JANG, SEONHEE. Molecular Dynamics Simulations of Plastic Deformation in Nanocrystalline Metal and Alloy. (Under the direction of Prof. Ronald O. Scattergood.)

Nanocrystalline metals have different mechanical properties from conventional grain sized metals. Hardness and yield strength have been found to increase with decreasing grain size in the nanocrystalline regime down to at least 15 nm on the basis of Hall-Petch mechanisms. Below grain sizes of ~10 nm, the strength decreases with further grain refinement, leading to the inverse Hall-Petch effect. Although the experimental evidence has found these deformation responses in nanocrystalline materials, the underlying mechanisms are not well identified. Molecular dynamics simulations were carried out for uniaxial tensile straining of two-dimensional columnar microstructures of aluminum (Al) and aluminum-lead (Al-Pb) alloys. Pure Al has a critical grain size at $d_c \approx 15$ to 20 nm, the crossover from ‘normal’ to ‘inverse’ Hall-Petch effect, accompanied with intra-grain mechanisms by partial dislocations and twins as grain sizes increases. With increasing grain size there exists a transition in plastic deformation mechanism from inter-grain processes to one that consists of both inter-grain and intra-grain processes. For Al-Pb alloys with a 10 nm grain size, Pb segregates completely to the grain boundaries and the grain boundaries become wider and more disorganized as the Pb content increases. A softening effect was observed in agreement with, but less than that found experimentally. As the Pb content increases, partial dislocation nucleation at grain boundaries is completely suppressed and the plastic strain is accommodated by mechanisms other than dislocation slip. As the grain sizes increase up to
15 or 20 nm, dislocation generation at grain boundaries is also suppressed. However, dislocation generation is not entirely suppressed at 3 equivalent at% Pb, compared to the 10 nm grain size showing complete suppression.
Molecular Dynamics Simulations of Plastic Deformation in Nanocrystalline Metal and Alloy

by

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DEDICATION

To my father: a gift of paper for his 60th birthday August 20, 2007
BIOGRAPHY

Seonhee Jang, born December 21, 1973 in Cheonan, Korea, has a family which her father was a government officer and her mother was affectionate. Her mother encouraged her to participate in a variety of activities such as science, music and paint. Among these experiences, she was especially interested in science. After graduation from high school in her hometown she entered SungKyunKwan University to study physics. During her senior year as an undergraduate, she took a tour to a semiconductor company for the first time and was impressed with how advanced technology devices are manufactured. She made a decision to specifically study semiconductor processing for her master degree in SungKyunKwan University. After her master degree, she worked as an assistant manager for a patent law firm for two and half years. In spite of her successful career working for company, she always had a dream of becoming a scientist so she decided to study abroad to get expert knowledge of materials science and engineering. She went on to attend the University of Utah and later transferred to North Carolina State University in 2003. She will get a Ph.D in December, 2007 and join Samsung Electro-Mechanics in Korea.
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CHAPTER 1
INTRODUCTION

1.1 GENERAL INTRODUCTION

Richard Feynman says in his famous book: Feynman’s Lectures on Physics [1]. “If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact, or whatever you wish to call it) that all things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.” The atomistic level for studying materials provides a most fundamental and for a fundamental understanding, we should capture the elementary physics of single atoms and expand the length scales of thousands of atomic layers. Atomistic simulations are widely used to investigate phenomena-structural, electrical, mechanical, and so on- at the atomic scale. Among those phenomena, for the functionality and reliability of “the next generation of creatures” such as microelectromechanical systems (MEMS), nanoelectromechanical systems (NEMS), integrated circuits, and micro- and nanoscale devices, mechanical properties of the nanocrystalline materials become important factors [2].
For the purpose of discussion throughout this dissertation, we need to define nanocrystalline metals and alloys as those with an average grain size smaller than 100 nm. Ultrafine crystalline metals and alloys have an average grain size in the 100-1000 nm range, whereas microcrystalline ones are taken to be those grain sizes of a micrometer or larger. FIG. 1.1 shows the variation of yield stress as a function of grain size in microcrystalline, ultrafine crystalline and nanocrystalline regimes [3]. In many metals and alloys with an average grain size of 100 nm or larger, i.e., microcrystalline and ultrafine crystalline regime, strengthening occurs with grain refinement on the basis of the Hall-Petch mechanism [4-6]. With further grain refinement, the stress peaks at an average grain size on the order of 10 nm in many cases and further decreasing in grain size can cause softening. This transition is the inverse Hall-Petch mechanism.
Several experimental techniques have been developed to produce nanocrystalline and ultrafine crystalline materials and these are used to obtain a clear mechanistic understanding of the mechanical response. They are classified into the following four groups: (1) mechanical alloying (including cryomilling) and compaction [7-10], (2) gas phase condensation of particulates and consolidation [11-13], (3) electrodeposition [14-17], and (4) severe plastic deformation [18]. Severe plastic deformation methods provide ultrafine grain sized material, whereas mechanical alloying, gas phase condensation and electrodeposition methods are capable of producing material with mean grain size in the tens of nanometers range. Mechanical alloying has been particularly successful in manufacturing aluminum alloys [9, 10]. The advantage of this method is that it produces reasonable size billets of material; however, its disadvantage is difficulty in controlling material purity and obtaining full density. Gas phase condensation has been used to produce nanocrystalline metals such as Cu, Ni and Pd. The process has several limitations including specimen volume and yield, purity issues, incomplete densification/porosity, and difficulties retaining the fine grain size during consolidation. Electrodeposition has been used to produce nanocrystalline metals (for example, Ni, Cu and Co) and binary alloys (for example, Ni-Fe and Ni-W). The grains often contain impurities such as carbon and sulfur because of the use of saccharin during processing. However, effort has been made to improve the synthesis of nanocrystalline metals using electrodeposition method.
Nanocrystalline material has been produced using the above synthesis methods and the mechanical properties of fcc metals (Cu, Ni, Pd, Al) characterized using uniaxial tension and microindentation loading have been reported [13, 16, 19-25]. Hardness and yield strength have been found to increase with decreasing grain size in the nanocrystalline regime (<100 nm) down to at least 15 nm. In this region, dislocation activity is primarily believed to originate and terminate at grain boundaries. Below grain sizes of ~10 nm, the strength decreases with further grain refinement, leading to an inverse Hall-Petch effect [26-30]. In this regime, grain boundary deformation mechanisms constitute the dominant deformation modes. Although the experimental evidence points to these unusual deformation responses in nanocrystalline materials, the underlying mechanisms are not well identified. Moreover, it is difficult to investigate deformation mechanisms as a function of grain sizes because of difficulty in preparing artifact free samples.

As the grain size decreases in nanocrystalline materials, computer simulations become a powerful tool for investigation of deformation mechanisms. The use of large-scale molecular dynamics (MD) simulations to obtain atomic level structural information in nanocrystalline fcc metals has significantly enhanced the understanding realized from experiments. Most simulations have been performed on fcc pure metals, such as Au, Ag [31-34], Cu [31, 35-39], Pt [31, 35], Ni [39, 40-43], Al [44] and several alloys [20, 40, 45]. A fully three dimensional (3D) nanocrystalline grain boundary network or a two dimensional (2D) columnar grain boundary network have been constructed for the simulations. The synthesis of three dimensional nanocrystalline materials can be accomplished by (a) cluster assembly followed
by compaction [46, 47], (b) cooling from the melt with pre-defined crystallization seeds [48, 49], or (c) using space filling techniques based on Voronoi construction [37, 50-53]. Two dimensional columnar model microstructures [44, 54-58] offer the possibility to extend these simulation studies on dislocation and twinning processes in single crystals to polycrystalline materials, while preserving many of the characteristics of fully three dimensional models. The limitations of the columnar model come mainly from the inability, due to geometrical constraints, to produce curved dislocation lines, i.e. all dislocation lines are constrained to be parallel to the columnar axis. This eliminates effects that involve the curvature of the dislocation loops in fully three dimensional systems, for example, nucleation of dislocations from grain boundaries. The evolution of microstructure is more easily visualized in the two dimensional models. As far as the mechanical behavior derived from the MD simulations is concerned, the following has been widely documented: Dramatically increased strength and hardness due to the Hall-Petch effect, however, at grain size below a critical grain size, $d_c$, typically 20-30 nm, the inverse Hall-Petch effect occurs-decreasing in the yield stress with decreasing grain size. Moreover, different deformation mechanisms are proposed in those two regions. For the larger grain sizes (of 50-100 nm) deformation is governed by intra-grain dislocation and twinning process, while for the smaller grain sizes (less than ~20 nm) deformation is dominated by inter-grain grain boundary processes. However, the mechanical properties of nanocrystalline materials still remain controversial.

Despite a large amount of research on the deformation mechanisms in pure nanocrystalline metals [37-39, 42-44, 51-53], a relatively small number of alloys systems have been studied.
There are many metal-metal systems with a miscibility gap in the liquid state such as Al-Pb, Cu-Pb and Al-Bi. Many of these have been used as bearing materials [59, 60]. Al and Pb are immiscible in the solid state and they have a wide miscibility gap in the liquid state [61]. There have been several reports showing the effect of Pb particles on the properties of Al. For example, melting behavior of nanosized Pb particles embedded in an Al matrix was investigated and the presence of Pb particles can lower or elevate the melting temperature of Pb from its bulk value [62-67]. There also has been an improvement of wear behavior of Al-Pb alloys [60]. If an insoluble element is added to a nanocrystalline matrix, it can produce second-phase particles or segregate to grain boundaries. Alloying elements could affect the Hall-Petch effect and show different deformation mechanisms. The effects of Pb on the mechanical properties for nanocrystalline Al are still uncertain based on several experimental results [68, 69]. In one case hardening was observed [68], while in the other there was a dramatic softening effect [69]. The latter investigators suggested that the Pb segregation to grain boundaries observed using Z-contrast high resolution transmission electron microscopy (HRTEM) was the cause of the softening.

In this dissertation, MD simulation has been used to study the deformation mechanisms in nanocrystalline aluminum and aluminum-lead alloys using uniaxial straining tests. We will discuss simulations on textured columnar structures which capture the critical grain size, $d_c$ where the crossover from “normal Hall-Petch” to “inverse Hall-Petch” behavior takes place with decreasing grain size in nanocrystalline aluminum. In aluminum-lead alloys,
microstructure changes due to Pb addition will be characterized and related to the deformation behavior.

The remainder of this chapter will be dedicated to a discussion of MD simulation, the potential energy function used in this work, a description of algorithms used in the computational code, and a description of visualization methods including a centro-symmetry parameter and local strain mapping method. This background will be helpful to understand the following chapters. In the following chapters, a general introduction of straining simulation will be given including a historical background, computational contributions from previous research groups, and a detailed description of the analysis of data from straining simulation.

In the second chapter, an overview of the techniques used for MD simulations of uniaxial tensile straining is given. It includes the parameters for the simulated material, the simulation setup and simulation process.

In the third chapter, the plastic deformation of nanocrystalline aluminum is investigated using MD straining simulations. The tensile deformation results of nanocrystalline aluminum with different grain sizes using a textured columnar microstructure are shown. The simulations provide insight into the interplay between the dislocation and grain boundary processes responsible for the mechanical behavior. These simulations also reveal how the
crossover from ‘normal’ to ‘inverse’ Hall-Petch behavior occurs and explain details based on the analysis of stress-strain curves, structure changes and local mapping techniques.

In the fourth chapter, plastic deformation of nanocrystalline aluminum-lead alloys is investigated. We also investigate the segregation of Pb atoms to the grain boundaries of Al using the Monte Carlo (MC) method and the modified embedded atom method (MEAM) potentials that we have developed for Al-Pb alloys. The effect of Pb addition on deformation mechanisms and grain boundaries in nanocrystalline Al-Pb alloys is also explained. These simulations show how deformation mechanisms of Al-Pb alloy are different from that of pure Al.

In the fifth chapter, deformation of nanocrystalline aluminum-lead alloys having larger grain sizes than that of Chapter 4 is investigated. MC simulations are carried out for producing aluminum-lead alloy microstructures and the results of uniaxial straining simulations are introduced to explain the mechanical behavior. These simulations show how deformation mechanisms changes as the grain size increases.

From the sixth through eighth chapters, the self contained reports are introduced based on manuscripts accepted by Materials Science and Engineering A, to be submitted to Acta Materialia, and to be submitted to Scripta Materialia, respectively.
1.2 MOLECULAR DYNAMICS SIMULATION

Molecular dynamics simulation consists of the numerical solution of classical equations of motion, e.g. Newton’s equation, which for a simple atomic system is written by [70]

\[ m_i \ddot{r}_i = f_i \]  \hspace{1cm} (1.1)

\[ f_i = -\frac{\partial}{\partial r_i} U \]  \hspace{1cm} (1.2)

In the simulations, we need to be able to calculate the forces \( f_i \) acting on the atoms, and these are derived from a potential energy \( U(r^N) \), where \( r^N \) represents the set of \( 3N \) atomic coordinates, \( r^N=(r_1, r_2, \ldots, r_N) \). In the system composed of atoms with coordinates \( r^N \) and potential energy \( U(r^N) \), the atomic momenta \( p^N=(p_1, p_2, \ldots, p_N) \) are introduced, in terms of which the kinetic energy is written as

\[ K(p^N) = \sum_{i=1}^{N} \frac{|p_i|^2}{2m_i}. \]

The energy or Hamiltonian is written as a sum of kinetic and potential energies, \( H = K + U \).

1.3 THE VERLET ALGORITHM

The potential energy is a function of the atomic positions of all the atoms in the system. The equations of motion should be solved numerically since there is no analytical solution. Many numerical algorithms have been developed for integrating the equations of motion, such as the Verlet algorithm [71], leap-frog algorithm [72, 73], velocity Verlet [74] and Beeman’s algorithm [75]. For choosing the algorithm, we should consider the following: (a) It should
conserve energy and momentum, (b) It should be efficient computationally, e.g. it should be fast and consume little memory, (c) It should permit a long time step for integration, and (d) It should be easy for programming.

Verlet [71] initially adopted one of the integration methods using a Taylor series expansion, so-called the Verlet algorithm, which uses the positions and accelerations at time \( t \) and the positions at time \( t-\delta t \) to calculate new positions at time \( t+\delta t \).

Later, Hockney and Potter [72, 73] made modifications to the basic Verlet algorithm and one of these is a leap-frog scheme. In this algorithm, the velocities first calculated at time \( t+1/2\delta t \) are used to calculate the positions, \( r \) at time \( t+\delta t \). The velocities leap over the positions and the positions leap over the velocities. Both the original Verlet and leap-frog algorithms do not handle the velocities in a completely satisfactory manner. The velocity Verlet algorithms [74] by Swope et al., requires storage of positions, velocities and accelerations at the same time \( t \). We have applied this algorithm to our simulation.

This algorithm takes the form as follows:

\[
r(t + \delta t) = r(t) + \delta t \, v(t) + \frac{1}{2} \delta t^2 a(t)
\]  
(1.3)

\[
v(t + \delta t) = v(t) + \frac{1}{2} \delta t \left [ a(t) + a(t + \delta t) \right ]
\]  
(1.4)

The new positions at time \( t+\delta t \) are calculated by the above equations and the velocities at mid-step \( t+1/2\delta t \) are calculated using

\[
v \left ( t + \frac{1}{2} \delta t \right ) = v(t) + \frac{1}{2} \delta t \, a(t)
\]  
(1.5)
The forces and accelerations at time $t + \delta t$ are then calculated and the velocity move is completed as

$$v(t + \delta t) = v\left(t + \frac{1}{2} \delta t \right) + \frac{1}{2} \delta t \ a(t + \delta t)$$  \hspace{1cm} (1.6)$$

Beeman’s algorithm [75] is closely related to the Verlet algorithm. This algorithm provides more accurate expressions of the velocities and better energy conservation, but the complex expressions compared to the other methods make for more expensive calculation.

\subsection*{1.4 THERMOSTAT}

It is impossible to fix the kinetic temperature of a system exactly at a set point in molecular dynamics since the temperature is defined by the ensemble average of kinetic energies of all the atoms as $\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{k_B T}{2}$ where, $k_B$ is a Boltzmann constant. The various types of thermostats, such as Berendsen [76], Langevin [77] and Nose-Hoover [78-80], have been introduced to control the atomic motions. A Berendsen thermostat [76] is a velocity rescaling method which corrects deviations of temperature from the set point by multiplying the velocities by a factor to control temperature. In the Langevin thermostat [77], a frictional force is added to the conservative force that is proportional to the velocity and it adjusts the kinetic energy of the particle so that the temperature matches the set point. The Hoover thermostat [78-80] has extended the analysis of Nose’ and introduced additional degrees of freedom (momentum) into the equations of motion from Nose’s Hamiltonian.
\[ \dot{r} = p/m \quad \text{(1.7)} \]
\[ \dot{p} = f - \xi p \quad \text{(1.8)} \]

where \( \xi \) is a friction coefficient given by the first-order differential equation
\[ \ddot{\xi} = \frac{f}{Q}(k_B \tau - k_B T) \quad \text{(1.9)} \]

and \( f \) is the number of degrees of freedom, \( Q \) is the thermal inertia parameter, \( \tau \) is the current kinetic temperature and \( T \) is the desired thermodynamic temperature. We have applied the Hoover thermostat to our simulation.

**1.5 MODIFIED EMBEDDED ATOM METHOD (MEAM)**

The embedded atom method (EAM), which is based on density-functional theory, renders a good description of many-body atomic interactions in metals [81, 82]. Baskes developed the modified embedded atom method (MEAM) for metals by adding directional bonding to the EAM [83]. The details of the MEAM formalism for bcc, fcc and hcp metals have been described in the literature [83-85]. The second nearest-neighbor MEAM formalisms were recently developed by Lee et al [86-88]. In the MEAM approach, the total energy of a system is given by
\[ E_{tot} = \sum_i \left( F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j 
eq i} \phi_{ij}(R_{ij}) \right) \quad \text{(1.10)} \]
where $F_i$ is the embedding function, $\overline{\rho}_i$ is the background electron density at site $i$, and $\phi_j(R_{ij})$ is the pair interaction between atoms $i$ and $j$ at a distance $R_{ij}$. The embedding energy function is given as follows:

$$F(\overline{\rho}) = AE_c \left( \frac{\overline{\rho}}{\rho_0} \right) \ln \left( \frac{\overline{\rho}}{\rho_0} \right)$$

(1.11)

where $A$ is an adjustable parameter, $E_c$ is the sublimation energy or cohesive energy, and $\rho_0$ is the background electron density for a reference structure. Normally, the equilibrium structure is taken as the reference structure for elements. The electron density $\rho_i^{(0)}$ is composed of spherically symmetric partial electron density and angular contributions $\rho_i^{(1)}$, $\rho_i^{(2)}$, $\rho_i^{(3)}$. These partial electron densities have the following forms:

$$\rho_i^{(0)} = \sum_{j \neq i} \rho_j^{(0)}(R_{ij})$$

(1.12a)

$$\left( \rho_i^{(1)} \right)^2 = \sum_{\alpha} \left\{ \sum_{j \neq i} \frac{R_{ij}^\alpha}{R_{ij}} \rho_j^{(1)}(R_{ij}) \right\}^2$$

(1.12b)

$$\left( \rho_i^{(2)} \right)^2 = \sum_{\alpha, \beta} \left\{ \sum_{j \neq i} \frac{R_{ij}^\alpha R_{ij}^\beta}{R_{ij}^2} \rho_j^{(2)}(R_{ij}) \right\}^2 - \frac{1}{3} \left\{ \sum_{j \neq i} \rho_j^{(2)}(R_{ij}) \right\}^2$$

(1.12c)

$$\left( \rho_i^{(3)} \right)^2 = \sum_{\alpha, \beta, \gamma} \left\{ \sum_{j \neq i} \frac{R_{ij}^\alpha R_{ij}^\beta R_{ij}^\gamma}{R_{ij}^3} \rho_j^{(3)}(R_{ij}) \right\}^2 - \frac{3}{5} \left\{ \sum_{j \neq i} \frac{R_{ij}^\alpha}{R_{ij}} \rho_j^{(3)}(R_{ij}) \right\}^2$$

(1.12d)

Here, $\chi_{ij}^\alpha = R_{ij}^\alpha / R_{ij}$, and $R_{ij}^\alpha$ is the $\alpha$ component ($\alpha = x, y$ or $z$) of the distance vector between atom $j$ and $i$. $\rho_j^{(a,b)}$ represents atomic electron densities from $j$ atom at a distance $R_{ij}$ from site.
Note that the expression for \((\rho_i^{(3)})^2\) is recently modified in order to make the partial electron densities orthogonal \([89]\). To combine the partial electron densities and compute the total background electron density, the following scheme is used:

\[
\bar{\rho}_i = \rho_i^{(0)} G(\Gamma)
\]

(1.13)

where \(G(\Gamma) = \frac{2}{1+e^{-\Gamma}}\), \(\Gamma = \sum_{h=1}^{3} t_i^{(h)} \left( \frac{\rho_i^{(h)}}{\rho_i^{(0)}} \right)^2\) and \(t_i^{(h)}\) are adjustable parameters. The atomic electron density is given as

\[
\rho_{\gamma^{(h)}}(R) = e^{-\beta^{(h)}(R/r_e-1)}
\]

(1.14)

where \(\beta^{(h)}\) are adjustable parameters and \(r_e\) is the nearest neighbor distance in the equilibrium reference structure.

