Multi-component solid solution and cluster hardening of Al–Mn–Si alloys

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Tensile tests on Al–Mn–Si ternary alloys show that a small amount of Si increases significantly the strength compared to Al–Mn binary alloys with the same concentration of Mn. This cannot be explained by classical theories for multi-element substitutional solid solution hardening under the assumption of no interaction between different alloying elements. A new simplified cluster strengthening model which addresses both the chemical and size misfit effects of atom dimers is proposed this work. The binding energies and misfit of dimers were estimated by first principles atomistic simulations. The prediction results of the model are reasonably consistent with the experimental results. It shows that the main strengthening contribution is due to the misfit of dimers.

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1. Introduction

The interaction between solute atoms and dislocations is an important strengthening mechanism for alloys. Solid solution hardening in binary alloys has been extensively studied and its principle has been well understood [1,2]. However, multi-element solution hardening, which is essential for commercial alloys, has been paid much less attention. The solute strengthening contribution from solute atoms of type i in binary alloys is denoted \( \Delta \tau_i \). Under the assumption that there is no interaction between solute atoms [3], the superposition of multi-element solution hardening is

\[
\Delta \tau^p = \sum_i \Delta \tau_i^p
\]

Here \( 1 \leq p \leq 2 \). Eq. (1) is a general superposition law at finite temperatures and in the athermal limit [4]. The value \( p=1 \) is justified when a high density of weak obstacles (e.g. solute atoms) are mixed with strong ones such as forest dislocations and non-shearable precipitates [5]. The choice \( p=2 \) is suitable for obstacles of similar strengths [5]. In literatures \( p=1.5 \) is often used for solute strengthening [6–8], which can be obtained from Labusch theory [9]. Simulations suggest that the value of \( p \) depends on the strength and density of obstacles in the athermal limit [10]. Eq. (1) describes well the multi-element solution hardening in several ternary alloys, for instance Cu–Si–Ge alloys [6], Pb–In–Tl alloys [7] and Mg–Gd–Y [11]. However, the predictions by Eq. (1) were found not to match experimental results of Al–Fe–Si alloys [12]. This is probably because the interactions between solute atoms in term of clustering cannot be neglected.

Solute clustering is found to occur in many aluminium alloys [13–17]. Clusters will influence the strength, for instance, the rapid hardening in Al–Cu–Mg alloys during ageing is attributed to the formation of co-clusters (containing various elements) [14,16,18]. Measurements of 3D atom probe tomography in [16,17] revealed that the majority of atom clusters in a naturally aged AlMgSi alloy and in as quenched or slightly aged AlMgCu alloys consisted of 2–4 atoms. Hence, it is common in theoretical analysis only to consider the dimers. In ternary alloys the dimers can contain two atoms of the same alloying element or one of each solute element.

Some models have been proposed to quantitatively explain the hardening effect of clusters. A simplified model for modulus hardening, which was originally proposed for precipitates [19], has been adapted for co-clusters [18]. Starink et al. proposed an analytic model, order strengthening model, considering the short-range order of clusters in Al–Cu–Mg [18] and Al–Mg–Si [17]. They demonstrated that the contribution of modulus hardening was less than 10% of order strengthening. Zhao [20] recently proposed a model that predicts that the elastic interactions between solute atoms and dislocations are significantly increased if the atoms are arranged in small few-atom clusters. The above-mentioned models usually consider the interaction between clusters and un-dissociated dislocations only. A more realistic picture should include the localized influence of clusters on dislocation dissociation and stacking fault. Monte Carlo simulation suggested that
solute clustering in Al–Cu–Ag might affect extended dislocation structure, increasing the separation between partial dislocations [21]. The atomic-scale simulations of Provile et al. [22,23] suggested that the interaction between solute atoms/dimers and two Shockley partials may not have the same magnitude, and that solute dimers are significantly stronger obstacles than isolated solute atoms for bypassing dislocations.

