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Developing an optimized homogenization process for Sc and Zr containing Al-Mg-Si alloys

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Abstract

Light-weighting of vehicles drives the development of Aluminium alloys with improved strength and formability. An opportunity to achieve this goal is using Scandium (Sc). The beneficial effects from Sc comes from the formation of nano-sized Al_3Sc dispersoids. Detrimental interactions between Sc and Silicon (Si) has limited the uptake of Sc in 6xxx alloys. The first step towards developing Sc containing 6xxx-series is to understand the as-cast microstructure and the effect of subsequent heat treatment on the dispersoids. This work uses isochronal ageing trials on a series of Al-Mg-Si-(Sc)-(Zr) model alloys. The evolution of hardness and conductivity is recorded to indirectly characterize the precipitate sequence. Transmission electron microscopy is used to further characterize the morphology and kinetics of MgSi precipitates and Sc/Zr dispersoids. The precipitation of Sc was altered by the presence of Si, and hence it is concluded that a non-traditional homogenization treatment is required for these alloys.

Introduction

The 6xxx series alloys are an age hardenable, medium strength aluminium alloys that are heavily used in the automotive industry. These alloys combine several desirable properties such as good corrosion resistance, processability and a high surface finish at a relatively low cost [1]. Due to the increasing demand for light-weighting in the automotive sector, there is a growing market for alloys with improved mechanical properties. One opportunity to achieve these goals, whilst retaining a good balance of corrosion resistance and formability, is the use of scandium (Sc).

In recent years, Sc has gained more attention in the Aluminium (Al) industry as a potential alloying element, especially in extrusion products [2, 3]. One of the primary obstacles to the widespread industrial use of Sc has been its prohibitive price. However, a high-grade deposit of Sc was discovered in Australia where Australian company Clean TeQ Ltd has developed an innovative cost-saving extraction technology. As a result, a significant reduction in Sc price in the near future is hence anticipated.

The main effects of Sc in Al alloys are improved strength [4, 5], improved resistance to hot cracking [6], and reduced grain size [5, 7]. Strength improvement is mainly provided through the formation of Al_3Sc nano-scale dispersoid particles [8, 9]. These dispersoids form during elevated temperature heat treatments, typically 300-400 °C, are very fine and uniformly distributed and provide strength through four main mechanisms: 1) Solid solution strengthening, 2) precipitation hardening, 3) grain structure control though inhibiting recrystallization, 4) potentially assisting nucleation of other strengthening phases [10, 11]. While Al_3Sc dispersoids are stable up to temperatures of 300 °C, the high temperature coarsening resistance of Sc can be further improved though the addition of Zirconium (Zr). Zr has a much lower diffusivity than Sc and as a result a multi stage ageing treatment can be utilised to form $\text{Al}_3(\text{Sc}_{1-x}\text{Zr}_x)$ dispersoids which display a core/shell type morphology, where most of the Zr segregates at the interface of the core Al_3Sc precipitates [12]. Recent work by Dorin et al. showed that these core-shell dispersoids are stable during high temperature extrusion [10].

Research on Sc containing 6xxx series alloys has been hampered due to potentially detrimental interactions between Sc and Silicon (Si). The presence of Si has been shown to alter the nucleation and precipitation kinetics of the Sc dispersoids in Al and at high Sc compositions, result in the formation of unwanted AlSc_2Si_2 ternary τ -phase [5, 13]. A study by Beeri et al. [14] demonstrated faster precipitation kinetics and a higher dispersoid number density, from the addition of impurity levels of Si (~0.025 at%) to a binary Al-Sc alloy. This acceleration has been attributed to a preferential partitioning of Si to the Al_3Sc precipitates, occupying the Al sublattice site [15]. This change in precipitation kinetics has several practical implications, specifically that while Sc is supersaturated during solidification in Al-Sc binary alloys under conventional cooling rates, Si appears to alter this behaviour to where addition of Si to Al-Sc was shown to result in discontinuous precipitation of coherent

Sc dispersoids during post-solidification cooling [16-19]. Furthermore, Si was also seen to accelerate the nucleation and growth of the Sc dispersoids, hence reducing the time to peak age but simultaneously decreasing their coarsening resistance [20].

