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Pb-induced solid metal embrittlement of Al-Mg-Si alloys at ambient temperatures

Kim, Young-Sub, Ph.D.
Case Western Reserve University, 1990
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Pb-INDUCED SOLID METAL EMBRITTLEMENT OF Al-Mg-Si ALLOYS

AT AMBIENT TEMPERATURES

by

YOUNG-SUB KIM

Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

Thesis Advisor: Dr. John J. Lewandowski

Department of Materials Science and Engineering
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May, 1990
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Young Sub Kim
Pb-INDUCED SOLID METAL EMBRITTLEMENT OF Al-Mg-Si ALLOYS AT AMBIENT TEMPERATURES

Abstract

by

YOUNG-SUB KIM

Minute amounts of Pb (i.e. 5ppm-500ppm) are shown to induce embrittlement of Al-Mg-Si alloys at ambient temperatures. In the high Pb alloys (i.e. >100ppm), Pb was usually associated with particles containing Si, Mn and Fe although isolated Pb signals were often found on the grain boundary. In the low Pb alloys (i.e. <20ppm), Pb was only found in association with Fe-containing particles. These sites of high Pb concentration are preferential sites for crack initiation.

It was observed in the tensile tests that grain boundary accommodation of deformation was predominant in the early stage of tensile deformation in high Pb alloys tested at slow strain rate, in contrast to transgranular slip which was predominant in specimens containing low Pb (i.e. 20ppm) and/or those tested at fast strain rates. Intergranular microvoid coalescence (IGMVC) was predominant in the fracture mode of the high Pb alloys tested at fast strain rate and the low Pb alloys tested at both strain rates, while low
ductility intergranular fracture (LDIGF) was predominant in the higher Pb alloys tested at slow strain rate.

The deleterious effect of Pb was also observed in the tensile interruption tests and the external Pb experiments.

It was found that the high Pb alloys exhibited lower fatigue life at low frequency (i.e. 9x10^4 Hz), while same alloys tested at high frequency (i.e. 0.5 Hz) revealed similar fatigue life with low Pb alloys tested at either low or high frequency. LDIGF was predominant in the fracture mode for high Pb alloys tested at low frequency while IGMVC was predominant for the same alloys tested at high frequency and for low Pb alloys at both low and high frequencies. Fatigue crack growth rate was found to be higher at low frequency than that at high frequency. Fracture mode transition from LDIGF to IGMVC was also observed with increasing stress intensity factor range. The fracture mode transition could be expected from the calculation of crack tip strain rate which was consistent with the tensile strain rate revealing LDIGF or IGMVC.

TEM foils were taken from tested specimens so that the details of deformation and void initiation could be obtained, while EDS analyses were able to reveal the presence of Pb in many cases.

It is proposed that locally segregated regions of Pb are preferential sites for cracking in a LDIGF mode either by decohesion or cracking of Pb-
containing particles, with subsequent Pb-assisted crack propagation occurring along grain boundaries. Propagation of fracture in a LDIGF mode requires a continual supply of Pb to the crack tip region, as supported by the tensile interruption tests and the external Pb tests which conclusively showed the increase in the amount of LDIGF, the decrease in the non-uniform strain and the increase in crack growth rate. In-situ deformation in SEM confirmed the effects of Pb on fracture behavior. It is appeared that the triaxial stress state is important for the Pb-assisted cracking.

The possible mechanisms are discussed in the regard of the crack tip strain rate, the semicohesive zone ahead of crack and the Pb surface diffusion, in addition to the reduction of surface energy by the addition of Pb.
Acknowledgements

I would like to express my gratitude to my advisor, Prof. John J. Lewandowski, for his guidance and support throughout this research. Special gratitude is extended to Dr. Henry Holroyd for his discussion and suggestions during this research. Also I would like to thank to Mr. Dick Howe and Mr. Chris Tuna for their invaluable help in the experimental matters.

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I. Introduction

1. General Introduction

The deformation and fracture behavior of precipitation hardened Al alloys has been extensively investigated in the past[1-5]. Many of the high strength precipitation hardened Al alloys exhibit low ductility and fracture via separation at or near the grain boundaries. Efforts have focussed on determining the role of various microstructural features on fracture, including: the grain size[1]; grain boundary precipitates[2]; the precipitate free zone[3]; the local deformation near the grain boundary[4]; and also the concentration of major alloying elements near the boundary[5]. The recent review by Vasudevan and Doherty[6] presents a summary of most of the major works conducted to date. In all studies, it must be remembered that grain boundary embrittlement and grain boundary fracture is not solely determined by grain boundary weakness, but may be affected by the relative strength of the matrix and the boundaries. Moreover, embrittlement may be facilitated by the initiation and growth of cracks in certain environments such as liquid or solid metal, aqueous solutions and hydrogen environments[7-14].

It has been suggested that systems exhibiting metal-induced embrittlement(MIE) typically are those in which the metal/embrittler couple
are immiscible (i.e. very limited or no solid solubility) and do not exhibit formation of intermetallic compounds[12]. In these cases, MIE typically occurs when a low melting point metal (i.e. embrittler) is in intimate contact with a normally ductile metal under the simultaneous action of tensile stress, with cracking occurring at abnormally low stress. MIE is also more likely to occur if the base metal and the embrittler have similar electro-negativity. In cases where embrittlement occurs when the low melting point metal is in the liquid state it is referred to as liquid metal embrittlement (LME), while embrittlement occurring below the embrittler melting point (i.e. solid state) is referred to as solid metal-induced embrittlement (SMIE).

It has been reported in the literature that a typical failure by MIE usually consists of an embrittler-controlled stage and final catastrophic failure. The embrittler-controlled stage includes crack initiation and propagation. First, an incubation period characterizes crack initiation which is enhanced by the embrittler. Second, crack propagation is controlled by the transport of the embrittler to the growing crack tip. Third, catastrophic failure occurs when the crack reaches the critical length at which the stress is sufficient to produce overload failure. Therefore, the final stage is typically not dependent on the presence of embrittler since the rupture is so fast that the transport of the embrittler can not keep up with the growing crack.

MIE is reportedly less common than other fracture process such as
hydrogen embrittlement (HE) and stress corrosion cracking (SCC). However, there are phenomenological similarities between LME/SMIE and HE/SCC. Therefore, there is a possibility that common mechanism(s) may exist. Thus, studying these MIE phenomena may provide a background to understanding HE and SCC.

This thesis investigates the effects of Pb on the mechanical behavior of Al-Mg-Si alloys. The literature review provides a background information into both LME and SMIE as they exhibit some similarities, while the focus of this thesis is on Pb (i.e. internal) induced SMIE of Al-Mg-Si alloys.
2. Literature Review

2.1. Liquid Metal Embrittlement (LME)

2.1.1. Prerequisites for LME

In LME, the ductility of the stressed metal or its alloy is essentially decreased by a liquid metal. However, apart from the reduction in ductility the stress-strain curve obtained in a smooth tensile test is not largely changed[15] as illustrated in Figure I-1. Cracks in polycrystalline materials typically propagate intergranularly in the presence of the liquid embrittler and the crack growth can be stopped if the supply of liquid embrittler is limited at the propagating crack tip. Tables I-1 & 2 summarize the variety of embrittlement couples in which LME has been exhibited.

It has been generally accepted that the necessary conditions for LME are: intimate contact between the base metal and the embrittler; tensile stresses to produce plastic deformation; and a suitable temperature range to ensure mobility of the embrittler[16-18]. It has been observed that oxide films on the surface of the base metal will prevent the intimate contact of the embrittler[16]. Therefore, the embrittlement can be delayed or inhibited unless oxide films are ruptured or any other contaminants on the surface are
cleaned to promote intimate contact.

By definition, LME usually occurs just above the melting point of the embrittler, because the atomic mobility is higher in the liquid than in the solid. Therefore, embrittlement is maximized at the melting point of the embrittler and then it is reduced as temperature is further increased, giving rise to an embrittlement trough as shown in Figure 1-2. Embrittlement which occurs well below the melting point of the embrittler (i.e. SMIE) will be reviewed in a later section. Early work[19] found that the embrittlement of leaded steel began from about 93°C below the melting point of Pb (i.e. 327°C) and was continuous up to Pb melting point. Lynn et al[18] also demonstrated that the embrittlement of 4140 steels began to occur at temperatures exceeding three quarters of melting point of the embrittler : 0.75Tm for Cd, 0.85Tm for Pb and Sn, and 0.95Tm for In and Zn (Tm: melting temperature of embrittler). The temperature range for the embrittlement was also shown to depend on the strain rate during the test on a given system[21-23].

For crack initiation via LME, there should be the simultaneous presence of stress and a sufficient supply of liquid metal. The presence of tensile stresses have been generally understood to produce LME regardless of the stress state (i.e. tension, bending). Therefore, it can be concluded that tensile stresses affect both deformation and crack initiation by the liquid metal, while
compressive stresses should produce deformation only. However, it has been recently reported that liquid metal induced fracture can initiate in compression in amorphous metals[24]. In that work, it was shown that bend specimens of several amorphous metals were embrittled equally by liquid Li placed on either the tensile or compressive surfaces of a bend sample, while the resulting fracture surfaces did not appear to indicate any differences with the applied stress state (i.e. tension vs. compression).

2.1.2. Variables for LME

The degree of LME is sensitive to metallurgical variables and test conditions which will determine whether a brittle crack will nucleate and/or propagate in a liquid metal environment. These factors include grain size, microstructure, alloying, type of test, and strain rate.

Alloys which have high strength are typically more severely embrittled[25]. For example, a 2024 Al alloy revealed more severe embrittlement by Hg in the peak-aged condition while embrittlement was reduced by overaging[26]. Furthermore, a 5083 Al alloy (Al-4%Mg) which does not appreciably age harden did not exhibit any embrittlement sensitivity to aging treatments[26]. These trends suggest that embrittlement in these cases was governed by the existence of coherent precipitates. Several
characteristics of embrittlement by liquid Hg were forwarded in this work[26]:

1) Solution-treated 2024 Al alloy fractured after macroscopic yielding.

2) Aged 2024 Al alloy fractured prior to yielding and the magnitude of embrittlement was greatest in the peak-aged condition, with the peak-aged alloy failing at only 70% of the yield strength of this alloy.

3) The combination of cold work and solution-treatment did not eliminate the occurrence of measurable yielding before fracture.

4) However, the combination of strain and aging-treatment led to the detrimental effect. At 20% prestrain, fracture of the peak-aged 2024 Al alloy occurred at only 20% of the yield strength, while prestraining the 5083 Al alloy showed a similar effect. In this case, 5% prestrain produced the maximum embrittlement of 5083 Al alloy.

The effect of prestrain on the degree of embrittlement depended on the grain size[27]. The fracture stress of a Cu-30%Zn alloy in Hg increased linearly with the amount of induced prestrain at the larger grain sizes (i.e. 0.16mm, 0.275mm, 0.366mm), while at a smaller grain size (i.e. 0.08mm) the
stress increased and then decreased, and at the smallest grain size (i.e. 0.032 mm) only a decrease was noted[27]. It was also observed[27] that:

1) the fracture strain in Hg decreased at all grain sizes as the prestrain increased,

2) the fracture strain in Hg first increased and then decreased as the grain size increased at constant prestrain,

3) the rate of decrease in fracture strain was only slightly sensitive to grain size.

In other instances[18] the fracture stresses for Zn in Hg, Ca in Ga, Brass and Cu alloys in Hg, and mild steel in Li varied linearly with the grain size. These grain size dependences followed the Cottrell-Petch relationship (i.e. the fracture stress varies linearly with the reciprocal of the square root of the grain size).

In addition to general microstructure, the structure and composition along grain boundaries may play an important role in LME. It has been known that the segregation of the impurities enhances the severity of hydrogen induced embrittlement and temper embrittlement[28,29]. However, the effect on LME is more variable. Dinda and Warke[30] reported that segregation of Sn or Sb caused an increase in susceptibility for the embrittlement of an AISI 4340 steel in liquid Pb and Sn while segregation of P or As caused a modest decrease in susceptibility. The beneficial effect of P in reducing embrittlement
of Cu-Ni alloys and Monel 400 in Hg has also been reported[31,32].

In addition to the effects of segregation, the nature of the grain boundary also has significant effects on LME[31-33]. It was reported that the fracture stress and strain associated with the embrittlement of Zn bicrystals by liquid Ga[33] depends strongly on the grain boundary misorientation angle, with a peak embrittlement at around 55° in <1010> tilt and twist boundary. Deformation ledges produced by the intersection of basal slip with the grain boundary played important roles for the intergranular fracture, and were proposed as capillary tube-notches. In a study[34] of Al bicrystals in liquid Ga it was shown that some specific grain boundaries (e.g. low angle boundary and coincidence boundary) had high resistance to the intergranular fracture, while acoustic emission events during the fracture test also depended on the type and misorientation of the grain boundary. In brass-Ga couples[35], cracks nucleated and propagated at random boundaries. The fracture mode transition from intergranular to transgranular or vice versa occurred under the type of the coincidence boundaries or low angle boundaries, which are resistant to the intergranular fracture. The frequency of occurrence of random high angle boundary and coincidence boundary(Σ3 - Σ25) was around 70% and 20%, respectively, and that of low angle boundary was about 10%, determined by electron channelling pattern.

Changes in composition of the solid can similarly alter the properties and
then affect the embrittlement of the solid. Alloying additions usually increase the strength and hence increase the yield and fracture stress of the solid[18]. Therefore, the usual effect of alloying is to make the solid stronger and consequently more readily embrittled[16]. Stacking fault energy can also be changed by alloying and then the slip mode altered from wavy or planar slip[36]. Stoloff et al[36] had shown that the susceptibility of solids to LME increased as their propensity for cross slip decreased. For example, additions of Al, Zn, Si or Ge to Cu increased the susceptibility of LME in Hg as the stacking fault energy was decreased, while additions of Co, Si and Al to Fe also increased susceptibility to LME. Other work[18] has documented that dilute additions of Cu or Au(0.1%) to Zn, as well as additions of 1 to 8% Ni to Fe, and additions of Be and others to Cu increased the susceptibility to LME by Hg.

Changes in the liquid composition can also affect the severity of embrittlement. Additions of up to 10% In to Hg increased the embrittlement of Cd but had the opposite effect on Ag[37]. Warke and Breyer[38] similarly demonstrated that Pb embrittlement in steels appeared to be more a function of the chemical composition of the Pb inclusions than that of the base composition of the steel or the prior austenitic grain size. A wide variety of leaded steels suffered a severe loss in ductility at elevated temperature tensile tests. The embrittlement trough did not vary in any systematic manner with
steel grade and the brittle-ductile transition temperature was not related to the Pb content of the steel. However, the steel containing less pure Pb inclusions, particularly those containing Sb and As, revealed a 66°C shift in the brittle-ductile transition temperature. In the later work[39], it was shown that in the Pb embrittlement of 4140 steel in tension that additions of 0.004 to 2.0% Sb to Pb produced a significant effect on the embrittlement, while the brittle-ductile transition temperature shifted 149°C at the maximum Sb content. However, such a linear correlation was not exhibited when Sn was added to Sb inclusions.

Most of LME have been reported to occur under the monotonic tensile stresses, while Stoloff[40] has summarized the limited number of investigations of LME in cyclic loading. From his summary it is demonstrated that Cu and Cu alloys in Hg, 7075 Al alloy in Hg and Ga, and steel in Na, Sn are embrittled under fatigue conditions, although notched bend tests of steel in liquid Sn and liquid Pb-Sn exhibited 65% and 90% increase in endurance limit, respectively. These increases were attributed to the formation of the intermetallic compound FeSn₂ during cycling. Recently several investigators[41-43] have reported LME in cyclic loading. Regan and Stoloff[41] reported the fatigue behavior of Cu-Al alloys in Hg where the fatigue lives of Cu-5.5% Al and 7.3% Al alloys exhibited a marked reduction in Hg, and fatigue strength in Hg varied inversely with grain size. The fatigue
crack growth rate for 6061-T651 Al alloy in Hg was higher than in air, and crack growth rate (m/cycle) at low frequency was greater than that at high frequency[42]. However, there was no Hg effect on fatigue crack growth below the critical value of ΔK. The fatigue crack propagation in Hg was studied from the superposition model:

\[
da/dN = (da/dN)_{\text{insert}} + (da/dN)_{\text{Hg}}
\]

This work also demonstrated the effects of R ratio (=K_{\text{min}}/K_{\text{max}}) on the fatigue crack propagation of a Ni-Cr-Mo high strength steel in Hg. Regardless of ΔK (i.e., different R from -0.6 to 0.6), the full effect of the environment could never be attained. Kamdar[43] studied the fatigue behavior of single-edge notched specimens of 4340 steel in Pb and Pb-Sb at temperatures from 357°C to 732°C. The brittle-ductile transition temperature of steel in fatigue was 260°C higher (i.e., 649°C) than that for smooth specimens in tension. The embrittlement by Pb was predominant at low temperatures (i.e., 316 to 371°C) and low concentrations of Sb (i.e., up to Pb-28% Sb), while the embrittlement of steel was primarily caused by Sb at high temperatures (i.e., 538 to 649°C) and high concentrations of Sb (i.e., Pb-35 to 75% Sb) in Pb-Sb solutions.
2.1.3. Proposed Mechanisms for LME

Although several mechanisms have been proposed up to this point, there is no unified mechanism that is generally accepted for LME. The most frequently suggested mechanisms are:

1) stress-aided dissolution[44]
2) adsorption-induced decohesion[45,46]
3) adsorption-enhanced shear[48]

Robertson[44] calculated the crack velocities in the presence of liquid metal. His calculations assumed that the crack propagated by solution of the solid in the liquid at the crack tip under the influence of the applied stress and diffusion of the dissolved solute away from the crack tip. This was reported as "dissolution-diffusion mechanism". His calculation considered:

1) the stress distribution around the crack tip establishes a gradient in the chemical potential at the tip, which causes a diffusion flux through the liquid away from the tip.
2) the solid-liquid interfacial tension against crack propagation since propagation requires creation of interfacial area.

This mechanism predicts high velocities, indicating that diffusion can contribute appreciably to crack propagation. However, this mechanism
predicts that the higher the solubility of the solid in the liquid, the more severe embrittlement. In nearly all cases, however, embrittlement is usually most severe when the solubility is very limited. In particular, it was found that this mechanism did not agree with experiments of the liquid Cd embrittlement of Ti[22].

The second suggested mechanism involves the particular interaction between the solid and liquid metals whereby the adsorption of the liquid reduces the binding energy of atomic bonds[45,46]. It was proposed that decreases in fracture stress and plastic deformation accompany the presence of liquid metals thereby promoting crack propagation. The crack grows by the successive rupture of atomic bonds. Figure I-3(a) illustrates the potential energies to break atomic bonds in the presence and absence of liquid metal, and stresses to separate atomic planes in the presence and absence of the liquid metal(Figure I-3(b)). The applied stress, \( \sigma_0 \), to extend the elastic crack tip was obtained in terms of the surface energy, \( \gamma \), from the Griffith theory:

\[
\sigma_t = \left( \frac{E\gamma}{2c} \right)^{1/2}
\]

where \( E \) is Young's modulus and \( c \) is the half-crack length. If the crack growth concerned with plastic deformation, then crack tip radius, \( r \), altered and the stress \( \sigma_t \) is given by
\[ \sigma_i = (E\gamma r/c\alpha)^n \]

where \( a_\alpha \) is the lattice parameter of the solid. The effective surface energy, \( w \), is then proportional to the elastic surface energy and the crack tip radius:

\[ w = \gamma r/a_\alpha \]

Westwood and Kamdar[46] suggested to define a coefficient of embrittlement, \( \rho \), since the embrittlement action should be independent of the radius of the crack tip. \( \rho \) is related to the energy adsorbed in breaking atomic bonds at the crack tip. The experimental observations on Zn-Hg embrittlement couple supported that the total energy involved in a propagating crack represented by:

\[ \Phi = \rho \gamma r \]

The crack propagating mechanism in the presence of the liquid was suggested from such energy considerations. The fracture energy in the basal plane of Zn was 90±10 ergs/cm², and this energy was 57 ergs/cm² in Hg and 42±13 ergs/cm² in Ga[46]. The reductions in the fracture surface energies of Zn indicate reductions in the strength of the atomic bonds in the basal plane by
these environments[18]. Their derivations[45,46] showed that cracking through lowering of elastic surface energy must inevitably lead to a lowering of plastic work.

