

Lawrence Berkeley National Laboratory

Recent Work

Title

THE INFLUENCE OF TERNARY PIDDITIONS ON THE STRENGTH OF AL-SC ALLOYS

Permalink

<https://escholarship.org/uc/item/0c0567dk>

Author

Morris, J.W.

Publication Date

1989-06-01

Center for Advanced Materials

CAM

Submitted to Metallurgical Transactions

The Influence of Ternary Additions on the Strength of Al-Sc Alloys

R.R. Sawtell and J.W. Morris, Jr.

June 1989

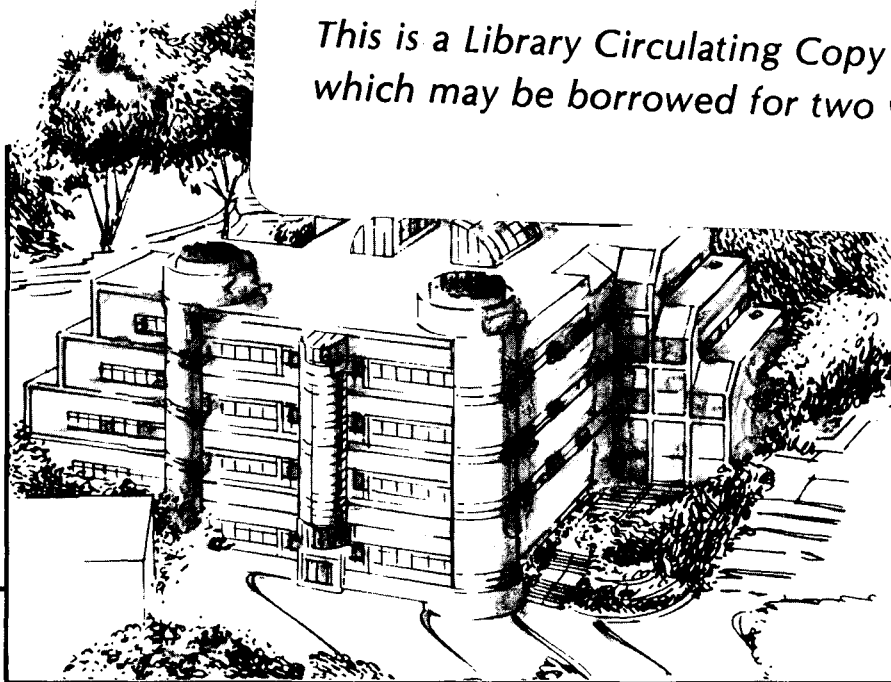
RECEIVED
LAWRENCE
BERKELEY LABORATORY

JAN 3 1990

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.*



Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory • University of California
ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

LBL-26913

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

**The Influence of Ternary Additions on the
Strength of Al-Sc Alloys**

Ralph R. Sawtell and J. W. Morris, Jr.

Center for Advanced Materials
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
1 Cyclotron Road
Berkeley, CA 94720
and
Department of Materials Science and Mineral Engineering
University of California

June 1989

This work is supported by Director, Office of Energy Research, Office of Basic Energy
Sciences, Materials Science Division of the U. S. Department of Energy under
Contract No. DE-AC03-76SF00098

The Influence of Ternary Additions on the Strength of Al-Sc Alloys

Ralph R. Sawtell and J. W. Morris, Jr.
Center for Advanced Materials, Lawrence Berkeley Laboratory
and
Department of Materials Science and Mineral Engineering
University of California, Berkeley

Abstract

While it has been known for some years that scandium is the most potent strengthening alloy addition in aluminum alloys, the potential of scandium additions has not been exploited. A major reason is the high cost of scandium. One possible method of improving both the cost and the properties of Al-Sc alloys is the addition of ternary elements that incorporate into the Al_3Sc strengthening precipitates. The purpose of this research was to select and test ternary alloy additions to improve precipitation hardening in Al-Sc alloys. The ternary additions were selected on the basis of a model that takes into account intermetallic compound formation, precipitation from solid solution and the strengthening efficiency of precipitates. The 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. Experimental results are presented showing that the peak strengths of Al-Sc alloys are increased by approximately 25 percent by the addition of Y or Gd. The increase apparently results from an improvement in the hardening efficiency of the L_{12} precipitate phase, as suggested by the model.

I. Introduction

The influence of scandium on the strength of aluminum alloys was first studied by Willey [1] 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. Later investigators found that Sc combines with Al to form a stable intermetallic phase that has the stoichiometric composition Al_3Sc and an ordered, L_{12} crystal structure [2]. The precipitates form coherent, spherical particles. Because of the relatively low equilibrium solubility of Sc in Al (0.3 atom per cent) 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 [3-5]. The Al_3Sc precipitate is also extremely effective in stabilizing the substructure of Al alloys, and hence facilitates strain hardening and stabilization treatments that 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 the binary alloys are too low to be of interest for advanced structural applications, 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 resistance [6].

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 (SPF) properties to Al-base alloys. Al-Sc-Mg alloys have been produced with superplastic forming characteristics that are superior to those of the currently accepted baseline for SPF Al alloys, alloy AA7475 [6].

One of the most exciting potential applications for Al-Sc-X alloys is in cryogenic tankage for space vehicles and hypersonic aircraft. Materials for such tanks must have good strength and high toughness at cryogenic temperatures, but must also be weldable. Recent results [7] indicate that Al-Sc-Mg alloys have combinations of strength and toughness at cryogenic temperatures that are significantly better than that of the 2219-T87 alloy which is currently used for such structures. In addition, Al-Sc alloys can be made weldable and their lower density (7 pct. lower for Al-6Mg-0.5Sc) offers significant weight reductions compared to the 2219.

Despite its obvious benefits Sc is not now used in commercial aluminum alloys. The primary reason is economic: Sc currently costs over \$40 per gram and has limited availability, at least in part because there is little commercial use for it. None of the alloys that have been investigated to date have offered sufficient performance improvements to offset the economic barrier. Moreover, relatively little fundamental research has been done on the Al-Sc system, which limits the knowledge base from which more attractive alloys can be designed. The purpose of this work was to extend the base of knowledge by exploring the use of ternary additions to augment alloy strength. If other alloying elements can be found that interact with Al_3Sc phase to improve precipitation hardening, alloy performance can be improved or the amount of Sc required (and cost) can be reduced. Either result could help launch this potentially important new system.

The research was done in three phases. The first was a theoretical study of potential ternary alloy additions to identify promising candidates. The most promising alloy additions appear to be yttrium and the group IIIA rare earth alloys. In the second phase ternary Al-Sc-X alloys were cast and tested, which established that significant strength improvements could be obtained with ternary additions of the types identified. The third phase included detailed microstructural studies of the Al-Sc-X alloys to gain further insight into the influence of ternary additions on the hardening precipitate phase. Results of the first two phases are reported below. The microstructural studies will be reported in a subsequent paper.

