# A Microstructural Engineering-Based Approach to 7xxx Series Alloy Optimisation

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Keywords: 7xxx series, strength, fracture toughness, precipitation, grain boundaries.

### Abstract

Work has been conducted on commercial 7xxx series (AI-Zn-Mg-Cu) aluminium alloys to obtain an optimum combination of strength and fracture toughness. Two compositions with different zinc to magnesium ratios were investigated, with copper and total solute content held constant. Ageing studies revealed that, for overaged T73-type conditions, lower zinc to magnesium ratio appears to provide greater strength retention for a given heat treatment practice. Preliminary results indicate that this may in turn lead to superior strength to toughness ratios. These results have been interpreted using DSC and TEM observations in order to relate microstructure to property changes.

# 1. Introduction

The desire to achieve high levels of fracture toughness and stress corrosion cracking resistance simultaneously with high strength in 7xxx series (AI-Zn-Mg-Cu) aluminium alloys has been the subject of attention over the years [1]. Such alloys are used in high integrity structural applications such as aerospace components, where careful control of both chemical composition and processing conditions is applied in order to deliver the necessary levels of performance. The development of similar alloys for use in high pressure gas cylinders has been described as being significant to the aluminium industry [2], and requires a particularly demanding combination of strength, toughness and stress corrosion cracking resistance. It has been shown that 7xxx series alloys such as AA7032 and AA7060 can provide adequate performance for high pressure gas cylinders [3, 4] and such products are increasingly being adopted as lighter weight alternatives to both conventional 6xxx series aluminium and steel cylinders. The aim of the present study is to control composition, processing and microstructure in order to maximise strength whilst maintaining adequate fracture toughness. The importance of factors such as the size and distribution of coarse intermetallic particles, quench rates, recrystallization and grain structure are well known for 7xxx series alloys and have been previously reported for the current system [5, 6]. Stress corrosion properties are to be reported at a later stage of the programme.

The strength of a 7xxx series alloy depends principally upon its compositional detail [7], since the precipitate phases promote the greatest strength contribution and these depend

upon Zn:Mg ratios and copper content. The main pattern of precipitation usually involves  $SSSSa \rightarrow GP_{zones} \rightarrow \eta' \rightarrow \eta$ .

The equilibrium precipitate  $\eta$  is generally referred to as MgZn<sub>2</sub>, although it can adopt a broad stoichiometric range and may be described as being based upon MgZn<sub>2</sub> with AlCuMg components [8]. The nomenclature  $\eta$ 1,  $\eta$ 2, and  $\eta$ 4 can also be used, depending on the specific composition and sequence of formation [9].

Duplex ageing practices are employed for 7xxx series alloys, which consist of an initial low temperature (T<sub>1</sub>) age in the range 100 – 120°C and a secondary (T<sub>2</sub>) age at 140 – 170°C [10], although higher T<sub>2</sub> temperatures have also been examined [11]. The  $\eta$ ' phase forms during the T<sub>1</sub> stage and peak strength (T6) is reached with a mixture of  $\eta$ ' and  $\eta$  following T<sub>2</sub> [12]. With overageing (T7x),  $\eta$  becomes more dominant [13]. Starink and Wang [14] have modelled the yield strength of 7xxx series aluminium alloys in the overaged condition on the basis of microstructural data. Toughness models for 7xxx series alloys are complex and include factors such as volume fraction and distribution of precipitates [15]. If grain size and external effects are ignored then strength depends upon the total alloying content (Mg + Zn + Cu) and the heat-treatment. In general, fracture toughness is at its highest in the underaged condition, passes through a minimum at peak strength then recovers again during overageing [1, 15].

### 2. Experimental

In this paper two 7xxx series alloy variants have been considered, whose compositions are listed in Table 1 and plotted on the quaternary (Al-Cu-Mg-Zn) equilibrium diagram at 460°C (figure 1, [16]). The Zn:Mg ratio was varied with copper content held constant. In both cases the total level of solute, i.e. Zn + Mg + Cu (at. %), was also kept constant in an effort to eliminate any inherent strength differences between the two alloys. Material was commercially DC-cast, stress-relieved and homogenised using a practice known to remove S-phase (CuMgAl<sub>2</sub>) from the as-cast microstructure.

