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A Model to Unravel the Beneficial Contributions of Trace Cu in Wrought Al-Mg Alloys

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Abstract

The softening and strengthening contributions in pre-deformed and aged Al-Mg-Cu alloys containing 3wt.%Mg and 0.5wt.%Cu are evaluated by a combination of microscopy, mechanical testing and modelling. A refined phenomenological model for the work hardening response, accounting for the separate effects of recovery and precipitation, is shown to be suitable for an unambiguous determination of the precipitation hardening contribution in these alloys. Significantly, it is found that the mechanical response of these alloys is not strongly impacted by Cu content (in the low Cu content regime), pre-deformation level or aging temperature meaning that the alloys are robust with respect to variations in composition. This is interesting from the perspective of alloy design concepts based on ‘recycling friendly’ compositions in applications that include paint-baking.

Keywords: Precipitation, aluminum alloys, Al-Mg-Cu, yield strength, work hardening, atom probe tomography, recycling friendly alloys

1. Introduction

There is a growing recognition that the development of ‘recycling friendly’ aluminum alloys will be a necessary outcome of increasing wrought alloy con-

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sumption and the corresponding increase in scrap availability [1, 2]. The traditional approach of down-cycling wrought alloys into foundry alloys is becoming less tenable as the supply of scrap starts to outstrip the demand from casting applications [2]. One of the drivers for the increasing scrap supply is the rapid growth of aluminum in automobiles. Developing strategies that adapt existing wrought aluminum alloys (e.g. 3xxx, 5xxx and 6xxx series alloys) to tolerate, or even benefit from, increasing levels of ‘impurities’ (residuals) so as to achieve ‘recycling friendly’ alloys is one strategy that appears to have promise [2].

Wrought 5xxx series alloys are particularly challenging as ‘sinks’ for recycled wrought aluminum alloys given that they are primarily Al-Mg alloys with only ppm of Mn and Cr added for grain size control. For the alloy 5754, for example, Cu and Mn arriving from 3xxx and 6xxx series alloy scrap would strongly limit their use as part of the recycled scrap mix [2]. Finding ways for 5xxx (or 5xxx like) alloys to accommodate even small amounts of these elements would increase the ability to use a wider variety of scrap sources.

In the particular case of Cu, there is ample evidence that small additions, small enough so as not to be detrimental to corrosion resistance[3], can be beneficial in automotive 5xxx series alloys[4, 5, 3, 6]. Additions of less than 0.5at.%Cu to 5XXX series aluminum alloys can reduce or even eliminate the softening experienced by stamped parts during the automotive ‘paint bake’ cycle [4, 5, 3]. Given that up to 20% of the as-stamped strength can be lost to recovery during the paint bake cycle, allowing for an increased level of Cu could create a virtuous circle; improving properties to allow designs incorporating less material, and higher scrap fractions (and lower scrap quality) in the alloy fabrication.

While it has been known for 20 years [5] that as little as 0.2wt.%Cu can be used to eliminate softening in 5xxx alloys during paint baking, the phenomena that control the evolution of the strength have not been clearly identified. Recent work has shown that precipitation in Al-Mg alloys containing ~0.2 wt.%Cu results in the formation of clusters/GPB zones reminiscent of those formed in conventional 2xxx series Al-Cu-Mg alloys. Importantly, however, the composition of the clusters/GPB zones in the low Cu alloys are richer in Mg and leaner

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9 in Cu compared to those in 2xxx series alloys. This allows for a significant num-
10 ber density of particles and thus significant precipitation strengthening despite
11 the relatively low Cu content [6].
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14 Precipitation during the paint bake process can be expected to have two
15 coinciding effects on the mechanical properties. First, precipitation hardening
16 alone could act to counterbalance the softening induced by recovery. As noted
17 above, a significant amount of precipitation hardening was observed in Al-Mg-
18 Cu alloys after solution treating and aging at 160 and 200°C [6]. In parallel,
19 precipitation can also act to reduce the rate of dislocation loss through recovery
20 (see e.g. [7, 8]). Precipitation in the presence of a pre-existing dislocation
21 network can lead to heterogeneous nucleation on dislocations, this leading to
22 a stasis in the recovery kinetics, the duration of which is determined by the
23 balance between the coarsening behaviour of the precipitates and the driving
24 force for recovery (the dislocation density itself)[7]. In the case of Al-Mg-Cu
25 (and 2xxx series alloys as well) there is evidence that heterogeneous precipitation
26 of metastable S-like phases on dislocations is prevalent [9]. It was reported, for
27 example, that precipitation into a pre-deformed Al-Mg-Cu alloy accelerated
28 the formation of the S-phase at the expense of cluster/GPB zone formation
29 [9]. Similar observations have been observed for other alloys as well (see e.g.
30 [10, 11])
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33 Separating the effects of 1) strengthening by precipitation hardening and 2)
34 reduction of softening by precipitation is difficult, particularly when the kinetics
35 of recovery and precipitation coincide. One possible way to approach this prob-
36 lem, using mechanical property data alone, would be to recognize that the two
37 phenomena can have distinctly different effects on different parts of the stress-
38 strain response (see Figure 1). In the case of precipitation hardening by small,
39 shearable precipitates the effect is fully attributable to the yield strength, the
40 change in the work hardening rate being negligible. In contrast, softening by
41 recovery (through the loss of dislocations) would have an effect on both the yield
42 strength *and* work hardening rate. This idealized view is illustrated in Figure 1.
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44 If we take a solution treated alloy and pre-deform it, increasing its dislocation
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9 density, we find that the pre-deformed material when subsequently tested will
10 exhibit a work-hardening behaviour that falls along the same line as the original
11 solution treated alloy (Figure 1 b). Precipitation hardening by shearable pre-
12 cipitates will, in contrast, shift the curve for the material to the right without
13 changing its slope (Figure 1 c). Recovery, will reduce the dislocation density,
14 causing the behaviour to shift back along the work hardening curve¹(Figure 1
15 d). Ultimately, for a pre-deformed sample that has been aged under conditions
16 where both recovery and precipitation have taken place, prediction of the work
17 hardening rate (dependent on dislocation density only) and flow stress at yield
18 (dependent on dislocation density and precipitation hardening) can be used to
19 identify both contributions (Figure 1 d).
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26 In this work, we start from the concept outlined above with the aim of
27 identifying the individual contributions of recovery and precipitation to the
28 mechanical properties of a pre-deformed and aged Al-3%Mg alloy containing
29 0.5wt.%Cu (i.e. Al-3.33at.%Mg-0.21at.%Cu). This builds on our recent work
30 using the same alloy, where we have characterized the precipitation sequence,
31 kinetics and hardening in the absence of pre-deformation[6]. Here, we use low
32 temperature tensile tests to introduce pre-deformation as well as to character-
33 ize the flow stress and work hardening response following aging at 160°C and
34 200°C. Illustrative atom probe tomography (APT) has been employed to cir-
35 cumvent the challenge of characterizing precipitates with low atomic number
36 contrast (e.g. those containing neighbouring elements like Al and Mg) while
37 allowing for characterization of segregation on defects. We will show that the
38 idealized analysis shown in Figure 1 is too simple to be fully useful but that the
39 desired separation of flow stress contributions can ultimately be recovered using
40 a more sophisticated analysis of the work hardening behaviour. Based on this
41 analysis the relationship between pre-deformation level, Cu alloy content and
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53 ¹This is true, to a good approximation, when the properties are measured without strain-
54 path change between pre-deformation and post aging measurements. Introducing a strain
55 path change introduces further complexity not considered here.
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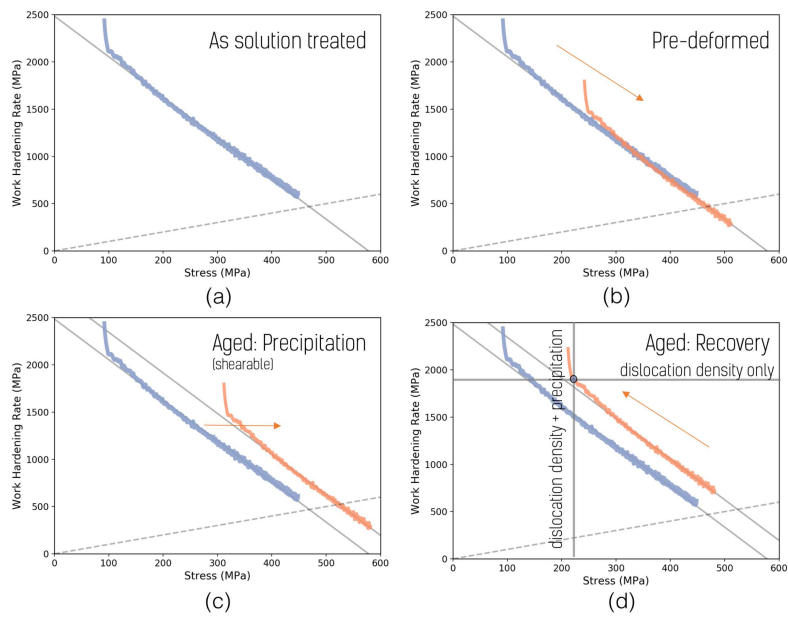


