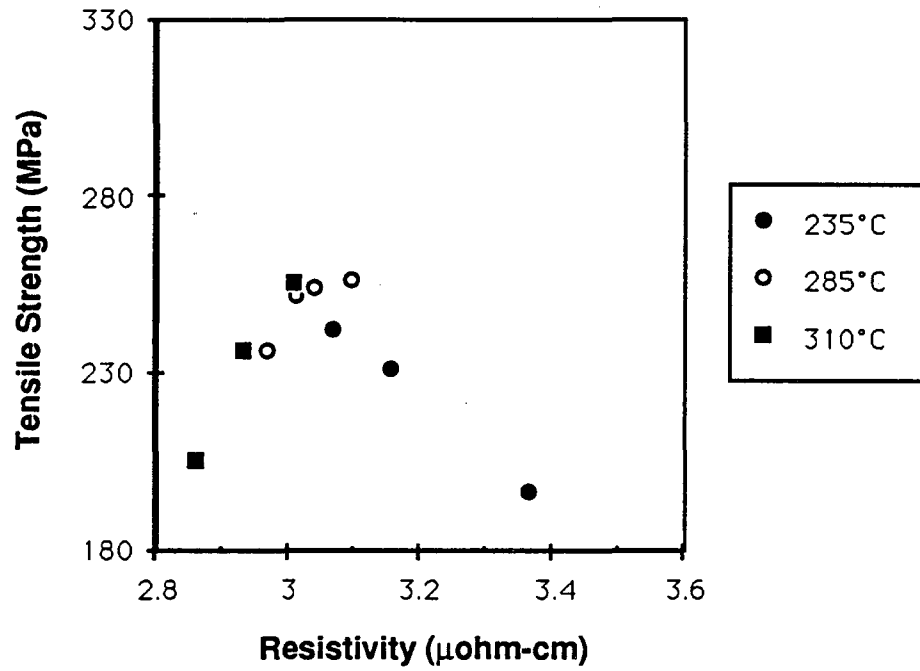


Figure 21. Ultimate tensile strength plotted versus resistivity for an Al-Sc alloy.

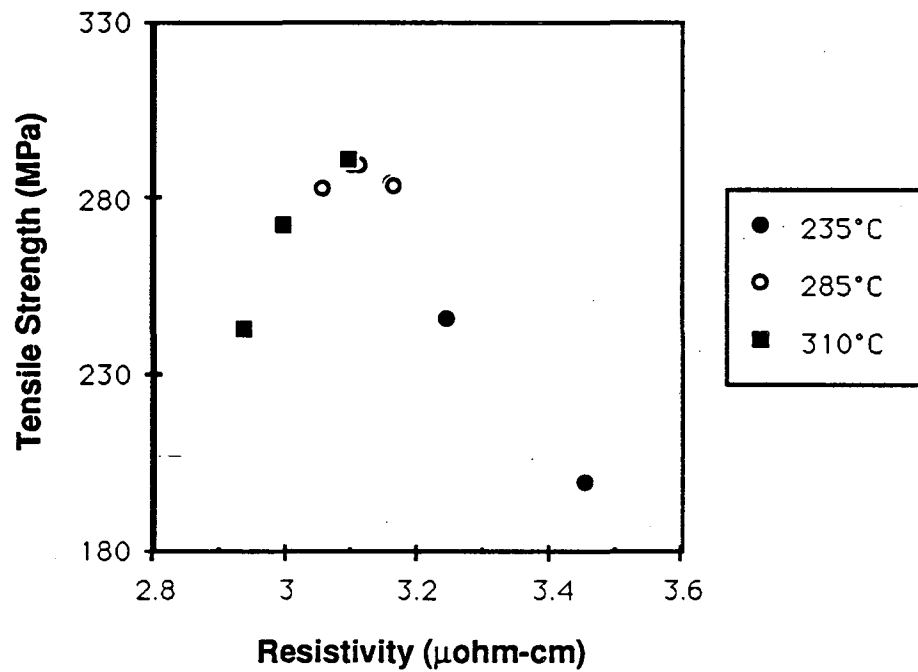


Figure 22. Ultimate tensile strength plotted versus resistivity for an Al-Sc-Y alloy.

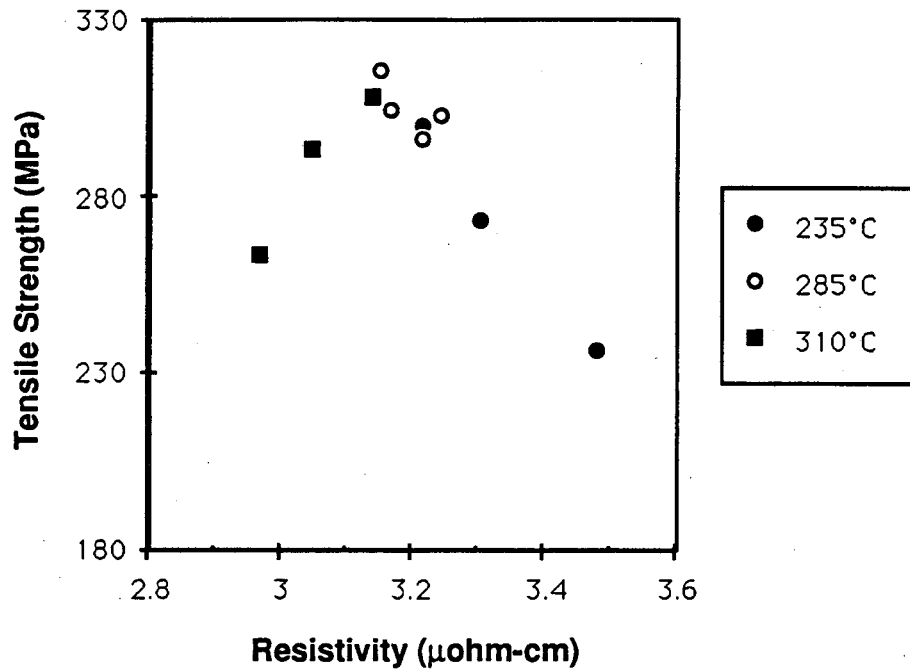


Figure 23. Ultimate tensile strength plotted versus resistivity for an Al-Sc-Gd alloy.

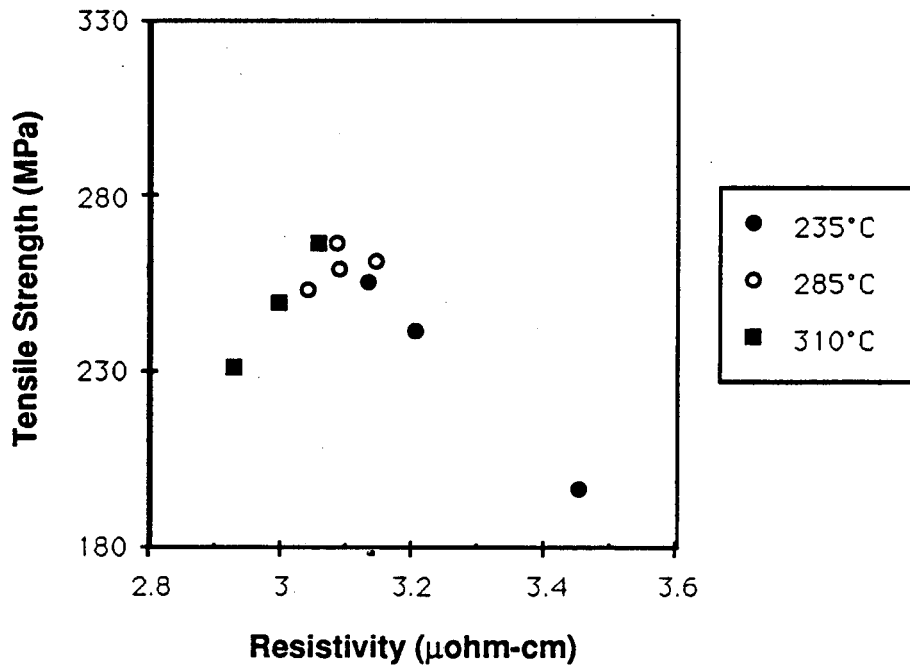


Figure 24. Ultimate tensile strength plotted versus resistivity for an Al-Sc-Ho alloy.

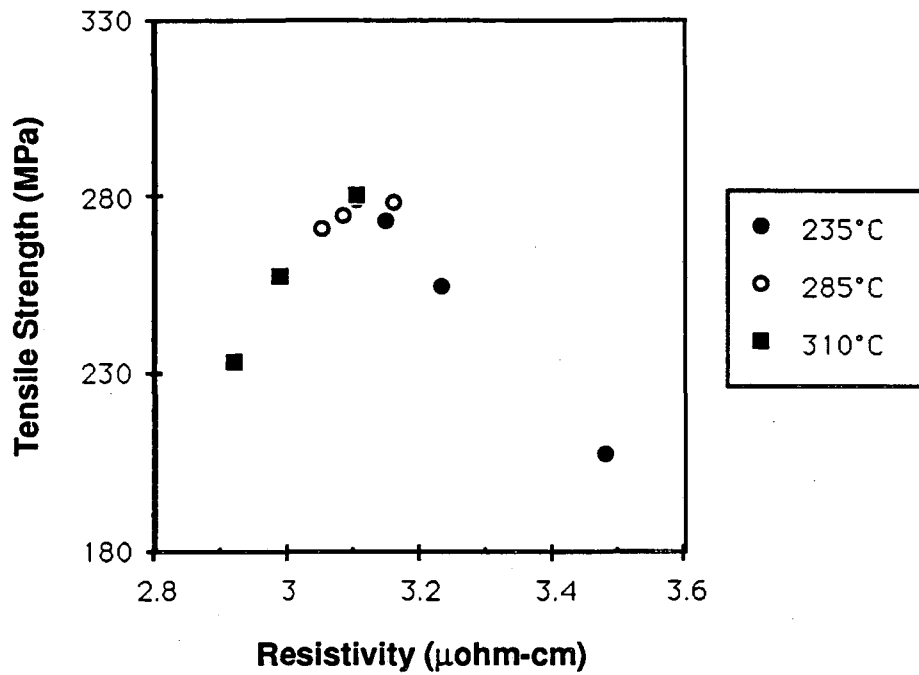


Figure 25. Ultimate tensile strength plotted versus resistivity for an Al-Sc-Er alloy.

Table XIII: Peak Strength and Resistivity at Peak Strength for Al-Sc-(RE) Alloys

Alloy	Peak Tensile Strength (MPa)	Resistivity at Peak Tensile Strength ($\mu\text{ohm-cm}$)	Ternary RE Radius (nm)
Al-Sc	251	3.033	--
Al-Sc-Er	278	3.094	0.1757
Al-Sc-Ho	262	3.073	0.1765
Al-Sc-Y	290	3.080	0.1800
Al-Sc-Gd	309	3.128	0.1801

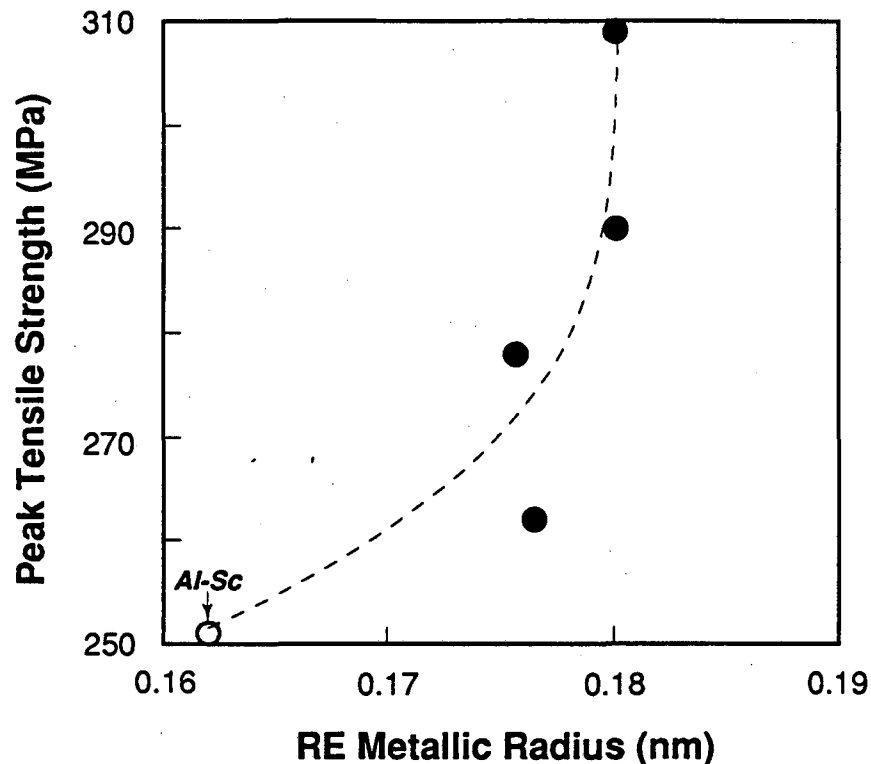


Figure 26. Peak tensile strength versus ternary RE radius for Al-Sc-RE alloys. Al-Sc data is shown for comparison.

It is also of interest to consider the strain hardening response of these alloys. Engineering stress / strain curves are shown for each of the alloys in the peak aged condition in Figure 27. The curves are quite similar varying only in the peak or ultimate tensile stress. Further, the strain hardening rates are quite low. This has been observed previously in binary Al-Sc alloys⁴⁸ and is consistent with the general observation that FCC alloys hardened by fine, coherent precipitates exhibit little strain hardening⁴⁹. This lack of strain hardening means that tensile and yield strengths are similar and follow the same trends. This fact will be the basis for analyzing tensile strength data using theory derived for yield phenomena in latter sections.