II. Alloy Design Considerations

The ternary additions of interest in this work are those that might interact with Sc to produce increased strength without compromising other properties. An attractive solution to this problem would be a ternary addition that incorporates into the Al_3Sc precipitate to

increase its resistance to dislocation glide. Given the paucity of prior work on the Al_3Sc phase it is necessary to identify promising ternary additions from indirect evidence and fundamental considerations. The ternary additions used here were chosen on the basis of three criteria. First, since the ternary addition should incorporate into the Al_3Sc precipitate, it should resemble Sc chemically and, preferably, form an L_{12} intermetallic with Al itself. Second, the ternary addition should increase the stability of the L_{12} precipitate. Third, the ternary addition should increase the strength of the precipitate: its resistance to shearing by a lattice dislocation. There is useful prior research on each of these subjects.

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 rare earth elements (RE). To begin an assessment of these elements to incorporate 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.

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

Table I: Radii and Electronegativity for Various Group III Elements

The electronic configurations of Sc, Y and the RE elements are similar in that one d electron and two s electrons contribute 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 close to that of Sc, with Y and the series Gd through Tm being the closest. These elements should, hence, strongly resemble Sc in their chemical interactions with Al. In contrast to the electronegativity values, there is a substantial difference between the metallic radii of Al and Sc (12%). Y and the other rare earth elements are all significantly larger than Sc. The rare earth elements that are closest to Sc in size are Y and the series Gd through Tm. We conclude from this that differences in the behavior of the IIIA alloying additions in Al will be dominated by size effects.

There is a reasonable body of experimental information on the intermetallic compounds that form between aluminum and the rare earth elements of interest that can also be used[8]. A review of this work reveals that the observed intermetallic structures can be divided into three types: (1) Al_3X compounds, (2) cubic Mg_2Cu -type Laves phases and (3) orthorhombic AlDy -type structures. These are all recognized to be so-called "size factor" compounds. We are primarily interested in the Al-rich phases with Al_3X stoichiometry. This category includes a variety of related crystal structures that are based on different stacking sequences of ordered {111} planes with triangular symmetry [9-11]. In all cases, the stable structure is the one that minimizes crystal volume and, to first order [12], the structure of the binary intermetallic is determined by the size mismatch between Al and the rare earth element in question.

As the 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 has been interpreted [13] in terms of the reorganization of the close packed planes to minimize interatomic potential energy. The Cu_3Au -type, L_{12} crystal structure, which is typified by Al_3Sc , is favored when the size difference is a minimum; the smallest rare earth elements (Er, Tm, Yb) form stable L_{12} structures and the next largest (Ho, Tb) transform into this structure at high pressure [14]. 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.

The influence of pressure on structural stability in Al_3X compounds apparently results from second order effects associated with compressibility or the gradient in the interatomic repulsive force with respect to distance [13]. 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, the pressure-induced transitions lead to structures that are characteristic of lower radius ratios. Yttrium, on the other hand, does not differ much from Al in compressibility and shows no pressure effect.

Although the trends observed in binary trialuminides are important in developing a basic understanding, ternary interactions 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 L_{12} structure and the stoichiometric formula

$\text{Al}_3(\text{Sc}_{1-x}\text{RE}_x)$. The L_{12} 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 L_{12} structure. A number of such ternary intermetallic compounds have been observed experimentally [15,16]. 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 general structural trends as the binary trialuminides. While the Y compounds are exceptions, the maximum reported solubility generally decreases as the rare earth size increases. However, the reduction in solubility is larger than expected; none of the ternary compounds achieves an effective radius near the limit found for the binary intermetallics (0.176 nm). The effective radius at maximum solubility decreases with increasing solute size. This effect may be a simple consequence of the distortion of the Sc-RE sublattice of the L_{12} structure caused by increasing size difference between Sc and the RE.

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

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

The elements that appear in Table II chemically resemble Sc and can be incorporated into the Al_3Sc intermetallic to at least some extent. They are, therefore, the ternary elements of interest in this work. All except Y are rare earths; for notational simplicity we shall use the symbol RE for all of them.

B. Precipitation

We next consider the possible precipitation of the ternary compounds from an Al solid solution. The thermodynamic driving force for precipitation at given temperature and external pressure, ΔG , is

$$\Delta G = V_{\beta}(\Delta g_c + \Delta g_e) + A_{\beta}(\gamma_{\alpha\beta}) \quad (1)$$

where V_{β} is the precipitate volume, Δg_c and Δg_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 focus on the differences in ΔG between the $L1_2$ Al_3RE precipitates it would seem a valid first approximation to neglect both the Δg_c and $\gamma_{\alpha\beta}$ terms because of the strong chemical similarities among the elements. With this approximation the differences in the driving force for nucleation for the various compositions is determined by differences in the elastic energy, ΔG_e .

The elastic contribution to the free energy change on forming a precipitate is,

$$\Delta G_e \approx N[e_p - e_s] \quad (2)$$

where N is the number of solute atoms in the precipitate, e_p is the elastic energy of the precipitate per solute atom, e_s is the elastic free energy per solute atom in the solution, and we have neglected the external pressure and the configurational entropy of the solute. The elastic energy has been evaluated for many precipitate-matrix combinations [17,18]. The simplest result, which may be adequate for our purposes, is obtained when the elastic constants are uniform and isotropic, in which case the elastic energy of a particular particle is

$$E_e = V_\beta \left(\frac{2}{9}\right) G \left[\frac{1+\nu}{1-\nu}\right] \epsilon_0^2 \quad (3)$$

where V_β is the volume of the elastic inclusion (precipitate or solute atom), G and ν are the shear modulus and Poisson's ratio, and ϵ_0 is the stress-free strain. For the solute atom,

$$\epsilon_0 \equiv 3(\delta r/r) \quad (4)$$

where r is the radius of an 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 this data is unavailable, we use the metallic radii of the atoms. For the precipitate,

$$\epsilon_0 \equiv 3(\delta a/a) \quad (5)$$

where a is the lattice parameter of the FCC unit cell, $\delta a = a' - a$ where a' is the lattice parameter of the $L1_2$ cell of the precipitate, and we have assumed complete precipitation of the available solute. Substituting these results into equation (2), the elastic contribution to the free energy change is approximately

$$\Delta G_e \approx 2(N)G \left[\frac{1+\nu}{1-\nu}\right] \left\{ v_s \left(\frac{da}{a}\right)^2 - \Omega_s \left(\frac{dr}{r}\right)^2 \right\} \quad (6)$$

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 , when the stress-free strain of the solute, (dr/r) , is computed from the free-atom radius it is much greater than the precipitate strain (da/a) , in every case of interest to us. The consequence is 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.

Equation (6) can also be used to estimate the elastic energy change for the formation of ternary precipitates. Calculations that use the experimental values of the lattice parameters of the ternaries show little difference in total elastic energy between an array of ternary $L1_2$ precipitates and 2 distinct arrays of binary precipitates. There may, however, be an additional driving force for the precipitation of ternary precipitates. If the ternary addition is disordered or only partly ordered on the Sc sublattice then the entropy of the ternary is higher than that of the ordered binaries.

