Aging characteristics of the Al-Si-Cu-Mg cast alloy modified with transition metals Zr, V and Ti

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Abstract. The hypoeutectic Al-7Si-1Cu-0.5Mg base alloy was modified with different contents of Zr, V and Ti. The wedge-shape samples with varying solidification rates during casting were subjected to isochronal aging at temperatures up to 500 °C. Moreover, as-cast and solution treated alloys were subjected to long-term isothermal aging at 150 °C. As a reference, the A380 alloy, seen as commercial standard for the automotive application target, was used. The modified alloys exerted different aging characteristics than the A380 grade with higher peak hardness and lower temperature of alloy softening. Besides, the influence of the applied solidification rates on hardness after aging was less pronounced in modified alloys than in the A380 grade. For three combinations of Zr, V and Ti tested with contents of individual elements ranging from 0.14 to 0.47 %, no essential differences in aging characteristics were recorded. The results are discussed in terms of the role of chemistry and heat treatment in generating precipitates contributing to the thermal stability of Al based alloys.

1. Introduction

The lightweighting features of Al-based alloys make them very attractive structural materials for automotive applications, including strategic powertrain components [1, 2]. It is well established that an improvement in effectiveness of the combustion engine requires increasing its service temperature and internal pressure. Thus, there is a search for new Al alloys with sufficient thermal stability at continuously increasing temperatures [3, 4, 5, 6].

The Al-Si based grades, i.e., Al-Si-Cu and Al-Si-Mg, have limited thermal stability and lose their strength above approximately 150 °C [6]. To improve the mechanical properties at elevated temperatures, the base Al-Si-Cu-Mg chemistry has to be modified and additions of transitional metals were found to be effective in this respect. According to recent findings, such elements as V, Zr, or Ti, combined with the Al-Si matrix, can improve high temperature stability [4, 6, 7, 8]. As documented in the literature, transition metals develop stable precipitates, which do not coarsen at temperatures as high as 300 °C [9, 10].

In our previous papers many aspects of the transition metals Zr, V and Ti in the Al-Si-Mg-Cu matrix were reported including work hardening and texture [11], tensile and compressive deformation behaviour [9, 12], hot deformation behaviour [13], role of dislocations during deformation at increased temperatures [14], fatigue behaviour [8, 9, 15] and thermal stability of (AlSi)(ZrVTi) intermetallic phases formed with transition metals [10]. However, the aging characteristics of the Al-Si-Cu-Mg modified with addition of Zr-V-Ti are still unknown. Thus, the objective of this study was to...
determine the alloy aging characteristics as a function of the alloy chemistry (Zr, V, Ti), the aging temperature and solidification rate.

2. Experimental details
Several alloy melts with experimental chemistries were prepared (table 1). The 30 kg batches were melted in an induction furnace by mixing commercial master alloys of Al–50%Cu, Al–35%Si, Al–6.1%Ti, Al–85%V, Al–10%Zr, Al–10%Sr and pure metals Mg and Al. Wedge-shaped castings were prepared in a copper mold cooled with flowing water at a temperature of 60 °C (figure 1). As a reference, the A380 alloy, seen as the commercial standard for the automotive application target, was used. To ensure melting of all ingredients, the alloy was overheated to 860 °C for approximately 20 minutes. The alloy temperature directly before pouring into the wedge mold was kept at 740 °C. The shape of the wedge castings after sectioning is shown in figure 2. The cooling rate of the wedge samples during solidification was measured using 3 k-type thermocouples positioned along the centerline at 25, 50 and 100 mm from wedge base as it was located in the casting mold, named as bottom, center and top. The typical cooling curves are shown in figure 3. The cooling rate varied from 9 °C/s at the top to 70 °C/s at the bottom of the mold.

Table 1. Chemistry of Al-Si-Cu-Mg alloys modified with addition of Zr-V-Ti and a reference alloy A380.

| Alloy ID | Si   | Cu  | Mg  | Fe  | Sr  | Mn  | Zr  | Ti  | V   | Al  |
|---------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| A       | 6.77 | 0.93| 0.51| 0.095| 0.010| 0.010| 0.14| 0.14| 0.22| Bal.|
| B       | 7.06 | 0.96| 0.51| 0.094| 0.047| 0.007| 0.42| 0.18| 0.17| Bal.|
| C       | 7.02 | 0.95| 0.48| 0.090| 0.012| 0.005| 0.47| 0.21| 0.30| Bal.|
| A380    | 9.5  | 3.4 | 0.07| 0.90 | <0.001| 0.19 | 0.0073| <0.001| 0.0087| Bal.|

Figure 1. Copper wedge mold with automatic pouring and cooling control with circulating water.
Figure 2. Wedge casting and slices (base 60 x 10 mm and height 120 mm) used for aging experiment and hardness measurements.

After casting, the wedges were sliced and hardness was measured as a function of the distance from the wedge base using a Rockwell hardness tester and F scale with a load of 60 kg and a 1/16” steel ball indenter. To examine the role of heat treatment the alloy was isochronally aged in 50°C
increments each lasting 15 min, beginning at 50 °C and terminating at 500 °C. After each aging step, specimens were water quenched and subjected to hardness testing. The solution treatment consisted of a two-step heating at 510 °C for 0.5 h and at 525 °C for 4.5 h, followed by water cooling. The isothermal aging of as-cast or solution treated alloys was conducted at 150 °C for time intervals up to 128 h.