Alloy ID	Mg	Zn	Cu	Cr	Fe	Zn+Mg+Cu (at. %)	Zn:Mg ratio
А	2.0	6.0	2.0	0.2	0.1	5.7	3:1
В	1.7	6.9	2.0	0.2	0.1	5.7	4.1:1

Table 1: Chemical compositions of the alloys investigated (in wt. % unless specified)



Figure 1: The quaternary system Aluminium-Copper-Magnesium-Zinc at 460°C and 6wt.% Zn. The compositions of the two alloys investigated are indicated. [16]

Both alloys were extruded at room temperature, under identical conditions, to a true strain of 1.87 (85% reduction in area). Solution treatment was performed at 475°C prior to quenching in cold water. Both alloys were then processed with typical 7xxx series duplex treatments consisting of an initial low temperature age ( $T_1$ ) at either 105 or 110°C followed by a second higher temperature ( $T_2$ ) exposure at 165 or 180°C.

Vickers hardness and tensile testing were used to monitor the ageing process, thus allowing T73-type overageing practices to be selected which would achieve target properties of 425MPa (0.2% proof stress), 500 MPa (UTS) and 12% elongation to failure. Fracture toughness was measured using a specially developed jig for curved specimens and, for certain heat treatment conditions, by pressurising cylindrical components containing pre-machined notches to failure [17]. This enabled toughness values to be calculated using a fracture mechanics-based approach. The final microstructures of both alloys were examined in a Jeol 2000fx TEM, whilst differential scanning calorimetry (DSC) was performed in a Perkin-Elmer DSC7 at a heating rate of 20°C min<sup>-1</sup> to follow the dissolution and precipitation reactions after partial treatments.

#### 3. Results

**Hardness:** Plots of hardness against time at the initial ageing temperature  $(T_1)$  for Alloys A and B are given in Figure 2a. Both alloys essentially achieve the same hardness level at the end of the initial  $T_1$  age, approximately 165 HV10, irrespective of whether aged at 105 or 110°C. Behavioural differences between the alloys were noted at the second ageing temperature  $(T_2)$ , however, which are best illustrated by tensile results.



Figure 2: (a) Vickers hardness as a function of the initial ageing time and temperature  $T_1$  for alloy A and B, (b) 0.2% proof strength as a function of secondary ageing time and temperature  $T_2$  for alloy A and B.

**Tensile properties:** Tensile tests were carried out on Alloys A and B after various times at second stage  $T_2$  treatment temperatures of 165 and 180°C. Figure 2b shows plots of the 0.2% proof stress values after these treatments. With the 180°C  $T_2$  age, both alloys reach a similar peak proof stress of around 510MPa within 2h. With Alloy A, the peak is at 2h and after 4h the proof stress is 445MPa. Alloy B, on the other hand, peaks within 1h and then overages more quickly, so that after approximately 4h the proof stress is 430MPa. Using the 165°C  $T_2$  age, both alloys reach similar peak proof stresses within 6h. However the disparity between the two alloys appears to be more exaggerated in this case, such that Alloy A reaches an overaged proof stress of 470MPa after 13.5h at 165°C whilst Alloy B has a proof stress of 445MPa after the same period. During the overageing sequence, as might be expected, more rapid kinetics were observed at 180°C than at 165°C.

However, for both temperatures investigated, Alloy A maintained a higher proof stress than Alloy B for a given overageing time. Tensile strength values of Alloy A and Alloy B were 508MPa and 492MPa respectively when processed with a 180°C T73-type practice. The 165°C T73-type treatment gave tensile strength values of 506MPa and 490MPa for Alloy A and Alloy B respectively. Elongation to failure of both alloys in the overaged condition remained in the range 14-15%.

**Microstructure:** TEM observations were made on both alloys after overageing to the same 0.2% proof stress level of 450MPa. Due to the aforementioned differences in kinetic behaviour, Alloy A required some 75 minutes longer than Alloy B at the 180°C T<sub>2</sub> ageing temperature to achieve the same strength level. The microstructure of Alloy A in this condition (Figure 3a) shows precipitate free zones (PFZs) of 40-50nm with precipitates of 30-40nm found in grain boundaries.

Observations made on alloy B (Figure 3b) revealed smaller precipitate free zones (10-20nm) and smaller precipitates on grain boundaries. Precipitate density within the grains was similar for each alloy.



Figure 3: Bright field transmission electron microscopy (TEM) of (a) Alloy A after ageing at 105 and 180°C to obtain a T73 temper and (b) Alloy B aged to equivalent hardness at the same ageing temperatures but with reduced 2<sup>nd</sup> stage ageing time.