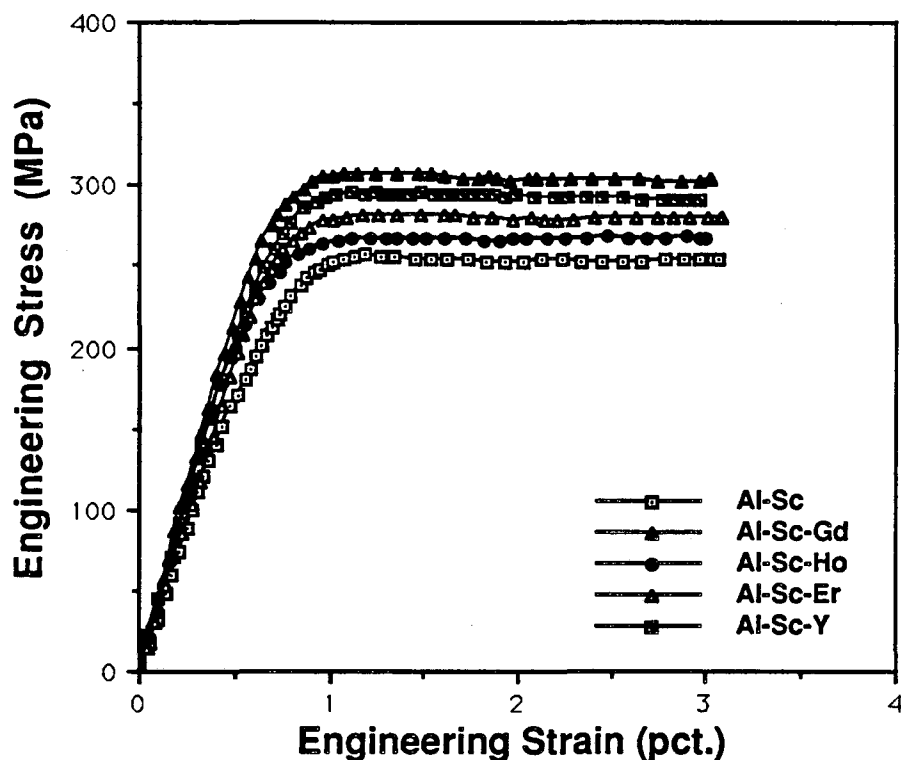


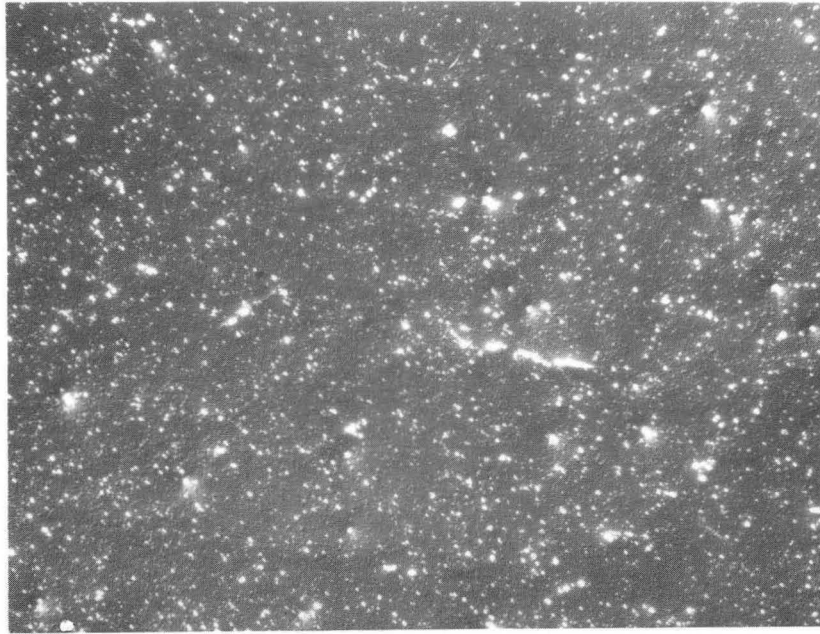
Figure 27. Engineering stress / strain curves for Al-Sc-(RE) alloys in the peak-aged condition. Very little strain hardening is observed.

C. Microstructural Characterization

1. Optical Metallography

Optical metallography was used to obtain a general perspective of the microstructures of both as-cast and fabricated samples. Optical micrographs of the as-cast samples and cross sections of the fabricated wires are presented in Figures 28 and 29 for the Al-Sc and Al-Sc-Gd alloys, respectively, as examples of the microstructures observed. Because of rapid solidification, the microstructures of the ingot samples were quite fine. The solidification cell size varied from 12 to 15 μm which translates to a cooling rate of approximately 50°C/sec.⁵⁰ Relatively few intermetallic particles are observed in the Al-Sc ingot (Figure 28a) but a pronounced cellular eutectic microstructure is evident for each of the ternary alloys as shown in Figure 29a for the Al-Sc-Gd alloy. This is not a complete surprise since the amounts of ternary elements added were known to be in excess of their equilibrium solubilities in aluminum.

The micrographs of the wire samples (Figures 28b and 29b) show that the distribution of intermetallic phases has been well refined by the extensive cold working employed in fabrication. Again, relatively fewer particles are observed in the Al-Sc alloy (Fig. 28b). The cellular structure observed in the ternary alloy ingot was completely eliminated by the cold working operation as shown in the micrograph of the Al-Sc-Gd alloy wire presented in Figure 29b.



(a)

50 μm

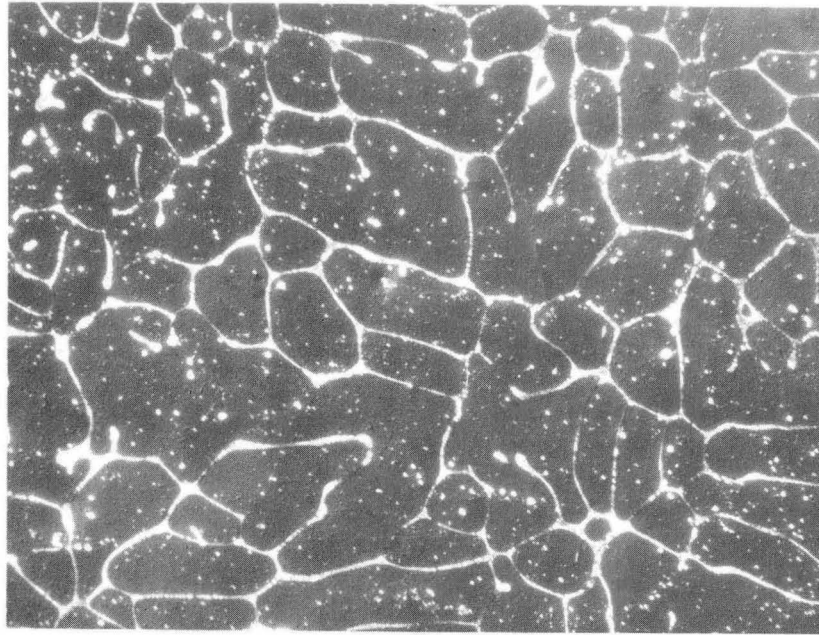


(b)

50 μm

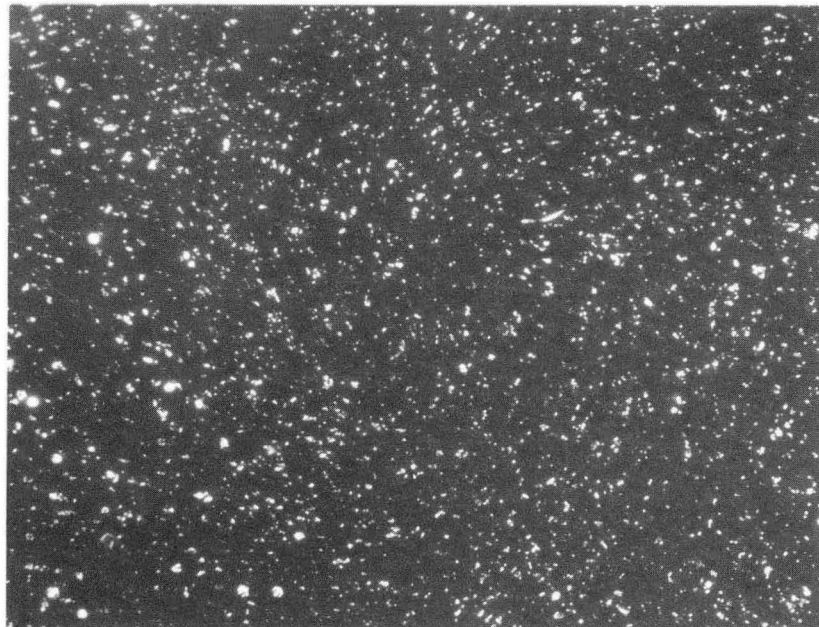
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Figure 28. Optical micrographs of Al-Sc ingot (a) and drawn wire (b). (polarized light with differential interference contrast)



(a)

50 μm



(b)

50 μm

XBB 880-9970

Figure 29. Optical micrographs of Al-Sc-Gd ingot (a) and drawn wire (b). (polarized light with differential interference contrast)

2. Guinier X-Ray Diffraction

Cold worked samples in both the aged and unaged condition were prepared for Guinier X-ray diffraction analysis. This technique is insensitive to the presence of precipitated phases in this system because of their small size so the prime purpose of this analysis was to determine the nature of the coarse phases formed during solidification.

As expected, no differences were observed between the aged and unaged samples for any of the alloys. Photographic positive prints of films obtained for the aged material are shown in Figure 30. Lattice spacings are presented in Tables XIV thru XVIII for the Al-Sc, Al-Sc-Y, Al-Sc-Gd, Al-Sc-Ho and Al-Sc-Er, alloys respectively. The I values shown are qualitative indications of relative intensity with 1 indicating the strongest lines. In each case, the significant lines could be accounted for by diffraction of known phases that have been observed in these systems before. A summary of the phase identifications are presented in Table XIX.

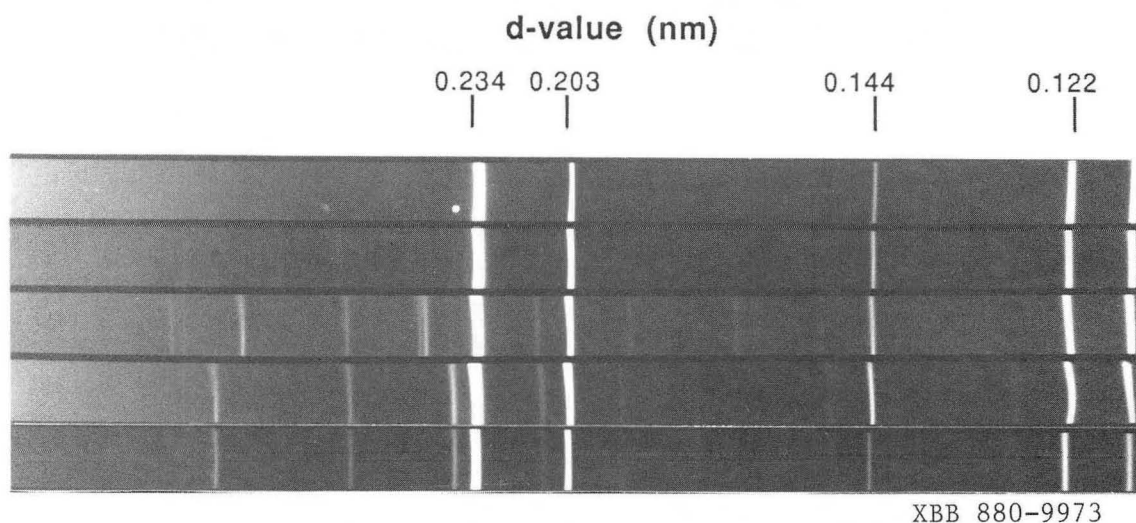


Figure 30. Photographic prints of Guinier X-ray diffraction results for Al-Sc-(RE) alloys. Starting at the top, Al-Sc, Al-Sc-Y, Al-Sc-Gd, Al-Sc-Ho, Al-Sc-Er. The more intense lines are due to the Al matrix.

Table XIV: X-Ray Diffraction Results for Cold Rolled and Aged Al-Sc

Al-Sc			
d (nm)	I	Phase	Plane
0.471	2	*	--
0.406	3	P1	{100}
0.286	3	P1	{110}
0.234	1	Al	{111}
0.203	1	Al	{200}
0.144	1	Al	{220}
0.122	1	Al	{311}
0.117	1	Al	{222}

* $\lambda/2$ line⁵¹

Al: aluminum solid solution matrix

P1: $L1_2$ - Al_3RE

Table XV: X-Ray Diffraction Results for Cold Rolled and Aged Al-Sc-Y

Al-Sc-Y			
d (nm)	I	Phase	Plane
0.471	2	*	--
0.426	3	P1	{100}
0.407	3	*	--
0.354	2		
0.310	2	P2	{110}
0.305	2	P1	{110}
0.286	3	*	--
0.266	3	P2	{201}
0.255	2	*	--
0.245	2	P1	{111}
0.240	2	P2	{204}
0.234	1	Al	{111}
0.227	3	P2	{205}
0.212	3	P1	{200}
0.203	1	Al	{200}
0.188	3	P2	{208}
0.155	3	P2	{220}
0.153	3	P1	{220}
0.144	1	Al	{220}
0.122	1	Al	{311}
0.117	1	Al	{222}

* $\lambda/2$ lines⁵¹

Al: aluminum solid solution matrix

P1: Cu₃Au-type, $Pm\bar{3}m$ ($L1_2$) structure

P2: Pb₃Ba-type, $R\bar{3}m$ structure^{11,52}

Table XVI: X-Ray Diffraction Results for Cold Rolled and Aged Al-Sc-Gd

Al-Sc-Gd			
d (nm)	I	Phase	Plane
0.580	2		
0.493	2	P3	{002}
0.474	2	*	--
0.424	3	P1	{100}
0.391	1	P3	{200}
0.371	3	P2	{104}
0.344	3		
0.322	2	P3	{003}
0.300	1	P3	{202}
0.287	3	*	--
0.260	2	P3	{113}
0.256	1	P3	{300}
0.253	2	P1	{111}
0.245	3	*	--
0.235	1	Al	{111}
0.225	3	P3	{302}
0.222	3	P3	{220}
0.213	2	P1	{200}
0.204	1	Al	{200}
0.196	3	P3	{312}
0.187	2	P2,P3	
0.179	3	P2,P3	
0.165	2	P2,P3	
0.161	2	P2,P3	
0.151	3	P1	{220}
0.144	1	Al	{220}
0.137	3	P1	{300},{221}
0.135	3		
0.130	3	P1	{311}
0.123	1	Al	{311}
0.117	1	Al	{222}

* $\lambda/2$ lines⁵¹

Al: aluminum solid solution matrix

P1: Cu₃Au-type, $Pm\bar{3}m$ ($L1_2$) structureP2: Pb₃Ba-type, $R\bar{3}m$ structure^{11,52}P3: Al₁₇Gd₂, $P6_3/mmc$ structure⁵²

Table XVII: X-Ray Diffraction Results for Cold Rolled and Aged Al-Sc-Ho

Al-Sc-Ho			
d (nm)	I	Phase	Plane
0.472	1	*	--
0.424	1	P1	{100}
0.407	3	P1	{100}
0.299	1	P1	{110}
0.289	3	P1	{110}
0.243	1	P1	{111}
0.234	1	Al	{111}
0.211	2	P1	{200}
0.204	1	Al	{200}
0.189	1	P1	{210}
0.173	1	P1	{211}
0.150	2	P1	{220}
0.144	1	Al	{220}
0.141	3	P1	{200}, {311}
0.127	3	P1	{310}
0.122	1	Al	{311}
0.117	1	Al	{222}

* $\lambda/2$ line⁵¹

Al: aluminum solid solution matrix

P1: Cu₃Au-type, $Pm\bar{3}m$ ($L1_2$) structure

Table XVIII: X-Ray Diffraction Results for Cold Rolled and Aged Al-Sc-Er

Al-Sc-Er			
d (nm)	I	Phase	Plane
0.470	1	*	--
0.420	1	P1	{100}
0.406	3	P1	{100}
0.297	1	P1	{110}
0.286	3	P1	{110}
0.242	1	P1	{111}
0.234	1	Al	{111}
0.210	1	P1	{200}
0.203	1	Al	{200}
0.188	2	P1	{210}
0.172	2	P1	{211}
0.149	2	P1	{220}
0.144	1	Al	{220}
0.140	3	P1	{221},{300}
0.133	3	P1	{221},{300}
0.126	2	P1	{311}
0.122	1	Al	{311}
0.117	1	Al	{222}
0.112	3	P1	{321}