In the present work, the tensile stress of a set of Al–Mn binary alloys and Al–Mn–Si ternary alloys are measured and compared to prediction of the model of Proville et al. [22,23] for solute clustering in Al. Atomistic calculations are performed to estimate input parameters for simplified models for cluster strengthening, which are applied to the Al–Mn–Si ternary alloys.

2. Experimental

Five alloys were cast, including the base material which was a 99.99% high purity Al (4NAl). First a pre-alloy was made where the 4NAl was mixed with 99.9% purity Mn in a ratio of 10:1. The pre-alloy was melted in a vacuum oven at a temperature of about 1673 K (1400 °C) and air cooled. At this temperature all the AlMn phases were dissolved in the melt. A melting pot made of 99.7% purity Al (4NAl) was mixed with 99.9% high purity Al (4NAl). First a pre-alloy was made where the base material was then mixed in a larger melting pot made of graphite clay but coated with Al2O3 and burned at 1473 K (1200 °C) and further coated with boron nitride to reduce diffusion of impurity elements into the melt. This was heated to about 1023 K (750 °C) to make sure that the AlMn phase in the pre-alloy dissolved. A mould of 7 cm × 7.5 cm × 20 cm cooling from one end was used for the final casting, where a uni-directional solidification structure with coarse grains with rotated [100] orientations around the longitudinal direction of the ingot was achieved. The chemical compositions were measured by a mass spectograph by Hydro R&D at Sunndalsøra and are listed in Table 1. The ingots were cut into 20 mm thick slabs that were homogenized by fast heating at 200 K/h to 908 K (635 °C) and further cooled with boron nitride to reduce diffusion of impurity elements into the melt. This was heated to about 1023 K (750 °C) to make sure that the AlMn phase in the pre-alloy dissolved. The compositions of alloys, temperatures for recrystallization (TREX), the grain diameter (Dg) and Taylor factor (M) of tensile specimens.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mn (wt%)</th>
<th>Si (wt%)</th>
<th>TREX (K)</th>
<th>Dg, 78 K (μm)</th>
<th>Dc, RT (μm)</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al99.99</td>
<td>0.00</td>
<td>&lt;0.01</td>
<td>598</td>
<td>185</td>
<td>65</td>
<td>3.0</td>
</tr>
<tr>
<td>AlMn0.25</td>
<td>0.22</td>
<td>&lt;0.01</td>
<td>623</td>
<td>108</td>
<td>29</td>
<td>2.9</td>
</tr>
<tr>
<td>AlMn0.5</td>
<td>0.44</td>
<td>&lt;0.01</td>
<td>623</td>
<td>116</td>
<td>25</td>
<td>2.9</td>
</tr>
<tr>
<td>AlMn1.0</td>
<td>0.93</td>
<td>&lt;0.01</td>
<td>673</td>
<td>150</td>
<td>37</td>
<td>2.7</td>
</tr>
<tr>
<td>AlMn0.25Si0.1</td>
<td>0.22</td>
<td>0.10</td>
<td>623</td>
<td>152</td>
<td>33</td>
<td>3.0</td>
</tr>
<tr>
<td>AlMn0.5Si0.1</td>
<td>0.46</td>
<td>0.11</td>
<td>648</td>
<td>276</td>
<td>–</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Fig. 1. Flow stress at various strain levels as a function of Mn content in solid solution (binary alloys in black; ternary alloys in red). Tensile tests were performed (a) at room temperature and (b) at 78 K. (For interpretation of references to colour in this figure legend, the reader is referred to the web version of this article.)
the critical resolved shear stress for coarse grained alloys, was estimated from the flow stress by
\[
\tau = \frac{1}{M} \left( \sigma - k \sqrt{D} \right),
\]  
(2)

where \( D \) is the grain size from Table 1, and \( \sigma \) is the measured tensile stress. At room temperature the Hall–Petch parameter \( k \) equals 1.27 MPa mm\(^{1/2}\), as given by [25]. The precise \( k \) value at 78 K is not known, but the same value as for room temperature was applied here. The Taylor factor \( M \) (Table 1) was calculated from the texture measured by EBSD mapping (of larger than one mm\(^2\)).

