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Abstract

The aging response of two Al-3Mg alloys with Cu addition <1 wt% has been tracked under simulated automotive paint bake conditions (∼ 20 min, 160 and 200°C) to quantify the processes controlling hardening. The decomposition of the solid solution, observed by atom probe tomography, has been interpreted using a novel pair correlation function approach and incorporated into a model for prediction of precipitation hardening. It is shown that the hardening is controlled by clusters/Guinier-Preston-Bagaryatsky (GPB) zones similarly to what has been previously observed in much higher Cu containing 2XXX-series alloys. Interestingly, it is shown that very small additions of Cu (< 0.1at%) can be used to catalyze a high number density of strengthening particles owing to the high enrichment in Mg compared to particles found in more conventional high Cu/low Mg alloys. This allows hardening during the first hour of aging that is as high as that obtainable in these high Cu alloys.

Keywords: Precipitation, aluminum alloys, yield strength, atom probe

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1. Introduction

There is evidence that additions of less than 0.5at%Cu to 5XXX-series aluminum alloys can counterbalance the softening experienced by stamped then 'paint baked' ($\sim$ 150-200°C for $\sim$ 20 min) automotive aluminum components [1, 2, 3]. Being able to retain the as-stamped strength in this way facilitates both reduced material usage and adoption of lower grade Cu-residual scrap in primary alloy production [4]. Finding the minimum Cu content to achieve this is essential to ensure that the weldability and work hardening capacity of the 5XXX alloy can be preserved.

Knowing how to choose the correct minimum level of Cu in this case requires an understanding of the microstructural changes and correlated mechanical response. To date, few studies of this kind have been performed for the low ($\lesssim$ 1wt.%) Cu Al-Mg alloys [3, 5, 6, 7, 8]. In contrast, many studies have been published on the related high ($\gtrsim$ 1 wt.%) Cu and low ($\lesssim$ 2 wt.%) Mg 2XXX series Al-Cu-Mg alloys [9, 10, 11, 12, 13, 14]. These precipitation hardenable alloys undergo a complex precipitation sequence,, from random solid solution to solute clusters, GPB zones, S" phase and finally S'/S phase(s) (see e.g. [15].

Both 2XXX-series alloys [16, 17] and Cu modified 5XXX-series alloys [7] exhibit a rapid increase in yield strength in the first few seconds of aging at temperatures between 150 and 200°C. In 2XXX-series alloys this has been linked to the formation of solute clusters and GPB zones [16, 17]. No similar experimental link has been made between precipitate phases and yield strength in the case of the low Cu/high Mg alloys [18, 7]

One of the challenges in both alloy classes is our poor understanding of the structure, composition and density of solute clusters/GPB zones existing at short aging times. While the structural model proposed by Kovarik et al. [19] was shown to be consistent with some of the experimentally observed characteristics of clusters/GPB zones [18, 20], it does not predict the composition of solute clusters/GPB zones measured by atom probe tomography in model [16], or commercial Al-Cu-Mg alloys [15]. Moreover, much of the available experi-

mental work on the structure and chemistry of these phases focuses on results obtained after long aging times (several hours) where characterization is notably easier [5, 19, 18, 20]. The relevance of such long term aging observations to the specific microstructure-hardening response in the paint bake cycle remains uncertain.

The aim of this work is to correlate precipitation to yield strength in Cu-modified Al-3Mg alloys at times and temperatures relevant to the industrial automotive paint bake cycle, emphasizing the effect of additions of < 0.5 at%Cu on the yield strength evolution. The evolution of the tensile mechanical properties and electrical resistivity are followed during aging at 160°C and 200°C for times of up to 7 hrs. To overcome the challenges of characterizing precipitates with low atomic number contrast (this limiting techniques such as STEM and SAXS), atom probe tomography has been used for characterization. A parameter free pair-correlation based technique has been used to identify the presence of clusters/particles and a model used to interpret their size and composition. These results are subsequently fed to a precipitation hardening model to predict the experimentally measured hardening response.

2. Materials and Experimental Method

Two laboratory cast and hot rolled 5 mm sheets were 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 were then artificially aged in an oil bath at 160°C or 200°C for up to 7 hrs. All uniaxial tensile tests were performed at 77 K, with an initial nominal strain rate of 10^{-3} s^{-1}. These conditions were selected so as to avoid the complicating effects of dynamic strain aging [21]. Resistivity measurements were also performed in a liquid nitrogen bath at 77K using a four-point probe with an applied current of approximately 20 mA and a reversion frequency of 30 Hz [22].

		Mg	Cu	Fe	Si	Ti	Ni	Mn	Zn	Cr
0.23 at.%Cu Alloy	(at.%)	3.23	0.229	0.048	0.048	0.008	0.003	0.0005	0.00008	0.0005
	(wt.%)	2.90	0.54	0.1	0.05	0.015	0.007	0.001	0.002	0.001
0.12 at.%Cu Alloy	(at.%)	3.20	0.115	0.046	0.046	0.007	0.003	0.0005	0.0012	0.0005
	(wt.%)	2.96	0.28	0.1	0.05	0.014	0.007	0.001	0.003	0.001

Table 1: Composition obtained by OES of alloys studied. Balance is aluminum.