In the MEAM, the energy per atom per for the reference structure is obtained from the universal equation of state by Rose et al.:

\[
F\left[\rho^0(R)\right] + \frac{1}{2} \sum \phi(R) = E^u(R) = -E_c \left( 1 + a^* + da^{*3} \right) e^{-a^*}
\]

(1.15)

where \(a^* = \alpha(R/r_e - 1)\) and \(\alpha = (9B\Omega/E_c)^{1/2}\). Here, \(E^u(R)\) is the universal function for a uniform expansion or contraction of the reference structure as a function of nearest neighbor distance \(R\), \(B\) is the bulk modulus and \(\Omega\) is the equilibrium atomic volume.

In the MEAM, the many body screening function \(S_{ij}\) between atoms \(i\) and \(j\) is defined as the product of the screening factor, \(S_{ikj}\), due to all other atoms between \(i\), \(j\) and \(k\). The screening factor, \(S_{ikj}\) is defined as a function of \(C\). \(C_{\text{min}}\) and \(C_{\text{max}}\), which are the limiting values of \(C\), determine the extent of screening.
\[ S_{ij} = \prod_{k \neq i,j} S_{ikj}, \quad S_{dj} = f_c \left( \frac{C - C_{\min}}{C_{\max} - C_{\min}} \right). \]  \hfill (1.16)

\( S_{ikj} \) is calculated using a simple geometric construction proposed by Baskes [90]. The equation of the ellipse is given by

\[ x^2 + \frac{1}{C} y^2 = \left( \frac{1}{2} R_y \right)^2. \]  \hfill (1.17)

The parameter \( C \) is determined by

\[ C = \frac{2(X_{ik} + X_{kj}) - (X_{ik} - X_{kj})^2 - 1}{1 - (X_{ik} - X_{kj})^2} \]  \hfill (1.18)

where \( X_{ik} = (R_{ik}/R_{ij})^2 \) and \( X_{kj} = (R_{kj}/R_{ij})^2 \). The \( R_{ij}, R_{kj} \) and \( R_{ik} \) are the distances between the corresponding atoms.

The smooth cutoff function \( f_c(x) \) assumes the following form.

\[ f_c(x) = \begin{cases} 1, & x \geq 1, \\ [1-(1-x)^4]^2, & 0 < x < 1, \\ 0, & x \leq 0. \end{cases} \]  \hfill (1.19)

**1.6 VISUALIZATION METHODS**

**1.6.1 Centro-symmetry parameter**

To study plastically deformed structures in detail, the location and type of defects presented in samples should be reliably identified. Centro-symmetric materials such as fcc metals remain centro-symmetric under elastic deformation [91]. Each atom has pairs of equal and opposite bonds to its nearest neighbors. With elastic distortion, these bonds will change
direction and length but they will remain equal and opposite. This relation no longer holds if a defect is introduced nearby. In other words, in the case of defected materials the equal and opposite relation will be changed for all of the nearest-neighbor pairs. Thus we can expect a centro-symmetry parameter which is zero for a centro-symmetric material under elastic deformation but nonzero under plastic deformation. The summation from 1 to 6 indicates summation over the six pairs of opposite atoms in a fcc lattice as seen FIG. 1.2. The centro-symmetry parameter for atom $i$ defined for an fcc lattice with 12 nearest neighbors $j$ is

$$P_i = \sum_{j=1,6} \left| R_{ij} + R_{ij+6} \right|^2$$

(1.20)

where $R_i$ and $R_{i+6}$ are the vectors or bonds corresponding to the six pairs of opposite nearest neighbors in the fcc lattice.

FIG. 1.2 Illustration of atomic pairs about a central atom $i$. On the left figure, $R_{ij} + R_{ij+6} = 0$ and on the right figure, $R_{ij} + R_{ij+6} \neq 0$.

The algorithm for calculating the centro-symmetry parameter is as follows:
(1) Find neighbors for all atoms $i$ using an order-$n$ binned neighbor search. While finding neighbors, save bond vector $R_{ij}$ for each neighboring atom.

(2) Create a pair list for each atom $i$ by finding the minimum value of the vector sum between atom $j$ and atom $k$ where atoms $j$ and $k$ are neighbors of $i$.

(3) Once the pairs are determined the centro-symmetry parameter is calculated using Eq. (1-20).

(4) Typically some tolerance is specified as a cut-off for the centro-symmetry parameter and all atoms with parameter values greater than the cut-off are output.

For reference, the centro-symmetry parameters for aluminum are introduced. The centro-symmetry parameter is zero for atoms in a perfect lattice, 3 Å$^2$ for surface/high-misfit atoms, 0.5 Å$^2$ for defect atoms including vacancies and dislocations, and 1 Å$^2$ for stacking faults.

1.6.2 Local strain analysis

The local strain mapping method [92, 93] was introduced to obtain deviatoric shear strain information associated with each atom. There are two coordinate files: a reference coordinates file (usually an undeformed system) and the current coordinates file (usually a deformed system). For each atom, the local environment is represented by the vectors to its nearest neighbors within a certain cutoff distance.

For one atom in the reference configuration:
\[ R_0 = \begin{pmatrix} x_0^1 & y_0^1 \\ x_0^2 & y_0^2 \\ x_0^3 & y_0^3 \\ \vdots \\ x_0^n & y_0^n \end{pmatrix} \]  \hspace{1cm} (1.21)

For the same atom in the current configuration:

\[ R = \begin{pmatrix} x^1 & y^1 \\ x^2 & y^2 \\ x^3 & y^3 \\ \vdots \\ x^n & y^n \end{pmatrix} \]  \hspace{1cm} (1.22)

Here \( n \) is the number of neighbors.

From the least square method, the linear transformation matrix is:

\[
\begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix} = (R_0^T R) (R_0^T R)^{-1} - I
\]  \hspace{1cm} (1.23)

where \( I \) is the identity matrix.

The matrix can be written as:

\[
\begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{pmatrix} = \begin{pmatrix} \frac{\varepsilon_{11} + \varepsilon_{22}}{2} \\ \frac{\varepsilon_{11} + \varepsilon_{22}}{2} \end{pmatrix} + \begin{pmatrix} \frac{\varepsilon_{12} - \varepsilon_{21}}{2} \\ \frac{\varepsilon_{12} - \varepsilon_{21}}{2} \end{pmatrix} + \begin{pmatrix} \frac{\varepsilon_{11} - \varepsilon_{22}}{2} \\ \frac{\varepsilon_{11} - \varepsilon_{22}}{2} \end{pmatrix}
\]  \hspace{1cm} (1.24)

The first term on the right hand side is a rigid expansion/contraction term. The second term is a rigid rotation term. The third term is a shear term. We define a deviatoric shear matrix as

\[ S = \begin{pmatrix} s \\ s \end{pmatrix} \]  \hspace{1cm} (1.25)
where $s$ is a positive deviatoric shear strain, $s$ is given by

$$s = \sqrt{\left(\frac{\varepsilon_{11} - \varepsilon_{22}}{2}\right)^2 + \left(\frac{\varepsilon_{12} + \varepsilon_{21}}{2}\right)^2} \quad (1.26)$$

The local strain mapping method was originally developed to facilitate the visualization of strain localization and shear band formation in amorphous structures. These are very difficult to analyze based on the centro-symmetry and local atomic environment methods. Local shear strain maps show the accumulated strain in the current configuration relative to the reference configuration. The method will also show accumulated deviatoric shear strain due to dislocation slip and twinning. Therefore, it is used in our work as a tool to aid in the visualization of local strain per atom during straining simulations. A novel feature is the ability to characterize discrete processes in crystal grains as well as those in disorganized grain boundaries. The local strain mapping method does not display changes due to pure volume expansion/contraction, or to rigid body grain rotation.

1.7 REFERENCES


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CHAPTER 2

MOLECULAR DYNAMICS STRAINING SIMULATIONS

The following chapter gives an overview of the techniques used for molecular dynamics (MD) simulations of uniaxial tensile straining. The first section shows the parameters for the simulated material, the second section the simulation setup and the third section the simulation process.

2.1 MEAM POTENTIAL

The molecular dynamics code PMEAM (Parallel Modified Embedded Atom Method) developed by C. Padgett and D. Irving was used for the straining simulations of microstructures of pure Al and Al-Pb alloys. The MEAM potential was developed to describe the interactions between Al-Al, Pb-Pb and Al-Pb atom pairs. The details of the MEAM formalism have been described in Chapter 1 and in the literature [1, 2].

Parameters for pure elements, Al and Pb were taken from Lee et al. [2], as given in Table 2.1. The parameters are: the cohesive energy $E_c$ (eV), the equilibrium nearest-neighbor distance $r_e$ (Å), the exponential decay factor for the universal energy function $\alpha$, the scaling factor for the embedding energy $A$, the four exponential decay factors for the atomic densities $\beta(i)$, the four weighting factors for the atomic densities $t(i)$ and the density scaling factor $\rho$. 
The parameters for the Al-Pb MEAM cross term were fitted to the lattice constant, cohesive energy and values of the elastic constants calculated for hypothetical Al-Pb alloys with B1 (NaCl) and B2 (CsCl) structures. These calculations were done using first principles density functional theory (DFT). B1 and B2 are reference structures in which an atom is surrounded by opposite-type neighbor atoms. The DFT parameters for the B1 structure were compared to the corresponding parameters of the B2 structure derived from MEAM and first principles calculations as shown below. Here, $\Omega$ is the lattice constant, $E^c$ is cohesive energy, $B$ is bulk modulus and $C_{11}$ and $C_{12}$ are elastic constant values.

1. Using first principles calculations, $B_{ij}$, $\Omega_{ij}$, $E^c_{ij}$ and $(C_{11}-C_{12})$ are calculated for each reference structure, B1 and B2.

2. Choose $B_{ij}$, $\Omega_{ij}$, $E^c_{ij}$ and $(C_{11}-C_{12})$ values of B1 from (1) and calculate $\alpha^{B1}_{ij} = \left( \frac{aB_{ij}\Omega_{ij}}{E^c_{ij}} \right)^{1/2}$

3. Calculate $\phi_{ij}$ from $\alpha^{NaCl}_{ij}$ and apply to the MEAM calculation to get $B_{ij}$, $\Omega_{ij}$, $E^c_{ij}$ and $(C_{11}-C_{12})$

4. Compare $B_{ij}$, $\Omega_{ij}$, $E^c_{ij}$ and $(C_{11}-C_{12})$ values from first principles calculations in (1) to the MEAM calculation in (3). Then the values of B1 reference structure can be matched, and those of the B2 reference structure should be matched in both calculations. If not, change the $C_{\text{min}}$ values until values of B1 and B2 structures match to the values from first principles calculations.
In Table 2.2, we show the fitted MEAM cross potentials between Al and Pb with first principles calculation results of lattice constants cohesive energies and two elastic constants for both B1 and B2 structures. Table 2.2 compares the calculated properties of B1 and B2, and shows satisfactory agreement between the MEAM and the DFT results.

Table 2.3 shows the angular screening parameters $C_{\text{max}}$ and $C_{\text{min}}$. Here, the middle atom is the “screening” atom and the outer atoms are the “interacting” atoms. $C_{\text{max}}$ values are 2.80 for all the combinations.

2.2. SIMULATION SETUP

The MD simulation uses a two-dimensional (2D) columnar microstructure similar to that used in ref. [3]. The $\langle110\rangle$-textured columnar microstructures used here consist of four grains of identical size, and regular-hexagonal shape, in the simulation cell illustrated in FIG. 2.1. The advantage over fully three dimensional (3D) microstructures is that considerably larger grain-sized samples can be considered. The four grains in the periodically repeated simulation cell are oriented relative to the tensile (x) axis by rotations about the [110] direction by the angles 0°, 30°, 60° and 90°. The [1-10] texture direction is chosen because it is the common axis of (111) and (11-1) planes in which dislocations nucleated from the grain boundaries can glide [3].

Schmid factors ($m$) and slip systems in face-centered cubic metals are described in FIG. 2.2. $m$ represents the Schmid factor for each glide plane with respect to the [1-10] direction. The
glide planes shown in FIG. 2.2 indicate the orientations of two sets of (111) planes at each grain. Slip is expected to occur in close-packed atomic directions. Slip planes should be those with the densest atomic packing, for they are characterized by the greatest separation between parallel crystal planes. In three dimensional microstructures, dislocations, following their nucleation, can glide on any of the 12 slip systems (illustrated by the Thompson tetrahedron [4, 5]) However, the high degree of periodicity in the [1-10] direction (in two dimension) allows the system to have only four slip systems, which are sufficient to maintain compatible plastic deformation. Table 2.4 gives the slip systems, including slip planes and slip directions, in the fcc structure in three dimensional and two dimensional systems. Slip in fcc metals is consistent with the slip directions and planes: <110> directions and {111} planes. The number of combinations of slip planes and directions provided by the crystallography of a crystal structure determines the number of slip systems. The fcc structure has 12 slip systems that result from there being four geometrically distinct planes of the {111} type, each of which contain three distinct <110> type directions. The simulation cell contains 14(1-10) planes in the z-direction, the net effect being that any dislocations nucleated from the grain boundaries are constrained to being straight lines. The thickness is determined by the interplanar spacing of \( \frac{\sqrt{2}}{4}a_0 \) \( (a_0=4.05 \text{ Å}) \). Since our simulation cell has a very small thickness in the z-direction, only straight dislocations (i.e., kink-free) with lines parallel to [1-10] direction are possible. The x-y plane size is determined by the grain size and we consider simulation cells with grain sizes ranging from 5
nm (giving a total of 7,532 atoms) to 30 nm (280,546 atoms). Table 2.5 shows the total number of atoms in the simulation system at each grain size, 5 to 30 nm.

FIG. 2.1 Schematic view of the columnar structure containing four grains in the shape of regular hexagons.
FIG. 2.2 Orientations of two sets of (111) planes for each grain. Two planes are inclined to each other at an angle of 70.53°. $m$ represents the Schmid factor for each glide plane with respect to the [110] direction.

Table 2.1 Parameters for the MEAM potentials of Al, Pb and Al-Pb

<table>
<thead>
<tr>
<th></th>
<th>$E_c$</th>
<th>$r_e$</th>
<th>$\alpha$</th>
<th>$A$</th>
<th>$\beta(0)$</th>
<th>$\beta(1)$</th>
<th>$\beta(2)$</th>
<th>$\beta(3)$</th>
<th>$t(0)$</th>
<th>$t(1)$</th>
<th>$t(2)$</th>
<th>$t(3)$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.36</td>
<td>2.86</td>
<td>4.69</td>
<td>1.16</td>
<td>3.20</td>
<td>2.6</td>
<td>6.0</td>
<td>2.6</td>
<td>1.0</td>
<td>3.05</td>
<td>0.51</td>
<td>7.75</td>
<td>1.31</td>
</tr>
<tr>
<td>Pb</td>
<td>2.04</td>
<td>3.5</td>
<td>6.38</td>
<td>1.01</td>
<td>5.42</td>
<td>2.2</td>
<td>6.0</td>
<td>2.2</td>
<td>1.0</td>
<td>3.10</td>
<td>3.91</td>
<td>1.25</td>
<td>0.98</td>
</tr>
<tr>
<td>AlPb</td>
<td>2.39</td>
<td>2.98</td>
<td>5.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.2 Comparison of the calculated properties of B1 (NaCl) and B2 (CsCl) structures using the MEAM potentials and first principles calculations.

<table>
<thead>
<tr>
<th>Properties of NaCl (reference)</th>
<th>MEAM</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>5.97</td>
<td>5.97</td>
</tr>
<tr>
<td>Heat of mixing (eV)</td>
<td>0.315</td>
<td>0.315</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>40.65</td>
<td>40.66</td>
</tr>
<tr>
<td>Elastic constant (C_{11}-C_{12}) (GPa)</td>
<td>74.91</td>
<td>75.72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties of CsCl</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (Å)</td>
<td>3.66</td>
<td>3.71</td>
</tr>
<tr>
<td>Heat of mixing (eV)</td>
<td>0.28</td>
<td>0.275</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>53.95</td>
<td>44.57</td>
</tr>
<tr>
<td>Elastic constant (C_{11}-C_{12}) (GPa)</td>
<td>0.42</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Table 2.3 Angular screening parameters for the MEAM potentials. C_{max} values are 2.80 for all the combinations

<table>
<thead>
<tr>
<th></th>
<th>AlAlAl</th>
<th>AlAlPb</th>
<th>AlPbAl</th>
<th>PbAlAl</th>
<th>PbPbAl</th>
<th>PbAlPb</th>
<th>AlPbPb</th>
<th>PbPbPb</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{min}</td>
<td>0.49</td>
<td>1.0</td>
<td>1.4</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Table 2.4 Slip systems in face-centered cubic structure (3-dimension and 2-dimension)

<table>
<thead>
<tr>
<th>Slip system in face-centered cubic (3-dimension)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slip planes</td>
</tr>
<tr>
<td>{111}; (111), (-111), (1-11), (11-1)</td>
</tr>
<tr>
<td>Slip directions</td>
</tr>
<tr>
<td>&lt;1-10&gt;; [110], [101], [011], [-110], [-101], [0-11]</td>
</tr>
<tr>
<td>Number of slip systems (12)</td>
</tr>
<tr>
<td>(111); [-110], [-101], [0-11]</td>
</tr>
<tr>
<td>(-111); [110], [101], [0-11]</td>
</tr>
<tr>
<td>(1-11); [110], [011], [-101]</td>
</tr>
<tr>
<td>(11-1); [101], [011], [-110]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slip system in face-centered cubic (2-dimension)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slip planes</td>
</tr>
<tr>
<td>{111}; (111), (11-1)</td>
</tr>
<tr>
<td>Slip directions</td>
</tr>
<tr>
<td>&lt;1-10&gt;; [011], [101], [01-1], [10-1]</td>
</tr>
<tr>
<td>Number of slip systems (4)</td>
</tr>
<tr>
<td>(111); [01-1], [10-1]</td>
</tr>
<tr>
<td>(11-1); [011], [101]</td>
</tr>
</tbody>
</table>

Table 2.5 The total number of atoms in the simulation system by grain size.

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>Total number of atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7,532</td>
</tr>
<tr>
<td>8</td>
<td>19,670</td>
</tr>
<tr>
<td>10</td>
<td>30,807</td>
</tr>
<tr>
<td>15</td>
<td>69,713</td>
</tr>
<tr>
<td>20</td>
<td>124,285</td>
</tr>
<tr>
<td>30</td>
<td>280,546</td>
</tr>
</tbody>
</table>
2.3 UNIAXIAL STRAINING SIMULATIONS

MD simulations using the MEAM potential at a finite temperature of 300K are done, and the Newtonian equations of motion for the atoms are solved numerically. Before the deformation is applied, the system is relaxed to equilibrium at 300K using Hoover thermostats. The equilibrium procedure brings the system close to the minimum in energy. When the relaxation is done, the system is ready to simulate deformation.

MD tensile straining simulation in the [110] x-direction was performed at a constant strain rate of $6.67 \times 10^9 \text{s}^{-1}$ as shown in FIG. 2.3. The strain rate is very high compared to experimental testing. Periodic boundary conditions are adopted in the x, y and z directions during simulation. Strains in the y and z directions were imposed to maintain the stresses $\sigma_{yy}$ and $\sigma_{zz}$ close to zero. The temperature was maintained at 300K and the MD time step for our potential was $\Delta t = 1 \text{fs}$. These simulation conditions are used for pure Al and Al-Pb alloy straining simulations in Chapter 3 through Chapter 5. After carrying out straining tests, unloading simulations are performed. FIG. 2.4 shows the schematic diagram of a stress-strain curve for loading and unloading. The reversible strain and $\sigma/E$ correction for unloading curves from the total strain of 10% used for the simulations are shown. The $\sigma_2$ value is the end point obtained from stress-total strain curves. Reversible strain from the unloading curves is $\varepsilon_1$, and the $\sigma/E$ correction calculated from the curve is $\varepsilon_2$. Simulation results show that $\varepsilon_1 \approx \varepsilon_2$. 
FIG. 2.3 Schematic diagram of the setup for the molecular dynamics straining simulation.

The straining direction, x-axis is along a $<110>$ direction and the z-axis is oriented in the $<001>$ direction. Periodic boundaries are held in the x, y and z directions.
FIG. 2.4 Schematic diagram of a stress-strain curve for loading and unloading.