These calculations suggest that the thermodynamic driving force for the formation of $L1_2$ precipitates from an Al-Sc-RE solid solution increases with the size of the RE atom. 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. Thus, the ternary addition should be decidedly beneficial if it does not diminish the strengthening effect of the precipitate phase.

C. Strengthening

We now consider the potential effect of ternary additions on the strengthening efficiency of the precipitates. The general subject of precipitation hardening has been reviewed often [19-21]. 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 dislocation glide depends on whether the precipitate particles are passed by shearing through the precipitates or looping around them.

When the precipitates are small they are inevitably sheared, irrespective of their dominant hardening mechanism. The critical resolved shear stress in the regime where the precipitates are sheared is approximated by the relation

$$\tau_c \approx \left[\left(\frac{6\Gamma^2}{\pi b^2} \right)^{1/2} \right] f^{1/2} \frac{Q\beta_c^{3/2}}{\langle r \rangle} \quad (7)$$

where f is the volume fraction of precipitate, b is the magnitude of the Burgers vector, Γ the dislocation line tension, $\langle r \rangle$ is the average particle radius, Q is a constant of order unity, β_c is the effective obstacle strength, and we have ignored the influence of the distribution of precipitate sizes [22]. The critical resolved shear stress that is given by equation (7) increases with the average radius, $\langle r \rangle$, irrespective of the dominant source of hardening, since $\beta_c^{3/2}$ increases more rapidly than $\langle r \rangle$. However, when the obstacle strength reaches a critical value of approximately 0.7 [23] the dislocations begin to pass the obstacles by Orowan looping, and the obstacle strength remains constant for all further increases in particle size.

The behavior that is predicted on the basis of this model is drawn schematically in Fig. 1. As a function of the particle size, the critical resolved shear stress increases so long as the obstacles are passed by shear, but decreases when Orowon looping intrudes. Hence the maximum strength falls at the transition between shear and looping. Note that as the strength of the particles increases, that is, as β_c increases for given $\langle r \rangle$, the maximum strength increases and the maximum falls at a smaller value of the mean particle size.

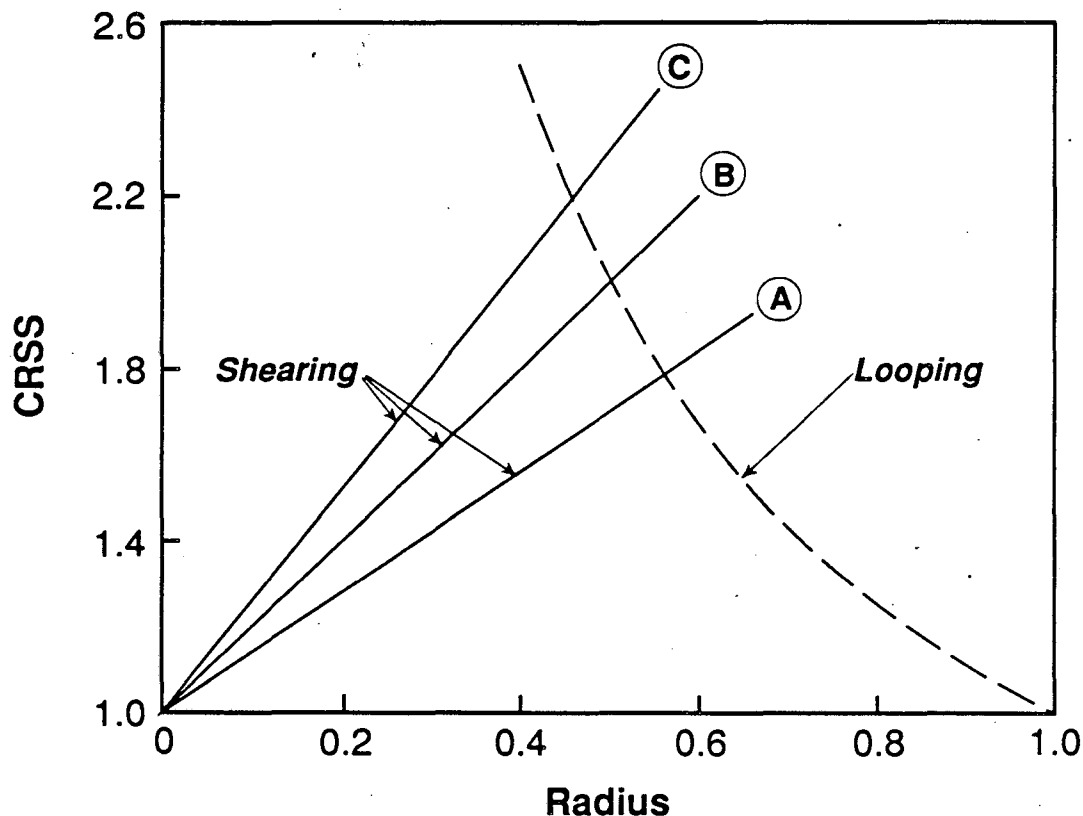


Figure 1: Schematic drawing showing CRSS as a function of particle radius in both the looping and shearing regimes. The hardening efficiency increases on moving from points A to B to C.

The ultimate value of τ_c depends on the particular mechanism that dominates the dislocation-obstacle interaction. In an alloy strengthened by ordered, $L1_2$ precipitates, strengthening will be dominated by coherency, order or modulus hardening. The maximum strength when the strain field of the precipitate dominates the interaction (coherency hardening) has the qualitative form

$$\tau_{\max}^e = KGe f^{1/2} \quad (8)$$

where K is a constant, G is the shear modulus, ϵ the strain between the precipitate and the matrix and f the volume fraction. When the interaction is dominated by the difficulty of glide through the precipitate (order hardening) the maximum strength has the form

$$\tau_{\max}^0 = K \left(\frac{\gamma_{\text{apb}}}{b} \right) f^{1/2} \quad (9)$$

where γ_{apb} is the antiphase boundary energy and b is the magnitude of the Burgers vector. The interaction may also be dominated by the modulus difference between the precipitate and the matrix. While there is no simple solution for the maximum stress in this case, the expected increment in τ_c should be proportional to the 3/2 power of an appropriate measure of the modulus difference.

The change in the strength of Al-Sc alloys with RE additions depends on the RE influence on the precipitate volume fraction and the obstacle strength. We concluded in the previous section that RE additions should increase the volume fraction, and, hence, should increase the maximum strength. The RE addition should also increase the effective obstacle strength if the dominant mechanism is coherency or order hardening. Coherency hardening increases with the precipitate strain, which increases on addition of relatively large third-atom. In the case of order hardening, the peak strength increases with the antiphase boundary energy. To a first approximation, γ_{apb} increases with the stability of the precipitate phase relative to the disordered solution [24,25]. It should, therefore, increase with the difference between the elastic energy of the precipitate and that of the solution. The efficiency of order hardening may also increase with RE size because of effective solute hardening within the precipitate. 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 under which circumstances this effect should be relatively small.