The increase of the critical resolved shear stress because of the added amount of Mn and Si in solid solution results in a difference between the critical resolved shear stresses of a coarse grained alloy \( \tau_{\text{Mn+Si}} \) and the critical resolved shear stress of the pure aluminium \( \tau_{\text{PA}} \) given by
\[
\Delta \tau_{\text{Mn+Si}} = \tau_{\text{Mn+Si}} - \tau_{\text{PA}}.
\]  
(3)

This strength contribution will first be modelled from classical theory without solute interactions. Next atomistic modelling is presented and models taking into account these modelling results are included.

### 3.1. Modelling without solute interactions

Eq. (1) applied to estimate the solid solution hardening of ternary AlMnSi alloys, can be written.
\[
(\Delta \tau_{\text{Mn+Si}})^2 = (\Delta \tau_{\text{Mn}})^2 + (\Delta \tau_{\text{Si}})^2.
\]  
(4)

Here \( \Delta \tau_{\text{Mn}} \) and \( \Delta \tau_{\text{Si}} \) are the Mn and Si contributions. Based on the tensile tests in Fig. 1 for binary AlMn alloys and by the use of Eq.(2), the contribution to the strengthening from Mn in solid solution was estimated to be \( \Delta \tau_{\text{Mn}} = 3.6 \) MPa for the case of AlMn0.25Si0.1. The solid solution contribution from Si was extrapolated from a work on high-purity Al–Si binary alloys [26] as \( \Delta \tau_{\text{Si}} \approx 0.9 \) MPa with the Labusch theory applied. Alternatively \( \Delta \tau_{\text{Si}} \) can be estimated to be in the range from 0.8 MPa to 1.2 MPa from the tensile testing of water quenched or air cooled Al–Si alloys reported in [27]. In this work \( \Delta \tau_{\text{Si}} = 1.2 \) MPa is used as an upper estimate. The pure solid solution strengthening under the assumption of no interactions is calculated from Eq. (4) as \( \Delta \tau = 4 \) MPa using \( p = 1.5 \). This value is smaller than the measured value 5.8 MPa, indicating the assumption of no interaction is questionable. Therefore, solute interaction/clustering is considered.

### 3.2. Atomistic modelling

Interactions between solutes were quantified from first principles calculation using density functional theory as implemented in the Vienna ab initio simulation package (VASP) [28,29]. The PBE generalized gradient approximation was employed [30], using a plane wave basis set with an energy cut-off of 350 eV and the projector augmented wave method to treat the core region [31]. Solutes were introduced into cubic super-cells consisting of 108 atoms (3 x 3 x 3 conventional cubic unit cells). Electronic self-consistency required difference in energy between consecutive iterations less than \( 10^{-6} \) eV. The density of integration points in the Brillouin zone was less than 0.17 Å\(^{-1}\) in each direction (3 x 3 x 3k points). The super cells were relaxed in size simultaneously as the atomic coordinates, and the relaxation criterion was that the forces had to be smaller than 1 meV/Å.

Pairs of solutes based on Si and Mn were investigated. The interaction energy between such pairs was defined as the difference between the electronic energy of a model with two solutes (i.e. X and Y) and that of the sum of electronic energies of models with single solutes, balanced by the number of Al atoms:
\[
E_{\text{int}} = E(\text{Al}100XY) + E(\text{Al}108) - E(\text{Al}107X) - E(\text{Al}107Y)
\]  
(5)

\( E_{\text{int}} \) is a function of the distance between the solutes within the cluster, displayed in Fig. 2. Negative energies indicate attraction between the atoms in a pair of solutes.

