Power Law Scaled Hardness of Mn Strengthened Nanocrystalline Al-Mn Non-Equilibrium Solid Solutions

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Abstract

In this work, the effects of Mn on lattice parameter, electron work function (EWF), bonding charge density, and hardness of nanocrystalline Al-Mn non-equilibrium solid solutions are investigated. We show how the enhancement of the EWF contributes to the observed improvement of the hardness of Al-Mn solid solutions. It is understood that the physical mechanisms responsible in our model, using the EWF coupled with a power law scaled hardness, are attributed to the redistribution of electrons caused by the presence of Mn solute atoms, supporting an atomic and electronic basis for the coupling of solid solution and grain refinement strengthening mechanisms.

Keywords: Bonding charge density; Electron work function; Solid-solution Hardening;
Grain refinement strengthening

Al alloys are one of the most versatile lightweight structural materials in our society today [1-7]. Over the past several decades, advancements in developing higher strength Al alloys have focused on optimizing solid solution hardening, grain refinement, and precipitation strengthening mechanisms [8-12]. More recently, nanocrystalline or nanostructured Al-Mn based alloys have been investigated extensively [9, 10, 13, 14], showing complex microstructural features such as non-equilibrium solid solutions, icosahedral and decagonal quasicrystalline dispersoids, and a range of amorphous/nanocrystalline phases [9, 15-20]. Such unique combination of these phases have given rise to remarkable increases in strength levels, where estimated yield strengths over 1.0 GPa have been reported [9-11, 21] along with enhanced bending ductility [11] and toughness [9, 10, 13, 22]. However, despite reporting these remarkable properties, very little has been done to separate and quantify the contributions from the various strengthening mechanisms in these alloys, such as grain size refinement, particle strengthening, and the formation of nonequilibrium solid solutions.

In the literature, mechanical properties of materials (e.g., Young's Modulus, hardness, and yield strength) have been correlated to basic chemical and physical parameters, including fundamental electronic quantities (bonding charge density, $\Delta\rho$ [23, 24], and electron work function, EWF, ϕ [25]), specific wavelength [26, 27], topological bonding features [28-30], energy gap between the lowest unoccupied and the highest occupied molecular orbitals [29, 31], and physics-based models connecting yield strength and stacking fault spacing [32]. Traditional descriptions of solid solution hardening (SSH) are based on models that consider the elastic interaction forces (due to size and modulus misfits of solute and solvent) between dislocations and solute element, yielding the phenomenological models. Through considering the electronic interactions/redistributions, the additional contributions to SSH could be recognized. As such, characterizing the chemical bonding between atoms within a solid is

crucial to understanding its mechanical properties [31], providing a physics-based model. This is because the chemical bonding reveals the nature of the macroscopic solid mechanics [31]. The electronic/bonding features determined by the local atomic arrangements are the primary causative basis for those models mentioned above. The EWF represents the energy required to move an internal electron from the Fermi Surface of a solid to its external surface, revealing the interactions between electrons and nuclei in the bulk solid. It has been found that the aforementioned properties are strongly dependent on the EWF raised to the sixth power [33-36], ϕ^6 . Similarly, $\Delta\rho$ [23, 37-39] captures the electron rearrangement and lattice distortion and, in turn, can be utilized to account for the enhanced hardness and understand how the solute atoms alter the bonding and strengthening character.

In the present work, the influence of Mn on the Al-Mn solid solution lattice parameter, ϕ , $\Delta\rho$, and hardness are investigated via first-principles calculations based on density functional theory (DFT) [40]. Eight Al-Mn alloys are studied: $\text{Al}_{179}\text{Mn}_1$, $\text{Al}_{159}\text{Mn}_1$, $\text{Al}_{143}\text{Mn}_1$, $\text{Al}_{119}\text{Mn}_1$, $\text{Al}_{95}\text{Mn}_1$, $\text{Al}_{79}\text{Mn}_1$, $\text{Al}_{63}\text{Mn}_1$, and $\text{Al}_{31}\text{Mn}_1$. The supercells used in the first-principles calculations are generated through enlarging a FCC Al unit cell (consisting of 4 atoms) by $5\times3\times3$, $5\times4\times2$, $4\times3\times3$, $5\times3\times2$, $4\times3\times2$, $5\times2\times2$, $4\times2\times2$, and $2\times2\times2$ with one of the Al atoms replaced by Mn. These first-principles calculations at 0 K are carried out using the Vienna *ab initio* simulation package (VASP) [40] (the setting parameters in the calculations can be found in the supplementary information). The bonding charge density (also known as the deformation electron density) is calculated through the charge density difference for the fully relaxed structure with and without the self-consistent calculations [23, 38] and used to characterize the bond structures of Al and the Al-Mn solid solutions. The isosurface structures with different values of $\Delta\rho$ are generated using the visualization for electronic and structural analysis (VESTA) code [41]. The EWF is obtained using the Halas-Durakiewicz model [25, 42, 43], which is discussed in the supplementary information. The first-principles