D. Summary

The considerations discussed above suggest that the volume fraction, stability and hardening effect of precipitates in an alloy containing a given amount of scandium should be improved by adding any of the RE elements. The volume fraction of precipitate is expected to vary as the inverse of RE size, while the strength and stability of the precipitates should improve with increasing RE size. It is also anticipated that the transformation stress (pressure) of precipitation will increase the solubility of the RE as in the pure intermetallics and, thus, mitigate the negative effects of increased RE size on precipitate volume fraction. The optimal addition will be determined by the relative importance of these various effects, and should be determined by a balance between the expected decrease in precipitate volume fraction that accompanies an increase in the strength of the hardening precipitates.

The conclusion is that additions of Y or RE to Al-Sc alloys may significantly improve alloy strength. The possibility was tested experimentally in the work reported below.

III. Experimental Materials and Procedures

A. Alloys

The Al-Sc-RE alloys that were studied in this program are listed in Table III. The Y and rare earth additions were selected to provide a systematic variation in solute size. Equal atom fractions of Sc and the RE were used. The nominal composition of the alloys were, in atom percent, Al-0.3Sc-0.3RE, which fixes the total atom fraction of solute for all alloys except the Al-0.3Sc control. The amount of alloy addition was chosen in the expectation that it would exceed the constrained $L1_2$ solubility limit for the larger ternary additions, but not for the smaller ones, and would hence clarify the balance between the expected increase in precipitate strength and decrease in precipitate volume fraction with solute size.

B. Melting and Casting

The alloys were melted and alloyed in air in a MgO crucible that was heated to 775°C in a resistance furnace. The alloying elements used were 99.999 pct. pure. The aluminum base was 99.99 pct. pure. The crucibles were periodically removed from the furnace and stirred with a graphite rod during melting. When all alloying additions were dissolved, the melt was skimmed using a stainless steel mesh and poured into a rectangular Cu mold that was preheated to approximately 200°C. This produced an ingot 0.635 cm. thick with an average cooling rate of approximately 50°C/sec.

System	RE Radius (nm)	Composition, actual (nominal) wt.%				
		Sc	Er	Ho	Gd	Y
Al-Sc	--	0.52 (0.5)				
Al-Sc-Er	0.1757	0.51 (0.5)	1.75 (1.8)			
Al-Sc-Ho	0.1765	0.51 (0.5)		1.91 (1.8)		
Al-Sc-Gd	0.1801	0.50 (0.5)			1.72 (1.7)	
Al-Sc-Y	0.1802	0.52 (0.5)				0.96 (1.0)

Table III: Alloy Compositions (nominal compositions are, in atom percent, 0.3Sc, 0.3RE)

The actual compositions of the alloys were determined by atomic absorption spectrometry and are shown in Table III. Spectrographic analyses confirmed that the impurity element concentrations were all below 0.02 wt. pct.

C. Fabrication

After casting the ingots were trimmed of solidification defects and sectioned. The sections were machined into cylindrical samples and then cold swaged to approximately 1.5 mm diameter. They were then cold drawn to 0.44 mm wires. Prior work [1] suggests that

optimum tensile properties are obtained in the Al-Sc system when the alloys are aged in the as-cast and fabricated condition without solution annealing. This procedure was used. All thermal treatments were carried out in circulating air furnaces maintained within ± 2 °C of the set point. In all cases, samples were placed into a furnace that had been stabilized at the nominal process temperature.

D. Precipitation

The precipitation reactions were studied with differential scanning calorimetry (DSC). The DSC 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. The scan rate was varied from 10 to 80 °C/min. Both the extent of the precipitation reaction and the temperature of the maximum reaction rate were determined.

Electrical resistivity and tensile properties were used to monitor changes in the Al-Sc-(RE) alloys after aging. The electrical resistance was determined using a standard 4-point probe configuration employing a Kelvin bridge for measurement. The sample and the probe contacts were immersed in an oil bath maintained at 21 ± 1 °C during measurement. The resistance is converted to resistivity by the formula

$$\rho = \left(\frac{A}{l} \right) R \quad (12)$$

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

A dedicated tensile testing machine was constructed to measure the tensile properties of the wire specimens. The ends of the wire were secured by epoxy in blocks that fit into the grips of a digital load frame of the type described by Fultz [26], with a constant 2.54 cm gauge length. They were tested at a constant applied stroke rate. Due to the high relative stiffness of the load frame, the stroke rate closely approximates the strain rate in the wire specimen, which was $\approx 10^{-2}$ per minute in all tests. Because of the unusual sample configuration, no attempt was made to place strain gauges on the samples. Hence the measured property was the ultimate tensile strength determined by the peak load. Typical breaking loads were on the order of 45 N.

IV. Results

A. Differential Scanning Calorimetry

Each of the alloys was scanned by differential scanning calorimetry (DSC) at heating rates of 10, 20, 40 and 80 °C/min. A typical scan is shown in Figure 2. The exothermic peak is due to precipitation of the $L1_2$, $Al_3(Sc,RE)$ phase. Its magnitude is a measure of the heat of reaction. The heats of precipitation that were measured on heating from the as-cast condition are shown in Table IV along with the ternary RE radii. The data are

plotted in Figure 3. The heats of precipitation for the ternary alloys are significantly greater than that of the Al-Sc binary, and increase sharply with the RE radius. This result indicates that the RE elements are incorporated into the L_{12} phase, since it is unlikely that an independent precipitation of Al_3RE would occur at the same temperature, and also suggests that the ternary reaction increases with the RE radius. Unfortunately, the data do not distinguish the change in the specific heat of reaction from the change in total volume of precipitate phase.