Specimens for APT were prepared by solution treating and artificially aging sheet material, following the procedure described above. Samples were cut following aging and turned into needle-shaped specimens using a conventional 2-stage electrochemical polishing technique employing perchloric acid [23]. Atom probe data was acquired on a Cameca LEAP 5000 XS at a base temperature of 50K, in high-voltage pulsing mode, with 20% pulse fraction, with the DC voltage adjusted to maintain a detection rate of 1 ion per 100 pulses. Data reconstruction was performed in the commercial software package IVAS 3.6.14, and using the calibration methods outlined in ref. [24, 25]. Precipitates were visualized by means of isocomposition surfaces [26] and composition of individual object by composition profiles derived from the regions-of-interest.

3. Experimental Characterization of Aging Response

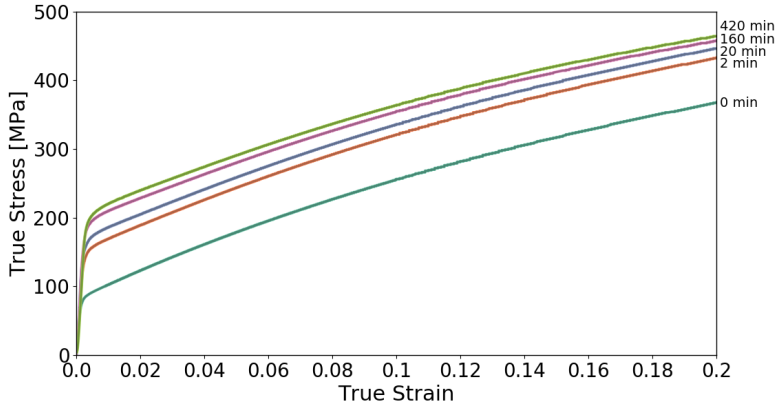
The tensile response of the 0.23at%Cu alloy aged at 200°C (Figure 1) shows that its yield strength rises rapidly from 87 MPa to 150 MPa within the first 2 minutes. This is followed by a gradual but continuous increase of the yield strength over the following 18 hours (1100 min). Aside from the evolution of the yield strength, no other changes in the stress-strain response were noted. The lack of change in work hardening rate (Figure 1(b)) is particularly notable as it suggests that the hardening phase(s) are predominantly small and shearable (see e.g. [21]). The second factor that might be expected to effect the work hardening rate (via dynamic recovery [27]) is the change of solute in solid solution. As will be shown shortly, the amount of solute removed from solid solution during aging is too small to have a noticable effect on the work hardening rate

(cf. Tables 2 and 3). This result mirrors the behaviour observed for all other aging conditions tested.

Figure 2 presents the 0.2% offset yield strength evolution for the two alloys aged at 200°C and the 0.23at.%Cu alloy aged at 160°C. Interestingly, the yield strength is seen to evolve at a similar rate for all conditions beyond the first 2 minutes of aging. This matches the linear evolution of yield strength with logarithmic time reported by Court and Lloyd [1] on similar alloys tested at room temperature after aging. Moreover, the similarity of the aging response of the 0.23at.%Cu alloy at 160 and 200°C agrees with the results presented for similar alloys by Ratchev *et al.* [2]. Comparing the behaviour of the 0.12 and 0.23wt%Cu alloys, it is impressive that alloy containing ∼50% less Cu is able to provide 75% of the strength of the 0.23at.%Cu alloy.

Electrical resistivity has been widely used as a mean-field characterization technique in cluster and precipitation hardening aluminum alloys [28, 29, 30]. Changes in resistivity reflect both the loss of solute from solid solution and, in the case of sufficiently fine clusters/precipitates, an increase in scattering arising from phase interfaces. While disentangling the effects of solid solution and interfaces in these alloys can be challenging [31], the method gives an independent measurement for comparison against the tensile data and more local microstructural information obtained from APT or (S)TEM.

Figure 3 shows the change in electrical resistivity for those samples whose yield strength is shown in Figure 2. The higher as-quenched resistivity for the 0.23at.%Cu alloy compared to the 0.12at.%Cu alloy reflects the higher overall solute content. Consistent with the 'rapid hardening' behaviour illustrated in Figure 2, the resistivity also increases rapidly within the first 2 minutes of aging, the magnitude of the jump being much larger in the case of the 0.23at.%Cu alloy compared to the 0.12at.%Cu alloy. This rapid increase is consistent with the formation of small solute clusters that contribute significantly to conduction electron scattering (cf. results on 2XXX-series alloys [32, 33]). Following the rapid initial resistivity jump, both alloys exhibit a long period (> 100 min) of nearly constant resistivity followed by a slow decrease for the 200°C samples.



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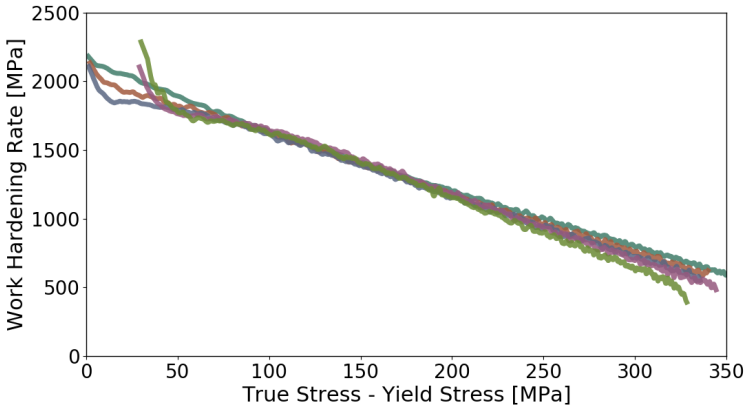


(b)

Figure 1: a) The tensile true stress- true strain response for the alloy containing 0.23at.%Cu in the solid solution state (0 min of aging), after 2 min, 20 min, 160 min and 420 min aging at 200°C. b) The same data as in (a) but plotted as a Kocks-Mecking plot showing the collapse of the work hardening rates when the yield strength is subtracted from the flow stress.

