CHARACTERISATION OF NANOPRECIPITATION MECHANISMS DURING ISOCHRONAL AGEING OF A PSEUDO BINARY AL-8.7LI AT % ALLOY

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" The addition of Lithium to Aluminium alloys is known to afford the dual advantages of increasing mechanical performance while lowering density. These characteristics make Al-Li alloys particularly desirable for aerospace applications"

Abstract

The addition of Lithium to Aluminium alloys is known to afford the dual advantages of increasing mechanical performance while lowering density. These characteristics make Al-Li alloys particularly desirable for aerospace applications. However, the complex precipitation pathways and extensive nanometre sized decomposition products, termed "nanoprecipitates", makes characterisation difficult and thus limits optimisation of the property sets of commercial alloys. This investigation uses thermal analysis and electrical resistivity methods to further understanding of the evolution of the various nanoprecipitates during isochronal ageing of an Al-8.7 at% Li alloy. The results indicate decomposition via the following pathway: Spinodal-Ordering $\rightarrow$ Congruent Ordering + Spinodal Decomposition + Dissolution of Small Spinodally ordered regions $\rightarrow$ Growth of d` $\rightarrow$ Dissolution of d` $\rightarrow$ Nucleation & Growth followed by Dissolution of d phase.

Introduction

The nature of precipitates, their composition, size distribution, locations, and the nature of there interface with the matrix strongly influences the mechanical and physical properties of advanced alloys. In many Aluminium alloys clusters, ordered domains and other forms of "nanoprecipitation" make a significant contribution to the overall property sets of alloys. The small size of these nanoprecipitates makes investigation of their decomposition pathways difficult in commercial alloys as their physical effects are often masked by the effects of conventionally sized second phase precipitation. In the Al-Li system this issue is further compounded by the low lattice misfit, relatively low volume fraction, massive precipitation of the primary strengthening phase, d`, as well as a similar composition and structure to both the matrix and to d`. These factors make characterisation of the nanoprecipitate structure and thus an investigation of the decomposition mechanisms extremely challenging.

Several authors have carried out both theoretical and experimental investigations that aim to predict the decomposition of binary Al-Li alloys. The theoretical work of Khachaturyan et al noted a number of flaws in previous models and produced what is considered to be the leading thermodynamic sub-phase model, Figure 1. High resolution transmission electron microscopy work by Mijasato et al, Radmilovic et al and Sato et al supported much of the Khachaturyan findings. Schmitz et al also imaged ordered domains using HREM but argued that this did not constitute conclusive support for the decomposition pathways proposed. Several diffraction studies by Fujikawa et al, Sato & Kamio discovered evidence which also partially supported the models. Mahadev et al, using X-ray scattering, found no evidence for the congruent ordering or spinodal pathways predicted by the models in an 11.4at.%Li alloy and suggested that d' formed by a classical nucleation and growth. Further, Williams & Eddington noted that X-ray sidebands, which are normally associated with a spinodal reaction, were lacking from the available data on Al-Li alloys. However, it has since been pointed out by Yu & Chen that sideband prediction is based on the linear, harmonic theory of Cahn & Hilliard, and as such may not always be detected as the theory is only applicable at the early stages of decomposition which is difficult to characterise due to the rapid precipitation kinetics in the system.

The importance of these alloys combined with the uncertainties in the existing literature and the difficulties in obtaining reliable data by the techniques traditionally used to investigate nanoprecipitation phenomena i.e. TEM, X-ray and neutron diffraction are the drivers for the

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present work. In this work a combined study using isochronal resistivity and differential scanning calorimetry have been used to further understanding of the evolution of the

Figure 1: Khachaturyan et al sub-phase diagram[1]

nanoprecipitate structure in an Al-8.7 at% Li alloy. These techniques have the advantage that they can characterise the products of nanoprecipitation reactions on bulk samples thus allowing meaningful sample volumes to be investigated. In addition, both techniques allow the samples to be kept below room temperature during the early stages of ageing thus allowing interrogation of the early stages of decomposition.

Experimental Methodology

A pseudo binary Al-8.7Li-(0.07Zr) alloy, was prepared by induction melting, extrusion followed by hot rolling into 1.6mm think sheets. Standard four point resistivity specimens, as shown in Figure 2, were wire cut from the sheet, solution treated (823K for 15minutes) and quenched into iced brine (254K). Further details regarding the sample preparation procedure can be obtained from Noble & Bray.