While limited, a few studies have explored the addition of Sc in 6xxx series alloy, though with varying degrees of efficacy. A recent study by Rohklin and colleagues [21] reported a significant increase in strength (80-85 MPa) in a Sc and Zr containing 6xxx series alloy that was hot rolled directly from the as cast condition. The alloys were subsequently solution treated and aged. This strength increase was attributed to the presence of Sc/Zr dispersoids formed during high temperature processing. In a similar study by Rohklin et al, this strengthening effect was not observed when this heat treatment was utilised in a Zr free alloy [22] suggesting that the increased stability provided by Zr is necessary in this process. Lityńska and colleagues [16] experimented with a series of different casting methods in an attempt to maximize the strengthening benefit of Sc and Zr. After a multi stage homogenization treatment a fine dispersion of 10-20nm Sc/Zr dispersoids of the L_{12} structure was observed in the Al matrix, regardless of casting method. These dispersoids were attributed to a hardness increase of ~15HV over a Sc/Zr free alloy.

Conversely, other authors have observed negligible or even detrimental effect of Sc additions on mechanical properties. Royset et al [23] compared the mechanical properties and processability of an AA6082 alloy with and without the addition of 0.13 wt% Sc and 0.13 wt% Zr. A minor decrease in the yield stress (-20 MPa) and increase in the UTS (+9 MPa) was observed in the Sc containing alloy but no reason was cited for this change. An isochronal trial developed by Vlach et al [24] compared the ageing response of a standard AA6082 alloy with an alloy augmented with 0.2 wt% Sc and 0.1 wt% Zr. While the initial hardness was observed to be higher in the Sc and Zr containing alloy, owing to the precipitation of Sc and Zr during solidification, the peak hardness throughout the trial was observed to be slightly higher in the standard AA6082 alloy. The addition of 0.3 wt% Sc and 0.14 wt% Zr to an AA6061 alloy was seen as extremely detrimental to the final mechanical properties in a study by Kwon et al [25]. The artificial ageing behaviour at 190 °C was assessed after an extensive prior mechanical/heat treatment schedule, revealing a drop of ~45 MPa in the peak yield strength of the Sc and Zr augmented alloy. Transmission electron microscopy (TEM) imaging revealed coarse incoherent Sc and Zr dispersoids and β' precipitates in the modified alloy while the base alloy contained mostly fine β'' precipitates. A difference in the ageing behaviour and kinetics of the Mg/Si precipitates in the presence of Sc/Zr was attributed to this strength loss, though this phenomena has been disputed by other authors [26].

The conflicting results around the strengthening ability of Sc in 6xxx series alloys may be related to the different solidification, cooling, homogenization and processing approaches chosen. To the author's knowledge, there are no detailed studies looking at tailoring the homogenization process for the optimized precipitation of Sc/Zr dispersoids prior to subsequent processing in a 6xxx series alloy. Detailed understanding of this process is required to create high strength Sc and Zr augmented 6xxx alloys with a fine distribution of both the Al_3Sc/Al_3Zr dispersoids and the β'' MgSi precipitates. This work uses isochronal ageing trials on a series of Al-Mg-Si-(Sc)-(Zr) model alloys. The evolution of hardness and conductivity is recorded to indirectly characterize the precipitation sequence. The morphology and kinetics of MgSi precipitates and Sc/Zr dispersoids are investigated using a combination of transmission electron microscopy and atom probe tomography. We explain how these findings will be utilised for the development and assessment of novel homogenization methods for Sc containing 6xxx-series alloys.

Methodology

The model alloys used in this study were prepared using 99.999% pure Al and five master alloys: Al-25wt.%Mg, Al-20wt.%Si, Al-33wt.%Cu, Al-2wt%Sc and Al-5wt%Zr. Alloy melting was performed in a small induction furnace. The molten metal was maintained at 710 °C for 20 minutes under an argon atmosphere, before casting into a steel mould. The mould was cylindrical in shape (80mm in diameter x 200 mm height), and had a large steel base to provide directional solidification. The final weight of each of the castings was approximately 4kgs.

In order to evaluate the interactions between each of the alloying elements in the modified Al-Mg-Si alloys, four Al-Mg-Si-(Sc)-(Zr) alloy variants were cast, as well as an additional Al-Sc-Zr binary alloy for the basis of comparison. These alloys were developed to isolate the effect of the alloying elements on the precipitation evolution during high temperature heat treatment. To achieve this, alloys were developed to include additions of Sc and Zr both individually and when combined. The composition of the alloys was measured using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES) from samples cut from the centre of the castings, and is given in Table 1 below.