2.4 REFERENCES

Molecular dynamics (MD) straining simulations were used to investigate the plastic deformation of nanocrystalline aluminum. The tensile deformation of nanocrystalline aluminum with different grain sizes using a textured columnar microstructure was observed. The simulations provide insight into the interplay between the dislocation and grain boundary processes responsible for the mechanical behavior. These simulations also reveal how the crossover from ‘normal’ to ‘inverse’ Hall-Petch behavior occurs and explain details based on the analysis of stress-strain curves, structure changes and local mapping techniques.

3.1 BACKGROUND AND INTRODUCTION

Since Herbert Gleiter proposed that nanocrystalline metals will show drastically different properties compared to conventional metals, and may open a new technological field [1], there has been a considerable interest in experiments and atomistic simulations to investigate their structural and mechanical properties. The mechanical properties of pure nanocrystalline metals have been investigated by many research groups [2-10] and the deformation scenario widely accepted is that (a) at larger grain sizes (50-100 nm) a dislocation-based deformation process takes place, leading to increased strength and hardness; this is known as “Hall-Petch
effect” and (b) for the smaller grain sizes (less than 20 nm), deformation is dominated by a
grain boundary-mediated deformation process, which produces the “inverse Hall-Petch
effect” resulting in a reduction of yield stress with decreasing grain size. This crossover from
“normal” to “inverse” Hall-Petch behavior takes place at a critical grain size, $d_c$ which
implies a “strongest grain” [2]. Below $d_c$, plastic deformation is governed by inter-grain
mechanisms. Above $d_c$, intra-grain mechanisms due to dislocation slip and twinning
dominate.

Recent results reported in the literature identify the atomic-level mechanisms for dislocation
nucleation and annihilation at the grain boundaries [9-11]; the prediction [6] and recent
experimental verification [12] of mechanical twinning in nanocrystalline Al [13]; the
elucidation of the mechanistic causes for the crossover from a dislocation to a grain
boundary-based deformation mechanism with decreasing grain size [14].

3.2 RESULTS

FIGS. 3.1a-f show the stress-strain curves for straining simulations of Al microstructures
with grain sizes of 5, 8, 10, 15, 20 and 30 nm, respectively. Each figure shows the results for
three different initial microstructures for the same conditions. The individual curves at
smaller grain sizes in FIGS. 3.1a-c are somewhat less reproducible than at larger grain sizes.
At the 5 nm grain size, the fluctuations in the stress-strain curves increase above a strain of
3%. The difference in fluctuations becomes smaller as the grain size increases, and the
differences are suppressed when the grain sizes are 20 and 30 nm. Even a minor change in the equilibrium procedure, or a perturbation of the atomic coordinates in a small grain-sized sample, will result in different fluctuations in the stress-strain curves. One set of simulations at each grain size was taken from FIG. 3.1, and these are shown in FIG. 3.2a as the stress $\sigma$ vs. total strain $\varepsilon_T$ curves. FIG. 3.2b shows the stress $\sigma$ vs. plastic strain $\varepsilon_p$ curves obtained from FIG. 3.2a. The plastic strain was evaluated using $\varepsilon_p = \varepsilon_T - \sigma / E$.

FIGS. 3.3a-c show the effective Young’s modulus (E), 0.5% plastic strain offset yield stress ($\sigma_{0.5}$), and peak stress ($\sigma_p$) for pure Al with different grain sizes from 5 nm to 30 nm. Average values of E, $\sigma_{0.5}$ and $\sigma_p$ for three simulation runs at each grain size are shown and standard deviation values are indicated. The E values are in the range of 51-63 GPa compared to the experimental value of E~70 GPa for polycrystalline Al. As the grain size increases, E values also increase. A (vertical) plastic strain offset 0.5% was used to define the offset yield stress $\sigma_{0.5}$ in conjunction with the $\sigma$ vs. $\varepsilon_p$ curves in FIG. 3.2b. The $\sigma_{0.5}$ values will increase if the offset is increased, but the relative differences remain similar up to 2% plastic strain. The $\sigma_{0.5}$ values are found to be in the range of 0.92-2.07 GPa. The highest value of 1.82-2.07 GPa occurs when the grain size is 15 nm. The $\sigma_p$ values increase as the grain size increases.

The effective modulus E in the [110] direction was obtained from the initial slopes of the $\sigma$ vs. total strain $\varepsilon_T$ curves. E depends on the elastic constants C11, C12 and C44 and it varies with grain orientation. C11, C12 and C44 are 1.143, 0.619 and 0.316 taken from ref. [15] and $E_{\text{max}}$, $E_{\text{min}}$ and $E_m$ were calculated from Eqs. 3.1. $E_{\text{max}}$ is the value in the <111> direction,
E\textsubscript{min} is in the \textlangle 100 \rangle direction and \textit{E} \textit{m} is in the \textlangle 110 \rangle direction. The three independent stiffness coefficients \( C_{11}, C_{12} \) and \( C_{44} \) are related to the three independent compliance coefficients, \( S_{11}, S_{12} \) and \( S_{44} \) by Eqs. 3.1.

\[
C_{11} = \frac{S_{11} + S_{12}}{(S_{11} - S_{12})(S_{11} + 2S_{12})} \quad (3.1a)
\]

\[
C_{12} = \frac{-S_{12}}{(S_{11} - S_{12})(S_{11} + 2S_{12})} \quad (3.1b)
\]

\[
C_{44} = \frac{1}{S_{44}} \quad (3.1c)
\]

For a cubic crystal the modulus in an arbitrary \([hkl]\) direction can be expressed in terms of stiffnesses or compliances. It is more convenient to use compliances as given by

\[
\frac{1}{E_{hkl}} = S_{11} - 2\left(S_{11} - S_{12} - \frac{1}{2}S_{44}\right)\left(\alpha^2 \beta^2 + \alpha^2 \gamma^2 + \beta^2 \gamma^2\right) \quad (3.2)
\]

where \( \alpha, \beta \) and \( \lambda \) are the direction cosines of the \([hkl]\) direction and the \([100], [010], \) and \([001]\) directions, respectively. For \([111]\), \( \left(\alpha^2 \beta^2 + \alpha^2 \gamma^2 + \beta^2 \gamma^2\right) = 1/3 \), for \([100]\), \( \left(\alpha^2 \beta^2 + \alpha^2 \gamma^2 + \beta^2 \gamma^2\right) = 0 \), and for \([110]\), \( \left(\alpha^2 \beta^2 + \alpha^2 \gamma^2 + \beta^2 \gamma^2\right) = 1/4 \). From the Eq. 3.1, \( S_{11}, S_{12} \) and \( S_{44} \) are obtained. When the above equations, 3.1 and 3.2 are solved, \( E_{\text{min}} = 70.8 \text{GPa}, \ E_{\text{max}} = 83.7 \text{GPa} \) and \( E_{\text{m}} = 80.1 \text{GPa} \) are obtained. The \( E \) values in FIG. 3.3a are below \( E_{\text{min}} \).

Unlike large-grain size polycrystalline metals, the large fraction of grain boundary atoms in nanocrystalline metals can reduce the modulus. The fraction of grain boundary atoms increases as the grain size decreases and the modulus of small grain-sized microstructures has lower values than that of larger grain-sized ones.
The $\sigma_{0.5}$ values increase as the grain size increases up to 15 nm and then decrease as the grain size increases above 15 nm. While the $\sigma_{0.5}$ at the 30 nm grain size is higher than that at 20 nm grain size, all $\sigma_{0.5}$ values above 15 nm grain size are smaller. This indicates onset of the inverse Hall-Petch effect. The critical grain size for maximum strength of nanocrystalline Al in this simulation therefore appears at $d \sim 15$ nm. We observe the inverse Hall-Petch effect transition at a critical grain size of 15 nm. Yamakov et al. [14] reported the critical grain size is 18 nm and Shimokawa et al. [16] 30 nm. Yamakov et al. used a three dimensional microstructure, so there can be a difference from our columnar microstructure. Shimokawa et al. used a similar columnar microstructure, but the grain size was measured by the distance between two parallel sides of the hexagonal grains. In the previous two simulations, the strain rates have the same order of $10^8$ s$^{-1}$. However, deformation conditions are constant stress simulation for Yamakov’s and constant strain for Shimokawa’s study. They also have different embedded atom method potentials and different stacking fault energies, 122 mJ/m$^2$ in Yamakov’s and 158 mJ/m$^2$ in Shimokawa’s model. In our model, the deformation mode is constant strain rate, the strain rate is higher than those two models and the stacking fault energy has the value, 141 mJ/m$^2$.

FIGS. 3.4a-c illustrate the deformation structures of pure Al with a 10 nm grain size at strains of 4.7%, 7.6% and 8.6%, respectively. The structures are colored using the centro-symmetry parameter $P$. The color scheme is $P = 0$ Å$^2$ for perfect fcc atoms, $P = 0.5$ Å$^2$ for defects including dislocations, $P = 1$ Å$^2$ for stacking faults and $P = 3$ Å$^2$ for surface and high-misfit grain boundary atoms. In FIG. 3.4a, the simulations show the emission of partial dislocations
from grain boundaries, or in the vicinity of a triple junction. Most dislocations are nucleated from the 60° tilt boundaries. The boundary between grains 30° and 90° is changed to a zigzag shape. The leading partial dislocations (seen as the terminating green atoms in white circles) are successively emitted and connected by stacking faults (yellow atoms). At this lower strain, only leading partial dislocations are generated. At higher strains, both leading and trailing partial dislocations are emitted and connected by stacking faults. From the straining simulations, three modes of deformation by the emission of dislocations from grain boundaries are revealed: (1) full dislocations; (2) partial dislocations; and (3) twins. Simulations reported in the literature show different dislocation mechanisms: only partial dislocations are observed in three dimensional microstructures whereas full dislocations occur in two dimensional columnar microstructures [6, 11]. In our simulations, both partial and full dislocations are observed. As the strain increases to 7.6% in FIG. 3.4b, more dislocations are produced and extended dislocations travel across the grains on slip planes (lower white rectangle) until they annihilate in the opposite grain boundary (upper white rectangle). Some dislocations move across grains without any trailing dislocations.

As strain increases, extrinsic stacking faults can transform to twins, as seen in the red circles in FIG. 3.4b. The extrinsic faults appear as two yellow layers and one blue layer. Although twins are not observed in coarse-grained Al, the formation of deformation twins occurs in nanocrystalline microstructures [13]. In FIG. 3.4c, the 60° tilt grain boundary is converted to a 70.5° twin boundary (white rectangle). Twinning occurs when the grain boundaries nucleate partial dislocations successively.
FIG. 3.5 shows the number of dislocations observed at each value of total strain for grain sizes from 5 nm to 30 nm. In the 5 nm sample, only one or two dislocations are formed during the simulation. A few more dislocations are formed at the 8 nm grain size. Significantly increased dislocation activity occurs as the grain size increases above 10 nm and the number of dislocations increases as total strain increases. As the grain size is reduced, the fraction of Al atoms belonging to the grain boundaries increases: 24.70%, 15.20%, 12.39%, 8.36%, 6.34% and 4.37% for 5, 8, 10, 15, 20 and 30 nm grain sized samples, respectively. As the fraction of atoms in grain boundaries increases with decreasing grain size, inter-grain deformation processes become easier than dislocation slip and this leads to the inverse Hall-Petch effect. Y. Champion et al. reported that the large fraction of atoms located at the grain boundaries was responsible for plastic deformation at decreasing stress and that grain boundary diffusion controls the deformation process in this regime [17]. However, as the grain size increases above 15 nm in our simulations, dislocations are nucleated more readily from grain boundaries or triple junctions, and this produces the transition to dislocation-controlled Hall-Petch behavior.

FIGS. 3.6a-e show the plastic strain ($\varepsilon_p$) vs. dislocation strain ($\varepsilon_d$) as a function of strain in 5, 10, 15, 20 and 30 nm grain sized samples, respectively. $\varepsilon_p$ values are taken from FIG. 3.2b and $\varepsilon_d$ values are calculated by the following procedure. The schematic of a hexagon grain shown in FIG. 3.7 is used to calculate tensile strain due to dislocation motion. FIG. 3.7 illustrates dislocation movement in the hexagonal grain in our simulation system. From FIG.
3.7, the area of the grain is $2.6D^2$. $\gamma$ is shear strain due to a dislocation moving a distance $x$ from the grain boundary

$$\gamma = \frac{bx}{A_g} = \frac{bx}{2.6D^2} = \text{amount of shear (}\gamma > 0) . \quad (3.3)$$

The dislocation strain $\varepsilon_{ij}$ in 1, 2 and 3 (x, y and z) axes is given by

$$\varepsilon_{ij} = \frac{1}{2} \gamma (n_i s_j + n_j s_i) \quad (3.4)$$

$\varepsilon_{11}$ is dislocation tensile strain is given by

$$\varepsilon_{11} = \gamma n_1 s_1 = \gamma M = \frac{Mbx}{2.6D^2} \quad (3.5)$$

where $M$ is Schmid factor.

The total dislocation strain is the linear sum over all dislocations that undergo slip on the active slip systems in all grains.

In FIG. 3.6, $\varepsilon_p$ increases up to 6.7%, 7.0%, 5.1%, 5.6% and 5.1% for 5, 10, 15, 20 and 30 nm grain size, respectively, as total strain increases. However, $\varepsilon_d$ for 5 nm is in the range of 0.06-0.5%, $\varepsilon_d$ for 10 nm is in the range of 0.2-2.6%, $\varepsilon_d$ for 15 nm is in the range of 0.01-1.4%, $\varepsilon_d$ for 20 nm is in the range of 0.05-2.3%, $\varepsilon_d$ for 30 nm is in the range of 0.05-1.4%. Since more dislocations are formed in 10 nm grain size than in 5 nm, as seen in FIG. 3.5, strain due to dislocation motion in 5 nm grain sized simulations is very low compared to the value at 10 nm. This is consistent with the inverse Hall-Petch transition. The strain difference between $\varepsilon_p$ and $\varepsilon_d$, ($\varepsilon_p - \varepsilon_d$) is caused by twinning and grain boundary mechanisms for plastic deformation.
The value of $(\varepsilon_p - \varepsilon_d)$ for 5 nm is in the range of 0.1-6.2% and the value of $(\varepsilon_p - \varepsilon_d)$ for 10 nm is in the range of 0.2-4.4%. If dislocations can form, the plastic deformation is governed partially by dislocation activity. If there are very few dislocations produced, the plastic deformation is dominated by other mechanisms.

FIGS. 3.8a and b show $\varepsilon_d/\varepsilon_p$ and (b) $(\varepsilon_p-\varepsilon_d)/\varepsilon_p$ vs. total strain for different grain sizes. In FIG. 3.8a, $\varepsilon_d$ for 5 nm grain size is very small (<20%) and remains nearly constant over the total strain range. For 8 and 10 nm grain sizes, $\varepsilon_d$ is initially 67% and 50%, respectively, and decreases to about 40% at a total strain of 6% and remains constant thereafter. At 15 and 20 nm grain sizes, $\varepsilon_d$ is small initially (<20%) and increases up to 40%. At a 30 nm grain size, $\varepsilon_d$ is also small initially (<20%) and increases up to 34%. It decreases at a total 9% strain and finally reduces 28% at the total 10% strain. This appears to be caused by the decreasing number of dislocations generated at the total 9% strain in FIG. 3.5. At the total 10% strain, the relative contribution of dislocations to the plastic strain saturates to the range 30-40% for all grain size > 5 nm.

In FIG. 3.8b, the $(\varepsilon_p - \varepsilon_d)$ the strain due to sources other than dislocations remains at 80-90% for the 5 nm grain size simulation. For 8 and 10 nm grain sizes, $(\varepsilon_p - \varepsilon_d)$ increases up to 60% at a total strain of 6%, and then saturates. For 15 and 20 nm grain sizes, $(\varepsilon_p - \varepsilon_d)$ values decrease to 60%. For 30 nm grain size, $(\varepsilon_p - \varepsilon_d)$ decreases to 66% at a total 9% strain and increases to 72% at the total 10% strain. The reason that $\varepsilon_d$ values for 8 and 10 nm grain sizes are lower than those of larger grain sizes is due to the initial dislocation nucleation process. For
example, at a total strain of 4%, 4 to 5 dislocations are generated and have moved to opposite grain boundaries for 8 and 10 nm grain sizes. Accordingly, the contribution to deformation by dislocation nucleation is less at the earlier stage of straining in 15 to 30 nm grain sized samples.

Schiotz *et al.* [18] observed extensive partial-dislocation nucleation from the grain boundaries and showed that these dislocations were responsible for only about 1/3 of the total plastic strain. Although the accommodation process required for grain boundary sliding was not addressed, it was concluded that grain boundary sliding is the dominant deformation mechanism rather than dislocation slip. Swygenhoven *et al.* [3, 4, 10, 19] showed that grain boundary sliding and grain rotation were the elementary mechanisms responsible for the deformation behavior, and that grain boundary sliding takes place through atom shuffling and stress-induced grain boundary diffusion. Whereas grain boundary sliding was the sole deformation mechanism for small grain sizes (<10 nm), dislocation processes contributed to the deformation behavior along with grain boundary sliding for larger grain sizes.

Dao *et al.* [20] concluded that only a small amount of plasticity mediated by grain boundary sliding processes contribute to the deformation mechanisms, while partial (or perfect) dislocation processes interacting with grain boundaries are dominant. Therefore, the current status as to whether the dominant deformation mechanism for plasticity involves grain boundaries or dislocations is not conclusive. Our results in FIG. 3.8 indicate that dislocations do not contribute significantly to plastic strain at the 5 nm grain size. As the grain size
increases, dislocations play an increasing role as total strain increases for 8 and 10 nm grain sizes and, in contrast, a decreasing role for 15 to 30 nm grain sizes. At the 10% total strain, the dislocation contribution is 30-40% for all grain sizes above 5 nm. This trend was reproducible in the simulations and we attribute this to an interplay of mechanisms through the range of the inverse Hall-Petch transition.

FIGS. 3.9a-f show deformation structures for 5 to 30 nm grain size at strains of 2, 4, 6 and 8%, along with stress-strain curves. In FIG. 3.9a (5 nm), there is no emission of dislocations until at a strain of 4% one dislocation is emitted. Above a strain of 4%, one or two dislocations are generated. In FIG. 3.9b (8 nm), dislocations are nucleating at a strain of 2%, four dislocations are emitted from grain boundaries at a strain of 4% and these move across the grains until they annihilate at the opposite grain boundaries. At a strain of 8%, more dislocations are generated and a twin is formed after a dislocation nucleates on a parallel slip plane. In FIG. 3.9c (10 nm), no dislocation activity is found at a strain of 2%. At a strain of 4% five dislocations are generated from grain boundaries, and at a strain of 6% more dislocations are formed and move along the slip planes to the opposite grain boundaries. At a strain of 8%, a twin is formed. In FIG. 3.9d (15 nm), no dislocation activity is found until 6% strain when dislocations are generated from grain boundaries. More dislocations are emitted at a strain of 8%. As the grain size increases to 20 and 30 nm in FIGS. 3.9e and f, respectively, dislocations are generated at 4% strain and the number of dislocations increases as strain increases. In the larger grain sizes (20 and 30 nm), dislocations moving in a slip plane interact with dislocations moving in the other slip plane in the same grain. As the grain
size increases, the strain at which dislocations are first nucleated from grain boundaries is delayed.

FIGS. 3.10a-e show the maps for the total accumulated local strain per atom at 7% total strain for grain sizes of 5, 8, 10, 15 and 20 nm, respectively. To enhance visualization, only atoms with a local strain greater than 7% are shown in FIGS. 3.10f-j, corresponding to FIGS. 3.10a-e, respectively. The color coding scheme is: purple (low strain) ⇒ blue ⇒ green ⇒ yellow (high strain). The initial (unstrained) structure was used for the reference configuration in this study, and the local strain contour maps presented here show the accumulated deviatoric shear throughout the total strain history. This includes plastic shear produced by dislocation motion, as well as other plastic shear straining mechanisms. At 5 nm grain size in FIG. 3.10f, the local strain values are distributed along grain boundaries. As grain size increases in FIGS. 3.10g-j, features on the maps corresponding to dislocation motion and twins can be seen in addition to local strain in the grain boundaries.

FIGS. 3.11a-e show the accumulated local strain maps at 9% of total strain for grain sizes of 5, 8, 10, 15 and 20 nm, respectively. Likewise, FIGS. 3.11f-j show the maps for local strain above 9%. At 9% strain, the number of dislocations increases and stacking faults and twins are formed, however, little dislocation activity is observed at 5 nm grain size. At 5 nm grain size, most of the local strain is concentrated in grain boundaries, whereas in other grain sizes, the local strain is distributed away from grain boundaries.
FIGS. 3.12a-e show the local strain maps at 9% total strain using the maps at 8% total strain as the reference configuration, i.e., the incremental local strain accumulated between 8 and 9% strain. To enhance visualization, only local strain values above 5% are shown (close to the thermal noise threshold). At 5 nm grain size, local strain accumulates around triple junctions. At larger grain sizes, the local strain is distributed along dislocation slip traces.