Figure 1: An idealized view of the changes of flow stress and working hardening, illustrated via a Kocks-Mecking plot, for a precipitation hardenable alloy (containing shearable precipitates) during strain aging. a) The as-solution treated (fully recrystallized) mechanical behaviour b) Upon predeformation, the dislocation density is raised causing the flow stress to increase and the work hardening rate to drop c) The addition of shearable precipitates (without recovery) would shift the flow stress without changing the work hardening rate d) recovery with precipitation would cause a lowering of the dislocation density, causing a reduction of the flow stress and an increase in the work hardening rate. The ultimate result is that the yield stress and work hardening rate at yield could (in theory) be used to separate the effects of precipitation and recovery in a strain aged material.

strength is proposed. This work highlights the possibility of adjusting the thermomechanical processing strategy based on minority (residual) element levels to give desirable properties using recycling friendly alloy compositions.

2. Materials and Experimental Method

A laboratory cast and hot rolled 5 mm sheet was provided for this study by the Novelis Global Technology Centre (see Table 1). This material was cold rolled to a thickness of 1 mm (80% reduction in thickness). Tensile samples were cut and solution treated at 550°C for 10 min, then quenched immediately in water. These samples were then deformed in tension to introduce deformation prior to aging. These tests were performed at 77 K **within a liquid nitrogen bath**, at a nominal strain rate of 10^{-3} s^{-1} . These conditions were selected so as to avoid the complicating effects of dynamic strain aging [12] as well as to reduce solute mobility during deformation. Deformation was performed to raise the flow stress by $\Delta\sigma = 44 \text{ MPa}$ or 176 MPa , corresponding to ~ 2 and 10% tensile strain respectively. The samples were then stored in liquid nitrogen until ready to be aged. Aging of the pre-deformed samples was conducted at 160°C or 200°C in a stirred oil bath. Following aging, samples were immediately tested in tension following the same procedure as used for pre-deformation. **In the case of pre-deformed samples, tests were repeated in most cases for two-independently prepared conditions. It was found from these tests that the maximum variation in yield strength between samples was $\pm 5 \text{ MPa}$.**

	Mg	Cu	Fe	Si	Ti	Ni	Mn	Zn	Cr
(wt.%)	2.90	0.54	0.1	0.05	0.015	0.007	0.001	0.002	0.001

Table 1: Composition of studied Al-3Mg-0.5Cu alloy obtained by optical emission spectroscopy. Balance is aluminum.

Specimens for transmission electron imaging in a scanning electron microscope (STEM-in-SEM) and APT were cut from the gauge section of pre-deformed

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9 and aged samples. STEM samples were prepared by grinding the sample to re-
10 duce its thickness, followed by punching out 3 mm diameter discs. These disks
11 were electropolished in a nitric acid methanol solution to perforation. Samples
12 were observed using a FEI Versa dual beam microscope at 30 keV, with the
13 STEM detector operating in bright field mode.
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17 For APT, needle-shaped samples were prepared via a 2-stage electrochemical
18 polishing technique [13, 6]. Data was collected using a Cameca LEAP 5000
19 XS. Experiments were performed using a base temperature of 50K, in high-
20 voltage pulsing mode, with 20% pulse fraction. The DC voltage was adjusted
21 to maintain a detection rate of 1 ion per 100 pulses. Data reconstruction was
22 performed in the commercial software package IVAS 3.6.14 using the calibration
23 methods outlined elsewhere [14, 15]. Isocomposition surfaces have been used to
24 highlight regions of enhanced solute (segregation, precipitation) [16] and the
25 composition of individual objects was approximated by composition profiles
26 across features of interest.
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34 **3. Experimental Characterization of Strain Aging Response**

35 *3.1. Yield Strength and Microstructure Evolution*

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38 As a first insight into the aging response, Figure 2 shows the evolution of the
39 yield strength for three conditions; the material with no pre-deformation and the
40 two pre-deformed cases aged at 160°C and 200°C. In the case of aging starting
41 from the as-solution treated material, it has been shown [6] that the hardening
42 is the result of increasing cluster/GPB zone size. For the material pre-deformed
43 to $\Delta\sigma = 44$ MPa ($\sim 2\%$ strain) the evolution of the yield stress is nearly the
44 same as that found when aging starts from the solution treated material, the
45 offset between the two sets of data being approximately 15 MPa. In the case of
46 the material pre-deformed by $\Delta\sigma = 176$ MPa ($\sim 10\%$ strain) an initial drop in
47 yield stress is observed if one compares the as-deformed yield stress to the yield
48 stress after 2 minutes of aging. Further aging, however, leads to continuous
49 strengthening, the rate being very close to that of the material starting from
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the solution treated state and the samples pre-deformed to $\Delta\sigma = 44$. The aging temperature (160°C or 200°C) makes no significant change in the response for the pre-deformed samples, this being consistent with what was shown for a range of alloy compositions for the as annealed material [6].