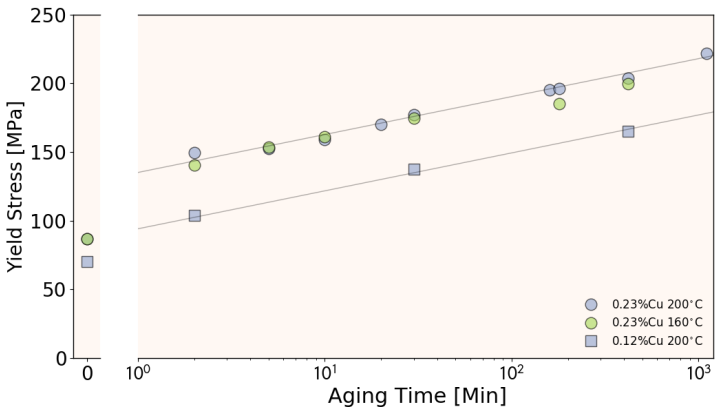


Figure 2: The evolution of the 0.2% offset yield strength for the 0.23at.%Cu alloy aged at 160 and 200°C and the 0.12at.%Cu alloy at 200°C for times ranging from 2 min to 1100 min. The yield strength of the solution treated sample is shown on the far left side of the plot. Lines are drawn as a guide to the eye.

It is notable that the resistivity evolution of the 0.23at.%Cu alloy aged at 160 and 200°C are nearly identical. This observation matches the nearly identical yield strength response shown in Figure 2.

To investigate the microscopic origin of the observed changes in yield strength and resistivity, atom probe tomography was performed on samples taken from the 0.23at. %Cu alloy after aging at 200°C for 20 min (typical paint bake time) and 160 min of aging (end of the resistivity plateau in Figure 3). Ideally, one would like to compliment such local observations with other cluster/GPB zone sensitive techniques such as HR-TEM, STEM and/or SAXS/SANS to provide better statistics to these observations. As pointed out earlier, however, the lack of atomic number contrast in these alloys drastically limits the options for complimentary techniques. This has, in our opinion, been the major stumbling block for previous studies on the early stages of aging in this alloy system. Figure 4(a) shows an APT volume measured on a sample aged for 20 min. Within this volume iso-surfaces reveal a distribution of small Mg and Cu enriched particles. The one-dimensional composition plots for the selected particles reveal the

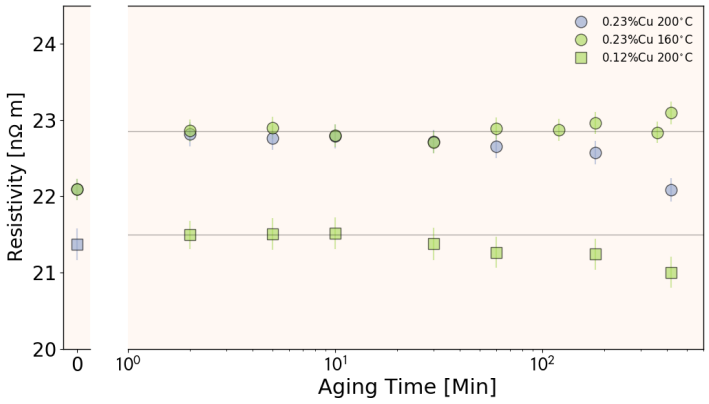
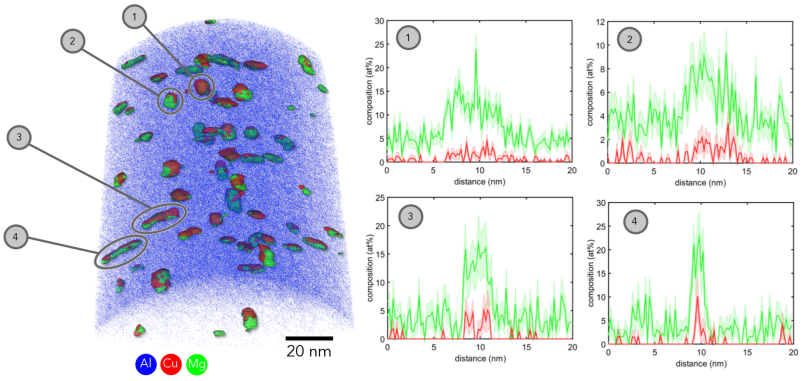