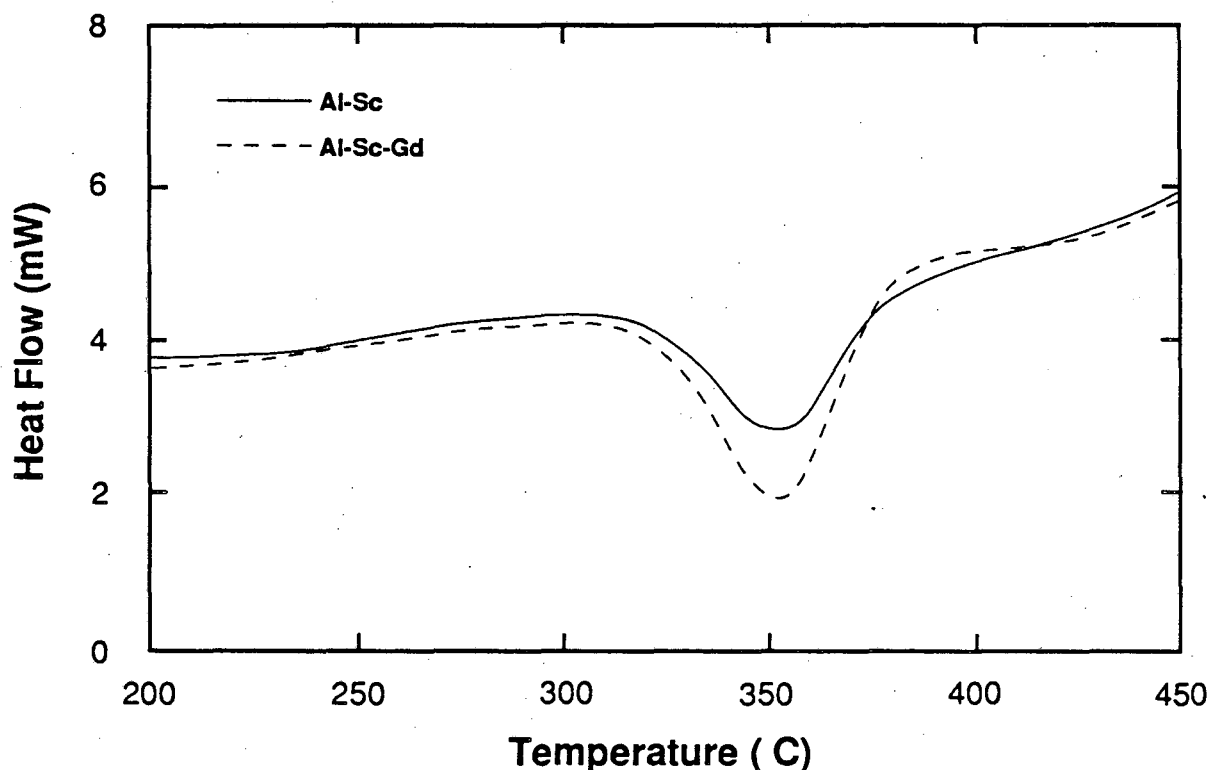


Figure 2. Plot of heat flow versus temperature for as-cast Al-Sc and Al-Sc-Gd alloys obtained using a heating rate of 40 °C/min. Note the exothermic reaction peaks.

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

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

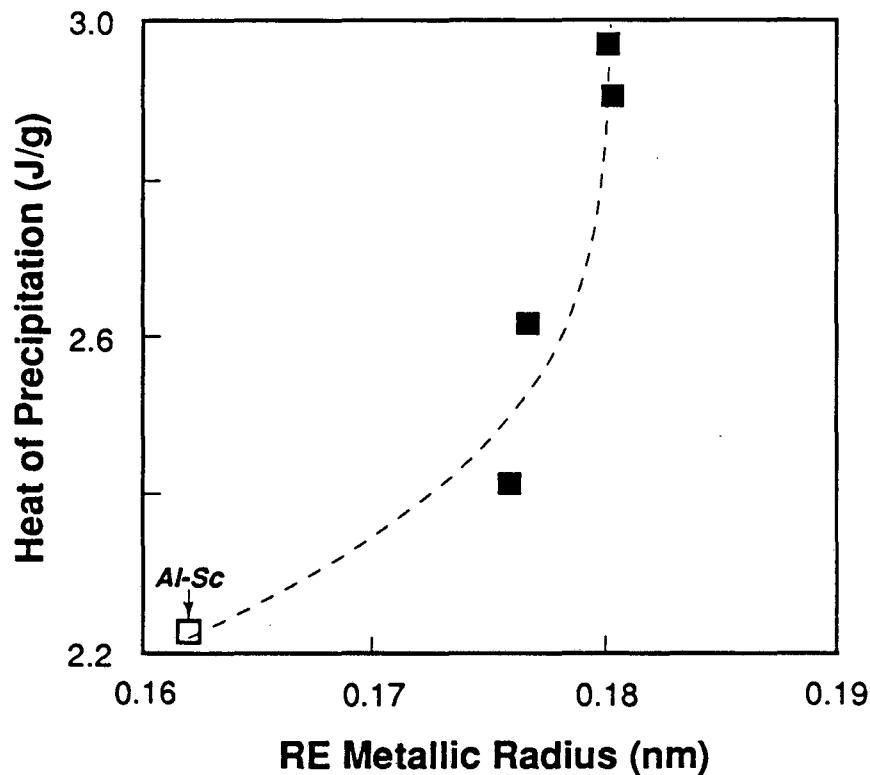


Figure 3. Specific heat of precipitation versus ternary RE radius for Al-Sc-RE alloys. Al-Sc data is shown for comparison.

The temperature that yields the maximum dynamic reaction rate in the DSC was also recorded for each alloy at a variety of heating rates. Assuming first order kinetics, this information yields the activation energy (E) and frequency factor (Z) for the precipitation reaction [27-29]. The calculated values of E and Z are given in Table V. The kinetic parameters for the ternary alloys are quite similar to those of Al-Sc; no clear trends were noted with respect to RE radius. The calculated isothermal precipitation kinetics for the Al-Sc alloy are shown in Figure 4 as an example of the expected behavior. Note that full reaction occurs in less than 1 hour at temperatures above 260° C.

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

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

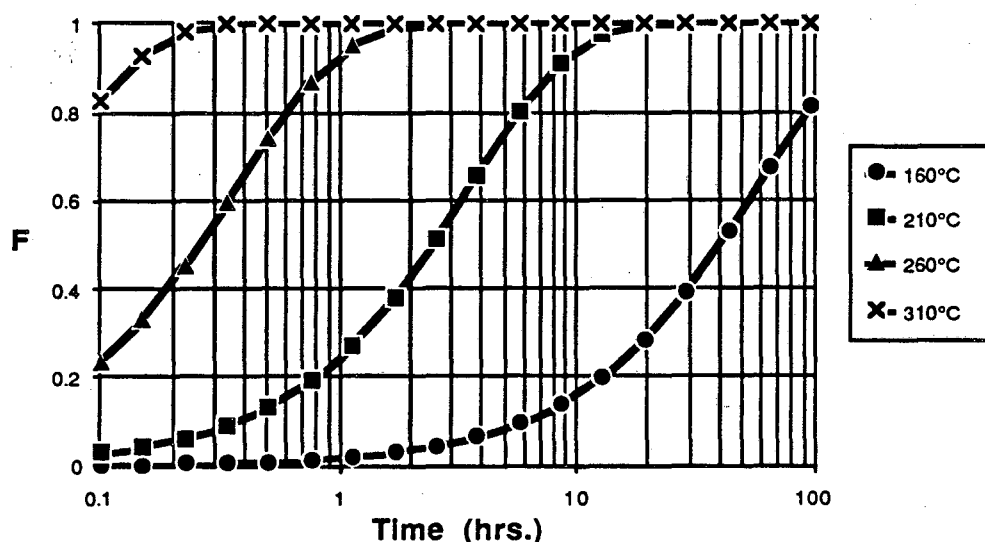


Figure 4. Calculated fraction precipitated (F) versus time for cold worked Al-Sc at a variety of temperatures.