calculations are carried out using the projector augmented wave (PAW) method to describe the electron-ion interaction with generalized gradient approximations of GGA-PW91 and GGA-PBEsol pseudopotentials. The energy-volume relations are obtained using the four-parameter Birch-Murnaghan (BM4) equation of state (EOS) fits.

Figure 1 shows the effect of the Mn content on the total energy, volume, and lattice parameter of the Al-Mn solid solutions. Fitted by the BM4-EOS, the total energies of the Al-Mn alloys predicted by PAW-GGA-PBEsol as a function of volume are presented in **Figure 1(a)** along with the data points from the first-principles calculations (additional results are shown in **Table S1** of the supplementary information). The corresponding lattice parameters are plotted in **Figure 1(b)** with the solid symbols from the BM4 EOS fitting and the solid blue line being a linear fit to the experimental data points (solid-open symbols) measured by Darling *et al.* [10, 21]; there is also good match to the experimentally measured lattice parameters in dash lines, reported by Jones (which includes the results of Bletry, Babic, and Stump and Jansen) [44-46], and Ruan and Schuh [9]. It is noted that the lattice parameter differences between our calculations (at 0 K) and those measurements (at room temperature) are reasonable and can be attributed to the thermal expansion of the solid solution. The first-principles calculations using PAW-GGA-PBEsol result in a smaller lattice parameter (-3.2%) and equilibrium volume (-2.3%) than those obtained via PAW-GGA (as shown in **Table S1** of the supplementary information) for the pure elements. For the Al-Mn solid solutions, PAW-GGA-PBEsol yields similar lattice parameters to those obtained from PAW-GGA, and our calculated lattice parameters of $\text{Al}_{63}\text{Mn}_1$ and $\text{Al}_{31}\text{Mn}_1$ agree well with previous predictions by Uesugi and Higashi [47]. In general, the predicted lattice parameters of Al-Mn alloys match well with those of the experimental observations as illustrated in **Figure 1(b)**.

To correlate the lattice parameter and hardness of the Al-Mn solid solutions [10, 21, 44], the effects of Mn on the EWF are studied through comparing two different

pseudopotentials. The predicted EWF values together with the key parameters in the Halas-Durakiewicz model [25, 42, 43] for Al, Mn, and the Al-Mn solid solutions are summarized in **Table S1** of the supplementary information, which are also compared with available experimental and theoretical data in the literature. It is noted that the EWF of Al predicted by PAW-GGA-PBEsol is closer to that of the experimentally obtained value than that obtained using PAW-GGA. Therefore, the PAW-GGA-PBEsol value is chosen in the present work. For the Al-Mn solid solutions, it is found that Mn decreases the volume and increases the EWF values of the Al-Mn solid solutions due to the smaller atomic radius and more valence electrons of Mn. The fitted value of the EWF of pure Al is 4.005, in line with our predictions via the first-principles calculations (4.004 from PAW-GGA-PBEsol). A linear relationship between the EWF values and Mn content is obtained as $\phi = 4.005 + 0.006x_{\text{Mn}}$, shown in **Figure 2**. Moreover, the most recent measurements by Darling *et al.* [10, 21] show that the hardness of the nanocrystalline Al-Mn solid solutions improves linearly with increasing Mn concentration. Moreover, Ruan and Schuh [9] report that the hardness of macrocrystalline Al-Mn solid solutions increases from 1 GPa to 2.8 GPa with adding Mn from 0 at.% to 7.5 at.%, which also have a significant decrease in grain size. Therefore, it is worthwhile to further investigate the atomic and the electronic basis of Mn strengthened Al-Mn solid solutions via EWF coupled with the Hall-Petch relationship.

