**Title:** Promotion or Retention of Desired Metastable and Ultrafine Microstructures with an Electric Field or Current

**Authors:** H. Conrad, K. Jung and J. Narayan

**Abstract:**

The influence of an electric field on the equilibria and kinetics of grain growth and phase transformations in metals and the resulting mechanical properties were determined, with attention to ultrafine and nanometer microstructures. The phenomena and materials considered were: (a) precipitation in Al-Mg-Si alloys, (b) phase coarsening in 60Sn40Pb solder joints, (c) grain growth in electrodeposited Cu and (d) dependence of the plastic flow stress on grain size. Regarding (a), a field applied during solutionizing increased the solubility of the pertinent constituents and in turn the tensile properties in the naturally-aged temper. Thermodynamic considerations along with HRTEM and SAED studies indicated that the field reduced the Gibbs free energy of solution, increased the size of the naturally-aged precipitates and changed their crystal structure. Regarding (b), a field retarded coarsening of the Sn and Pb phases and changed...
14. ABSTRACT (Continued)

their volume fractions. The effect of the field on phase coarsening appeared to be through its effect on the diffusion coefficient. Regarding (c), a field retarded grain growth. Whether the field retarded grain boundary mobility or enhanced the annihilation of the crystal defects responsible for the driving force was not clear. Regarding (d), analysis of the effect of grain size $d$ on the flow stress of metals and compounds over the range from nanometers to millimeters indicated three regimes: Regime I ($d>\sim 10^{-6}$m), Regime II ($d=10^{-8}$-$10^{-6}$m) and Regime III ($d<10^{-6}$m). Dislocations are active in I and II and absent in III. The mechanism governing Regime III appears to be grain boundary shear accommodated by grain boundary diffusion.

Unique pulsed laser vapor deposition techniques were employed to fabricate: (a) metals and compounds with nanometer grain size, (b) $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$/ZnO heterostructures and (c) nanodot metals embedded in ceramic matrices, and their respective novel mechanical or electrical properties were determined.
Final Report

PROMOTION OR RETENTION OF DESIRED METASTABLE AND ULTRAFINE MICROSTRUCTURES WITH AN ELECTRIC FIELD OR CURRENT

ARO Contract/Grant Number: DAA19-02-1-0315

Table of Contents

1. Statement of Problem Studied ................................................................. 1

2. Summary of the Most Important Results .................................................. 1
   2.1. Precipitation Hardening of Al Alloys .............................................. 1
   2.2. Phase Coarsening in Solder Joints .................................................... 8
   2.3. Grain Growth ..................................................................................... 10
   2.4. Effect of Grain Size on the Flow Stress ............................................ 11
   2.5. Consideration of the Physical Basis for the Effect of
        an Electric Field on Phase Equilibria and Kinetics in Metals ............ 14
   2.6. Novel Microstructures by Pulsed Laser Vapor-Deposition ................... 15
   2.7. Summary of “Firsts” ........................................................................ 16
   2.8. Bibliography .................................................................................... 17

3. List of all Publications and Technical Reports ......................................... 18
   (a) Papers Published in Peer-Reviewed Journals .................................... 18
   (b) Papers Published in Non-Peer Reviewed Journals or in
       Conference Proceedings .................................................................... 19
   (c) Papers Submitted at Meetings, but not yet Published in
       Conference Proceedings .................................................................... 20
   (d) Manuscripts Submitted but not yet Published ................................... 20
   (e) Technical Reports Submitted to ARO ............................................... 20

4. Participating Scientific Personnel ............................................................. 21

5. Report of Inventions ............................................................................... 21

6. Technology Transfer ................................................................................ 21

List of Appendixes

Appendix I: Calculation of the effect of electric field on thermodynamic
solubility parameters determined from resistivity $\rho$ measurements ........ 23

Appendix II: Analysis of natural aging kinetics of the Al-Mg-Si alloys in terms of
the Johnson-Mehl, Avrami, Kolmogorov (JMAK) model ......................... 24

Appendix III: Simplified model for the effect of an electric field on the
solubility of Si in Al .................................................................................. 25
1. Statement of Problem Studied

Materials science deals with the production and control of microstructure having the aim of optimizing or improving the properties of materials. Of considerable interest in recent years has been the development of metals and ceramics with an ultrafine microstructure extending into the nanometer range. In view of the high internal energy associated with the interfaces in such ultrafine microstructures, they tend to be unstable and coarsen, thereby losing beneficial properties. Desirable therefore are means for promoting and retaining desired metastable and ultrafine microstructures.