* $\lambda/2$ line⁵¹

Al: aluminum solid solution matrix

P1: Cu₃Au-type, $Pm\bar{3}m$ ($L1_2$) structure

P2: Pb₃Ba-type, $R\bar{3}m$ structure^{11,52}

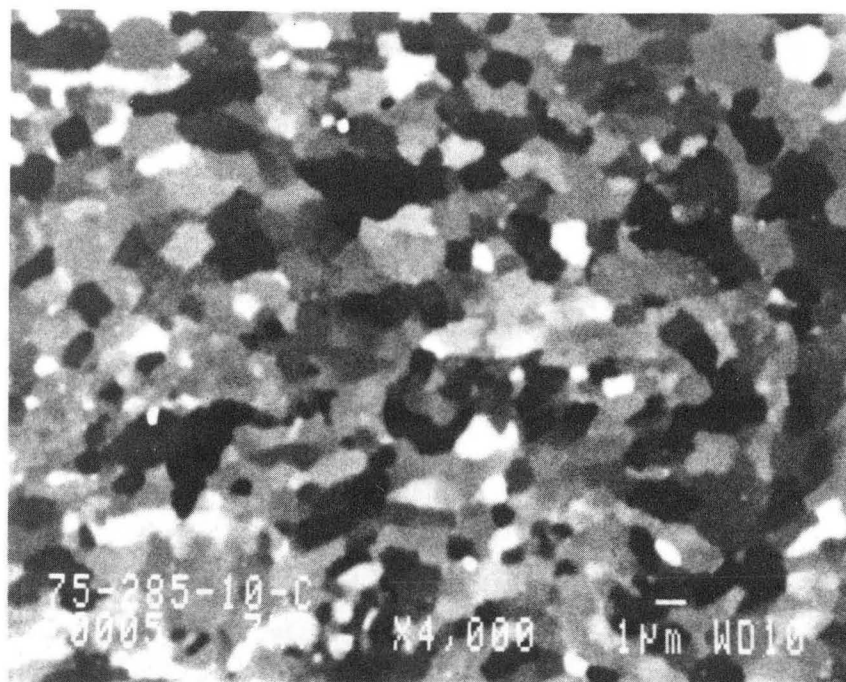
Table XIX: Intermetallic Phases Present in Cold Rolled and Aged Al-Sc-(RE) Alloys

Alloy	Structure Type			
	Al	Cu ₃ Au	Pb ₃ Ba	Al ₁₂ Gd ₂
Al-Sc	X	X		
Al-Sc-Y	X	X	X	
Al-Sc-Gd	X	X	X	X
Al-Sc-Ho	X	X		
Al-Sc-Er	X	X		

The actual compositions of the phases detected in the ternary alloys could not be determined by the X-ray data alone but it is quite likely that the L1₂ phase, for example, contains both Sc and the RE. It should also be noted that the Pb₃Ba type structure would not be expected to form at equilibrium in these systems. This phase is observed only at high pressure in binary Al-Y and Al-Gd intermetallics¹².

3. Scanning Electron Microscopy

Although transmission electron microscopy is often used to evaluate grain structure, using channeling enhanced backscattered contrast in the SEM allows sampling of a much greater area and, thus, provides better counting statistics. Samples of the wire material were examined using this technique for a variety of artificial aging temperatures and at a number of locations along the wire radius. All examinations were conducted on faces perpendicular to the wire drawing axis. As an example of the images produced by channeling enhanced backscattered contrast, a micrograph of the Al-Sc alloy wire, is provided in Figure 31. The detail produced is reminiscent of that produced in optical metallography when using polarized light on specimens that have been electropolished.



XBB 880-9972

Figure 31. Scanning electron micrograph of Al-Sc alloy wire obtained with channeling enhanced backscattered electron contrast.

Because small differences in grain size can have appreciable influence on strength, the SEM images were analyzed quantitatively. The measure of grain size used was linear grain boundary intercept length which, for idealized grain shape, can be translated to grain diameter through a multiplicative factor of 1.68³¹. Histograms of linear and natural log intercept length are shown for Al-Sc alloy wire in Figure 32 as examples of the behavior observed. As demonstrated by the upper figure, the distribution of intercept lengths was approximately log-normal.

No significant differences in boundary intercept length were observed between samples of a given alloy aged at different temperatures ranging from 235 to 310°C. There were also no observable differences in intercept length across the wire diameter.

Mean and most probable grain boundary intercept lengths are shown for the various alloys in Table XX along with calculated strength based on substructure hardening only. The substructure strengthening calculations were made with the aid of equation (22). Very little difference is observed in the average grain intercept lengths and the differences that were observed would represent insignificant effects on alloy strength (maximum ~6 MPa).

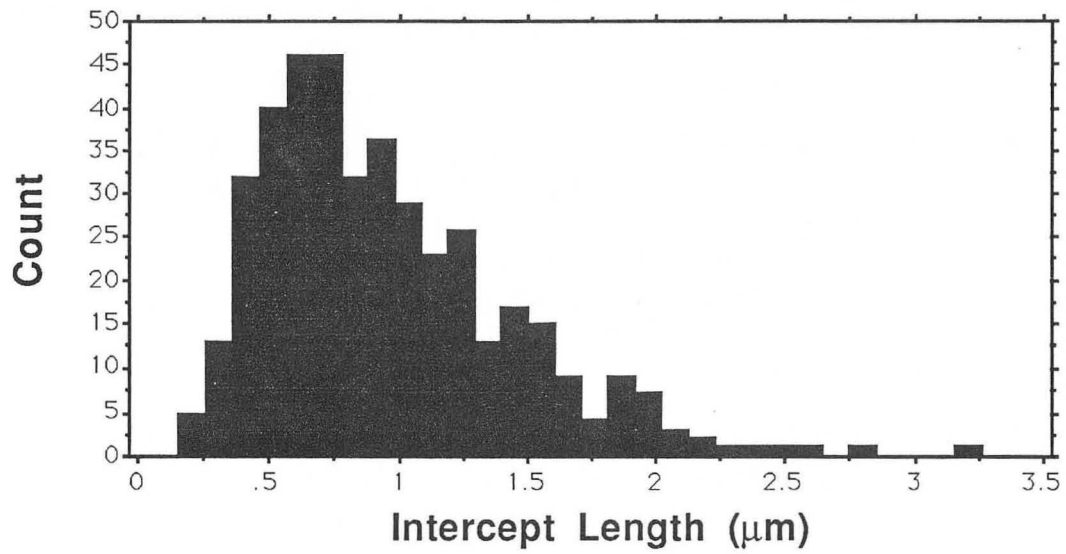
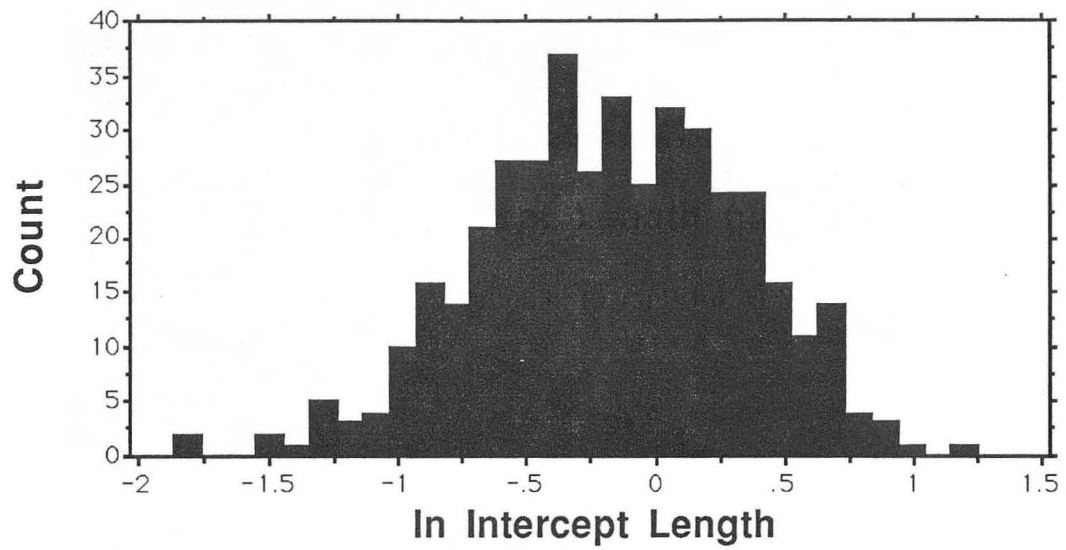


Figure 32. Grain intercept length distribution histograms for Al-Sc alloy wire.

Table XX: Grain Size Data for Al-Sc-(RE) Alloy Wires

Alloy	Average Grain Intercept Length (μm)	Most Probable Grain Intercept Length (μm)	Calculated* Strength (MPa)
Al-Sc	1.001	0.8	109.9
Al-Sc-Y	1.054	0.7	105.6
Al-Sc-Gd	1.058	0.75	105.3
Al-Sc-Ho	1.034	0.75	107.2
Al-Sc-Er	1.081	1.05	103.6

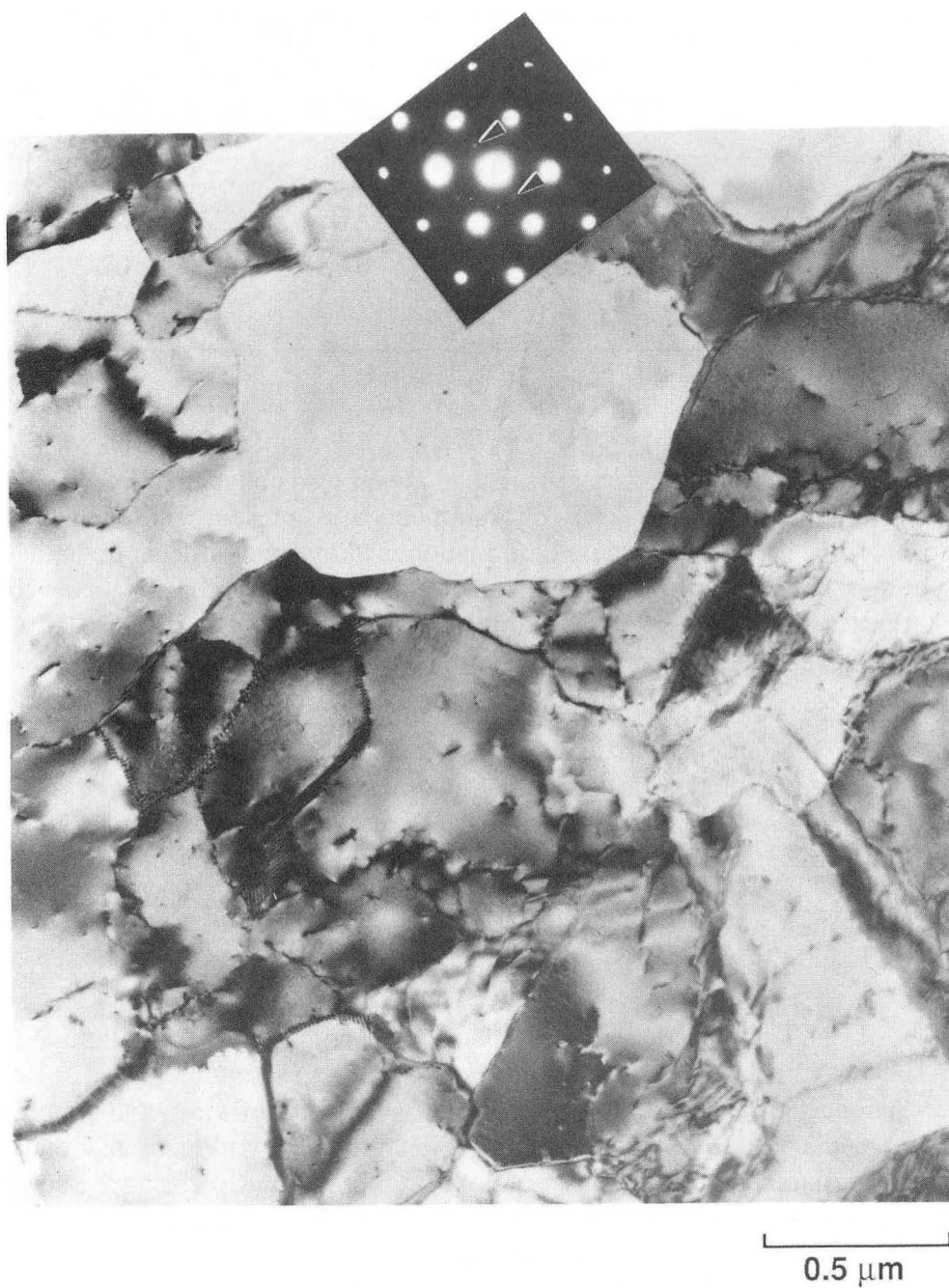
* Calculated using equation (20)

A limited study of grain boundary misorientation was also conducted in the SEM using EBSD. It showed that the vast majority of grain boundaries present were high angle (>5 - 10 deg.). This is not surprising because deformation in alloys with little strain hardening is known to be very nonuniform with a preponderance of slip bands and resultant severe local lattice rotations. Since there is little if any true recrystallization in these alloys, the recovered subgrain structure is representative of this deformation structure.

4. Transmission Electron Microscopy

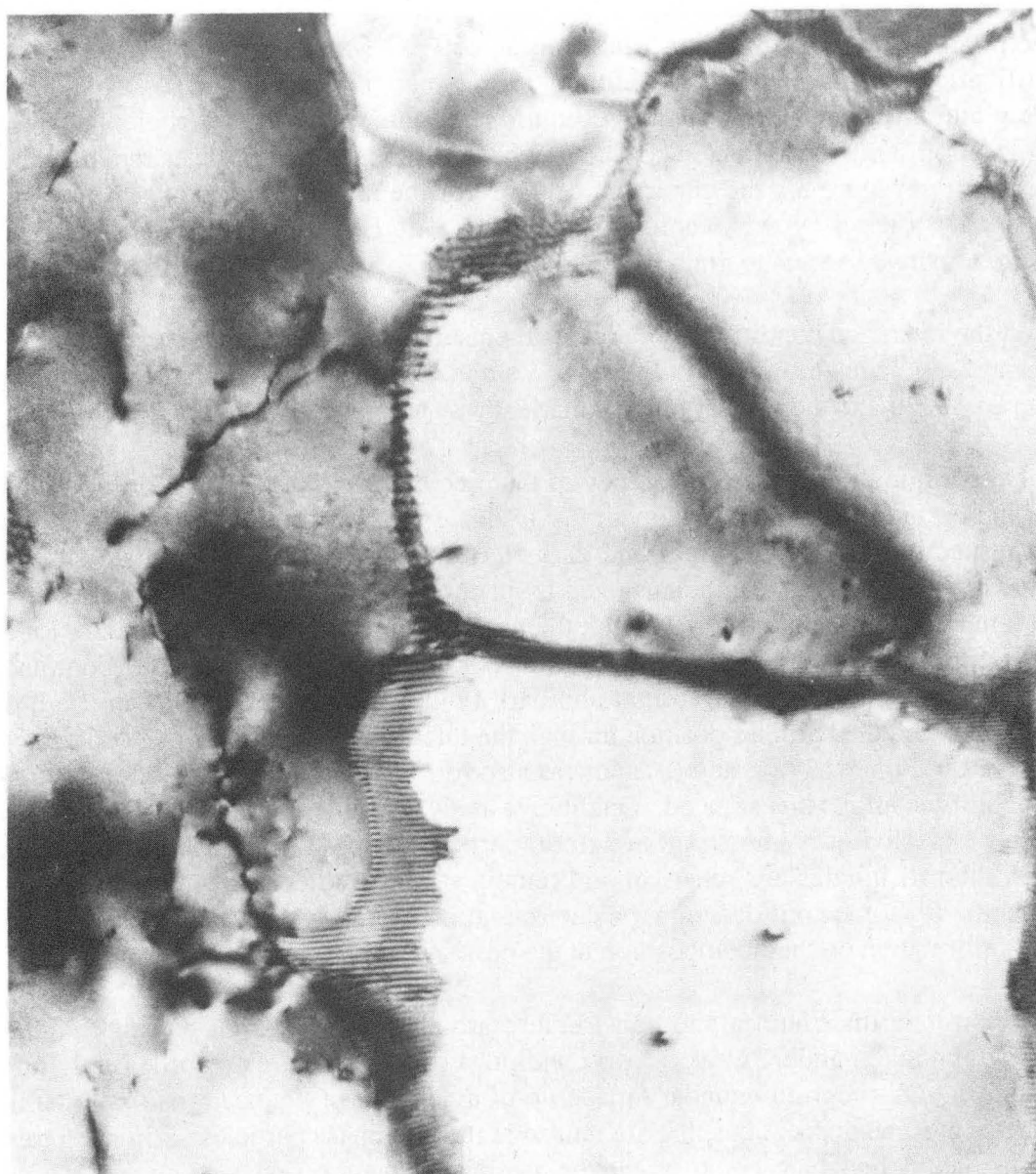
TEM was used primarily to ascertain the chemical and structural nature of the L_{12} precipitates in the alloys studied. Observations of the overall microstructure in the peak aged conditions were conducted using conventional TEM techniques. In addition, overaged samples were examined using analytical electron microscopy (AEM) and the peak aged microstructures were investigated using high resolution electron microscopy (HREM). The results obtained will be presented in this order.

