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Microhardness and Tensile Properties of a 6XXX Alloy Through Minor Additions of Zr

Karen M.C. Wong, A.R. Daud, and Azman Jalar

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The 6XXX series alloy is known to show inferior age-hardening response during the paint-bake cycle due to natural aging prior to the paint-bake. Many researchers have adopted the pre-aging process to offset the detrimental effect of the natural aging process. The alloy used in this study contained excess Si, and it had been reported elsewhere that such alloys do not show positive response to the pre-aging process. The present work is aimed to study the microhardness and tensile strength of the Al-1.2Si-0.5Mg-0.25Fe wrought alloy through Zr additions between 0.02 and 0.30 wt.%. Alloys containing 0.15 wt.% Zr and above heat-treated for 30 min gave higher microhardness and ultimate tensile strength values compared to that of Al-1.2Si-0.5Mg-0.25Fe without Zr which was heat-treated for 11 h. It was found that mechanical properties improved when the Zr content in the alloys increased. The improvement of mechanical properties was mainly attributed to formation of Zr-bearing intermetallic compounds formed in the alloy.

Keywords grain refinement, intermetallic compounds, mechanical properties, zirconium

1. Introduction

The 6XXX series aluminum alloys for automotive applications undergo solutionization followed by natural aging to enhance their age-hardening response. After a substantial natural aging, these alloys are paint-baked. A typical paint-bake carried out in automotive industries is baking at 180 °C for about 30 min. However, it is difficult to obtain superior paint-baking response in such a short period of time (Ref 1), which led to various studies on ways to enhance the paint-bake response of these alloys. Additional thermomechanical processing steps had been introduced to address this issue, with An et al. (Ref 2), Birol (Ref 3), Miao and Laughlin (Ref 4), Murayama and Hono (Ref 5), and Zhen and Kang (Ref 6) performing pre-aging on various 6XXX series alloy while Birol (Ref 7) carried out pre-straining shortly after solutionizing.

The alloy used in this study contains excess Si, and according to Gupta et al. (Ref 8), such alloys do not show positive response to pre-aging, thereby eliminating the need for this step as a measure to harden the alloy. Improvement of the age-hardenability of this alloy by means other than the usual thermomechanical route has been attempted. Addition of minor elements such as Cr, Cu, Sc, Zr, and Mn is known to improve mechanical properties of the 6XXX series alloy when added in suitable amounts.

Karen M.C. Wong, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, UTAR Setapak, Off Jalan Genting Kelang, 53300 Kuala Lumpur, Malaysia; and **A.R. Daud** and **Azman Jalar**, School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia. Contact e-mail: y2karenw@hotmail.com.

It is widely established that fine grains are favorable in obtaining materials with superior mechanical properties. The common practice for obtaining fine grains is by using materials which contain precipitates that impede grain boundary mobility, and thereby restricting grain growth. Therefore, addition of elements that could aid grain refinement in 6XXX series alloy is likely to improve the mechanical properties of the alloy. The obvious advantage of this route of improving the age-hardening response of the alloy would be the time saving factor of not having to implement additional steps to the original thermomechanical processing (TMP).

Zr is a well-known grain refiner for aluminum alloys (Ref 9) due to formation of precipitates. Besides their obvious effect on mechanical properties, these precipitates also help reduce corrosion in aluminium alloys with high Si content (Ref 10). This makes Zr an attractive minor element addition candidate to 6XXX alloy for automotive applications whereby corrosion resistance is an important factor to be taken into consideration. Mukherjee (Ref 11) added 0.16 wt.% Zr to a 6111 alloy containing Cr and found that the strength of the Zr containing alloy increased significantly compared to the alloy containing only Cr. Yin et al. (Ref 12) found that adding 0.2 wt.% Sc and 0.1 wt.% Zr can refine the grain size of an Al-Mg based alloy. Increase in the hardness for A319 cast alloy containing 0.15 wt.% Zr has been reported by Sepehrband et al. (Ref 13) while Ryum (Ref 14) in his study on an Al-0.5wt.%Zr alloy attributed the increase in recrystallization temperature of the alloy to presence of Al_3Zr precipitates which had the pinning effect on low- and high-angle grain boundaries.

The present work was carried out to study the effects of zirconium additions on some mechanical properties of the Al-1.2Si-0.5Mg-0.25Fe wrought alloy.