The external parameters generally employed in the processing and control of microstructures in materials are: (a) temperature, (b) pressure or stress, (c) environment (gas, liquid or solid) and (d) time. Usually neglected are electric and magnetic fields. However, it has been shown in previous work by the PI (H. Conrad) sponsored by ARO that electric fields can have a significant influence on the properties of metals, even though an effect is not expected. The major objective of the present study was therefore to further evaluate the effects of an electric field on the microstructure of metals, with the aim of promoting or retaining desired metastable and ultrafine microstructures.

2. Summary of the Most Important Results

2.1 Precipitation Hardening of Al Alloys: The alloys investigated were the commercial age-hardening Al-Mg-Si alloys AA6061, 6022 and 6111 with the compositions given in Table 1. They are based on the precipitate Mg₂Si and are finding increasing application in the automotive and aerospace industries. Alloy 6061 is a...
Table 1. Pertinent alloying constituents in wt.% in three 6××× Al-Mg-Si alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg₂Si</th>
<th>Excess Si</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>6061</td>
<td>1.51</td>
<td>0.07</td>
<td>0.01</td>
</tr>
<tr>
<td>6022</td>
<td>0.92</td>
<td>0.40</td>
<td>0.06</td>
</tr>
<tr>
<td>6111</td>
<td>1.23</td>
<td>0.19</td>
<td>0.79</td>
</tr>
</tbody>
</table>

nominally balanced Mg₂Si alloy, 6022 has an excess of Si and 6111 has the addition of Cu. The solubility of the pertinent solutes during the solution heat treatment (SHT) and the subsequent natural aging behavior of these alloys were monitored by conductivity Σ (resistivity ρ=Σ⁻¹) and Vickers hardness Hv measurements of water-quenched specimens. Tensile properties (YS, TS and % El.) were determined at the peak naturally-aged condition (T4 temper).

It was found that the application of an external dc electric field E during SHT at 450°-550°C of 6022 and 6111 decreased both the enthalpy ΔHₘ and entropy ΔSₘ of solution with a resulting decrease in the Gibbs free energy ΔGₘ=ΔHₘ-TΔSₘ, giving an increase in the solubility of Mg₂Si; see Fig. 1. The equations by which the solubility of Mg₂Si was determined from the resistivity ρ and hardness Hv measurements are given in Appendix I. The influence of alloy composition on the increase in solubility produced by the electric field is shown in Fig. 2. This shows that the increase depends on the presence of excess Si and the addition of Cu in the Al-Mg-Si alloys, which accounts for the fact that the field had no detectable effect on the 6061 alloy.

The dependence of the thermodynamic parameters of ΔHₘ, ΔSₘ and ΔGₘ on the strength of the electric field is shown in Fig. 3. All three parameters decrease with field...
Fig. 1. Increase in the solubility of Mg$_2$Si in Al-Mg-Si alloys by application of an electric field during solution heat treatment. The solubility in 6xxx alloys with E=0 taken from Gröng [1].

Fig. 2. Effects of Cu + excess Si on the increase in solubility $\Delta c$ of Mg$_2$Si at 475°-550°C produced by application of an electric field E=5 kV/cm. Strength up to ~1 kV/cm and then only slightly, if at all, at higher field strengths. The increase in solubility with field strength is given by (see Appendix I)

$$\overline{D}_m^m - \overline{D}_o^m = k_0 \exp(-Q/RT)t$$  \hspace{1cm} (3)

where $c_{Mg_2Si}$ is the concentration of Mg$_2$Si and $\Delta G_s(E)$ decreases with field strength $E$ according to Fig. 3.
Fig. 3. The effect of the electric field strength on the enthalpy $\Delta H_s$, entropy $\Delta S_s$, and Gibbs free energy $\Delta G_s=(\Delta H_s-T\Delta S_s)$ of solution of Mg$_2$Si in three Al-Mg-Si alloys 6061, 6022 and 6111.