B. Resistivity Measurements

The electrical resistivity was measured along with tensile properties to monitor artificial aging behavior in the Al-Sc-(RE) alloys at temperatures between 235 and 335 °C. In all cases the resistivity decreased monotonically with increasing aging time and temperature. Data for the Al-Sc alloy are shown in Figure 5 as an example of the behavior observed. When the samples were aged at higher temperatures, such as 335 °C, resistivity values approached those for pure aluminum (2.8 $\mu\text{ohm-cm}$). Given the DSC results, which indicate that precipitation is complete after very short times at temperatures in this range, we conclude that the resistivity changes reflect increasing precipitate size rather than alloying in solid solution. It is known that fine precipitates have a marked effect on resistivity [30] due to their efficiency in electron scattering [31].

C. Mechanical Properties

The effect of aging on tensile properties was determined for a restricted subset of the artificial aging conditions investigated using resistivity. An example of the data, the Al-Sc-Gd case, is given in Table VI, which includes the resistivity values. The ultimate tensile strength is very nearly a unique function of the resistivity, irrespective of the aging temperature. This dependence is illustrated in Figure 6, which is a superposition of the plots of tensile strength against resistivity of Al-Sc-Y for various aging temperatures. A composite plot of the data for all alloys is given in Figure 7. Since the resistivity decreases on aging the effective aging time increases to the left in these figures. Normal artificial aging behavior is observed; the strength increases to a maximum value and decreases on further aging. The peak strength and resistivity at peak strength for each alloy are given in Table VII along with ternary RE radius. These values were obtained by fitting a third degree

polynomial to the experimental data in Figure 7 and then employing standard mathematical analysis to determine the maximum.

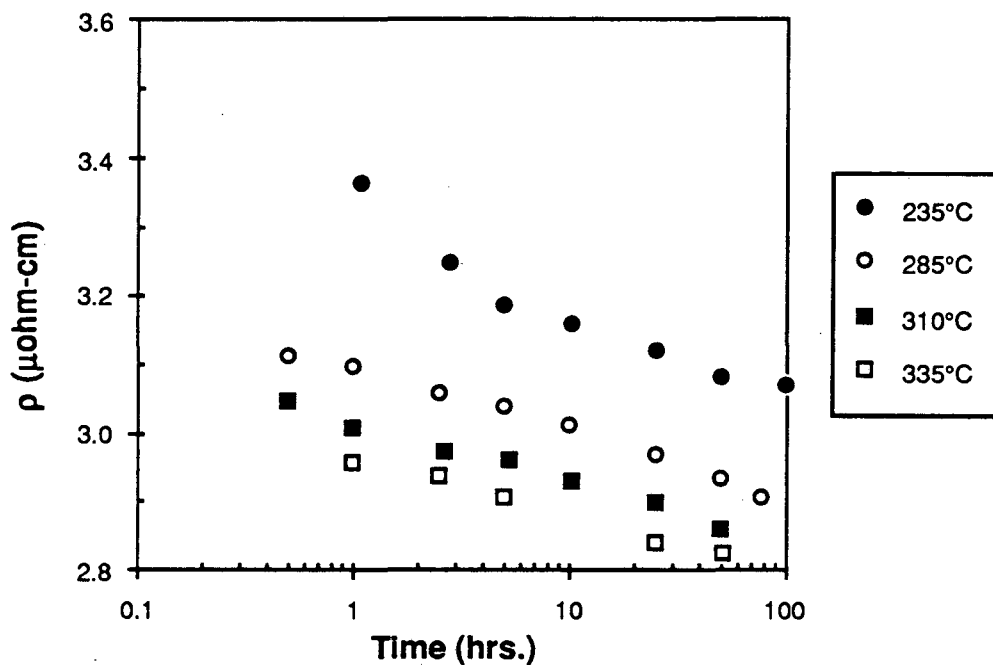


Figure 5. Resistivity (ρ) of an Al-Sc alloy shown as a function of artificial aging time and temperature.

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 VI: Artificial Aging Data for Cold Rolled Al-Sc-Gd

Three features of the aging data seem particularly significant. First, 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 about 25 percent. The strength increase indicates the importance of ternary interactions. If Sc alone were determining strength, the values should all be the same. Second, both the peak strength and the resistivity at peak strength increase with the RE radius. The variation of peak strength with RE radius is shown in Fig. 8. The associated increase in resistivity is documented in Table VII. Since the resistivity increases as the precipitate size decreases, this observation suggests that peak strength is attained at smaller precipitate sizes as the RE radius increases. Third, while the size of the hardening precipitate at peak strength apparently decreases as the RE radius increases, the aging time required to reach peak strength increases with Re size, from ≈ 5 hr. for Al-Sc to ≈ 6 hr. for Al-Sc-Er to ≈ 10 hr. for Al-Sc-Ho, Al-Sc-Y and Al-Sc-Gd.

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

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

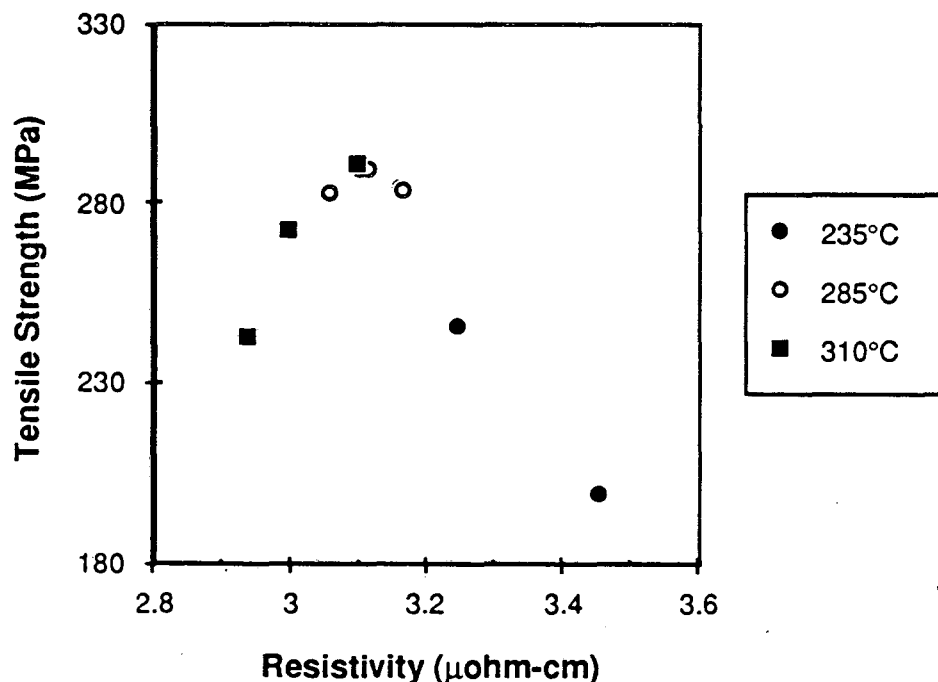


Figure 6. Ultimate tensile strength plotted versus resistivity for an Al-Sc-Y alloy.