Several workers have proposed that liquid metals reduce the surface free energy of the solid by adsorption of the liquid metal, in addition to reducing the cohesive force. Roth et al[47] calculated the reductions in fracture surface energy for three systems: Al-Bi, Al-Pb and Al-Cd. The reductions in fracture surface energy for these systems were 82, 80 and 67%, respectively. They[47] applied thermodynamic surface energy measurements to the grain boundary fracture of Al induced by liquid inclusions: the dihedral angle, $2\theta$, is related to the grain boundary energy, $\gamma_{gb}$, and the solid-liquid interfacial energy, $\gamma_{sl}$, by the equation

$$\gamma_{gb} = 2\gamma_{sl}\cos\theta$$

The severity of intergranular embrittlement was expressed in terms of the fractional reduction in the work of fracture, $\Delta W/W$, due to the presence of liquid:

$$\Delta W/W = 1 - 0.2(sec\theta - 1)(\gamma_{gb}/\gamma^*_{gb})$$
The relatively large dihedral angles observed in these systems indicated that the composition of the grain boundary and the liquid are very different, in other words, Bi, Cd or Pb do not adsorb at grain boundaries. Consequently, $\gamma_{gb}/\gamma_{gb}^*$ is approximately 1, resulting in $\Delta W/W = 0.88$ for Al-Bi, 0.86 for Al-Cd and 0.81 for Al-Pb. These values closely parallel the severity of embrittlement in these systems as measured by the impact energy obtained at the melting point of the inclusions, i.e. 1.5J for Al-Bi, 1.8J for Al-Cd and 5.4J for Al-Pb. Roth et al[47] concluded that the reduction of fracture surface energy when the inclusions are liquid facilitates both crack initiation and propagation. The major shortcoming of such a thermodynamic approach is that it is not particularly informative because it does not predict the embrittlement on an atomic or electronic scale.

Recently, Lynch[48] has proposed a mechanism where embrittlement is considered to occur by the reduction in the shear strength of interatomic bonds at the crack tip and thereby facilitate nucleation of dislocations at crack tip. Once a crack has nucleated, the dislocations move away from the crack tip. If more dislocations were emitted on one side of the crack than the other, a layer back stress would counteract further dislocation nucleation on the more active side. Therefore, roughly equal amounts of slip on planes on either side of the crack should generally occur(Figure 1-4(a)). Now if some general matrix slip also occurs and produces voids ahead of a crack, the crack
will grow with linkage of voids (Figure I-4(b)). The void is nucleated ahead of
the crack tip at perhaps a precipitate, inclusion or a subboundary in a single
crystal. The fracture occurs by ductile rupture mode with the appearance of
dimples on the fracture surfaces (Figure I-4(c)), and dimples on fracture
surface are generally quite shallow because strain and plastic zone around
the crack for LME are small and hence void does not grow extensively. Lower
strains at failure or subcritical crack propagation by the growth and linkage
of voids is then the measure of LME. From the experimental observations [48-
51], fracture surfaces of Al-6%Zn-3%Mg single crystal, bicrystal and alloys in
liquid metal environments were approximately parallel to \{100\} planes, crack
growth occurred in \(<110>\) directions, and extensive slip occurred on \{111\}
planes intersecting the cracks. Microscopic studies revealed shallow dimples
on cleavage fracture planes and the size of dimples depended on the
distribution of precipitates in a manner consistent with the nucleation of
voids by precipitates ahead of cracks. Observations consistent with the
enhanced shear model were also observed for LME of Ni single crystals, Fe-
2.6%Si single crystals, high strength steel, pure Mg and \(\alpha\)-Ti alloys. Those
metallographic and fractographic observations of environmentally assisted
cracking indicate that an adsorption-induced localized slip process is
responsible for cracking for the test conditions used. This proposed model
was also applied to HE and SCC, and remarkable similarities between HE,
SCC, and remarkable similarities between HE, SCC, and LME were observed[49].
2.2. Solid Metal-Induced Embrittlement (SMIE)

2.2.1. Characteristics of SMIE

Many ductile metals in intimate contact with low melting point metals which exhibit LME also manifest severe embrittlement at temperatures below the melting point of the embrittler. Therefore, prerequisites for SMIE are the same as those mentioned for LME in the previous section. Those for SMIE are:

1) the intimate contact between the base metal and the embrittler.

2) presence of tensile stress.

3) crack nucleates at the solid-embrittler interface from a barrier such as a grain boundary.

4) the presence of embrittling species at a propagating crack tip.

It has been observed that crack propagation rates for SMIE are much slower than that for LME, consistent with the significantly different magnitude of transport properties of the solid and liquid embrittler. Nucleation and propagation of cracks appear to be two separate processes in SMIE[52], while SMIE also occurs by the presence of internal embrittling elements in the base
metal. Fracture typically occurs by brittle intergranular or transgranular
mode, while Tables 1-3 & 4 show the documented occurrence of SMIE in steels
and non-ferrous alloys.

2.2.2. Occurrence of SMIE

The earliest work related to SMIE was the embrittlement of β-brass and
Sn-bronze by Pb[53]. The reduction of area in impact tensile tests was
decreased at 200°C, which is well below the melting point of Pb, 327°C.
Tiner[54] investigated SMIE of Zn by solid Hg. A decrease in the fracture
stress was obtained at -51°C, again below the melting point of Hg (i.e. -
39°C). Later work has similarly shown SMIE by Cd in steels[55-57], Ti
alloys[58,59] and Zr alloys[60] at temperatures below the melting point of
Cd (i.e. 321°C).

Iwata et al[55] observed the brittle failure of Cd plated steel nuts in the
temperature range of 200°C to 300°C. They also observed the delayed failure
of Cd, Zn and In plated 4340, 4140 and 18Ni Maraging steel. Delayed failure
in these cases was prevented by plating of Ni or Cu onto the steel specimens
to act as a diffusion barrier.

Hildebrand[55] investigated cracking due to solid Cd for high strength
low alloy steels. He used notched tensile specimens of Cd plated D6ac, 4340
and Maraging steels. The specimens were baked after plating to remove hydrogen which was introduced during Cd-plating. The Cd embrittlement occurred down to 121°C for D6ac steels, and he suggested the possibility of hydrogen embrittlement besides Cd embrittlement for 4340 and Maraging steels.

Cd embrittlement of steels was also reported by Fager and Spurr[57]. Crack propagation rates were increased with increasing temperature, while the activation energy for Cd diffusion on steels (i.e. 13.5 kcal/mole) was similar to the activation energy calculated from delayed failure tests, and is also the same as that for Cd diffusion on Ti from the earlier work[58]. In the work of SMIE of Ti alloys by Cd[58], transport of embrittler to the crack tip by vapor flow was not consistent with the experimental data and the concentration of Cd on SMIE fracture surface was found to decrease with increasing distance from the specimen surface. These observations suggested that surface diffusion of Cd over Ti was the embrittler transport mechanism. The recent work[59] of SMIE of Ti alloys by Cd illustrated the effect of cyclic loading as well as static loading. Cracks were initiated and grown by Cd under static stress at 149°C but there was no effect of Cd under cyclic loading at 2.5 and 30Hz. The author concluded that the cracks were self-limiting in depth, probably because of oxidation at the crack tip outfacing the arrival of Cd by surface diffusion when cracks exceeded 1 or 2mm depth.
Gangloff[60] reported Cd embrittlement of a Zr alloy. Textured, low strength Zircaloy-2 was severely embrittled by solid Cd during constant extension rate, plane strain tensile deformation at 300°C. Cracking occurred at or below the yield strength of the alloy, and propagated by near basal cleavage, in contrast to the equiaxed dimpled rupture obtained in an inert environment. Solid Cd embrittlement was strongly time dependent, and was suppressed at fast loading rates due to the kinetic limitations of Cd surface diffusion to the propagating crack tip. Increases in elongation at fracture with increasing loading rate were described by the surface diffusion coefficient and crack length according to:

\[
\varepsilon_n = \frac{2D_{\text{Cd}}}{x^2} \left( \frac{\delta_p}{b^o} \right)
\]

where \(\delta_p/b^o\) is the permanent gauge elongation i.e. cross head displacement/gauge length. The time dependence of embrittlement was inconsistent with Cd evaporation and vapor transport because of the impeding influence of atom-crack wall interactions. Cu additions to Cd reduced the susceptibility of Zr-2 to SMIE due to either reduction in the surface diffusivity of Cd or codiffusion and preferential adsorption of Cu. The author concluded that the inhibition of Cu on Cd induced SMIE was not
related to decreases in the rates of Cd evaporation or vapor transport since the equilibrium activity and vapor pressure of Cd associated with Cu/Cd alloys was high.

Premature fracture of internally or externally leaded steels[19,61-63,65] and Al alloys[66,67] was similarly observed at temperatures below the melting point of Pb. The influence of 0.3%Pb on the room and elevated temperature mechanical properties of a 4145 steel has been investigated by Mostovoy and Ereyer[19]. In that work[19], the reduction of area decreased rapidly between 204°C and the melting point of Pb, 327°C(621°F) as shown in Figure I-5 and fracture was found to follow intergranular paths initiated at the Pb inclusions. It was also found that increasing the strain rate of the tensile test shifted the onset of embrittlement to higher temperature; impact tests showed a loss in toughness above 316°C, just below the melting point of Pb. A subsequent extensive fractographic study[61] was performed by using specimens from the previous work[19]. This study[61] revealed that the intergranular regions were associated with Pb inclusions at the onset of embrittlement (i.e. 204°C to 316°C). These intergranular regions were also extended as the severity of the embrittlement increased (i.e. up to 482°C). This study indicated that the intergranular regions were restricted to within a grain diameter or two of an inclusion since the influence of the embrittler was more widespread as the temperature increased to the melting point of
was more widespread as the temperature increased to the melting point of Pb.

Later, the embrittlement of steel by Pb was reviewed by Warke et al[60]. They pointed out the four major features of embrittlement:

1) Severity of embrittlement increased with increasing strength.

2) Stress/Strain curves were not changed by the embrittlement except for stress and strain at fracture.

3) Some plastic deformation always occurred before fracture.

4) A recovery of ductility at a high temperature was observed.

In that review, fracture was propagation controlled for SMIE since multiple crack origins and secondary cracks had been observed, and fracture had been shown to be nucleation controlled for LME since only one crack had been observed.

Later, Warke and Breyer[38] investigated the embrittlement of different compositions of steels by either internal Pb or externally applied Pb. The onset of embrittlement was 261°C for externally wetted Pb while embrittlement was observed at 204°C for internal Pb in tests conducted on smooth tensile specimens. Embrittlement was found to be more severe for base metals with lower carbon or alloy content at an equivalent strength level. Additions of Sb, Sn, Zn or As to Pb also increased the severity of
embrittlement. However, refining the grain size or increasing the strain rate was found to decrease embrittlement.

Breyer and Gordon[63] described the service failure by Pb-induced cracking such as radial cracking of gear teeth, fracturing of shafts and die blocks of forging hammers, and failure of jet engine compressor disks. The temperature range for the failure was 204°C to 482°C which was same as the temperature range of the previously reported Pb-induced embrittlement. Trace amounts of impurities were able to cause the large increases in embrittlement. It was noted that cold work reduced the susceptibility to embrittlement, and additions of rare earth metals were also able to eliminate embrittlement. The fracture was described as two processes: formation and growth of intergranular microcracks at inclusions under load, followed by the linkage of these cracks by microvoid coalescence.

As described in LME, grain boundary segregation had some effects on SMIE by Pb[30]. They described the effect of trace amounts of Sb, Sn, P or As in 4340 steel in contact with Pb or Sn. Grain boundary segregation produced lower a reduction of area obtained under standard load tensile tests conducted with notched tensile specimens. It was observed that the embrittlement in sheet steel coated with a 55%Al-Zn alloy was inhibited by P segregating to the ferrite grain boundaries where it blocks intergranular diffusion of Zn[64]. The room-temperature ductility of sheet steel coated with
an Al-Zn alloy and containing less than 0.04%P was decreased by heating in the range 316 to 510°C. This reduction in ductility resulted from diffusion of Zn from coating along the grain boundaries. At temperatures outside the critical range, the rate of the intergranular Zn diffusion was low below 316°C and the rate of Zn volume diffusion exceeds the intergranular diffusion above 510°C, and thus the embrittlement did not occur.

Although changes in composition of the embrittler can affect the severity of LME, it was found to be unimportant for SMIE[39]. Other work for the alloying effect of the embrittler was demonstrated by Landow et al[65]. They described the embrittlement of 4140 steel in contact with 1)pure Pb, 2)Pb-Bi, 3)Pb-Zn or 4)Pb-Sn-Bi by tensile tests. The onset temperatures for SMIE were below the solidus temperatures for each alloy embrittler: 41°C for Pb-Bi, 117°C for Pb-Zn and 13°C for Pb-Sn-Bi. It was suggested that Zn pick-up from the flux residue trapped under the solder bead was affecting the embrittlement behavior at the onset temperature since the flux was known to contain ZnCl and that trace amounts of Zn can produce large changes in embrittlement behavior.

Later, Lynn et al[20] described SMIE of 4140 steel in contact with Zn, Pb, Cd, Sn or In. The onset temperature of the embrittlement was at about 3/4 Tm of the embrittler during the tensile tests as shown in Figure I-6. Crack propagation was also found to be influenced by the presence of the solid
embrittlers. Their observations suggested that the severity of embrittlement was limited by the supply of embrittler atoms to the crack tips. They concluded that multilayer surface self-diffusion of the embrittler over the crack surfaces is the most likely mechanism, such as a kind of "waterfall" effect, as illustrated in Figure I-7. It was also pointed out that both Zn and Sn make intermetallic compounds with Fe and severe embrittlement still occurred in contrast to the prerequisites for MIE. All embrittlement couples which exhibit LME were proposed to exhibit at least some SMIE under appropriate conditions.

Guttmann et al[66] indicated that small amounts of Pb induced embrittlement of Al-Mg-Si alloys in creep conditions at elevated temperatures. Severely reduced creep rupture lives of Al-Mg-Si alloys tested at 100°C were obtained by increasing the Pb content in the range of 10 - 165ppm. However, there was little observable effect of Pb content on either the room temperature Charpy impact toughness or smooth tensile behavior.

Recent work[67] on 6xxx series Al alloys has demonstrated the deleterious effects of Pb at ambient temperatures in sustained load cracking tests and slow strain rate tensile tests. Crack growth rates exceeding 100mm/yr were obtained for alloys containing 100ppm Pb in room temperature sustained load tests using bolt-loaded double cantilever beam(DCB) specimens. The threshold values of stress intensity factor, K,
additionally shown that the fracture morphology was affected by the Pb level and applied K. Fracture occurred in a low ductility intergranular mode (LDIGF) for high Pb alloys, while intergranular microvoid coalescence (IGMVC) was predominant in low Pb alloys. LDIGF was also observed in smooth tensile specimens of high Pb alloys tested at slow strain rate (i.e. <10⁻⁶/sec). It appeared that the rate of crack growth and the type of fracture mode was controlled by the availability of Pb.

SMIE during sustained-load conditions has been observed for Ti alloys by Au and Ag[68]. In that work, Cd embrittlement of Ti alloys was also investigated. The onset temperature of embrittlement by Au and Ag was 204°C to 232°C, which is about 0.38T/Tm in Kelvins, while Cd embrittlement is only about 0.59T/Tm. From the Auger analysis, surface diffusion of Cd or Ag was noted to be over the Ti oxide. It was pointed out that the rate of oxygen delivering to the crack tip was not virtually affected by crack length because of the vapor transport of oxygen. However, if the crack surfaces oxidize before sufficient amount of embrittler are supplied to the crack tip, embrittlement may be inhibited. It was also suggested that the prerequisites for LME may not hold for SMIE since Cd, Au and Ag make intermetallic compounds with Ti.

SMIE by In as well as Pb, Cd for steels[20,69,70] and Al alloys[72] has been studied in detail. Gordon and An[69] discussed MIE of 4140 steel by In
using delayed failure tensile tests. They concluded that crack initiation and
crack propagation were separate stages which were thermally activated with
quite different activation energies. For SMIE, crack propagation was much
slower than that for LME. The experimental results indicated that the
embrittler for LME supplied to the crack tip by the bulk liquid flow and for
SMIE the embrittler transport took place by surface self-diffusion of In
explained by waterfall effect. It was also concluded that crack initiation in the
embrittlement of 4140 steel by In can be explained by a mechanism involving
stress-aided embrittler diffusion penetration of base-metal grain boundaries.
Similar work[71] has been done for SMIE for In and In-Sn eutectic alloy in
vacuum($10^{-5}$ Torr). It was suggested that crack initiation was controlled by
the grain boundary diffusion of In into steel. The activation energy for crack
initiation was 34Kcal/mole for both solid and liquid state of both
embrittlers (i.e. In and In-Sn). They[71] determined the diffusion rate of In of
about $1x10^{-5}$cm$^2$/sec which was higher than that obtained by previous
work[69] by an order of magnitude, probably due to the vacuum
environment.

Lynch[72] has demonstrated SMIE by In for 7075 Al alloys using bolted
DCB specimens from -20°C to 150°C. Crack growth rate during SMIE
increased with increasing temperature, decreased with increasing crack
length (i.e. increasing distance from the source of In). It was proposed that
the rates of crack growth for long cracks (i.e. >1.5mm) were higher in the absence of air because surface diffusion over the oxidized crack surface was slower than over clean surfaces and the preferential adsorption of oxygen at the crack tip inhibited adsorption of In. Above the threshold stress intensity factor (i.e. \( K_{th} = 8 \text{MPa}\sqrt{m} \)) the crack growth rate was independent of \( K \).

Fractographic observations suggested that crack growth, which involves nucleation and growth of voids around grain boundary precipitates in the precipitate free zone, occurred by an adsorption-induced localized-slip process. He also mentioned that values of the surface diffusion coefficient calculated from SMIE data were underestimated since the diffusion distances were taken as the projected crack lengths. The actual diffusion distance was argued to depend on the roughness of the fracture surfaces and could be up to three to four times the projected crack lengths when crack growth is intergranular and when intergranular facets are not smooth.