The increase in $\rho$ (and in $H_v$) which resulted from the increase in solubility by the application of a field during SHT prevailed throughout the subsequent natural aging process; see for example Fig. 4. An analysis of the kinetics of the natural aging process in terms of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model [2-4] (Appendix II) gave that the application of the field during SHT had no clear effect on the subsequent natural aging kinetics.

The effect of applying an electric field during SHT at 475°-550°C on the tensile properties in the T4 temper (naturally-aged for 1mo.) of 6111 is shown in Fig. 5. An increase in tensile properties with application of a field is clearly evident. Of special note is that the application of only 200 V/cm during SHT at 500°C gave tensile properties equivalent to those at 550°C without a field. Reductions of 10°-20°C in the normal SHT temperature were obtained for 6022. Decreases in the SHT temperature of these magnitudes offer the potential for considerable savings in industrial SHT practice.
Fig. 4. Increase in resistivity $\rho$ with natural aging time $t_{\text{NA}}$ as a function of the field strength $E_{\text{SHT}}$ applied during the solution heat treatment of 6111 at 475°-550°C.

Fig. 5. Tensile properties of the 6111 alloy naturally-aged for 1 mo (T4 temper) as a function of the electric field strength applied during solution heat treatment at 475°-550°C.
Of interest is the change in microstructure which leads to the improved tensile properties in the T4 temper as a result of the application of an electric field during processing. For this, high resolution transmission electron microscopy (HRTEM) observations and selected area electron defraction (SAED) studies were performed on 6022 specimens which had been; (a) SHT at 525°C and naturally-aged for 2-3 yr without an electric field and (b) SHT with E=5 kV/cm plus an initial natural aging treatment (INA) for 15 min with E=5 kV/cm immediately following the water quench and (c) subsequently naturally-aged for 2-3 yr without a field. The application of the field during the initial natural aging (INA) as well as during SHT further enhanced slightly the tensile properties over those for applying the field only during SHT.

Examples of the precipitates are given in Fig. 6. In general, the precipitates in the specimen processed with the field were larger and spaced further apart than those without field. Their size distributions are shown in Fig. 7. An analysis of the diffraction rings in corresponding SAED patterns indicated that the crystal structure of precipitates without (a) E=SHT=0 and (b) E=SHT=5 kV/cm plus 15 min initial natural age (INA) with E=INA=5 kV/cm.

Fig. 6. HRTEM micrographs of 6022 solution heat treated for 10 min at 525°C, water quencher and naturally-aged for 2 yr: (a) E=SHT=0 and (b) E=SHT=5 kV/cm plus 15 min initial natural age (INA) with E=INA=5 kV/cm.
field was c-centered monoclinic $\beta''$, while that with the field did not correspond to any known crystal structure. *This is the first time that the size distribution and crystal structure of naturally-aged precipitates in an Al-Mg-Si alloy have been determined.*

The increase in tensile properties with application of a field can be attributed to the differences in the precipitate size, spacing, volume fraction and crystal structure. The yield stress due to precipitates in the peak naturally-aged state (T4 temper) is given by [5]

$$\sigma_{ppt} = \frac{M(F^*)^{1/2} f_{ppt}^{1/2}}{b(2\sqrt{3}\pi)^{1/2} \Gamma^{1/2} r^*}$$  \hspace{1cm} (2)

where $M$ is the Taylor factor, $F^*$ the interaction force between dislocations and the precipitates with average size $r^*$, $f_{ppt}$ the volume fraction of precipitates, $b$ the Burgers vector and $\Gamma$ the dislocation line tension. According to Eqn. 2 an increase in yield stress occurs when the product $[(F^*)^{1/2} f_{ppt}^{1/2} ]/r^*$ increases. Considering the increase in yield stress produced in the specimens processed with a field, it was found that although the
volume fraction of precipitates \( f_{ppt} \) increased with field, the corresponding increase in \( r^* \) was such that the ratio \( f_{ppt}^{1/2}/r^* \) decreased with field. Hence, it appears that the field produced an increase in the interaction force \( F^* \) through its effect on the size and crystal structure of the precipitates. This in turn gave the observed increase in yield stress.