Alloy No.	Designation	Al	Mg	Si	Fe	Sc	Zr
1	Al-Mg-Si	Bal	0.48 (0.5)	0.52 (0.5)	0.11 (-)	-	-
2	Al-Mg-Si-Sc	Bal	0.52 (0.5)	0.52 (0.5)	0.11 (-)	0.05 (0.05)	-
3	Al-Mg-Si-Zr	Bal	0.50 (0.5)	0.50 (0.5)	0.11 (-)	-	0.12 (0.1)
4	Al-Mg-Si-Zr-Sc	Bal	0.45 (0.5)	0.63 (0.5)	0.11 (-)	0.05 (0.05)	0.14 (0.1)

Table 1: Composition of the model alloys in wt%, as measured by ICP AES. The nominal composition is specified in brackets.

The model alloys were aged isochronally from 100 °C to 450 °C in 25 °C increments for a duration of 3 hours for each ageing step. After each ageing step the specimens were directly water-quenched where the precipitate evolution was monitored with Vickers microhardness and electrical conductivity measurements. The electrical conductivity measurements were performed at ambient temperature using a Simgascope eddy current apparatus. Four electrical conductivity measurements (given as a percentage of the International Annealed Copper Standard - %IACS) were recorded on each specimen at four different measurement frequencies (60, 120, 240, 480 kHz). The mean value of these conductivities is reported, while error bars represent one standard deviation. An increase in electrical conductivity corresponds to a decrease in the solute concentration in the matrix due to the precipitation of Sc/Zr dispersoids and Mg/Si precipitates [27, 28]. Hardness was measured using a Struers Durascan hardness tester. All samples were rough ground flat with 1200 grit SiC paper prior to testing. Vickers hardness using a 1 kg load and indentation time of 15 seconds was utilised for all hardness measurements. At least 6 diagonal widths between indentations was utilised to avoid misinterpretations of hardness due to retained deformation from the previous indentation. Hardness measurements are presented as the mean \pm one standard deviation, utilizing a minimum of 5 indents.

The isochronal trial was conducted with three starting conditions, each representing a different stage or condition in the industrial extrusion billet production processes:

- **As Cast (AC):** The state of the billet directly after casting.
- **Solution Treated - Solution treated at 575 °C for 5 hours and water quenched (ST):** The state of the billet after a high temperature homogenization and solutionisation process if a rapid cool from elevated temperature is employed.
- **Furnace Cooled - Solution treated at 575 °C for 5 hours and cooled in the furnace (FC):** The state of the billet after a high temperature homogenization process if a slow cool from elevated temperature is employed (as is common practice in 6xxx series alloys [29]). The temperature evolution of the furnace cooled samples was monitored during cooling. The cooling rate in the furnace was observed to be non-linear, initially displaying an approximate cooling rate of 150 °C/hour over the first 2 hours but slowing significantly as the temperature differential between the furnace and ambient temperature was reduced. Room temperature was reached after approximately 16 hours.

The precipitates distribution was characterized on a JEOL JEM 2100F transmission electron microscope (TEM) operated at 200 kV. TEM samples with a thickness of 60 – 100 μ m were prepared by electro-polishing in a solution of 33% nitric acid in methanol at a temperature of -20 °C.

Results and Discussion

Initial Conditions

The initial (a) conductivity and (b) hardness values for the model alloys in the three initial conditions is shown below in Figure 1. The conductivity results suggest that the percentage of elements in solute follows the following trend, where the elements in solute is highest in the solution treated condition, followed by the as cast condition and finally lowest in the furnace cooled condition. This is unsurprising, as in 6xxx series alloys rapid cooling from above the solidus temperature is generally employed to maximize the percentage of Mg and Si in solute. Furthermore, it is clear that the quantity of solute scales with the cooling rate from elevated temperature (after either casting or homogenization) as there is more time spent above the activation temperature for precipitation of the alloy elements - Mg/Si (room temperature), Sc (>250 °C) and Zr (>350 °C) [30]. The rapidly cooled water quenched (cooling rate of ~100 °C per second) solution treated samples have the fastest cooling rate and the lowest conductivity, suggesting most of the elements are retained in solid solution. The as cast condition has the second fastest cooling rate in which billets are initially solidified and rapidly cooled by the walls of the casting mould and then left to cool at ambient temperature. As the conductivity in this condition is higher than that of the solution treated samples, suggesting some precipitation has occurred during cooling. Finally, the furnace cooled samples have the slowest cooling rate (ranging from 100 °C/hour initially to 20 °C/Hour as cooling progresses) and the highest conductivity. It is apparent that significant precipitation has occurred during this period of extended slow cooling.