As can be seen from this figure, all pairs of solute atoms display attraction at some level. The weakest attraction is between Si atoms, where only 2nd nearest neighbours are attracted to each other with \( |E_{\text{int}}| > 1 \) kJ/mol. Si–Mn interactions are on the other hand much stronger, with an attraction of more than 7 kJ/mol for 2nd nearest neighbours. Pairs of Mn are repulsive between 2nd and 4th neighbours but attractive between nearest and 3rd neighbours. There is thus a thermodynamic drive towards formation of clusters based on all the solute pairs that we studied.

The volume misfit \( \Delta V \) was calculated from the definition of the bulk modulus \( B \):
\[
\Delta V = -\Delta PV/B.
\]  
(6)

where the pressure difference \( \Delta P \) of a reference volume \( V \) (the super cell used in the calculation) was calculated using VASP. The experimental value of 79.4 GPa at 0 K was used for \( B \) [32]; this is quite similar to the DFT calculated value of 78 GPa [33]. Three different concentrations of solutes were investigated for each impurity; 1, 2, and 4 solutes per super cell. The pressure difference of a single solute was calculated from a linear fit to \( \Delta P \) as a function of solute concentration, as shown in Fig. 3. The calculated misfit volume was 3.0 Å\(^3\) for Si, 14.2 Å\(^3\) for Mn, and 16.8 Å\(^3\) for the Si–Mn pair. The latter value is rather close to the sum of misfit volumes for the two constituent solutes.

![Fig. 2. The interaction energy \( E_{\text{int}} \) between the atoms in pairs of Si and Mn solutes. The energy is in kJ/mol per solute pair, and is relative to solutes infinitely separated.](image)

![Fig. 3. Pressure versus solute atoms in a 108-atoms super-cell for Si, Mn solutes and Mn–Si dimers. The dashed line is linear fit for Mn–Si dimers, which slope is used in Eq. (6).](image)
3.3. Strengthening due to chemical effect

The clusters are formed due to the interaction between solute atoms. A simplified model for chemical strengthening adapted here is similar as described in [17,18]. A dislocation is located between two [111] planes and the two atoms of the dimer will be in one of these two planes or with one atom in each of them. The clusters will in some cases be sheared apart by a dislocation passing by, i.e. when the relative position of the two atoms in a dimer is changed from first nearest neighbours to the second or third nearest neighbours. If both the dimer atoms are located in the [111] plane either below or above, then the dimer is simply shifted one Burgers vector subsequent to the dislocation has passed it. In some of the cases with one atom in each of the two [111] planes the dimer can still be sheared into a similar configuration as before, say into another closest neighbour configuration. Based on results from principle calculations in last section, only dimers of two atoms that are either closest or second closest neighbours will be considered. Guided by the atomistic binding energies, only dimers consisting of one Si atom and one Mn atom are considered here.

The breaking of a cluster will require extra energy $\Delta E_{ccl}$, which is the energy barrier of the transition, i.e. the activation energy. The value of $\Delta E_{ccl}$ is difficult to determine experimentally, so atomistic simulations are required. Ideally $\Delta E_{ccl}$ corresponds to a saddle point between the initial and the subsequent configuration. However, the difference between the energies of each configuration is much simpler to calculate from atomistic simulations and will here be used as first estimates for $\Delta E_{ccl}$. In theory this energy is lowered by the cases where a dimer is formed by that two atoms are brought together by the dislocation. In a dilute alloy this contribution is small and neglected. With increased strain many of the dimers become sheared apart, which might affect the work hardening, but this effect is not included in the modelling here.