2.2 Second Phase Coarsening: Solder joints in electronic packages frequently fail by low-cycle fatigue. This fatigue mechanism is enhanced by the coarsening (which occurs during operation) of the fine microstructure produced during the soldering operation. Of interest was the influence of an electric field on the coarsening of the Sn and Pb phases in 60Sn40Pb solder joints with initial phase sizes of \( \sim 1 \, \mu m \).

A reduction in the phase coarsening rate of both the Sn-rich phase and the Pb-rich phase in 60Sn40Pb solder joints by the field is shown in Fig. 8. It was determined that the reduction in coarsening rate corresponded to a decrease in the parameter \( m \) and the product \( k_o \exp(-Q/RT) \) in the usual coarsening equation

\[
\bar{D}^m - \bar{D}_o^m = k_o\exp(-Q/RT)t
\]  

(3)

where \( \bar{D} \) is the average phase size, \( \bar{D}_o \) the initial phase size, \( Q \) the activation energy, \( t \) the time and \( k_o \) and \( m \) constants. The influence of the field on phase coarsening varied from the outer surface to the center of the 4 mm dia solder joint, a greater retardation of the coarsening occurring near the outer surface compared to the center; see Fig. 9. This behavior is similar to that which occurred for the sintering of iron powder compacts [6], where it was found that the reduction in porosity produced by a field was greatest near the external surface. This was attributed to the migration of charged vacancies to the charged
surface produced by the field. *It was therefore concluded that the major effect of the field on phase coarsening in the 60Sn40Pb solder joints was through its reduction of the diffusion coefficient.*

![Diagram](image)

**Fig. 8.** Mean size $D$ of the individual Pb and Sn phases in 60Sn40Pb solder joints vs annealing time at 150°C as a function of electric field strength.

![Diagram](image)

**Fig. 9.** Gradients in the phase size and volume fraction of the respective phases in 60Sn40Pb solder joints annealed for 70 hr at 150°C without and with an applied electric field $E=25$ kV/cm.

Fig. 9 shows that besides the variation in phase size from the outer surface to the center of the solder joints there also occurred a difference in their respective volume fractions at these locations. Near the outer surface the volume fraction of the Sn-rich phase
was lower than the equilibrium value without a field, while the reverse was true at the center. *These results indicate that the field affected the equilibrium volume fraction of the respective phases in addition to retarding their coarsening rates.* The field also retarded the growth of the intermetallic compounds formed at the solder-Cu substrate.

### 2.3 Grain Growth

Reducing the grain size of metals generally leads to an increase in strength. As a result there has developed in recent years an increased interest in producing metals with an ultrafine grain size extending down to the nanometer range. However, because of the high energy associated with the grain boundaries, ultrafine-grained metals are usually unstable in that grain growth occurs under otherwise normally stable conditions. Since in prior work by the P.I. and coworkers [7] it was found that the application of an electric field during the annealing of cold-worked Al and Cu wire retarded recovery and recrystallization, the objective of this research activity was to determine whether an electric field might also retard grain growth in ultrafine-grained metals. The material chosen was electrodeposited Cu with an initial as-deposited grain size \( D = 600 \text{ nm} \), which is used in electronic packages.