When assessing the hardness results of the model containing alloys, the as cast samples were found to be significantly harder than the samples in the other two conditions. However, there was a period of several months between casting and hardness testing in the AC samples, allowing for a significant room temperature natural ageing to occur, which could explain the increased hardness. As both the ST and FC samples were tested directly after quenching/cooling the strength increase due to natural ageing in these alloys is minimal.

An increased hardness is observed in Sc (and Sc +Zr) containing alloys compared to those that do not contain Sc in both the AC and FC conditions. This observation is similar to prior work in alloys containing Sc and Si, and likely due to the formation of Sc precipitates during solidification and cooling [16-19]. Bright field TEM images of the Al-Mg-Si-Sc-Zr alloy in the AC condition (Figure 2) revealed the presence of a fine dispersion of precipitates with a size range 7.5 ± 2.5 nm (as well as coarse Mg/Si rods) which when of this size have been shown to effectively increase strength [16]. No such precipitates were observed in the alloys that did not contain Sc. As a result, it is highly likely that the observed dispersoids are those formed due to the discontinuous precipitation of Sc during cooling, as facilitated by Si. This trend is not observed in the solution treated alloys, where the hardness increases linearly with the percentage of alloy content. Furthermore, the associated low conductivity of the alloys suggests that the various alloying elements (including the Sc dispersoids) have been successfully solutionised during this process. The observed increase in strength alongside alloy content is likely a result of solid solution hardening.

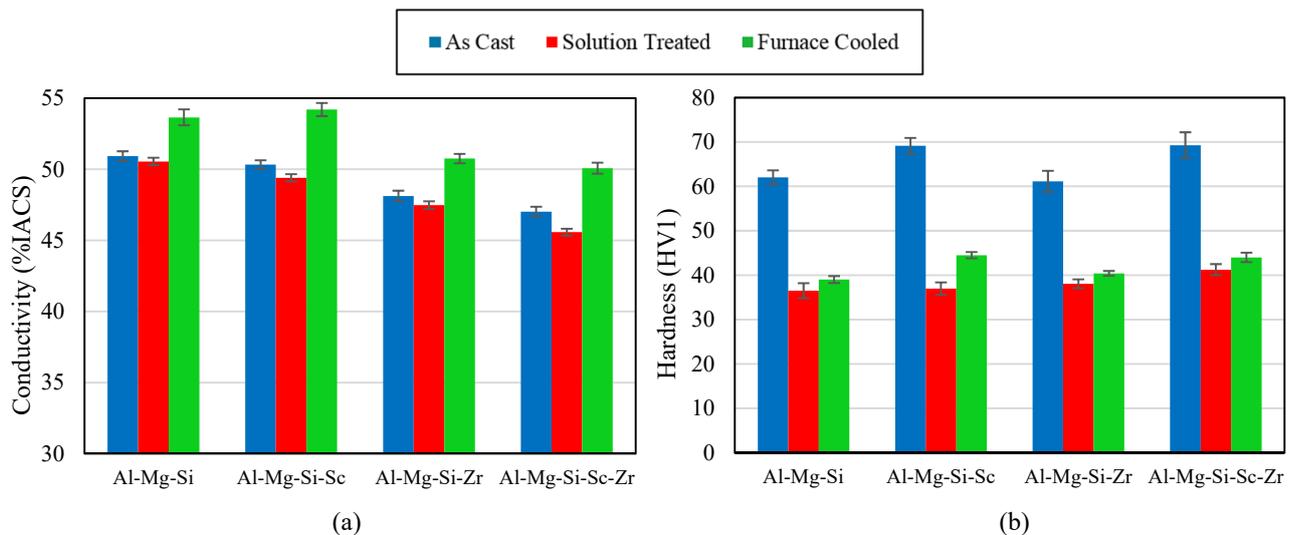


Figure 1: Initial (a) conductivity and (b) Hardness of the model alloys in the As Cast, Solution Treated and Furnace Cooled condition.