Figure 3(a) shows the 3D view of the measured hardness of Al and Al-Mn solid solutions. The hardness of nanocrystalline Al obtained by Darling *et al.* [10] (pink diamonds) displays the grain refinement strengthening (HV_d), which follows a Hall-Petch-type behavior [10] ($\sigma = \sigma_0 + kd^{-\alpha}$ [12] and $\text{HV} = 3\sigma$ [31, 48, 49] where σ_0 and k are size-independent constants, σ is the flow strength, and α is an exponent typically between 0.5 and 1 [12]). The macrocrystalline Al and Al-Mn solid solution samples examined by Ruan and Schuh (navy stars) show that there is insignificant variation in the composition between the bulk and grain

boundaries [9]. So, the improved hardness of these data (navy stars) with the increased Mn concentration is mainly attributed to the solid-solution hardening (HV_{ss}). For ultrafine to nanocrystalline grain size Al-Mn solid-solutions (green spheres), their hardness increase linearly with the reduced grain size and the increased x_{Mn} , revealing that the enhanced hardness/yield strength is mainly dominated by coupled solid solution hardening and grain size strengthening, mechanisms. Moreover, based on the projected blue data points of Al and Al-Mn shown in the grain size-hardness plane of **Figure 3(a)**, the grain refinement effect on the hardness still follows a Hall-Petch-type behavior ($HV \propto d^{-0.5}$). The values of the squared correlation coefficient (R^2) of $HV-\phi^6$ and $HV-d^{-0.5}$ being near 1 suggest a linear regression of HV in terms of ϕ^6 and $d^{-0.5}$.

Together with the aforementioned sixth power scaled hardness in term of EWF ($HV \propto \phi^6$) [33, 35], the coupling effects of HV_d and HV_{ss} on the hardness of Al-Mn solid solutions is initially expressed via the linear interpolation approach as

Equation 1
$$HV = HV_{ss} + HV_d = 1.0131 \times 10^{-2} \phi^6 - 41.1870 + k_d d^{-0.5}$$

with $k_d = 3.9550 \text{ MPa nm}^{0.5}$, the results of which are shown in **Figure 3(b)**. Through scaling, the hardness by a Red-Green-Blue (RGB) color gradient, those data points merging with the surface indicate a good agreement between our predictions and the experimental observations, shown in **Figure 3(b-1)**. The comparison of the hardness, shown in **Figure 3(b-2)**, highlights the divergence between our predicted hardnesses with the measured ones, which also implies that the hardnesses of Al and dilute Al-Mn are generally overestimated while those of the supersaturated Al-Mn solid solutions are underestimated. It is strongly suggested that a composition dependent slope (k_d) of Al-Mn should be considered when discussing the grain refinement strengthening with the Hall-Petch relation, which is mainly attributed to the segregation of solute atoms at grain boundaries [9, 50-54]. Based on prior Auger electron

spectroscopy and scanning transmission electron microscopy analysis of Al-Mn, there was an insignificant variation in composition between the bulk and the grain boundaries [9, 14], suggesting to derive an average Mn concentration dominated k_d . With the updated composition dependent k_d , $k_d = f(x_{Mn}) = \begin{cases} 2.4943 & \text{if } x_{Mn} = 0 \\ 4.06 + 1.4722 \ln x_{Mn} & \text{if } x_{Mn} > 0 \end{cases}$, our predicted results of Al and Al-Mn (open symbols) agree well with those measured by Darling *et al.* [10, 21] and by Ruan and Schuh [9] (solid symbols), shown in **Figure 3(c)**. It is worth to mention that the logarithmic function has fewer fitting parameters and with the larger values of the square of the correlation coefficient (R^2) than those obtained from a polynomial function. Thus, it is chosen here. Attributed to a similar atomic size [55] and valance electrons [25] between Mn and Cr, the correlation listed in **Equation 1** is also validated for the nanocrystalline Al-Cr solid solutions, yielding a good agreement with the measurement by Gupta *et al.* [49], which can be found in the **Figure S2** and **Figure S3** of the supplementary information.

Such correlation listed in **Equation 1** reveals the combined effects of solid solution hardening and grain refinement strengthening. On one hand, as presented by the slope changes of the green lines perpendicular to the axis of EWF in **Figure 3(b-1)** and of the open circles for a fixed EWF in **Figure 3(c-1)**, it is understood that the grain refinement of an Al-Mn solid solution plays an important role in improving its hardness. Thus, a high concentration of Mn is a promising way to further enhance the hardness of the Al-Mn solid solution, which is highlighted by the red regions in **Figure 3(b-1)**, **Figure 3(c-1)** and **Figure S4** of the supplementary information. Moreover, the gradient colors in **Figure 3(b-1)** and **Figure 3(c-1)** screen the critical theoretical conditions (such as d and x_{Mn}) to yield the hardness at a desired target level. For example, in order to process an ultra strong Al-Mn labeled by the red color ($HV \geq 3.5$ GPa), the boundary between the red and the yellow colors suggests the critical theoretical conditions of d and x_{Mn} to be followed.