For microstructural observations, samples were collected from several positions in the wedge. The surfaces were ground using SiC papers up to a grit number of 1200, polished using first an Al₂O₃ slurry and then colloidal silica. The microstructure was examined in the unetched condition using a light optical microscope equipped with a quantitative image analyser and SEM/EDX techniques. The average secondary dendrite arm spacing (SDAS) values were determined using the linear intercept technique, which involves measuring the distances between secondary dendrite arms along a line normal to the dendrite arms. For the cooling rate applied the approximate change in SDAS was between 10 and 35 μm.

3. Results and discussion

3.1. Alloy microstructure

The characteristic features of the experimental and reference A380 alloys are Al dendrites, surrounded by Al-Si eutectic structures with intermetallics distributed within the interdendritic region. It is well established that at relatively fast cooling rates, such as at the bottom of the wedge casting, and chemically modified alloy, the Al-Si eutectics are much finer and the silicon is seen as having a fibrous/spheroidal morphology (Figure 4). The SEM/EDX spectra across two intermetallics revealed the presence of Ti-, V- and Zr-containing phases with needle like shape, generally referred to as Al(TiVZr)Si [10, 16].

![Figure 4](Image)

**Figure 4.** Microstructure of the experimental alloy C from different locations corresponding to figure 3; top (a), center (b) and bottom (c) of the wedge mould in as-cast state.
At the same time, intermetallics observed in A380 are Fe-rich phases Al₁₅(FeMnCr)₃Si₂, mostly with a shape of a skeleton. In this alloy, the eutectic Si particles and Fe-phases can act as nucleation sites for Cu-rich phases. The Mg-containing Q-phase and Fe-containing π-phase are also present in both alloys. Such micro-size phases are believed to form as primary phases during initial alloy solidification. According to EDX analysis of element distribution, in the experimental alloys the particles contained mainly (Si, Zr, V, Ti) and (Mg, Cu). On the other hand, in the A380 alloy, particles with (Si, Fe, Mn, Cr) and (Mg, Cu) dominated. It is believed that these micro-size phases in the experimental alloy would, most likely, contribute to the strength retention at elevated temperatures since they were more thermally stable than Cu- and Mg-based phases.

As portrayed in Figure 5, heat treatment changed the alloy microstructure. The metallographic analysis of the T6 heat treated alloy with the optical microscopy and the SEM/EDS techniques confirmed primarily dissolution of Cu-containing phases. Some other phases including eutectic silicon experienced only partial dissolution. In addition to this, some phases were not affected by the solutionizing temperature of 510/525 °C, which indicates their high thermal stability. Details are published in our previous studies [10].

![Figure 5](image)

**Figure 5.** Typical LOM (a) and SEM (b) microstructures of the experimental alloy C in T6 heat treated condition at the center of the casting wedge.

3.2. **Hardness after isochronal aging**

The results of isochronal aging behaviour of the tested alloys are summarized in figure 6. For all alloys the peak aging conditions are attained at approximately 200 °C. There is a hardness difference at the peak between the experimental alloys and A380; 93HRF versus 87 HRF, respectively. It is of interest that for all three alloys A, B, C the peak hardness is almost identical. For other aging temperatures the hardness difference between A, B and C chemistries was rather small. The initial hardness of the A380 alloy of 83 HRF is over 10 units higher than that of the experimental A, B, and C alloys. For temperatures up to 150 °C, the A380 grade experienced hardness reduction instead of the increase observed for A, B, C alloys.

3.3. **Hardness after isothermal aging**

The results of isothermal aging of as-cast and solution treated alloys are plotted in figure 7. For as cast experimental alloys, the first hours of aging led to a reduction in hardness from 80-84 HRF to just below 80 HRF. Then, hardness increased attaining a maximum. It was revealed that as-cast A380 showed very similar hardness change, reaching a maximum of 92 HRF after approximately 50 h.

The solution treatment of experimental alloys at 510/525 °C reduced their hardness from 80-82 HRF to around 70 HRF. The subsequent aging led to an increase in hardness with a maximum close to 100 HRF after 50 h exposure and then a slight reduction for up to aging time of 100 h. The
solution treatment of the A380 alloy increased its hardness slightly, which after 10 h led to maximum of over 100 HRF, the highest value of all alloys tested.

![Graph showing hardness and temperature relationship](image)

**Figure 6.** Hardness of the experimental and reference alloys after isochronal aging.

![Graph showing effect of time on hardness](image)

**Figure 7.** Effect of time on hardness of as cast and solution treated alloys after aging at 150 °C.

3.4. General observations on aging behaviour

It should be stated that no substantial effect of cooling rate, especially in experimental alloys, on hardness measured directly after casting or after heat treatment was detected. Moreover, there was no distinct effect of the amounts of Zr, V and Ti added to experimental alloys on hardness measured. While comparing the experimental alloys with the A380 grade, the latter shows lower response to post-casting heat treatments, at the same time preserving higher hardness to higher temperatures, especially
above approximately 250 °C. The experimental alloys, however, showed during isochronal aging slightly higher hardness. It is obvious that observed differences in hardness after casting and heat treatments are caused by differences in alloy chemistry, in particular, by the presence of transition metals Ti, Zr and V. The precipitates they form, as identified and described earlier [10], are responsible for the observed hardness differences. This study revealed rather low sensitivity of alloy hardness to contents of transition metals but this requires additional verification. This verification is essential to find the optimum content of transition metals to generate the maximum effect in improving thermal stability of the Al-Si alloys.

4. Conclusions
During isochronal aging, the modified alloys exerted different aging characteristics than the A380 grade with a higher peak hardness and a lower temperature of alloy softening. Besides, the influence of the applied solidification rates on hardness after aging was less pronounced in modified alloys than in the A380 grade.

For three combinations of Zr, V and Ti tested with contents of individual elements ranging from 0.14 to 0.47 %, no essential differences in aging characteristics were observed.

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