2. Materials and Methods

The aluminum prepared for this study contained 1.2 wt.% Si, 0.5 wt.% Mg, 0.25 wt.% Fe and Zr varied between 0.02 and

0.30 wt.%. Melting was carried out at 850 °C under argon atmosphere using graphite crucible and cast in a steel mould to produce a 5-mm-thick plate. The plates were scalped along its later rolling direction, then homogenized at 550 °C for 24 h to reduce short-range intercellular segregation and to dissolve soluble phases in the alloy (Ref 15). This was followed by hot (50% reduction) and cold rolling to obtain sheets with the final thickness of 1 mm. The sheets were solution heat-treated at 550 °C for 30 min (Ref 5) followed by air-quenching to room temperature, then naturally aged for 14 days. The respective sheets were then heat-treated at 180 °C for 30 min as practiced in the paint-bake cycle in automotive industries and for 11 h to achieve peak hardness (Ref 16). Specimens for microstructural studies were mechanically wet-ground using SiC papers and polished with diamond spray to a 1-μm finish. Mechanical tests were used to determine the age-hardening response of the alloy. An improvement in mechanical properties of the alloy after the 30 min heat-treatment indicates that the age-hardening response of the Al-1.2Si-0.5Mg-0.25Fe alloy has improved. Vickers microhardness was chosen to determine the hardness of different microconstituents within a structure while the tensile test was used to determine the bulk strength of the alloys. The Vickers microhardness test was carried out using Shimadzu Microhardness Tester HMV-2000. A load of 300 g was applied for 15 s. Each microhardness value reported here is an average value of 12 measurements. Tensile specimens were prepared according to ASTM E8M standard. Tensile test was carried out at room temperature using a computerized 2.5 tons capacity Instron 5567 universal testing machine. Uniaxial tensile stress was applied with a speed of 1 mm/min. For microstructural study, the specimens were etched in Barker's reagent and observed under Carl Zeiss Axiotech 100 HD optical microscope. Leo 1450 variable pressure SEM equipped with energy-dispersive X-ray from Oxford Instrumentations was used to obtain SEM images.

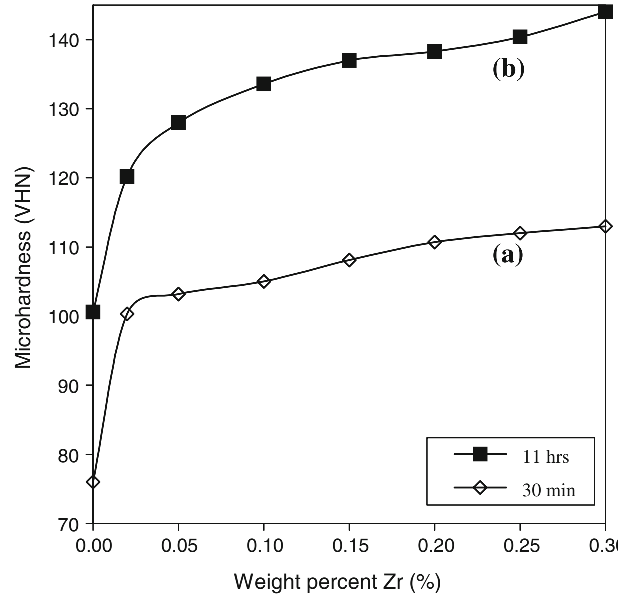

Fig. 1 Microhardness of Al-1.2Si-0.5Mg-0.25Fe with Zr additions: (a) natural aging for 14 days, followed by heat-treatment at 180 °C for 30 min, and (b) natural aging for 14 days, followed by heat-treatment at 180 °C for 11 h

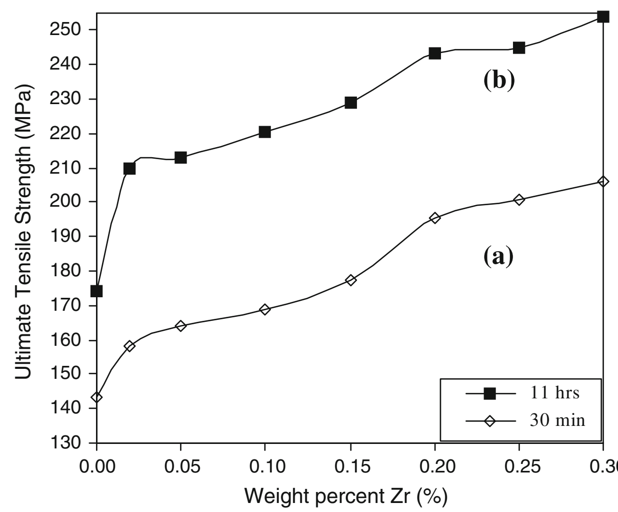

Fig. 2 Ultimate tensile strength of Al-1.2Si-0.5Mg-0.25Fe with Zr additions: (a) natural aging for 14 days, followed by heat-treatment at 180 °C for 30 min, and (b) natural aging for 14 days, followed by heat-treatment at 180 °C for 11 h

3. Results and Discussion

The solid-solubility of Zr in Al at 660 °C is 0.28 wt.% and by decreasing the temperature to about 427 °C, the solubility of Zr in Al is only 0.05-0.06 wt.% (Ref 17). Among all transition metals, Zr has the lowest diffusion flux in Al (Ref 14) and the largest negative enthalpy of mixing with Al, giving rise to a reduction in the Gibbs free energy of the system, thus formation of Al_3Zr is possible.

