

Solute Cluster and Precipitate Evolution in Early Ageing of Al-Zn-Mg

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1. Abstract

Sander and Meissner first recognized the superb age hardening properties of Al-Zn-Mg alloys in 1923. Today, through research and development, new Al-Zn-Mg(x) alloys with high tensile properties form integral aerospace and transport structures. Design of more complex alloys to produce desirable properties requires an intimate knowledge of the solute clustering and precipitate evolution in the base system. This poster presents a revealing insight into the nanostructure of Al-Zn-Mg phase transformations during very early T6 age hardening at 150°C.

According to Maloney et al (2000) at 150°C precipitation is first visible at 2 hours and bright field TEM studies at 1 and 3.5 min exhibit no features. We report that distinct clusters of solute atoms are observable at 30 seconds, and are widespread at 60 seconds. We report a nanostructure in the as quenched condition and relate it to subsequent decomposition. Cluster morphology and chemistry has been investigated, and relationships to the hardening and TEM detection explored.

2. Experimental

One scientific alloy was prepared using ingot metallurgy practice, Al-1.9Zn-1.7Mg (at.%). TEM work was performed on a Philips CM12 and atom probe tomography (APT) undertaken using an Imago LEAP™. Data was measured and scaled to reflect the d-spacing of identified poles. The core linkage algorithm developed by Stevenson et al was used for cluster analysis of APT data. The parameters used are 1st nearest neighbour, 2.76 point density, 0.6 nm d-link, 7 atoms n-min, and 0.6 nm enveloping. A 3 nm radial erosion of poles and surface was performed to maximise and maintain the highest quality data. Hardness was measured using a standard Vickers macro indenter under 5 kg. Samples were solution heat treated in a salt bath at 460 °C for 1 h, rapidly quenched into cold water, and aged at 150 °C for 30 and 60 seconds in silicone oil.

3. Results and Discussion

The early age hardening response at 150°C, corresponding transmission electron micrographs, and APT cluster maps are presented in Figure 1.

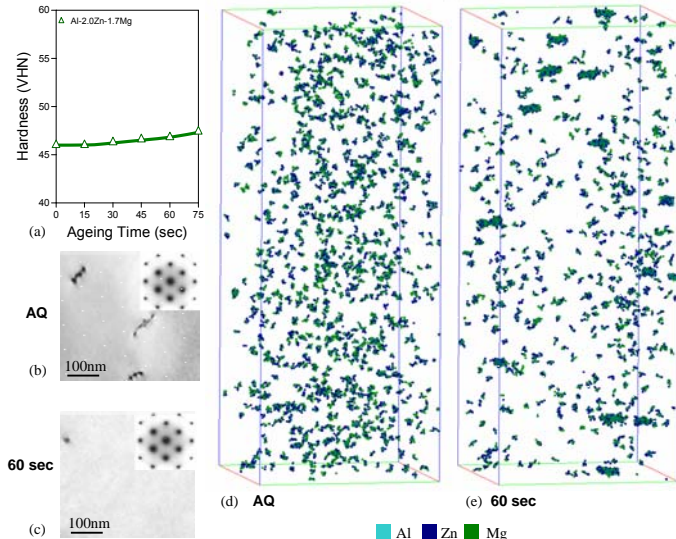


Fig. 1 (a) Age hardening at 150°C (b) Bright field micrographs at 0 sec, and (c) 60 sec recorded near <011> with SAED inset. (d) 40x40x100 nm APT cluster maps at 0 sec and (e) 60 sec

A very mild response during early ageing was observed, and we confirm the results of Maloney et al (2000) that no microstructure is discernible through conventional TEM. The APT cluster map qualitatively presents fine uniformly distributed clusters that reduce in number from the as quenched to 60 second condition. A surprising widespread occurrence of larger clusters up to 5nm across was observed at 60 seconds. This is a well studied system, the analytical research performed to date does not suggest substantial microstructural/nanostructural change at this stage, nor is it expected due to the very mild alteration of mechanical properties. The following studies attempt to characterise these observations.

Cluster morphology for each ageing time is presented in Figures 2 (a) to (c). Aspect ratio is width divided by length, and oblateness height divided by width. A spherical cluster, for example, would have values 1 and 1 on both scales. The size and colour of the data points illustrate each cluster's radius of gyration; brown to yellow, smallest to largest. Measurements of cluster radius of gyration features alongside in Figures 2 (d) to (f).