It was found that the application of an electric field during annealing at 150° - 195°C of the electrodeposited Cu retarded grain growth; see Fig 10. An analysis of the kinetics of the grain growth gave

\[
\frac{dD}{dt} = A_o \exp\left(-\frac{Q}{RT}\right)t^n
\]

with \( A_o \approx 10^{-5} \text{ m/s}^n \), \( Q \approx 11 \text{ kJ/mole} \) and \( n \approx 0.06 \). It was determined that the retarding effect of the field was through a reduction in \( A_o \) and \( Q \), but such that the product \( A_o \exp(-Q/RT) \) decreased with field. Further, the results indicated that the driving force for grain growth
Fig. 10. Log grain size $D$ vs. log annealing time $t$ for 18 $\mu$m thick electrodeposited Cu foil annealed at 150°-195°C without and with an electric field $E=5$ kV/cm. “Bottom” indicates side of the foil adjacent to the substrate.

was due to the presence of a high density of dislocations (and other crystal defects), which decreased with time during the annealing process as a result of their annihilation. Li’s [8] model for this process gives

$$\frac{dD}{dt}^{-1}=M^{-1}(P_o^{-1} + k_R t)$$

(5)

where $M$ is the grain growth mobility, $P_o$ the initial driving force and $k_R$ a second order dislocation annihilation constant. Employing Eqn. 5, the apparent activation energy $Q$ in Eqn. 4 is the difference between $Q_M$ and $Q_R$, i.e., $Q=Q_M-Q_R$, where $Q_M \approx 80$ kJ/mole is the activation energy for grain boundary mobility (by vacancy migration) and $Q_R \approx 70$ kJ/mole that for the annihilation of dislocations. The present data did not provide for an unequivocal statement regarding the relative effect of the field on $Q_M$ and $Q_R$, which gave the reduction in $Q$.

2.4 Effect of Grain Size on the Flow Stress: Since grain size is important in mechanical properties, it was deemed desirable as part of our research on the effect of an electric field
on grain growth to determine the effect of grain size over the wide range from millimeters to nanometers on the flow stress of metals and metal compounds, and in turn the governing mechanisms. Considered were the FCC metals Cu, Ag and Au, CPH Zn, a BCC Ti-15 at. % Mo alloy and several other metals and compounds including WC and TiN. The metals (Cu and Zn) and the compounds (WC and TiN) were produced with grain size $D<10$ nm by the Co-PI (J. Narayan) and his colleagues employing a unique pulsed laser vapor deposition technique; see for example Fig. 11.

Fig. 11. Hardness $H_v$ vs grain size $d$ showing grain size softening for WC films produced by pulsed laser vapor deposition.

Fig. 12. Log of the modulus-normalized flow stress $\sigma/\mu$ at strains $\epsilon=0.002$ and 0.20 vs the Burgers vector-normalized grain size $d/b$ for the FCC metals Cu, Ag and Au with grain size in the range from millimeters to nanometers.
As an example, Fig. 12 gives a plot of the modulus-normalized flow stress $\sigma/\mu$ vs. the Burgers vector-normalized grain size $d/b$ for the FCC metals Cu, Ag and Au. Three regimes are identified: (a) Regime I, $d/b \geq 10^4$ m, (b) Regime II, $d/b \approx 10^2-10^4$ m and (c) Regime III, $d/b < 10^2$. Grain size hardening occurred in Regimes I and II, while grain size softening occurred in Regime III. Dislocations were present in Regimes I and II, while they were absent in Regime III. Separation between Regimes I and II occurred when the grain size became smaller than the dislocation cell size, separation between Regimes II