Samples of each of the alloys in the peak aged condition were examined using conventional TEM to obtain a general perspective of the microstructures and microstructural differences among the alloys. Although quantitative analysis of grain and subgrain size was not attempted, qualitative observations were in agreement with the data obtained via SEM analysis presented in the previous section. A representative micrograph showing the general microstructure is presented in Figures 33 along with a selected area diffraction pattern obtained from this area. A portion of this area is shown at higher magnification in Figure 34. As shown in these figures, the orientation of the grain boundaries is quite irregular and not at all reminiscent of the equilibrium grain structure observed in aluminum. This is due to the pinning effects of the L_{12} precipitates. Although the precipitates are not readily visible at this level of resolution, the diffraction pattern shown in Figure 33 clearly indicates the presence of the L_{12} superlattice reflections. Isolated dislocations can also be observed but not in sufficient quantities to significantly alter alloy strength or resistivity.



XBB 880-10010

Figure 33. Bright field TEM micrograph showing the general microstructure of an Al-Sc-Ho alloy in the peak aged condition. A selected area diffraction pattern for the central region of this area showing (001) superlattice reflections is also included ([110] zone).



XBB 880-10017

0.1 μm

Figure 34. Bright field TEM micrograph showing the nonequilibrium subgrain structure in an Al-Sc-Ho alloy in the peak aged condition.

Because precipitates in the peak aged condition were found to be too small to analyze using conventional AEM techniques, samples of each alloy were overaged to coarsen the precipitates. A soak of 1 hour duration at 450 °C was used for this purpose. The justification for this approach is found in the recognition that elastic energy of the precipitate array (and thus, the phase equilibria) is unaffected by particle size. Hence, composition should also remain constant with size as long as the particles remain coherent. As shown in Figure 35, the general appearance of the microstructure of these alloys was not greatly altered by the overaging treatment. The $L1_2$, $Al_3(Sc,RE)$ precipitates still remain effective barriers to grain boundary migration.

In the overaged condition the particles themselves are also resolvable as shown in the BF and DF images presented in Figures 36 a and b. Average precipitate size was on the order of 30 nm and did not vary in any marked way among the various alloys.

Determining the state of coherency of the precipitates in this overaged microstructure was important to establishing the validity of this entire approach. Figures 37 (a) and (b) are, respectively, 2 beam bright and dark field images showing precipitate strain field contrast. Such contrast can be analyzed by methods popularized by Ashby and Brown⁵³ and latter refined by others^{54,55}. When the particles are coherent, light and dark lobes are observed with a line of no-contrast perpendicular to the operating g-vector. Contrast for a given particle varies between bright and dark field images depending on the sign of the strain field and the particles position through the thickness of the foil. Lobe contrast can be observed in Figures 37 (a) and (b) and was also found for alternate diffraction vectors and in each of the alloys investigated. Qualitative analysis of the strain field contrast indicates that, as expected, it is interstitial in nature (particle lattice parameter larger than matrix). Thus, the precipitates are spherical and remain coherent after coarsening. We can now proceed with some confidence that a determination of their chemistry can be expected to yield information on their composition in the peak-aged condition.

Precipitate distribution and substructure are shown in Figure 38 which contains a micrograph taken under "weak beam" conditions of the same area recorded in Figures 37 (a) and (b). A subgrain boundary made up of a network of dislocations is shown in this figure as are free dislocations that are pinned at the $L1_2$ phase particles. Strain contrast can also be seen in this micrograph, as can the precipitates themselves.

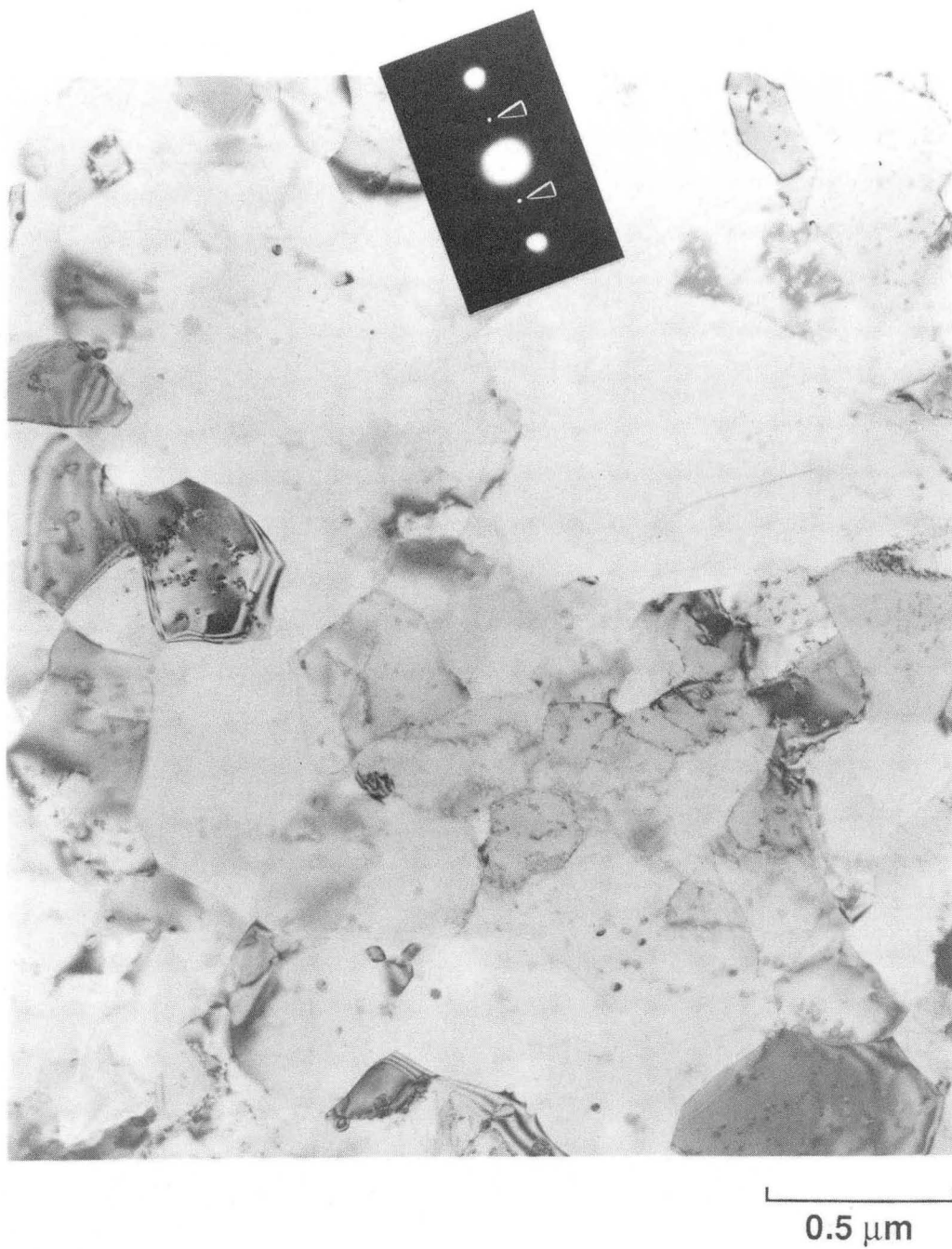
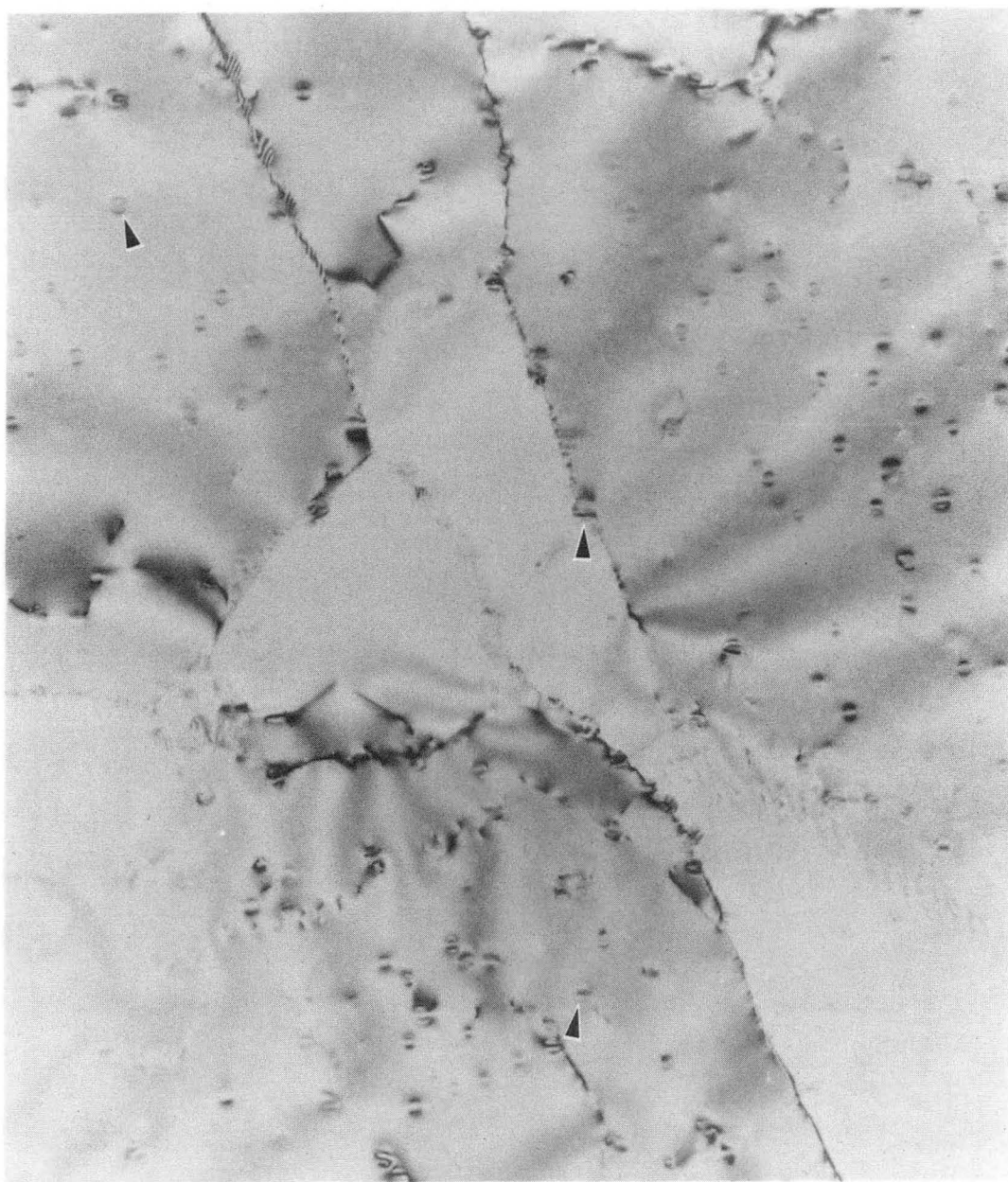


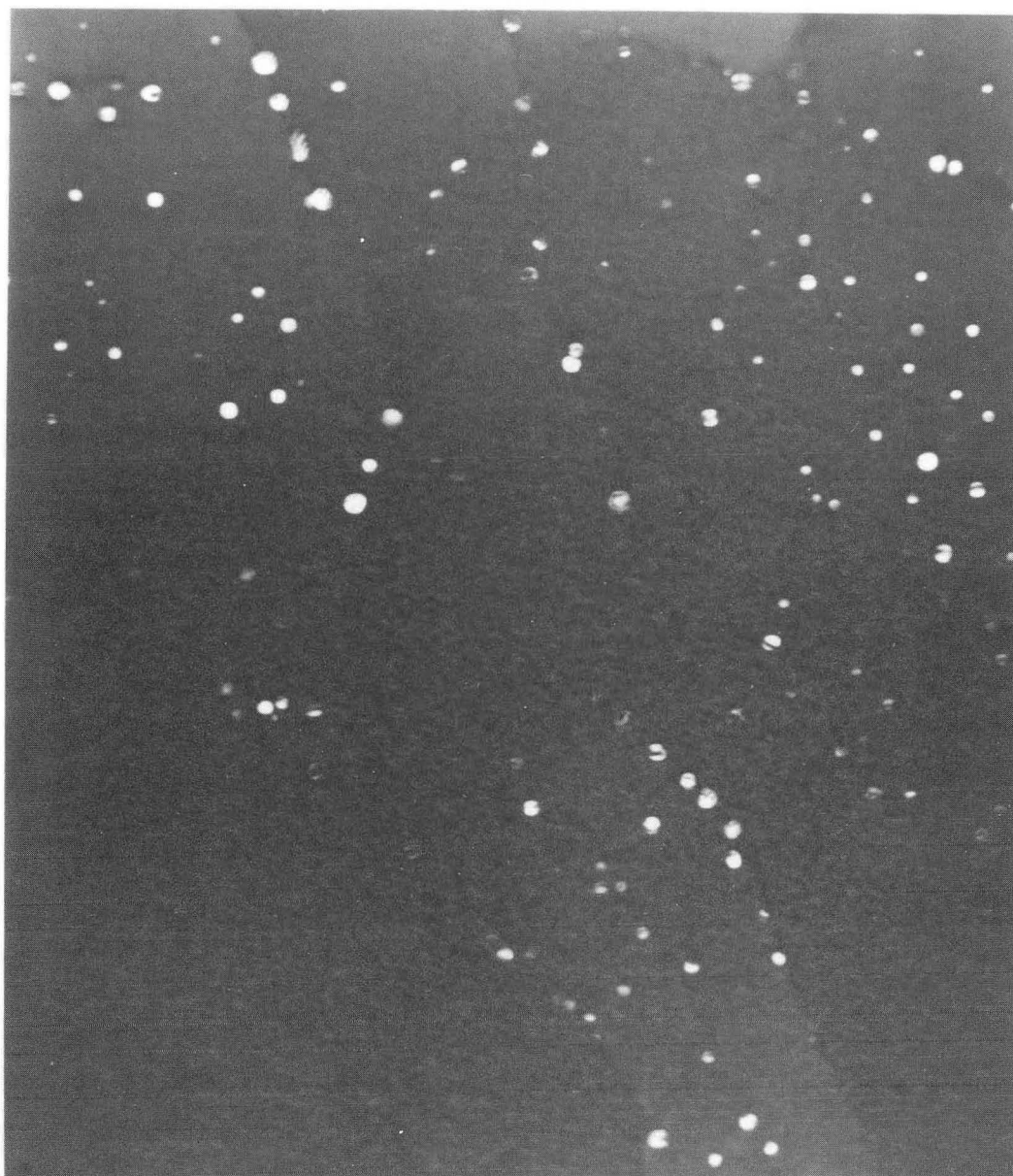
Figure 35. Bright field TEM micrograph showing the general microstructure of an Al-Sc-Gd alloy in the overaged condition. A selected area diffraction pattern for the left-hand region of this area showing (001) superlattice reflections is also included ([110] zone).