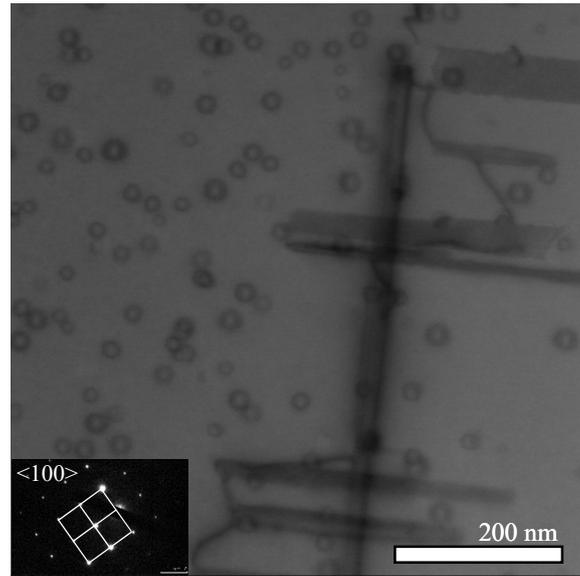


Figure 2: Bright field TEM image taken along the $\langle 100 \rangle$ zone axis of the Al-Mg-Si-Sc-Zr alloy.

Isochronal Trial

The (a) conductivity and (b) hardness evolution of the alloys during the isochronal trial as a function of the heat treatment temperature in the as cast condition is shown below in Figure 3. All of the model alloys show hardening from 100 – 175 °C and soften upon subsequent higher temperature ageing. This initial hardness increase is accompanied by a jump in the conductivity, signifying the precipitation of Mg and Si which occurs rapidly at this temperature [30].

The Sc containing alloys show a delayed softening behaviour at temperatures above 200 °C and 375 °C. This is likely due to the Sc dispersoids formed during solidification and cooling retaining the strength of the alloy at this elevated temperature, as they are substantially more stable than the MgSi precipitates at these temperatures.

All Zr containing alloys show reduced softening, or in the case of the Al-Mg-Si-Zr alloy, slight hardening at temperatures between 325 °C and 425 °C. As a result, alloys containing both Sc and Zr display delayed softening up to 425 °C. This is likely due to the precipitation of Zr forming the “shell” on the Sc dispersoids allowing the alloy to retain its strength at these temperatures, while Al₃Zr dispersoids are formed resulting in slight hardening in the Al-Mg-Si-Zr alloy.

A decrease in conductivity is observed in all Mg and Si containing alloys at a temperature of 400 °C. This is likely due to Mg and Si slowly returning into solution as it is very close to the solution temperature for these elements.

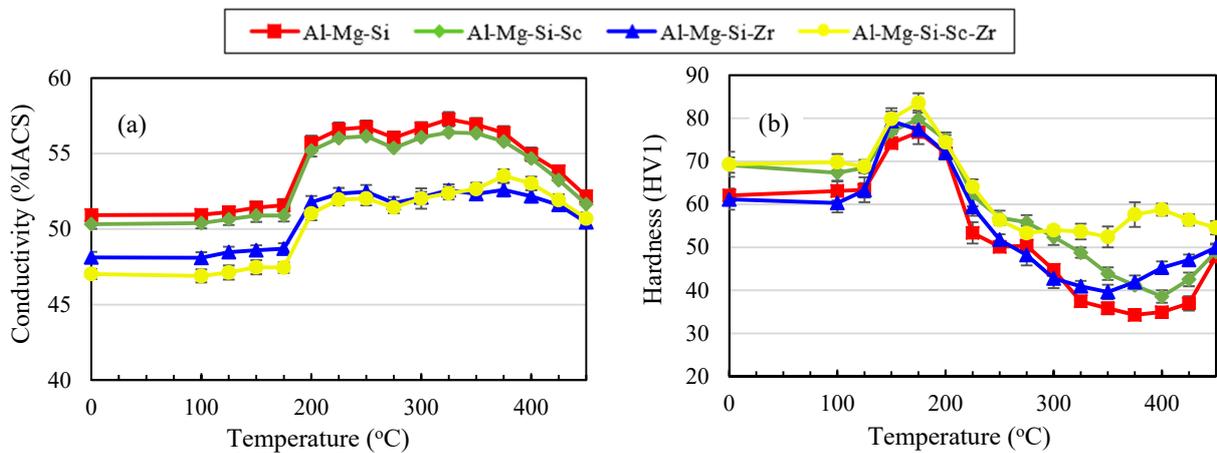


Figure 3: (a) Conductivity and (b) Hardness evolution of the four model alloys as a function of temperature during isochronal ageing from the as cast initial condition.