**Differential Scanning Calorimetry (DSC):** DSC plots were obtained at various stages during the ageing sequence. Figure 4a shows Alloy A immediately after solution treatment and water quenching, whilst Figure 4b shows the same alloy after an initial age at 110°C T<sub>1</sub> temperature. After quenching, an exothermic peak was observed at 240°C, an endothermic peak at 275°C and a broad endothermic reaction starting at 440°C. These can be interpreted as the precipitation and subsequent dissolution of  $\eta$  from solid solution, followed by dissolution of T-phase [9]. An additional endothermic peak was observed at 180°C following the T<sub>1</sub> age, which may be attributed to the dissolution of  $\eta$ ' that had formed at 110°C. Furthermore, Figure 4b also shows that the exothermic peak at 240°C had now split into two discrete reactions, which are probably associated with the transformation of  $\eta$ ' to  $\eta_2$  and the formation of  $\eta_1$  phase.



Figure 4: Differential scanning calorimetry (DSC) plots for (a) Alloy A solution treated for 1h at 475°C, and water quenched and (b) Alloy B solution treated, water quenched and aged for 2h at 110°C.

**Fracture Toughness:** Figure 5a shows fracture toughness measurements for the two alloys obtained from cylindrical components with pre-machined notches. Alloy A consistently achieves higher toughness ( $K_{max}$  or  $K_{1C}$ ) than Alloy B, despite its higher proof strength. Fracture toughness has also been determined for Alloy A as a function of proof stress in a variety of heat treatment conditions, as shown in figure 5b.

These results are characteristic of 7xxx series strength-toughness behaviour, although the  $K_{max}$  values in the present study are higher than those reported in the literature (represented by the shaded region in Figure 5b [1]).



Figure 5: (a) Fracture toughness comparison between Alloy A and B, (b) Fracture toughness (Kmax) results for Alloy A as a function of 0.2% proof stress. The shaded region represents published 7xxx series data [1].

#### 4. Discussion

Both 7xxx series alloys investigated in this paper appeared to go through a similar precipitation process, which allowed 0.2% proof strength values in the range 440MPa to 470MPa to be generated via an overageing, T73-type treatment. These practices make use of a primary and secondary age at two different temperatures, denoted  $T_1$  and  $T_2$ . The peak strength level achieved by both alloys was essentially the same, as might be predicted from their solute contents, and furthermore was found to be insensitive to the  $T_2$  ageing temperature. However, some quite significant differences were observed between the ageing kinetics of the two compositions, with Alloy B (higher Zn:Mg ratio) overageing at a faster rate than Alloy A.

The primary  $T_1$  age promotes a major increment in strength relative to the as-quenched condition, shown clearly by the hardness increase from approximately 90 Hv10 to 165 Hv10 in Figure 2a. The supersaturated solid solution present after quenching undergoes an exothermic reaction at around 240°C, shown in Figure 4a, which corresponds to the

precipitation of  $\eta$ . Conversely, the 180°C endothermic peak in Figure 4b indicates that  $\eta'$  phase had formed during the initial T<sub>1</sub> age, thus accounting for the significant increase in hardness. The exothermic doublet present at 240°C after initial T<sub>1</sub> age indicates the presence of two products. It is thought that this is due to a combination of an in-situ transition from  $\eta'$  to  $\eta$  ( $\eta_2$ ) followed by the direct nucleation of  $\eta$  ( $\eta_1$ ) [9]. It would appear then, that the presence of  $\eta'$ ,  $\eta_1$  and  $\eta_2$  phases is responsible for peak strengthening which, for both alloys, occurred within 2 hours at the 180°C T<sub>2</sub> temperature and coincided with a proof stress of 510MPa (Figure 2b).

After peak ageing, more of the  $\eta$ ' is replaced by  $\eta$  and ultimately precipitate coarsening takes place. TEM observations (Figure 3a and 3b) demonstrate that, at an equivalent overaged strength level of approximately 450MPa proof stress, the precipitate size distribution is very different for the two alloys. In this condition Alloy A exhibits a more overaged appearance to the microstructure in terms of the grain boundary characteristics, despite the strength levels being the same. This is perhaps to be expected since additional time is required at the T<sub>2</sub> ageing temperature in order to achieve the same strength level.