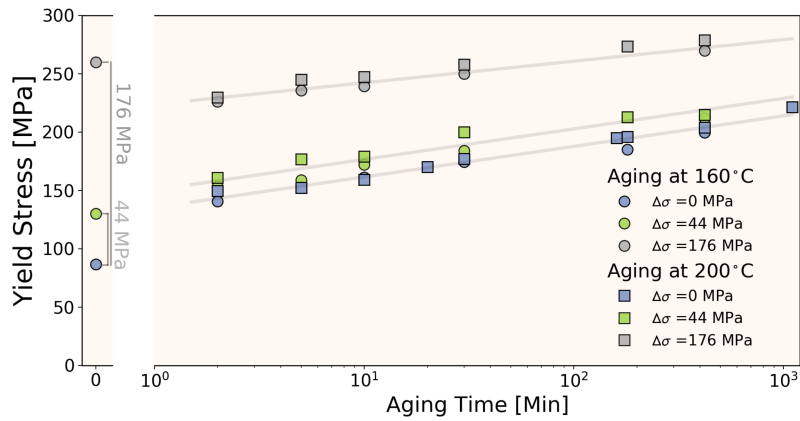


Figure 2: The evolution of the 0.2% offset yield strength aging at 160 and 200°C and for the as-solution treated sample as well as samples pre-deformed to $\Delta\sigma = 44$ MPa and $\Delta\sigma = 176$ MPa. The yield strength of the solution treated sample and as-deformed samples is shown on the far left side of the plot. Lines are drawn as a guide to the eye. Each symbol represents the average of measurements from two samples, the maximum difference between measurements was less than ± 5 MPa, this being the size of the markers used in plotting.

The similarity of the increase in yield strength for all of the conditions at times longer than 2 min suggests that recovery dominates the flow stress at short times (particularly for $\Delta\sigma = 176$ MPa) but that precipitation hardening dominates the yield strength evolution at longer times. In the case of the solution treated and aged samples, it has been shown that the hardening is dominated by a high density of small clusters/GPB zones, similar in morphology and density to those found in 2xxx series alloys but containing much lower Cu contents [6]. It was shown that the volume fraction of these features did not change significantly over the aging times shown in Figure 2 but that the size of the particles did, this leading to the observed strengthening.

Figure 3 shows illustrative atom probe tomography analyses for two samples

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9 aged at 200°C for 160 min with a) no pre-deformation and b) pre-deformation
10 to 176 MPa ². The tomographic reconstructions are displayed at the same scale.
11 For both, sets of iso-contour plot are superimposed onto the point cloud (only
12 approx. 1% of the detected Al ions are shown), in order to highlight the popu-
13 lation of clusters/GPB zones. In the aged sample 3 variants of small, elongated
14 precipitates are visible. One-dimensional composition profiles calculated in 5-
15 nm-diameter cylinders positioned perpendicular to the long axis of the feature
16 (indicated by coloured arrows) are also shown. The particles are mostly Mg-
17 rich, reaching typically close to 25 at.% Mg, with 2-5 at % Cu (i.e. 22 wt.% Mg
18 and 5-6.5 wt.% Cu).
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25 In contrast, for the pre-deformed material, the distribution of the solute
26 elements is much more heterogeneous, both spatially and compositionally, as
27 highlighted by the iso-contours showing solute rich regions. The geometry of the
28 features suggests segregation and/or precipitation along dislocations. Indeed,
29 some regions along these features appeared to have Mg:Cu ratios close to those
30 observed for clusters/GPB zones in the solution treated and aged samples (e.g.
31 Figure 3a) while others had a Mg:Cu ratio closer to 1. Generally, the particles
32 are larger and less well dispersed in the pre-deformed and aged sample compared
33 to the sample aged directly from the as-solutionized state.
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39 Aging of pre-deformed samples leads to the formation of S-phase precipi-
40 tates preferentially along dislocations, by-passing the more typical sequence of
41 clusters/GPB zone formation followed by S-phase formation [9]. A similar pro-
42 cess has also been reported for other alloys, including an Al-Cu-Li alloy [10].
43 This is visible in samples prepared here, where lath-like S-phase can be seen
44 along dislocations in Figure 4. The composition of some of the larger particles
45 imaged by APT in Figure 3b is consistent with the S-phase, **Al₂CuMg having a**
46 **1:1 Cu:Mg ratio [17]**, as well.
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52 The microstructural differences between the solution treated+aged and pre-
53 deformed+aged samples belies the very similar rates of hardening shown in
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56 ²A more detailed analysis of samples aged with no-predeformation can be found in [6]
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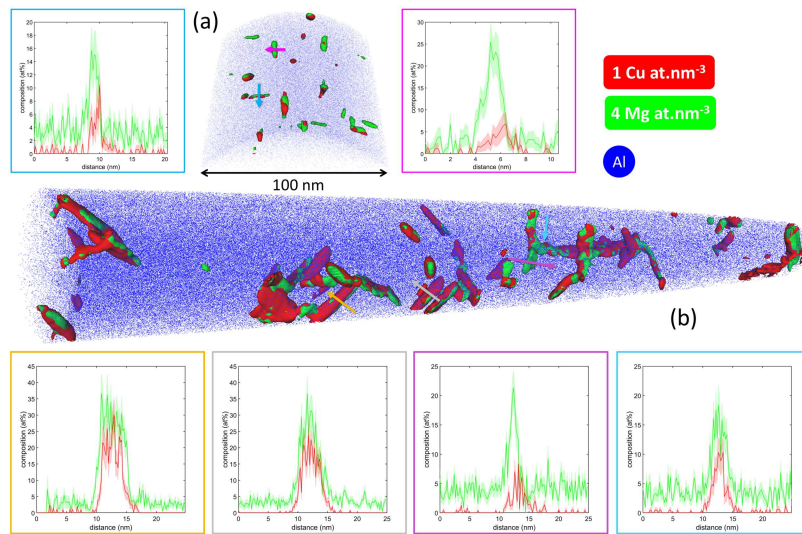


Figure 3: APT reconstruction of specimens prepared from samples solution treated then a) aged for 160 min at 200°C (no pre-deformation) and b) pre-deformed to 44 MPa then aged for 160 min at 200°C. Iso-concentration surfaces are superimposed on the data to highlight the presence of precipitates. Both reconstructions are displayed with the same scale. One-dimensional composition profiles for some of the particles found in each of the data sets are displayed alongside the reconstruction, and for each, an arrow of the same colour is included in the reconstruction to indicate which microstructural object was interrogated. The shaded area corresponds to the 2σ of the counting statistics in each of the 0.2 nm bin of the profile.