3.3 SUMMARY

MD straining simulations for pure Al indicated that the yield stress decreases as the grain size increases above 15 nm, indicating the Hall-Petch effect, and decreases as the grain size decreases below 15 nm, showing the inverse Hall-Petch effect. The number of dislocations nucleated from grain boundaries increases and the plastic strain contribution from dislocations increase as the grain size increases. Local strain mapping showed that high local strains are associated with slip in larger grain sizes, and this will transition to grain boundaries at the smallest grain sizes.

3.4 REFERENCES

FIG. 3.1 Three sets of stress-strain curves for pure Al microstructures with grain size of (a) 5 nm, (b) 8 nm, (c) 10 nm, (d) 15 nm, (e) 20 nm and (f) 30 nm.
FIG. 3.2 (a) Stress-total strain $\varepsilon_T$ curves and (b) stress-plastic strain $\varepsilon_p$ curves of nanocrystalline Al with different grain sizes of 5-30 nm.
FIG. 3.3 (a) The effective Young’s modulus (E), (b) 0.5% offset yield stress ($\sigma_{0.5}$) and (c) peak stress ($\sigma_p$) values from three sets of pure Al stress-strain curves as a function of grain size.
FIG. 3.4 Structural changes at strains of (a) 4.7%, (b) 7.6% and (c) 8.6% with a grain size of 10 nm. The visualization is according to the centro-symmetry parameter.

FIG. 3.5 The number of dislocations generated during straining simulations as a function of total strain in pure Al microstructures with different grain sizes of 5-30 nm.
FIG. 3.6 The plastic strain $\varepsilon_p$, strain by dislocation $\varepsilon_d$ and the difference between two ($\varepsilon_p - \varepsilon_d$) for pure Al with grain sizes of (a) 5, (b) 10, (c) 15, (d) 20 and (e) 30 nm.
strain, $\varepsilon_T$

(a) plastic strain, $\varepsilon_p$
strain by dislocation, $\varepsilon_d$
$\varepsilon_p - \varepsilon_d$

(b) plastic strain, $\varepsilon_p$
strain by dislocation, $\varepsilon_d$
$\varepsilon_p - \varepsilon_d$

(c) plastic strain, $\varepsilon_p$
strain by dislocation, $\varepsilon_d$
$\varepsilon_p - \varepsilon_d$

55
strain, $\varepsilon_T$

(e) [Graph showing plastic strain, strain by dislocation, and their difference $\varepsilon_p - \varepsilon_d$.]
FIG. 3.7 The dislocation movement in the hexagonal grain in the simulation system.
FIG. 3.8 (a) $\varepsilon_d/\varepsilon_p$ and (b) $(\varepsilon_p-\varepsilon_d)/\varepsilon_p$ with dislocation strain ($\varepsilon_d$) and plastic strain ($\varepsilon_p$) for pure Al with different grain sizes of 5-30 nm.
FIG. 3.9 Deformation structures at strains of 2, 4, 6 and 8% of grain sizes of (a) 5, (b) 8, (c) 10, (d) 15, (e) 20 and (f) 30 nm with showing stress-strain curves.
Figure 6.6: Comparison of stress-strain curves under different strain levels.

(a) Strain levels of 2%, 4%, 6%, and 8% for sample A.

(b) Strain levels of 2%, 4%, 6%, and 8% for sample B.
stress, \( \sigma \) (GPa)

strain, \( \varepsilon \)

\( \varepsilon \approx 2, 4, 6, 8\% \)
stress, $\sigma$ (GPa)

strain, $\varepsilon$

$\varepsilon \sim 2, 4, 6, 8\%$

$0.00 \ 0.02 \ 0.04 \ 0.06 \ 0.08 \ 0.10$

$0 \ 1 \ 2 \ 3$

$\varepsilon \sim 2, 4, 6, 8\%$

stress, $\sigma$ (GPa)

strain, $\varepsilon$
FIG. 3.10 The accumulated local strain at 7% of total strain for pure Al with grain sizes of (a) 5, (b) 8, (c) 10, (d) 15 and (e) 20 nm. The atoms having local strain value less than a total strain of 7% are deleted and shown in (f)-(j) corresponding to (a)-(e).
FIG. 3.11 The accumulated local strain at 9% of total strain for pure Al with grain sizes of (a) 5, (b) 8, (c) 10, (d) 15 and (e) 20 nm. The atoms having local strain value less than a total strain of 9% are deleted and shown in (f)-(j) corresponding to (a)-(e).
FIG. 3.12 The 8-9% incremental deformation having local strain less 0.05 (remove thermal noise) for pure Al with grain sizes of (a) 5, (b) 8, (c) 10, (d) 15 and (e) 20 nm.
CHAPTER 4
PLASTIC DEFORMATION OF NANOCRYSTALLINE ALUMINUM-LEAD ALLOY BY UNIAXIAL STRAINING SIMULATIONS

Plastic deformation of nanocrystalline Al-Pb alloys was investigated using molecular dynamics (MD) simulations. We also have investigated the segregation of Pb atoms to the grain boundaries of Al using the Monte Carlo (MC) method and MEAM potentials that we developed for Al-Pb alloys. The effect of Pb addition on deformation mechanisms and grain boundaries in nanocrystalline Al-Pb alloys was studied. These simulations show that deformation mechanisms of Al-Pb alloy are different from that of pure Al. The details are discussed in terms of stress-strain curves, structure changes and local mapping techniques.

4.1 BACKGROUND AND INTRODUCTION

There are many metal-metal systems with a miscibility gap in the liquid state such as Al-Pb, Cu-Pb or Al-Bi. Some of these have been used as bearing materials [1, 2]. Al and Pb are immiscible in the solid state and they have a wide miscibility gap in the liquid state [3]. There have been several reports showing the effect of Pb particles on the properties of Al. For example, melting behavior of nanosized Pb particles embedded in an Al matrix was investigated and the presence of Pb particles can lower or elevate the melting temperature of Pb from its bulk value [4-9].
When Al-Pb alloys are made by ion implantation or rapid solidification, Pb inclusions form in the grain boundaries. The boundary inclusions are larger than inclusions embedded in the Al matrix. Grain boundaries provide diffusion paths for the growth of Pb particles. Al and Pb have an fcc structure, and there is a 22% difference in lattice parameter \(a_{\text{Al}}=4.05\text{Å},\ a_{\text{Pb}}=4.95\text{Å}\). Pb inclusions in Al usually form strongly faceted particles in parallel topotaxy and free of defects [10, 11]. Dahmen et al. observed the effect of size and interface structure on premelting behavior of nanoscale Pb inclusions embedded in Al, using grain boundary particles that have two different interfaces. Premelting first initiates at the large-angle interface and the topotaxial interface does not premelt until the particle melts completely and its shape is changed upon exceeding the bulk melting point [12].

In spite of a large amount of research on the thermal behavior and recrystallization of Pb inclusions embedded in an Al matrix, the deformation mechanisms in Al-Pb alloys have not been investigated. Moreover, a relatively small number of MD simulations have been reported on the effect of alloying elements on the deformation mechanisms in nanocrystalline metals [13], whereas numerous simulations of pure metals [14-20] have been performed. If an insoluble element is added to a nanocrystalline matrix, it can produce second-phase particles or segregate to grain boundaries. Since nucleation of partial dislocations from grain boundaries along with grain boundary sliding and rotation have been shown to facilitate deformation in fcc nanocrystalline metals, grain boundary segregation is expected to have an influence on the deformation mechanisms.
The effects of Pb on the mechanical properties on nanocrystalline Al are conflicting based on several experimental studies [21, 22]. FIG. 4.1a shows the hardness as a function of Pb content in Al-Pb alloys from Rajulapati et al. [22] and FIG. 4.1b shows a Z-contrast transmission electron microscopy (TEM) image of Al-Pb. Al and Pb are immiscible in the solid state [3]. Rajulapati et al. [22] observed a dramatic decrease in hardness with Pb addition of only a few atomic percent, as shown in FIG. 4.1a. In contrast, Sheng et al. [21] found that Pb additions to a nanocrystalline Al matrix increases hardness. The reasons for these differences are not understood, but appear to be related to Pb segregation to grain boundaries, as observed by Z-contrast high-resolution TEM in [22]. Motivated by this, we extended the straining simulations to Al-Pb alloys.

4.2 RESULTS

4.2.1 Monte Carlo (MC) simulations

MC simulation methods have been successfully used in previous surface segregation calculations for various alloys (for example, Al-Mg [23], Ni-Cu [24] and Pt-Ni [25]. MC methods have advantages for studying segregation phenomena in an alloy system since these methods can avoid slow physical dynamic process such as diffusion, while providing an average composition profile over a thermodynamic equilibrium ensemble. The MC simulations use the Al-Pb MEAM potential with statistical mechanics based on a canonical ensemble, i.e., the total number of atoms, volume and temperature are held
constant. After a required number of Pb atoms are introduced randomly into the Al matrix, MC simulations are done to obtain the equilibrium configuration of Pb atoms in the matrix and grain boundaries at 300K.

In this method, starting from a given atomic configuration, the successive configurations are generated in proportion to the probabilities of a configuration occurring in the equilibrium ensemble. The algorithm for the MC simulation exchanges a randomly selected pair of Al and Pb atoms. First, randomly selected atoms were displaced from their original positions by a small amount in a random direction. Second, two randomly selected atoms with different element types (Al and Pb) were exchanged. The first operation accounts for the relaxation and vibration processes and the second operation accounts for the inter-diffusion process in the system. According to the Boltzmann distribution, the probability \( (P_{AB}) \) of the configuration transformation (for example, from A to B) is given by a Boltzmann factor for the change in energy \( (\Delta E = E_B - E_A) \).

\[
P_{AB} = \exp\left(-\frac{\Delta E}{k_B T}\right)
\]

(4.1)

Here, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. If the energy of the new configuration is less than that of the previous one, the exchange is accepted; otherwise it is accepted based on the thermodynamic probability of \( P_{AB} \). The simulation is terminated when the energy change is less than a cutoff limit.
The straining simulations for Al-Pb alloys discussed in this chapter were done for a grain size of 10 nm. The range of the Pb content used was 1, 2, and 3 at% Pb. This range was selected based on an estimate of the amount of Pb needed to produce a monolayer along otherwise perfect crystal grains of Al. FIG. 4.2 shows a schematic of a hexagonal grain in the columnar microstructure model. We assume that there is a Pb monolayer on Al grain boundaries. The lengths of \( D \) and \( d \) are defined as shown in FIG. 4.2 and \( \delta \) is a grain boundary width in the columnar model.

The total hexagon volume, \( V_0 \) is

\[
V_0 = V_m + V_g
\]  

(4.2)

where \( V_m \) is the volume of the matrix and \( V_g \) is the volume of the grain boundary.

The volume per hexagonal grain for Al atoms, \( V_h \) is

\[
V_h = 6 \times 2 \times \frac{1}{2} \times \left( \frac{D}{2} \right) \left( \frac{D}{2} \tan 30^\circ \right) = \frac{3}{2} D^2 \tan 30^\circ = 0.866D^2
\]  

(4.3)

The volume of the matrix, \( V_m \) is

\[
V_m = 6 \times 2 \times \frac{1}{2} \times \left( \frac{D - \delta}{2} \right) \left( \frac{D - \delta}{2} \tan 30^\circ \right) = \frac{3}{2} (D - \delta)^2 \tan 30^\circ = 0.866(D - \delta)^2
\]  

(4.4)

The volume of the grain boundary, \( V_g \) is

\[
V_g = V_h - V_m = \frac{3}{2} \tan 30^\circ \left[ D^2 - (D - \delta)^2 \right] = 0.866 \left[ D^2 - (D - \delta)^2 \right]
\]  

(4.5)

\[
\frac{V_m}{V_g} = \frac{(D - \delta)^2}{D^2 - (D - \delta)^2} = \frac{1}{1 - \frac{\delta^2}{D^2}} \approx \frac{D}{2\delta} - 1
\]  

(4.6)
$v_m$ and $v_g$ are the volume per atom in the matrix and the grain boundary, respectively. $N_m$ and $N_g$ are the number of atoms in the matrix and the grain boundary, respectively. These are

$$N_m = \frac{V_m}{v_m}; \quad N_g = \frac{V_g}{v_g}$$

(4.7)

The atom fraction $f$ in the grain boundary is

$$f = \frac{N_g}{N_g + N_m} = \frac{1}{1 + \frac{N_m}{N_g}} = \frac{1}{1 + \frac{V_m}{V_g} \frac{v_g}{v_m}} = \frac{1}{1 + \frac{v_g D}{v_m 2\delta}}$$

(4.8)

For the fcc structures, $v_{fcc} = \frac{16}{(\sqrt{2})^3} r^3 = 5.66 r^3$, where $r$ is the atom radius.

Assume that $v_m = v_{Al(fcc)}$; $v_g = v_{Pb(fcc)}$; $\delta = v_{Pb}^{1/3}$

Therefore, the atom fraction $f_{gb}$ of Pb to produce a grain boundary monolayer with perfect Al grains is given by

$$f_{Pb} = \frac{1}{1 + \frac{v_{Pb}^{2/3} D}{v_{Al} 2}} = \frac{1}{1 + \frac{v_{Pb}^{2/3} d}{v_{Al} 2.31}}; \quad d \text{ in nm}$$

(4.9)

Here, $r_{Pb} = 0.175$ nm and $r_{Al} = 0.143$ nm.

$$\frac{v_{Pb}^{2/3}}{2.31 v_{Al}} = \frac{(5.66)^{2/3} r_{Pb}^2}{2.31(5.66)r_{Al}^3} = 2.544$$

(4.10)

Therefore, $f_{gb}$ is obtained as

$$f_{Pb} = \frac{1}{1 + 2.544d}; \quad d \text{ in nm}$$

(4.11)
FIG. 4.3 shows \( f_{Pb} \) as a function of grain size \( d \) from Eq. (4.11). At \( d = 10 \) nm, we have that 

\[
f_{Pb} = \frac{1}{(1 + 2.544d)} = 0.038,
\]

which gives 3.8 at% Pb for a monolayer at a grain size \( d = 10 \) nm. Thus, Pb contents of 1, 2 and 3 at% should indicate well the trends as the ideal monolayer saturation limit is approached. Note that \( f_{Pb} \) scales approximately as \( 1/d \) so if the grain size is doubled to 20 nm the atomic % Pb should be reduced by 50% for comparison to the 10 nm results.

Al-Pb alloy structures generated by the MC simulation method are illustrated in FIG. 4.4 using centro-symmetry visualization. The structure of pure Al is shown in FIG. 4.4a for comparison. The structures were relaxed by equilibration at 300K. The atomic percentages of Pb are 1, 2 and 3, respectively in FIGS. 4.4b-d. FIGS. 4.4e-g show only the Pb atoms from FIGS. 4.4b-d, respectively. As is seen, virtually all Pb atoms are segregated to grain boundaries after the MC simulation. The thickness of the grain boundaries in FIG. 4.4 appears to increase with the Pb content. This was confirmed by the total percentage of Al+Pb atoms that are found in grain boundaries, which is 14.1%, 16.7% and 19.2% for 1 to 3 at% Pb, respectively, which is compared to 12.4% for pure Al.

### 4.2.2. MD straining simulations

FIGS. 4.5a-c show stress-strain curves for Al-Pb microstructures with 1, 2 and 3 at% of Pb, respectively. Each figure shows the results of three different initial structures for the same
conditions of straining. The individual curves are very reproducible with Al-1at% Pb alloy having the largest variations at total strain above 6%.

One set of simulations at each grain size was taken from FIG. 4.5 and shown in FIG. 4.6a as the stress-total strain $\varepsilon_T$ curves. FIG. 4.6b shows the stress vs. plastic strain $\varepsilon_p$ curves obtained from FIG. 4.6a. The plastic strain is evaluated using $\varepsilon_p=\varepsilon_T-\sigma/E$.

FIGS. 4.7a-c show the effective Young’s modulus (E), 0.5% offset yield stress ($\sigma_{0.5}$) and peak stress ($\sigma_p$) for pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb. Average values of E, $\sigma_{0.5}$ and $\sigma_p$ are shown and standard deviations for the three simulations are indicated. The E values are in the range of 50-59 GPa compared to the experimental value of $E \approx 70$ GPa for polycrystalline Al. As the Pb content increases, E values decrease. A (vertical) plastic strain offset 0.5% was used to define offset yield stress $\sigma_{0.5}$ in conjunction with the $\sigma$ vs. $\varepsilon_p$ curves in FIG. 4.6b. The $\sigma_{0.5}$ values will increase if the offset is increased, but the relative differences remain similar up to 2% plastic strain. The $\sigma_{0.5}$ values are found to be in the range of 1.33-1.77 GPa. When the Pb content increases the $\sigma_{0.5}$ value decreases. The $\sigma_p$ values decrease as the Pb content increases. The $\sigma_{0.5}$ values and $\sigma_p$ values decrease by ~17% and ~6%, respectively, as the Pb content increases to 3 at%. For the experimental results reported in [22], the hardness decreases by ~40% for 33 nm grain size Al-Pb alloy with ~0.55 vol% addition of Pb. The simulations do not account for the very large strength decrease observed in these experiments, and they cannot capture the 3D grain structure and low strain rates in the latter, but they do indicate the onset of a softening effect as a result of Pb segregation to grain boundaries.
FIGS. 4.8a-d show deformation structures and stress-strain curves of pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb at strains of 2, 4, 6 and 8%. In FIG. 4.8a, number of dislocations is increased as strain increases. In FIG. 4.8b, no dislocations are generated until a strain of 6% where dislocations begin to form. At a strain of 8% a twin and a dislocation lock are formed. In FIG. 4.8c, only one dislocation is generated at a strain of 8%. In FIG. 4.8d, no dislocation generation is observed throughout the simulation up to 10% strain.

FIGS. 4.9a-d illustrate the effect of Pb on the deformation structures at 7% total strain, as revealed by centro-symmetry. Structural changes at 7% deformation are shown for pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb in FIGS. 4.9a-d, respectively. The accumulated local strain maps are shown in FIGS. 4.9e-h, corresponding to FIGS. 4.9a-d, respectively. The color coding scheme for local strain maps is: purple (low strain) → blue → green → yellow (high strain). To enhance visualization, the atoms having local strain value less than 0.07 are deleted and shown in FIGS. 4.9i-l corresponding to FIGS. 4.9e-h, respectively. For the pure Al shown in FIG. 4.9a, partial dislocations and dislocation pairs (green) with intrinsic stacking faults (yellow) are nucleated at grain boundaries and triple junctions. The dislocations travel across the grains on the slip planes and are absorbed into grain boundaries on the opposite side. Extrinsic stacking faults and twin lamella can also be observed. As the Pb content increases from 1 to 3 at% in FIGS. 4.9b-d, the nucleation of dislocations from 60° tilt grain boundaries is reduced in each figure until, at 3 at% Pb in FIG. 4.9d, no dislocations are generated during straining. The total number of dislocations decreases with increasing Pb.
content. The formation of stacking faults and twins are observed less in Al-1at% Pb than in pure Al. Only one dislocation connected by one intrinsic stacking fault is observed in Al-2at% Pb and no dislocations in Al-3at% Pb. Compared with the MD simulations of pure Al nanostructures, the results show that the addition of Pb suppresses the formation of partial dislocations at the grain boundaries while at the same time increases the overall thickness of grain boundaries. A larger amount of disorder is also found in the grain boundaries in the alloys. Increasing disorder is seen in FIGS. 4.9b-d, where the grain boundaries appear thicker compared to the pure Al grain boundary structure in FIG. 4.9a. The percentages of Al+Pb atoms in grain boundaries in the Al-Pb alloys are 14.12%, 16.70% and 19.24% in 1, 2 and 3 at% Pb, respectively, compared to 12.39% in pure Al. The relative percentage of Pb atoms in the Al+Pb grain boundaries are 7.13%, 12.05% and 15.69% in 1, 2 and 3 at% Pb, respectively.

FIGS. 4.10a-d are representations similar to FIGS. 4.9a-d, but at 9% total strain. FIGS. 4.10e-h show the local strain maps corresponding to FIGS. 4.10a-d, respectively. To enhance the displays for localization, FIGS. 4.10i-l and FIGS. 4.10m-p show the local strain maps with atoms having local strains above 0.09 and 0.16, respectively, corresponding to FIGS. 4.10e-h. FIG. 4.10a shows that the total number of dislocations increases, and stacking faults and twins are formed for pure Al. These features are suppressed as the Pb content increases in FIGS. 4.10b-d. One twin and one partial dislocation connected to an intrinsic stacking fault are seen at Al-1%Pb in FIG. 4.10b. There is one twin at Al-2%Pb in FIG. 4.10c and no dislocation or twin activity at Al-3%Pb in FIG. 4.10d. Pure Al in FIG. 4.10m has high local
strain distributed at grain boundaries and stacking faults connected by dislocations. However, in the Al-Pb alloys in FIGS. 4.10n-p, the high local strain becomes increasingly concentrated on grain boundaries until at 3 at% Pb in FIG. 4.10p there is complete suppression of intra-grain local strain. The accumulated strain is very low in boundaries that lie parallel to the horizontal straining direction.