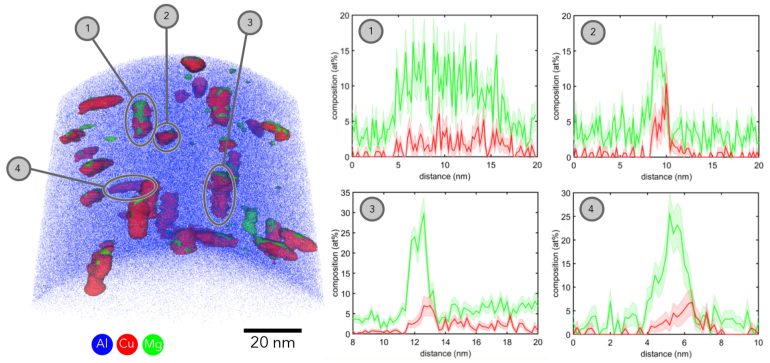
Figure 3: The time evolution of electrical resistivity for the 0.23at%Cu alloy at 200°C and 160°C and the 0.12at.%Cu alloy aged at 200°C for the same aging times used to produce Figure 2. The resistivity of the solution treated samples is shown on the far left. Error, shown as the bars on each data point, was calculated based on the uncertainty in measured resistance and area. The lines are shown as a guide to the eye.

particles to contain approximately 80-90at.%Al, 10-15at.%Mg and 1-5at.%Cu. Further aging to 160 min (Figure 4(b)) led to only minor changes in the composition and sizes of the particles based on iso-surface and one-dimensional composition plots. In both cases, the compositions were found to be similar to, but distinct from, those previously reported for clusters/GPB zones in an AA2024 alloy (4.3 wt%Cu, 1.3wt%Mg) [15].

Relying on conventional cluster finding algorithms has drawbacks owing to the underlying assumptions that one must make [34]. Cluster-finding methods are usually prone to parameter-selection biases [35] in particular for cases where multiple morphologies of features are present [36]. As an alternative method, a pair correlation based approach has been adopted here to interpret the results in Figure 4. This radial distribution function based method for extracting information on clusters and precipitates [37], and its direct relationship to the formalism conventionally used in small angle scattering, has been established [38, 39] and used recently for studying clustering in aluminum alloys by Ivanov



(a)



(b)

Figure 4: Atom probe volumes measured on samples aged for a) 20 min and b) 160 min at 200°C. In each case, iso-surfaces corresponding to a) 3.13 atoms/nm^3 Mg and 0.5 atoms/nm^3, and b) 3.5 atoms/nm^3 Mg 1.0 atoms/nm^3 Cu are plotted to reveal the presence of small Mg and Cu rich particles. One dimensional composition plots are provided along two perpendicular directions, the results being representative of the observations made in the other particles.

et al. [40]. The pair correlation approach used here has the advantage of providing a self-consistent, parameter free description of the solute distribution within the dataset. This can then be interpreted to obtain information on particle size and composition when combined with a suitable model.

We use a modified definition of the pair correlation function (PCF) compared to the one introduced in [41]. The form used here allows the PCF to be expressed in an equivalent way to the form used in small angle scattering in the case of an isotropic two-phase system where the composition is uniform within the two phases [42, 43, 38, 40]. We define a pair correlation function as,

$$\gamma_{i-j}(r) = c_0^i c_{i-j}(r) - c_0^i c_0^j \tag{1}$$

where c_0^j is the average concentration of species j in the alloy and $c_{i-j}(r)$ is the concentration of species j at a distance r from an atom of species i averaged over all atoms of species i. $\gamma_{i-j}(r)$ is the correlation between the concentration fluctuations in element i and element j, i.e. $\left\langle \Delta c^i \Delta c^j \right\rangle$. Equation 1 can be written in terms of two contributions,

$$\gamma_{i-j}(r) = \gamma_{ij}(0)\,\gamma_0(r) \tag{2}$$

The function $\gamma_0(r)$ is a normalized correlation function, such that $\gamma_0(0) = 1$ and $\gamma_0(r \to \infty) = 0$. The meaning of $\gamma_0(r)$ is particularly intuitive in the case of a single object in a (infinitely) large homogeneous volume. In this case $\gamma_0(r)$ is the normalized autocorrelation; it is the intersection volume of the object and its 'ghost' displaced by a distance r normalized by the object volume. For simple shapes, this function can be determined analytically. For example, for spherical particles of radius R, $\gamma_0(r)$ is [44],

$$\gamma_0^{sphere}(r) = \begin{cases} 1 - \frac{3r}{4R} + \frac{r^3}{16R^3}\,(r \leq 2R) \\ 0\,(r > 2R) \end{cases} \tag{3}$$

In the case of randomly distributed precipitates whose radii are distributed

(e.g. following a log-normal distribution) a volume weighted numerical integration of Equation 3 can be performed to obtain $\gamma_0(r)$.

It is important to note that $\gamma_0(r)$ is a unique function of the size and geometry of the second phase. The effect of matrix/particle composition enters entirely through $\gamma_{i-j}(0)$ which is a measure of the compositional contrast between the phases. In the case of the correlation between atoms of the same type,

$$\gamma_{i-i}(0) = f_v(1-f_v)\left(c_p^i - c_m^i\right)^2 \tag{4}$$

while in the case of the correlation between two different types of atoms we obtain,

$$\gamma_{i-j}(0) = f_v(1-f_v)\left(c_p^i - c_m^i\right)\left(c_p^j - c_m^j\right) \tag{5}$$