The evolution of the hardness and conductivity of the samples in the solution treated condition is very similar to those that were observed in the as cast condition. The magnitude of the observed increase in hardness and conductivity between temperatures of 100 – 175 °C in the solution treated alloys is significantly higher than in the as cast condition. This is due the solution treatment putting most of the Mg and Si in solution where it is available for subsequent precipitation, whereas it was observed that some coarse Mg/Si precipitates formed during cooling after solidification in the as cast condition. Delayed softening is observed in the Sc containing alloys at temperatures between 325 °C and 425 °C. Due to the observed progressive increase in conductivity (when compared to the Sc free alloy) and the lower initial hardness of the Sc containing alloys this suggests that these dispersoids have formed during the elevated temperature isochronal trial, rather than prevailing throughout the trial from the as cast microstructure. Furthermore, this also suggests that the precipitation and hardening response of the Sc and Zr dispersoids is not completely negated in the presence of Mg and Si.

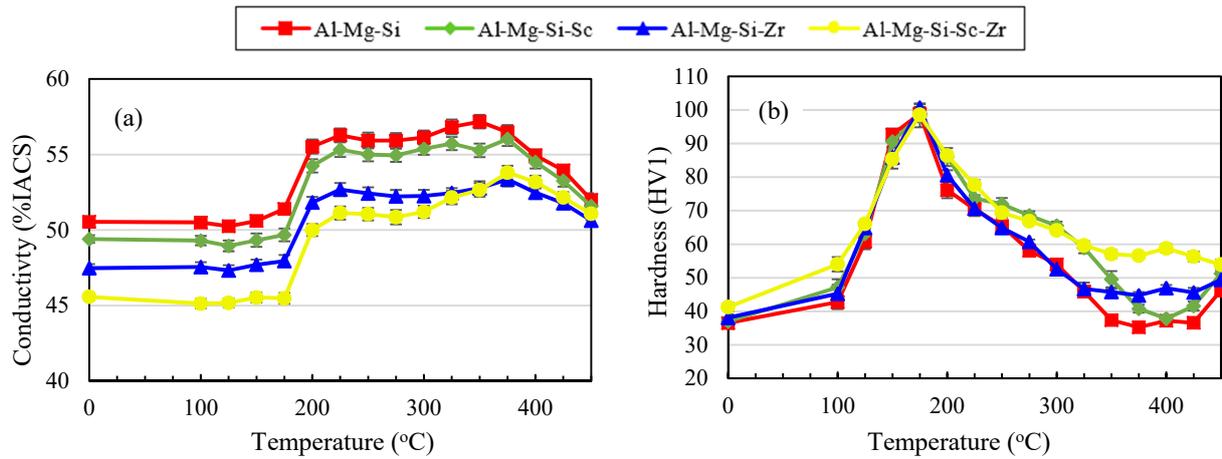


Figure 4: (a) Conductivity and (b) Hardness evolution of the four model alloys as a function of temperature during isochronal ageing from the solution treated initial condition.

The furnace cooled (Figure 5) samples show similar trends to those observed in the as cast and solution treated samples, however with significantly reduced magnitudes. The increase in conductivity and hardness is smaller as for the as-cast or solution treated samples, signifying substantial prior precipitation of both Mg/Si precipitates and Sc/Zr dispersoids during the furnace cool. As a result, these elements are unavailable for subsequent precipitation during the isochronal trial and only minimal hardening increases and changes in conductivity are observed.