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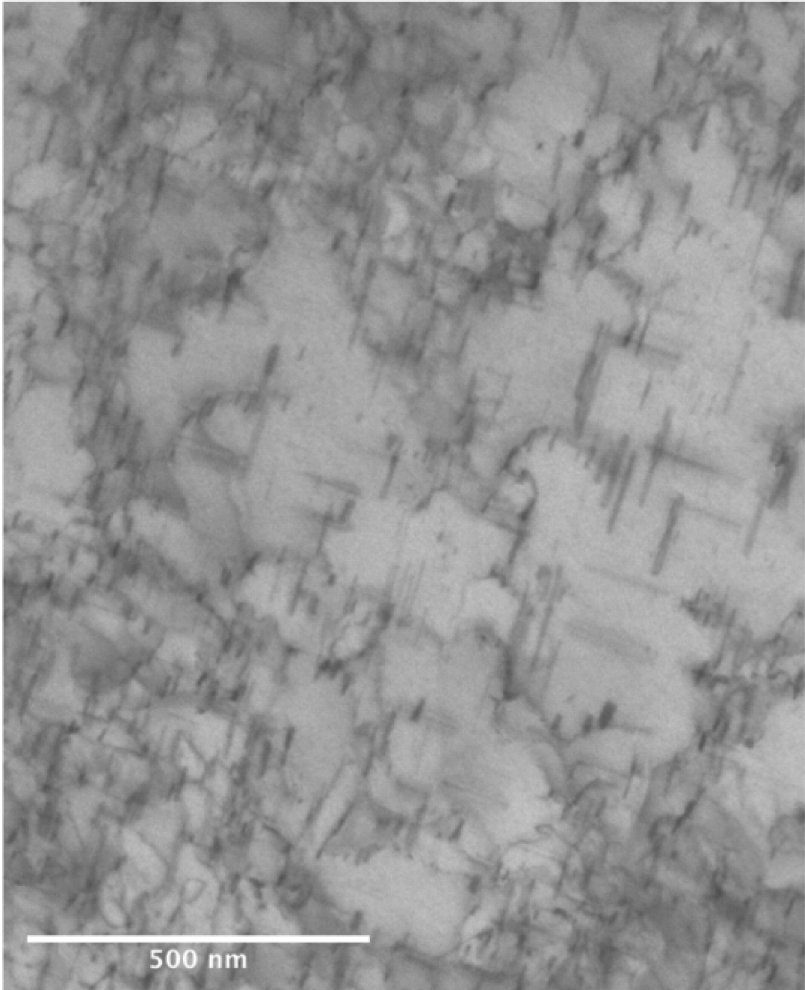


Figure 4: Bright field STEM-in-SEM image from a sample pre-deformed to $\Delta\sigma=44$ MPa and aged at 200°C for 1600 min illustrating the formation of S-phase laths preferentially along dislocations.

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Figure 2. While in our previous work on the hardening response of solution treated and aged samples we were able to use information directly from APT experiments to parameterize a precipitation hardening model, here the complexity of the segregation/precipitation in the pre-deformed samples does not allow for such an approach. Rather, to more quantitatively evaluate the precipitation hardening we can look at the work hardening behaviour (Figure 5).

3.2. Work Hardening Analysis: Separating the Effects of Recovery Induced Softening and Precipitation Hardening

A cursory observation of Figure 5 shows that the real response of the alloy is more complex than the idealized response illustrated in Figure 1. The most noticeable discrepancy between Figures 1 and 5 is the (transient) low work hardening rate ($d\sigma/d\epsilon$) at the onset of yielding. A more careful inspection of Figure 5 also shows that, unlike the idealized response, the work hardening vs. flow stress curves for the as-solution treated and pre-deformed and aged samples are not parallel to one another. Rather, it appears that parallelism is approached asymptotically at high flow stresses. This is particularly notable in Figure 5d.

Very similar behaviour has been recently reported and discussed for a non-precipitation hardenable Al-Mg alloy pre-deformed and aged under very similar conditions to those used here [18]. Therein, a simplified version of the Kubin and Estrin [19] two-internal state variable model was developed. In that case, it was argued that solute-dislocation interactions amplified by the low temperature aging treatment led to changes in the static and dynamic recovery response of forest dislocations. Here, we adapt this model to the case of Al-Mg-Cu alloys. The precipitates are considered as shearable particles and we retain the basic concept outlined in Figure 1 as our method for separating the effects of recovery and precipitation hardening on the yield and flow stress. Here we present the most salient aspects of the model, including the modifications to include the effect of precipitation hardening. We start by writing the flow stress

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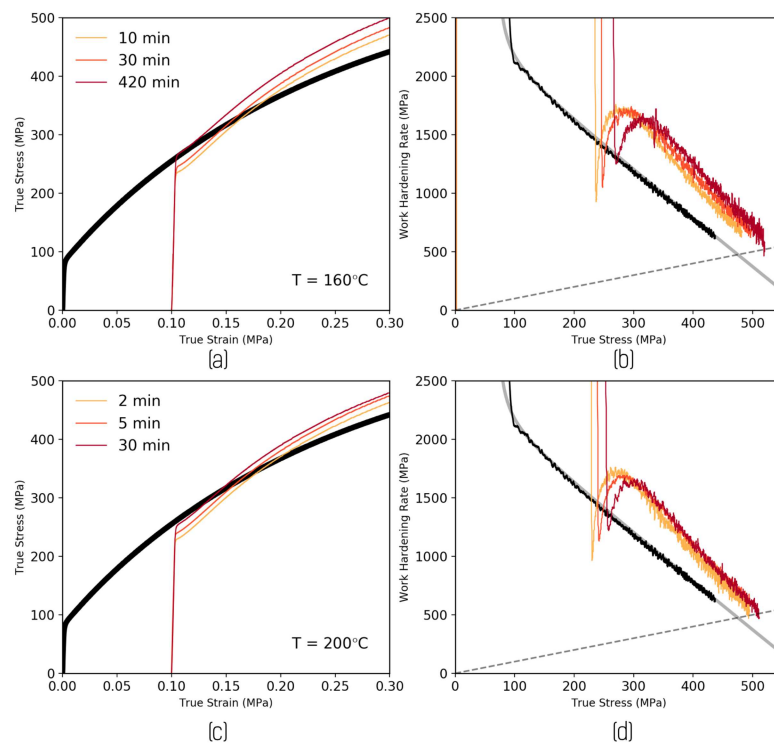


Figure 5: Evolution of the stress-strain (a,c) and work-hardening behaviour (b,d) of a sample pre-deformed to $\Delta\sigma = 176$ MPa.

as a function of the strain rate and forest dislocation density (ρ_f).

$$\sigma = \sigma_0 + \sqrt{\sigma_{ss}^2 + \sigma_{ppt}^2} + M\alpha Gb\sqrt{\rho_f + \rho_f^*} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0}\right)^m \quad (1)$$

In this expression σ_0 is a friction stress including effects of lattice resistance and the grain size. The next two terms $\sqrt{\sigma_{ss}^2 + \sigma_{ppt}^2}$ are the contributions of solid solution strengthening and precipitation strengthening, these being added based on the density of obstacles based on the expectation that the contributions from these two terms will be similar [6].

The reference strain rate, $\dot{\epsilon}_0$ is assumed to be proportional to the mobile dislocation density $\dot{\epsilon}_0 = \beta\rho_m$ and was assumed to evolve as,

$$\frac{1}{\rho_m^s} \frac{d\rho_m}{d\epsilon} = \eta \left(1 - \frac{\rho_m}{\rho_m^s}\right) \quad (2)$$

Where η is a parameter related to the rate of mobile dislocation density generation and ρ_m^s is a saturation mobile dislocation density. The mobile dislocation density will rise with strain to ρ_m^s corresponding to $\dot{\epsilon}_0 = \dot{\epsilon}$, or $\rho_m^s = \beta^{-1}\dot{\epsilon}$. Note that in eqn. 2 one only needs to identify the ratio ρ_m/ρ_m^s , not the absolute value of ρ_m .