In the above equations, c_p and c_m refer to the particle and matrix compositions, c_0 to the average compositions and f_v to the volume fraction of particles. It is important to note that for a pseudo-binary situation, i.e. if only one type of objects are present, the 3 PCFs $\gamma_{i-i}(r), \gamma_{j-j}(r)$ and $\gamma_{i-j}(r)$ should all be proportional, the factor of proportionality being related to the fraction of objects and the composition contrast. Moreover, based on the definitions given above,

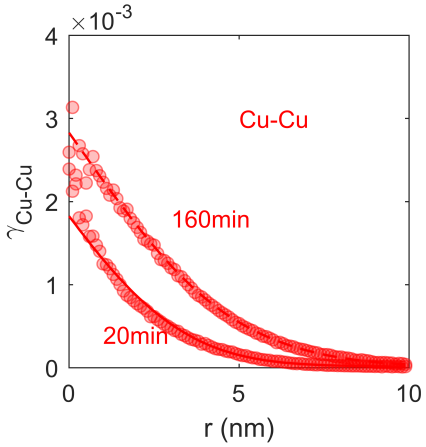
$$\gamma_{i-j}(0) = \sqrt{\gamma_{i-i}(0)\,\gamma_{j-j}(0)} \tag{6}$$

In the present case, we have calculated the Mg-Mg, Cu-Cu and Mg-Cu pair correlations (Figure 5) from the APT data shown in Figure 4. If the particles observed in Figure 4 belonged to a single population with a uniform composition, then all three pair correlation functions should be proportional to one another. Careful observation of the Mg-Mg and Cu-Cu pair correlations shows that this can't be true as the correlation length for the Cu-Cu pair correlations is noticeably longer than that for the Mg-Mg pair correlations.

The results in Figure 5 can be interpreted in terms of particle/matrix compositions and particle sizes if a model for the phases is proposed. Here, it has been assumed that the particles in the APT volumes are spherical, the radii of the particles following a log-normal size distribution. Analysis of the iso-contour data in Figure 5 suggests that the aspect ratio of the particles increases on aging from ∼1 at 20 min to close to 2 at 160 min of aging. We have, nevertheless, retained the assumption of spherical particles so as to keep the number of fitting parameters as small as possible. Moreover, the effect of this approximation on the prediction of yield strength based on particle size presented below, is expected to be nearly insensitive to this assumption for such small aspect ratios [45].

To account for the fact that the pair correlations in Figure 5 do not scale with one another, we have considered that two populations of particles exist, one being richer in Cu with a larger correlation length compared to the other. From fitting $\gamma_{Mg-Mg}(0)$, $\gamma_{Cu-Cu}(0)$ and $\gamma_{Cu-Mg}(0)$ one would like to be able to independently obtain the particle compositions and volume fractions (for the assumed two particle types) as well as the matrix composition. In order to do this one extra piece of information needs to be supplied. In the present case we have assumed that the particles contained 80 at% Al based on the profiles in Figure 4.

Under the above assumptions it was possible to obtain two size distributions and particle compositions from the APT volumes (Figure 6). The resulting fits to the pair correlations are shown as solid, coloured, lines superimposed on the experimentally determined pair correlations (symbols) in Figure 5. The values obtained from the fit are also given in Table 2. Consistent with the composition profiles shown in Figure 4, the particles are seen to be systematically richer in Mg than Cu, with the Cu:Mg ratio being highest in the largest precipitates. With increased aging time, both distributions are seen to shift to larger particle sizes, again qualitatively consistent with the results from the isocomposition plots (Figure 4). Interestingly, the volume fractions of the two populations are observed to remain constant, suggesting a process of coarsening rather than



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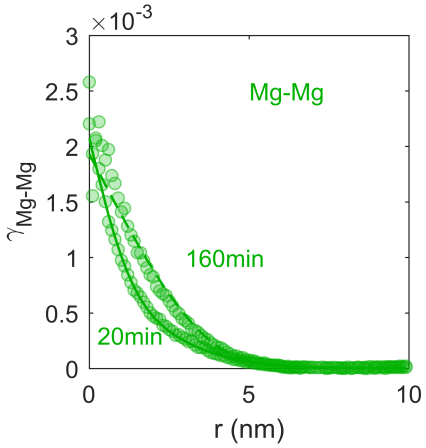

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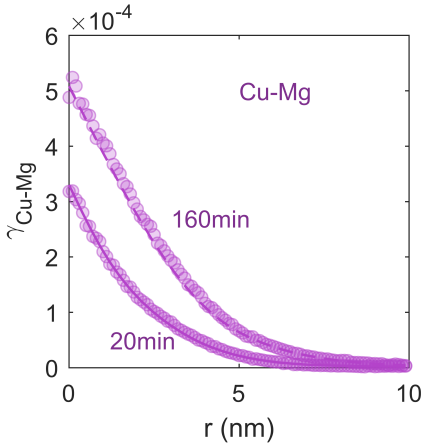

(c)

Figure 5: Experimental (symbols) and fit (coloured lines) pair correlation functions for a) Cu-Cu pairs, b) Mg-Mg pairs and c) Mg-Cu pairs from the APT datasets shown in Figure 4. If all particles belonged to the same population having a uniform composition, then the three figures should simply scale with one another.

growth. This interpretation would also be consistent with our resistivity results (Figure 3) when interpreted using resistivity models [46, 47] that predict cluster contributions to the resistivity proportional to volume fraction, and provide also an explanation for the resistivity decrease at long aging times observed at 200°C, likely due to the coarsening of the particle distribution.