0.2 μm

XBB 880-10015

Figure 36a. Bright field TEM micrograph showing precipitates in an Al-Sc-Gd alloy (multibeam).



0.2 μm

XBB 880-10014

Figure 36b. Dark field TEM micrograph showing precipitates in an Al-Sc-Gd alloy (multibeam, centered on (001) superlattice reflection).

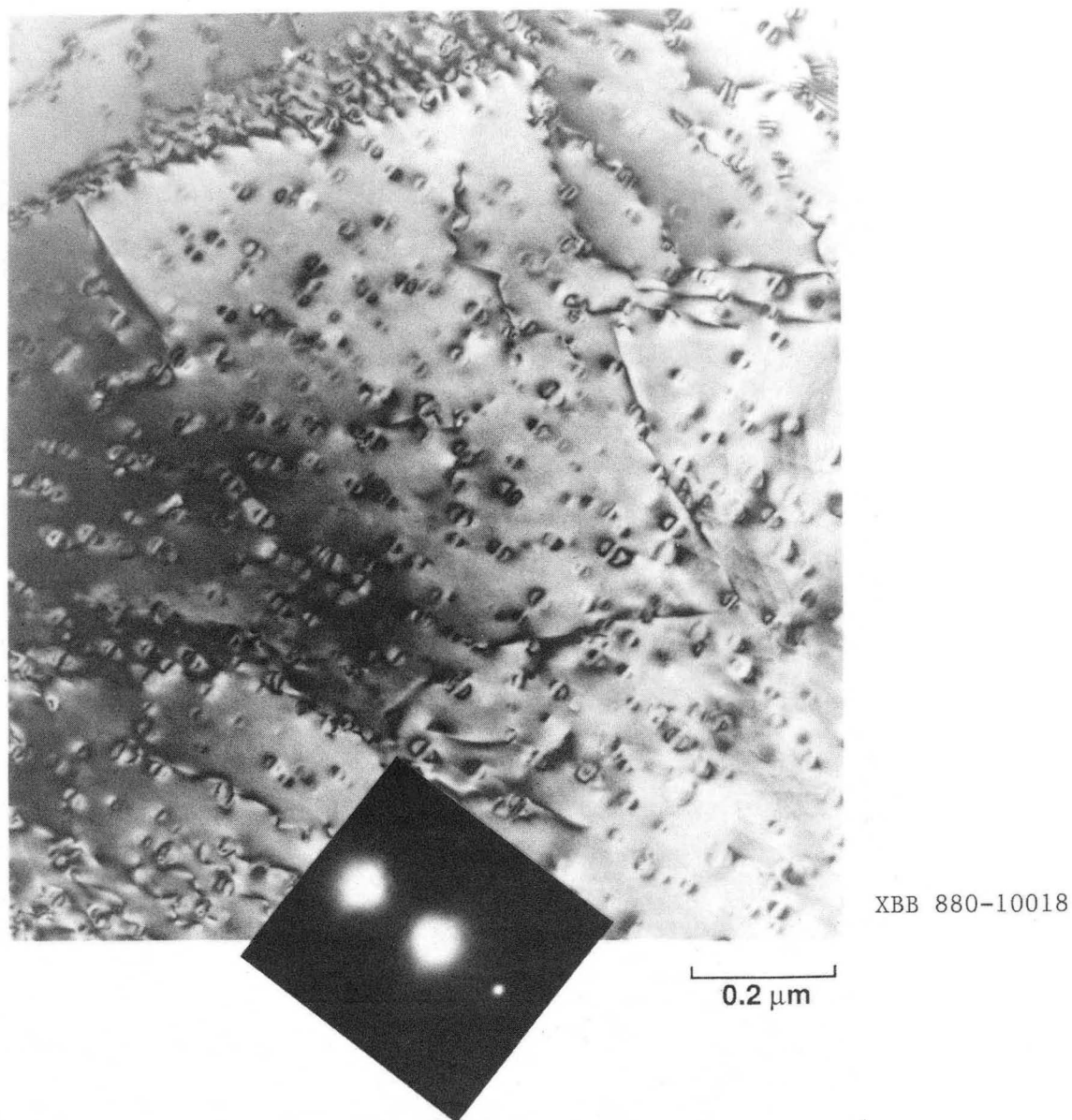
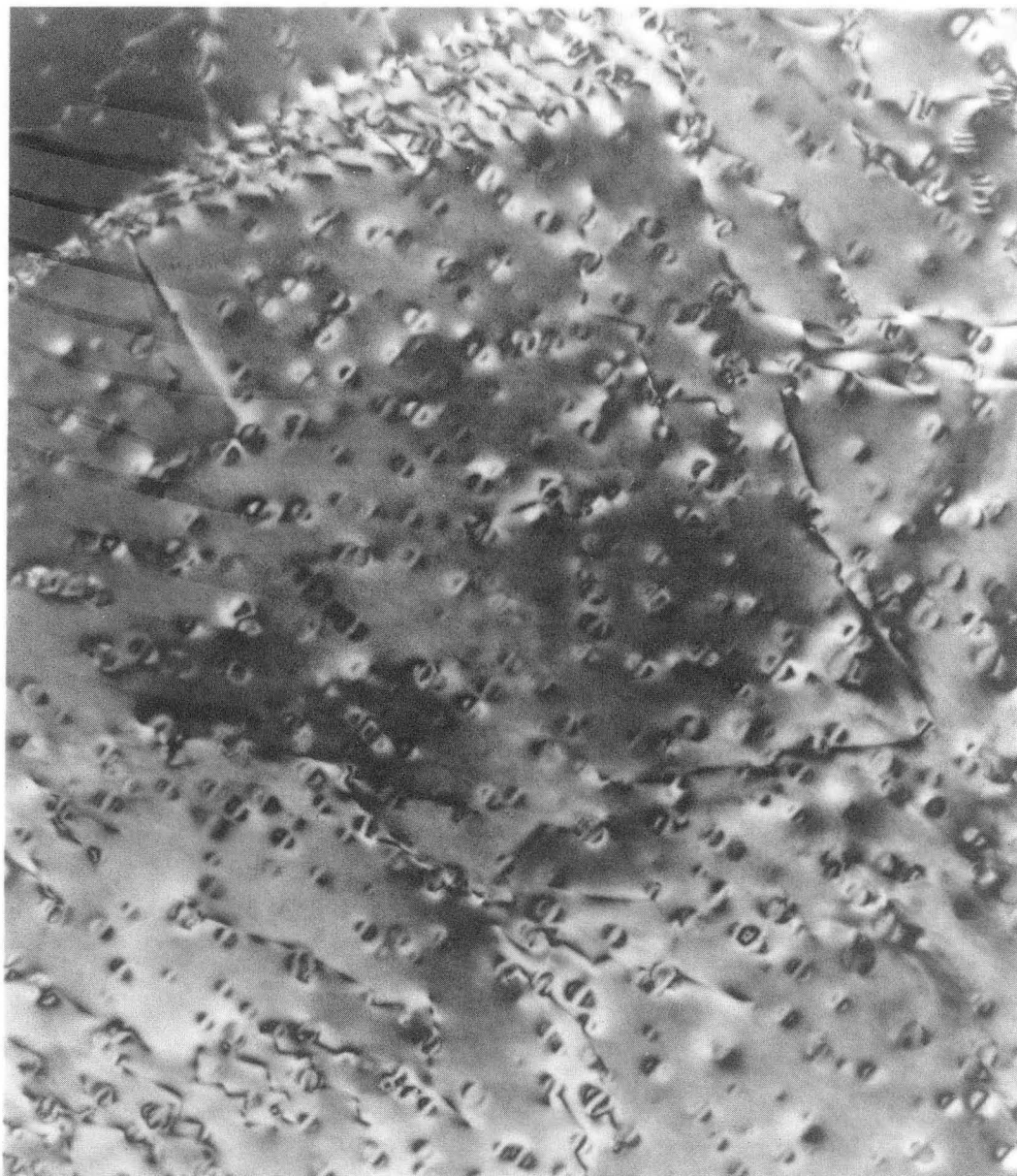


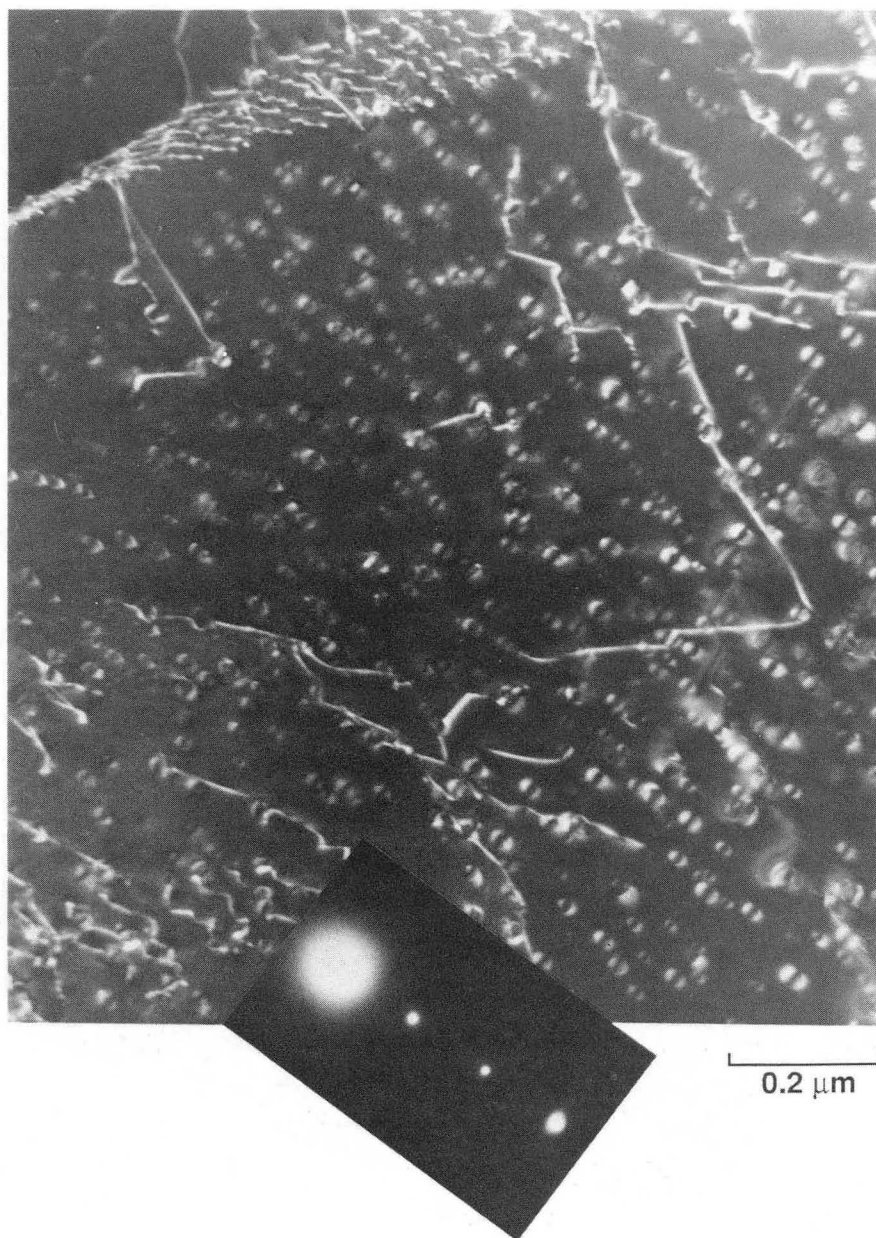
Figure 37a. Bright field TEM micrograph showing precipitate strain fields in an Al-Sc-Gd alloy ($g=(002)$ 2-beam). Diffraction pattern showing imaging condition is also shown ($[110]$ zone).



XBB 880-10019

0.2 μm

Figure 37b. Dark field TEM micrograph showing precipitate strain fields in an Al-Sc-Gd alloy ($g=(002)$ 2-beam). Diffraction pattern showing imaging condition shown in Figure 37a.



XBB 880-10016

Figure 38. Weak beam TEM micrograph showing dislocation networks in subgrain boundaries and free dislocations pinned by precipitates in an Al-Sc-Gd alloy. Diffraction pattern showing imaging condition is also shown, $g=(002)$.

Actual analysis of the precipitate compositions was conducted using more or less standard AEM technique employing energy dispersive spectrometry (EDS). In AEM work there is always a trade-off between spatial resolution and EDS count rate, which determines the accuracy of chemical analysis. In this case, the minimum probe size that would afford an acceptable count rate (based on sample drift, contamination etc.) was slightly larger than the average size of the particles to be analyzed. Because of this, and the fact that the particles were generally contained within the foil, some matrix was included in each analysis. Thus, the absolute values of Sc and RE recorded could not be used directly. Instead, ratios of Sc to RE based on atomic percentages were used. Between 8 and 10 particles were analyzed for each alloy. A number of analyses of matrix composition were also recorded and in all cases Sc and RE levels were below detectable limits. An example of a typical EDS spectrum for the precipitates is shown in Figure 39 for an Al-Sc-Ho alloy. These data are in the form of frequency histogram where the number of characteristic X-rays of a given energy are plotted versus that energy. Once these raw spectra are recorded, the background is modeled and subtracted, the peaks deconvoluted and integrated. Composition is then calculated based on ratios of integrated intensity. Details of this procedure are presented elsewhere⁵⁶. The average values of Sc/RE composition ratio measured in the $L1_2$ precipitates, along with the limits of a 95 pct. confidence interval are shown in Table XXI. Fractions of RE in the $Al_3(Sc_{1-x}RE_x)$ phase (value of x) were calculated from these values and are shown, along with the experimentally determined bulk values^{17,18}, in Table XXII. These data are also shown plotted versus ternary RE radius in Figure 40. Before interpreting these results, it should be pointed out that the limit of substitution of RE in the $L1_2$ phase based on the choice of alloying level, was 0.5. This assumes that all of the Sc was available for formation of $L1_2$ precipitates. Metallographic and X-ray results presented earlier show that some of the ternary RE were tied up in large incoherent phases formed during solidification further reducing the amounts available for formation of precipitates (and thus the maximum level of substitution). Hence, it is possible that the values recorded for RE substitution in the Al-Sc-Ho and Al-Sc-Er alloys are more reflective of the limited RE available than they are the coherent phase equilibria. Taking into account the inconsistency in the bulk Al-Sc-Y data noted in earlier sections, the results for RE substitution in the the Al-Sc-Gd and Al-Sc-Y alloys are remarkably close to the values that would be anticipated from bulk data.