FIGS. 4.11a-d show histograms of local strain values at a total strain of 9% in pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb, respectively. The inset pictures for each histogram are plotted for strain values above the total nominal strain of 9%. Using the histograms, the deformation participation ratio (DPR) is obtained from FIGS. 4.11a-d as the fraction of atoms having a local strain larger than the 9% nominal strain. An upper bound of 0.5 for the DPR indicates a limit of uniform strain in the sense that the probability of local strain per atom being larger or smaller than the nominal value is equal. In contrast, lower values of the DPR indicate non-uniform strain localization. If strain is localized entirely within discrete shear bands, then the DPR approaches the ratio of the deformed-to-undeformed volumes, which can be quite small for extreme localization.

FIG. 4.12 shows the DPR plotted as a function of at% Pb. The DPR decreases as Pb content increases, and reaches a saturation limit at 2 and 3 at%. At 2 and 3 at% Pb, the DPR is a half of that for pure Al. The higher DPR for pure Al represents a more uniform strain distribution while smaller values of DPR for the Al-Pb alloys represent a more localized strain distribution in grain boundaries.
FIGS. 4.13a-d show an enlarged atomic configuration of the same 60° tilt grain boundary for pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb using the centro-symmetry parameter, respectively. FIGS. 4.13e-h illustrate the same boundary structures colored by local strain maps, corresponding to FIGS. 4.13a-d, respectively. To enhance visualization, only the atoms having local strain values higher than 0.09 are presented in FIGS. 4.13e-h. For pure Al in FIGS. 4.13a and e, there are three sites (black circles) from which partial dislocations are nucleated. The nucleation and emission of partial dislocations occurs with reorganization of the remaining grain boundary including the grain boundary nucleation sites. Swygenhoven et al. reported that at the atomic level, atomic shuffling and stress assisted free-volume migration play a significant role in plastic deformation in pure nanocrystalline metals [26]. They suggested that atomic shuffling causes both grain boundary plastic strain and dislocation nucleation. Shuffling is accompanied by a stress-assisted free-volume migration [17, 26]. The free-volume migration is often observed in connection with emission of partial dislocations from grain boundaries [17, 27]. From this observation, we expect there is free-volume migration in the three sites in FIGS. 4.13a and e. For Al-Pb alloys with 1 to 3 at% Pb in FIGS. 4.13c-e and f-h, Pb atoms in the grain boundary cluster in the same sites as those for dislocation emission for pure Al. Therefore, in Al-Pb alloys, it appears that those sites that favor nucleation of partial dislocations in pure Al also attract Pb atoms that cluster, thereby suppressing the free-volume migration and related effects that allow partial dislocation emission.
4.3 SUMMARY

A MEAM potential was developed and used for MD straining simulations of Al-Pb alloys with a grain size of 10 nm and Pb content up to 3 at%. MC simulations done at 300K indicated that all the Pb is segregated to the grain boundaries in these alloys. As the Pb content increases, partial dislocation nucleation at grain boundaries is suppressed, the grain boundaries are more stable with respect to disruption or decomposition and the plastic strain is accommodated by mechanisms other than dislocation slip. The increasing Pb content was accompanied by a reduction in the yield and peak stress values. This lends support to the hypothesis that Pb segregation to grain boundaries causes the drop in hardness observed by Rajulapati et al. [22].

4.4 REFERENCES


FIG. 4.1 Experimental data of (a) hardness as a function of Pb contents and (b) transmission electron microscopy (TEM) picture from Rajulapati et al.
FIG. 4.2 The hexagonal shaped grain in the columnar microstructure model.

FIG. 4.3 The atomic fraction $f_{Pb}$ of Pb vs. grain size needed to produce a grain boundary monolayer surrounding perfect Al grains.
FIG. 4.4 The relaxed simulation cell at 300K with grain boundaries for (a) pure Al and Al-Pb alloy structures with (b) 1, (c) 2 and (d) 3 at% of Pb. The structures are colored by the centro-symmetry parameter. Only Pb atoms are shown in (e), (f) and (g) corresponding to (b), (c) and (d), respectively.
FIG. 4.5 Three sets of stress-strain curves for Al-Pb alloy structures with (a) 1, (b) 2 and (c) 3 at% Pb.
FIG. 4.6 (a) Stress-total strain $\varepsilon_T$ curves and (b) stress-plastic strain $\varepsilon_p$ curves for pure Al and Al-Pb alloys of 1-3 at% Pb with a grain size of 10 nm.
FIG. 4.7 (a) The effective Young’s modulus (E), (b) 0.5% offset yield stress ($\sigma_{0.5}$) and (c) peak stress ($\sigma_p$) from three stress-strain curves of pure Al and Al-Pb alloy as a function of Pb.
FIG. 4.8 Deformation structures at strains of 2, 4, 6 and 8% for (a) pure Al and Al-Pb alloy of (b) 1, (c) 2 and (d) 3 at% Pb with showing stress-strain curves.
(a) stress, $\sigma$ (GPa) vs strain, $\varepsilon$ for $\varepsilon \sim 2, 4, 6, 8\%$

(b) stress, $\sigma$ (GPa) vs strain, $\varepsilon$ for $\varepsilon \sim 2, 4, 6, 8\%$
FIG. 4.9 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb. The accumulated local strain maps are shown in (e)-(h) corresponding to (a)-(d). The atoms having local strain value less than total strain of 0.07 (macroscopic strain) are deleted and shown in (i)-(l) corresponding to (e)-(h).
FIG. 4.10 Structural changes during 9% deformation in (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb. Local strain mapping at a strain of 9% with different Pb contents; (e) pure Al and Al-Pb alloys with (f) 1, (g) 2 and (h) 3 at% Pb. The atoms having local strain less than 0.09 and 0.16 are removed showing in (i)-(l) and (m)-(p) corresponding to (e)-(h), respectively.
FIG. 4.11 Histograms of local strain values at a strain of 9% with different Pb contents; (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb. Inset pictures are local strain mappings having values above 0.09.
FIG. 4.12 Deformation participation ratio (DPR) measured at a strain of 9% plotted as a function of at% of Pb.
FIG. 4.13 The enlarged atomic configuration of the same 60° tilt grain boundary for (a) pure Al and (b) 1, (c) 2 and (d) 3 at% Pb, respectively, using the centro-symmetry parameter. Local strain maps of (e)-(h) are illustrated corresponding to (a)-(d), respectively.
CHAPTER 5
PLASTIC DEFORMATION OF NANOCRYSTALLINE ALUMINUM-LEAD ALLOY BY UNIAXIAL STRAINING SIMULATIONS:
DEPENDENCE ON THE GRAIN SIZE

Deformation of nanocrystalline aluminum-lead alloys having larger grain sizes than that of Chapter 4 is investigated. Monte Carlo (MC) simulations were carried out for constructing the Al-Pb alloy microstructures using MEAM potentials. Uniaxial straining simulations were performed to study mechanical behavior. The Pb content at the larger grain size was scaled based on grain size in order to compare results to the 10 nm grain size in Chapter 4. These simulations show how deformation mechanisms of Al-Pb alloy change as the grain size increases. The details are discussed in terms of stress-strain curves, structure changes and local mapping techniques.

5.1 SIMULATION SETUP

MC simulations with Al-Pb MEAM potentials were used to build equilibrated Al-Pb microstructures for 15 and 20 nm grain sizes. The Pb content for 15 and 20 nm grain size simulations in this chapter was scaled by the grain size ratios for comparison with 10 nm grain size alloys in Chapter 4. The atomic fraction of Pb needed to obtain a grain boundary monolayer for the columnar microstructure in FIG. 5.1 is \( \frac{1}{(1 + 2.55d)} \approx \frac{1}{2.55d} \) for \( d \geq 10 \) nm.
Pb contents in 15 and 20 nm grain sizes must then be 2/3 and 1/2 that for 10 nm alloys to maintain similar monolayer fractions. The “equivalent” at% Pb values used for the simulations are given in Table 5.1.

Table 5.1 The equivalent at% Pb values required for 10, 15 and 20 nm grain sizes.

<table>
<thead>
<tr>
<th>Equivalent at% Pb</th>
<th>Actual at% Pb</th>
<th>10 nm</th>
<th>15 nm</th>
<th>20 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.67</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1.5</td>
<td></td>
</tr>
</tbody>
</table>

Al-Pb alloy microstructures generated by the MC simulation method are shown in FIG. 5.1 using centro-symmetry visualization. The structures of pure Al with grain sizes of 15 and 20 nm are also illustrated in FIGS. 5.1a and f, respectively. Al-Pb alloys with 1 and 3 equivalent at% Pb for 15 nm grain size are illustrated in FIGS. 5.1b and c, respectively and for 20 nm in FIGS. 5.1g and h, respectively. FIGS. 5.1d, e, i and j show only the Pb atoms (red color) from FIGS. 5.1b, c, g and h, respectively. As is seen, all Pb atoms are segregated to grain boundaries after the MC simulation. The thickness of the grain boundaries in FIG. 5.1 increases with the Pb content. This was confirmed by the total percentage of atoms that are found in grain boundaries, which is 9.61% and 13.10% for 1 and 3 equivalent at% Pb, respectively. This is compared to 8.36% for pure Al in 15 nm grain sized samples. The percentages are 8.67% and 9.96% for 1 and 3 equivalent at% Pb, respectively compared to 6.34% for pure Al in 20 nm grain sized samples.
5.2 MD STRAINING SIMULATIONS

FIGS. 5.2a and b show three sets of stress-strain curves for Al-Pb microstructures having a 15 nm grain size with 1 and 3 equivalent at% of Pb, respectively. Each figure shows the results of three simulations using different initial microstructures. The individual curves are very reproducible with small variations at total strain above 8%. FIGS. 5.3a and b show stress-strain curves for Al-Pb microstructures having a 20 nm grain size with 1 and 3 equivalent at% of Pb, respectively. As in FIG. 5.2, three different initial equilibrated structures were used for the simulations and the individual curves are very reproducible.

FIGS. 5.4a-c show stress vs. total strain $\varepsilon_T$ curves for grain sizes of 10, 15 and 20 nm, respectively. FIGS. 5.5a-c show typical stress vs. plastic strain $\varepsilon_p$ curves for grain sizes of 10, 15 and 20 nm, respectively. The plastic strain was evaluated using $\varepsilon_p=\varepsilon_T-\sigma/E$ as described in Chapter 3. The stress-strain curves shift downward and the peak stresses decrease as Pb content increases.

FIGS. 5.6a-c show the effective Young’s modulus (E), 0.5% offset yield stress ($\sigma_{0.5}$) and peak stress ($\sigma_p$) for pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb having grain sizes of 10, 15 and 20 nm. The results for 2 at% Pb for the 10 nm grain size are also included. The E values are in the range of 50-63 GPa compared to the experimental value of E~70 GPa for polycrystalline Al. As the Pb content increases to 3 equivalent at%, E values decrease except for the 15 nm grain size, where the E value increases. The $\sigma_{0.5}$ yield stress decreases
by ~17%, ~40% and 3% for 10, 15 and 20 nm grain sizes, respectively, as the Pb content increases to 3 equivalent at%. For the case of 20 nm, the $\sigma_{0.5}$ values are not much changed with variation of Pb content. At 1 equivalent at% Pb, $\sigma_{0.5}$ values are almost the same at each grain size. At 3 equivalent at% Pb, the $\sigma_{0.5}$ value is the highest in 20 nm grain size and $\sigma_{0.5}$ value for 15 nm has lowest. The peak stress values decrease by ~7%, ~16%, and 16%, respectively for 10, 15 and 20 nm grain sizes, as the Pb content increases to 3 equivalent at%.

FIGS. 5.7a-d illustrate the effect of Pb on the deformation structures of 10 nm grain size at 7% total strain, as revealed by centro-symmetry. The accumulated local strain maps are shown in FIGS. 5.7e-h and the atoms having local strain value less than 0.07 are deleted in FIGS. 5.7i-l. Details of these results are discussed in Chapter 4.

FIGS. 5.8a-c illustrate the deformation structures of 15 nm grain size at 7% total strain, as revealed by centro-symmetry. Structural changes during 7% deformation are shown in Al and Al-Pb alloys with 1 and 3 equivalent at% Pb in FIGS. 5.8a-c, respectively. The accumulated local strain maps are shown in FIGS. 5.8d-f, corresponding to FIGS. 5.8a-c. To enhance visualization, the atoms having local strain value less than 0.07 are deleted and shown in FIGS. 5.8g-i. For the pure Al shown in FIG. 5.8a, a sequence of leading dislocations connected by intrinsic stacking faults are generated from the 60° tilt grain boundary (lower right). The addition of Pb suppresses dislocation generation in FIGS. 5.8b and c. At 1 equivalent at% Pb, two leading dislocations are formed from two triple junctions (white circles). At 3 equivalent at% Pb, only one dislocation is generated from the triple
The local strain maps in FIGS. 5.8d-i show that deformation transfers from partial dislocations connected by stacking faults to grain boundary deformation processes as the Pb content increases. However, compared to the 10 nm grain size in FIG. 5.7d, dislocation generation still occurs at 3 equivalent at% Pb.

FIGS. 5.9a-c illustrate the effect of Pb on the 20 nm grain size deformation structures at 7% total strain, as revealed by centro-symmetry. Structural changes during 7% deformation are shown in Al and Al-Pb alloys with 1 and 3 equivalent at% Pb in FIGS. 5.9a-c, respectively. The accumulated local strain maps are shown in FIGS. 5.9d-f, corresponding to FIGS. 5.9a-c. To enhance visualization, the atoms having local strain value less than 0.07 are deleted and shown in FIGS. 5.9g-i corresponding to FIGS. 5.9d-f, respectively. For the pure Al shown in FIG. 5.9a, leading dislocations connected by intrinsic stacking faults are generated from grain boundaries and triple junctions. More dislocations are generated than for the system corresponding to a 15 nm grain size. At 1 equivalent at% Pb as shown in FIG. 5.9b, the dislocation formation is suppressed and the number of dislocations generated decreases. At 3 equivalent at% Pb shown in FIG. 5.9c, two dislocations are generated from the triple junction and the adjacent grain boundary. The local strain maps in FIGS. 5.9d-i show that local strain is transferred to grain boundaries as the Pb content is increased. FIGS. 5.7 to 5.9 clearly indicate that increasing grain size increases dislocation activity. Furthermore, dislocation activity is not entirely suppressed at 3 equivalent at% Pb at larger grain sizes.
FIGS. 5.10a-c show the histograms of the local strain values at a total strain of 9% for 15 nm grain size in pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb, respectively. The inset pictures for each histogram show local strain maps for the atoms having local strain above 9%. The average local strain values determined from the histograms were 9.5, 8.9 and 8.3% for pure Al and Al-Pb alloys with 1 and 3 equivalent % Pb, respectively. As seen in FIG. 5.10a, the pure Al sample shows that high local strain is distributed at grain boundaries and dislocations connected by stacking faults. Local strain values in the middle range of the color-scale illustrated in the bar are distributed around dislocation trails and grain boundaries. For Al-Pb alloys as seen in FIGS. 5.10b and c, high local strain is distributed dominantly at grain boundaries.

FIGS. 5.11a-c show the histograms of the local strain values at a total strain of 9% for 20 nm grain size in pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb, respectively. The inset pictures for each histogram show local strain maps for the atoms having local strain above 9%. The average local strain values determined from the histograms were 9.4, 9.0 and 8.3% for pure Al and Al-Pb alloys with 1 and 3 equivalent % Pb, respectively. All three maps show the local strain distribution in the grain boundaries and dislocations connected by stacking faults. As seen in FIG. 5.11a, pure Al has local strain values in the middle range of color-scale bar, which are distributed along dislocation trails and inside grains. This feature disappears as the Pb content increases.
FIG. 5.12 shows the deformation participation ratio (DPR) obtained at a strain of 9% for 10, 15 and 20 nm grain sizes plotted as a function of equivalent at% Pb. The DPR is plotted as the value relative to pure Al in FIG. 5.12. This eliminates variations in the absolute values, which have no direct physical interpretation, and shows that the normalized decrease is similar for all grain sizes. This indicates a similar transfer of intra-grain deformation processes to inter-grain processes with the equivalent at% Pb. It also suggests that the saturation effect for the DPR is related to equivalent fractional values of a Pb monolayer over the range of grain sizes.

5.3 SUMMARY

MD straining simulations of Al-Pb alloys with grain sizes of 15 and 20 nm and Pb contents of 1 and 3 equivalent at% were carried out to investigate deformation mechanisms and compare to the results of 10 nm grain size. MC simulations show the segregation of Pb to the grain boundaries. With increasing Pb additions, both grain sizes show that dislocation nucleation from the grain boundaries are suppressed. As Pb content increases to 3 equivalent at%, one or two dislocations are generated during whole straining simulation. The straining simulations also indicated that Pb additions in Al-Pb alloys reduce the yield stress relative to pure Al, however for the case of a grain size of 20 nm the yield stress decreases only by a few percent. In contrast, the peak stresses show a stronger decrease for larger grain sizes. The DPR also decreases as Pb contents increase. High local strains are distributed in the grain boundaries and dislocations connected by stacking faults. The addition of Pb atoms reduces...
the number of dislocations generated in Al grains and the features on the local strain maps corresponding to dislocation motion are reduced in the Al-Pb alloys.
5.4 FIGURES

FIG. 5.1 The relaxed simulation cell at 300K with grain boundaries for (a) pure Al and Al-Pb alloys with (b) 1 and (c) 3 equivalent at% Pb for 15 nm and for (f) pure Al and Al-Pb alloys with (g) 1 and (h) 3 equivalent at% Pb for 20 nm. The atoms are colored by centro-symmetry parameter. Only Pb atoms are shown in (d), (e), (i) and (j) corresponding to (b), (c), (g) and (h), respectively.
FIG. 5.2 Three sets of stress-strain curves for Al-Pb alloy structures with (a) 1 and (b) 3 equivalent at% Pb for 15 nm grain size.
FIG. 5.3 Three sets of stress-strain curves for Al-Pb alloy structures with (a) 1 and (b) 3 equivalent at% Pb for 20 nm grain size.
FIG. 5.4 Stress-strain curves of (a) 10, (b) 15 and (c) 20 nm grain sizes for pure Al and Al-Pb alloys with 1 and 3 equivalent at % Pb.
FIG. 5.5 Stress-plastic strain $\varepsilon_p$ curves for (a) 10, (b) 15 and (c) 20 nm grain sizes for pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb.
FIG. 5.6 (a) The effective Young’s modulus (E), (b) 0.5% offset yield stress ($\sigma_{0.5}$) and (c) peak stress ($\sigma_p$) from three stress-strain curves of pure Al and Al-Pb alloy with grain sizes of 10, 15 and 20 nm as a function of equivalent at% Pb.
Modulus, $E$ (GPa) equivalent at% Pb

Peak stress, $\sigma_p$ (GPa) equivalent at% Pb

(a) 10nm grain size
(b) 15nm grain size
(c) 20nm grain size

0.5% offset yield stress, $\sigma_{0.5}$ (GPa) equivalent at% Pb
FIG. 5.7 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 equivalent at% Pb with 10 nm grain size. The accumulated local strain maps are shown in (e)-(h) corresponding to (a)-(d). The atoms having local strain value less than 0.07 are deleted and shown in (i)-(l).
FIG. 5.8 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys of (b) 1 and (c) 3 equivalent at% Pb with 15 nm grain size. The accumulated local strain maps are shown in (d)-(f) corresponding to (a)-(c). The atoms having local strain value less than 0.07 are deleted and shown in (g)-(i).
FIG. 5.9 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys of (b) 1 and (c) 3 equivalent at% Pb with 20 nm grain size. The accumulated local strain maps are shown in (d)-(f) corresponding to (a)-(c). The atoms having local strain value less than 0.07 are deleted and shown in (g)-(i).
FIG. 5.10 Histograms of local strain values at a strain of 9% of 15 nm grain size; (a) pure Al and Al-Pb alloys with (b) 1 and (c) 3 equivalent at% Pb. Inset pictures are local strain mappings having values above 0.09.
FIG. 5.11 Histograms of local strain values at a strain of 9% of 20 nm grain size; (a) pure Al and Al-Pb alloys with (b) 1 and (c) 3 equivalent at% Pb. Inset pictures are local strain mappings having values above 0.09.
FIG. 5.12 Normalized deformation participation ratio (DPR) measured at a strain of 9% plotted as a function of equivalent at% of Pb for 10, 15 and 20 nm grain sizes.
CHAPTER 6

MOLECULAR DYNAMICS SIMULATIONS OF DEFORMATION IN
NANOCRYSTALLINE AL-PB ALLOYS

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6.1 INTRODUCTION

A large amount of research using molecular dynamics (MD) simulations has been done on
the deformation mechanisms in pure nanocrystalline metals [1-7]. In contrast, a relatively
small number of MD simulations have been reported on the effect of alloying elements on
the deformation mechanisms in nanocrystalline metals [8]. If an insoluble element is added to
a nanocrystalline matrix, it can produce second-phase particles or segregate to grain
boundaries. Since nucleation of partial dislocations from grain boundaries along with grain
boundary sliding and rotation have been shown to facilitate deformation in fcc
nanocrystalline metals, grain boundary segregation is expected to have an influence on the
defformation mechanisms.