<table>
<thead>
<tr>
<th>Material</th>
<th>Grain Size Regime</th>
<th>Grain Size Hardening or Softening Mechanism</th>
<th>Rate-Controlling Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu, Ag, Au (FCC)</td>
<td>I</td>
<td>Dislocation density hardening</td>
<td>Intersection of dislocations</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>Disloc. pile-up and grain boundary shear</td>
<td>Grain boundary shear</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>Grain boundary shear</td>
<td>Grain boundary shear</td>
</tr>
<tr>
<td>Zn (CPH)</td>
<td>I</td>
<td>Dislocation density hardening</td>
<td>Intersection of dislocations</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>Ditto</td>
<td>Ditto</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>Grain boundary shear</td>
<td>Grain boundary shear</td>
</tr>
<tr>
<td>Ti-15at% Mo (BCC)</td>
<td>I</td>
<td>Dislocation density hardening</td>
<td>Overcoming solutes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC (Hex)</td>
<td>I</td>
<td>Dislocation density hardening or dislocation pile-up</td>
<td>Peierls-Nabarro stress</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>Ditto</td>
<td>?</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>Grain boundary shear</td>
<td>Grain boundary shear</td>
</tr>
<tr>
<td>TiN (Cubic)</td>
<td>I</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td></td>
<td>III</td>
<td>Texture softening</td>
<td>?</td>
</tr>
<tr>
<td>TiAl, ZrTi</td>
<td>III</td>
<td>Grain boundary shear</td>
<td>Grain boundary shear</td>
</tr>
</tbody>
</table>
and III when the grain size became smaller than the elastic interaction spacing between dislocations. Similar grain size regimes were identified in the other metals and in metal compounds. A summary of the mechanisms concluded to be governing the grain size dependence of the flow in each of the three regimes and the corresponding rate-controlling plastic deformation mechanism are presented in Table 2.

2.5 Consideration of the Physical Basis for the Effect of an Electric Field on Phase Equilibria and Kinetics in Metals: As pointed out in the Statement of the Problem section,

![Graph](image)

Fig. 13. As-quenched resistivity ratio ΔR/R₀ vs the reciprocal of the annealing temperature without and with application of an external electric field of ~1 kV/cm.

normally an effect of electric field on solid state phenomena in conductors such as metals is not expected. An effect could however occur if there exist charged defects (e.g., vacancies, dislocations, grain boundaries) within the specimen. The charged crystal defects could interact directly with the applied electric field or indirectly with the charged exterior surface produced by the field. The results obtained in the present and previous ARO-sponsored research suggest that either or both mechanisms could be operative with the application of an electric field during solid-state phenomena in metals. A speculative consideration of the interaction between a charged vacancy-solute complex and an
externally applied electric field is given in Appendix III.

Preliminary studies [Fig. 13] indicated that an electric field of the order of a kV/cm had no detectable effect on the concentration of vacancies in high purity Al (99.999) at 200°-500°C. This suggests that the charge on vacancies alone, as contrasted to vacancy-solute complexes, may be insufficient to give a significant change in their concentration with a field of ~1 kV/cm. However, since an electric field produced a significant increase in the solubility of the pertinent alloying constituents in Al-Mg-Si alloys with the presence of excess Si and/or Cu addition, it appears that the charge on vacancy-solute complexes may be of sufficient magnitude for an interaction with the field. Additional work is needed to determine the effects of an electric field on the concentration and mobility of vacancies in metals and alloys, especially since only very preliminary results (Fig. 13) have been obtained to-date.

2.6 Novel Microstructures Fabricated by Pulsed Laser Vapor Deposition: Rectifying La$_{0.7}$Sr$_{0.3}$MnO$_3$/ZnO (LSMO/ZnO) heterojunctions were grown on a sapphire substrate using a pulsed excimer laser. These junctions provide an effective way to control the electrical and magnetic characteristics of giant magnetoresistive LSMO films by using the built-in electric field at the LSMO/ZnO interface. They also provide an opportunity to investigate various magnetic and magneto-resistant properties of manganites with nonlinear optical and optoelectronic applications of ZnO.

Self-assembled, nanocrystalline metal particles (nanodots) were embedded in various ceramic matrices (see for example Fig. 14) employing a novel pulsed laser vapor-deposition technique. Photoluminescence spectra of Au nanodots in ZnO matrix showed
Fig. 12. Nanodot arrays produced by the pulsed laser deposition technique. Left: cross section <110> TEM image of Ni nanodots embedded in alumina matrix on Si (100). Right: high resolution TEM image of one Ni nanodot.

a sharp excitonic peak at 3.22 ± 0.05 eV without any signature of green band emission.