In equation 1, two separate forest dislocation densities are introduced, ρ_f and ρ_f^* . During pre-deformation at low temperature we expect to generate forest dislocations ρ_f , which have interacted with approximately immobile solute (due to the low temperature of pre-deformation). Upon aging, two processes will be activated. First, some of these forest dislocations will be lost due to static recovery. At longer times, we anticipate some fraction of these dislocations to be modified due to solute segregation to them and/or precipitation on them. These phenomena are anticipated to change both the rate of static recovery as well as the rate of dynamic dislocation storage and annihilation on reloading following aging. The density of dislocations identified by ρ_f^* are those that have been decorated by solute (or precipitates) during artificial aging. The total forest dislocation density at the end of aging ($\rho_f + \rho_f^*$) is expected to be less than that at the end of pre-straining due to recovery.

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9 The low temperature deformation after aging is expected to only reduce ρ_f^* ,
10 this having been taken in [18] to follow,
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$$12 \quad \frac{d\rho_f^*}{d\epsilon} = -k_4^* \rho_f \left[1 - \exp \left(-\sqrt{\frac{\rho_f^*}{\rho_f}} \right) \right] \quad (3)$$

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16 The important concept here is that the density ρ_f^* recovers (dynamically)
17 more slowly than those dislocations generated by deformation (ρ_f), this leading
18 to an enhanced rate of work hardening over the initial portion of the stress-strain
19 curve.
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22 During deformation, the evolution of ρ_f is assumed to obey,
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$$24 \quad \frac{d\rho_f}{d\epsilon} = k_2 \frac{\rho_m}{\rho_m^s} + k_3 \sqrt{\rho_f} + k_3^* \sqrt{\rho_f^*} - k_4 \rho_f \quad (4)$$

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26
27 where different rates of storage are attributed due to the interaction with
28 ‘solute loaded’ and ‘solute unloaded’ forest dislocations.
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31 In the above system of equations, there are several parameters that need to
32 be set to predict the mechanical properties. In the case of a solution treated
33 sample it is assumed that ρ_f^* can be approximated as zero meaning that eqn. 4
34 depends only on k_2 , k_3 and k_4 . In the limit where $\rho_m = \rho_m^*$ then this further
35 simplifies as the first term in eqn. 4 becomes a constant, this reducing to the
36 classic Kocks-Mecking analysis (Figure 1 with an initial non-linearity (at low
37 stress) controlled by the value of k_2 .
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42 The value of σ_{ss} can be obtained directly from the alloy content of the
43 sample, the value used here being the same as the value used in [6]. One
44 complicating factor is the fact that precipitation can act to deplete solute from
45 the matrix, this making σ_{ss} a function of the aging condition. In our work on
46 aging starting from the as-solution treated state [6] it was shown that the solid
47 solution strengthening was dominated by Mg and that the amount of Mg and
48 Cu found in clusters/GPB zones was insufficient to lead to a significant change
49 in σ_{ss} . Here, for simplicity, we also assume that σ_{ss} can be taken to be constant,
50 independent of the aging condition.
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Taking the above points into consideration, a single test on a solution treated sample, allows one to establish values for σ_0 , k_2 , k_3 and k_4 , the values found for the alloy studied here being given in Table 2.

Parameter	Value	Comment
Material Properties		
b	0.4 nm	Burgers vector
μ	25 GPa	Shear modulus
M	3	Taylor factor
α	0.3	Saada constant
m	0.01	Rate sensitivity
Hardening Law Parameters (Solutionized)		
σ_0	5 MPa	Friction stress and grain size
σ_{ss}	65 MPa	Solid solution strengthening from [6]
ρ_f^0	$2 \times 10^{12} \text{ m}^{-2}$	From σ_0 and experimental yield stress
k_2	$22 \times 10^{13} \text{ m}^{-2}$	Non-linear response at low stress
k_3	$5.7 \times 10^8 \text{ m}^{-1}$	Asymptotic linear fit at high stress
k_4	8.4	Asymptotic linear fit at high stress
Hardening Law Parameters (Pre-deformed + Aged)		
η	50	generation rate of ρ_m
k_3^*	$2.3 \times 10^8 \text{ m}^{-1}$	Taken to be equal to $0.4k_3$
k_4^*	4.2	Taken to be equal to $0.5k_4$

Table 2: Parameters used in modelling the work hardening response using equations 1, 2, 4.

The remaining parameters in eqn. 4, k_3^* and k_4^* , were obtained as a single best fit to all of the pre-deformed and aged conditions used in this study. Following the findings in [18], we restrict the values of k_3^* and k_4^* to be of the same order of magnitude as k_3 and k_4 . The remaining global parameter to identify is η in eqn. 2. As was shown in [18] the exact value is not sensitive to the resulting fit,

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9 therefore this parameter was taken to be identical to the value used in [18].

10 The remaining parameters that are required, and which depend on the level
11 of pre-strain and the aging time/temperature are, i) the density of forest disloca-
12 tions following aging ii) the ratio of the density of mobile dislocations (ρ_m/ρ_m^s)
13 following aging and iii) the precipitate contribution to the flow stress, σ_{ppt} . The
14 density of dislocations (mobile and forest) following pre-straining are estimated
15 from the fit to the solution treated stress-strain curve at $\Delta\sigma = 176$ MPa. Fol-
16 lowing aging, the density of mobile dislocations is expected to be reduced as
17 some mobile dislocations are locked and converted to forest dislocations while
18 others are lost due to recovery. In the case of the forest dislocation density
19 following aging, we need to distinguish between solute locked forest dislocations
20 (ρ_f^*) and non-solute locked forest dislocations (ρ_f). Owing to recovery, we ex-
21 pect that $\rho_f + \rho_f^*$ will be less than the density of forest dislocations present at
22 the end of pre-straining.

23 As described in [18], the value of ρ_m following pre-straining and aging affects
24 mainly the value of the (low) work hardening rate at the onset of yielding and
25 does not significantly impact the stress-strain response beyond $\sim 1\%$ strain.
26 Indeed, according to eqn. 2, mobile dislocations are rapidly generated with the
27 onset of plasticity for the parameters used here. The value of σ_{ppt} only impacts
28 on the yield strength after aging while the values of ρ_f and ρ_f^* , have a significant
29 impact on both the yield strength and work hardening rate.

30 The values of σ_{ppt} and $\rho_f + \rho_f^*$ can be established by fitting to the yield
31 strength of the material as well as the initial (high) work hardening rate following
32 the initial (transient) minimum in the work hardening rate. A more direct
33 estimate of σ_{ppt} can be obtained from the flow stress-work hardening relationship
34 at high flow stress. At high flow stress, the effect of ρ_f dominates that from
35 ρ_f^* leading to the recovery of a linear relationship between flow stress and work
36 hardening rate, as obtained in a classical Kocks-Mecking analysis. As pointed
37 out before, this behaviour is clear in Figure 5d where the solution treated and
38 aged samples are seen to become parallel at high stress.

39 Under these conditions, σ_{ppt} is recovered unambiguously from the separation
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between the parallel solution treated and aged work hardening curves, as illustrated in the case of the simplified analysis presented in Figure 1. Knowing σ_{ppt} , one can then use the yield strength to obtain $\rho_f + \rho_f^*$. To separate these two values, one can then use their distinctly different effect on the work hardening response.