Al and Pb are immiscible in the solid state [9]. Sheng et al. [10] found that Pb addition to a
nanocrystalline Al matrix increases hardness, whereas Rajulapati et al. [11] reported a
dramatic decrease in hardness with Pb addition of only a few atomic percent. The reasons for
these differences are not understood, but appear to be related to Pb segregation to grain
boundaries as observed by Z-contrast high-resolution electron microscopy in [11]. Motivated by this, we are currently developing MD simulations to study the effect of Pb addition on deformation mechanisms and grain boundaries in nanocrystalline fcc Al-Pb alloys. Initial results obtained from the MD straining simulations are reported in this paper. The effects of Pb segregation on grain boundary energy, obtained from separate Monte Carlo (MC) simulations, are reported in a companion paper [12].

6.2 SIMULATION PROCEDURE

The MD simulation uses a two-dimensional columnar microstructure similar to that used in [13]. The simulation cell contains four hexagonal grains as illustrated in FIG. 6.1. The grain size $d$ is defined as the distance between two opposite vertices. A grain size $d = 10$ nm was used for all the simulations reported here. The individual grains are rotated by misorientation angles of 0°, 30°, 60°, and 90° about the [1-10] texture axis (z-direction), which produces high-angle grain boundaries. Periodic boundary conditions are used in the x, y and z directions. The [1-10] texture direction is chosen because it is the common axis of (111) and (11-1) planes in which dislocations nucleated from the grain boundaries can glide [13]. This geometry provides a sufficient number of dislocation slip systems to maintain compatible deformation. The simulation cell in FIG. 6.1 contains 14 (1-10) planes in the z-direction; the thickness is determined by the interplanar spacing $\frac{\sqrt{2}}{4} a_0$ ($a_0=4.05\text{Å}$). The total number of atoms in the simulation cell is 30807. A modified embedded atom method (MEAM) potential
was developed to describe the interactions between Al-Al, Pb-Pb and Al-Pb atom pairs [14, 15]. First principles calculations for the B1 (NaCl) and B2 (CsCl) Al-Pb crystal structures were performed, and the MEAM parameters for Al-Pb alloys were fit to the results of these calculations. Details are given elsewhere [16].

Al-Pb alloy microstructures were generated using MC simulations described in Section 6.3.1. The microstructures obtained from the MC simulations were used as input to the MD straining simulations described in Section 6.3.2. All microstructures were equilibrated at 300K. Visualization of the results was done using a centro-symmetry parameter that distinguishes between atoms in an fcc environment and those in hcp and defect environments. The range of the centro-symmetry parameter distinguishes between the different environments [17]. A local strain mapping method described in [18] was used as a second visualization tool. The local environment of an atom is represented by a set of vectors to the nearest neighbor atoms within a specified cutoff distance. A reference configuration and current configuration must be defined. The local shear strain distributions (Von Mises effective deviatoric strain) are derived from this. Hydrostatic strain and lattice rotations are not revealed. The initial (unstrained) structure was used for the reference configuration in this study and local strain contour maps presented here show the accumulated shear throughout the total strain history. This includes plastic shear produced by dislocation motion, as well as other plastic shear straining mechanisms.
6.3 SIMULATION RESULTS

6.3.1 MC simulations

The MC simulations use the Al-Pb MEAM potential with statistical mechanics based on a canonical ensemble, i.e., the total number of atoms, volume and temperature are held constant. After a required number of Pb atoms are introduced into the Al matrix, MC simulations are done to obtain the equilibrium distribution of Pb atoms in the matrix and grain boundaries at 300K. The algorithm for the MC simulation exchanges a randomly selected pair of Al and Pb atoms. The new configuration of atoms is accepted or rejected according to its energy and thermodynamic probability $e^{-(E_f-E_i)/k_BT}$. If the energy of the new configuration is less than that of the previous one, the exchange is accepted; otherwise it is accepted based on the thermodynamic probability. The simulation is terminated when the energy change is less than a cutoff limit.

An equilibrated pure Al grain microstructure is illustrated in FIG. 6.2a using centro-symmetry visualization. The color-coding scheme is blue ⇒ fcc atoms, yellow ⇒ hcp atoms, green ⇒ defect atoms (vacancies, dislocations) and red ⇒ surface/high-misfit grain boundary atoms. Grayscale printing may not clearly reveal the different types. Color is included in the figures available at http://www.mse.ncsu.edu/CompMatSci/. FIGS. 6.2b-d show the Al-Pb microstructures containing 1 to 3 at% Pb, respectively. FIGS. 6.2e-g show only the Pb atoms from FIGS. 6.2b-d, respectively. As is seen, virtually all Pb atoms are segregated to grain boundaries after the MC simulation. For comparison, a simple estimate
shows that ≈ 7 at% Pb is needed to produce a grain boundary monolayer for grain size d = 10 nm. The thickness of the grain boundaries in FIGS. 6.2b-d appears to increase with the Pb content. This was confirmed by the total percentage of atoms that are found in grain boundaries, which is 14.1%, 16.7% and 19.2% for 1 to 3 at% Pb, respectively, which is compared to 12.4% for pure Al.

6.3.2 MD straining simulations

Tensile straining in the [110] x-direction (arrow in FIG. 6.1) was done at a constant strain rate of $6.67 \times 10^9 \text{s}^{-1}$. Periodic boundary conditions are maintained in the x, y and z directions during straining. Strains in the y and z directions were imposed to keep the stresses $\sigma_{yy}$ and $\sigma_{zz}$ close to zero. The MD temperature was maintained at 300K and the time step was $\Delta t = 1\text{fs}$.

The stress $\sigma$ vs. plastic strain $\varepsilon_p$ curves obtained from the simulations are shown in FIG. 6.3a. The inset shows the stress vs. total strain $\varepsilon_T$ curves. An effective Young’s modulus $E$ in the [110] straining direction was obtained from the initial slopes of the $\sigma$ vs. $\varepsilon_T$ curves. $E$ depends on the elastic constants $c_{11}$, $c_{12}$ and $c_{44}$ and it varies with grain orientation. The large fraction of grain boundary atoms at $d = 10$ nm can also affect the modulus. The plastic strain is evaluated using $\varepsilon_p = \varepsilon_T - \sigma / E$. This does not account for non-linear reversible strain. Nevertheless, unloading curves from the 10% total strain used for the simulations showed
that approximately 4% of the strain was reversible, and this was close to the $\sigma/E$ correction. Various procedures, including strain offset, have been proposed to define yield or flow stress in MD straining simulations [19, 20]. There is no established basis for adopting these procedures, and the limitations for defining a yield stress for very small-scale MD simulation models like the 4-grain simulation cell in FIG. 6.1 must be recognized. For the purpose of characterizing the effect of at% Pb on strength for fixed simulation conditions, a (vertical) plastic strain offset of 0.5% was used here to define yield stress in conjunction with the $\sigma$ vs. $\varepsilon_p$ curves in FIG. 6.3a. The yield stress values will increase if the offset is increased, but the relative differences remain similar up to 2% plastic strain. Results are shown in FIG. 6.3b for the modulus E, the 0.5% yield stress $\sigma_{0.5}$ and the peak (ultimate) stress $\sigma_p$ as a function of at% Pb. The E values are in the range of 50-58 GPa compared to the experimental value of E $\approx 70$ GPa for polycrystalline Al. The $\sigma_{0.5}$ values and $\sigma_p$ values decrease by $\approx 17\%$ and $\approx 6\%$, respectively, as the Pb content increases to 3 at%.

A decrease in hardness of $\approx 40\%$ was observed experimentally in [11] for 33 nm grain size Al-Pb alloys with $\approx 1.5$ at% addition of Pb. The MD simulations do not account for the very large strength decrease observed in these experiments, and they cannot capture the macroscopic size scales and low strain rates in the latter, but they do indicate the onset of a softening effect as a result of Pb segregation to grain boundaries. MD simulations for grain sizes in the range of 30 to 40 nm are currently in progress to determine the effect of Pb addition at larger grain sizes.
FIGS. 6.4a-d illustrate the effect of Pb on the deformation structure at 7.2% total strain, as revealed by centro-symmetry. For the pure Al shown in FIG. 6.4a, partial dislocations and dislocation pairs (green) with intrinsic stacking faults (yellow) are nucleated at grain boundaries and triple junctions. The dislocations are observed to travel across the grains on slip planes and are absorbed into grain boundaries on the opposite side. Extrinsic stacking faults and twin lamella can also be observed. The 0-60° grain boundary (FIG. 6.1) in the lower right grain in FIG. 6.4a is being converted into a 70.5° twin boundary as straining progresses. The (horizontal) 60-90° grain boundary in the lower right grain is undergoing decomposition near the adjoining triple junction. These features require relative rotation of the adjacent grains. As the Pb content increases from 1 to 3 at% in FIGS. 6.4b-d, the nucleation of partial dislocations from grain boundaries is diminished until, at 3 at% Pb in FIG. 6.4d, no dislocations are generated during the entire straining history. Decomposition phenomena associated with grain boundaries is also diminished with increasing Pb content, and the grain boundaries are thicker and more stable.

FIGS. 6.5a-d illustrate local strain maps corresponding to the frames in FIGS. 6.4a-d. The maps represent the relative amount of accumulated shear strain at each atom. The color coding scheme is: purple (low strain) ⇒ blue ⇒ green ⇒ yellow (high strain). As the Pb content increases, the features on the maps corresponding to dislocation motion in FIG. 6.4 diminish, until at 3 at% Pb only strain signatures generated within the grain boundaries remain. It also appears that the accumulated strain is lower in boundaries that lie parallel to the straining direction (FIG. 6.1). The atomic mechanisms that facilitate plastic straining due
to grain boundaries and grain rotation, and their interactions with segregated Pb atoms, are being analyzed in more detail and will be discussed in a forthcoming publication.

FIGS. 6.6a-d are representations similar to FIGS. 6.4a-d, but at a total strain of 8.8%. Extensive dislocation activity is observed for pure Al in FIG. 6.6a. A fully formed twin boundary is now present in the lower right grain in FIG. 6.6a. The 60-90° grain boundary in the lower right grain has undergone further decomposition. This grain boundary is eliminated at higher strain, producing a stress driven grain growth effect discussed in [21]. The trends with increasing Pb content follow those in FIG. 6.4. No dislocation activity is observed in the 3 at% Pb alloy. The corresponding strain maps in FIG. 6.7 show trends similar to FIG. 6.5, but with higher accumulated shear strains manifest by the increasing amounts of yellow coloration.

6.4 SUMMARY AND CONCLUSIONS

MD simulation using a two dimensional columnar straining model for 10 nm grain size Al-Pb alloys was implemented in conjunction with a new MEAM potential developed for Al-Pb. MC equilibration at 300K showed that all of the Pb segregates to grain boundaries for Pb contents up to 3 at%. With increasing Pb additions, dislocation nucleation from grain boundaries is suppressed, and the grain boundaries are more stable with respect to disruption or decomposition. The straining simulations also indicated that Pb additions reduce the yield and peak stresses relative to pure Al. These results indicate that the Pb segregation has a
significant influence on the deformation mechanisms and grain boundary response. It is not clear at this point how the Pb segregation influences the atomic configurations and mobility to produce the phenomena observed. There may also be an effect of grain size that has not been investigated. These issues will be addressed in more detail in a forthcoming publication that will also present additional simulation results for a range of larger grain sizes.

6.5 REFERENCES


6.6 FIGURES

FIG. 6.1 The columnar model containing four hexagonal grains with the xyz crystal reference directions indicated. The grain rotations correspond to counter-clock wise (ccw) rotation about the z-axis.

FIG. 6.2 (a)-(d) The MC equilibrated initial microstructures for 0, 1, 2 and 3 at% Pb, respectively. (e)-(g) The Pb atom positions highlighted for frames (b)-(d), respectively.
FIG. 6.3 (a) Stress vs. plastic strain obtained from MD straining simulations for Al and Al-Pb alloys as indicated. (b) The effective Young’s modulus, 0.5% offset yield stress and peak stress values obtained from the curves in (a).
FIG. 6.4(a)-(d) Microstructures obtained after 7.2% total strain for 0, 1, 2 and 3 at% Pb, respectively. Representations are given using centro-symmetry visualization. The color coding scheme used in FIGS. 6.2, 6.4 and 6.6 is: blue ⇒ fcc atoms, yellow ⇒ hcp atoms, green ⇒ defect atoms (vacancies, dislocations), and red ⇒ surface or high-misfit grain boundary atoms.

FIG. 6.5 (a)-(d) Microstructures are the same as in FIG. 6.4. Representations are given using local strain mapping. The color coding scheme used in FIGS. 6.5 and 6.7 is: purple (low strain) ⇒ blue ⇒ green ⇒ yellow (high strain).
FIG. 6.6 (a)-(d) Microstructures obtained after 8.8% total strain for 0, 1, 2 and 3 at% Pb, respectively. Representations are given using centro-symmetry visualization.

FIG. 6.7 (a)-(d) Microstructures are the same as in FIG. 6.6. Representations are given using local strain mapping.
CHAPTER 7

MOLECULAR DYNAMICS SIMULATIONS OF NANOCRYSTALLINE ALUMINUM AND ALUMINUM-LEAD ALLOYS

To be submitted for publication in Acta Materialia

7.1 INTRODUCTION

Since Gleiter proposed that nanostructured materials can have dramatically different properties compared to their conventional counterparts [J. Horvath, R. Birringer and H. Gleiter, Solid State Communications 62, 319-322 (1987)], there has been active research on the mechanical properties of nanocrystalline metals involving both experiments and atomistic simulations. The mechanical properties of pure nanocrystalline metals have been investigated by many research groups, and it is generally agreed that: (a) in larger grain size nanocrystalline metals, a dislocation-based intra-grain deformation process occurs leading to increased strength with decreasing grain size (Hall-Petch effect), and (b) at very small grain sizes an inter-grain deformation process not involving slip dislocations or twins occurs leading to decreased strength with decreasing grain size (inverse Hall-Petch effect) [1-7]. This transition from normal to inverse Hall-Petch behavior takes place at a critical grain size \( d_c \), which implies a “strongest grain size” [1].
While extensive research has been done on the deformation mechanisms in pure nanocrystalline metals, the effects of alloy additions to nanocrystalline matrices are poorly understood. There are many metal-metal systems with a miscibility gap in the liquid state, for example, Al-Pb, Cu-Pb or Al-Bi [8, 9]. In particular, Al and Pb are immiscible in the solid state and they have wide miscibility gap in the liquid state [10]. The large size difference between the Al and Pb atoms can produce phase separation, non-equilibrium solid solutions, and of particular interest in the case of nanocrystalline alloys, the formation of grain boundary segregates. There have been several studies showing the effects of Pb additions to Al. The melting behavior of nanosized Pb particles can be higher or lower than the bulk value [11-16]. Pb additions to Al improve the wear behavior [9]. The effects of Pb on the mechanical properties of nanocrystalline Al are conflicting [17, 18]. In one case significant strengthening was observed [17] while in the other pronounced softening was observed [18]. The latter investigators observed Pb segregation on Al grain boundaries using Z-contrast electron microscopy, and suggested that softening might be related to the Pb segregation. Thermodynamic models predict that the segregation of large size-misfit solutes (22 % in the case of Pb in Al) to grain boundaries from solid solution can reduce the effective grain boundary energy, and it is possible to get zero or even negative values of the energy [19, 20]. Solute segregation has therefore been proposed as an important strategy for stabilizing nanoscale microstructures. Based on empirical models, Seah [21] developed a ranking scheme to predict changes in the grain-boundary cohesive energy for specified solute atoms in different elemental matrices. Pb additions to Al are predicted to reduce the cohesive energy. These effects and the conflicting experimental results on mechanical properties were
motivation for the current molecular dynamics (MD) straining simulation studies on Al-Pb alloys.

Tensile straining simulations at fixed strain rate for pure nanocrystalline Al and Al-Pb alloys were done using two-dimensional columnar microstructures for which the distribution of Pb in Al is obtained using the Monte Carlo technique. In addition to reducing the demands on computational resources, the straining evolution in the columnar structure is more easily obtained and displayed compared to full three-dimensional simulations. The deficiencies of the columnar model have been discussed [22]. Three-dimensional simulations provide the most fundamental atomistic information on mechanisms such as nucleation paths for partial dislocations and twins from grain boundaries and triple junctions. Our primary aim in this work is to characterize the phenomenological effects of Pb on the deformation behavior in Al-Pb alloys, compared to the pure Al matrix.

7.2 SIMULATION PROCEDURE

The MD simulation uses a two-dimensional columnar microstructure similar to that reported in [22]. The simulation cell contains four uniform hexagonal face centered cubic (fcc) grains as illustrated in FIG. 7.1a. The individual grains are rotated by angles of 0°, 30°, 60°, and 90° about the [1-10] texture axis (z-direction), which produces high-angle tilt grain boundaries between the grains. The grain size $d$ is defined here as the distance between two opposite vertices. Periodic boundary conditions are used in the x, y and z directions. The [1-10]
texture direction is chosen because it is the common axis of (111) and (11-1) planes on which partial dislocations nucleated from the grain boundaries can glide, and it provides sufficient slip systems for compatible plastic straining [22]. The glide planes are shown in FIG. 7.1b, as two sets of (111) planes in each grain. \( m \) represents the Schmid factor for each glide plane with respect to the [110] straining direction. The simulation cell contains 14 (1-10) planes in the z-direction and the thickness is determined by the interplanar spacing \( \frac{\sqrt{2}}{4} a_0 \) \((a_0=4.05\text{Å})\). The x-y plane size is determined by the grain size and we use simulation cells with grain sizes ranging from 5 nm (7,532 atoms) to 30 nm (280,546 atoms).

Various methods are available to develop interatomic potentials for binary alloy systems, for example, the modified analytic embedded atom method (EAM) potentials [23], and glue type empirical potentials [24]. For this study, we use the modified embedded atom method (MEAM) [25, 26] to describe the interactions between Al-Al, Pb-Pb and Al-Pb atom pairs. The MEAM potential is similar to the embedded atom method (EAM) [27], but it includes angular contributions of electron density to calculate the embedding term [26]. Since no experimental data is available for the immiscible Al-Pb system, first-principles calculations using B1 (NaCl) and B2 (CsCl) crystal structures were done to obtain values for the bulk modulus, shear modulus, cohesive energy and lattice parameter parameters for the corresponding (hypothetical) Al-Pb structures. These values were used to fit parameters required for the MEAM potential [27].
Al-Pb alloy microstructures were generated using Monte Carlo (MC) simulation. Details of the MC method are given in [28]. One benchmark for describing solute segregation to grain boundaries follows from the amount of solute atoms needed to form a boundary monolayer along otherwise perfect crystal matrix grains. Assuming that the atomic volumes $v_{Al}$ and $v_{Pb}$ in the Al-Pb alloys are the same as for the corresponding elemental fcc crystals, and that the Pb monolayer width $\delta = v_{Pb}^{1/3} << d$, the atomic fraction of Pb needed to produce a monolayer for columnar model grains (FIG. 7.1a) is $f_{gb} \approx 1/(1+2.55d)$ with grain size $d$ in nm. At $d = 10$ nm, 3.8 at% Pb would represent the fully saturated limit for grain boundary monolayer segregation. Based on this, microstructures for Al-Pb alloys were generated using a 10 nm grain size with 1, 2 and 3 at% Pb additions. Microstructures for pure Al were generated for a range of grain sizes from 5 nm to 30 nm.

Two visualization methods were used to display microstructural features, a centro-symmetry method and a local strain mapping technique. The centro-symmetry parameter $P$ proposed by Kelchner et al. [29] is defined by:

$$P_i = \sum_{j=1,6} |R_{ij} + R_{ij+6}|^2$$

where $R_{ij}$ and $R_{ij+6}$ are the bond vectors corresponding to pairs of atoms. $P$ distinguishes between atoms in an fcc environment and those in hcp and defect environments. Using appropriate normalization, we have that $P = 0$ Å$^2$ for perfect fcc atoms, $P = 0.5$ Å$^2$ for defects including dislocations, $P = 1$ Å$^2$ for stacking faults and $P = 3$ Å$^2$ for surface and high-misfit grain boundary atoms. The atoms in FIGS. 7.2a-d are colored according to $P$ value: blue for
perfect fcc, green for defects including dislocations, yellow for stacking faults and red for surface and high-misfit grain boundary atoms (Al vs. Pb atoms are not distinguished, however virtually all red atoms are Pb).