### 2.2.3. Proposed Mechanisms for SMIE

The proposed mechanisms for SMIE are similar to those forwarded for LME because of the similarities exhibited between the phenomena as well as the observation that the metal/embrittler couples for LME also exhibit SMIE. Based on such factors, others [17-21, 25] have suggested that SMIE occurs via
a reduction in cohesion at atoms in the grain boundaries and thus is similar to the "adsorption-induced decohesion" mechanism discussed in the previous section of LME. A similar mechanism is described in the work of Gordon and An[69] which elaborated on the experimental data on Krishtal's idea[70], in which the embrittler diffuses into the grain boundary in the base metal and creates a high dislocation density along the diffusion path. The activation energy of crack initiation is considered to represent the energy for stress-aided diffusion of embrittler into the base metal grain boundaries. Crack initiation thus occurs by the diffusion penetration of the embrittler followed by the lowering the crack resistance of the boundaries. In such a mechanism, crack nucleation occurs at grain boundary dislocation pile-ups when sufficient penetration of embrittler (i.e. about tens of atoms diameters) has taken place. They[69] proposed that the rate-controlling process is the diffusion penetration (i.e. stress-aided diffusion) of embrittler atoms. Once the crack initiates, crack propagation is controlled by embrittler transport which takes place by embrittler surface self-diffusion via the so-called waterfall effect[20]. The activation energy for crack propagation should thus represent the energy for surface self-diffusion of the embrittler.

Recently Lynch[72] proposed that the adsorption-enhanced localized-slip mechanism which was also proposed for LME[48-51] is also applicable in the case of SMIE. In such a model, the interatomic bond strength at the interface
between the base metal and the embrittler is reduced by adsorption, not by diffusion of embrittler, and thereby facilitates the nucleation of dislocations from the crack tips. These dislocations are injected from crack tips and hence produce crack growth. Therefore, smaller strains are required for crack growth by the coalescence of voids. Figure 1-8 illustrates this mechanism schematically. Lynch has also shown much experimental evidence of plastic deformation on cleavage-like fracture surfaces in single crystals[48-51].

2.3. Al-Mg-Si Alloys

2.3.1. Characteristics of Al-Mg-Si Alloys

Commercial Al alloys in the 6xxx series contain Mg and Si as the main alloying elements. Mg and Si are required to form an intermetallic compound, Mg$_2$Si (Magnesium Silicide), with the Mg:Si ratio of 1.73. The alloys are sometimes referred to as quasi-binary systems since it can be treated as consisting of Al and Mg$_2$Si as shown in Figure 1-9, which shows the quasi-binary section of this alloy. The solid solubilities of Mg and Si in Al decrease with decreasing temperature as shown in Figure 1-10. This reduction in solubilities is associated with the age-hardening ability of this system[73]. The terms "excess Mg" and "excess Si" are used to describe alloys which
depart from balanced alloys. Excess Si over that necessary to form Mg$_2$Si can be introduced without reducing the maximum amount of Mg$_2$Si that will go into solution[73]. However, excess Mg causes a decrease in the solubility of Mg$_2$Si[73]. Therefore, excess Si produces higher strength without loss of formability and weldability, but some tendency to intergranular corrosion while excess Mg leads to better corrosion resistance but lower strength and formability [74].

2.3.2. Effect of Aging

Since it is clear that microstructural effects may be important in the embrittlement of metals via SMIE, a review of the microstructural development in Al-Mg-Si alloys is provided. In Al-Mg-Si alloys the maximum strength can be attained by precipitating in the matrix. It has been well known[75-77] that the precipitation reactions (i.e. aging process) include:

1) solid solution

2) rod shaped Mg$_2$Si along $<100>$ matrix($\beta''$)

3) plate-shaped equilibrium Mg$_2$Si($\beta$)

Aging starts with the formation of G.P. zones. The zones are needle-shaped aligned along $<100>$ matrix. The needles have a monoclinic unit cell
of with the lattice parameters \(a=b=6.16\text{Å}, c=7.1\text{Å}, \alpha=\beta=90^\circ, \gamma=82^\circ\), with orientation relationships:

\[
(111)_{\text{needle}} \parallel (110)_{\text{matrix}}
\]
\[
[110]_{\text{needle}} \parallel [001]_{\text{matrix}}
\]

The needles give rise to very faint streaks parallel to \([100]\) and \([010]\) matrix directions on electron diffraction pattern. These precipitates are exactly coherent with the matrix, with only small elastic coherency strain involved[75].

The needles change into rods by further reaction. The rods are semi-coherent with matrix. The rods are consistent with a fcc lattice with \(a=6.42\text{Å}[75]\), or hexagonal unit cell with \(a=7.05\text{Å}, c=4.05\text{Å}[77]\), with orientation relationship:

\[
(001)_{\text{rod}} \parallel (100)_{\text{matrix}}
\]
\[
[100]_{\text{rod}} \parallel [011]_{\text{matrix}} \text{ or } [011]_{\text{matrix}}
\]

The final equilibrium phases are plates. The plates are fcc lattice(CaF₂ structure) with \(a=6.39\text{Å}\), with orientation relationship:

\[
(100)_{\text{plate}} \parallel (100)_{\text{matrix}}
\]
\[
[110]_{\text{plate}} \parallel [001]_{\text{matrix}}
\]
The solid solution begins to decompose at room temperature if aging treatment is delayed after solution treatment, and clustering occurs. The zones are distinguished by temperature range: those formed below 70°C and above 70°C[78]. The zones formed above 70°C are not considered as a distinct precipitate[79]. They are divided into the initial disordered stage and the ordered stage. Recently, it has been shown[80] that the precipitation formed above 100°C before the intermediate phase is not considered as zone precipitation. It was sometimes observed that two different forms of intermediate phase, \( \beta'' \) and \( \beta' \), were present after the G.P. zone formation and before the formation of equilibrium Mg_2Si. Therefore, the aging sequence can be rearranged as follows[76]:

1) Solid solution

2) G.P. zone (at room temperature and above 70°C)

3) needle-shape (100-200°C)

4) rod-shape (160-250°C)

5) plate-shape (250-350°C)

The peak-aged structure in fact consists of a dense distribution of needles[73]. It has been shown that the density of needles markedly increases with increasing Si content, whereas their size decreases[81].

It has been well documented that heat treatment variables in addition to the final aging time and temperature can have a marked effect on the
hardening of Al alloys. These are (1) natural aging and (2) preaging. The time interval between quenching and the start of artificial aging can have a significant effect on final aged properties. It is believed to be associated with the growth of very fine precipitate during the delay period [73]. Some alloys (i.e. balanced high Mg$_2$Si alloys and excess Si high Mg$_2$Si alloys) have a drop in aged properties with increasing delay time (i.e. natural aging) but the reverse effect is observed for the others (i.e. balanced low Mg$_2$Si alloys) [73, 76]. The Al-Mg-Si alloys develop only medium hardness on natural aging, with some loss of ductility. Hardening is fairly rapid in the first few hours unless refrigeration or reversion treatments are used [73]. For high Mg$_2$Si alloys a delay of 1 day or more will result in a permanent loss of about 10% of the mechanical properties while in low Mg$_2$Si alloys a drop in properties occurs between 1 and 10 hours of delay. Usually preaging immediately after quenching prevents much of the loss in properties. For low Mg$_2$Si alloys (i.e. 0.6% Mg$_2$Si) the hardness of the final aged alloys is increased by a 2 hours preaging at 150°C while 0.9% Mg$_2$Si alloys do not appear to be significantly affected by this preaging [82]. For high Mg$_2$Si alloys (i.e. 1.2% Mg$_2$Si) preaging leads to either hardening or softening of the final aged alloys [76, 83]. The above results have been explained using the concept of a critical temperature, above which homogeneous nucleation does not take place. This temperature depends on Mg$_2$Si concentration as shown in Figure I-
11. Cold work accelerates aging and reduces the hardening but the decrease in age hardening is more than compensated by the work hardening if the amount of deformation is sufficient[74].

2.3.3. Effect of Alloying Element

An excess of Si accelerates precipitation and increases the hardening, but it makes the depleted matrix negative to the saturated part and therefore some susceptibility to intergranular stress corrosion cracking may occur. An excess of Mg, on the other hand, does not affect appreciably the corrosion resistance[74].

Fe combines with some of the Si to form an Al-Fe-Si complex, thus reducing the amount available to form Mg$_2$Si:  Si available for Mg$_2$Si = %Si - 1/4(%Fe + %Mn)[82].

Cu up to 0.3% improves the strength without impairing the other properties[73,84], and reduces the effect of the delay in aging[76]. Alloys containing Cu in the absence of Mn and Cr appear to be more susceptible to preferential grain boundary precipitation as a result of the increased rate of precipitation. Therefore, alloys containing Cu alone are more susceptible to intergranular corrosion[84].

Mn and Cr reduce grain boundary precipitation, thus reducing
embrittlement and susceptibility to intergranular corrosion [74,84]. The behavior of Cr is similar in every respect to that of Mn, with the exception that on a weight percentage basis it appears to be twice as effective and the maximum addition is about 0.25%[84]. Mn additions improve the mechanical behavior of Al-Mg-Si alloys by reducing the tendency of intergranular fracture[85-87]. Fine Mn dispersoids promote transgranular fracture, thus leading to increased toughness[85]. Dowling and Martin[86] additionally investigated the deformation behavior in peak aged Mn-bearing alloys. The Mn dispersoids caused lateral spreading of the slip bands, giving rise to significantly smaller stress concentrations at the head of slip bands. However, the Mn-free alloys deformed to form narrow slip bands, giving rise to high stress concentrations at the head of the slip bands and leading to the intergranular failure. Figure 1.12 illustrates the change in slip band spacing for the Mn additions (i.e. 0.21% Mn and 0.5% Mn) as a function of compressive engineering strain. Busby et al[87] reported the aging effect on tensile properties of Mn-bearing alloys. Mn dispersoids are shown to increase ductility by slip homogenization as shown in the previous work[82]. This slip homogeneity increases with dispersoid content and with the presence of overaged (rather than underaged) precipitates. Ductilities in underaged alloys are greater than that in overaged alloys because of stronger grain boundaries in the former. Work-hardening rates also increase with dispersoid content,
while underaged alloys have a higher work-hardening rate than overaged alloys and much less sensitivity to dispersoid content. The addition of Mn in peak aged Al-Mg-Si alloys additionally results in a substantial improvement in the resistance to fatigue crack propagation[88].
3. Objective

Pb is virtually insoluble in solid Al (see Figure I-13) and is often intentionally added in the 1-3 wt% range to certain Al alloys to increase their machinability. In free-machining alloys these low melting point additions enhance machinability by liquefying during machining, thereby aiding the formation of metal chips[89]. While enhanced machinability is achieved at these levels, minute amounts of Pb (i.e. <500ppm) may be detrimental to the mechanical properties both at intermediate (i.e. 100°C)[66] and low (i.e. -4°C, 25°C)[67] temperatures.

Guttmann et al[66] have indicated that small amounts of Pb (e.g. <165ppm) may induce embrittlement of Al-Mg-Si alloys in creep conditions at elevated temperatures but no effect was obtained in either tension or toughness tests. Auger and X-ray analysis revealed that Pb was essentially in precipitate form, and that it spread on the surface by diffusion immediately after fracture. Pb globules were preferentially associated with large AlFeSi inclusions at which transgranular dimples initiated, producing a dimpled intergranular surfaces. Their discussion focussed on Pb surface diffusion with the Pb-(AlFeSi) association being responsible for the embrittlement by Pb in creep conditions.

Recent work[67] on 6xxx series Al alloys has demonstrated the
deleterious effects of Pb at ambient temperatures in sustained load cracking tests and in slow strain rate testing. Figure [1-14 illustrates the effects of Pb level and applied stress intensity, $K$, on the crack velocity in bolt-loaded DCB specimens tested at (a)-4°C, (b)25°C and (c)80°C. The crack growth rate increased with increasing stress intensity, increasing grain size and increasing Pb content. Fracture under sustained load was primarily affected by the Pb content and the stress intensity level. Low Pb alloys exhibited predominantly intergranular microvoid coalescence (IGMVC), while low ductility intergranular fracture (LDIGF) was predominant in the high Pb alloys. Microanalysis by a Laser Microprobe Mass Spectroscopy (LMMS) revealed that Pb was present on the fresh fracture surface as well as in subsurface cracks. It was shown in the slow strain rate tensile tests that grain boundary accommodation of slip was predominant regardless of Pb content in the alloys.

The present work was undertaken to identify the locations of Pb in the microstructure, in addition to performing experiments designed to characterize deformation of Al-Mg-Si alloys containing Pb and then to elucidate the possible mechanisms of Pb assisted failure. A variety of analytical techniques were used in combination with sequential straining tests, tensile interruption tests and fatigue tests, in addition to Auger fracture tests, in-situ deformation studies and experiments conducted to determine the
effects of an external supply of Pb.
II. Experimental Procedures

This investigation was conducted on Al-Mg-Si alloys (6xxx series) intentionally doped with various levels of Pb. For this material, it is possible to conduct experiments in laboratory air without any environmental effects (e.g. stress corrosion cracking) affecting the results because of the general resistance of these alloys to stress corrosion cracking[90]. As reviewed earlier, while large amounts of Pb or Bi may enhance machinability[91], trace amounts of impurities from scrap may promote detrimental effects on the mechanical properties. The experiments outlined below were conducted to investigate the effects of minute (e.g. <500ppm) quantities of Pb on the mechanical properties.

1. Materials

Al-Mg-Si alloys corresponding to alloy composition 6351 containing various amounts of Pb (i.e. 5ppm - 500 ppm) were utilized for this investigation. Their chemical compositions are listed in Table I1-1. These alloys were D.C. cast by Alcan International Ltd., Banbury, UK., and homogenized at either 450°C for 12 hours or 570°C for 2 hours followed by:

1) 50% cold working
2) anneal at 400°C for 1 hour
3) 12% cold working
4) solution heat treatment at 535°C for 2 hours
5) aged to peak strength at 175°C for 7 hours

The materials were received in the peak-aged condition (i.e. condition 5).

2. Microstructural Evaluation

2.1. Optical Metallography

Optical metallography was utilized to characterize the microstructure. Metallographic specimens were mechanically polished using diamond paste up to 0.25 micron grade. Polished specimens were then etched in two kinds of solutions: Keller's reagent\(^1\) for micro-etching; Poulton's reagent\(^2\) for macro-etching. Some of the polished specimens were electro-etched to reveal grain boundaries in a 20%HNO\(_3\)-Methanol solution at 20V, -20°C. Etched samples were then examined in a Zeiss Ultraphot optical microscope, while grain size was measured in a Zeiss Videoplan by manually tracing the grain boundaries.

---

\(^1\) 2ml HF, 3ml HCl, 20ml HNO\(_3\), 175ml Water

\(^2\) 10ml HF, 120ml HCl, 60ml HNO\(_3\), 10ml Water
in a photograph.

2.2. Transmission Electron Microscopy (TEM)

TEM was utilized to characterize the microstructural features on undeformed as well as deformed specimens, while energy dispersive X-ray spectroscopy (EDS) analysis on a TEM was used to chemically analyze the features present using 100nm spot size. Thin foils (500μm) were first cut using slow rate diamond saw parallel to the longitudinal axis of extension and parallel to loading axes of test specimens which were in the longitudinal orientation. These foils were ground to about 100μm thick using #400 grit paper. Then 3mm discs were cut out and thinned down to about 60μm using #600 grit paper. These discs were jet-polished in a Tenupol 2 at 15V, -20°C in 25% HNO₃-Methanol solution. The prepared foils were then kept in a vacuum dessicator prior to being introduced in a TEM to prevent oxidizing. Subsequent examinations of perforated foils were performed in a Phillips 400T Analytical TEM at 120KV.

A collaborative TEM work was made at Harwell Laboratories, Didcot, Oxon, U.K. to analyze the microstructure and the grain boundary chemistry of an alloy containing 500ppm Pb high detail. The perforated foils were examined in a Phillips EM400 and a fine scale energy dispersive X-ray
spectroscopy (EDS) analysis was undertaken on a VG HB 501 FEG/STEM, both operating at 100KV. This high resolution STEM has a spatial resolution of 3nm.

2.3. Surface Analysis

High resolution (i.e. 500Å) surface analyses were obtained on polished, undeformed, and ion sputter cleaned specimens in a Perkin-Elmer PHI660 Scanning Auger Microprobe (SAM) operated at 10KV and 110µA, in an attempt to identify the source(s) and location(s) of Pb in the microstructure. A focused electron beam impinging on a specimen surface causes numerous beam-specimen interactions to take place, as shown in Figure II-1. Auger electrons are generated in the first few atomic layers of a specimen (e.g. 10Å). Therefore, Auger spectra can provide the elemental composition of the specimen surface. Auger surveys were taken at 1eV/step with a wide energy range (e.g. 30-2030eV) and Auger maps were obtained to see the two dimensional surface distribution of elements. Auger line scans were performed across grain boundary regions in both high Pb and low Pb alloys, schematically shown in Figure II-2. Auger line scans show the relative concentrations of individual elements along a sample traverse. The scans are collected by stepping the electron beam point by point along a selected line.
In the present case, the resolution of each line was 256 steps and survey time was 15ms/step.

2.4. Ga Embrittlement Experiments

These experiments were conducted in an additional attempt to locate the sources of Pb in the microstructure. The Al-Ga system as shown in Figure II-3 reveals that the general requirements for susceptibility to grain boundary penetration (i.e. low intersolubility) are present and it is well known that Ga will produce intergranular embrittlement in Al alloys with little macroscopic deformation[93].

A small specimen (1 cm³) of large- or small-grained alloy containing 500ppm Pb was used in these experiments. The specimen surface was finished to #600 grit paper and immersed in 10%HF solution to remove the oxide scale as described elsewhere[94]. The specimen was placed on a clean glass slide and was then heated to 50°C on a hot plate. Ga was dropped on a specimen surface. The specimen surface was scratched by a sharp knife to make intimate contact of Ga. The test arrangement is shown schematically in Figure II-4. Once Ga was collected at the bottom of specimen, the specimen was cooled and sliced to the thickness of 2mm, and the thin specimen was fractured gently in a hand vice. The fractured specimen was cleaned in
distilled water to remove the excess Ga on the fracture surface. Ga was
removed by the exothermic reaction and the cleaning was continued until
clear water remained. The specimen was subsequently introduced into the
Auger chamber to determine the fracture surface chemistry, followed by SEM
examination to observe the fracture surface produced by such a study.

3. Mechanical Testing

3.1. Tensile Tests

Tensile tests were conducted on smooth flat tensile specimens as
well as smooth cylindrical specimens. The former were used for room
temperature tests while the latter were used for high temperature tests. Their
dimensions are illustrated in Figure II-5. All tensile tests were conducted in an
Instron 1125 machine. Flat tensile specimens were polished prior to testing
using diamond paste up to 0.25 micron grade and carbon grids were
deposited on a surface to determine surface deformation in detail.

3.1.1. Grid Technique

Examination of the surface of deformed specimens can provide valuable
evidence concerning the deformation behavior of materials: slip line patterns and the offsets from grain boundary sliding. In this investigation, a grid technique was used to determine surface strain accommodation during tensile loading. The technique can be used to identify the deformation zones ahead of cracks and the strain distribution following deformation of complex shapes. This technique has been proved to be most useful in other work [95], while aims of the present experiments are described elsewhere [96]. The stencil method of grid production uses a very fine orthogonal mesh, consisting of a uniform array of square holes in a very thin metal sheet. It is important that the grids should be fine enough to discriminate between local strains at grain boundaries and grain centers. A fine Ni mesh of 2000 lines/inch was purchased from Buckbee-Mears & Co., St. Paul, Minnesota. The required size of this mesh was immersed in a 20% glycerol-ethanol solution and the excess solution allowed to drain off when the mesh was lifted out from the solution. This mesh was then placed in the gage section of a polished specimen surface. The remaining solution on the mesh allowed to adhere flat and firmly on the specimen surface. Carbon was then vacuum-deposited onto the specimen. Removal of the Ni mesh revealed a regular array of square carbon dots of 8μm size and 6μm spacing, as shown in Figure II-6.