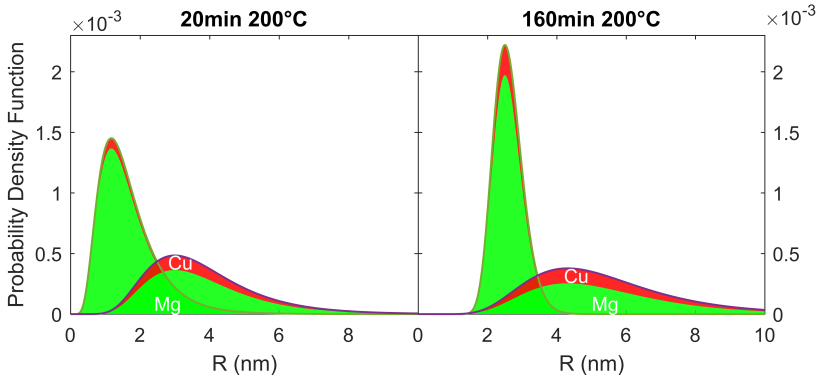

Figure 6: The best fit log-normal size distributions corresponding to the pair correlations shown in Figure 5. Left: aging for 20 min at 200°C. Right: aging for 160 min at 200°C. The green and red areas account for the respective amounts of Cu and Mg in the particles. The results are given as a volume weighted distribution, or $\frac{\mathrm{d}f_v}{\mathrm{d}R}$.

Aging Time	Particle	$\langle R \rangle$	S	f_v	N_v	Al (at%)	Cu (at%)	Mg (at%)
20 min	Cu Lean Particles	0.73 nm	0.48	0.23%	4.9×10^{23} m^{-3}	80	1	19
	Cu Rich Particles	2.2 nm	0.4	0.16%	1.8×10^{22} m^{-3}	80	5	15
160 min	Cu Lean Particles	2.4 nm	0.16	0.23%	3.6×10^{22} m^{-3}	80	2	18
	Cu Rich Particles	3.2 nm	0.4	0.17%	6.3×10^{21} m^{-3}	80	7	13

Table 2: The mean particle size ($\langle R \rangle$) and standard deviation (S) of assumed log-normal particle size distribution, volume fraction (f_v), number density and composition of particles obtained by fitting to the data in Figure 5 assuming two log-normal particle size distributions in each aging condition. The Al content was fixed at 80 at% based on the composition profiles extracted in Figure 4.

4. Predicting Yield Strength Evolution from Microstructural Observations

If the features seen in APT (Figures 4) are responsible for the evolution in yield strength reported in Figure 2 it should be possible to use the data from Figure 6 to predict the evolution of yield strength with time. Calculating the strength of such a distribution of precipitates must be done carefully as the way in which one chooses to calculate the average strength of such an assembly can have a strong influence on the prediction [21, 48]. Here, for simplicity, We take a slightly modified approach to the one originally proposed by Deschamps *et al.* [49] where the average strength of a distribution of obstacles is calculated as the average of the individual obstacle strengths [21]. It has been shown, by comparing to the results of areal glide simulations, that this approach provides a lower limit estimate to the strength of a distribution of obstacles, the predictions being better for narrower and weaker obstacle populations [48].

We start by assuming that the strength of an individual particle is proportional to the radius of the circle (r) formed by the intersection of the spherical particle and the glide plane [50]. The distribution of circle radii ($f(r)$) formed by cutting the spherical particles (having a distribution of radii $g(R)$, where R is the sphere radius) can be calculated from Wicksell's fundamental integral equation [50, 51],

$$f(r) = \frac{r}{\bar{R}} \int_0^\infty \frac{g(R)\, dR}{\sqrt{R^2 - r^2}} \tag{7}$$

where $\bar{R}$ is the mean value of the sphere radii.

The contribution of the precipitates to the macroscopic yield stress is defined as,

$$\sigma_{ppt} = M \frac{Gb}{\bar{L}_s} \bar{\tau}^* \tag{8}$$

where M is the Taylor factor, G is the shear modulus of aluminum and b is the magnitude of the Burgers vector. The average square spacing of precipitates in

the glide plane, $\bar{L}_s$, is taken following Ardell [52] as,

$$\bar{L}_s = \left(\frac{2\pi}{3f}\right)^{1/2} \bar{R} \tag{9}$$

The normalized average strength of the ensemble of particles, $\bar{\tau^*}$ is calculated as,

$$\bar{\tau^*} = \int_0^\infty \tau\left(r\right)^* f\left(r\right) dr \tag{10}$$

In this expression, $\bar{\tau^*}$ is the strength of a randomly distributed population of particles whose size in the glide plane is r. In the approach originally proposed by [49] the strength of obstacles was assumed to obey Friedel's law, this only being strictly valid in the limit of weak obstacles. This approach was generalized by [21] to include obstacles of all strengths by using the classic result of Foreman and Makin [53] Here, we take the same approach, but use an updated relationship between obstacle strength and particle size arising from computer simulations [54],

$$\tau\left(r\right)^* = \begin{cases} 0.9\left(\frac{r}{r_c}\right)^{3/2}\left(1-\frac{1}{6}\left(\frac{r}{r_c}\right)^5\right) & \text{if } r < r_c \\ 0.75 \text{ if } r \geq r_c \end{cases} \tag{11}$$

The parameter r_c in this expression is the critical size at which the particles transition from being shearable to non-shearable. It was noted, in relation to Figure 1, that the lack of change in work hardening indicates the presence of shearable particles. When considering a distribution of particle sizes one must, however, consider the possibility of sizes that span a range of sizes from below to above r_c.