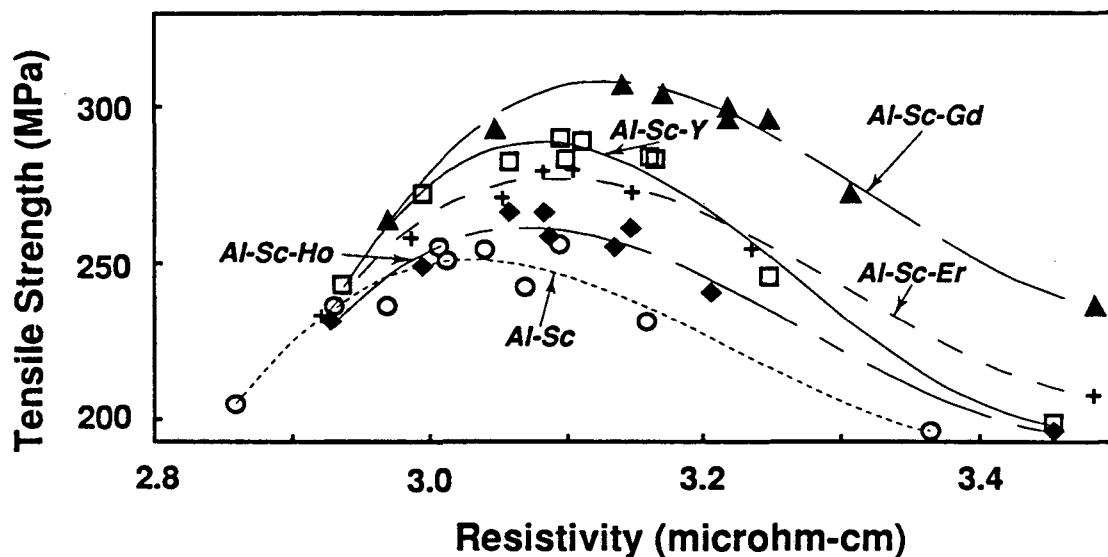


Figure 7. Ultimate tensile strength plotted versus resistivity for an Al-Sc-Y alloy.

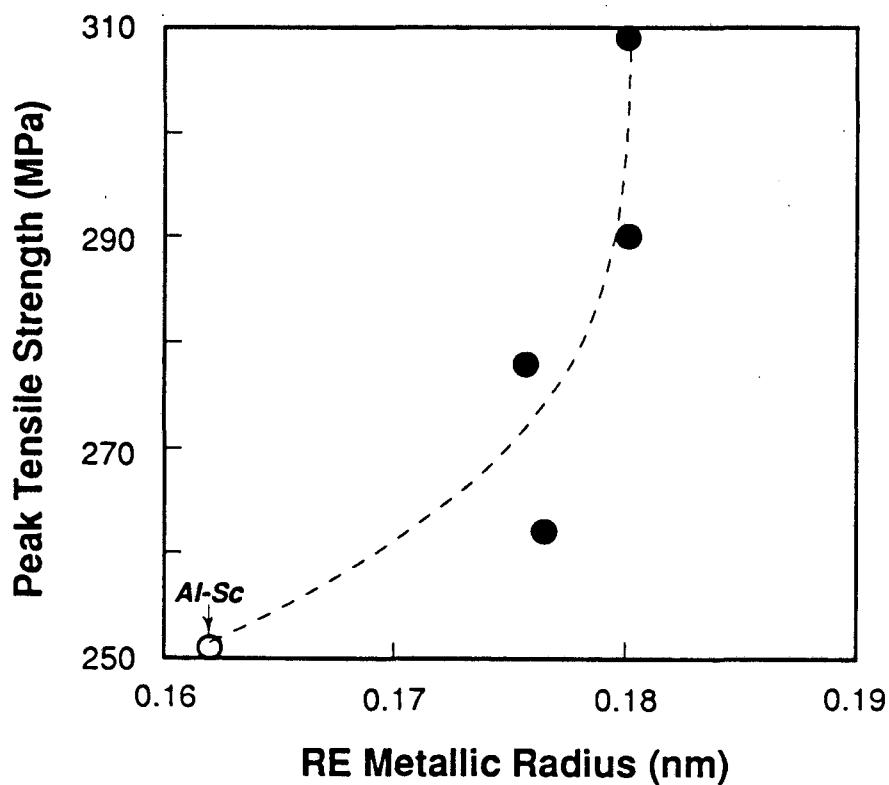


Figure 8. Peak tensile strength versus ternary RE radius for Al-Sc-RE alloys. Al-Sc data is shown for comparison.

V. Discussion

From the point of view of the original alloy design goals the two most important results of this work are that the strengths of the ternary Al-Sc-RE alloys are greater than that of Al-Sc and that they increase with increasing RE size. Both are indications that the ternary species incorporate into the $L1_2$ precipitate, a hypothesis that is also supported by the DSC data.

The resistivity at peak strength and its variation with RE size is also important. As a practical matter, the resistivity at peak strength can be used in concert with plots of resistivity against time and temperature to determine the optimal aging time as a function of temperature. More fundamentally, the increase in resistivity at peak strength suggests that the peak occurs at smaller precipitate size as RE radius increases, which indicates that the RE elements increase the effective strength of the precipitate phase. This effect is illustrated in Figure 1, which plots the consequences of the simple model in which peak strength is obtained when the strength of the hardening precipitates becomes so great that Orowan looping replaces shearing as the dominant mechanism for dislocation glide. The model predicts that peak strength falls at smaller obstacle radii as the efficiency of hardening increases.

Fig. 1 should roughly illustrate the aging behavior of the Al-Sc-RE alloys. The precipitation reaction is apparently complete after very short aging times, so the precipitates coarsen at constant volume fraction. Neglecting any differences in the volume fraction, the increase in strength at given particle radius is due to the increment in strength imparted by the RE addition to the precipitate. The greater the contribution of the RE atom to the strength of the Al_3X hardening precipitate, the more rapid the increase in strength with particle size, the higher the peak strength, and the smaller the particle size at which peak strength is attained. This is the behavior observed in the Al-Sc-RE alloys as RE size is increased from Er through Gd. The peak strength increases and the radius at peak strength decreases.

As discussed in Section II, there are at least two mechanisms that suggest an increasing hardening efficiency with increasing RE radius. If the RE solute is fully incorporated into the precipitate, both the elastic coherency strain and the antiphase boundary energy should increase with increasing RE radius. The results presented here do not distinguish between the two strengthening mechanisms. Microstructural studies that will be presented elsewhere suggest that the primary effect is the antiphase boundary energy of the hardening precipitate.

The kinetics of artificial aging also suggest that the RE additions are incorporated into the $L1_2$ precipitate. The 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. As a point of comparison, the peak is attained after 5 hours in the binary Al-Sc. These trends are observed even though precipitate size at peak strength decreases with increased RE size. Hence the precipitate coarsening rate must decrease with RE size. It is well known that coarsening in such systems is diffusion controlled. Although diffusion data in Al are not

available for many of the RE elements there is a strong trend toward decreasing diffusion rates with increasing RE size [32]. Thus, slower diffusion and decreased coarsening rates would be expected for Al-Sc-Y and Al-Sc-Gd, as is apparently observed.