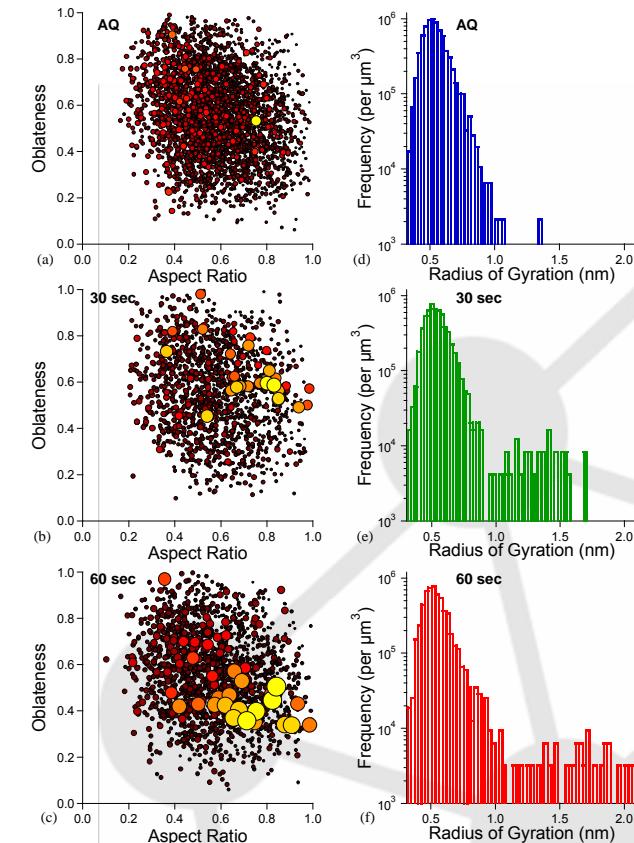


Fig. 2 (a) (b) and (c) are morphology graphs of as quenched, 30 sec, and 60sec ageing times respectively. (d) (e) and (f) are radius of gyration frequency graphs for as quenched, 30 sec and 60 sec respectively.

It may be observed from the morphology graphs that a reduction in the number of small clusters occurs from as quenched to 30s. This coincides with the growth of clusters with larger radii. Additionally, the frequency graphs describe a reduction in the number of ~0.5 nm clusters from ~1,000,000 per μm^3 , to ~800,000. Our results suggest that solute clusters evolve from random shapes of approximately 0.5 nm, to flat ellipsoidal and disc profiles up to 2.1 nm. This morphology is similar to the reported disc shape of the meta-stable η' precipitate.

Mg and Zn concentration in clusters of 0.7 nm radius and larger in the 60s condition are presented in Figure 3 (a). A ~300,000 nm^3 dataset has been used. The η' and η'' precipitates are often described in terms of solute ratios. Figure 3 (b) represents the Zn to Mg cluster chemistry as a ratio. The size and colour of the data points represent the number of atoms in each cluster. Clusters of similar sizes in the as quenched, and 30s condition, had consistent chemistries so are not presented for the purpose of clarity.

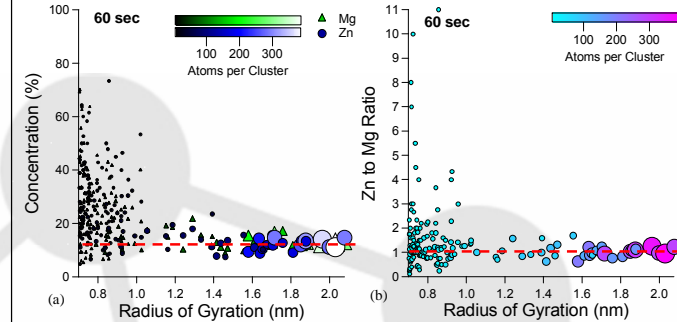


Fig. 3 (a) Graph of Mg and Zn concentration in clusters with a radius >0.7 nm (b) Ratio of Mg to Zn within the clusters. The markers on both graphs are proportional to the number of atoms.

The solute concentration of clusters smaller than 1.0 nm varies from ~4 % to ~75 %. From 1 nm onwards both solutes converge to an average concentration of ~14 %. Figure 3 (b) indicates that the ratio within the developed clusters converges to a 1 to 1 ratio; the mean ratio is 1.07 Zn to Mg. This ratio is similar to the ~1:1 reported in the literature. at 2 hours for η' . None of the well developed clusters (>1.6 nm) displayed a ratio close to 2:1 characteristic of the equilibrium η precipitate.

4. Conclusion

- A surprising rapid nanostructural decomposition led to large widespread solute clusters being observed in the 30 and 60 seconds ageing condition.
- Despite being up to 5nm across, the clusters were still not detectable in bright field and SAED CTEM. We suggest that these clusters precede any discrete phase transformations or small scale ordering that would cause contrast diffraction.
- The absence of dramatic hardening due to the wide spread clustering indicates that these clusters do not significantly impede dislocation movement and supports our previous suggestion of full coherency with the matrix. As no other structures exist, this clustering is most likely responsible for the very mild hardening response.
- It appears evident that these larger clusters evolved from a nanostructure of fine clusters. We suggest these fine clusters were 'quenched in' during the experimental process.
- The emerging clusters take on a plate to ellipsoidal morphology.
- Within clusters > 1 nm radius of gyration, the solute species have a composition ratio of ~1:1 and mean concentration of ~14%.
- The chemistry and morphology are most similar to the literature definitions of the η' meta-stable precipitate. Further investigation into proceeding ageing times may tie together the link between the embryonic development of solute clustering and precipitates.

5. Acknowledgements

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