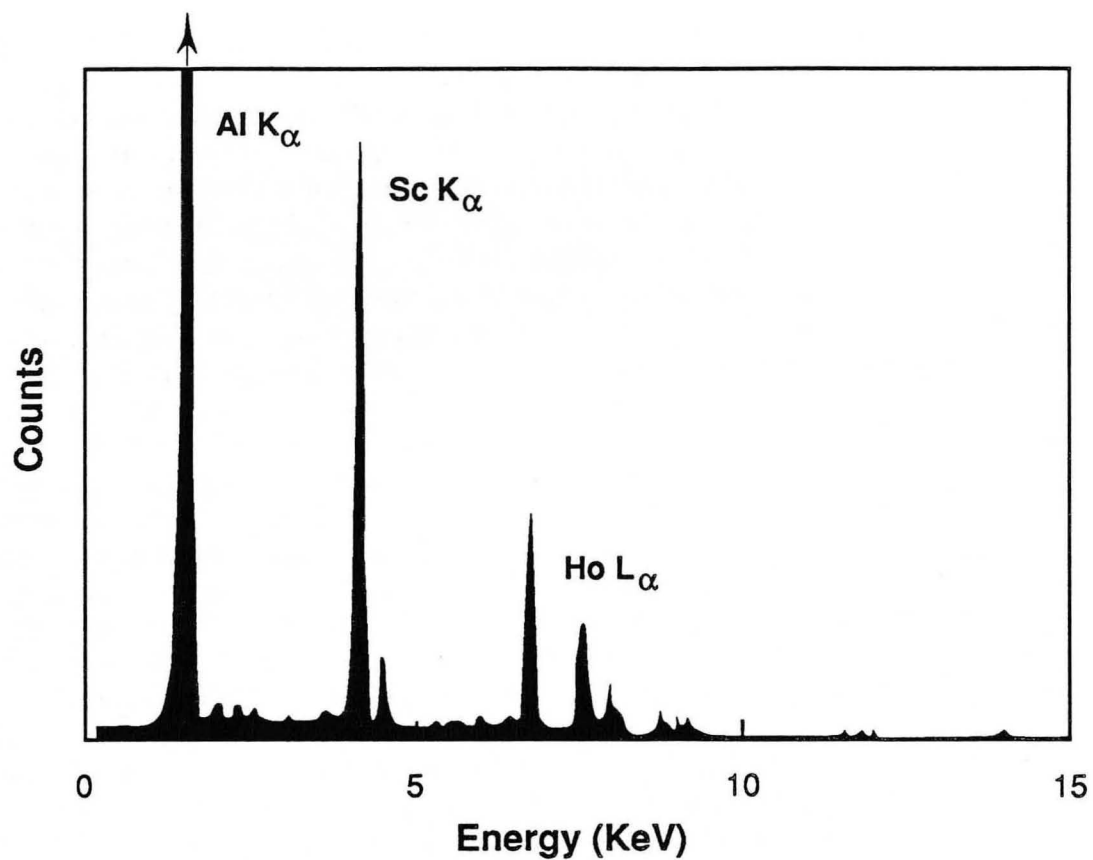


Figure 39. EDS spectrum for a coherent precipitate in an Al-Sc-Ho alloy.

Table XXI: Sc/RE Composition Ratio for Coherent Precipitates in Al-Sc-RE Alloys

Alloy	Sc/RE Composition Ratio		
	Mean	95 Pct. Conf. Int.	
		Upper	Lower
Al-Sc-Er	2.56	3.47	1.66
Al-Sc-Ho	2.05	2.71	1.39
Al-Sc-Y	3.93	5.01	2.85
Al-Sc-Gd	4.83	5.59	4.07

Table XXII: Calculated Fraction RE in $\text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$ Precipitates

Alloy	RE Radius (nm)	RE Substitution			
		Precipitate			Bulk
		Mean	Upper	Lower	
Al-Sc-Er	0.1757	0.294	0.364	0.224	0.90
Al-Sc-Ho	0.1765	0.335	0.394	0.275	0.72
Al-Sc-Y	0.1800	0.211	0.249	0.173	0.60
Al-Sc-Gd	0.1801	0.175	0.198	0.152	0.15

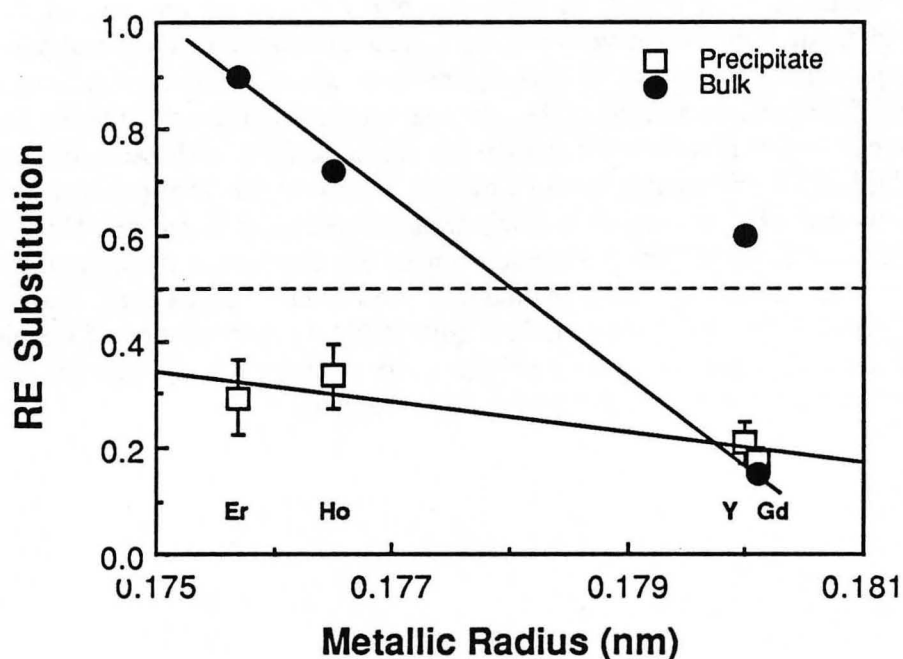
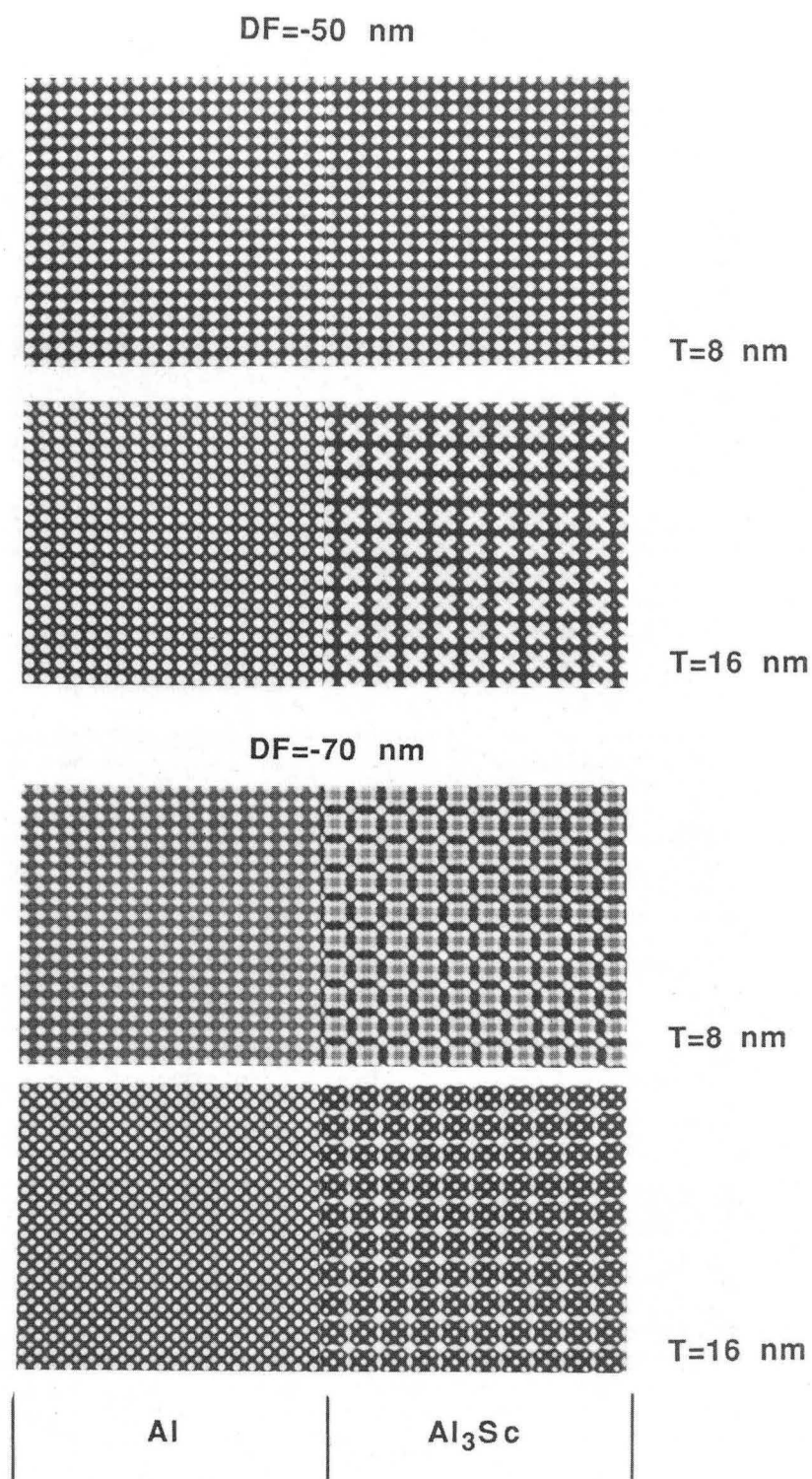


Figure 40. Re substitution as a function of RE metallic radius for bulk and precipitated $\text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$ phases. Note that in both cases substitution increases with decreasing RE radius.

Although electron diffraction had already indicated the presence of an L_{12} precipitate phase in each of the alloys, HREM was used to determine the configuration of the precipitates in the peak aged condition. HREM relies on phase rather than amplitude contrast imaging. As a result, the type of microscope and excitation conditions for the various lenses differ somewhat from conventional electron microscopy. In short, one desires low chromatic (C_c) and spherical (C_s) aberration and the shortest possible wavelength. Because wavelength is more important than C_s in determining the Scherzer or

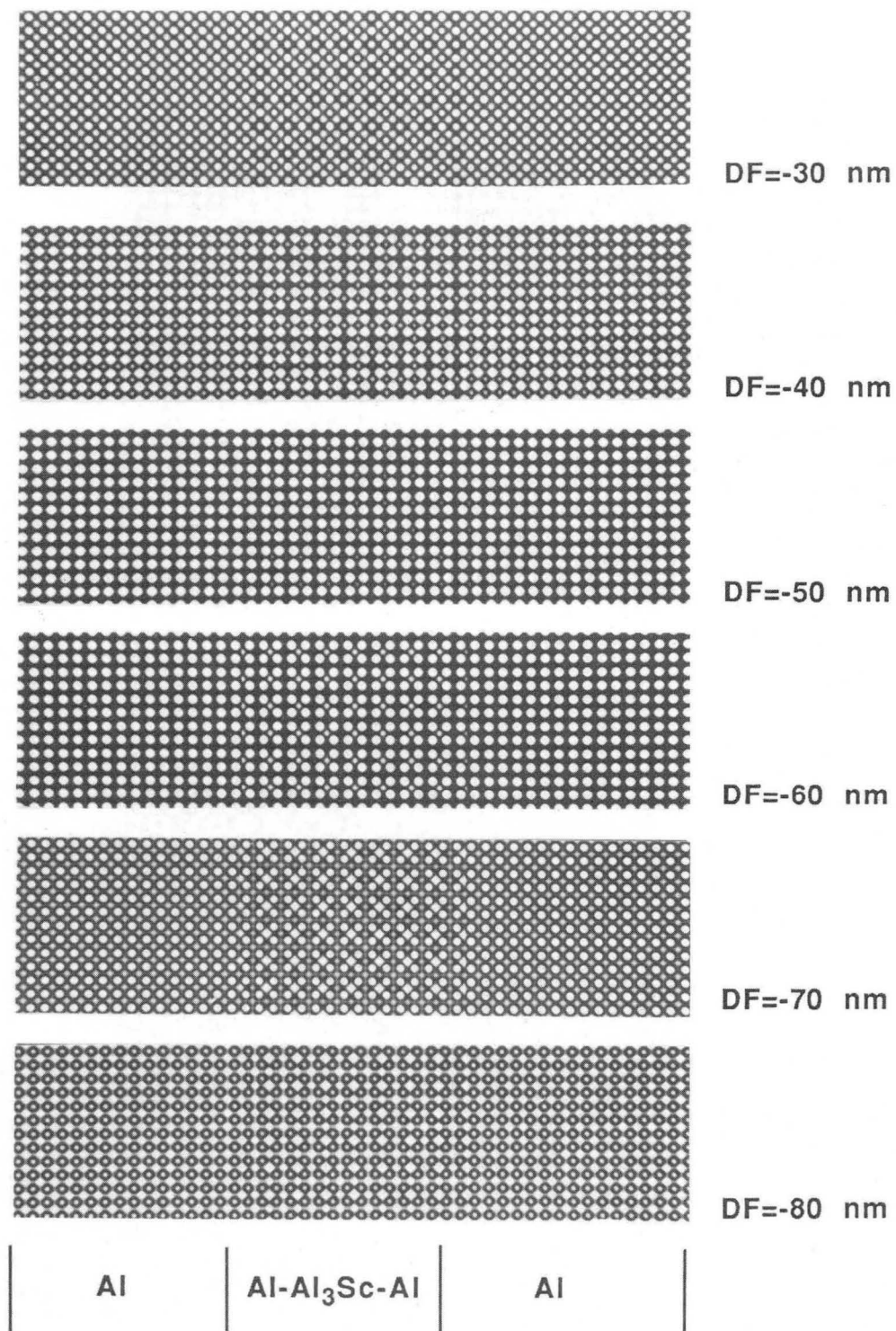
structure resolution, high voltage microscopes are often employed for phase contrast imaging. The instrument used in this investigation was the best available for this type of work: the Atomic Resolution Microscope (ARM) located at the National Center for Electron Microscopy.