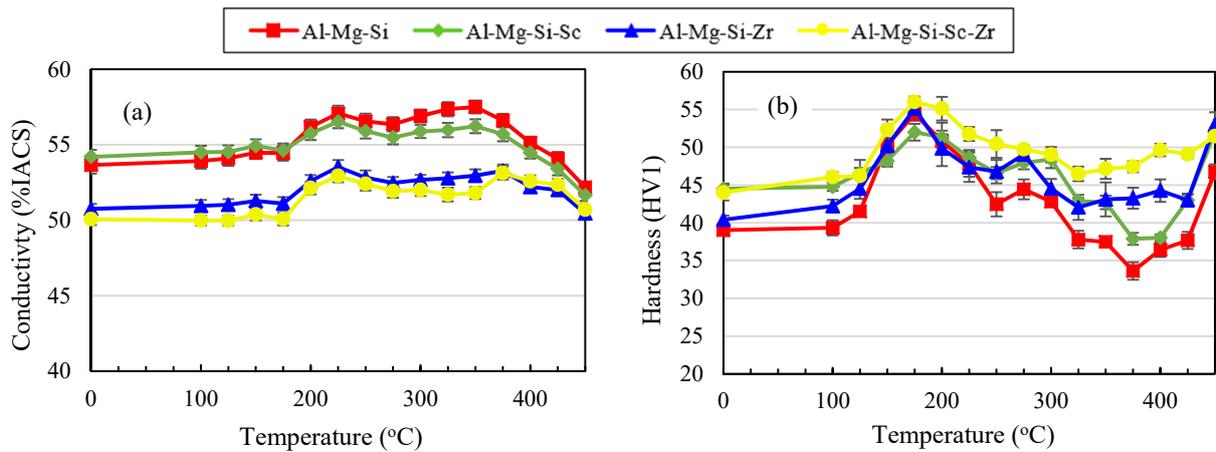


Figure 5: (a) Conductivity and (b) Hardness evolution of the four model alloys as a function of temperature during isochronal ageing from the furnace cooled initial condition.

In order to get a visual image of the effect of Sc and Zr during the isochronal treatment, the hardness values of the Al-Mg-Si-Sc-Zr alloy were subtracted from the baseline hardness values for the Al-Mg-Si ternary alloy. The hardness increment are obtained and plotted as a function of the isochronal heat treatment temperature and compared across the three initial conditions in Figure 6. These hardness increment curves better highlight the trends previously observed in the isochronal trial. The hardness remains relatively unchanged between the two alloys at temperatures below 250 °C where Mg and Si precipitation is the primary strengthening mechanism. A significantly increased hardness is observed in the Sc and Zr containing alloy during the ageing steps between 250 °C and 425 °C where Sc and Zr precipitation is known to occur [12]. Only minimal differences in the hardness increment is observed between the solution treated and as cast condition, suggesting that the hardness increase due to the Sc dispersoids formation is effective regardless whether they are formed during solidification cooling or throughout

the ageing trial. Significantly reduced hardening is observed in the case of the furnace cooled condition, due to the aforementioned prior precipitation of coarse Sc and Zr dispersoids during the slow cooling process.

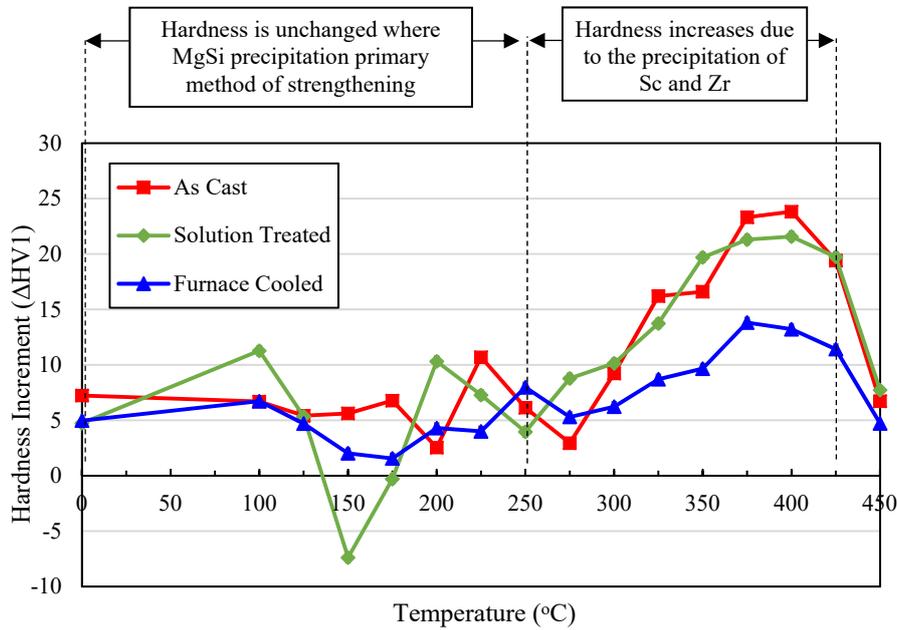


Figure 6: Hardness increment between the Al-Mg-Si-Sc-Zr alloy and Al-Mg-Si alloy throughout the isochronal ageing trial for the three initial conditions.