A qualitative study of surface deformation can then be made from the displacements of the initially uniform array of fine, square dots. An other
application of this technique is the Moire technique of surface strain measurement[97]. The deformed grid is viewed through a master grid to produce Moire fringes. The displacement of the fringe ($\delta f$) at any point is then related to actual offset ($S$) when the fringes are perpendicular to the grain boundary as

$$S = (\delta f / f)g$$

where $f$ is the fringe spacing and $g$ is the grid pitch. The Moire technique is of limited application with fine-grained materials (less than 100 $\mu$m).

3.1.2. Sequential Tensile Tests

Smooth, flat tensile specimens as shown in Figure II-5 were tested at room temperature at either $10^6$/sec or $10^3$/sec. Tensile specimens were sequentially loaded to higher strains in the uniform strain range, while the details of surface deformation were investigated using Nomarsky Interference Microscopy in combination with the utilization of a carbon grid deposited on the polished flat surfaces prior to testing. The surface deformation was subsequently studied by photographing the displacement of the initially uniform grid, while the level of local strain was compared to the
macro-strain, as Figure II-7 illustrates. The change in the edge-to-edge distance of the dots (i.e., spacing of dots) in the tensile direction was utilized to monitor the local strain.

3.1.3. Tensile Interruption Tests

Tensile interruption tests were conducted to determine the effects of Pb level on the non-uniform strain. The metallographically polished flat tensile specimens were strained to UTS at room temperature at 10°/sec, unloaded, and subsequently reloaded at the same rate after holding for 24 hours at either room temperature or 80°C. Figure II-8 illustrates the schematic test sequence on stress-strain curve. Total elongation and reduction of area were measured at the UTS and at failure, while the orientation of grain boundary failure with respect to the stress axis were measured near fracture surface.

3.1.4. High Temperature Tensile Tests

The following tests were designed to determine if the large voids surrounded by low ductility intergranular fracture (LDIGF) were potential sources of Pb. Round tensile specimens as shown in Figure II-5 were prepared from material containing 500 ppm Pb. Three different kinds of tests were
conducted:

1) The specimen was elongated to the UTS at 450°C, then cooled to room temperature. The specimen was subsequently tested to failure (test 1).

2) The specimen was heat-treated at 450°C for 30 minutes and water quenched, followed by tensile testing at room temperature (test 2).

3) The specimen was solution-treated at 535°C for 2 hours and aged to peak strength at 175°C for 7 hours, and subsequently tested at room temperature (test 3).

3.2. In-Situ Auger Test

Auger fracture tests were performed on alloys containing 500ppm Pb to determine the locations of Pb on the internal crack surfaces. Notched Auger fracture specimens (Figure II-9) were prepared and pre-strained to the UTS at slow strain rate (10^-6/sec) in an Instron 1125 machine to produce Pb-induced low ductility intergranular cracks since impact will not induce low ductility failure. These specimens were unloaded and kept in LN₂ (Liquid Nitrogen) prior to being introduced in an Auger chamber. The specimen was then fractured by impact in an UHV Auger chamber and analyses were performed
on areas exhibiting fractographic features consisted with embrittlement by Pb. In this way, the notched specimens produce sub-notch root microcracks that are not contaminated with the environment and, hence, contamination is not a problem as has been shown elsewhere[98,99].

Auger depth profiling was conducted both on LDIGF and IGMVC regions to identify the fracture path with respect to the microstructural details provided by the TEM investigations. The surface of the specimen was sputtered by Ar ion bombardment and Auger spectra were collected in the center of the sputter etched area. Changes in Auger signal amplitudes during ion-etching indicate changes in specimen composition with depth, yielding a depth-composition profile. In the present case, the sputter rate was 3Å/sec.

3.3. Impact Tests

Impact tests were performed to determine effects of Pb on dynamic fracture energy. A modified Charpy V-notched specimen, as shown in Figure II-10, was used in this test. Test temperatures were varied from room temperature to 450°C (i.e. above the melting point of Pb), and specimens containing different levels of Pb were tested. Fractured specimens were kept in dry-ice or LN₂ to maintain surface chemistry (especially Pb on fracture surface) prior to being introduced in a SEM, and metallographic observations
were conducted in a optical microscope to examine near the fracture surface.

3.4. Fatigue Tests

Two different kinds of fatigue tests were conducted to determine the effects of different loading conditions on SMIE by Pb, where both the Pb level and loading rate were changed. Smooth flat tensile specimens (Figure II-5) with carbon grids on them were used at two different rates in an Instron 1125 machine. Cross head speeds of 0.01 mm/min produced a cyclic loading frequency of $9 \times 10^{-4}$ Hz while a 5 mm/min produced a cyclic frequency of 0.5 Hz. Cycle shapes and load ranges utilized are schematically shown in Figure II-11. These were chosen based upon previous work on monotonically deformed specimens. In these tests, maximum load was increased when the macroscopic strain reached about 1.5%. Macroscopic and local strain measurements were made on the surfaces of the deformed, cycled specimens, after a fixed numbers of cycles. Measurements were followed by the same methods with those in the sequential tensile test, while the amount of grain boundary sliding at a fixed number of cycles was determined by measuring the offset of a grid line across the grain boundary.

Notched bend specimens of 500 ppm Pb were used to determine Pb effects on the fatigue crack growth. The specimen geometry is illustrated in Figure II-
12. Three-point bending fatigue was conducted at two different frequencies (i.e. 20Hz, 0.2Hz) in a MTS machine corresponding to the loading rates used in the smooth specimen tests. The fracture toughness, \( K \), for three point bending specimen was evaluated using the following relationship from ASTM E399:

\[
K = \frac{PS}{Bw^{3/2}}
\]

\[
3\sqrt{\frac{a}{w}}\{1.99 - \frac{a}{w}(1-a/w)(2.15 - 3.93a/w + 2.7(a/w)^2)\}
\]

where \( f(a/w) = \frac{1}{2(1+2a/w)(1-a/w)^{3/2}} \)

\( P \) = applied load.

\( S \) = span distance (=40mm).

\( B \) = specimen thickness (=10mm).

\( w \) = specimen width (=10mm).

\( a \) = crack length.

All tests were performed at room temperature. Specimens were precracked to about 1mm with an initial \( \Delta K = 5\text{MPa}\sqrt{\text{m}} \), \( R = 0.5 \) (i.e. \( K_{\text{min}}/K_{\text{max}} \)) at 30Hz by decreasing \( \Delta K \) to the threshold, to produce a starting crack ratio \( (a/w) \) of about 0.35. The load was reduced by 10% at every 0.2mm crack growth, which produced an amount of crack growth in excess of the plastic zone size of the previous load. Rising \( \Delta K \) Fatigue tests were performed with \( R = 0.5 \)
starting at $\Delta K_{th}$, and the load was maintained in order to increase $\Delta K$ during testing, thereby producing the entire da/Dn vs. $\Delta K$ curve.

3.4.1. Electric Potential Measurements

Crack length was monitored by means of the potential drop technique. The entire system for the potential measurement is schematically shown in Figure II-13. A reference specimen was used to compensate the potential variations due to the environments such as temperature. Since all material and instrument variations are also included in the reference measurements, subtracting the reference potential from the test potential reveals the potential variation due to crack growth only. Use of reference potential measurements can significantly increase crack length resolution. Cu washers were utilized to connect the current input to the specimen in order to reduce the amount of specimen heating by the direct connection. A small hole was drilled (#44) and tapped (#4-40) on either side of the notch to measure the potential drop across the notch by flowing a direct current of 18A. Crack length was calculated from the potential measurements of[100]:

$$\frac{v}{v_o} = \sqrt{a^2+u^2}/\sqrt{(a_o^2+u^2)}$$
where \( v_0 \) = initial potential.

\( v \) = changed potential due to crack growth.

\( a_0 \) = initial crack length.

\( a \) = crack growth.

\( u \) = distance between potential probes.

Calibration revealed 14\( \mu \)V/mm of crack growth.

3.4.2. Surface Roughness Measurements

The roughness of fatigue fractured surface was measured using perthometer S8P in a Perthen at Alcan international Ltd., Banbury, Oxon, U.K. to determine the effects of crack closure during fatigue. Roughness was measured by scanning a fine laser beam along a selected line on fracture surface. The maximum resolution of the laser beam was 0.5\( \mu \)m in depth. The minimum scan distance was 5\( \mu \)m in horizontal direction. The roughness measured mean roughness, mean peak-to-valley height, maximum roughness, waviness depth and profile height.

3.5. External Pb Tests

While the previous tests are utilized the presence of internal Pb, tests
were conducted to determine the effects of externally applied Pb. Solid Pb was applied to the external surface of a variety of low Pb DCB (bolt-loaded Double Cantilever Beam) specimens in which cracks had grown and stabilized: 5ppm Pb large-grained alloy, 5ppm Pb small-grained alloy and 20ppmPb small-grained alloy. The geometry of the DCB specimen is illustrated in Figure II 14. The Pb source for the 5ppm Pb large-grained alloy was a Pb-Bi alloy, chosen because its melting temperature was so low (i.e. 125°C), thereby increasing the mobility of the diffusing species at the test temperature (i.e. 80°C).

Thin foils of Pb-Bi alloy were placed on both external surfaces of the DCB specimen and was held in place by a C-clamp. This specimen was then placed in a vacuum oven at 80°C. Crack length was monitored optically at various times and converted to the stress intensity factor, K.

The Pb sources for 5ppm Pb small-grained alloy and 20ppm Pb small-grained alloy were pure Pb foils. Tests were conducted in the same manner as with 5ppm Pb large-grained alloy. In order to identify regions of Pb-induced slow crack growth, these specimens were subsequently fatigued to failure and analyzed in the SEM to determine any changes in fracture mode due to external Pb.

Additional Auger fracture tests were conducted to determine the crack tip chemistry of DCB specimens tested in the presence of external Pb. Auger
specimens were taken both at the edge and in the middle of the crack tip region which was grown by the external Pb. Figure II-15 illustrates the locations of Auger specimens in DCB specimen containing 5ppm Pb. Auger specimens were cut to include the crack in thickness direction using low speed diamond saw. The square rod shape of the Auger specimen fit in the regular Auger fracture stage. The specimens were cleaned using ultrasonic cleaner first in acetone and then methanol. The prepared specimen was fractured by impact in a Auger chamber and examined near the original crack tip region.

4. Fractography

4.1. Scanning Electron Microscopy(SEM)

The sequentially strained tensile specimens and fracture surfaces were examined to elucidate the details of deformation and fracture in a JEOL 35CF SEM operated at 15KV, while the in-situ SEM straining observations were conducted in a JEOL 840A SEM. Some of the cold-mounted metallographic specimens were vacuum-coated with Au-Pd to ensure good conductivity and clarity prior to examine in SEM.
4.2. In-Situ SEM Observation

A deformation stage in a SEM was used to observe the details of Pb assisted crack growth under a sustained load. In-situ observations were conducted on single-edge notched (SEN) specimens of 500ppm and 5ppm Pb small-grained alloys. The specimen geometry is shown in Figure II-16. Specimens were polished and electro-etched at 15V, -20°C in a 20% HNO₃-Methanol solution. A specimen was placed on the deformation stage contained in a JEOL 840A Scanning Electron Microscope and loaded to the K value corresponding to 24.9MPa√m at the rate of 1.4Kg/min. The load was maintained for about 68 hours, while the deformed surface was monitored at regular time intervals. The 500ppm Pb alloy was reloaded to K=15MPa√m after unloading from the initial load.

4.3. High Resolution SEM

An additional SEM study was made at Alcan International Ltd, Banbury, Oxon, U.K. to observe fracture surfaces in detail. The purpose of this work was to identify the fine features such as micro-dimples on the fracture surfaces induced by Pb which were usually shown smooth and relatively featureless in a conventional SEM. A high resolution SEM (i.e. the spatial
resolution: 100nm) was undertaken in a ISI DS130 operating at 15KV. A small sample (maximum sample size is 4mmx4mmx2mm) including fracture surface was cut using low speed diamond saw. This sample was washed using ultrasonic cleaner in acetone and then rinsed in ethanol. The sample was glued with silver paste on a round specimen mount and was introduced into the high resolution SEM.
III. Results

1. Microstructure

1.1. General Features

The present alloys were homogenized prior to the thermomechanical treatments as described in section II-1. Homogenization at 570°C for 2 hours produced grain sizes in excess of 1 mm, while homogenization at 450°C for 12 hours produced grain sizes about 30 μm. Figure III-1 shows two different grain sizes produced by the two different homogenizing temperatures. It is known that the homogenizing treatments control the recrystallized grain size of cold-rolled and annealed Al-Mg-Si alloys[73]. When Mn and/or Cr-rich precipitates are present in the alloy, grain growth is inhibited by pinning the grain boundary[73]. The degree of recrystallization depends on the size of precipitates (i.e. homogenization temperature). Therefore, higher homogenizing temperature (e.g. 570°C) induce more complete recrystallization than lower temperature (e.g. 450°C) because of the greater precipitates at the higher temperature. Figure III-2 illustrates the effect of Mn on grain sizes as peak-aged for two different homogenizing temperatures. When the alloy does not contain Mn but some of Cr, recrystallization is less
inhibited and then the grain sizes are similar for the two homogenizing
temperatures (Figure III-2(a)). This phenomenon disappeared with the
additions of Mn (Figure III-2(b) & (c)). TEM studies of alloys homogenized at
450°C revealed that the Cr-rich precipitates are relatively smaller than the
Mn-rich precipitates (Figure III-3). The latter were slightly
different in their sizes for two homogenizing temperatures as indicated in
Figure III-5. Figure III-4 shows Mn-dispersoids in the 100ppm Pb alloys
homogenized at (a) 450°C and (b) 570°C. Dispersoid sizes are slightly
increased with the Mn amount as shown in Figure III-5. Since the alloys
containing 0%Mn and 0.25%Mn have 0.26%Cr and 0.17%Cr, respectively,
the average dispersoid size will be affected by the fine Cr particles. Therefore,
the overall dispersoid size would be increased with the Mn addition in the
alloy. The alloy containing 0.55%Mn shows the different particle sizes for the
different homogenizing temperatures: the high homogenizing temperature (i.e.
570°C) reveals slightly bigger particle size. The relative frequencies and
cumulative frequencies of those particle sizes in the alloy containing
0.55%Mn are shown in Figure III-6 for the homogenizations at
450°C((a)&(b)) and 570°C((c)&(d)). The average particle size for the alloy
homogenized at 570°C is slightly bigger than that for the alloy homogenized
at 450°C even though the cumulative frequencies are very similar for the two
different homogenizations.
It has been well known that the Al-Mg-Si alloys are hardened by the aging precipitates(Mg2Si) in matrix due to the strain around precipitate by the coherency between the precipitate and the matrix[75]. These semi-coherent precipitates lie in three mutually perpendicular directions parallel to the <100> directions of the Al matrix(Figure III-7). The spots in Figure III-7 are fine precipitates lying perpendicular to the plane of the photograph which includes some dislocations. These precipitates give rise to streaks in electron diffraction pattern as shown in the inset of Figure III-7. A precipitate free zone(PFZ) along the grain boundary was observed in all alloys and its width was usually 0.2μm(Figure III-8(a)). EDS analyses indicate that the solutes(i.e. Mg and Si) are depleted in the PFZ(area B in Figure III-8(b)). This solute depletion may be caused by the grain boundary precipitation.

TEM foils taken from undeformed specimens containing various amounts of Pb revealed small(i.e. <0.5μm), slightly faceted particles at the grain boundary as well as in the matrix, as shown in Figure III-9. These are identified as aging precipitates and Mn-rich intermetallics by analyses of diffraction data and the EDS spectra. The distribution of grain boundary precipitates was determined after intergranular decohesion using liquid Ga. Figure III-10 illustrates the grain boundary surface produced in this manner in a 500ppm Pb alloy homogenized at 450°C. The scanning electron micrographs reveal the distribution of grain boundary precipitates, while
matching surface fractography of grain boundaries produced by decohesion with liquid Ga showed grain boundary precipitates and matching depressions on the opposite grain surface. The average sizes of grain boundary precipitates were 0.34 μm (standard deviation = 0.14) for the small-grained alloy (i.e. homogenized at 450°C) and 0.41 μm (standard deviation = 0.2) for the large-grained alloy (i.e. homogenized at 570°C). This measurement was performed using Zeiss Videoplan by manually tracing particles on the SEM micrograph.

In addition to the above constituents, these alloys contain large (i.e. >1 μm) Fe-rich particles in the matrix and in the grain boundary regions. These particles are usually identified as Al(Mn,Fe)Si phases (Figure III-11), while, in the absence of Mn in the alloy, the particles are identified as AlFeSi phases (Figure III-12).

1.2. Locations of Pb

TEM-EDS analyses of the small-grained 100 ppm Pb alloy indicated that Pb was often associated with the small faceted grain boundary particles at the grain boundary and was detected on the grain boundary region as shown in Figure III-13, in addition to being detected in association with the large Fe-containing particles both at the grain boundary and in the grain. Figure III-14
shows a secondary electron image of an Fe particle in the small-grained 100ppm Pb alloy, in which the presence of Pb was identified by Auger survey and Auger mapping. Auger line scans, schematically described in Figure II-14, across a grain boundary of the polished, ion sputter cleaned, undeformed 500ppm Pb containing alloy is presented in Figure III-15. Pb signals were detected both at the grain boundary and within the grain as Figure III-15 illustrates. These Pb signals disappeared when the same Auger line scan was performed in the same locations after 2 days in an UHV chamber as shown in Figure III-16 although the other signals were not affected. Additional analyses revealed that the Pb was often associated with Mn, Fe and Si, although isolated Pb signals were detected in the absence of these elements.

Another high resolution (i.e. 3nm) EDS analysis in an alloy containing 500ppm Pb revealed no significant segregation of Pb to the grain boundary or at the interface with Fe-containing particles[101]. In this analysis[101], however, low levels of Pb was detected near (i.e. 5-10nm) the grain boundary or the interfaces of Fe-containing particles. These results are summarized in Table III-1. The microstructural observations revealed the similar results with the present work (i.e. B'rods, Fe-containing particles and PFZ's along the grain boundaries as shown in Figure III-17).

Auger analyses were conducted on the fracture surfaces of Ga embrittled specimens. Surface analyses were performed on surfaces which were oriented
normal to the electron beam in Auger chamber. The orientation of the surfaces was confirmed by taking stereo pairs to verify that the surfaces were indeed at 90° to the incident beam. Auger spectra taken around large voids (e.g. regions 1, 2, 4 in Figure III-18) revealed that Pb was present at these large voids and was sometimes detected at the precipitates near large voids as Figure III-18 illustrates.

In the commercial processing of this alloy, the alloy is heat treated at temperatures above the melting point of Pb (i.e. 327°C). These materials are homogenized at 450°C or 570°C, annealed at 400°C, and solution-treated at 535°C, respectively. During such temperature excursions, Pb would tend to accumulate while the volume change associated with re-solidification (i.e. contraction) might produce small, pre-existing voids containing Pb. At the very least, the Pb globules accumulated in these regions would be poorly bonded to the Al matrix. Therefore, these large voids are believed potentially to be the major sources of Pb. The average size of these Pb containing, large voids was 4.85μm (standard deviation=1.27) for the small-grained 500ppm Pb alloy and 5.4μm (standard deviation=2.13) for the large-grained 500ppm Pb alloy, while the area fraction present on the fracture surface was measured as 0.82% and 1.0%, respectively.