A key adjunct to experimental HREM is the simulation of phase contrast images via digital computer. In cases where complex structures are to be analyzed, simulation is vital for determining causal correlation between proposed structures and recorded images. In the case of simple structures, like the $L1_2$ phase of interest in this work, simulations are perhaps most useful in defining imaging conditions that provide the best contrast between matrix and precipitate phases. For any given microscope the most common imaging variables are specimen orientation, thickness (which varies whether you like it or not) and objective lens defocus. As far as orientation is concerned, the $[001]$ zone is a convenient choice because only the $\{002\}$ matrix and $\{001\}$ $L1_2$ superlattice reflections need be considered. The effects of thickness and defocus on imaging in this orientation are depicted in Figure 41 which contains simulated images of Al_3Sc and pure Al for a series of conditions. The point of this figure is to show the wildly differing contrast of the individual phases as well as the extreme variations in the *differences* in contrast between them. From this it is clear that not all conditions will be conducive to identifying $Al_3(Sc,RE)$ precipitates in an Al matrix. The situation is even more extreme in the more likely case of a small Al_3Sc precipitate embedded in an Al matrix. This situation is depicted in Figure 42 for a 4 nm particle surrounded top and bottom by equal amounts of matrix (12 nm total), under a variety of defocus conditions. In this case, distinguishing the area containing the simulated particle is quite difficult. Substitution of RE on the Sc sublattice of the $L1_2$ phase improves particle/matrix contrast a small amount owing to the much higher atomic scattering factors for these elements.



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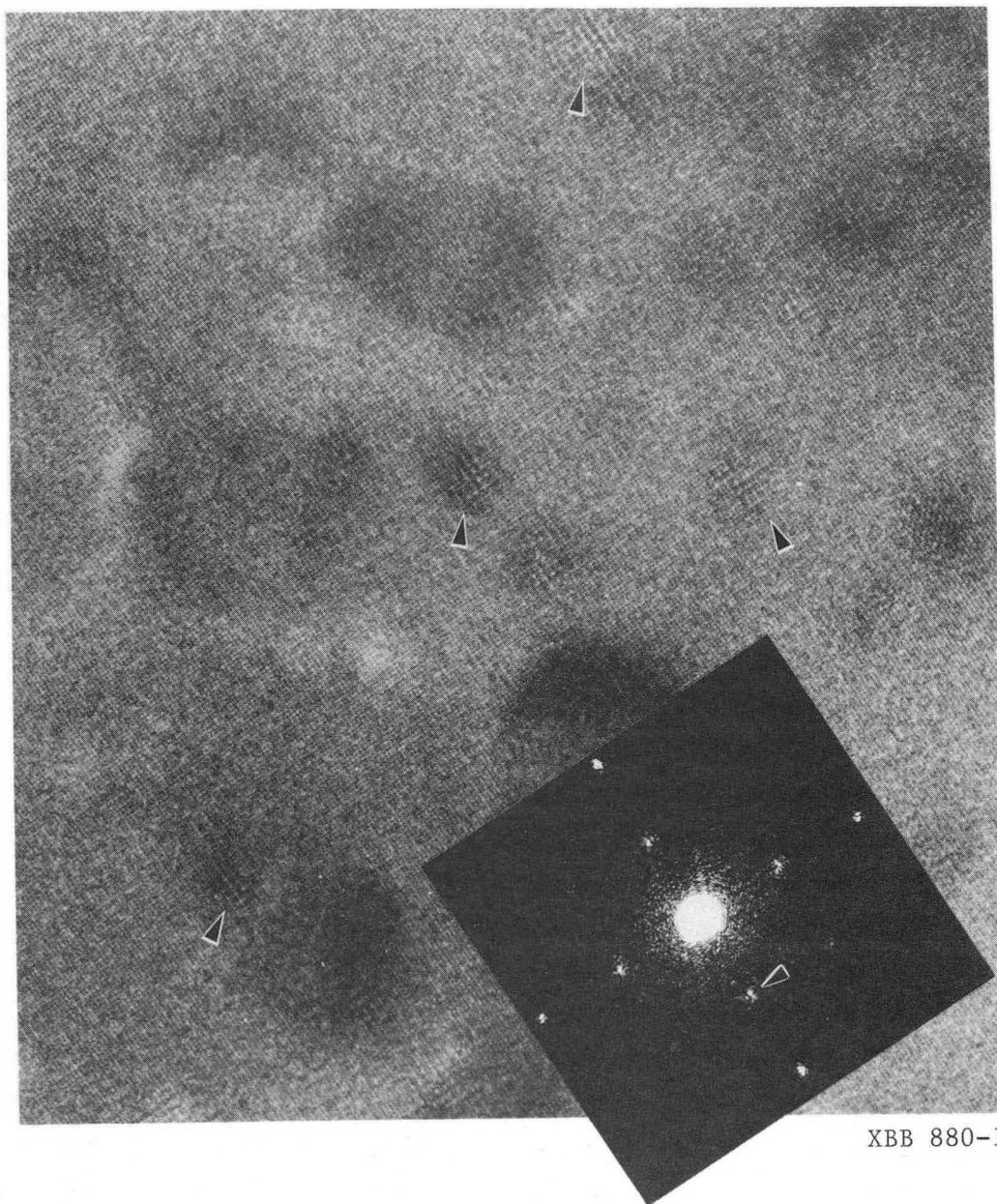
Figure 41. Simulated images for Al (right) and Al₃Sc (left) under a series of different thickness (**T**) and defocus (**DF**) conditions. ([001] zone)



XBB 880-9975

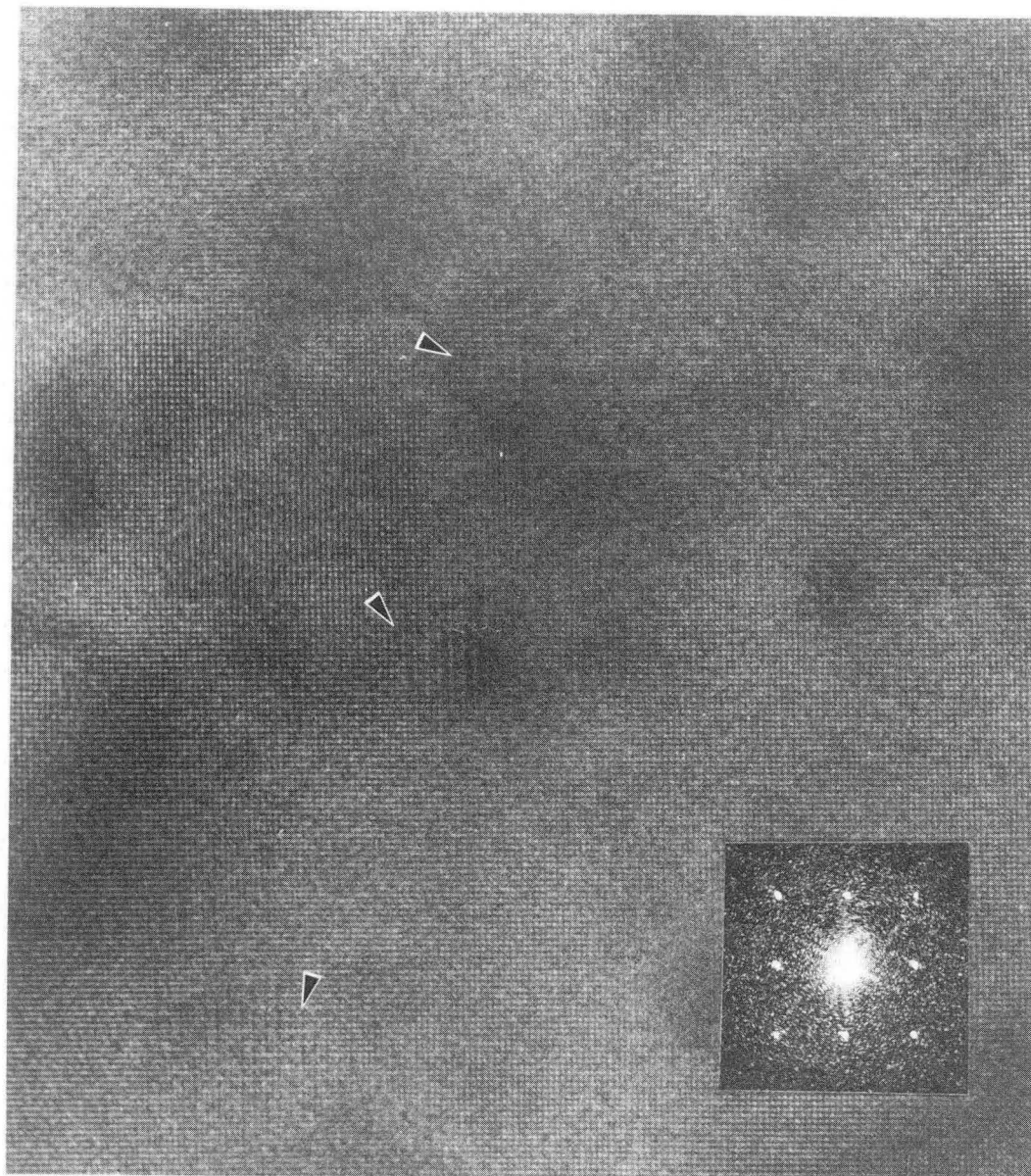
Figure 42. Simulated images for Al and an Al-Al₃Sc-Al composite 12 nm thick under a series of different defocus conditions. ([001] zone)

Despite the aforementioned difficulties, precipitates were imaged in the peak aged condition and representative micrographs showing the precipitate shapes and distributions for the Al-Sc-Gd (highest strength, lowest RE substitution) and Al-Sc-Ho (lowest strength, highest RE substitution) alloys are presented in Figures 43 and 44. An example of a larger particle detected in the Al-Sc-Ho alloy is shown in Figure 45. In each of the figures, optical diffraction patterns⁵⁷ are provided showing the structure of the precipitate phase compared to that of the Al matrix. An aperture corresponding to ~12 nm at the sample plane was used to obtain these patterns. The precipitate patterns each show the characteristic superlattice reflections of the L1₂ phases which are absent in the matrix patterns. Although several areas of each sample were viewed and imaged, this is far too little information to provide a *statistically valid* average precipitate size or spacing. Qualitatively, however, the distribution of precipitates appears uniform with an average diameter of 3 nm for both alloys.



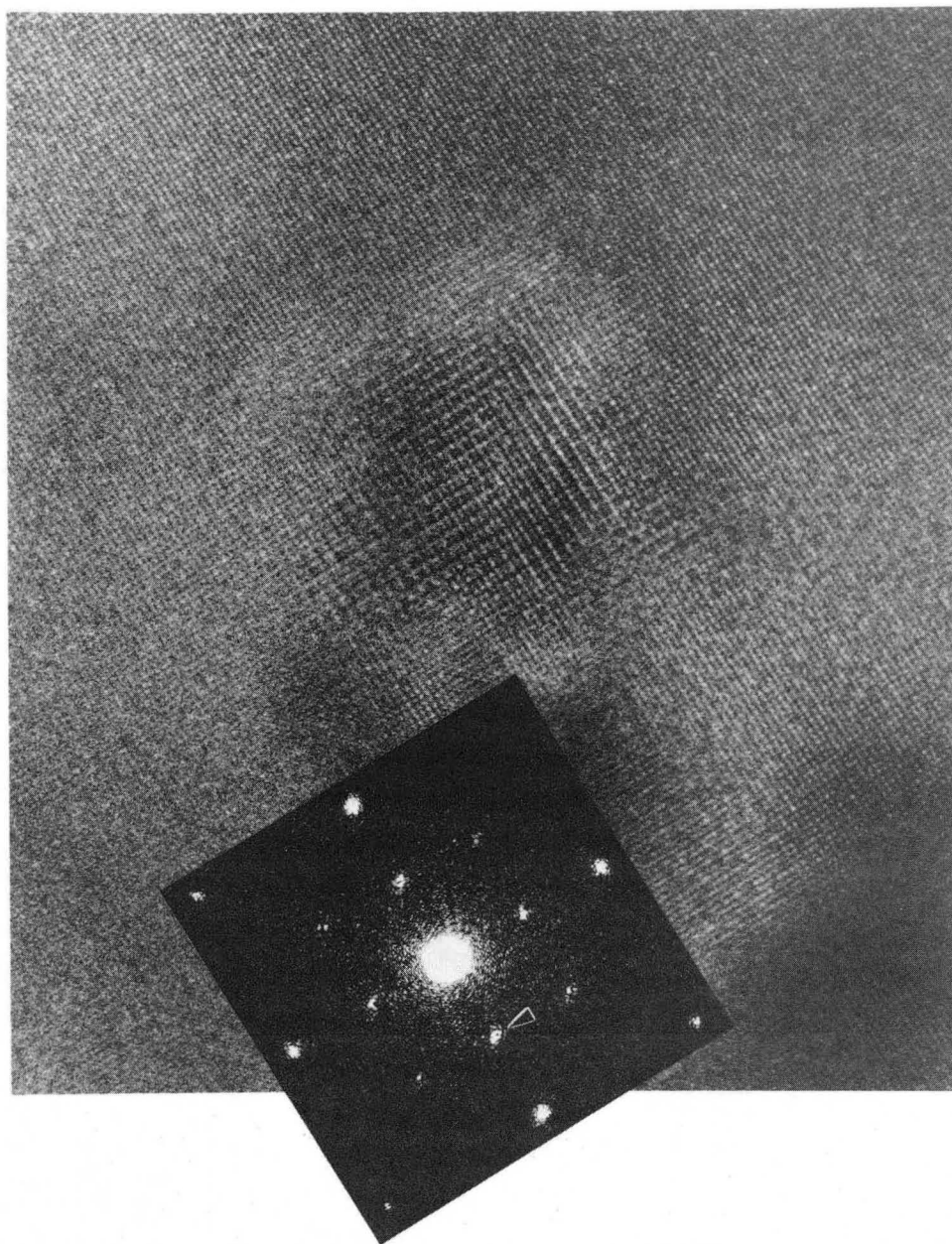
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Figure 43. HREM micrograph showing $L1_2$ precipitates (lattice fringe doubling) in a peak aged Al-Sc-Ho alloy. Optical diffraction pattern shows evidence of (001) superlattice reflection. Matrix fringe spacing is 0.2025 nm. Precipitates are ~15 fringe spacing or 3 nm in diameter. ([001] zone)



XBB 880-10623

Figure 44. HREM micrograph showing $L1_2$ precipitates (lattice fringe doubling) in a peak aged Al-Sc-Gd alloy. Optical diffraction pattern shows evidence of (001) superlattice reflection. Matrix fringe spacing is 0.2025 nm. Precipitates are ~15 fringe spacing or 3 nm in diameter. ([001] zone)



XBB 880-10013

Figure 45. HREM micrograph showing a larger $L1_2$ precipitate in a peak aged Al-Sc-Ho alloy. Optical diffraction pattern shows evidence of (001) superlattice reflection. Matrix fringe spacing is 0.2025 nm. ([001] zone)

VI. Discussion

To begin discussion of these results the goals of this program and the approach used will be summarized. The results will then be reexamined and attempts will be made to provide interpretations in light of the theoretical background provided in Section III. At the end of this section these interpretation will be integrated and an approach for further alloy design and development in this system will be presented.