To capture the results found here, it was found necessary to take $\rho_f^* \gg \rho_f$ following aging. This would suggest that nearly all dislocations that do not recover during the aging treatment are segregated to and/or precipitated on, a result that would seem intuitive given the similarity of the segregation profile to split edge and screw dislocations in Al-Mg alloys [20].

Figure 6 shows experimental data and modelling fits for the material that had been pre-deformed by $\Delta\sigma = 176$ MPa and aged for 10 minutes at 200°C. Here one can explicitly see how, at high flow stresses, the work hardening rates of the solution treated and aged materials become parallel, the separation between the two giving the value of σ_{ppt} .

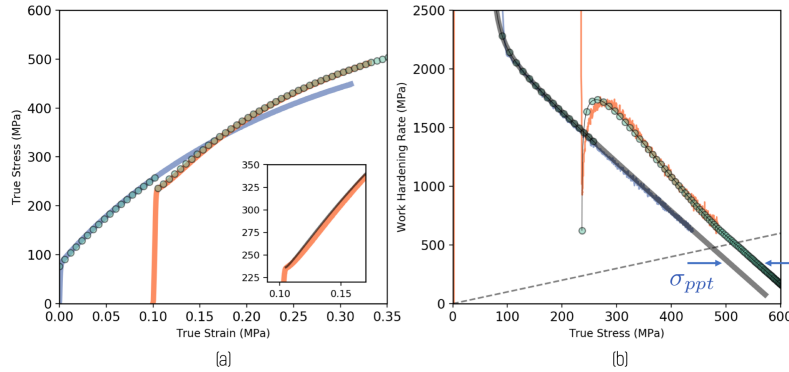


Figure 6: Illustration of the fit of the model (eqns. 1, 4 and 2) to a) the stress-strain response of the solution treated material (blue) and the material pre-strained to $\Delta\sigma=176$ MPa then aged for 10 minutes at 200°C (orange). Experimental data are shown as lines while the model fits are shown as circles. Shown in (b) is the flow stress-work hardening relation for the same materials. Here it is shown how the experimental data and model prediction lead asymptotically to linear behaviour at high flow stresses and how this can be used to deduce the magnitude of σ_{ppt} .

Following the approach outlined above, we have deduced a best fit to the stress-strain response of the materials pre-deformed to $\Delta\sigma = 176$ MPa and aged at 160°C and 200°C for various times. Figure 7 shows the experimental stress-strain curves (solid lines) along with the fits of the model (symbols).

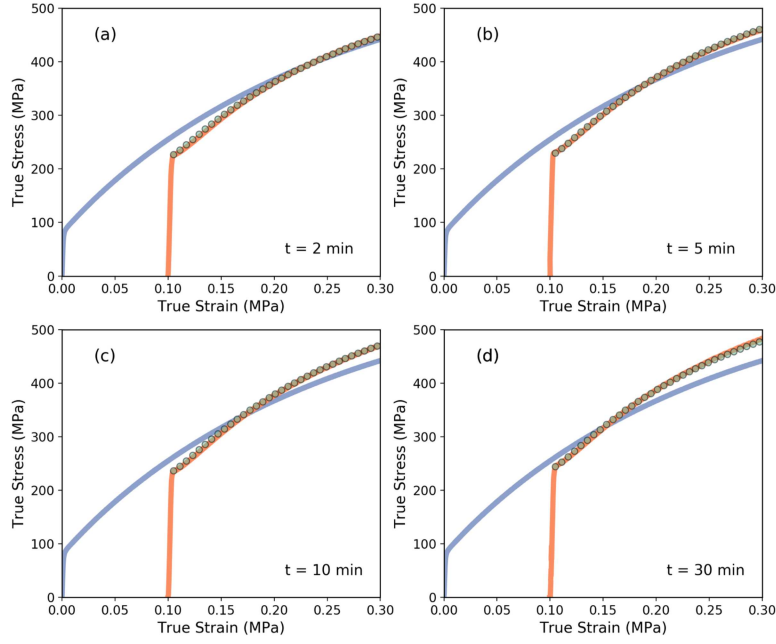


Figure 7: Illustration of the fit of the model to the stress-strain response following aging at 200°C for the indicated times. Experiments are solid lines (blue = solution treated, orange = aged) and symbols are model predictions.

As can be seen, the fits reproduce the stress-strain response very well, the two main parameters that need to be adjusted with aging time being the forest dislocation densities directly after aging (ρ_f and ρ_f^*) and the precipitation contribution to the strength, σ_{ppt} . It was found that the combined best fit values of $\rho_f + \rho_f^*$ were nearly identical for all but the two shortest annealing times at 160°C (Figure 8). This would suggest that recovery happens much more quickly than precipitation, reducing the forest dislocation density to $\sim 37\%$ the value that was present directly after reloading.

The fact that further recovery seems not to take place may be a consequence of solute segregation and precipitation on those dislocations that had not recovered earlier. This should be contrasted with the results obtained from applying the same model to very similar experimental results for a binary (non-precipitation hardening) Al-Mg alloy [18] where it was observed that recovery continued obeying classic Bailey-Orowan recovery kinetics. These results would be in line with the view presented in the case of Al-Mg-Sc alloys where a stasis in the recovery was observed owing to dislocation/precipitate interactions [7].

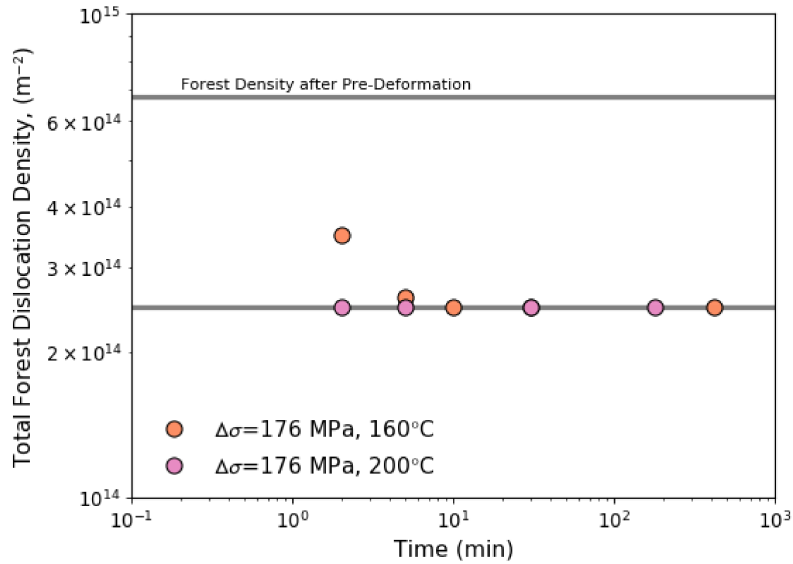


Figure 8: The estimated total forest dislocation ($\rho_f + \rho_f^*$) following pre-deformation and aging.