Isochronal aging for the resistivity (ICR) experiments were carried out in a high temperature oil bath with a simu-

Figure 2: Four point probe resistivity samples

lated heating rate of 20K / min (temperature control ± 2K). Resistivity measurements were recorded after placing the sample in liquid nitrogen using a Cuprico D500 high precision ohmmeter capable of measuring changes in resistivity down to the nano ohm range. Differential scanning calorimetry (DSC) samples were prepared by punching out 6mm diameter disks from the solution treated alloy sheets after which both surfaces were removed by grinding in a custom made chilled grinding block. DSC thermograms were obtained from a Perkin Elmer DSC 7 equipped with a liquid nitrogen chilled cooling block at a heating rate of 20K/min.
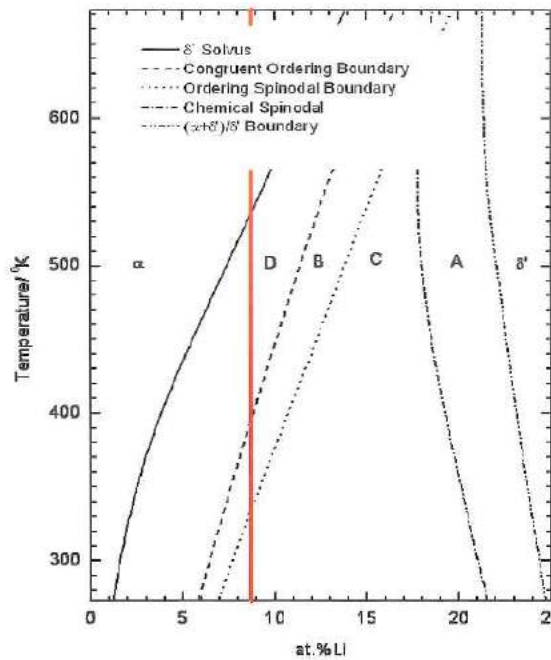
Results from Isochronal Resistivity Experiments

The high resolution 4-point resistivity measurements carried out after isochronal aging the Al-8.7Li pseudo binary alloy indicates various phase transformations occur during decomposition of the supersaturated solid solution (SSSS), Figure 3. Isochronal aging at the first two temperatures (273 & 293K), resulted in a decrease in resistivity, Figure 4. This early aging treatment (273-373K) was repeated several times on equivalent samples to confirm that it was a real observation, in each case an equivalent resistivity decrease was observed. Resistivity decreases are associated with either an increase in lattice order over length scales larger than the mean free path of the electrons or a decrease in lattice scattering associated with events such as lowering of the solute content of the matrix. As the temperature is relatively low it is unlikely that true precipitates will have had sufficient time to form and grow beyond a size which causes scattering. Thus the rapid reaction kinetics support the hypothesis that a ordering event occurs at low temperatures, such events require only local atom exchanges rather than the bulk diffusion needed to form an extensive network of large precipitates. Higher aging temperatures result in a small increase in resistivity up to a peak (380K) followed by a large decrease. At such low aging temperatures a resistivity increases during the decomposition of a SSSS are most typically associated with the formation of a large number of small scattering centres which shorten the mean free path
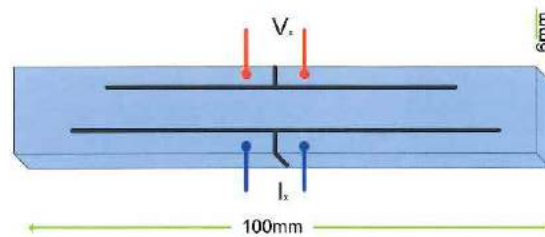
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of the conduction electrons. The subsequent decrease from the resistivity peak could either be associated with the growth of these small scattering centres beyond this size or the nucleation of new, small secondary precipitates and their rapid growth. The magnitude of the resistivity decrease is relatively large suggesting extensive removal of solute from the supersaturated lattice.

At isochronal ageing temperatures above 500K the resistivity increases indicates an increase in solute content of the matrix. Higher temperatures result in another decrease to a second valley followed by an increase to a value near the as quenched resistivity. At these relatively high temperatures this event is associated with the formation of an equilibrium phase which lowers the solute content as it forms and grows before it starts to dissolve at higher temperatures returning solute into solution and thus increasing lattice scattering. Higher temperatures resulted in a progressive decrease in resistivity which is most probably associated with the loss of lithium from the sample during high temperature aging. This together with a lower vacancy concentration compared to the as-quenched alloy are the most likely reasons why the resistivity does not return to the as- quenched value. This portion of the curve will not be considered further in this work.
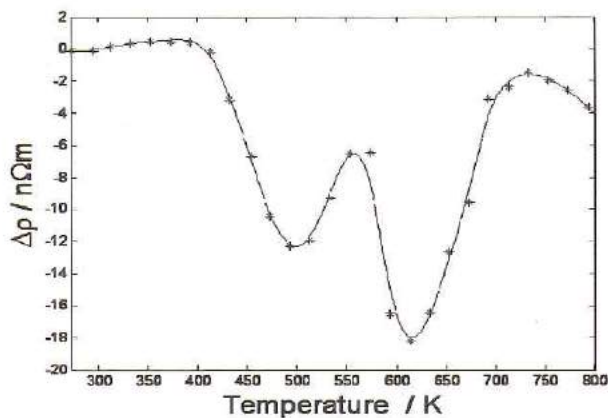