The local strain mapping method [30] was developed to obtain accumulated deviatoric shear strain information associated with each atom. The local environment of an atom is represented by a set of vectors to the surrounding neighbor atoms within a specified cutoff distance. Two coordinate files are used for this analysis: a reference configuration file and current configuration file. The deviatoric shear strain at each atom position is obtained by a least-square fitting of the differential coordinate file displacements. This result represents the local accumulated strain associated with atoms in the current configuration relative to zero strain in the reference configuration. The local strain mapping technique was developed to aid in visualization of localized shear bands in amorphous structures [30]. We adopt the method here to for analysis of the effects of Pb on strain localization in straining simulations. The method reveals accumulated strain history for disorganized structures such as grain boundaries, as well as dislocation slip and twinning within grains. It does not capture local volume changes or rigid-body rotations.

The starting microstructures for the straining simulations were equilibrated at 300K. Typical Al and Al-Pb alloy microstructures are shown in FIGS. 7.2a-d. Centro-symmetry was used to generate the color visualization. FIGS. 7.2e-g highlight Pb atoms (white) from FIGS. 7.2b-d, respectively. All of the Pb atoms initially placed in solid solution are segregated to grain
boundaries after MC simulation. Experimentally, one must produce this kind of segregation for immiscible systems by non-equilibrium processing, as was done using ball milling in [18]. The width of the grain boundaries in FIGS. 7.2b-d increases with the Pb content. The relative increase in red atoms in the grain boundaries also indicates an increased degree of disorganization. The percentage of the Al + Pb atoms in grain boundaries was 14, 17 and 19% for 1, 2 and 3 at% Pb, respectively, compared to 12% for the pure Al grain boundaries.

7.3 STRAINING SIMULATION RESULTS

7.3.1 Pure Al

MD tensile straining in the [110] x-direction was performed at a constant strain rate of 6.67×10^9 s^{-1}. Periodic boundary conditions were adopted in the x, y and z directions during straining. Strains in the y and z directions were imposed to maintain near-zero normal stresses in those directions. The temperature was thermostated at 300K and the simulation time step was 1 fs. The same conditions were used for pure Al and the Al-Pb alloys. Each straining simulation was repeated three times for reproducibility using different initial equilibrated microstructures.

FIG. 7.3 shows the stress-strain results for the simulations on pure Al plotted as tensile stress σ vs. plastic strain ε_p. The plastic strain was derived from the total strain ε_T using the relation ε_p = ε_T - σ/E where E is the effective Young’s modulus. The values for E were obtained from the initial slope of the σ vs. ε_T curves (FIG. 7.3 inset). Unloading curves obtained at the end
of the simulations showed that the overall recoverable strain was given to a good approximation by $\sigma / E$.

FIG. 7.4a shows the modulus $E$ for grain sizes from 5 nm to 30 nm. The scatter bars on data points in this and succeeding figures correspond to $\pm$ one standard deviation for the three simulation runs at each grain size. $E$ depends on the elastic constants $c_{11}$, $c_{12}$ and $c_{44}$ and can vary by 13 GPa for pure Al depending on the crystal straining direction. The different grain orientations in FIG. 7.1b produce an effective average value of $E$. The large fraction of grain boundary atoms at the smaller grain sizes also affect the modulus, and it is apparent that $E$ tends to decrease at smaller grain sizes. $E$ values are in the range of 51-63 GPa compared to the experimental value of 70 GPa for polycrystalline Al.

FIGS. 7.4b and c show, respectively, the average values of the yield stress and the peak stress as a function of grain size obtained from simulation curves in FIG. 7.3. For the results reported here, we determined the yield stress $\sigma_{0.5}$ from $\sigma$ vs. $\varepsilon_p$ curves using a 0.5% plastic strain offset criterion (a vertical line at $\varepsilon_p = 0.005$ in FIG. 7.3). Both the offset criterion and the offset value are arbitrary and there is no standardized procedure for extracting yield stress values from MD straining simulations. The small number of grains in the simulation models, two-dimensional vs. three-dimensional microstructures, high strain rates and stresses, and boundary conditions can all contribute to variation. Different investigators have adopted different definitions for the yield stress in previous research [31, 32]. In our case, the values will increase if the offset is increased, but trends remain quite similar up to about 2% plastic
strain offset. We therefore expect the trends to give a reasonable approximation for the onset of “global” plasticity in the simulations.

The yield stress values in FIG. 7.4b increase as the grain size increases up to about 15 to 20 nm, and then gradually decrease indicating an inverse Hall-Petch effect at a critical grain size $d_c \approx 15$ to 20 nm. There is an added variation in FIG. 7.4b due to the apparent increase in stress from 20 nm to 30 nm grain size. The cause of this second increase was not clear, and we take the trend line in FIG. 7.4b as that due to the Hall-Petch transition. The peak stress values in FIG. 7.4c do not show this transition. Yamakov et al. [33] and Shimokawa et al. [32] reported critical grain sizes of 18 nm and 30 nm for pure Al straining simulations using three-dimensional and two-dimensional microstructures, respectively. Simulations were done at constant stress in [33] and constant strain rate in [32] using different definitions for the yield/flow stress. Given that different atomic potentials and methodology were used in [32] and [33] vs. the current study, the values for the critical grain size for pure Al obtained here appear to be in reasonable agreement with previous simulations.

FIGS. 7.5a-c show deformation microstructures for 10 nm grain-size pure Al at total strains of 4.7%, 7.6% and 8.6%, respectively. The microstructures are colored the same as in FIGS. 7.2a-d using the centro-symmetry parameter. FIG. 7.5a shows the emission of leading partial dislocations at grain boundaries and triple points (white circles). Only leading partials were observed at this strain value. When the strain increases to 7.6% in FIG. 7.5b, leading and trailing partial dislocations can be observed (white squares) and the extended dislocation
pairs travel across the grains and are absorbed into grain boundaries. The purple and red circles show, respectively, the formation and growth of twins as a result of partial dislocation generation. At 8.6% strain in FIG. 7.5c, an extended twin due to partial dislocation emission on parallel planes can be observed (white circle). In addition, the original 60° tilt boundary in the lower right corner (FIG. 7.1b) has been converted to a 70.5° twin boundary (white square). FIGS. 7.5a-c reveal the gradual conversion to the twin boundary by partial dislocation emission and grain rotation.

Dislocation activity similar to that seen in FIG. 7.5 was more extensive at larger grain sizes and diminished at smaller sizes. FIG. 7.6 shows the number of leading/trailing partial dislocations observed at each value of total strain for the range of grain sizes used in the simulations. At the smallest grain size of 5 nm, there is almost no dislocation activity. At the 10 nm grain size shown in FIG. 7.5 there is an onset of significant dislocation activity during straining. This occurs even though the grain size is smaller than the critical size $d_c \approx 15$ to 20 nm for the inverse Hall-Petch transition. The relative contribution of dislocation slip to the total plastic strain is shown in FIGS. 7.7a and b, respectively. The dislocation strain was determined by tracking the total area swept by partial dislocations during the simulation, converting this to tensile strain using appropriate orientation factors for each grain and taking the linear sum. It is seen that at the 5 nm grain size, virtually all of the plastic strain is generated by processes not involving dislocation slip. These must be due to inter-grain controlled processes [3, 34, 35]. At the 10 nm grain size, about 35% of the total plastic strain
is due to dislocation slip. The total plastic strain due to dislocation slip saturated at about 35-40% in the larger grain sizes.

The straining simulations for pure Al over the range of grain sizes investigated here show features similar to those reported by previous investigators [32, 33]. Details differ, which can be expected for different atomic potentials, straining conditions and simulation methodology. Except at the smallest grain size of 5 nm, leading partial dislocations and fully extended leading/partial pairs were observed in our simulations, above certain threshold straining values. Deformation twinning was also observed along with grain-boundary dissociation and rotation converting a tilt boundary into a twin boundary. The remaining part of this study deals with the effect of Pb additions on the baseline straining simulations for 10 nm grain size pure Al. Larger grain sizes for Al-Pb alloys are currently under investigation and results will be reported in a future publication [36]. In addition, we are using the Al-Pb MEAM potential and ab initio calculations to study the energetics and stability for Pb segregation to specific tilt boundary orientations in Al, and results from the companion studies will be reported in future publications [37].

7.3.2 Al-Pb alloys

FIG. 7.8 shows a set of straining simulations for 10 nm grain-size pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb. Similar to FIG. 7.3, $\sigma$ is plotted vs. $\varepsilon_p$ using the effective modulus $E$ from $\sigma$ vs. $\varepsilon_T$ curves (inset). FIG. 7.9a shows the effective Young’s modulus as a function of
at % Pb. There is an overall decrease in E of approximately 9% relative to pure Al. FIG. 7.9b shows an overall decrease in the 0.5% offset yield stress of approximately 17% while the peak stress values in FIG. 7.9c show a smaller decrease of approximately 4%. A softening effect due to Pb grain boundary segregation in nanocrystalline Al is observed in our simulation results, but is less dramatic than the $\approx 40$ to 45% drop in hardness for Al-Pb nanocrystalline alloys found experimentally in [18]. Limitations of the MD simulation model preclude any quantitative comparison with the experimental results, nonetheless, our observation of softening lends support to the hypothesis in [18] that grain boundary Pb segregates produce the softening effect observed. In the remaining part of this section, we discuss the phenomenological aspects of the microstructure changes due to Pb additions to pure Al at the 10 nm grain size.

FIGS. 7.10a-d show deformation microstructures visualized by centro-symmetry at 7.2% total strain for pure Al and 1, 2 and 3 at% Pb alloys, respectively. Leading and trailing partial dislocations (white circles) and twins (white square) can be seen for pure Al in FIG. 7.10a, similar to what was observed in FIG. 7.5b at a comparable strain of 7.6%. The addition of 1 at% Pb in FIG. 7.10b suppresses some of the partial dislocation emission/absorption observed in FIG. 7.5a (white circles and square). At 2% Pb, only a single partial dislocation is evident in FIG. 7.10c (white circle). At 3 at% Pb, FIG. 7.10d reveals a complete absence of partial dislocations and twins. As noted earlier for the initial microstructures, the grain boundaries are wider and more disorganized as the Pb content increases. The grain boundaries with Pb segregates also prove to be robust since these features are retained during
straining. As a further indication of robustness, the conversion of the 60° tilt boundary (lower right) to form a twin boundary in pure Al was suppressed.

FIGS. 7.11a-d show the same sequence as in FIG. 7.10, but for an increased total strain of 9%. Partial dislocations (white circles) and twins (white squares) are again observed in diminishing numbers up to 2 at% Pb. At 3 at% Pb, no partial dislocations or twins are observed. These trends persist up to the final total strain of 10%. No dislocation emission or twinning activity was observed for 3 at% Pb throughout the entire straining history.

FIGS. 7.12a-d show local deviatoric shear strain maps corresponding to the deformation microstructures at 9% strain in FIGS. 7.11a-d. The reference configuration used for the strain maps FIGS. 7.12a-d was the initial microstructure, i.e., the maps in FIG. 7.12 show the total accumulated strain per atom during the deformation history up to 9% strain. As the Pb content increases, the intra-grain plastic strain contribution from partial dislocation slip and twinning in pure Al (FIG. 7.7b) is transferred to inter-grain processes. At 3 at% Pb, FIG. 7.12d shows that local strain is accumulated exclusively within grain boundaries and triple points. The blue shading apparent within the bottom grain in FIG. 7.12d is a stress concentration signature for the dislocation slip activity seen in FIGS. 7.12a-c. There is no accumulation of local strain in grain boundaries parallel to the straining direction in FIG. 7.12. In order to enhance the visualization of the dominant localization, FIGS. 7.12e-f is a re-plot of the maps in FIGS. 7.12a-d, respectively, showing only local strain values greater than 0.16.
Additional information can be extracted from local strain maps using strain distribution histograms. FIGS. 7.13a-d shows histograms of the local strain per atom along with local strain maps (insets) plotted for strain values above the total nominal tensile strain of 9%. The average local strain values determined from the histograms were 11.1, 9.5, 8.5 and 8.1% for pure Al and 1, 2 and 3 at% Pb, respectively. The deformation participation ratio (DPR) can be used as a measure of the overall strain localization during deformation [38]. The DPR is obtained from histograms in FIGS. 7.13a-d as the fraction of atoms having a local strain larger than the 9% nominal strain (dashed line). An upper bound of 0.5 for the DPR is proposed as a limit of uniform strain in the sense that the probability of local strain per atom being larger or smaller than the nominal value is equal [38]. In contrast, lower values of the DPR indicate more intensive, non-uniform strain localization. FIG. 7.14 shows the DPR values as a function of at% Pb, obtained from the histograms in FIG. 7.13. The decreasing trend is consistent with a transfer of the intra-grain contribution to plastic straining in pure Al to inter-grain local strain in Al-Pb alloys. FIG. 7.14 indicates a saturation effect as the Pb content increases. This can be rationalized on the basis of the previous geometric calculation, $f_{gb} \approx 1/(1+2.55d)$, which shows that a grain boundary monolayer in Al would be fully saturated with Pb at 3.8 at% Pb for $d = 10$ nm.

The straining simulations for Al-Pb alloys reveal a pronounced effect of Pb additions on suppressing grain-boundary nucleation of partial dislocations and twins. We have examined these effects using centro-symmetry, local strain maps and stress-strain curves. Our
simulations based on columnar microstructures show the formation of grain boundary segregates for Pb additions up to 3 at% in 10 nm grain-size Al, consistent with the prediction of thermodynamic models for large size misfit solutes. This can be accompanied by a decrease in the effective grain boundary energy, and we have observed that effect in a companion study [39]. A decrease in the grain boundary energy must contribute in part to the stabilization of the grain boundaries, relative to pure Al, observed during straining. Empirical correlations further predict a reduction in the cohesive energy due to additions of Pb to Al [21]. Our simulation results are also consistent with this effect as manifest by the transfer of intra-grain plastic strain to inter-grain plastic strain and a reduction in yield stress due to the “softer” grain boundaries.

FIGS. 7.15a-d show an enlarged atomic configuration of the same 60° tilt grain boundary for pure Al and Al-Pb alloys with 1, 2 and 3 at% Pb using the centro-symmetry parameter, respectively. FIGS. 7.15e-h illustrate the same boundary structures colored by local strain maps, corresponding to FIGS. 7.15a-d, respectively. To enhance visualization, the atoms having local strain value higher than 0.09 are presented in FIGS. 7.15e-h. For pure Al in FIGS. 7.15a and e, there are three sites (black circles) from which partial dislocations are nucleated. The nucleation and emission of partial dislocations occurs with reorganization of the remaining grain boundary including the grain boundary nucleation sites. Swygenhoven et al. reported that at the atomic level, atomic shuffling and stress assisted free-volume migration play a significant role for plastic deformation in pure nanocrystalline metals [31]. They suggested that atomic shuffling causes both grain boundary plastic strain and
dislocation nucleation. Shuffling is accompanied by a stress-assisted free-volume migration [4, 31]. The free-volume migration is often observed in connection with emission of partial dislocation from grain boundaries [4, 32]. From this observation, we expect there is free-volume migration in the three sites in FIGS. 7.15a and e. For Al-Pb alloys with 1 to 3 at% Pb in FIGS. 7.15c-e and f-h, Pb atoms in the grain boundary cluster in the same sites as those for dislocation emission for pure Al. Therefore, in Al-Pb alloys, it appears that those sites that favor nucleation of partial dislocations in pure Al also attract Pb atoms that cluster, thereby suppressing the free-volume migration and related effects that allow partial dislocation emission.

7.4 SUMMARY AND CONCLUSIONS

Monte Carlo simulations and straining simulations using a two-dimensional columnar microstructure were done for pure Al with a range of grain sizes, and for Al-Pb alloys at a 10 nm grain size with 1, 2 and 3 at% Pb. Details of the microstructure changes were characterized using centro-symmetry and local strain visualization techniques. Pure Al shows an inverse Hall-Petch transition at $d_c \approx 15$ to 20 nm, but significant intra-grain plastic strain due to partial dislocations and twins is retained at a 10 nm grain size. Pb segregates completely to the grain boundaries at this grain size. The grain boundaries become wider and more disorganized as the Pb content increases. These features are retained throughout the straining simulations, indicating that the grain boundaries are robust compared to pure Al. Additions of Pb result in a 17% decrease in the yield stress. The softening effect is in
agreement with, but significantly less than that found experimentally for Al-Pb alloys. The stabilization of the grain boundaries due to Pb additions and the softening associated with the transition to inter-grain plastic straining processes are consistent with thermodynamic models in the literature that predict a possible reduction in the effective grain boundary energy and the cohesive strength due to grain boundary segregation. The nucleation of partial dislocations from specific sites in a 60° grain boundary in pure Al was increasingly suppressed as the Pb content increased up to 3 at%. The dislocation nucleation sites were furthermore the sites favored for Pb segregation.

7.5 REFERENCES


[37] Y. Purohit, D. Irving, C. Padgett, R. O. Scattergood and D. Brenner (to be submitted)
FIG. 7.1a Schematic view of the columnar structure containing four grains in the shape of regular hexagon.

FIG. 7.1b Orientations of two sets of (111) planes for each grain. Two planes are inclined each other at an angle of 70.53°. \( m \) represents the Schmid factor for each glide plane with respect to the [110] direction.
FIG. 7.2 The relaxed simulation cells at 300K with grain boundaries for (a) pure Al and Al-Pb alloy structures with (b) 1, (c) 2 and (d) 3 at% of Pb, The structures are colored by centro-symmetry parameter. Only Pb atoms (white) are shown in (e), (f) and (g) regarding to (b), (c) and (d), respectively.
FIG. 7.3 Stress vs. plastic strain obtained from one set of straining simulations for pure Al with different grain sizes. Inset graph is stress-total strain curves.
FIG. 7.4a The effective Young’s modulus (E) for three sets of pure Al stress-strain curves as a function of grain size.

FIG. 7.4b The 0.5% offset yield stress ($\sigma_{0.5}$) for three sets of pure Al stress-strain curves as a function of grain size.
FIG. 7.4c The peak stress ($\sigma_p$) values for three sets of pure Al stress-strain curves as a function of grain size.

FIG. 7.5 Structural changes at strains of (a) 4.7%, (b) 7.6% and (c) 8.6% with a grain size of 10 nm. The visualization is according to the centro-symmetry parameter.
FIG. 7.6 The number of dislocations vs. strain at each grain size.

FIG. 7.7 Plastic strain ($\varepsilon_p$) vs. strain by dislocation ($\varepsilon_d$) in (a) 5 nm and (b) 10 nm grain size samples.
FIG. 7.8 Stress vs. plastic strain obtained from the one set of straining simulations for pure Al and Al-Pb alloy with different Pb contents. The grain sizes are all 10 nm. Inset graph is stress-strain curves.
FIG. 7.9a The effective Young’s modulus (E) for three sets of stress-strain curves of pure Al and Al-Pb alloy as a function of atomic % of Pb.

FIG. 7.9b The 0.5% offset yield stress ($\sigma_{0.5}$) for three sets of stress-strain curves of pure Al and Al-Pb alloy as a function of atomic % of Pb.
FIG. 7.9c The peak stress ($\sigma_p$) for three sets of stress-strain curves of pure Al and Al-Pb alloy as a function of atomic % of Pb.

FIG. 7.10 Structural changes during 7.2% deformation in (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb.
FIG. 7.11 Structural changes during 9% deformation in (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb.

FIG. 7.12 Local strain mapping at a strain of 9% with different Pb contents; (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb. The atoms having local strain less than 0.16 are removed, showing in (e) pure Al and Al-Pb alloys with (f) 1, (g) 2 and (h) 3 at% Pb.
FIG. 7.13 Histograms of local strain values at a strain of 9% with different Pb contents; (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb. Inset pictures are local strain mappings having values above 0.09.
FIG. 7.14 Deformation participation ratio (DPR) measured at a strain of 9% plotted as a function of at% of Pb.
FIG. 7.15 The enlarged atomic configuration of same 60° tilt grain boundary of (a) pure Al and (b) 1, (c) 2 and (d) 3 at% Pb in Al-Pb alloys using the centro-symmetry parameter, respectively. The high misfit/surface atoms (red) revealed by centro-symmetry correspond to Pb atoms. Local strain maps of (e)-(h) are illustrated corresponding to (a)-(d), respectively.
8.1 INTRODUCTION

The mechanical properties of nanocrystalline metals have been reported by many research groups. These are characterized by using uniaxial tension and microindentation tests [1-7]. Hardness and yield strength have been found to increase with decreasing grain size in the nanocrystalline regime (<100 nm) down to at least ~15 nm. In this region, dislocation activity is primarily believed to generate and annihilate at the grain boundaries. Below grain sizes of ~10 nm, the strength decreases with further grain refinement, leading to the inverse Hall-Petch effect. In this region, grain boundary deformation mechanisms constitute the dominant deformation modes. While much research has been done on the deformation mechanisms of pure nanocrystalline metals, involving both experiments and atomistic simulations [1-7], the effects of alloy additions to nanocrystalline matrices are poorly investigated. Among the many metal-metal systems such as Al-Pb, Cu-Pb or Al-Bi [8, 9] with a miscibility gap in the liquid state, experiments on Al-Pb alloy were performed to study the effects of Pb on the mechanical behavior of nanocrystalline Al [10, 11]. Sheng et al. [10] found that Pb addition to a nanocrystalline Al matrix increases hardness, whereas Rajulapati et al. [11] reported a
dramatic decrease in hardness with Pb addition of only a few atomic percent. The latter author proposed that softening could be the result of Pb segregation to the grain boundaries.