Figure 9 shows the predicted evolution of σ_{ppt} with aging time and temperature for these samples. Also shown here are results from the same alloy aged at 200°C from the solution treated state [6]. Coinciding with the results in Figure 2 we see that, except for short aging times at 160°C, the aging response follows the same trend regardless of aging temperature. This also mirrors the aging response that was reported for the as-solution treated samples [6]. What is notable here, however, is the fact that the precipitation contribution to the flow

stress is *lower*, compared at equal aging time, for the samples that had been pre-deformed compared to those that were aged starting from the as-solutionized state. This would suggest that pre-deformation leads to less efficient precipitation hardening.

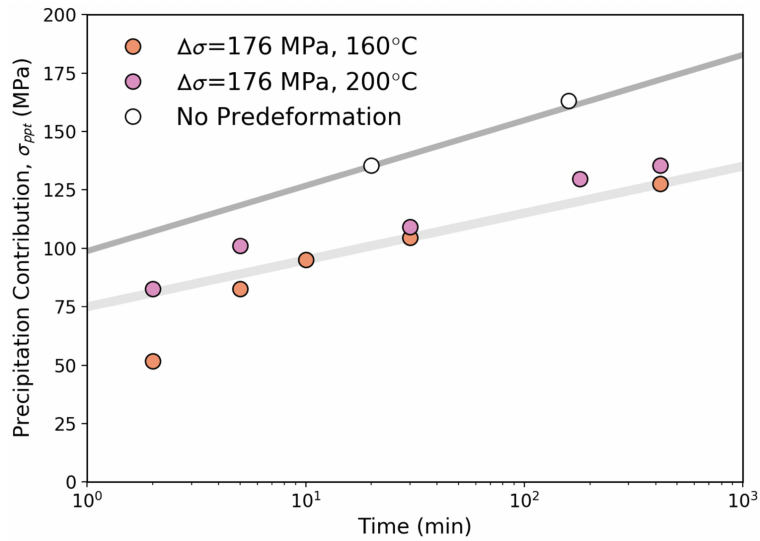


Figure 9: The estimated contribution to the flow stress from precipitation hardening, σ_{ppt} as a function of aging time and temperature. Also shown are the results obtained from samples that had been aged without pre-deformation [18].

While the results in Figures 6 and 7 indicate a very good ability of the model to reproduce the experimental stress-strain response, this was not true for all cases. In particular the sample aged for the longest time (420 min) at 200°C could not be satisfactorily fit by the model. Figure 10 shows the experimental results for this condition. It is notable here that the yield stress of the pre-deformed and aged sample is slightly higher than the flow stress of the material at the end of pre-deformation. Given that recovery has happened, this suggests significant precipitation hardening. However, if one looks at the flow-stress, work hardening plot (Figure 10b) one sees that the slope of the work hardening rate of the aged sample at high flow stress does not approach parallel with that

of the solution treated sample. Indeed, the two curves appear to cross close to the point of necking. Given the arguments made above regarding the effect of σ_{ppt} this would seem inconsistent.

This observation is a likely consequence of a majority of precipitates no longer being shearable. Indeed, in our detailed work on the precipitation hardening in the absence of pre-deformation [6] it was found that a significant portion of the observed precipitates were above the estimated shearable/non-shearable transition after aging for 160 minutes at 200°C. With further over-aging of the sample, the precipitates will influence not only the yield strength but also the work hardening rate of the material, these effects not being properly accounted for in the model used here.

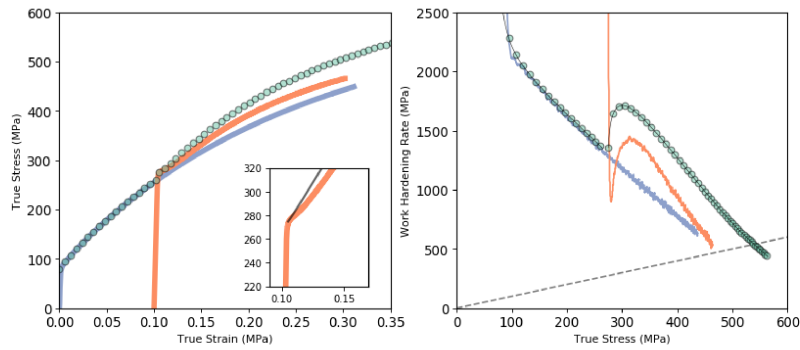


Figure 10: The a) stress-strain and b) work hardening response for a sample aged at 200°C for 420 minutes. The model results (symbols) have been obtained using the same values of ρ_f and ρ_f^* as for shorter times and a value of $\sigma_{ppt} = 85$ MPa, this being in line with the trend shown in Figure 9. It is clear, however, that the model cannot reproduce the shape of the stress strain (work hardening rate) in this case. This can be linked to the fact that the precipitates are likely non-shearable (S-phase) by this stage of aging.

3.3. Mechanisms Contributing to The Mechanical Response

The work detailed above shows that the evolution of the yield strength with aging is dominated by precipitation hardening in the case of pre-deformed samples. Recovery occurs rapidly at short times but then stagnates once significant