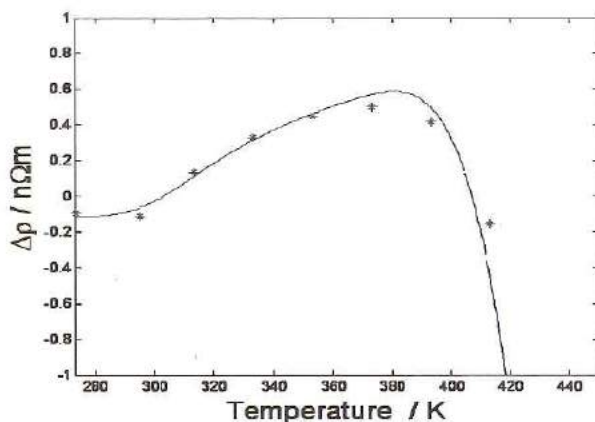Figure 3: Change in resistivity during isochronal ageing

Figure 4: Change in resistivity during the early stages of isochronal ageing

Results from Isochronal Differential Scanning Calorimetry

The thermogram from the differential scanning calorimeter, obtained at an equivalent heating cycle as the resistivity experiment and also indicates a number of phase changes occur during isochronal ageing. Within the inevitable short, near room temperature, exposure during preparation of the DSC samples, it can be expected that the first event observed in the resistivity experiment, a resistivity decrease, Figure 4, has occurred before the DSC analysis. The first observation on the DSC thermogram is a low temperature endotherm characteristic of a dissolution event. As the dissolution temperature is low it is reasonable to assume that the phase dissolving is extremely small, i.e. dissolution of a nanoprecipitate. The second event is an exotherm characteristic of the formation of a
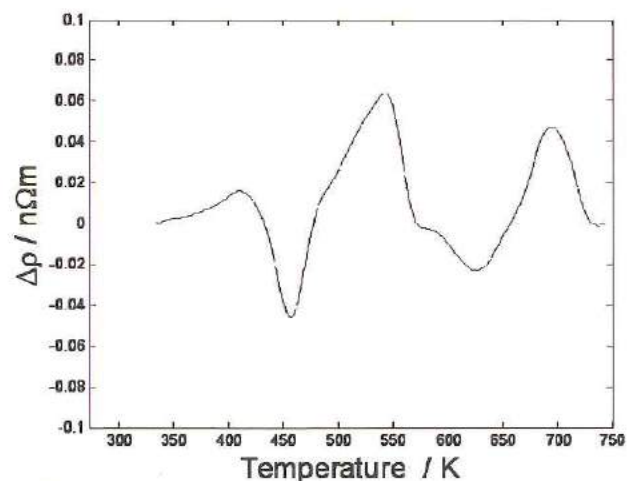

Figure 5 : Differential scanning calorimetry analysis

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true precipitate. As the scanning temperature increases, a second endotherm of a size comparable to the previous exotherm is observed. The similar size of peaks and the lack of other events suggests the formation and then dissolution of the same phase as temperature increases. At higher temperatures a second pair of exo - endotherms suggests the precipitation and dissolution of a high temperature phase.

Discussion

Noble and Bray[12] used similar solution treatment and quenching conditions to examine an Al-9.0Li-0.14Zr alloy in the as-quenched condition. They assumed the starting state of the alloy was a supersaturated solid solution with a high vacancy concentration and a partially ordered matrix containing discrete d`-nuclei. DSC analysis resulted in the detection of a small initial exotherm not detected in the thermograms discussed in this paper. Their analysis attributed this event to a continuation of the ordering process, which had begun during quenching. According to the phase diagram proposed by Khachaturyan et al this alloy would be in a thermodynamic sub-phase region expected to undergo continuous ordering of the matrix. This observation supports the association of the initial resistivity decrease observed in Figure 4 with a large scale increase in lattice order rather than a lowering of lattice solute concentration due to the formation of large precipitates. Therefore it appears that the alloy undergoes a spinodal-ordering reaction producing ordered domains throughout the entire lattice during the short room temperature exposure which occurs during DSC sample preparation and the initial ageing treatment during ICR. This spinodal-ordering explanation is supported by the high resolution transmission electron microscopy work of Radmilovic et al who in a similar alloy, (Al-2.4Li) found that ice brine quenching resulted in modulated order/disordered regions. This was taken as firm evidence for the occurrence of spinodal-ordering.