The strengthening due to shearings clusters apart is clearly different from classical order strengthening, which creates an anti-phase boundary, and from chemical strengthening, which creates two ledges of interface. The work per slip area done by a gliding dislocation is $W_{ord} = \tau_{ord}b$. This work is assumed to equal the change in binding energy due to shearing apart dimers across the adjacent two slip planes. This energy equals the energy change per broken dimer $\Delta E_b$, multiplied with the number of such dimers per slip area. The dimers crossing the slip plane contains one atom from each adjacent plane, so the number of dimers per slip area equals the number of atoms per area that are part of such dimers in any of the two adjacent atom planes. The concentration of Mn atoms being part of any closest or second closest neighbour dimer is $c_{cl}$. A certain fraction $P_{sh}$ of the dimers are modified by the gliding dislocation. The work energy balance gives

$$\Delta \tau_{ord} = \frac{\Delta E_{ccl} - 2c_{cl}P_{sh}}{3A_{111}} \Delta E_{b}$$

Here $A_{111} = \sqrt{3}b^2/2$ is the [111] area occupied per atom. The statistical chance that an arbitrarily chosen atom at one of the adjacent [111] planes is Mn or Si and part of a dimer equals $2c_{cl}$. There are 12 different closest neighbour dimer configurations and additional six second closest neighbour configurations to choose, from which only three of each crosses the glide plane. When a dislocation is gliding between these two planes, one of the closest neighbour dimers would remain a closest neighbour, one would become a second closest neighbour and the third would become third closest neighbour. One second closest neighbour would become closest neighbour while the two others would become more distant. Hence three out of 18 dimers are modified from first or second to more distant neighbours, i.e. $P_{sh} = 1/6$.

3.4. Strengthening due to size misfit of clusters

Zhao [20] proposed a model considering the elastic effect of size misfit of small clusters, which is adapted from solute strengthening theory. Basic assumptions are that the volume misfit of a small cluster is assumed to be approximately the sum of misfits of all the atoms in the cluster and the clusters can be treated as point obstacles. Since the atomistic simulations confirmed the assumption that the misfits can be added for the dimers considered in this investigation, the model of Zhao should be applicable. The methodology by Leyson et al. [8] to predict solute strengthening by combining the Labusch theory with first-principles calculations, are adapted here to estimate the strengthening due to the volume misfit of dimers in the matrix. It is assumed that since the size of a dimer is small, its misfits can be treated similar as single substitutional atoms.

According to Ref. [8], solute strengthening at 0 K is approximately given by

$$\Delta \tau_{s} \approx A_{s} \Delta V^{4/3} C^{2/3}$$

Here $\Delta V$ is the volume misfit; $c$ is atomic fraction of solutes; $A_{s}$ is a constant, $-31.1 \text{ MPa \AA}^{-4}$. The yield stress will be reduced due to the atomic thermal motion at elevated temperature. The temperature dependence is given by

$$\Delta \tau_{s}(T) = \Delta \tau_{s0} \left[ 1 - \exp \left( \frac{kT}{\Delta E_{b}} \ln \frac{\bar{\epsilon}_{0}}{\bar{\epsilon}} \right)^{2/3} \right]$$

or

$$\Delta \tau_{s}(T) = \Delta \tau_{s0} \exp \left( \frac{-kT}{0.51\Delta E_{b}} \ln \frac{\bar{\epsilon}_{0}}{\bar{\epsilon}} \right).$$

$$\Delta E_{b} \approx A_{s} \Delta V^{2/3} C^{1/3}$$

$T$ is temperature; $k$ is Boltzmann constant; $\Delta E_{b}$ is the energy barrier; $A_{s}$ and $\bar{\epsilon}_{0}$ are constants, $A_{s} = 1.31 \text{ eV \AA}^{-2}$ and $\bar{\epsilon}_{0} = 10^{-4} \text{ s}^{-1}$. Eq. (9) is used for low temperature such as 78 K, and Eq. (10) for more elevated temperature.