Analyses of low Pb specimens (i.e. 20ppm) were not as successful in locating the site(s) of Pb in the alloy in the present work. However,
fractographic analyses using Backscattered Electron Image (BEI) has revealed that Pb is only found in association with Fe-containing particles in these low Pb alloys[102].

2. Mechanical Testing Results

2.1. Tensile Results

The local (i.e. micro) strain as a function of macro-strain of the sequentially loaded flat tensile specimens, calculated via the technique described in Figure II-6, are presented in Figure III-19[96]. Calculation of local strain were performed both across grain boundary regions and within the matrix for the two strain rates. Figure III-19(a) indicates a strong effect of Pb level on the micro-strains obtained for a given macro-strain, which is measured across grain boundaries in slow strain rate tests. Direct comparison of the behavior of the 500ppm Pb alloy (570°C) and the 20ppm Pb alloy (450°C) is provided by the solid lines in Figure III-19. Increased grain boundary accommodation of deformation is evident in higher Pb materials, and was more pronounced at the larger levels of macro-strain, while deformation by matrix slip was more prevalent for low Pb alloys tested at the same rate (Figure III-19(b)). Figure III-19(C) and (d) indicate that there was
no measurable effect of Pb on the balance of deformation by grain boundary
or matrix slip for specimens tested at fast strain rate. Appearances of
deformed grids for different Pb contents and strain rate are presented in
Figure III-20. Figure III-21 shows deformed grids of specimen surfaces for the
comparison between (a) large-grained 500ppm Pb alloy and (b) large-grained
20ppm Pb alloy both strained to about 2% by slow strain rate. Arrows
indicate the deformed grain boundary regions in (a) and the matrix slip in
(b).

The non-uniform strain decreased with an increase in Pb content. As
detailed earlier, additional specimens were unloaded at the UTS, and were
subsequently reloaded after holding in vacuum for 24 hours at either room
temperature or 80°C. The non-uniform strain to failure obtained after
reloading, summarized in Figure III-22, was strongly
affected by both the Pb level and the holding temperature. Holding at room
temperature for 24 hours produced no measurable effect on the subsequent
non-uniform strain to failure at either Pb level, whereas significant decreases
were obtained for both low and high Pb specimens held at 80°C prior to
reloading. Greater losses were obtained with higher Pb levels. However,
heating at 80°C for 24 hours prior to tensile testing did not exhibit the effect
on the non-uniform strain to failure as indicated in Figure III-22. The
orientation of grain boundaries exhibiting failure was determined with respect
to the tensile axis on the tensile interruption tests. Figure III-23 summarizes the cumulative total of grain boundaries exhibiting fracture as well as their orientation with respect to the tensile axis. High Pb alloys exhibited a predominance of failure in boundaries oriented at 90° to the tensile axis, while grain boundary failure for low Pb alloys did not reveal any orientation preference.

A TEM micrograph of a small-grained alloy containing 100ppm Pb deformed to 0.3% plastic strain is shown in Figure III-24. These dislocations tend to pile-up at grain boundary regions as shown in Figure III-25. Further increases in deformation induces dislocation bands as shown in Figure III-26, illustrating slip bands in the matrix of the small-grained 100ppm Pb alloy strained to 0.4%. On increasing the deformation, the bands did not disappear but instead become diffuse: they become wider and then the slip band spacing becomes narrower. At increasing amount of strain (e.g. above 1.5%), the deformation bands are no longer resolvable. It was observed that dislocation debris were left around Mn dispersoids which are incoherent with the matrix, as shown in Figure III-27. Alloys not containing these dispersoids (i.e. the Mn-free alloys) allow dislocations to cut through the aging precipitates and subsequently promote dislocation glide preferentially along the local path of the slip plane, thereby concentrating slip in narrow bands, as also shown in other work [86]. It was additionally found in the present
work that Mn dispersoids changed the slip band spacing. Figure III-28 illustrates the reduction in the slip band spacing with increasing Mn level in the alloys strained to 1.2% plastic strain. Figure III-29 shows representative TEM micrographs of the different slip band spacings obtained for alloys containing different Mn levels. The alloys containing 0%Mn and 0.25%Mn revealed the wider slip band spacing even though these alloys contain 0.26%Cr and 0.17%Cr, respectively. Therefore, the Mn dispersoids would be more effective than the Cr dispersoids in promoting cross slips (i.e., becoming narrow slip band spacing). Dislocations were found to arrange into the bands parallel to \{111\} as shown in Figure III-30. Dislocation half-loops were found in the PFZ's as shown in Figure III-31. It was also found that dislocations were locked at the border of PFZ and matrix at the early stage of deformation (Figure III-31). Later these dislocations move into the matrix and then relatively dislocation-free in PFZ as shown in Figure III-32.

TEM micrographs of tensile specimens strained various amounts revealed microvoid initiation both at the grain boundary and at cracked large Fe-containing particles within the grain. The grain boundary microvoids were typically associated with the small faceted particles shown earlier (i.e., Figure III-9) at which Pb was detected. Figure III-33 shows a TEM micrograph of a large-grained 500ppm Pb specimen subjected to the tensile interruption test held at 80°C, and subsequently tested to failure. Pb was associated with the
particle shown in Figure III-33, while the grain boundary void was associated with the precipitate free zone. Figure III-34 shows the cracked Fe-containing particles in the large-grained 100ppm Pb alloys strained to 5% plastic strain at slow strain rate and to 6% plastic strain at fast strain rate, respectively. EDS analyses revealed Pb in association with these particles. TEM and SEM observations of tensile tested specimens revealed the cracked or decohered Fe-containing particles at all Pb levels regardless of the applied strain rate. Figure III-35 shows a SEM micrograph of a large-grained 500ppm Pb alloy strained to 10.3% at slow strain rate, revealing the cracked Fe particles at the boundary and in the matrix.

High temperature tensile tests have been done to determine the effect of large voids as the potential sources of Pb as described earlier. Flow stresses from three different kinds of tensile tests are summarized in Table III-2. Both test 1 and 2 showed extremely low flow stress due to the loss of matrix strength at high temperature. It was only 7.5MPa when specimen was strained at 450°C, and it was increased to 91MPa when this specimen was strained at room temperature after cooling. This value (i.e. 91MPa) was comparable to that of test 2, 77MPa. The flow stress from test 3 was recovered by reaging.

2.2. In-Situ Auger Fracture Results
In-situ Auger fracture of the large-grained 500ppm Pb alloy revealed the uniform coverage of Pb on the fracture surface as shown in Figure III-36(a). This uniform Pb coverage decayed after 2 days kept in an UHV Auger chamber. Figure III-36(b) illustrates the reduced coverage of Pb on the fracture surface as indicated by an Auger mapping of Pb. Auger spectrum taken after 1 week in an UHV Auger chamber indicated that Pb disappeared completely(Figure III-36(c)).

Auger depth profiles were conducted to identify the fracture path of LDIGF and IGMVC as schematically shown in Figure III-37(a) &(b). Depth profiles obtained on LDIGF regions exhibited only Al initially followed by alloying elements such as Mg and Si after depth of 0.1μm(area 2 in Figure III-37(c)). This distance is roughly equivalent to the half of the precipitate free zone. In contrast to LDIGF, alloying elements were detected from the beginning of depth profile on IGMVC region(area 1 in Figure III-37(c)), strongly suggesting that the base of dimple is the boundary between PFZ and the matrix. It is proposed from these results that LDIGF fracture proceeds directly along the grain boundary, while IGMVC lies along the PFZ and boundary as shown in the schematic(Figure III-37(a)).

2.3. Impact Results
The impact energies obtained for the different Pb contents as a function of temperature is presented in Figure III-38, while the results are also summarized in Table III-3. The impact energies were not significantly affected by Pb below the melting point of Pb (i.e. 327°C). However, the difference in impact energy between the 5ppm Pb alloy and the 100ppm Pb alloy was noted at 350°C, which is above the melting point of Pb. The further increase in temperature to 450°C induced the recovery of the difference in impact energy between the 5ppm Pb alloy and the 100ppm Pb alloy. One possible explanation of the similar behaviors of the low and high Pb specimens at high (i.e. 450°C) temperatures is that the specimens were overaging during heating at these test temperatures. Therefore, the matrix strength is much lower than that of grain boundary. This low strength of matrix induced the high ductility: the increase in impact energy and fracture occurred transgranularly. Only the 100ppm Pb alloy tested at 350°C fractured completely into two pieces: the remaining specimens tested at temperatures above the melting point of Pb did not break into two pieces. The metallographic observations near the fracture surface of specimens tested above the melting point of Pb indicated that alloys containing 100ppm Pb revealed higher void density than 5ppm Pb alloys as shown in Figure III-39. Specimens containing these higher void densities exhibited lower impact energies. SEM-EDS revealed Pb on the fracture surface of 100ppm Pb alloy
tested at 350°C as shown in Figure III-40. In this case, Pb was associated
with AlFeMnSi particle on the transgranular fracture surface.

2.4. Fatigue Results

The effects of Pb on fracture has been studied under cyclic loading
conditions at room temperature. Smooth flat tensile specimens were fatigued
at two different frequencies (i.e. 9x10^4Hz and 0.5Hz) and the surfaces were
monitored as described earlier. The deformed grid surface and polished
surface of the 500ppm Pb alloy fatigued at 9x10^4Hz are shown in Figure III-
41. The number of cycles to failure for two different frequencies and two
different Pb content are summarized in Figure III-42. The high Pb alloy (i.e.
500ppm) failed after 1,275 cycles when cycling was conducted at the slow
rate (9x10^4Hz), and the identical alloy failed after 36,492 cycles when cycled
at the fast rate (0.5Hz). The low Pb alloy (i.e. 5ppm) failed after 31,853 cycles
when cycled at a fast rate, and the same alloy cycled at a slow rate was
removed after 4,500 cycles because the fatigue life tended to the similar result
with the latter. The actual time to failure of this alloy (i.e. 5ppm Pb) would be
a several months at a slow rate fatigue test. Their fracture strains were much
lower than those of monotonic tensile tests as shown in Table III-4. The
amount of grain boundary sliding, measured by the offset of grid line across a
grain boundary, as a function of macro-strain is presented in Figure III-43. The high Pb alloy fatigued at a slow rate revealed a lower amount of grain boundary sliding in comparison to the others which exhibited a similar trend of relatively high amount of grain boundary sliding. This difference in grain boundary sliding is illustrated in Figure III-44. Figure III-44 shows the difference of the grain boundary sliding amount by small arrows across grain boundaries for 500ppm Pb alloy fatigued at two different frequencies and their plastic strains were about 2%.

Additional fatigue tests were performed to determine the fatigue crack growth rate of the alloy containing 500ppm Pb both at 20Hz and 0.2Hz. The crack growth rate (da/dN) as a function of stress intensity factor range (ΔK) is presented for both 20Hz and 0.2Hz in Figure III-45(a). The crack growth rate (mm/cycle) in the case of 0.2Hz was higher than 20Hz at the same K value. However, the actual crack velocity (m/sec) for 20Hz was faster than that for 0.2Hz(Figure III-45(b)).

TEM foils taken from the cyclically loaded specimens to failure revealed the similar dislocation structure with the monotonic tensile tests. However, in the fatigue tests, the dislocation bands were more dense and much dislocation debris was observed between bands(Figure III-46). TEM foils were taken from the 500ppm Pb alloy tested to failure at 9x10⁴Hz. Slip bands were parallel to {111} as indicated by the solid line. Since there are incoherent dispersoids in
the matrix, dislocations can not shear but are accumulated at the dispersoids during cyclic loading (Figure III-47).

2.5. External Pb Tests

Figure III-48 shows the specimen surface for the large-grained 500ppm Pb alloy at various times after the Pb-Bi alloy was applied to the outside surfaces. The arrow in Figure III-48 denotes the farthest point of crack extension in each picture. Crack growth was observed after 160 hours, with additional crack growth at 325 hours. In the absence of external Pb, no crack growth was observed for the testing times and temperature (i.e. 80°C) utilized. The crack growth and stress intensity factor (K) changes are illustrated in Figure III-49, for the bolt-loaded DCB specimen. This parabolic shape of crack growth has also been observed for SMIE of 7075 Al alloy by In[72]. The pure Pb foil was applied to the small-grained 5ppm Pb and 20ppm Pb alloys. Their crack growth and stress intensity factor changes are also presented in Figure III-50. These specimens were reloaded by the bolt when the crack growth was stable, and were thereby tested again for a short time. The stress intensity factor changes indicated that the threshold values were lowered by the external Pb. A plot of crack velocity vs. stress intensity factor (γ-K) curve illustrates this in Figure III-51.
Auger fracture specimens were taken from the crack tip region both at the edge and the middle of low internal Pb DCB specimen tested by external Pb as described in Figure II-15. Auger elemental mapping of in-situ fracture surface revealed the uniform coverage of Pb both on LDIGF and IGMVC surfaces as shown in Figure III-52, giving the same result as the in-situ Auger fracture test of an alloy containing 500ppm Pb. Local accumulation of Pb was found at the sites of large dimples which are apparently the sites of the original Pb in the alloy. As mentioned earlier, this uniform coverage of Pb gradually disappeared after several days in the UHV Auger chamber, with complete disappearance of the Pb signal in one week.

3. Fractography

3.1. Fracture Mode Transition

The fractography of fractured specimens similarly revealed an effect of Pb level and strain rate on the fracture mode. The high Pb alloy (i.e. 500ppm) exhibited regions of Low Ductility Intergranular Fracture (i.e. LDIGF) surrounding large (i.e. >5μm) voids in the slow strain rate tensile test as shown in Figure III-53(a). In contrast, the fast strain rate tests as well as the low Pb alloys exhibited Intergranular Microvoid Coalescence (i.e. IGMVC), as
shown in Figure III-53(b). SEM stereo pairs of the fracture surfaces revealed that LDIGF was typically present in regions normal to the stress axis. Figure III-54 exhibited LDIGF around large voids even in low Pb alloy tested at slow strain rate and the stereo pair revealed that these LDIGF were normal to the stress axis.

Fracture surfaces of specimens in high temperature tensile tests exhibited large voids surrounded by low ductility intergranular fracture (LDIGF) in test 3 while most of the fracture surfaces revealed transgranular ductile rupture (Figure III-55). The density of large voids surrounded by LDIGF was 65/mm². This value was lower than that of normal tensile fractured surface (i.e. 150/mm²) produced at room temperature. However, the area fraction of voids was slightly higher (i.e. 0.2%) in test 3 than normal tensile fractured specimen (i.e. 0.16%). Liquidified grain facets existed on the fracture surface of test 1 as shown in Figure III-55(a).

Fracture surfaces of most of the impact specimens revealed IGMVC and/or TGMVC as indicated in Table III-3. Figure II-56(a) shows the fracture surface of the small-grained 50 ppm Pb alloy tested at room temperature, revealing dimples on the fracture surface. The identical alloy tested at 100°C exhibited a similar fracture mode. Figure III-56(b) indicates particles inside of dimples (arrows) on the fracture surface of the small-grained 5ppm Pb (with Mn+Cr) alloy tested at room temperature. Figure III-57 illustrates the
transgranular fracture surfaces of (a) the small-grained 100ppm Pb alloy tested at 250°C, and (b) the identical alloy tested at 350°C. EDS analysis indicated that Pb was detected in association with Mn, Fe, Si containing particle (arrow in Figure III-57(b)) as shown in Figure III-40.

Generally, a fracture mode transition occurred from IGMVC to LDIGF as the Pb content increased and strain rate decreased, as shown in Figure III-58. This fracture mode transition was also observed on the fatigue fracture surface. LDIGF was predominant in the small-grained 500ppm Pb alloy tested at low frequency (i.e. 9x10^-4Hz) while IGMVC was predominant in the same alloy tested at high frequency (i.e. 0.5Hz) as shown in Figure III-59. The IGMVC will be predominant in the small-grained 5ppm Pb alloy regardless of frequency. A fracture mode change from LDIGF to IGMVC was observed on the fracture surfaces of the fatigue crack propagation tests. Figure III-60 shows the fatigue fracture surface of the small-grained 500ppm Pb alloy fatigued at 20Hz. The fracture surface includes regions of LDIGF, IGMVC and transgranular fatigue crack propagation. The LDIGF mode changed to IGMVC mode as the stress intensity factor range (ΔK) increased. This is observed as one moves from the fatigue precrack into the regions of fatigue crack growth. In other words, LDIGF was predominant in the low ΔK regime (i.e. threshold and low da/dN), while IGMVC was prevalent in the high ΔK (i.e. >9MPa√m) as shown in Figure III-61. However, LDIGF was exhibited at high ΔK's for the
same alloy fatigued at 0.2Hz. Figure III-62 shows the fatigue fracture surface of this alloy. A fracture mode change from LDIGF to IGMVC occurred at higher ΔK than that for the 20Hz fatigue. As illustrated in Figure III-63 the most IGMVC was observed at ΔK=15MPa√m which is in the dynamic fracture region, even though small areas of dimples start to show from ΔK=9.7MPa√m.

The roughness of fatigue fracture surface indicates that the fracture surface of 20Hz fatigue shows slightly smoother than that of 0.2Hz fatigue, as summarized in Table III-5. The fracture surface of 20Hz fatigue includes more amount of cleavage and less amount of LDIGF than that of 0.2Hz fatigue. Since the fracture surface of 0.2Hz has more grain facets due to LDIGF then this surface seems to be slightly rough. Figure III-64 illustrates the examples of surface profile both for (a)20Hz and (b)0.2Hz. The horizontal scale is 1.25mm(i.e. scan distance) and the vertical scales are 36.75µm for 20Hz and 29.73µm for 0.2Hz. The general crack growth direction is from right to left on the graph.

The fracture mode transition observed due to external Pb application is shown on the fracture surface of a large-grained DCB specimen containing 5ppm Pb fatigued to failure in Figure III-65(a). SEM fractography clearly revealed that LDIGF was induced by external Pb(areas 1 and 2 of Figure III-65(b)). Some LDIGF was additionally observed in regions containing
predominantly IGMVC (areas 3 and 4 of Figure III-65(b)), which was probably due to the fracturing of unfractured ligaments which occurred during the original crack growth without the external Pb. High resolution SEM (i.e. 0.1 μm) revealed that LDIGF showing relatively featureless did not contain micro-dimples on that surface but contain many cusps on that surface (Figure III-66).