On the other hand, an elaboration of the electronic basis of nanocrystalline Al-Mn in terms of the EWF serves to bridge composition and mechanical property. It can be seen that the EWF-scaled hardness of nanocrystalline Al-Mn non-equilibrium solid solutions, without requiring considerations for deformation mechanisms (i.e., ordinary dislocation-mediated plasticity or deformation twinning [12]), is a simple and concise approach which, in turn, can be used to gain a better understanding of the complex strengthening mechanisms operating in these alloy systems. For example, due to the decreased grain size by the increasing Mn concentration, the grain refinement strengthening via dislocation mechanism is highlighted by the second term in the Taylor hardening equation ($HV = 3[\sigma_0 + M\alpha Gb\rho^{1/2}]$) for nanostructured materials, where σ_0 is the frictional stress, M is the Taylor factor, α is a constant, G is the shear modulus, and ρ is the dislocation density [48]. The correlation listed in **Equation 1** is in line with the Taylor hardening equation, which, in its present form, is a concise composition-property relation that supports more complex mechanisms.

Furthermore, it gradually becomes clear that a detailed knowledge of the chemical bonding between the atoms of nanocrystalline Al-Mn solid solutions is crucial to an understanding of mechanical properties [31]. The physical mechanisms responsible for the correlations listed in **Equation 1** are intrinsically dominated by the bonding charge density (or bonding strength), which, in turn, affects the mechanical properties of the material [29, 31, 33, 34, 37, 43, 56-58]. A larger value of ϕ corresponds to a higher stability of electrons in metallic bonds, therefore, requiring a greater driving force to achieve electron rearrangement during a certain mechanical deformation [34]. Thus, this work shows that electron rearrangement caused by solute atoms and lattice distortion can be tracked and captured by $\Delta\rho$ [23, 38], which then can be utilized to study the enhanced mechanical properties of nanocrystalline Al-Mn non-equilibrium solid solutions.

The nature of the bond structure of Al and Al-Mn is illustrated by various $\Delta\rho$ isosurfaces in **Figure 4**. Comparing with quantitative convergent-beam electron diffraction, QCBED, measurements of Al [23] in the literature, the $\Delta\rho=0.0035 \text{ e}^-\text{\AA}^{-3}$ and $\Delta\rho=0.0025 \text{ e}^-\text{\AA}^{-3}$ isosurfaces (corresponding to $0.53\Delta\rho_{\text{max}}$ and $0.38\Delta\rho_{\text{max}}$, respectively), in the positive and the negative modes, present the typical tetrahedral bonding of Al, shown in **Figure 4(a)**. The selection of different $\Delta\rho$ isosurface levels will cause the bond structure to be different. Note, the bond structure of Al determined by DFT (i.e., $0.53\Delta\rho_{\text{max}}$) and QCBED (i.e., $0.5\Delta\rho_{\text{max}}$) are almost the same characterized by the tetrahedral bonds, though, there are some quantitative differences in $\Delta\rho$ [23]. Due to the higher electron density of Mn than that of Al, a higher value of $\Delta\rho$ ($\Delta\rho = 0.006 \text{ e}^-\text{\AA}^{-3}$) is required to plot the tetrahedral bond feature of Mn for an Al-Mn solid solution. For example, the electron redistribution range of the Mn solute atoms in $\text{Al}_{31}\text{Mn}_1$ reaches out to the second nearest neighbors when $\Delta\rho = 0.0035 \text{ e}^-\text{\AA}^{-3}$ is chosen, while it only reaches to the first nearest neighbors when the setting is $\Delta\rho = 0.006 \text{ e}^-\text{\AA}^{-3}$, see **Figure 4(b)**. With an increasing amount of Mn, the Mn-centered bond structure changes from a “double-drum” type (two tetrahedrons merging together), when $x_{\text{Mn}} < 1 \text{ at.}\%$ (i.e., $\text{Al}_{179}\text{Mn}_1$, $\text{Al}_{159}\text{Mn}_1$, $\text{Al}_{119}\text{Mn}_1$, and $\text{Al}_{143}\text{Mn}_1$), to the typical tetrahedral type, when $x_{\text{Mn}} > 1 \text{ at.}\%$ (i.e., $\text{Al}_{95}\text{Mn}_1$, $\text{Al}_{79}\text{Mn}_1$, $\text{Al}_{63}\text{Mn}_1$ and $\text{Al}_{31}\text{Mn}_1$); this transition is shown in **Figure 4(c)**. These isosurfaces reveal that the electron redistribution, caused by the Mn solute atoms, contributes to the enhancement of the EWF, and thus to improve the hardness of Al-Mn solid solutions (as presented by the green lines on surface plot in **Figure 3(b)**, which are perpendicular to the axis of grain size). The characterizations of electronic structures of materials in terms of the EWF and $\Delta\rho$ provide an insight into the understanding the topological constraint theory [58, 59], which has the potential to be used as an effective predictive tool to optimize the mechanical properties of materials.