Electrical resistivity measurements showed these films to be highly conducting with a room temperature resistivity of 3.4 ± 0.2 mΩ-cm.

2.7 Summary of “Firsts”: The following are some of the more significant “first time ever results” obtained on the present project.

(1) Determined that an electric field increased the solubility of pertinent alloying constituents in commercial Al-Mg-Si alloys. The increase in solubility gave an increase in tensile properties for a given solution heat treatment temperature $T_{SHT}$, or allowed for a decrease of 10°-50°C in $T_{SHT}$ and still obtain nominal tensile properties.

(2) Employing HRTEM and SAED determined for the first time the size distribution and crystal structure of the precipitates in a naturally-aged Al-Mg-Si alloy.

(3) Determined that an electric field retarded grain growth in ultrafine-grained (D=600
nm) electrodeposited Cu. Further, it was shown how the activation energy $Q$ and
time exponent $n$ in the grain growth equation were related to: (a) existing crystal
defects, (b) their annihilation with time and (c) grain boundary mobility.

(4) Determined that an electric field influenced phase equilibria and retarded phase
coarsening in 60Sn40Pb solder joints.

(5) Correlated the grain size dependence of the flow stress of a number of metals and
compounds over the entire range of the grain size from nanometers to millimeters
and proposed the governing mechanisms.

(6) Produced “artifact-free” nanocrystalline (including d<10 nm) metals and compounds
employing a unique pulsed laser deposition (PLD) technique.

(7) Fabricated novel materials including metal nanodots in ceramic matrices employing
PLD.

2.8 Bibliography

1. Ø. Gröng, Metallurgical Modeling of Welding, 2nd Ed. The Inst. Of Materials, The


8. J. C. M. Li, in Recrystallization, Grain Growth and Textures, ASM, Metals Park,
3. List of all publications and technical reports

(a) Papers published in peer-reviewed journals


(b) Papers published in non-peer reviewed journals or in conference proceedings


(c) Papers submitted at meetings, but not yet published in conference proceedings
None.

(d) Manuscripts submitted but not yet published


(e) Technical reports submitted to ARO

2. H. Conrad, J. Narayan and K. Jung, Annual report for the period 1/01/03-12/31/03 on
DAA19-02-1-0315, 41893-MS. Report Date: 12/31/03.


4. Participating Scientific Personnel

1. Prof. H. Conrad, P.I.
2. Prof. J. Narayan, Co-P.I.
3. Dr. K Jung, post-doctoral fellow
4. S. Ramachandren, graduate student, passed PhD qualifying exam
5. Wes Crill, undergraduate student, received B.S. degree; enrolled in graduate school.

5. Report of Inventions


6. Technology Transfer

(a) H. Conrad

(1) Through visits, seminar presentations and communications have maintained continued interactions with the Al industry (Dr. D. Lloyd, Alcan, Dr. R. Ramage, Alcoa, and Dr. B. Das, Secat) and the automotive industry (Drs. M. Demeri and A. Sherman, Ford Scientific Laboratory) regarding results and potential benefits of applying an electric field in the processing of Al alloys.

(2) Initiated with Dr. R. Becher, ORNL, a research project on the effect of an electric field on the plastic deformation of oxide ceramics.
Upon invitation gave a seminar on our work and spent several days with Drs. R. Armstrong, J. House and R. DeAngelis, Materials Laboratory, Eglin Air Force Base, FL. discussing mutual research activities including the effects of electric fields on metals and ceramics.

Developed interactions with Dr. H. Merchant, Gould Electronics, regarding the influence of an electric field on the properties of electrodeposited Cu used in electronic packages.
Appendix I: Calculation of the effect of electric field on the thermodynamic solubility parameters determined from resistivity $\rho$ measurements

\[ \rho_s = \rho_w - \rho_o = \alpha c^n = \alpha \exp(\Delta G_s/RT)^n \]  (I-1)

\[ = \alpha \exp(n\Delta S_s/R) \exp(-n\Delta H_s/RT) \]  (I-1a)

\[ = \beta \exp(-Q/RT) \]  (I-2)

$\rho_o$ = resistivity due to insoluble constituents; $c$ is the concentration of the soluble constituents, $\rho_s$ the resistivity due to the soluble constituents, $\rho_w$ that of the as-quenched state and $\Delta H_s$, $\Delta S_s$ and $\Delta G_s$ are the enthalpy, entropy and Gibbs free energy of solution. $\alpha$ and $n$ are constants.