The presence of two particle distributions (one lower in Cu, the other higher in Cu) leads to a question of whether one should use different r_c for each distribution. It has been argued, though not proved definitively, that precipitation/cluster hardening in Al-Cu-Mg alloys is sensitive to the composition of the phases present [16]. Here, we have chosen to fix a single value of r_c so as to minimize the number of adjustable parameters. Even with a single value of r_c,

the two particle distributions (Figure 6) lead to two values of σ_{ppt} according to Equation 8. Considering that the strengths and densities of these two particle distributions will be similar, the most appropriate method for their addition is by (see e.g. [55]).

$$\sigma_{ppt} = \sqrt{\sigma_{ppt,1}^2 + \sigma_{ppt,2}^2} \tag{12}$$

Finally, in order to calculate the total yield strength, we also have to factor in the solid solution contribution. From the particle compositions and volume fractions, we can calculate the remaining Cu and Mg in solid solution based on the bulk composition of the alloy. As in the case of the precipitate contribution to the yield strength, the net contribution from the two solid solution alloys is expected to follow [55, 48].

$$\begin{aligned} \sigma_{ss} &= \sqrt{\sigma_{ss-Cu}^2 + \sigma_{ss-Mg}^2} \\ &= \sqrt{\left(k_{Cu} X_{Cu}^{2/3}\right)^2 + \left(k_{Mg} X_{Mg}^{2/3}\right)^2} \end{aligned} \tag{13}$$

where the solid solution hardening coefficients, k_{Cu} = 81.8 MPa/at.%$^{2/3}$ and k_{Mg} =27MPa/at.%$^{2/3}$ are taken from [56].

Table 3 provides the various contributions from precipitates and solid solution to the overall yield strength. The relative average precipitate strength is also reported where $\beta = F_m/2\Gamma$ where Γ is the dislocation line tension and β = 1 corresponds to the Orowan strength ($r = r_c$). To compute the total yield strength, the precipitate and solid solution contributions are summed as in Equation 13 and 12 owing to their similar magnitudes. Finally, a constant term, σ_0 , has been added to account for the effect of grain size,

$$\sigma_{ys} = \sigma_0 + \sqrt{\sigma_{ss}^2 + \sigma_{ppt}^2} \tag{14}$$

The value of σ_0 was obtained directly by measuring the yield strength of a fully solution treated sample and subtracting the solid solution contribution calculated from Equation 13.

Using the above methodology with the particle size distributions from Figure 6 there remains only one unknown parameter(r_c) needed to calculate the yield stress. In order to fit the yield strength measured after 20 min of aging at 200°C (170 MPa), a value of $r_c = 3.95$ nm needs to be used. This is very close to the equivalent value ($r_c = 5$ nm) used by Deschamps *et al.* to describe the precipitation hardening response of an Al-1.1at%Cu-1.7at%Mg alloy [17].

Aging Time at 200°C	σ_0 **(MPa)**	σ_{ss-Cu} **(MPa)**	σ_{ss-Mg} **(MPa)**	r_c **(nm)**	σ_{ppt} **(MPa) (Cu Rich)**	β **(Cu Rich)**	σ_{ppt} **(MPa) (Cu Lean)**	β **(Cu Lean)**	σ_{ys} **(MPa) Predicted**	σ_{ys} **(MPa) Experimental**
20 min	20	30	58	3.95	104	0.5	87	0.2	170	170
160 min	20	29	58	3.95	106	0.7	124	0.5	195	196

Table 3: Parameters used/calculated in predicting the yield strength of the alloy after aging for 20 min and 160 min at 200°C. The relative strengths of the particles ($\beta = F_m/2\Gamma$) are also reported

Having established a value for r_c one can test the method's ability to predict the yield stress after aging of 160 min, the results being shown in Table 3. One can see that our predicted value of the yield stress (195 MPa) is nearly identical to that measured experimentally (196 MPa). It is important to note that this good prediction would not have been possible if, in Equation 8 we would have used the mean radii of the distributions to calculate $\bar{\tau}^*$ [21]. Indeed, fitting the yield stress after 20 min of aging would require $r_c = 3.8$ nm leading to a predicted yield stress of 211 MPa in contrast to the experimental value of 196 MPa.

As noted in the introduction, the qualitative similarity of the hardening response of the low Cu alloys studied here and more conventional 2XXX series alloys has been interpreted as evidence of similar microstructural evolution on aging. Comparison of the observations presented here to those from more conventional Al-Cu-Mg alloys [16, 15] suggests similarities *and* differences. In the APT observations reported in [16] and [15], following aging similar to that used here, the dominant feature of the microstructure was reported as solute clusters. Such clusters were described as roughly spherical solute enriched regions containing on average 24 solute atoms [15]. Upon aging up to peak strength (80 hours at 170°C) three different features were found to dominate; solute clusters

(up to 100 atoms in size, $<$ 4 nm in diameter), rod-like GPB zones ($<$ 4nm in diameter and 10-60 nm in length) and large plate like S-phase precipitates.