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9 solute segregation or precipitation on dislocations occurs. In this case, the abil-
10 ity of small Cu additions to reduce the strength loss on aging would appear to be
11 a combined effect arising both from precipitation strengthening and the cessa-
12 tion of dislocation loss via slowed recovery. The last question to examine is why
13 the precipitation hardening appears to be slower in the case of pre-deformed
14 samples.
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18 It is believed that vacancies play a vital role in determining the formation
19 of solute clusters in the early stages of aging in Al-Cu-Mg and Al-Mg-Cu al-
20 loys (see e.g. [21, 22, 23, 24]). In the as-quenched state the microstructure
21 can be described as being composed of a random solid solution with a low den-
22 sity dislocations. Quenched in excess vacancies from solution treatment will
23 allow for accelerated formation of clusters due to accelerated diffusion of solute
24 [25, 26, 27], with some vacancies becoming incorporated into the clusters/GPB
25 zones, possibly to thermodynamically stabilize small clusters [28, 29, 21]. Those
26 excess vacancies not captured within clusters/GPB zones may annihilate at
27 other defects (dislocations and/or grain boundaries) or they may cluster to
28 form dislocation loops [30]. STEM observation on solution treated and aged
29 samples revealed classical helical dislocations and small dislocations loops in
30 the alloys studied here, similar to observations made in commercial Al-Cu-Mg
31 alloys [31, 32]. The loss of these excess vacancies would be expected to i) slow
32 the formation/growth of clusters/GPB zones due to reduced diffusivity and ii)
33 lower the rate of cluster/GPB-zone nucleation. Such an explanation would ac-
34 count for the ‘rapid hardening effect’ observed for the present alloy, aged from
35 the undeformed state [6].
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40 If the solution treated material is pre-deformed (here at 77 K) then one
41 can have the further generation of deformation induced vacancies [33]. Taking
42 parameters typical of Al-Mg alloys and considering the relatively small levels
43 of pre-deformation used here, we expect only a small change in the concentra-
44 tion of vacancies due to our pre-deformation [34]. Upon aging, the presence
45 of dislocations can have a significant effect on reducing the vacancy concentra-
46 tion. Dislocations act as sinks for vacancies and the much higher density of
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9 dislocations in the pre-deformed sample compared to the as-solutionized sam-
10 ple leads to a potential competition between vacancy annihilation and vacancy
11 incorporation into clusters/GPB-zones. The recent work of Fischer *et al.* [35]
12 has shown the importance of dislocation density on the rate of vacancy an-
13 nihilation. We find, using the Fischer model parameterized for Al-Mg alloys
14 [34], that samples containing a low dislocation density ($\rho \approx 10^{10} - 10^{11} \text{ m}^{-2}$,
15 consistent with a solution treated sample) will retain a large fraction of their
16 excess vacancy concentration over aging times of minutes. In contrast, samples
17 containing $\rho \approx 10^{13} - 10^{14} \text{ m}^{-2}$ (consistent with the dislocation densities in the
18 pre-deformed samples studied here) would lose their excess vacancies within sec-
19 onds, potentially even during the process of heating to the aging temperature.
20 Thus, it is proposed here that the origins of the reduced precipitation hardening
21 for pre-deformed samples arises from the rapid loss of excess vacancies due to
22 the higher density of sinks.
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31 Finally, reflecting back on the original aim to distinguish between precipita-
32 tion hardening and recovery induced softening on the yield strength evolution
33 in these alloys, one may ask the question of whether the results presented here
34 are representative of conditions more typical to those found in the automotive
35 paint bake cycle. Here, for example, deformation was performed at 77 K so
36 as to explicitly avoid the challenges associated with dynamic strain aging at
37 room temperature. We can, however, compare the results obtained here to
38 those reported by Court and Lloyd [4] who studied very similar alloys (contain-
39 ing 3wt.%Mg and 0.2 and 0.6wt.%Cu) pre-strained in room temperature tensile
40 tests to 10% plastic strain (very similar to the pre-deformation to $\Delta\sigma = 176$
41 MPa used here). Comparing first the yield strength data from their study (Fig-
42 ure 11a) we see that the yield strength of the sample containing 0.6wt.%Cu is
43 higher than that of the sample containing 0.2wt.%Cu. This, however, is compli-
44 cated by the fact that the yield strength following pre-deformation was slightly
45 higher than the latter. When these are compared with the 0.5wt.%Cu alloy
46 studied here, we see that rather than lying between these two, the 0.5wt.%Cu
47 alloy is situated at much higher stresses. This, however, arises from the much
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9 higher flow stress obtained, despite the similar level of pre-deformation, due to
10 the much lower temperature of deformation (77 K vs. room temperature).
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12 To approximately remove this difference, the data has been re-plotted as
13 the difference between the time evolving yield stress and the yield stress of the
14 as-pre-deformed sample (before aging) in Figure 11b. This clearly collapses
15 the data more closely together. Reflecting on eqn. 1, we see that the data in
16 Figure 11b is given by,
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$$20 \quad \sigma_{ys}(t) - \sigma_{ys}(0) = \sqrt{(\sigma_{ss}^2 + \sigma_{ppt}^2)} + (\sigma_{\rho_f} - \sigma_{\rho_{f,0}}) - \sigma_{ss} \quad (5)$$

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22 In the case of all three samples, σ_{ss} is nearly the same since it is domi-
23 nated by the Mg content of the alloy. If we take the term relating to recovery,
24 $(\sigma_{\rho_f} - \sigma_{\rho_{f,0}})$ to be a constant (cf. Figure 8) then the only time evolution should
25 arise from the time evolution of σ_{ppt} . In the case of the samples from [4], we can
26 assume that amount of recovery is very similar thus, the slightly higher stress
27 for the samples containing 0.6wt.%Cu likely reflects a slightly higher level of
28 precipitation hardening. In the case of the sample containing 0.5wt.%Cu such
29 an increase is not seen but this is likely due to the fact that one cannot assume
30 the same amount of recovery. Owing to the higher flow stress (and thus disloca-
31 tion density) in the pre-deformed state one would expect a faster rate of initial
32 recovery.
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42 Despite the points made above, the three samples in Figure 11 show remark-
43 ably similar results despite quite different chemistries, loading conditions and
44 aging temperature. Indeed, the lines shown in each case use the trend line for
45 σ_{ppt} shown in Figure 9 to predict the evolution of the yield strength. Overall,
46 this points to the fact that variations in chemistry between 0.2-0.6wt.%Cu and
47 aging temperatures between 160 and 200°C will have little effect on the overall
48 rate of strengthening during the paint baking of these alloys and that this evo-
49 lution is ultimately predictable with limited experimental validation as long as
50 all of the contributions to the strength are properly accounted for.
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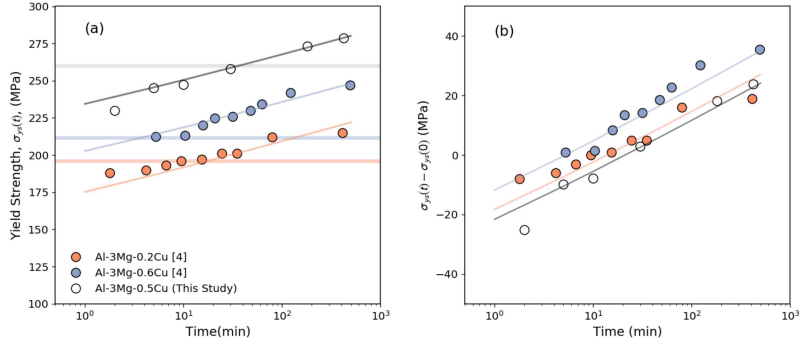


Figure 11: a) The evolution of yield strength with aging time collected by Court and Lloyd [4] for Al-3Mg-0.2Cu and Al-3Mg-0.6Cu (in wt.%) alloys pre-strained to 10% strain in tension at room temperature then aged at 180°C. Also plotted are the results obtained here for an Al-3Mg-0.5Cu alloy pre-deformed to $\Delta\sigma = 176$ MPa ($\sim 10\%$ strain) at 77 K). The horizontal lines show the yield strength of the three alloys directly after pre-deformation (without aging) b) The same data as in (a) but where the yield strength of the pre-deformed material (with no aging) has been subtracted. The solid lines use the trend line for σ_{ppt} shown in Figure 9

4. Conclusion

It has been shown that the contributions of precipitation hardening and recovery induced softening in pre-deformed Al-Mg-Cu alloys can be separated based on a careful accounting for their unique contributions to the flow stress and work hardening rate. A recently proposed model that accounts for solute-dislocation interactions has been used here to separate these two contributions showing that the evolution of the yield strength with aging is dominated by precipitation hardening. The effect of recovery induced softening saturates within the first minute of aging. The magnitude of precipitation hardening was found to be lower than that obtained in solution treated (non-pre-deformed samples), this being attributed to the loss of vacancies annihilating at dislocations. Finally, comparing the results obtained here to results reported in the literature, we see that the beneficial effects of small Cu additions are relatively insensitive to the Cu content (between 0.2 and 0.6wt.%Cu), the deformation temperature

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9 and the aging temperature. This lack of sensitivity means that one can achieve
10 improved properties without very tight composition control on the minor ele-
11 ment (Cu) making these a good starting point for the development of 'recycling
12 friendly' alloys. Studies broadening this work to investigate a wider range of
13 compositions and other important characteristics (e.g. corrosion resistance [3])
14 should be undertaken to better understand the limits of composition flexibility.
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