- Knowing $\Delta H_s$ and $\Delta S_s$ for $E=0$ (from Gröng [1]) we can obtain the effect of $E_{SHT}$ on $c$ from a plot of $\rho_s$ vs. $1/T_{SHT}$. 
Appendix II: Analysis of natural aging kinetics of the Al-Mg-Si alloys in terms of the Johnson- Mehl, Avrami, Kolmogorov (JMAK) model

- The JMAK model gives

\[ f_r = 1 - \exp(-kt^{n_{NA}}) \]  \hspace{1cm} (II-1)

\( f_r \) = relative volume fraction of precipitate, \( t_{NA} \) = natural aging time, \( k \) and \( n \) are constants.

- \( f_r \) is given by

\[ f_r = \frac{f_c}{f_c^*} = \frac{\rho_c}{\rho_c^*} \]  \hspace{1cm} (II-2)

\( f_c \) = actual volume fraction of precipitate at \( t_{NA} \), and \( f_c^* \) that at the peak-aged state.

\( \rho_c \) = resistivity due to the precipitate at \( t_{NA} \) and \( \rho_c^* \) that at the peak-aged state.

- Assume

\[ \rho = \rho_o + \rho_c + \rho_s \]  \hspace{1cm} (II-3)

\( \rho_o \) = resistivity of Al matrix, \( \rho_c \) that due to precipitate and \( \rho_s \) that due to solutes remaining in solution.

- One then obtains \( \rho_c = (\rho - \rho_w)/(1-\alpha) \) and \( \rho_s = (\rho_w-\rho_o) - \alpha \rho_c \), so that

\[ f_r = \frac{(\rho - \rho_w)}{(1-\alpha)(\rho^* - \rho_o)} \]  \hspace{1cm} (II-4)

\( \alpha = \rho_s/\rho_c \) and \( \rho^* \) is the resistivity of the peak-aged state.

- Rearranging Eqn. 1 and taking double logarithms gives

\[ \ln \ln \left[ \frac{1}{(1-f_r)} \right] = \ln k + n \ln t_{NA} \]  \hspace{1cm} (II-5)

or

\[ \log \log \left[ \frac{1}{(1-f_r)} \right] = \log(k/2.3) + n \log t_{NA} \]  \hspace{1cm} (II-5a)

- Insert Eqn. II-4 for \( f_r \) into Eqn. II-5a and plot left hand side of Eqn. II-5a vs \( \log t_{NA} \) to obtain \( n \) from the slope and \( k \) from the intercept of the line.
Appendix III: Simplified and Speculative Model for the Effect of an Electric Field on Solubility of Si in Al

Based on: A.D. LeClaire (1978) and Shewmon (1989)

- Vacancy with electron cloud results in negative charge on the vacancy.

- Attractive force between negatively-charged vacancy and positively-charged Si ion gives binding energy $E_b$.

- Energy of vacancy thus decreases and their concentration increases.

\[ C_v = A \exp\left[-\frac{(E_v - E_b)}{kT}\right] \]  

(III-1)

- Electrostatic potential $V(r)$ around the solute ion is

\[ V(r) = \frac{Ze}{r} \exp(-q(r)) \]  

(III-2)

$Z =$ No. of excess electrons per ion  
$e =$ Charge on an electron  
$q =$ Screening parameter  
$r =$ Radial distance from ion

- Effect of electric field $E$

\[ V_E(r) = \left[\left(\frac{Ze}{r}\right)\exp(-q(r))\right] - Ex \]  

(III-3)

$x =$ distance over which the electric field acts

Refs.