3.2. In-Situ Deformation

Sustained load tests were conducted in a SEM by applying an initial load corresponding to $K = 24.9 \text{MPa} \sqrt{\text{m}}$ which was near $K_{\text{th}}$ of low Pb alloy (i.e. 5 ppm). The notch root areas upon the initial load are shown in Figure III-67 for both 500 ppm and 5 ppm Pb alloys. The sequential observations for both alloys revealed that the 500 ppm Pb alloy exhibited crack growth in vacuum after 68 hours, while no crack growth occurred in the 5 ppm Pb alloy after same amount of time. Figure III-68 shows cracks in detail of 500 ppm Pb alloy after 68 hours. The observations of crack surfaces indicated that LDIGF was predominant for cracks occurring during sustained load (areas 1, 2, 4 and 7 in Figure III-68(b)) while intergranular microvoid coalescence (IGMVC) was predominant for cracks induced upon loading (areas 3, 5 and 6 in Figure III-68(b)). These LDIGF surfaces were usually normal to the stress axis and were
also associated with large voids. This specimen was subsequently reloaded to
the value corresponding to $K=15\text{MPa\sqrt{m}}$, which is above $K_{th}(\approx 9-10\text{MPa\sqrt{m}})$
for this alloy. Figure III-69 shows the reloaded external surface of the
500ppm Pb alloy after 40 hours in the SEM. There was no macroscopic crack
growth, but sub-critical cracks had opened and were beginning to link-up.
The observations of the crack surfaces revealed that the cracking which
occurred upon reloading was IGMVC(area 1 in Figure III-69) with ductile
rupture around large constituents(area 2 in Figure III-69). Area 3, in Figure
III-69, is the crack surface produced by the initial load which opened by
reloading.
IV. Discussion

1. Locations of Pb

The present work indicates that Pb-induced embrittlemenent may occur in Al-Mg-Si alloys at room temperature and possibly lower temperatures, as shown in a recent work[67,113]. However, these temperatures are somewhat lower than typical SMIE which occurs near the melting temperature of the embrittler[52,71]. The present work exhibits many similarities with HE[7]. All brittle failure involve the initiation and propagation of cracks. The embrittlement is sensitive to strain rate and then diffusion of hydrogen or Pb. Therefore there exists the crack incubation period, the slow crack propagation and the final catastrophic failure. The following discussion focuses on rationalizing the locations of Pb in the alloys studied and their effects on the macroscopic and microscopic deformation and fracture behavior in these materials.

Although Pb exhibits some solubility in liquid Al, essentially zero solubility exists in the solid state as shown in Figure I-13. Thus, Pb will segregate during solidification due to the wide density difference between Al\(^1\)

\[ \rho(\text{Al}) = 2.71 \text{g/cm}^3 \]
and Pb\(^2\). The present results from the various experiments such as TEM-EDS and Auger analyses indicate that the Pb distribution is affected by Pb level. In the low Pb alloys, Pb was typically observed at large Fe-containing inclusions which are very stable during heat treatments. In contrast, high Pb specimens exhibited a variety of locations for Pb. Pb peaks were detected at incoherent particles (i.e. Al(Mn,Fe)Si or AlMnSi) and inclusions (i.e. AlFeSi), at the grain boundary, and within grains. Pb was also detected at the boundary region (see Figure III-13) with alloying elements such as Mg and Si. The Harwell report [101] indicated that there was no significant Pb segregation on the grain boundary in the material containing 500ppm Pb but the low levels of Pb was detected at or near the grain boundary and the interface with Fe-containing particles. They interpreted that even though Pb may segregate in a submonolayer no indications of Pb at the grain boundary or the interface with Fe-containing particles are caused by the diffusion away from the electron beam in the plane of the interface due to the high mobility of Pb.

TEM investigation of foils taken below the fracture surface of failed specimens containing 500ppm Pb held at 80°C in the tensile interruption test and failed in the LDIGF mode revealed preferential crack initiation at Pb containing grain boundary particles (see Figure III-33). Figure III-23 additionally showed that the high Pb alloys show a strong preference for

\[ \rho(\text{Pb}) = 11.34 \text{g/cm}^3 \]
grain boundary failure by LDIGF for boundaries oriented normal to the stress axis. These cracks subsequently grow in a LDIGF mode by the continual supply of Pb from the process zone ahead of the growing crack. It was also noticed that most of LDIGF features on fracture surfaces were centered on large shallow voids (e.g. 5μm) on the surface as shown in Figures III-53&54, and that the frequency of these features increased with increasing Pb content in the alloy. One plausible explanation for the source of these features is that this alloy is subjected to heat treatments at temperatures above the melting point of Pb (i.e. 327°C), and upon cooling the liquified Pb would tend to contract during solidification. Thus, an Al matrix containing poorly bonded Pb globules exists in these sites. Therefore, the Pb globules in the shallow voids at the grain boundary, in addition to the Pb-containing Fe particles and other poorly bonded regions are major sources of Pb. Support for the influence of Pb containing regions as potential void sites is provided by the impact and high temperature tensile tests which indicated that the area fraction of voids observed in metallographic cross sections increased with Pb level. Since the large second phase particles in this alloy (i.e Al(Fe,Mn)Si intermetallics) are very stable after homogenizing treatment, it is likely that the number of Pb containing regions is the controlling factor for the change of the density of voids. In support of this, the Ga embrittlement experiments of Figure III-18 revealed that Pb was usually detected with particles in the shallow voids and
was also detected at particles near these shallow voids.

Recently, Guttman et al[66] concluded that Pb does not segregate to the grain boundary and is often associated with AlFeSi inclusions which initiate transgranular dimples. In its work[66], no preferential association of Pb was present in the intergranular areas since the intermetallic inclusions formed at high temperatures are not preferentially located on grain boundaries. However, in the present work, the intermetallic inclusions, sometimes associated with Pb, are observed at the grain boundary regions and Pb exists at or near the grain boundaries as indicated by the large shallow voids on the low ductility intergranular fracture surfaces.

Before discussing some of the fracture experiments in more detail, the deformation characteristics of these alloys in relation to the microstructure will be discussed.

2. Deformation Characteristics

The present alloy contains soft PFZ's along the grain boundaries which are surrounded by the precipitate-hardened matrix. In the slow strain rate tests on smooth specimens, grain boundary deformation was predominant while matrix slip was prevalent at the same strain level in the fast strain rate tests as shown in Figure III-19. It is logical in these conditions that the soft
PFZ's are preferentially deformed under stress, thereby possessing a dislocation density which is initially higher in the PFZ than in the matrix. The intervention of grain boundary failure depends on both loading rate and Pb level as discussed shortly. In previous work[103-106] it has been demonstrated that these dislocations were generated at grain boundaries in materials containing PFZ's, while in-situ TEM observations of strained Al polycrystalline foil at room temperature[103] showed that lattice dislocations were generated at grain boundaries without any interactions with pre-existing lattice dislocations. In the present work, it was shown in Figure III-31 that half-loops of dislocations emerge from the grain boundary of a specimen deformed to 0.3% strain and dislocations are gathering on the border of the PFZ/matrix interface. As the PFZ is relatively weak, the PFZ becomes relatively dislocation free upon further deformation. Dislocations can easily cross it under lower stress. Slip bands subsequently nucleate and develop from the PFZ/matrix interface, and these then impinge on the grain boundaries. The optical metallographic observations of deformed tensile specimens revealed the different contrast of the slip lines on different sides of a grain boundary, presumably resulting from two sets of slip lines originating from the two opposite grain boundaries, as similarly mentioned by Vasudevan and Doherty[6].

It was proposed by Ryum[4] that deformation occurs in narrow slip bands
through the matrix. In the present work, TEM foils of deformed specimens revealed narrow slip bands in Mn-free Al-Mg-Si alloys as shown in Figures III-28 & 29. It has been shown [86] that dislocations will shear the aging precipitates (Mg₂Si) and this will soften the slip plane, so that subsequent dislocations will glide along this path. Thus, dislocations will be concentrated in a narrow band which produce a local stress concentration at a boundary. Subsequently, the grain boundaries are subjected to tensile stresses, often producing intergranular fracture in the peak-aged condition. However, dislocations will not shear the Mn-dispersoids (α-AlMnSi) in the Mn-bearing alloy. Instead, dislocation loops will be left around particles as by the mechanism shown schematically in Figure IV-1 and evidenced by Figure III-27. Figure III-26 illustrates the dislocation debris around particles. This will harden each slip plane and cause cross slip to adjacent planes [86]. Slip is then homogenized through the matrix. Therefore, Mn has the effect of lateral spreading the slip bands, giving rise to smaller stress concentration at the head of the slip bands and improving the toughness.

In the peak-aged condition, the shearing mechanism is predominant for the interaction between dislocations and precipitates [86]. It has been well known that the hardening of the peak-aged Al-Mg-Si alloys is mainly due to the fine coherent or semi-coherent aging precipitates. However, Banizs [108] has shown that the hardening is due to two factors which behave differently.
against dislocations. The total shear stress, $\tau_{pr}$, to move a dislocation through a precipitate is divided into the stress due to the coherent strain of the precipitate, $\tau_{coh}$, and the shear stress due to the order of the precipitate, $\tau_{sh}$, i.e. the energy required to shear the precipitates[108]:

$$\tau_{pr} = \tau_{coh} + \tau_{sh}$$

When $\tau_{coh} >> \tau_{sh}$, shearing of a precipitate by a dislocation does not lower the shear stress for the next dislocation penetration. However, if $\tau_{sh} >> \tau_{coh}$, a dislocation will cut a precipitate and there is no dislocation hardening. Thus dislocations will be concentrated in a narrow slip band and produce a brittle intergranular fracture as mentioned in the Mn-free Al-Mg-Si alloys[86]. Figure IV-2 illustrates the interactions of precipitates lying in the $<100>$ directions by the dislocations moving in the direction of $[110]$ on a $(111)$ plane. The cross-sectional areas of the precipitates are reduced after shearing by a dislocation as shown in Figure IV-2 and this reduction of cross-section area gives rise to the lower resistance for the next dislocation motion, subsequently softening the slip plane.

TEM investigations of foils taken from fatigue fractured specimens in Mn containing materials revealed similar dislocation structure obtained during tensile deformation. Slip distribution was homogeneous as shown in Figure
III-46 but intense slip occurred by cyclic loading. This slip homogeneity was caused by Mn dispersoids as indicated in the tensile deformation. The influence of Mn dispersoids on fatigue behavior is well described[88,109], in addition to its beneficial influence on tensile properties[86] and toughness[110,111]. Mn dispersoids promote hardening within the slip bands and hence the slip distribution is homogenized. Edwards and Martin[109] described that mobile dislocations are reduced in each slip band for a given strain as the volume fraction of dispersoids increased. Therefore the rate of cyclic softening will be reduced by the slip homogenization[109].

It is appropriate at this point to define the local strain within the PFZ at which crack initiation and fracture occurs. Generally the local strain within the PFZ can be estimated by[117]:

$$\epsilon_{PFZ} = \mu/W$$

where $\mu$ is the amount of grain boundary sliding, $W$ is the width of PFZ. This estimation yields a high value of local deformation but the contribution to the overall macroscopic strain is very small. The contribution of the grain boundary sliding to total elongation was calculated by Brunner and Grant[123]. Their calculation assumes the following:

1) Shear plane(or grain boundary) extends through the thickness
of the specimen and normal to the surface of the specimen.

2) No significant interaction between the shear interface and the edge of the specimen.

The contribution of grain boundary sliding to total elongation is expressed by:

$$\delta = \frac{1}{W} \int_{-c'}^{+c'} \mu dt = \frac{1}{W} \int_{-c'}^{+c} \mu dx$$

where $\delta$ is the amount of contribution to total elongation, $W$ is the specimen width, $\mu$ is the amount of the grain boundary sliding, $\beta$ is the grain boundary angle to the stress axis as shown in Figure IV-3, and $c$ and $c'$ are the projections of the grain boundary to the vertical and horizontal axis, respectively. It was found that the contribution of grain boundary sliding to the total elongation was less in the high Pb alloys at slow strain rate tensile test than at fast strain rate or in the low Pb alloys both at slow and fast strain rate tensile tests. It was also found that the contribution of grain boundary sliding was greater in the high frequency fatigue tests (0.5Hz) than in the low frequency fatigue tests (9x10^-4Hz). This indicates that the shear deformation along grain boundary (i.e. PFZ) is predominant in the high Pb alloys at fast strain rate tensile tests or in the low Pb alloys at fast and slow strain rate tensile tests, as opposed to normal fracture to the grain boundary which occurs via tensile decohesion. This interpretation is also applicable to
the cyclic loading tests. However, the contribution to the total elongation is extremely small (i.e. maximum a few hundreds Å). If the matrix does not deform plastically at all and all PFZ's show the maximum displacement, then the macroscopic strain due to the deformation of PFZ's can be estimated [117]:

\[ \varepsilon_{PFZ} = \ln \left( \frac{D + \mu \sin \theta}{D} \right) \]

where \( D \) is the grain size, \( \theta \) is the angle between tensile axis and the normal of the specific grain boundary plane. This estimation shows that only a small amount of macroscopic strain arises due to local grain boundary deformation. Figure IV-4 shows the strain in the PFZ as a function of macroscopic strain for monotonic and cyclic loading experiments. Therefore, it can be concluded that the macroscopic strain is mainly determined by the plastic deformation of the age-hardened matrix [117].

Gerberich and Moody [118] have proposed for the micromechanisms of fatigue crack growth that the crack front region is described as a semicohesive zone, recognized first by Beevers et al [119-121] and McEvily [122] that the crack front is moving in a discontinuous manner near threshold with the front being held up at various points by microstructural obstacles. Figure IV-5 illustrates schematically the semicohesive zone ahead of main crack. Thus this concept can be applied to the mechanisms of fatigue
crack propagation in the Al-Mg-Si alloys containing Pb. If the intergranular fracture strain required to cause LDIGF is low, regions of LDIGF will be separated by the remaining unfractured ligaments. The brittle failure (i.e. LDIGF) of the ligaments during fatigue will depend on the applied ΔK and the crack tip strain rate.

At low levels of ΔK, the crack tip strain rate is low and the static mode failure is very small but some LDIGF may occur due to the low interfacial strength in the alloy containing high Pb. Therefore the fatigue crack propagation rate is controlled by the failure of remaining ligaments within the semicohesive zone. Since the crack tip strain rate is low enough to allow Pb diffusion to the crack tip during the low frequency fatigue the failure of the ligaments will occur by LDIGF at low fatigue crack propagation rate. Thus the fraction of LDIGF during fatigue crack propagation within the semicohesive zone will decrease with increasing frequency and increasing ΔK.

At high levels of ΔK, the crack tip strain rate is high and the static mode failure increases significantly as ΔK increases. For low frequency, the crack tip strain rate is still low enough to cause Pb diffusion to the crack tip but the degree of voiding ahead of the crack tip increases due to high ΔK. These voids will grow by LDIGF because of the low crack tip strain rate. However, for high frequency, the static mode of failure is predominant due to the high crack tip strain rate. The remaining ligaments are then subjected to high
stresses (i.e. $K_{\text{max}}$) as the fraction of voiding increases due to high $\Delta K$.

Therefore, IGMVC mode increases as $\Delta K$ increases. Subsequently the crack propagation rate across the ligament within the semicohesive zone will increase with $K_{\text{max}}$ as the crack tip opening displacement increases due to the high stresses.

It is now possible to estimate the local stress intensity factors causing the interactions of macrocrack with microcracks at the crack tips within the semicohesive zone. Rubinstein[114] calculated the local stress intensity factors at the macrocrack tip and microcrack tips. The macrocrack is represented as a semi-infinite crack and a collinear microcrack is located ahead of the macrocrack tip as shown in Figure IV-6. The local stress intensity factors are given in terms of macrocrack stress intensity factor (i.e. in the absence of microcrack) $K_I(\infty)$ by:

$$
\frac{K_I(0)}{K_I(\infty)} = \sqrt{\left(\frac{D}{D+2C}\right)} \frac{\Sigma \left[ 1 - \frac{D}{D+2C} \right]}{\Gamma \left[ 1 - \frac{D}{D+2C} \right]}
$$

$$
\frac{K_I(A)}{K_I(\infty)} = \left\{ \frac{D+2C}{D} \frac{\Sigma \left[ 1 - \frac{D}{D+2C} \right]}{\Gamma \left[ 1 - \frac{D}{D+2C} \right]} - 1 \right\} + \sqrt{(2C/D)}
$$
\[
\frac{K_t(B)}{K_t(\infty)} = \left\{ 1 - \frac{D}{D+2C} \right\} \sqrt{1 - \frac{D}{D+2C}} + \Gamma\left(1 - \frac{D}{D+2C}\right)
\]

where \(K_t(O), K_t(A)\) and \(K_t(B)\) are the local stress intensity factors at the macrocrack tip, \(O\), and microcrack tips, \(A\) and \(B\), \(\Gamma\) and \(\Sigma\) are the first and second complete elliptic integrals given by:

\[
\Gamma(m) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1-m^2\sin^2 \theta}}
\]

\[
\Sigma(m) = \int_0^{\pi/2} \frac{\sqrt{1-m^2\sin^2 \theta}}{\sqrt{1-m^2\sin^2 \theta}} d\theta
\]

Recently Shang and Ritchie[125] have applied this calculation to fatigue crack growth in SiC-reinforced Al alloy composites, revealing that the stress intensity at the microcrack tip nearest to the macrocrack tip may be as high as 74% of the applied \(K\) on the macrocrack. In their calculation[125] for the case of non-coplanar microcracks, the stress intensity at the microcrack tip near to the macrocrack tip is enhanced 40% of the applied \(K\) on the macrocrack. These high stress intensity factors at the microcrack tips may produce the fast failure of the ligaments between the microcrack and
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macrocrack. The crack growth rate will be controlled by the applied $K$ and the size of the ligament (i.e. the distance between the macrocrack and microcrack). If the size of the ligament is larger than the microcrack by two times there will be no interaction between the macrocrack and the microcrack[114]. Further growth of the microcrack will reduce the distance between the macrocrack and the microcrack. Therefore, the overall growth rate is controlled by the failure of the ligament (i.e. the growth of the microcrack).

Crack closure during fatigue crack growth has been known to be induced by the mechanisms such as oxide-induced closure, plasticity-induced closure or roughness-induced closure[129]. It was indicated that roughness-induced closure is prevalent near the threshold stress intensity range during fatigue crack propagation[129]. From the geometrical consideration as shown in Figure IV-7, the crack closure effect during fatigue is expressed by:

$$\frac{K_{cl}}{K_{max}} = \frac{2\gamma x}{\sqrt{1+2\gamma x}}$$

where $\gamma$ is the fracture surface roughness factor ($=h/\alpha d$, $d$ is the grain size and $\alpha$ is the ratio from $w=\alpha d$). The crack closure ratio ($K_{cl}/K_{max}$) is plotted as a function of the roughness factor in Figure IV-7 for various values of $x$ (i.e.
the ratio of Mode I and Mode II displacement)[129]. From the experimental
data[129] Mode II displacement was significant at low stress intensity ranges.
However, the roughness-induced crack closure can only occur at low load
ratio (i.e. R) due to the premature contact of fracture surfaces, and hence there
exists the critical ratio above which the crack closure effect can not be
considered. The critical load ratio[129] is:

\[ R_{ct} = \sqrt{h/\delta_{max}} \]

\( R_{ct} \) will be 0.2 even though Mode II displacement is maximum (i.e. \( x=1 \) in
Figure IV-7). In the present case, however, since the load ratio was 0.5, the
closure effect is not considerable for the present case.

3. Effects of Pb on Mechanical Behavior

**Tensile Tests**

It is well demonstrated by the tensile tests that the grain boundary
accommodation of deformation is predominant for the alloys containing high
Pb (i.e. >100ppm) at slow strain rate conditions, while the low Pb alloys (i.e.
<50ppm) are prevalent for the matrix deformation at the same conditions.
LDIGF is predominant for alloys containing high amount of Pb (i.e. >100 ppm) at slow strain rate condition (<10⁶/sec), while fracture is typically GMVC as the amount of Pb decreases and strain rate increases as shown in Figure III-58.

The deleterious effects of Pb were particularly well demonstrated in the tensile interruption tests. While it appears that Pb is released either from cracking or decohesion of inclusions, or from decohesion of Pb globules from the matrix, the tensile interruption tests demonstrate the effect(s) of allowing additional Pb diffusion to the crack surfaces (i.e. internal). High Pb alloys held at 80°C prior to retesting produced additional reductions in total elongation to failure. Low Pb alloys as well as those held only at room temperature exhibited considerably less reduction in ductility. Therefore, the availability of Pb appears to be a major controlling factor in this embrittlement phenomenon. However, the availability of Pb is accomplished only under the stress. Preheating at 80°C did not exhibited additional reduction in non-uniform strain as shown in Figure III-22. Thus, the Pb-induced embrittlement occurs by the dynamic Pb surface diffusion.