Development of Homogenization Methods for 6xxx-series alloys with Sc and Zr

Homogenization treatments of wrought Al alloys are commonly used for the following reasons: formation of dispersoids, solutionisation of solute elements and spheroidization of coarse intermetallics [29]. The homogenization methods of 6xxx-series alloys are standardised and routinely conducted in the extrusion industry. However, there is currently no consensus in the literature on how to homogenize 6xxx-series alloys that contain Sc and Zr.

An effective homogenization process for an Al-Mg-Si-Sc-Zr alloy will result in: 1) the formation of stable and strengthening Sc and Zr dispersoids, 2) the effective solutionisation of Mg and Si (this stage could also possibly include the subsequent controlled re-precipitation of Mg and Si during cooling in the form of fine lath-shaped β' precipitates that will readily re-solutionize during the subsequent thermomechanical processing).

In the present project, hardness and conductivity measurements during isochronal trials were used to indirectly characterise the formation of precipitates in a range of carefully selected model alloys. This information proves extremely useful to design a suitable homogenization treatment for these alloys. The initial condition from which the alloy will be homogenized is crucial. Dispersoids former elements tend to stay in solution in the as-cast condition and hence it is common to heat treat to the suitable temperature for dispersoids formation directly from the as-cast condition. This was recently shown to be the case for an Al-4Cu-Sc-Zr alloy, where both Sc and Zr were shown to stay in solution after solidification [10]. In the present case, our TEM observations revealed the presence of a high number density of dispersoids in the as-cast condition. As a consequence, we chose three starting condition for our isochronal trials: 1) from the as-cast state, in that case the as-cast dispersoids will most likely keep growing, 2) from a solutionised and quenched state, in this case, most Sc and Zr should be back in solution and 3) a solutionised and furnace cooled. This latest condition was conducted as it is common in the industry to slowly cool large billets after solutionisation.

The furnace cooled condition showed significantly reduced changes in hardness which indicates that fewer elements were available for precipitation. Furthermore, the actual hardness achieved were much lower as compared to the other conditions trialled. In that case, the slow cooling from elevated temperature resulted in the formation of coarse Sc, Zr, Mg and Si features

that are not efficient for strengthening. As a result, this initial state was discarded for the design of an effective homogenization process. Further work will be dedicated to finding the slowest cooling rate achievable from the solutionisation temperature in order to still retain a supersaturated solution in Sc and Zr.

The hardness increments, from the formation of Sc and Zr dispersoids, observed when starting from the as-cast or solutionised and quenched conditions were found to be similar (Figure 6). As a result, both these starting conditions will be investigated further as a possible suitable starting point for and appropriate homogenization heat treatment. In order to ensure the formation of fine core-shell dispersoids, the utilisation of a multi-step homogenization approach will most likely be required [10, 12, 31, 32]. The core-shell morphology should then ensure thermal stability of the dispersoids when solutionizing the Mg and Si, and during subsequent processing and ageing. The development, evaluation and optimization of a modified homogenization treatment for an Al-Mg-Si-Sc-Zr alloy based on these ideas is part of an ongoing project and will be addressed in subsequent work.

Conclusions

In the present study, the impact of adding Sc and Zr to an Al-Mg-Si alloy was investigated during isochronal ageing from three initial conditions and approaches for developing a modified homogenization cycle for these alloys were discussed. The main conclusions are as follows:

1. The quantity of the total elements in solid solution scales with the cooling rate from elevated temperature.
2. Sc dispersoids precipitate during solidification and cooling, increasing the as cast alloy hardness compared to a Sc free alloy.
3. Sc and Zr dispersoids precipitate between temperatures of 250 °C and 425 °C during isochronal ageing, providing a significant strengthening benefit.
4. An as cast and solution treated condition were determined to be potential starting points for the development of a homogenization treatment for an Al-Mg-Si-Sc-Zr alloy.
5. Excessive slow cooling from an elevated temperature resulted in the unwanted precipitation of coarse Sc and Zr particles and a significantly reduced strengthening increment. As a result, this must be avoided when developing an effective homogenization cycle for these alloys.

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