It follows that the first endotherm in Figure 5 is due to the dissolution of these spinodally ordered regions. Thermodynamically it will be the smallest of these ordered domains which dissolve first. Khachaturyan et al predicts that these domains may undergo spinodal decomposition to form true d`, an event not predicted to result in a net endothermic reaction. It is also apparent from the progressive increase in resistivity (rather than a step change) within this temperature region that this event does not occur spontaneously, thus it may be that the alloy has moved into region C of the sub-phase diagram (Figure 1) and new ordered domains are also being formed by a congruent ordering processes. The formation or formation then decomposition of congruently ordered domains could cause an increase in resistivity if there size was lower than the mean free path. However, such an event would not be expected to result in an endothermic peak in the DSC thermogram which suggests the dissolution of the spinodally ordered regions formed during the initial exposure is also occurring. The real situation is likely to be a combination of development of those pre-existing ordered regions that are sufficiently large to decompose into nanosized d` (causing scattering and a small exothermic contribution), the formation of new congruently ordered regions (causing scattering and a small exothermic event) and the dissolution of the smallest ordered regions (which will lower scattering and result in a net small endothermic event). Additional evidence for a number of convoluted processes occurring can be seen from the irregular shape of initial peak in the DSC thermogram.

As temperature of the isochronal age increases beyond ~400K, the d` grows removing solute from solution and causing the decrease in resistivity and the initial exothermic event at 550K. Dissolution of d` then occurs as the solvus temperature is approached, this results in the second DSC endotherm and the resistivity increase as solute is returned to solution. According to the phase diagram the event observed at higher temperatures results in the precipitation and dissolution of the equilibrium d-phase, this does not feature any further in the current work as commercial heat treatments are designed to avoid production of the equilibrium phase.

Conclusion

The isochronal decomposition pathways leading to the evolution of nanoprecipitation within the Al-Li binary systems are complex and not fully understood. The application of electrical resistivity and differential scanning calorimetric methods provide complimentary data to more conventional electron imaging and diffraction studies. The investigation indicates that the thermodynamic models developed agree with the physical observations; however, there are still areas of uncertainly regarding the specifics of the decomposition mechanisms and the position of the sub-phase boundaries. The results indicate that upon isochronal aging a supersaturated Al-8.7Li At % alloy undergoes a spontaneous ordering process. Uncertainty still exists on

COLLOQUIA ON COMPOSITES

Siti Haslina Bt Ramli (R), Chairman of the IMM Composites Committee, presiding at the second colloquium

The Composites Committee of the Institute of Materials, Malaysia (IMM) together with The Institute of Materials, Minerals & Mining, (IOM3) and Petronas organised two half -day talks during the first half of the year.

Dr KH Leong (L) with Dr Brett Suddell of IOM3 UK

The first talk by Dr Karen Kozielski & Dr Wendy Tian, 2 senior researchers from the Commonwealth Scientific & Industrial Research Organisation (CSIRO), Australia, was held on 6th February 2009. Karen presented "Toughening of a Carbon Fibre Reinforced Epoxy Anhydride Composite Using an Epoxy Terminated Hyperbranched Modifier" whilst Wendy elaborated on "Accelerated Ageing versus Realistic Ageing in Advanced Composite Materials Hot/Wet Ageing Effects in Low Temperature Cure Epoxy Composites".

On 9 April, 2009, another colloquium entitled "Low Environmental Impact Materials" by Dr Swee L Mak, Deputy Chief (Industry), CSIRO Materials Science and Engineering, CSIRO was held. Dr Mak spoke on how selection of materials, appropriate designs, construction practices, waste generation and service life performance of a structure can impact the environment, especially in construction worldwide. Dr Mak argued that the use of new generation of materials may increased the sustainability of concrete construction.

Dr Brett Suddell of IOM3 UK graced the occasion at this event.

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the pathway by which discrete d˘ is formed, the results indicating that it could be through the spinodal decomposition of the previously ordered regions, the formation of congruently ordered regions and there subsequent decomposition or a combination of methods. The present research suggests the following decomposition pathway: Spinodal-Ordering → Congruent Ordering + Spinodal Decomposition + Dissolution of Small Spinodally ordered regions → Growth of d˘ → Dissolution of d˘ → Nucleation & Growth followed by Dissolution of d phase.

Acknowledgments

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