The most surprising result of this work is that strength monotonically increases with RE size. We anticipated that Gd would be a less effective addition because so little of it should be incorporated into the L₁₂ phase. This strong contribution of Gd to the peak strength suggests that either Gd is incorporated in amounts well beyond its anticipated solubility or that small Gd additions have a significant effect on the precipitate strength. This issue is explored further in the microstructural studies reported in the companion paper.

While the results of this study provide strong, indirect evidence that the RE elements are incorporated into hardening precipitates in Al-Sc alloys, there is no *direct* evidence that the RE are incorporated, and if so, at what level. Factors other than RE incorporation into the hardening precipitates could be responsible for the observed variations in alloy strength. The possibilities include solid solution strengthening, co-precipitation of hardening phases that contain RE, and substructure strengthening. Solid solution strengthening seems unlikely because of the low solubility of the solute species at normal temperatures. Significant co-precipitation also seems unlikely since no evidence for it appears in the DSC data. Substructure or grain size strengthening could be a significant effect if variations in precipitate volume fraction or nature alter the grain size or dislocation substructure [33-36]. These issues are addressed in the companion paper.

VI. Conclusions

The following conclusions are drawn from this work.

1. The elements Y, Gd, Er and Ho are effective in increasing the strength of Al-Sc alloys. The addition of Gd is particularly effective. The tensile strength of Al-0.3Sc-0.3Gd is $\approx$ 25% higher than that of Al-0.3Sc.
2. The strengthening effect of the ternary alloy additions increases with atomic size, and apparently results from the incorporation of the ternary specie into the Al₃Sc precipitate. The latter conclusion is based on the increased heat of precipitation in the ternary alloy and the smaller mean size of the hardening precipitate at peak strength, as inferred from resistivity measurements.
3. The results obtained here are insufficient to determine the extent of incorporation of the ternary addition in the Al₃Sc precipitate or whether the principle contribution to hardening is through the precipitate strain, the antiphase boundary energy, or some other cause. Microstructural studies are underway to complete the analysis.

Acknowledgements

The authors appreciate helpful conversations with A.G. Khachaturyan, S. Verzasconi and J. Glazer, Center for Advanced Materials, LBL. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract No. DE-AC03-76SF00098, and by a research gift from Alcoa, who also provided the research materials.

References

1. L.A. Willey, *U.S. Patent 3,619,181*, 1971
2. M. E. Drits, S. G. Pavlenko, L. S. Toropova, Yu. G. Bykov and L. B. Ber, *Sov. Phys. Dokl.*, 1981, vol. 26, pp 344-346.
3. M. E. Drits, L. S. Toropova and Yu. G. Bykov, *Metallovedenie. i Termicheskaya. Obbrabotka. Metallov*, 1983, vol. 7, pp 60-63.
4. V. I. Elagin, V. V. Zakharov and T. D. Rostova, *Metallovedenie. i Termicheskaya. Obbrabotka. Metallov*, 1983, vol. 7, pp 57-60.
5. N. Blake and M. A. Hopkins, *J. Mat. Sci.*, 1985, vol. 20, pp 2861-2867.
6. R. R. Sawtell, P. E. Bretz and C. L. Jensen, *U.S. Patent 4,689,090*, 1987.
7. S. L. Verzasconi, Center for Advanced Materials, Lawrence Berkeley Laboratory, *unpublished work*.
8. A. Iandelli and A. Palenzona, *Handbook on the Physics and Chemistry of Rare Earths*, Ed. Gschneidner and Eyring, North Holland, 1979.
9. J. H. Van Vucht and K. H. J. Buschow, *J. Less-Common Metals*, 1965, vol. 10, pp 98-107.
10. J. F. Cannon and H. T. Hall, *J. Less-Common Metals*, 1975, vol. 40, pp 313-328.
11. M. Gasgnier, G. Schiffmacher and P. Caro, *J. Less-Common Metals*, 1976, vol. 50, pp 177-188.
12. J. H. Van Vucht, *J. Less-Common Metals*, 1966, vol. 11, pp 308-322.
13. E. E. Havinga, *J. Less-Common Metals*, 1975, vol. 41, pp 241-254.
14. J. F. Cannon and H. T. Hall, *J. Less-Common Metals*, 1975, vol. 40, pp 313-328.
15. O. I. Zalutskaya, V. G. Kontsevov, N. I. Karamyshev, V. R. Ryabov and I. I. Zalutsky, *Dop. Akad. Nauk. Ukrain. RSR [A]*, 1970, vol. 8, pp 751-753.
16. O. I. Zalutskaya, V. R. Ryabov and I. I. Zalutsky, *Dop. Akad. Nauk. Ukrain. RSR [A]*, 1970, vol. 3, pp 255-259.
17. J. D. Eshelby, *Proc. Roy. Soc. A*, 1957, vol. 241, pp 376-?; 1959, vol. 252, pp 561-?.
18. A.G. Khachaturyan, *The Theory of Structural Transformations in Solids*, J. Wiley, New York, 1983
19. A. Kelly and R. B. Nicholson, *Progr. Mat. Sci.*, 1963, vol. 10, pp 149-154.
20. L. M. Brown, and R. K. Ham, *Strengthening Methods in Crystals*, A. Kelly and R. B. Nicholson, eds., Halsted Press, John Wiley & Sons, New York, NY, 1971, p 9.

21. A. J. Ardell, *Met. Trans. A*, 1985, vol. 16A, pp 2131-2165.
22. Glazer and Morris, *Acta Met.*, 1988, vol 36, pp. 907-915
23. Bacon, Kocks and Scattergood, 1973, *Phil.Mag A*, vol 28, pp. 1241-1263
24. P. A. Flynn, *Trans. AIME*, 1960, vol. 218, pp 145-154.
25. A. G. Khachaturyan and J. W. Morris, *Phil. Mag.*, 1987, vol. 56, pp 517-532.
26. B. Fultz, R. Kopa and J. W. Morris, Jr., *J. Metals* , April, 1986, pp 58-59.
27. J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Std.*, 1966, vol. 70A, pp 487-523.
28. T. Ozawa, *J. Thermal Analysis*, 1970, vol. 2, pp 301-324.
29. A. A. Duswalt, *Thermochimica Acta*, 1974, vol. 8, pp 57-68.
30. P. Wilkes, *Acta Met.*, 1968, vol. 16, pp 863-866.
31. A. J. Hillel, *Acta Met.*, 1970, vol. 18, pp 253-259.
32. S. P. Murarka and R. P. Agarwala, *Indian Atomic Energy Commision Report BARC-368*, 1968, pp 30-33.
33. N. Hansen, *Met. Trans. A*, 1985, vol. 16A, pp 2167-2190.
34. S. K. Varma and B. G. LeFevre, *Met. Trans. A*, 1980, vol.11A, pp 935-941.
35. D. J. Lloyd and D. Kenny, *Acta Met.*, 1980, vol. 28, pp 639-649.
36. D. Kalish and B. G. LeFevre, *Met. Trans. A*, 1975, vol. 6A, pp 1319-1324.

*LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720*