The goal of this work was to establish an alloy design methodology to optimize the precipitation hardening component of strengthening in Al-Sc-X alloys. To achieve this, elements were sought that would interact synergistically in the L_{12} , Al_3Sc phase. Based on similarities in chemical properties the group IIIA elements were chosen as likely candidates. Although there is no way of knowing at present whether limiting alloying variations to the family of RE elements was the best approach, it has produced some interesting results and generally facilitated use of a more structured alloy design process relying on metallurgical theory and understanding rather than statistics and empirical procedures. Further consideration of known principles led to the conclusion that RE size was the key variable in Al-Sc-RE alloys and that an understanding of its effects could lead to a productive alloy design methodology. To facilitate development of such an understanding, an experimental design was devised that would eliminate all variations except that of RE size. Since phase equilibria information was unavailable, the choice for alloying level had to be somewhat arbitrary. Unfortunately, as shown by optical metallography and X-ray phase analysis, the amounts of RE added were in excess of the solubility limit and coarse phases were formed during solidification. This occurred despite the fact that attempts were made to suppress these reactions by using rapid solidification. As a result, the effective levels of alloying in solution and available for participation in precipitation reactions was not completely constant. This complicates, but does not preclude analysis of the true effects of RE size.

Considering the results obtained with regard to the commercial goals of this work, the most important piece of information emerging is that maximum tensile strength is increased by RE additions and that the strength increment increases with increasing RE size. The key metallurgical question is: why? A number of possible effects of variation in RE size were introduced in Section III. These effects will be reexamined in light of the experimental results in the discussions below. In an attempt to sort out the various competing effects, a number of the experimental results have been treated quite literally. Of particular concern is reliance on the limited AEM precipitate composition data to infer a number of key precipitate characteristics.

The first effect to consider is precipitate volume fraction. Volume fraction of precipitate can be calculated if it is assumed that all of the Sc is incorporated into precipitates and that the average level of RE incorporated is adequately described by the data presented in the Section V-C-4. These calculations lead to the values shown in Table XXIII which also contains values of calculated lattice parameter and peak tensile strength. As mentioned previously, the increase in RE substitution and, thus, precipitate volume fraction with decreasing RE size is consistent with the published information for bulk phases. Interestingly, the maximum tensile strength varies *inversely* with respect to calculated

volume fraction. If this were the only effect to be considered it would be in direct conflict with the well known laws of precipitation hardening presented in Section III-C. Thus, volume fraction can not be the controlling variable in determining alloy strength in this system.

Table XXIII: Calculated Lattice Parameters and Volume Fractions of $\text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$ Precipitates

Alloy	RE Radius (nm)	RE Substitution	Lattice Parameter (nm)	Volume Fraction (pct.)	Peak Strength (MPa)
Al-Sc	--	0	0.4583	1.20	251
Al-Sc-Er	0.1757	0.294	0.4697	1.70	278
Al-Sc-Ho	0.1765	0.335	0.4720	1.80	262
Al-Sc-Y	0.1800	0.211	0.4690	1.52	290
Al-Sc-Gd	0.1801	0.175	0.4673	1.45	309

One alternative could be that other forms of strengthening (besides precipitation strengthening) dominate. However, it was shown in Section V-C-3 that grain size did not vary, hence, substructure hardening is eliminated as a possibility. In principle, solid solution strengthening could be a factor but AEM results presented in Section V-C-4 show that there is no appreciable amount of solute remaining in solution after aging to peak strength. Even given the fact that the minimum detectable mass fraction of RE is probably on the order of 0.1-0.3 weight percent⁵⁶, differing solid solution hardening effects can probably also be eliminated. This line of reasoning leads inexorably to the conclusion that precipitation hardening efficiency (effective obstacle strength) has been altered and that these effects override the effect of variation in precipitate volume fraction. This is perhaps not surprising when one considers the general form of equation (14) which shows that CRSS (τ_c) varies linearly with respect to obstacle strength and with the square root of volume fraction. This conclusion is also consistent with the observation made in Section V-B-2 that precipitate size at peak strength decreases. The explanation of these effect is aided by Figure 46 which shows a schematic rendition of CRSS as a function of precipitate radius for particles of various effective strengths. In order to construct such a diagram the obstacle strength must be separated into its geometrical and physical parts. To do this it is assumed that the geometrical contribution to the obstacle strength scales as the square of average radius for shearable particles and is constant after the looping threshold. Mathematically (referred to (16)),

$$\tau_c = \Omega (f^{1/2} \beta'(r)) \quad (32)$$

for shearing, and

$$\tau_c = \Omega \left(\frac{f^{1/2}}{\langle r \rangle} \right) \quad (33)$$

for looping

where f is volume fraction, $\langle r \rangle$ is average particle radius and β' is an obstacle strength function.

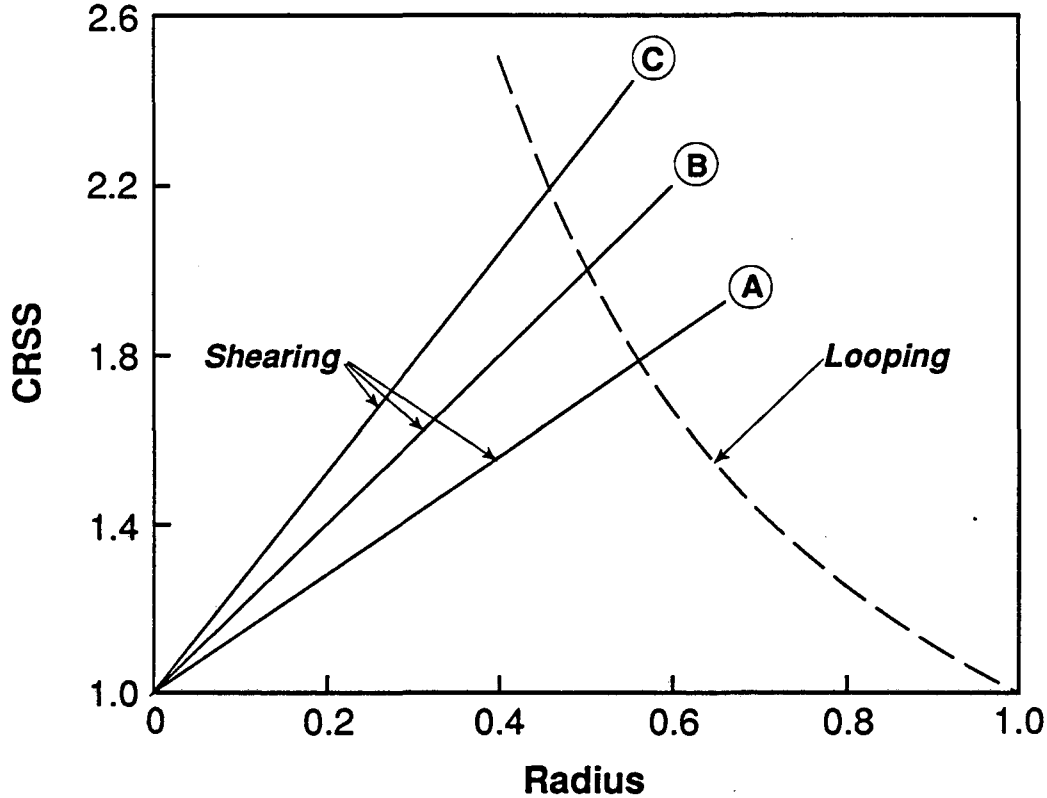


Figure 46. Schematic drawing showing CRSS as a function of particle radius in both the looping and shearing regimes. Effective obstacle strength is increasing moving from points A to B to C.

Moving from smaller to larger particle size on this diagram is believed to be illustrative of what occurs during artificial aging for the Al-Sc-RE alloys. Based on DSC results it is known that the precipitation reaction is complete after very short aging time. Hence, for the times studied in this work, the precipitates are coarsening at constant volume fraction. Thus, precipitate size increases monotonically as does spacing. Strength increases initially because the larger particles are more effective barriers regardless of their internal structure. This is the geometrical contribution. Eventually, the looping radius is reached and CRSS begins to decrease. β' assumes a value of 1 at this point. Peak strength is reached at the

point where the shearing and looping curves intersect. (e.g. points A, B and C). As the inherent physical strength of the particles increase, β' increases leading to more rapid rise in CRSS and higher peak strength. Under these conditions, the intersection of the shearing and looping curves (and, hence peak strength) occurs at ever smaller particle radii, as observed.

Having established the hypothesis that the higher strengths observed in alloys containing larger ternary RE additions are due to greater inherent obstacle strength, the next question to be considered is; how is the "strength" of the $L1_2$ phase altered by RE radius. Two mechanisms were given in Section III-C as a basis for the original hypothesis that greater strengthening efficiency was to be expected from larger RE additions;

1. Increased coherency strains (depends on relative level of substitution as well as size)
2. Greater APB energy (due to greater relative stability of the $L1_2$ phase and greater atomic size mismatch)

Since precipitate chemistry is now known, the first possibility is easy to evaluate. Calculated lattice parameters for the precipitate phases were presented in Table XXIII. These data show relatively little variation and little or no correlation to the peak strength values. If anything, the trend runs in the wrong direction (higher misfit gives lower strength). Thus, increased misfit does not appear to be the dominating factor.

Given the likelihood that increases in APB energy with increased RE size is the cause for increased strength in the $L1_2$ phase one should consider the relative roles of elastic contributions to phase stability versus the "solid solution" strengthening effects of larger RE. Unfortunately, separating these two possibilities does not appear to be possible given the data that presently exists. Both effects are due to internal rearrangements of the $L1_2$ phase that result from size differences among the atomic constituents of this system and are heavily interrelated. The DSC results may provide some insight, however. When the DSC phase stability results were originally presented in Section V-A-1, there remained a question of whether the higher heats of precipitation recorded for the alloys containing larger RE were the result of variations in volume fraction or greater inherent phase stability. Given the aid of the volume fraction calculations presented above, it is clear that the $L1_2$ phase containing larger RE are indeed more stable with respect to the Al solid solution. Higher heats of precipitation are recorded for the alloys containing larger RE even though the precipitate volume fraction decreases. This was anticipated in Section III-B as a result of the elastic energy effects and indicates that this component of the proposed increase in ABP energy with RE size is at least plausible.

The observed artificial aging kinetics are also consistent with the generalized interpretation that RE are incorporated in the $L1_2$ precipitate. It was noted in section V-B-2 that longer times were required to reach peak strength for the Al-Sc-Y and Al-Sc-Gd alloys even though the precipitate size at peak strength is *smaller*. Thus, coarsening kinetics in these alloys must be reduced. It is well known that coarsening in such system is diffusion controlled. Although diffusion data in Al are not available for many of the RE elements

there is a strong trend toward decreased diffusion rates with increasing RE size⁵⁸. Thus, slower diffusion and diminished coarsening rates would be expected for Al-Sc-Y and Al-Sc-Gd, as apparently observed.

From the point of view of commercial development, this work has been a clear success. The best alloys containing Y or Gd in addition to Sc were found to develop strengths 50-60 MPa higher than the binary Al-Sc control. This is a useful increment in performance that could help make commercial variants of these alloys containing solid solution strengtheners like Mg and or Li quite competitive. From a practical point of view, Y would probably be the best choice of the additions studied here because of its greater equilibrium solubility lower density and relatively lower cost. Given appropriate processing, however, Gd additions have been shown to produce the highest strength.

Finally, the goal of developing an alloy design strategy based in metallurgical understanding has also been a success. The trends in alloy strength appear to be well understood and this knowledge can be used to guide future alloy development in this or similar systems.

VII. Summary

The overall commercial goal of this work has been to improve the cost/performance balance in Al-Sc-X alloys by optimizing the precipitation hardening component of strengthening in these alloys. The approach involved selecting ternary additions that would interact with Sc in the L_{12} phase precipitates known to form in Al-Sc alloys, modifying the precipitates and increasing overall precipitate volume fraction. The rare earth (RE) elements were chosen as candidates because of their chemical similarity to Sc. In the next step, stabilities of various phases in the Al-RE and Al-Sc-RE systems were considered with emphasis on conditions favorable to formation of the L_{12} $Al_3(Sc,RE)$ phase. It was found that atomic size was the dominant factor in determining phase stability and that formation of the L_{12} phase was favored when RE size is at a minimum. The thermodynamics of precipitation of this phase in an Al matrix was then considered and it was discovered that precipitation of ternary $Al_3(Sc,RE)$ phases was favored for any combination of Sc and RE and that the driving force increases with RE size. Having established the likelihood of interaction of various RE in L_{12} precipitates attention was turned to effects of these variations in precipitate character on relative strengthening efficiency. It was shown that the precipitates become more effective obstacles as size of the RE addition increases. This effect is due to increased coherency strains and greater APB energy. An experimental program was developed to investigate effects of RE size at a constant level of alloying on the trade-off between effects of greater precipitate strengthening efficiency provided by larger RE and the accompanying reduction in degree of substitution and, thus, volume fraction. It was found that the maximum strength of these alloys increased significantly with increasing RE size. Detailed investigation of the precipitation reactions and precipitates themselves showed that precipitate stability increased as predicted and that the precipitates contained significant amounts of RE. Since maximum strength was found to be inversely proportional to apparent precipitate volume fraction, it was concluded that increases in precipitation strengthening efficiency with increasing RE size far outweighed the effects of reduced volume fraction. It was concluded that strengthening efficiency increased because of higher APB energy and not coherency strains. APB energy increases with increasing RE size because of internal rearrangements in the L_{12} phase. Finally, the precipitates themselves were imaged using HREM and found to be uniformly distributed spheres on the order of 3 nm in diameter in the peak aged condition.

VIII. Conclusions

1. Strong interactions occur between Sc and the RE elements in Al base alloys resulting in modification of the $L1_2$ precipitate phase and significantly increased strength.
2. As a result of modification of the $L1_2$ phase, substantial differences in tensile properties are observed with higher strengths recorded for RE with larger atomic radii.
3. Strength increases with increasing size of RE substituting on the Sc sublattice because it increases the effective strength of the precipitate, thus, greatly increasing the strengthening efficiency of the precipitate array.
4. Precipitate strength increases with RE size because of higher APB energy.
5. Because of its greater solubility, lower density and generally lower cost Y additions are recommended as most promising for commercial Al-Sc-X alloys.

IX. Future Work

From a theoretical point of view it would be most interesting to separate the various physical manifestations of the internal rearrangement of the $L1_2 \text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$ phase to determine the key factor responsible for increasing precipitate APB energy and "strength".

Continued commercial optimization of the Al-Sc-RE system will require investigation of at least 3 additional effects;

1. Variations in Sc/RE ratios and total amounts of alloying in the Al-Sc-RE system,
2. Larger RE in ternary Al-Sc-RE alloys,
3. Unwanted interactions among the RE and potential quaternary additions like Mg or Li.

Item 1 should be evaluated through additional work in the Al-Sc-Ho and Al-Sc-Gd systems which demonstrated the extremes of behavior in this study. These results would indicate the extent to which RE can be substituted for Sc as well as the ultimate performance of this subset of Al-Sc-RE alloys. For item 2, Ce might be a good choice to study because Ce is less expensive and more available than most of the RE. This study would indicate the limits of property improvement with increasing RE size. Item 3 could, perhaps, be the subject of a theoretical investigation considering potential intermetallics that might form but could also be evaluated empirically.

When alloying effects in the Al-Sc-RE system have been completely defined systematic studies should be undertaken to evaluate the effect of solid solution strengtheners like Li and Mg with the ultimate goal of producing optimized structural materials.

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XI. References

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