Impact Tests

The effect of Pb on the impact energy does not exhibit at low
temperatures (i.e. <250°C). On the other hand, the difference in the impact energy exhibit between the high Pb alloy (i.e. 100ppm) and the low Pb alloy at the temperatures above the melting temperature of Pb (i.e. 327°C). A SEM-EDS on the fracture surface of the alloy containing 100ppm Pb tested at 350°C revealed that Pb was associated with the large Fe-containing particle (see Figure III-40). The extensive cavitation was observed near the fracture surface of the alloy containing 100ppm Pb at temperatures above the melting temperature of Pb (see Figure III-39). Because Pb is liquid at these temperatures, these liquid Pb sites act as voids and promote cavities at these sites, and subsequently decrease the impact energy.

Fatigue Tests

The fracture strain of an alloy containing 500ppm Pb was reduced markedly in cyclic loading tests. The significant effect of Pb in cyclic loading tests was also shown in fracture mode transition. From the measurements of grain boundary sliding, the 500ppm Pb alloy loaded at 9x10^{-4}Hz exhibits lower amount of grain boundary sliding than that of other conditions. It is believed that crack initiation in the 500ppm Pb alloy at 9x10^{-4}Hz occurs by the tensile decohesion rather than the shear localization due to grain boundary sliding. Although it is not enough to determine the effect of Pb on
fatigue crack propagation, the present results revealed that the Pb effect on the fatigue crack propagation was predominant in the low frequency fatigue test (i.e. 0.2 Hz).

The fracture mode transition occurred at a higher stress intensity range (i.e. about 15MPa√m) at low frequency than that (i.e. about 9MPa√m) at high frequency (20 Hz). This difference is probably developed by the difference in the crack tip strain rate, in other words, the time available for the supply of Pb to the crack tip. Perkins[116] developed the crack tip strain rate model for a single crack subjected to cyclic loading during stress corrosion cracking. From his derivation[116], the crack tip strain rate given as the average plastic displacement rate for both triangular and sinusoidal waveforms is:

\[
\delta_{AV} = \frac{1}{2T G \sigma_y} (\Delta K)^2
\]

where \(T\) = one period of loading time
\(\Delta K\) = stress intensity factor range
\(G\) = shear modulus
\(\sigma_y\) = yield stress.

Crack tip strain rates will increase as frequency or \(\Delta K\) increases. Therefore
crack velocity increases and the transition in fracture mode from LDIGF to IGMVC occurs as $\Delta K$ increases. Figure IV-8 indicates the crack tip strain rate as a function of $\Delta K$ for different frequencies in the 500ppm Pb alloy. Figure IV-9 plots crack growth rate as a function of crack tip strain rate. The limits of crack tip strain rate for LDIGF are similar with the strain rate revealing Pb-induced SMIE in the monotonic tensile tests. The lower crack tip strain rate gives more more for Pb diffusion to the crack tip to induce LDIGF. The boundary for the transition in fracture mode will change with the amount of Pb in the alloy: the lower the amount of Pb the steeper the slop of the boundary between LDIGF and IGMVC. Eventually the region of LDIGF will disappear and IGMVC will be predominant in the low Pb alloy regardless of frequency during fatigue.

**External Pb Tests**

Crack growth was observed when Pb was supplied externally although crack growth was nonexistent and the stress intensity factor was below the threshold value before applying the external Pb to DCB specimens containing low amounts of Pb (i.e. 5 and 20 ppm). Auger fracture tests of crack tip regions indicated that Pb was covered uniformly over entire surface, revealing the likelihood that surface diffusion of Pb provided Pb to the crack tip.
regions. The crack growth rate, however, did not behave like an alloy containing high Pb in the sustained load tests. Auger analyses on those specimens revealed that an O signal was also detected on the fracture surface, indicating the presence of pre-existing O. It is then supposed that Pb surface diffusion or adsorption to the crack tip is inhibited by the barrier like oxides because the crack surface was exposed to laboratory air during measuring crack length. Recently, Lynch[72] has demonstrated that external In-induced crack growth in an Al alloy was decreased when the test was conducted in the air.

It was observed that crack growth was faster in the plane strain region indicated by bowing out of crack tip in the middle of crack surface even though Pb was supplied normal to the crack growth direction from the side surfaces. Then it is appeared that the triaxial stress state is important for Pb assisted fracture.

The effect of stress state on Pb assisted fracture was also shown in blunt notched and DCB specimens[67,113], where cracks initiated in the high stress region ahead of the notch and in the plane strain region. It was observed in the sustained load experiments[67] using bolt-loaded DCB specimens that IGMVC is typical at high K level regardless of amount of Pb in the alloy, while, at low K, LDIGF is predominant for alloys containing high amount of Pb. Consequently, in the absence of triaxial stress conditions, it is difficult to
obtain LDIGF under slow strain conditions unless high Pb levels are tested.

Auger Fracture Tests

In-situ Auger fracture tests revealed that the Pb signal observed on the freshly exposed surface decayed with exposure time in the UHV chamber. This can be rationalized by a variety of possibilities including volatilization of Pb from the surface. First, one may need to calculate the activity of Pb in the free surface of Al to get the vapor pressure of Pb. The thermodynamic activity of Pb on the fracture surface can be defined as\[131:\]

\[ a_{PB}^{Al(Surf)} = \frac{p_{PB}^{Al}}{p_{PB}^{o}} \]

where \( p_{PB}^{Al} \) is the partial pressure of Pb in Al, \( p_{PB}^{o} \) is the vapor pressure of Pb in the standard state which is shown in Figure IV-10. Therefore if we know the activity of Pb in Al we can get the partial pressure of Pb on the fracture surface. This activity is then related to the mole fraction in a non-ideal solution:
where $X_{\text{Al}}^{\text{Pb}}$ is the mole fraction of Pb and $\gamma_{\text{Pb}}$ is the activity coefficient. From the reference data[128], the activity coefficient of Pb is about 78.5 in the liquid state which is the extreme positive deviation from the ideal state. This value can be higher in the solid state of Pb due to the zero-solubility of Pb in Al. The fraction of Pb on the fracture surface is about 0.34a/o which was obtained from the measurement of the Auger peak height ratio $(I_{\text{Pb}}/I_{\text{Al}})$ in Figure III-36. Therefore the activity of Pb in Al is 26.69, or can be much higher than this value in the solid state because of the calculation in the liquid state and of the zero-solubility. This activity will be greater at the free surface of Al like a fracture surface. Then the partial pressure of Pb on the fracture surface is greater than the standard state. Hence the volatilization of Pb is considered as a possibility at ambient temperature. Next one may hypothesize that the oxidation of Pb and/or other element(i.e. Al, Si, Mg etc) inhibit the detection of Pb on the surface. Every element like Al, Mg, Si, Fe or Mn except Pb was detected on the specimen surface after long times in UHV Auger chamber as shown in Figure III-16. Figure III-36 of in-situ Auger fracture test indicates that an Al Auger spectrum changes with increasing time in chamber. It was experimentally observed that the Auger spectrum line shapes change as chemical states of elements are change at surfaces[115].
Figure IV-11 shows changes in the differential Al Auger spectrum as Al oxide forms on the surface[115]. Therefore the specimen surface oxidizes after a certain time even in UHV chamber but Pb should be still detected, like other elements in the alloy. Hence this may not be considered the possibility of decay of Pb. Therefore, the volatilization of Pb in UHV may be the most likely explanation for the decay of Pb on the fracture surface.

4. Proposed Mechanisms for SMIE

LDIGF is not typically observed in aluminum alloys tested under monotonic conditions. Although previous work[85,86,109-112] has indicated that Mn removal may promote intergranular fracture of a dimpled nature in fracture toughness and tensile tests, the present materials contain sufficient Mn to prevent low ductility intergranular fracture at fast strain rates. It follows that Pb facilitates both crack initiation and propagation. Under slow strain rate conditions, the PFZ's are preferred sites for deformation which promotes the tensile stress across the grain boundary. In high Pb alloys, cracks will preferentially initiate at the interfaces of Pb-containing particles situated in these regions as schematically shown in Figure IV-12(a). In contrast, the stronger interfaces in the low Pb alloys require additional stress and strain to decohere the interfaces. Thus, in the latter case, higher shear
stresses along the grain boundary result, thereby promoting dimpled fracture (Figure IV-12(b)). Crack nucleation rate on the grain boundary will increase as the amount of Pb in the alloy increases. Once a crack has initiated the crack will propagate with a continual supply of Pb (i.e. internal) to the crack tip. Therefore, the observation that LDIGF is not obtained in low Pb or high Pb alloys tested at fast strain rates, can be rationalized as due to the mobility of Pb which is insufficient to keep up with the growing crack.

Although there is no unified mechanism that is generally accepted for SMIE, it has been suggested that crack propagation is controlled by surface self-diffusion of embrittler over embrittler[20,69]. In such a transport of the embrittler[20], the rate of the embrittler surface self diffusion in multilayer is faster than that of monolayer diffusion because embrittler diffusion in multilayer would be like embrittler diffusion over embrittler, and the lower atomic layer of embrittler atoms are formed by "waterfall" effect rather than diffusion on substrate (see Figure I-7). Thus, this transport of embrittler is the most probable mechanism. The present results, although not quantitative, support such a mechanism since additional embrittlement as measured as loss in non-uniform strain was obtained in the tensile interruption tests where it is expected that additional Pb diffusion may occur during holding at high temperature. Embrittlement was also significantly enhanced by the external supply of Pb. Auger fracture tests of the crack tip region grown by the
external Pb indicates that the transport of Pb occurred by surface diffusion from the external source. Lewandowski et al.[113] calculated the activation energy of about 8.1 kcal/mol for the maximum crack velocity of the alloy containing 100 ppm Pb in the sustained load experiments, which is consistent with the activation energy for surface self-diffusion of Pb on Pb.

In the present work, the surface diffusion coefficient of Pb, $D_s$, was calculated from the area of LDIGF in the fatigue fracture surface using the random-walk diffusion equation:

$$D_s = \frac{x^2}{4t}$$

where $x$ is the diffusion distance (i.e. crack growth by LDIGF at a certain $\Delta K$ level). The surface diffusion of Pb calculated from this equation was about $10^{-12} \text{ m}^2/\text{sec}$ at room temperature. Now the crack velocity can be estimated by[51]:

$$v = \frac{2D_s}{r_p \frac{x^2}{x^2}}$$

where $r_p$ is the plastic zone size. For plane strain condition this crack velocity
can be expressed by:

\[ v = \frac{K^2D_s}{3\pi \sigma_y^2 x^2} \]

where \( \sigma_y \) is the yield stress. This calculation gives crack velocities in the range obtained experimentally as shown in Figure IV-13. The difference in crack velocities between calculation and experiments may be caused by the estimation of \( D_s(Pb) \) which was obtained on a two dimension surface assuming linear random-walk diffusion and not by taking into account three dimension sources.

The value of Pb surface diffusion calculated from the random-walk diffusion is included in Figure IV-14[72] to compare with the surface self-diffusion coefficients from other metals and other SMIE couples. This value is slightly different from data for clean surface self-diffusion obtained by the sintering of small particles, decay of scratches and grain boundary grooving[126,127] but it is reasonably close to the surface self-diffusion data range.

The fracture surface produced by Pb-induced SMIE is relatively featureless (e.g. Figure III-58) and some areas exhibit dimple-like cusps, indicating that the interaction of particle with PFZ left incomplete
cusps. It has been proposed[48-51,72] in LME that brittle fracture surfaces actually exhibit shallow dimples which are too shallow to be resolved by conventional SEM. Therefore crack growth involves nucleation and growth of voids around grain boundary precipitates[48-51,72]. In the present case, however, the shallow dimples on LDIGF were not observed even in the high resolution SEM, indicating that Pb weakens the interface with the matrix and thereby facilitates the nucleation of brittle crack-like voids, and crack growth occurs by the coalescence of these brittle voids.

A general approach to the embrittlement phenomena can be made using the Griffith equation[130]:

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi c}}$$

where $\sigma_f$ is the breaking stress, $E$ is Young's modulus, $\gamma'$ is the total energy required per unit increase in area of crack, comprising the true surface energy and plastic work done by the stress concentration at the moving crack tip, and $c$ is the half-crack length. McLean[132] rearranged this equation by replacing $\gamma'$ to the true surface energy $\gamma$ and a term $\alpha \sigma_f$ (where $\alpha$ is a constant) to represent the plastic work:
\[ \sigma_f = \left( \frac{2E_\gamma}{\beta \pi c} \right)^{1/2} \]

where \( \beta = (1-2E\alpha/\pi c) \). Now \( \gamma \) is the important factor controlling the amount of plastic work done. For a cleavage fracture, \( \gamma = 2\gamma_s \) where \( \gamma \) is the fracture surface energy, while for an intergranular fracture

\[ \gamma = (2\gamma_s - \gamma_b) \]

where \( \gamma_b \) is the grain boundary energy per unit area, since the energy of the two new fracture surfaces is partly offset by the grain boundary along which fracture is taking place.

If an impurity segregates to the grain boundary by the Gibbs surface adsorption, the surface energy of solid metals can be reduced not by reducing \( \gamma_b \) but by reducing the much larger term \( 2\gamma_s \) since the grain boundary impurity is the surface-active[132]. In particular, Pb can be a highly surface-active impurity in the present alloy. Then the surface activity of Pb can be calculated using the Gibbs adsorption equation for a dilute solution[131]:

\[ \frac{\partial \gamma_s}{\partial X} = - \frac{RT \Gamma}{X} \]
where $X$ is the bulk concentration of impurity and $\Gamma$ is the excess concentration. For the present system, $X_{\text{pb}}=6.5\times10^3$ a/o (i.e. 500ppm) and $\Gamma=1.46\times10^6$ mole/m$^3$[131], then the adsorption parameter i.e. the surface activity of Pb in Al is:

$$\gamma_s \quad = \quad 5.52\times10^3 \text{erg/cm}^2 \text{ a/o}$$

This value is comparable with the value of $8\times10^3$ erg/cm$^2$ for the Cu alloy exhibiting embrittlement by the addition of Sb in creep tests[133]. Even though the embrittlement of Cu-Sb system is different with the present work in the regard of LDIGF, the reduction in the surface energy may induce the embrittlement effect by the addition of Pb. At equilibrium (no plastic flow) $\gamma_s=1220$ erg/cm$^2$ and $\gamma_b=405$ erg/cm$^2$ in Al[134]. Then, the true surface energy $\gamma(=2\gamma_s-\gamma_b)=2035$ erg/cm$^2$ in Al for the intergranular fracture, while $\gamma=330$ erg/cm$^2$ in the Al-Pb system[47]. Subsequently the breaking stress($\sigma_b$) required to initiate fracture on the Griffith model is reduced by the reduction of $\gamma$ from 2035 erg/cm$^2$ to 330 erg/cm$^2$ due to the Pb segregation on Al. Therefore the embrittlement effect of Pb for the present work is the consequence of the reduction in the surface energy even though these values obtained in the liquid state of Pb.
The development of brittle failure may be considered with reference to Figure IV-15. The crack-like void will initiate at the weak interface containing Pb within the PFZ. Under stress condition, the continual supply of Pb from the three dimensional sources occurs to the internal and external crack tip. Pb diffusion to the crack surface leads to an appreciable reduction in the surface energy. Thus the brittle crack can develop which greatly reduce the stress required to initiate LDIGF.
V. Conclusions

1. The sources of Pb and LDIGF sites have been identified:
   
   In low Pb alloys, Fe-containing inclusions provide the primary source of Pb while a variety of sites were identified for the high Pb material.

2. Increasing the availability of Pb enhances the following during deformation:
   
   a) Grain boundary accommodation of slip
   
   b) Reduction of non-uniform strain to failure

3. Fracture mode transition from IGMVC to LDIGF occurred as the amount of internal Pb increases and strain rate (i.e. crack tip strain rate) decreases.
   
   The deleterious effect of Pb was also observed by the external Pb.

4. LDIGF occurred along the grain boundary by the continual supply of Pb to the crack tip region.

5. The cracks ahead of main crack indicate the importance of triaxial stress state in the Pb-assisted fracture.

6. The rapid coverage of Pb on the Auger fracture surface indicates the rapid surface diffusion of Pb from the Pb sources on the fracture surface.
VI. Proposed Future Works

The rapid coverage of Pb on the Auger fracture surface decayed with time in the UHV chamber. Even though the plausible explanations indicated the possibility of the volatilization of Pb in the UHV chamber, the reason why Pb disappears from the surface remains elusive because Pb was detected in the material from the depth profiling with time both in the air and in vacuum[67,113]. In those experiments[67,113], Pb was vapor-deposited onto the Pb-free polycrystalline Al alloy. The subsequent depth profiling revealed that Pb signals were detected in the material and the depth for detecting of Pb was increased with increasing time, while Pb signals decayed on the surface of the material at room temperature in the air as well as in vacuum. Thus the volatilization and the diffusion of Pb appear to be competitive. Therefore it is necessary to conduct the analysis in more detail. Pb deposit on the small-grained polycrystalline Al alloy. Subsequently the high resolution Auger depth profiling is utilized on the surface in UHV chamber. The specimen will be kept both in air and in UHV chamber. The sequential Auger depth profiling will provide the dominant process (i.e. volatilization or surface diffusion) depending on the condition. The volatilization would be dominant in the UHV chamber as discussed in section IV-2, while the diffusion through the material would be possible in the air due to the extremely low vapor
pressure of Pb.

Many of the observations obtained from the present work are similar to a creep mechanism. However, the present work and previous work[67] has demonstrated that large-grained material exhibited more embrittling effects in the presence of internal Pb than did the small-grained materials, in contrast to the conventional creep. The measurement of grain boundary sliding indicated the difference depending on the amount of Pb in the material and the loading rate. Thus the grain boundary sliding is the another controlling factor to elucidate the mechanisms for deformation because several mechanisms including creep can be applied to the present embrittlement. Therefore, creep experiments for the present material will provide the additional information for the mechanisms of Pb-induced embrittlement.

It has been reported in the literature that Al and Al alloys are embrittled by elements such as Bi, Cd, In, Ga, Hg, Sn, Na, Sn-Zn and Pb-Sn in the liquid state of the embrittler. From the result of the present work, the present alloy (i.e. 6351 Al alloy) is expected to embrittle by the other low melting point elements such as Bi, In or Sn at room temperature. This proposed embrittlement system will provide the guidance for understanding the mechanisms of the Pb-assisted fracture of the present system.
References


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Tables
Table I-1. Occurrence of LME in Ferrous Alloys\cite{15,16&25}.

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Table I-2. Occurrence of LME in Non-Ferrous Alloys[15,16&25].

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Table I-3. Occurrence of SMIE in Ferrous Alloys[71].