The features seen in Figure 4 and quantified via the pair correlation analysis in Figure 6 seem to situate somewhere between the features reported at short aging times and long aging times in the Al-Cu-Mg alloys noted above [16, 15]. The solute clusters reported in [15] after 30 min of aging at 170°C are similar in size and morphology to the average size of the Cu lean particles in Figure 6 after 20 min of aging. At the longer aging times, the size of the Cu rich particles along with the tendency for more rod-like morphologies suggests a transition towards more GPB like particles, according to their definition in [16].

A significant difference between the clusters/GPB zones reported in [15] and the particles observed here are the particle chemistries. While the cluster/GPB zones in [15] were found to have Mg:Cu ratios on the order of 1.1-1.3, here the Mg:Cu ratio was found to range from as high as 16 (in the Cu lean particles at 20 min of aging) to as low as 2 (in the Cu rich particles after 160 min of aging). What is consistent with regard to chemistry across both studies, however, is that in all cases the particles are predominantly made up of Al; $\sim$ 80 at% in this study and between $\sim$ 85 and $\sim$ 90at% in [15]. The enrichment in Mg found here may not be entirely surprising considering the much higher bulk Mg:Cu ratio (14:1) for the alloy studied here compared to 0.97:1 in the alloy studied in [15]. This enrichment, combined with the high Al content of the particles, is a significant factor in the relatively high number density of particles ($N_v \approx 10^{23}$ m^{-3}) despite the low Cu levels employed. It is interesting to note that the behaviour seen here where small amounts of Cu can catalyze precipitation in Al-Mg alloys qualitatively mirrors the behaviour seen in Al-Cu alloys where rapid hardening is only observed when small additions of Mg are made to the alloy [16]. Indeed, the precipitation strengthening observed here is quite comparable to that reported in more conventional Al-Cu-Mg alloys despite a lower number density of particles. For example, an Al-2.5wt%Cu-1.5wt%Mg alloy has been reported to harden by $\Delta\sigma \approx 80$ MPa after 100-200 min of aging at 200°C [17]. In the case of the 0.23at%Cu alloy studied here, $\Delta\sigma = 108$ MPa evaluated after

160 min of aging at the same temperature. The strengthening potential of these clusters/GPB zones may relate to a point made in relation to strengthening in Al-Cu-Mg alloys [16] where it was argued that particles richer in Mg seemed to be more effective at hardening compared to those rich in Cu.

The ability of even very small Cu additions to efficiently catalyze the formation of a relatively high number density of predominantly Al-Mg strengthening particles at short aging times is emphasized by the results obtained for the alloy containing only 0.12at%Cu (Figure 2). One can double the solutionized yield strength of both alloys studied here ($\Delta\sigma = 90$ MPa for 0.23at.%Cu and $\Delta\sigma = 67$ MPa for 0.12at.%Cu) by aging for 20 min at 200°C, this despite the fact that one alloy has half as much Cu as the other. These results support those originally reported in [1] where strengthening was achieved for alloys containing as little 0.08at%Cu. This is important given the aim of counterbalancing the $\sim$ 25% loss in strength during the paint bake cycle [1] with the minimal addition of Cu.

Finally, we point to the significant potential for further studies focused on better understanding the precipitation sequence and kinetics in these alloys. As noted above, the nearly identical aging response at 160°C and 200°C is surprising. This observation suggests that there may be competing mechanisms leading to an optimal strengthening in this temperature range. Indeed, tests performed at lower temperature (100°C, not shown here) show lower strength for the same aging time. The competition between the kinetics of excess vacancy annihilation and vacancy trapping by solute clusters may be a fruitful area for further exploration in regards to this phenomenon [REF]. The observed linear dependence of yield strength on logarithmic time also warrants further study. As noted above, this behaviour is not unique to the work reported here but has also been reported by both Court and Lloyd [1] and Ratchev *et al.* [2]. It was suggested that the lack of variation in volume fraction of clusters/GPB zones on aging at 200°C is most coherent with an interpretation of particle coarsening. Further to this point, if one were to adopt a simple model for coarsening kinetics see e.g. [57] then one would expect an aging response that was nearly linear in log time and

whose slope would be independent of aging temperature and composition. To be able to confidently confirm or deny this interpretation would require many further studies on other alloys and other aging temperatures.

5. Summary

It has been shown that additions of as little as 0.12at.%Cu to a binary Al-Mg alloy can lead to significant precipitation hardening, the observed precipitates being similar in size and chemistry to clusters/GPB zones previously reported in more conventional 2XXX-series alloys and model Al-Cu-Mg alloys. Using data extracted directly from APT measurements, the size distribution of particles could be used to predict the yield strength after aging 160 min at 200°C following calibration of the shearable/non-shearable radius from data collected after 20 min of aging. While the strengthening particles share similar size and geometry to clusters/GPB zones in higher Cu/lower Mg alloys [15], the chemistry of the particles observed here were much leaner in Cu. This observation helps explain the relatively large number density of clusters/GPB zones despite the low bulk Cu content. Given the appreciable strengthening observed in these low Cu alloys, precipitation hardening in alloys containing very low Cu contents should be able to readily compensate for recovery induced softening in the industrial paint bake cycle. The question of the effectiveness of precipitation hardening in pre-deformed alloys, however, is the subject of ongoing work.

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