In this work, Eqs. (8)–(11) are adapted for misfit strengthening of dimers. The dimer is treated similar to a single atom. Its volume misfit is assumed to be approximately the sum of misfits of the two atoms in the dimer,

$$\Delta V_{cl} \approx \Delta V_{Mn} + \Delta V_{Si}.$$  

The volume misfit of a cluster does not increase linearly with the number of atoms per cluster, but linearity can be an approximation for very small clusters. The atomistic simulation in Section 3.2 has verified Eq. (12). A combination of Eq. (12) with Eqs. (8)–(11) provides an estimate of the misfit strengthening, with the concentration $c$ in Eqs. (8) and (11) replaced by the cluster concentration $c_{cl}$.

4. Application of the models

As shown in Section 3.2, Mn and Si attract each other with interaction energies of 6–8 kJ/mol at the first and second nearest neighbour sites. The attractions between Si–Si pairs and between Mn–Mn pairs are much weaker, smaller than 2 kJ/mol for nearest and 2nd nearest neighbours. The strong attraction between dimers of Mn and Si suggests that these are favourable clusters, while Si–Si and Mn–Mn pairs are less likely to occur. As a simplification, only Mn–Si pairs were thus considered as clusters in the present work.

The interaction energy of Mn–Si pairs at the first nearest neighbour site was found to be $-6.4 \text{ kJ/mol}$ from the first principle calculations, i.e. the enthalpy of formation of Mn–Si pairs...
from a random solution. It is reasonable to assume that Mn–Si clusters form and make a significant contribution to the strength. The interaction energy of Mn–Si pairs at the second and third nearest neighbour sites were found to be $-7.5 \text{kJ/mol}$ and $-0.6 \text{kJ/mol}$ (repulsive), respectively, from the atomistic calculations. For the sake of simplicity the value of $\Delta E$ was set as $7 \text{kJ/mol}$ for both first and second closest neighbour dimer configurations in this work.

As the most extreme case it was assumed that all the Si atoms formed clusters (pairs) with Mn atoms, i.e. spending all Mn and Si atoms giving an atomic fraction $c_{\text{Si}} = 0.11$. The experimental strain rate was $\dot{\varepsilon} = 10^{-3} \text{s}^{-1}$. The volume misfits of Mn and Si for misfit strengthening are taken from [8]. The total strengthening becomes the sum of misfit strengthening and order strengthening, given by

$$\Delta \tau_{\text{MS}} = \Delta \tau_{\text{Mn-Si}} + \Delta \tau_{\text{MS-f}}$$

The predicted values of $\Delta \tau_{\text{Mn-Si}}$ of cluster strengthening in Al–Mn–Si ternary alloys and pure solute strengthening in the Al–Mn alloys are plotted in Fig. 4. Here only the measured yield strength variations are considered. For the experiments performed at 77 K the smallest strain of 0.01 are used as an estimate of the yield strength. The results are qualitatively valid also for flow stress at larger strains, but then also work hardening must be accounted for. For cluster strengthening in Al–Mn–Si ternary alloys, the contribution due to the binding energy of dimers is only $\sim 0.2 \text{MPa}$. It can be seen that the misfit strengthening plays the major role in the ternary alloy, while the cutting of the dimer hardly contribute. The trend line of Al–Mn binary alloys illustrates the prediction ability of the solute strengthening model [8]. As noted in Ref. [8], the prediction of Eq. (8) deviates up to $\pm 30\%$. The main contribution from the clusters follows from the same equation by replacing single atoms by dimers, and then the predicted value of $\Delta \tau_{\text{Mn-Si}}$ fits well this trend line.

5. Conclusion

It is found that the yield strength of an Al–Mn–Si ternary alloy is larger than the multi-element hardening prediction under the assumption of no interaction between alloying elements. This implies that solute clustering may occur and contribute to higher strengthening. Models for cluster strengthening were applied, including chemical and elastic effects of clusters based on simplified assumptions and input from atomistic simulations. The predictions are reasonably consistent with experimental results. The models should be applicable to other alloys containing clusters. Atomistic simulations are required to further develop the models for cluster strengthening. It is concluded that misfit strengthening due to clusters makes the major contribution in the investigated case.

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