In this first-principles computational effort, we have demonstrated the effects of Mn on the lattice parameter, the bonding charge density, and the EWF of Al-Mn solid solutions. From our study, it is shown how the enhancement of the EWF contributes to the observed improvement of the hardness of experimentally fabricated Al-Mn solid solutions. It is understood that, for nanocrystalline Al-Mn non-equilibrium solid solutions, the physical mechanisms responsible in our model, use of the EWF, coupled with a power law scaled hardness, are attributed to the redistribution of electrons caused by the presence of Mn solute atoms. In turn, such detailed description of the chemical bonding between the constituent atoms within nanocrystalline Al-Mn non-equilibrium solid solutions is a necessary step in improving our understanding of the complex mechanisms underpinning the observed composition-property relationships.

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Figure Caption

Figure 1. Effect of Mn on total (bonding) energy, volume and lattice parameter of Al-Mn solid solutions, (a) first-principles calculations (PAW-GGA-PBESol) predicted total energies of Al-Mn as a function of volume fitted by four-parameter Birch-Murnaghan (BM4) equation of state (EOS); and (b) reduction of lattice parameter of Al-Mn with increasing Mn concentration. The gradient colored arrow highlights the decreased equilibrium volume caused by the alloying of Mn solute atoms. The experimentally obtained lattice parameters, shown by dashed lines (Blety, Babic *et al.*, and Stump and Jansen) are reported in Jones [44] and Ruan and Schuh [9]. The navy solid line is based on the experimental data points (solid-open symbols) measured by Darling *et al.* [10, 21]. The solid symbols are obtained from first-principles calculations.

Figure 2. Contributions of Mn to the hardness and EWF of Al-Mn solid solutions. Solid-open symbols indicate the measured hardness of Al-Mn by Darling *et al.* [10] and Ruan and Schuh [9] while the solid symbols present the calculated EWF in this work.

Figure 3. The solid-solution hardening (HV_{ss}) and the grain refinement strengthening (HV_d) of Al-Mn solid solutions, (a) 3D view of the measured hardness by Darling *et al.* [10] (spheres and solid diamonds) and Ruan and Schuh [9] (solid stars); (b) and (c) the coupling effect of HV_{ss} and HV_d on the hardness of Al-Mn solid solutions (labeled as b-1 and c-1) together with the comparison of the predicted hardnesses with the measured ones (labeled as b-2 and c-2), which utilize the constant k_d and the composition dependent k_d , respectively. The solid circles and open diamonds in (a) present the projected data by Darling *et al.*, while the open stars display the projected ones by Ruan and Schuh. The values of the correlation coefficient squared (R^2) of $HV-\phi^6$ and $HV-d^{-0.5}$ are also listed in (a). The minimum and maximum values for the Red-Green-Blue (RGB) color gradient are fixed at 0.5 GPa and 3.5

GPa for the hardness, and at 0 at.% and 4.0 at.% for the Mn concentration, respectively. The hardness falls outside this RGB scaling range will be highlighted by either blue ($HV < 0.5\text{GPa}$) or red ($HV > 3.5\text{GPa}$).

Figure 4. Bonding charge density ($\Delta\rho$) isosurfaces of Al and Al-M solid solutions, (a) $\Delta\rho = 0.0025\text{ e}^-\text{\AA}^{-3}$ and $\Delta\rho = 0.0035\text{ e}^-\text{\AA}^{-3}$ isosurface of Al shown in the positive (gaining electrons) and the negative (losing electron) modes; (b) $\Delta\rho = 0.0035\text{ e}^-\text{\AA}^{-3}$ and $\Delta\rho=0.006\text{ e}^-\text{\AA}^{-3}$ isosurface of $\text{Al}_{31}\text{Mn}_1$ shown in the positive mode; and (c) $\Delta\rho = 0.006\text{ e}^-\text{\AA}^{-3}$ isosurface of Al-Mn solid solutions shown in the positive and negative mode. All these plots are generated via VESTA [41]. The blue colored dashed line highlights the supercell used in the first-principles calculations.

Figure 1

Figure 2

Figure 3

Figure 4