The influence of alloy Zn:Mg ratio on precipitation kinetics has been previously reported [7, 13]. Furthermore, Zn:Mg ratio within the precipitates is known to vary throughout the ageing process in 7xxx series alloys, whereby initially high ratios have been found to reduce with increasing ageing time [12]. Since the alloys in this study were processed under identical conditions, the observed differences are likely to be due to the relative levels of solute within the matrix.

These results show that it is possible to process 7xxx series alloys with the same inherent strength, to the same overaged strength level, yet generate quite different microstructures. It is interesting to consider the influence of the observed microstructural differences upon grain boundary-influenced properties, such as fracture toughness and SCC resistance. The toughness of 7xxx series alloys has been shown in the past to be dependent on strength level, which in turn behaves in a linear fashion with the total solute content (Zn + Mg + Cu) expressed as atomic percent. This, of course, assuming a given distribution of coarse intermetallic particles and thermomechanical processing history.

For the overaged condition selected in this study, the fracture toughness behaviour of the two alloys was observed to be different. The preliminary results presented in Figure 5a show that Alloy A, with its more overaged nature, is consistently able to deliver higher fracture toughness than Alloy B at a given strength. Figure 5b shows that Alloy A displays classic 7xxx series behaviour, with toughness passing through a minima at the peak strength level before increasing again during overageing. While SCC performance is not presented in this paper, it is generally acknowledged that a larger grain boundary precipitate size improves SCC resistance in 7xxx series alloys [18, 19].

# 5. Concluding Remarks

The results of this study indicate that it may be possible to engineer the microstructure of 7xxx series alloys in order to produce a more favourable balance of strength, toughness and SCC resistance. Inherent alloy strength was found largely to be in agreement with a model based on total solute content.

However, when processing to overaged T73-type conditions, Zn:Mg ratio was observed to influence both the ageing kinetics and final microstructure. Preliminary tests have shown that this could ultimately lead to increased fracture toughness at a given strength level.

This work is part of a larger programme aimed at optimising the strength-toughness relationship in 7xxx series alloys.

#### References

- [1] I.J. Polmear, Light Alloys: Metallurgy of the Light Metals, Edward Arnold (publishers) London, 1981.
- [2] A.R. Woodward, Alum. Today, 12, 21, 1997.
- [3] N.J.H. Holroyd, W. Hepples, U.S. Patent 5,932,037, 1999.
- [4] N.J.H. Holroyd, W. Hepples, European Patent EP 0 694 084 B1, 2001.
- [5] W. Hepples, M.R. Clinch, D.M. Banks, N.J.H. Holroyd, Mater. Sci. Forum, 217-222, 1807, 1996.
- [6] M.R. Clinch, S.J. Harris, W. Hepples, N.J.H. Holroyd, J.V. Wood, proc. ICAA6, 1107, 1998.
- [7] S.K. Maloney, K. Hono, I.J. Polmear, S.P. Ringer, Scripta Mater., 41, 1001, 1999.
- [8] J.A. Wert, Scripta Mater., 15, 445, 1981.
- [9] J.K. Park, A.J. Ardell, Mater. Sci. & Eng., A114, 197, 1989.
- [10] J.C. Werenskiold, A. Deschamps, Y. Brechet, Mater. Sci. & Eng., A293, 267, 2000.
- [11] L.B. Ber, Mater. Sci. & Eng., A280, 91, 2000.
- [12] T. Engdahl, V. Hansen, P.J. Warren, K. Stiller, Mater. Sci. & Eng., A327, 59, 2002.
- [13] X. Li, M.J. Starink, Mater. Sci. Forum, 331-337, 1071, 2000.
- [14] M.J. Starink, S.C. Wang, Acta Mater., 51, 5131-5150, 2003.
- [15] T. Pardoen, D. Dumont, A. Deschamps, Y. Brechet, J. Mech. Phys. Solids, 51, 637, 2003.
- [16] D.J. Strawbridge, W. Hume-Rothery, A.T. Little, J. Inst. Met., 74, 191, 1948.
- [17] J.T. Evans, G. Kotsikos, R.F. Robey, Eng. Fracture Mech., 50, 295, 1995.
- [18] N.J.H. Holroyd, proc. EICM, 311, 1989.
- [19] A.Zielinski, E. Renaud, M. Puiggali, J.M. Olive, M. Cid, D. Desjardins, J. Mater. Proc. Tech, 53, 491, 1995.