We have reported the result of molecular dynamics (MD) straining simulations on the mechanical behavior of Al and Al-Pb alloys for a grain size of 10 nm [12, 13]. Pure Al shows an inverse Hall-Petch transition at \( d_c \approx 15 \) to 20 nm, however significant intra-grain plastic strain due to partial dislocations and twins is retained at a 10 nm grain size [13]. Straining simulation results for Al-Pb alloys with 1-3 at\% Pb for 10 nm grain size were reported in [12, 13]. As the Pb content increases, partial dislocation nucleation at grain boundaries is suppressed, and the plastic strain is accommodated by mechanisms other than dislocation slip. The increasing Pb content was accompanied by a reduction in the yield and peak stress values. Additions of 3 at\% Pb result in a 17\% decrease in the yield stress. The softening effect is in agreement with, but significantly less than that found experimentally for Al-Pb alloys [11]. Moreover, Pb segregation on Al grain boundaries was confirmed by Monte Carlo (MC) simulations. The investigators in ref. 11 observed Pb segregation using Z-contrast transmission electron microscopy, which suggested that softening might be related to Pb segregation. The stabilization of the grain boundaries due to Pb additions and the softening associated with the transition to inter-grain plastic straining processes are consistent with thermodynamic models in the literature that predict a possible reduction in the effective grain boundary energy and the cohesive strength due to grain boundary segregation [14-16].
In this study, we extend the simulations of Al-Pb alloys from the previous study to larger grain sizes of 15 and 20 nm. These simulations were intended to show how the deformation mechanisms change as the grain size increases. The straining simulation results are discussed in terms of stress-strain curves and structure changes displayed using centro-symmetry and local mapping techniques.

8.2 SIMULATION PROCEDURE

The MD simulation uses a two-dimensional columnar microstructure identical to that used in [12, 13]. The simulation cell contains four uniform hexagonal face centered cubic (fcc) grains. The individual grains are rotated by misorientation angles of 0°, 30°, 60°, and 90° about the [1-10] texture axis (z-direction), which produces high angle grain boundaries between grains. The grain size, \( d \) is defined as the distance between two opposite vertices. Periodic boundary conditions are used in the x, y and z directions. The [1-10] texture direction is chosen because it is the common axis of (111) and (11-1) planes in which dislocations nucleated from the grain boundaries can glide [17]. The simulation cell contains 14(1-10) planes in the z-direction and the thickness is determined by the interplanar spacing of \( \frac{\sqrt{2}}{4} a_0 \) (\( a_0 = 4.05\text{Å} \)). The x-y plane size is only determined by the grain size and specifically we consider our simulation cells with grain sizes of 10 nm (giving a total of 30,807 atoms), 15 nm (69,713 atoms) and 20 nm (124,285 atoms).
In this study, the modified embedded atom method (MEAM) is used to describe the interatomic interactions between Al-Al, Pb-Pb and Al-Pb. The MEAM potential is similar to the embedded atom method (EAM) [18] but allows angular contributions of electron density to calculate embedding term of MEAM formalism [19]. First principles calculations for the B1 (NaCl type-6 neighbors) and B2 (CsCl type-8 neighbors) phases was carried out to fit the parameters for Al-Pb for the MEAM potential such as bulk modulus, cohesive energy, lattice parameter and \((C_{11}-C_{12})\) value [18].

Al-Pb alloy structures were generated using MC simulation. Details of this method are given in the previous work [12]. The MC simulations with Al-Pb MEAM potentials were used to build equilibrated Al-Pb microstructures. In this paper, the pure Al microstructures of 15 and 20 nm grain sizes are used to produce Al-Pb alloy microstructures that can be compared with 10 nm grain size microstructures containing with 1 and 3 at% Pb. The Pb content for 15 and 20 nm grain size simulations was scaled by the grain size ratios for comparison with 10 nm grain size alloys. The atomic fraction of Pb needed to obtain a grain boundary monolayer for the columnar microstructure in FIG. 8.1 is \(\frac{1}{(1+2.55d)} \approx \frac{1}{2.55d}\) for \(d \geq 10\) nm [20]. Pb contents for 15 and 20 nm grain sizes must therefore be 2/3 and 1/2 that for 10 nm grain size alloys to maintain similar monolayer fractions. The “equivalent” at% Pb values used for the simulations are given in Table 1.
Table 8.1 The equivalent at% Pb values required for 10, 15 and 20 nm grain sizes.

<table>
<thead>
<tr>
<th>Equivalent at% Pb</th>
<th>Actual at% Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 nm</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

We used two visualization methods, centro-symmetry parameter and local strain mapping. First, the centro-symmetry parameter $P$ proposed by Kelchner et al. [21] is defined by:

$$P_i = \sum_{j=1,6} |R_{ij} + R_{ij+6}|^2$$  \hspace{1cm} (8.1)

where $R_{ij}$ and $R_{ij+6}$ are the bond vectors corresponding to pairs to atoms. $P$ distinguishes between atoms in an fcc environment and those in hcp and defect environments. By calculating $P$ in the normalization form, we found that $P=0$ Å$^2$ for perfect fcc atoms, $P=0.5$ Å$^2$ for defects including dislocations, $P=1$ Å$^2$ for stacking faults and $P=3$ Å$^2$ for surface and high-misfit grain boundary atoms. The atoms are colored according to $P$ value, appearing in blue with perfect fcc, green with defects including dislocations, yellow with stacking faults and red with surface and high-misfit grain boundary atoms.

Second, the local strain mapping method [22] is introduced to obtain the strain information associated with each atom. The local environment of an atom is represented by a set of vectors to the nearest neighbor atoms within a specified cutoff distance. There are at least two coordinate files needed for this analysis: a reference configuration file and current
configuration file. The deviatoric shear strain is obtained through a least-square fitting of the atomic displacements of neighboring atoms within a cutoff distance.

Al-Pb alloy microstructures generated by MC simulation method are shown in FIG. 8.1 using centro-symmetry visualization. The structures of pure Al with grain sizes of 10, 15 and 20 nm are also illustrated in FIGS. 8.1a, e and h, respectively. Al-Pb alloys with 1, 2 and 3 equivalent at% Pb for 10 nm grain size are illustrated in FIGS. 8.1b-d, respectively, with 1 and 3 equivalent at% Pb for 15 nm grain size in FIGS. 8.1f and g, respectively and for 20 nm in FIGS. 8.1i and j, respectively. All Pb atoms are segregated to grain boundaries after the MC simulation. The thickness of the grain boundaries in FIG. 8.1 appears to increase with the Pb content. This was confirmed by the total percentage of Al+Pb atoms that are found in grain boundaries, which is 14.1%, 16.7% and 19.2% for 1 to 3 at% Pb, respectively, which is compared to 12.4% for pure Al in 10 nm grain sized samples. The total percentage of atoms are found in grain boundaries, which is 9.61% and 13.10% for 1 and 3 at% Pb, respectively, which is compared to 8.36% for pure Al in 15 nm grain sized samples. The percentages are 8.67% and 9.96% for 1 and 3 at% Pb, respectively compared to 6.34% for pure Al in 20 nm grain sized samples.

8.3 MD STRAINING SIMULATIONS

MD tensile straining in the [110]-direction was performed at a constant strain rate of $6.67 \times 10^9$ s$^{-1}$. Periodic boundary conditions are adopted in the x, y and z directions during the
simulation. Strains in the y and z directions were imposed to maintain the stresses $\sigma_{yy}$ and $\sigma_{zz}$ close to zero. The temperature was maintained at 300K and the MD time step was $\Delta t=1$ fs.

FIGS. 8.2a-c show the results for the straining simulations on pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb plotted as tensile stress $\sigma$ vs. plastic strain $\varepsilon_p$ for 10, 15 and 20 nm grain sizes, respectively. The results for 2 at% Pb for the 10 nm grain size are also indicated from the previous paper [13]. Inset figures are stress $\sigma$ vs. total strain $\varepsilon_T$ curve. Each simulation of pure Al and Al-Pb alloys was repeated three times for reproducibility using a different initial microstructure. One set of simulations at each grain and Pb content was taken and shown in FIGS. 8.2a-c. The plastic strain is evaluated using $\varepsilon_p=\varepsilon_T-\sigma/E$ where E is the effective Young’s modulus obtained from the initial slope of each inset curve.

FIGS. 8.3a-c show the effective Young’s modulus (E), 0.5% offset yield stress ($\sigma_{0.5}$) and peak stress ($\sigma_p$) for pure Al and Al-Pb alloy with 1 and 3 equivalent at% Pb having grain sizes of 10, 15 and 20 nm. The results for 2 at% Pb for the 10 nm grain size are also indicated. The E values are in the range of 50-63 GPa compared to the experimental value of E~70 GPa for polycrystalline Al. As the Pb content increases to 3 equivalent at%, E values decrease except for the 15 nm grain size, where the E value increases. The $\sigma_{0.5}$ yield stress decreases by ~17%, ~40% and 3% for 10, 15 and 20 nm grain sizes, respectively, as the Pb content increases to 3 equivalent at%. For the case of 20 nm, the $\sigma_{0.5}$ values are not much changed with variation of Pb contents. At 1 equivalent at% Pb, $\sigma_{0.5}$ values are almost the same for each grain size. At 3 equivalent at% Pb, $\sigma_{0.5}$ value is the highest in 20 nm grain size and $\sigma_{0.5}$
value for 15 nm is lowest. The peak stress values decrease by $\sim7\%$, $\sim16\%$ and $16\%$, respectively for 10, 15 and 20 nm grain sizes, as the Pb content increases to 3 equivalent at%.

FIGS. 8.4a-d illustrate the effect of Pb on the deformation structures for the 10 nm grain size at 7% total strain, as revealed by centro-symmetry. Structural changes during 7% deformation are illustrated in Al and Al-Pb alloys with 1, 2 and 3 at% Pb in FIGS. 8.4a-d, respectively. The accumulated local strain maps are shown in FIGS. 8.4e-h, corresponding to FIGS. 8.4a-d. To enhance visualization, the atoms having local strain value less than 0.07 are deleted and shown in FIGS. 8.4i-l, according to FIGS. 8.4e-h. Details of these results are discussed in the previous paper [13]. FIGS. 8.5a-c illustrate the effect of Pb on the deformation structures of 15 nm grain size at 7% total strain, as revealed by centro-symmetry. Structural changes during 7% deformation are illustrated in Al and Al-Pb alloys with 1 and 3 equivalent at% Pb in FIGS. 8.5a-c, respectively. The accumulated local strain maps are shown in FIGS. 8.5d-f, corresponding to FIGS. 8.5a-c. To enhance visualization, the atoms having local strain value less than 0.07 are deleted and shown in FIGS. 8.5g-i, according to FIGS. 8.5d-f. For the pure Al shown in FIG. 8.5a, leading dislocations connected by intrinsic stacking faults are generated from $60^\circ$ tilt grain boundary, and glide across the grain until they are absorbed at the opposite grain boundary. The addition of Pb in the grain boundaries suppresses dislocation generation in FIGS. 8.5b and c. At 1 equivalent at% Pb, two leading dislocations are formed from two triple junctions, however, at 3 equivalent at% Pb, only one dislocation is generated. As shown in the local strain maps corresponding to the deformation
microstructures at a strain of 7% from FIGS. 8.5d-i, the deformation becomes more localized to grain boundaries as the Pb content increases.

FIGS. 8.6a-c illustrate the effect of Pb on the 20 nm grain size deformation structures at 7% total strain, as revealed by centro-symmetry. Structural changes during 7% deformation are shown in Al and Al-Pb alloys with 1 and 3 equivalent at% Pb in FIGS. 8.6a-c, respectively. The accumulated local strain maps are shown in FIGS. 8.6d-f, corresponding to FIGS. 8.6a-c. To enhance visualization, the atoms having local strain value less than 0.07 are deleted and shown in FIGS. 8.6g-i corresponding to FIGS. 8.6d-f, respectively. For the pure Al shown in FIG. 8.6a, leading dislocations connected by intrinsic stacking faults are generated from grain boundaries and triple junctions. More dislocations are generated than for the corresponding to 15 nm grain size. At 1 equivalent at% Pb as shown in FIG. 8.6b, the dislocation formation is suppressed and the number of dislocations generated decreases. At 3 equivalent at% Pb shown in FIG. 8.6c, two dislocations are generated from the triple junction and the adjacent grain boundary. The local strain maps in FIGS. 8.6d-i show that local strain is transferred to grain boundaries as the Pb content is increased. FIGS. 8.4 to 8.6 clearly indicate that increasing grain size increases dislocation activity. Furthermore, dislocation generation is not entirely suppressed at 3 equivalent at% Pb at the larger grain sizes. It is completely suppressed at the 10 nm grain size at 3 at% Pb.

FIGS. 8.7a-c show the histograms of the local strain values at a total strain of 9% for 15 nm grain size in pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb, respectively. The inset
pictures for each histogram show local strain maps for the atoms having local strain above 9%. The average local strain values determined from the histograms were 9.5, 8.9 and 8.3% for pure Al and Al-Pb alloys with 1 and 3 equivalent % Pb, respectively. As seen in FIG. 8.7a, the pure Al sample shows high local strain distributed at grain boundaries and dislocations connected by stacking faults. Local strain values in the middle range of the color-scale illustrated in the bar are distributed around dislocation trails and grain boundaries. For Al-Pb alloys in FIGS. 8.7b and c, high local strain distributed dominantly at grain boundaries.

FIGS. 8.8a-c show the histograms of the local strain values at a total strain of 9% for 20 nm grain size in pure Al and Al-Pb alloys with 1 and 3 equivalent at% Pb, respectively. The inset pictures for each histogram show local strain maps for the atoms having local strain above 9%. The average local strain values determined from the histograms were 9.4, 9.0 and 8.3% for pure Al and Al-Pb alloys with 1 and 3 equivalent % Pb, respectively. All three maps are showing the local strain distribution in the grain boundaries and dislocation connected by stacking faults. As seen in FIG. 8.8a, pure Al shows that local strain values in the middle range of the color-scale bar are distributed between dislocation trails and inside grains. This feature disappears as the Pb content increases.

FIG. 8.9 shows the deformation participation ratio (DPR) obtained at a strain of 9% for 10, 15 and 20 nm grain sizes plotted as a function of equivalent at% Pb. The DPR is plotted as the value relative to pure Al in FIG. 8.9. The normalized DPR decreases falls on the same trend line for all grain sizes. This indicates a similar transfer of intra-grain deformation
processes to inter-grain processes with increasing equivalent at% Pb. It also suggests that the saturation effect for the DPR is related to equivalent fractional values of a Pb monolayer over the range of grain sizes.

8.4 SUMMARY AND CONCLUSIONS

MD straining simulations of Al-Pb alloys with grain sizes of 15 and 20 nm and Pb contents of 1 and 3 equivalent at% were carried out to investigate deformation mechanism. The results are compared to previous work using a 10 nm grain size. MC simulations show complete segregation of Pb to the grain boundaries at all grain sizes. With increasing Pb additions, dislocation nucleation from the grain boundaries is suppressed. As Pb content increases to 3 equivalent at%, only one or two dislocations were generated during whole straining simulation. The simulations also indicated that Pb additions in Al-Pb alloys reduce the yield stress relative to pure Al. However for the case of a grain size of 20 nm the yield stress decreases by a few percent. DPRs also decrease as Pb contents increase. High local strains are distributed in the grain boundaries and dislocations connected by stacking faults. The addition of Pb atoms reduces the number of dislocations generated and increase strain localization in grain boundaries.

8.5 REFERENCES


FIG. 8.1 The relaxed simulation cell at 300K with grain boundaries for (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 at% Pb for 10 nm, for (e) pure Al and Al-Pb alloys with (f) 1 and (g) 3 equivalent at% Pb for 15 nm and for (h) pure Al and Al-Pb alloys with (i) 1 and (j) 3 equivalent at% Pb for 20 nm grain sizes. The atoms are colored by centro-symmetry parameter.
FIG. 8.2 Stress vs. plastic strain obtained from the one set of straining simulations for pure Al and Al-Pb alloy with 1 and 3 equivalent at% Pb. The grain sizes are (a) 10 nm, (b) 15 nm and (c) 20 nm. Inset graphs are stress-strain curves.
FIG. 8.3 (a) The effective Young’s modulus (E), (b) 0.5% offset yield stress ($\sigma_{0.5}$) and (c) peak stress ($\sigma_p$) from three stress-strain curves of pure Al and Al-Pb alloy with grain sizes of 10, 15 and 20 nm as a function of equivalent at% Pb.
FIG. 8.4 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys with (b) 1, (c) 2 and (d) 3 equivalent at% Pb with 10 nm grain size. The accumulated local strain maps are shown in (e)-(h) with respect to (a)-(d). The atoms having local strain value less than 0.07 are deleted and shown in (i)-(l).
FIG. 8.5 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys of (b) 1 and (c) 3 equivalent at% Pb with 15 nm grain size. The accumulated local strain maps are shown in (d)-(f) with respect to (a)-(c). The atoms having local strain value less than 0.07 are deleted and shown in (g)-(i).
FIG. 8.6 Structural changes during 7% deformation in (a) pure Al and Al-Pb alloys of (b) 1 and (c) 3 equivalent at% Pb with 20 nm grain size. The accumulated local strain maps are shown in (d)-(f) with respect to (a)-(c). The atoms having local strain value less than 0.07 are deleted and shown in (g)-(i).
FIG. 8.7 Histograms of local strain values at a strain of 9% of 15 nm grain size; (a) pure Al and Al-Pb alloys with (b) 1 and (c) 3 equivalent at% Pb. Inset pictures are local strain mappings having values above 0.09.
FIG. 8.8 Histograms of local strain values at a strain of 9% of 20 nm grain size; (a) pure Al and Al-Pb alloys with (b) 1 and (c) 3 equivalent at% Pb. Inset pictures are local strain mappings having values above 0.09.
FIG. 8.9 Deformation participation ratio (DPR) measured at a strain of 9% plotted as a function of equivalent at% of Pb for 10, 15 and 20 nm grain sizes.
The uniaxial tensile straining simulations were carried out to investigate the deformation mechanisms of two dimensional columnar microstructures of pure Al and Al-Pb alloys. The simulations results of pure Al show that a transition to the inverse Hall-Petch occurs at a critical grain size at \( d_c \approx 15-20 \) nm. At the smallest grain size of 5 nm, grain boundary deformation constitutes the dominant deformation mode. As grain size increases, dislocations play an increasing role as total strain increases for 8 and 10 nm grain sizes and, in contrast, a decreasing role for 15 to 30 nm grain sizes. With increasing grain sizes, plastic deformation mechanism transitions from inter-grain processes to one that consists of both inter-grain and intra-grain processes. From Monte Carlo simulations, Pb atoms segregate completely to the grain boundaries. As Pb content increases, the total percentage of Al and Pb atoms in the grain boundaries increases and grain boundaries become wide and more disorganized. A softening effect with increasing Pb content was observed in agreement with, but less than that found experimentally. The addition of Pb suppresses the nucleation of partial dislocations at the grain boundaries and with increasing of Pb content the number of partial dislocation nucleated at grain boundaries decreases. The deformation participation ratio (DPR) shows that pure Al represents a more uniform strain distribution while the Al-Pb alloys represent a more localized strain distribution in grain boundaries. This indicates the transfer of intra-grain deformation processes to inter-grain processes with Pb content. In Al-Pb alloys, it appears that the sites that favor nucleation of partial dislocations in pure Al also
attract Pb atoms that cluster, thereby suppressing the free-volume migration and related
effects that allow partial dislocation emission.

For future work, the straining simulations for larger grain sizes in nanometer range than those
of this work can be performed to verify the Hall-Petch behavior. More analysis of atomic
mechanisms in the grain boundaries will be required to investigate the mechanisms of
dislocation nucleation and Pb effects on the grain boundaries. Three dimensional
microstructures of pure Al and Al-Pb alloys can be simulated to study deformation
mechanisms and compare to two dimensional columnar microstructures. Other metal-metal
alloys such as Cu-Pb and Al-Bi with a miscibility gap will be simulated to study if the same
segregation mechanism to the grain boundaries will be observed.