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<td></td>
<td>Cd</td>
<td>38 C</td>
<td>DF</td>
<td>S</td>
</tr>
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<td></td>
<td>Zn</td>
<td>400 C</td>
<td>DF</td>
<td>N</td>
</tr>
<tr>
<td>4340M</td>
<td>Cd</td>
<td>38 C</td>
<td>DF</td>
<td>S</td>
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<td>288 C</td>
<td>ST</td>
<td>S</td>
</tr>
<tr>
<td>8620 leaded</td>
<td>Pb</td>
<td>204 C</td>
<td>ST</td>
<td>S</td>
</tr>
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<td>A-4</td>
<td>Pb</td>
<td>288 C</td>
<td>ST</td>
<td>S</td>
</tr>
<tr>
<td>A-4 leaded</td>
<td>Pb</td>
<td>204 C</td>
<td>ST</td>
<td>S</td>
</tr>
<tr>
<td>D6ac</td>
<td>Cd</td>
<td>149 C</td>
<td>DF</td>
<td>N</td>
</tr>
</tbody>
</table>

Key:
DF - Delayed Failure Tensile Test
ST - Standard Tensile Test
N - Notched Specimen
S - Smooth Specimen
NA - No Available Data
Table I-4. Occurrence of SMIE in Non-Ferrous Alloys[71].

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Brittle</th>
<th>Temperature (°C)</th>
<th>Test Method</th>
<th>Specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Mg-Si</td>
<td>In</td>
<td>-4 - 80</td>
<td>SUS</td>
<td>DCB</td>
</tr>
<tr>
<td>Al-Zn-Mg</td>
<td>Cd</td>
<td>38</td>
<td>SUS</td>
<td>DCB</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Cd</td>
<td>149</td>
<td>BE</td>
<td>S</td>
</tr>
<tr>
<td>Ti-8Al-1Mo-</td>
<td>Cd</td>
<td>149</td>
<td>BE</td>
<td>S</td>
</tr>
<tr>
<td>1V</td>
<td></td>
<td>149</td>
<td>BE</td>
<td>S</td>
</tr>
<tr>
<td>Ti-3Al-14V-</td>
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<td>149</td>
<td>BE</td>
<td>S</td>
</tr>
<tr>
<td>11Cr</td>
<td></td>
<td>149</td>
<td>BE</td>
<td>S</td>
</tr>
<tr>
<td>Ti-6Al-6V-</td>
<td>Cd</td>
<td>204-232</td>
<td>BE</td>
<td>S</td>
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<td>BE</td>
<td>S</td>
</tr>
<tr>
<td>Ag</td>
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<td>Au</td>
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<td>S</td>
</tr>
<tr>
<td>Cu-Bi(U)</td>
<td>Hg</td>
<td>-48</td>
<td>ST</td>
<td>S</td>
</tr>
<tr>
<td>Cu-Bi(S)</td>
<td>Hg</td>
<td>-46</td>
<td>ST</td>
<td>S</td>
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<td>S</td>
</tr>
<tr>
<td>Cu-1%Zn(S)</td>
<td>Hg</td>
<td>-51</td>
<td>ST</td>
<td>S</td>
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<tr>
<td>Sn Bronze</td>
<td>Pb</td>
<td>300</td>
<td>ST</td>
<td>S</td>
</tr>
<tr>
<td>Zn</td>
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<td>S</td>
</tr>
<tr>
<td>Inconel</td>
<td>In</td>
<td>300</td>
<td>ST</td>
<td>S</td>
</tr>
<tr>
<td>Zr-2</td>
<td>Cd</td>
<td>300</td>
<td>ST</td>
<td>S</td>
</tr>
</tbody>
</table>

U-Unsegregated  
S-Segregated  

SUS-Sustained load test  
DF-Delayed failure test  
BE-Bending test  
ST-Standard tensile test  
IM-Impact tensile test  
RE-Residual stress test  

DCB=Double cantilever beam  
SF-Smooth flat tensile  
S-Smooth specimen
Table II-1. Chemical Compositions of Alloys.

<table>
<thead>
<tr>
<th>Mg</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Fe</th>
<th>Zr</th>
<th>Ti</th>
<th>Pb</th>
<th>Al</th>
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</thead>
<tbody>
<tr>
<td>.62</td>
<td>1.06</td>
<td>.55</td>
<td>.001</td>
<td>.24</td>
<td>.02</td>
<td>.014</td>
<td>.0005</td>
<td>Rem</td>
</tr>
<tr>
<td>.62</td>
<td>1.01</td>
<td>.59</td>
<td>.007</td>
<td>.25</td>
<td>.02</td>
<td>.013</td>
<td>.002</td>
<td>Rem</td>
</tr>
<tr>
<td>.62</td>
<td>.99</td>
<td>.58</td>
<td>.007</td>
<td>.23</td>
<td>.02</td>
<td>.017</td>
<td>.005</td>
<td>Rem</td>
</tr>
<tr>
<td>.62</td>
<td>1.00</td>
<td>.55</td>
<td>.007</td>
<td>.24</td>
<td>.03</td>
<td>.012</td>
<td>.01</td>
<td>Rem</td>
</tr>
<tr>
<td>.62</td>
<td>1.02</td>
<td>.56</td>
<td>.007</td>
<td>.23</td>
<td>.03</td>
<td>.016</td>
<td>.05</td>
<td>Rem</td>
</tr>
</tbody>
</table>
Table III-1. FEG/STEM EDS results for an alloy containing 500ppm Pb[101].

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Al</th>
<th>Mg</th>
<th>Si</th>
<th>Cu</th>
<th>Pb</th>
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</thead>
<tbody>
<tr>
<td>Rod Precipitate</td>
<td>88.7</td>
<td>2.6</td>
<td>8.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>73.7</td>
<td>6.7</td>
<td>18.9</td>
<td>0.2</td>
<td>0.1</td>
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<tr>
<td>Grain Boundary</td>
<td>99.4</td>
<td>-0.8</td>
<td>0.5</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Ppt. Interface</td>
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<td>-0.6</td>
<td>6.8</td>
<td>0.3</td>
<td>0.2</td>
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<tr>
<td>Matrix -50nm</td>
<td>99.4</td>
<td>-0.5</td>
<td>0.9</td>
<td>0.2</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td>100.2</td>
<td>-0.8</td>
<td>0.5</td>
<td>0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td></td>
<td>99.9</td>
<td>-0.8</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>-0.7</td>
<td>0.5</td>
<td>0.2</td>
<td>-0.1</td>
</tr>
<tr>
<td>Grain Boundary 0nm</td>
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<td>0.4</td>
<td>0.7</td>
<td>0.1</td>
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<tr>
<td>Matrix +5nm</td>
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<td>-0.7</td>
<td>0.5</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>99.7</td>
<td>-0.7</td>
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<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>99.8</td>
<td>-0.8</td>
<td>0.6</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>99.9</td>
<td>-0.9</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
</tr>
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</table>
Table III-2. Flow stresses of high temperature tensile tests.

<table>
<thead>
<tr>
<th>Pb Level (ppm)</th>
<th>Homogenize (°C)</th>
<th>RT</th>
<th>Test1 (MPa)</th>
<th>Test2 (MPa)</th>
<th>Test3 (MPa)</th>
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</thead>
<tbody>
<tr>
<td>5</td>
<td>450</td>
<td>270</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>20</td>
<td>450 570</td>
<td>290</td>
<td>282 312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>450 570</td>
<td>259</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>450 570</td>
<td>255</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>450 570</td>
<td>277</td>
<td>7.5*, 9f**</td>
<td>77</td>
<td>292</td>
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</table>

* 450°C
** R.T.
Table III-3. SEM observations of impact specimens.

<table>
<thead>
<tr>
<th>Temp(°C) Pb(cpsm)</th>
<th>RT</th>
<th>100</th>
<th>250</th>
<th>350</th>
<th>450</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>S</td>
<td></td>
<td>TGMVC</td>
<td>DNF</td>
<td>DNF</td>
<td></td>
<td>Low void density above Pb mp</td>
</tr>
<tr>
<td>5(-Mn+Cr)</td>
<td>IGMVC</td>
<td>TGMVC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>IGMVC</td>
<td>TGMVC</td>
<td>IGMVC</td>
<td>TGMVC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>TGMVC</td>
<td></td>
<td>TGMVC Pb w/Fe-Mn-Si inclusions</td>
<td>DNF</td>
<td>High void density above Pb mp</td>
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</tbody>
</table>

IGMVC: Intergranular Microvoid Coalescence
TGMVC: Transgranular Microvoid Coalescence
DNF: Did Not Fracture
Table III-4. Comparison of fracture strain for monotonic and cyclic tensile tests.

<table>
<thead>
<tr>
<th>Pb Level (ppm)</th>
<th>Homogenize (°C)</th>
<th>Tensile test*</th>
<th>Fatigue</th>
<th>Elongation (%)</th>
<th>Tensile Interruption test</th>
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<tr>
<td>5</td>
<td>450</td>
<td>12</td>
<td>-</td>
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<td>16.3 14.7</td>
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<tr>
<td></td>
<td>570</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>450</td>
<td>10</td>
<td></td>
<td></td>
<td>16.3 14.7</td>
</tr>
<tr>
<td></td>
<td>570</td>
<td>16</td>
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<td></td>
<td>570</td>
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<td></td>
</tr>
<tr>
<td>100</td>
<td>450</td>
<td>9</td>
<td></td>
<td></td>
<td>15.5 14.3</td>
</tr>
<tr>
<td></td>
<td>570</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>450</td>
<td>7</td>
<td>4.5 6.7</td>
<td></td>
<td>14.1 12.0</td>
</tr>
<tr>
<td></td>
<td>570</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 6x10^-6 / sec  
f1=9x10^6 Hz  
f2=0.5Hz  
RT=Room temperature holding after interruption  
80 C=80 C holding after interruption
Table III-5. Comparison of roughness of fatigue fracture surface.

<table>
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<tr>
<th>Parameter</th>
<th>20Hz</th>
<th>0.2Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Peak-to-Valley</td>
<td>34.55μm(12.56μm)</td>
<td>46.70μm(11.81μm)</td>
</tr>
<tr>
<td>Height</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean Roughness</td>
<td>6.73μm(2.49μm)</td>
<td>9.46μm(2.86μm)</td>
</tr>
<tr>
<td>Max. Roughness</td>
<td>53.99μm(27.82μm)</td>
<td>62.21μm(19.44μm)</td>
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<tr>
<td>Waviness Height</td>
<td>65.49μm(21.0μm)</td>
<td>89.84μm(30.26μm)</td>
</tr>
</tbody>
</table>

*Standard deviation*
Figures
Figure I-1. The schematic illustrates the effect of liquid metal environment on the stress-strain.
Figure I-2. Effect of temperature on embrittlement due to liquid and solid metals[40].
Figure I-3. (a) Potential energy functions $u(r)_s$ and $u(r)_a$ vs. $r$ in the presence and absence of liquid metal. (b) Stresses $\sigma_s$ and $\sigma_a$ to separate atomic planes in the presence and absence of liquid metal [45 & 46].
Figure I-4. Diagram illustrating crack growth in liquid metal environment[48].
Figure I-5. Ratio of reduction of area for leaded to non-leaded 4145 steel as a function of strength level showing SMIE and LME[19].
Figure I-6. Comparison of normalized fracture strength and reduction of area as a function of homologous temperature for 4140 steel surface wetted by several embrittlers[20].
Figure 1-7. Two possible mechanisms of embrittler surface diffusion. 
(a) Diffusion of embrittler atoms in a monolayer along the steel crack surface. Embrittler atoms move by heterogeneous surface diffusion steel substrate atoms. 
(b) Multilayer movement of embrittler on substrate by surface self-diffusion of embrittler over its own surface[20].
Figure 1-8. Diagram illustrating mechanism of intercrystalline crack growth in Al alloys, involving nucleation and growth of voids in soft precipitate-free zone containing grain boundary precipitates in embrittling solid-metal environments[72].
Figure I-9. Quasi-binary section of Al-Mg-Si alloys[73].
Figure I-10. Solute solubility limits of Al-Mg-Si alloys[73].
Figure I-11. Estimate of critical temperatures as a function of the amount of \( \text{Mg}_2\text{Si} \) in Al-Mg-Si alloys[82].
Figure I-12. The effect of Mn on slip band spacing as a function of compressive engineering strain[86].
Figure I-13. Al-Pb phase diagram.
Figure I-14. The effects of Pb level and applied stress intensity factor, $K$, on the crack velocity in bolt-loaded DCB specimens tested (a)-4°C, (b) room temperature and (c) 80°C[67].
Figure 1-14 (cont'd).
Figure II-1. Schematic of electron-specimen interaction[92].
Figure II-2. Schematic showing the locations of Auger line scans across grain boundary.
Figure II-3. Al-Ga system.
Figure II-4. Arrangement for Ga embrittlement experiment.
Figure II-5. Dimensions of (a) smooth flat and (b) smooth round tensile specimens.
Figure II-6. Regular array of carbon grids on a polished flat tensile specimen. (a)200x (b)500x.
Figure II-7. Schematic showing macro- and local-strain measurements in a tensile specimen.
Figure II-8. Schematic illustrating the tensile interruption test in stress-strain curve.
Figure II-9. Specimen dimension for Auger fracture test.
Figure II-10. Dimension of an impact specimen.
Figure II-11. Cycle shapes and load ranges for (a) $9 \times 10^{-4}$ Hz (b) 0.5 Hz in axial fatigue test of smooth flat tensile specimen.
Figure II-12. Dimension of a three-point bending fatigue specimen showing the locations of current probe and potential probe.
Figure II-13. Block diagram of potential drop (PD) system for crack growth measurement during three-point bending fatigue.
Figure II-14. Dimension of a bolt-loaded DCB specimen.
Figure II-15. Schematic illustrating the locations of Auger fracture specimens in a DCB specimen containing 5ppm Pb tested by external Pb.
Figure II-16. Specimen dimension for in-situ SEM observation.
Figure III-1. Optical micrographs revealing two different grain sizes by homogenizing at (a) 570°C/2hrs and (b) 450°C/12hrs.
<table>
<thead>
<tr>
<th></th>
<th>450 °C</th>
<th>570 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Mn + 26Cr</td>
<td><img src="a.png" alt="Image" /></td>
<td><img src="a.png" alt="Image" /></td>
</tr>
<tr>
<td>b. 25Mn + 17Cr</td>
<td><img src="b.png" alt="Image" /></td>
<td><img src="b.png" alt="Image" /></td>
</tr>
<tr>
<td>c. 42Mn + 17Cr</td>
<td><img src="c.png" alt="Image" /></td>
<td><img src="c.png" alt="Image" /></td>
</tr>
<tr>
<td>d. 55Mn</td>
<td><img src="d.png" alt="Image" /></td>
<td><img src="d.png" alt="Image" /></td>
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</table>

Figure III-2. Optical micrographs showing Mn effect on grain size for two different homogenizing temperatures.
Figure III-3. TEM micrographs of alloys containing (a) 0.55% Mn and (b) 0.23% Cr. Both alloys were homogenized at 450°C.
Figure III-4. TEM micrographs of 100ppm Pb alloys homogenized at (a) 450°C and (b) 570°C.
Figure III-5. Dispersoid size as a function of Mn addition.
Figure III-6. Relative and cumulative frequencies of particle sizes for 100ppm Pb alloy homogenized at (a,b)450°C and (c,d)570°C.
Figure III-7. A TEM micrograph showing fine aging precipitate $\text{Mg}_2\text{Si}$ in the 100ppm Pb alloy homogenized at 450°C and deformed to fail at tensile strain rate of $10^4$/sec.
Figure III-8. (a) A TEM micrograph showing PFZ along the grain boundary. (b) EDS analyses from the locations of A, B and C across a grain boundary in (a).
Figure III-8 (cont'd).
Figure III-9. A TEM micrograph showing faceted particles (arrows) at grain boundary in the 100ppm Pb alloy homogenized at 450°C.
Figure III-10. SEM micrograph of (a) grain boundary precipitates and (b) the matching grain boundaries after decohesion by the liquid Ga showing grain boundary precipitates and the matching depressions on the opposite grain surface of a 500ppm Pb alloys homogenized at 450°C.
Figure III-11. (a) A TEM micrograph of large Fe-containing particle in the small-grained 5ppm Pb alloy and (b) its EDS analysis showing the elements of Al, Si, Mn and Fe.
Figure III-12. (a) A TEM micrograph of large Fe-containing particle in the small-grained 5ppm Pb alloy (with Mn+Cr) and (b) its EDS analysis showing the elements of Al, Si and Fe.
Figure III.13. (a) A TEM micrograph showing the locations of EDS analyses across grain boundary of a small-grained 100ppm Pb alloy and (b) their EDS spectra indicating Pb peaks at the grain boundary region and a particle on the grain boundary.
Figure III-14. (a) A secondary electron image of the particle in a large-grained 500ppm Pb alloy, (b) an Auger map for Pb and (c) an Auger spectrum indicating Pb association with a Fe-containing particle.
Figure III-15. Auger line scans of (a)Pb, (b)Si, (c)Fe and (d)Mn across the grain boundary in a large-grained 500ppm Pb alloy.
Figure III-16. Auger line scans of same location shown in Figure III-15 after 2 days.
Figure III-17. A TEM micrograph showing $\beta'$ rod in the matrix, Mn-Fe intermetallic and PFZ along the grain boundary in a small-grained 500ppm Pb alloy[101].
Figure III-18. (a) A secondary electron image of the grain boundary surface fractured by the liquid Ga showing the locations of Auger survey and (b) Auger analyses showing Pb in and near a large void.
Figure III-19. Local strain vs. macro-strain measurements for the different Pb levels at slow((a),(b)) and fast((c),(d)) strain rate. Solid lines compare data for the 500ppm and 20ppm Pb specimen.
Figure III-20. Deformed grid surfaces of (a) a large-grained 500ppm Pb alloy, (b) a large-grained 20ppm Pb alloy, (c) a small-grained 5ppm Pb-Mn-Cr alloy tested at slow strain rate and (d) a small-grained 100ppm Pb alloy tested at fast strain rate.
Figure III-20 (cont'd)
Figure III-20(cont'd). (c)
Figure III-21. Deformed grid surfaces of (a) a large-grained 500ppm Pb alloy at 2.2%, (b) a large-grained 20ppm Pb alloy at 2% by slow strain rate tensile test. Arrows indicate the grain boundaries in (a) and the matrix slip lines in (b).
Figure III-22. Non-uniform strain to failure vs. Pb level. Data obtained in the tensile interruption tests.
Figure III-23. Cumulative locations of grain boundary failure vs. angle to stress axis.
Figure III-24. A TEM micrograph showing dislocation structure of the small-grained 100ppm Pb alloy strained to 0.3% by slow strain rate.
Figure III-25. A TEM micrograph showing dislocation pile-ups in the same alloy of Figure III-24.
Figure III-26. A TEM micrograph showing planar slip bands in the same alloy strained to 0.4% of Figure III-24.
Figure III-27. A TEM micrograph of dislocation cutting through aging particles and dislocation debris around Mn dispersoids. Specimen taken from the small-grained 5ppm Pb alloy strained to 1.2% by slow strain rate.
Figure III-28. Slip band spacing as a function of Mn level in the alloys at 1-1.2% plastic strain.
Figure III-29. TEM micrographs showing slip bands in the alloys of Figure III-28. (a)6061 alloy, and 6351 alloys containing (b)-Mn+0.26%Cr, (c)0.25%Mn+0.17%Cr and (d)0.55%Mn.
Figure III-30. TEM micrographs showing slip bands parallel to \{111\} in a 5ppm Pb alloy containing -Mn+Cr.
Figure III-31. A TEM micrograph of the small-grained 100ppm Pb alloy strained by slow strain rate, showing dislocation half-loops in the PFZ and dislocation locking at the border of PFZ and matrix. Beam direction [001].
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Figure III-69(cont'd).
Figure III-69 (cont'd).
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