By adding 0.02-0.30 wt.% Zr to Al-1.2Si-0.5Mg-0.25Fe both microhardness and ultimate tensile strength (UTS) increased for heat-treatments of 30 min and 11 h. Increasing Zr content gave better mechanical properties (Fig. 1-3). For additions of Zr above 0.15 wt.%, both microhardness and UTS for the alloys heat-treated for 30 min are higher than the values of Al-1.2Si-0.5Mg-0.25Fe without Zr addition despite being heat-treated for 11 h. This implies that addition of Zr has enhanced the bake-hardenability of the Al-1.2Si-0.5Mg-0.25Fe alloy significantly.

Zr-containing precipitates (Fig. 4-6) are believed to have contributed to this increase in mechanical properties. These precipitates are believed to be Al_3Zr from the Al-Zr phase diagram. Besides the formation of precipitates, the grain sizes have been obviously refined with the addition of Zr (Fig. 7). Al_3Zr precipitates effectively block grain boundary mobility by causing the pinning effect on dislocations (Ref 18). Second phase particles have a major inhibiting effect on boundary migration and are particularly effective in the control of grain size. The pinning process arises from surface tension forces exerted by the particle-matrix interface on the grain boundary as it migrates past the particle. The grain boundary is assumed to move rigidly through the particles and experiences a retarding force, *F*, from each particle. The pinning force per unit area of boundary, P_z, is given by (Ref 19)

$$P_z = \frac{3 V_v \gamma}{2r} \quad \text{(Eq 1)}$$

where V_v is the volume fraction of particles, r the radius of particles assumed to be spheres, and γ is the boundary energy per unit area.

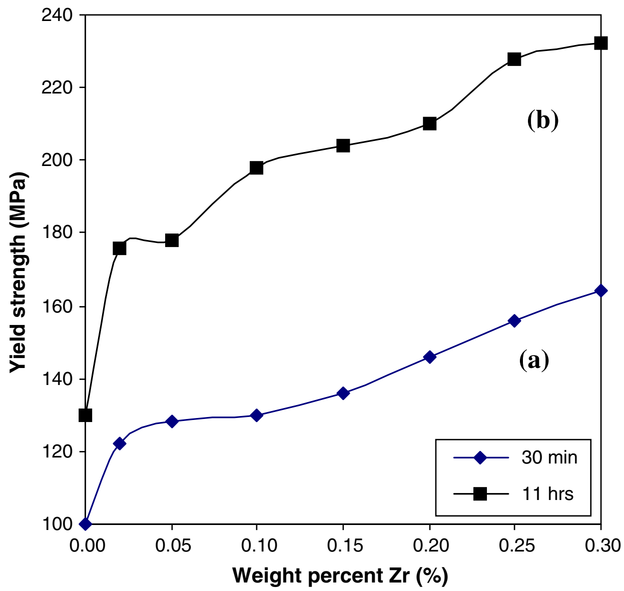

Fig. 3 Yield strength of Al-1.2Si-0.5Mg-0.25Fe with Zr additions: (a) natural aging for 14 days, followed by heat-treatment at 180 °C for 30 min, and (b) natural aging for 14 days, followed by heat-treatment at 180 °C for 11 h

From Eq 1, it is apparent that the pinning process is more effective with increasing precipitates density, which can be achieved by increasing content of Zr in the alloy.

From Fig. 7, it can be seen that grain size reduction after heat-treatment for 11 h is not proportional to that of such lengthy aging time when compared to the grain size reduction obtained for the 30 min heat-treatment. However, the strengthening from heat-treatment of 11 h is rather large, indicating that the grain size strengthening effect due to the addition of Zr is not as potent as the pinning effect caused by the presence of precipitates.

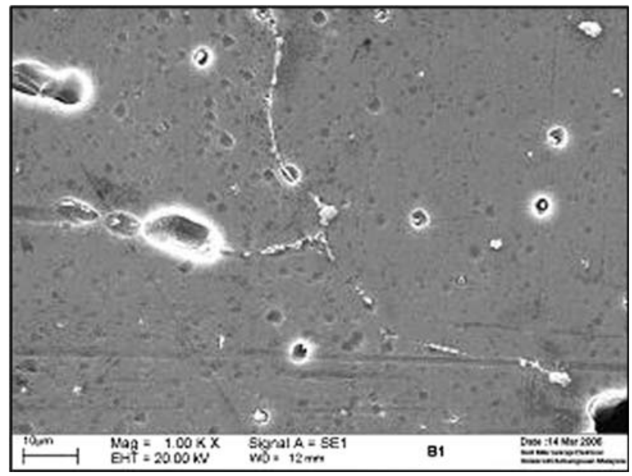

Fig. 5 SEM micrograph of Al-1.2Si-0.5Mg-0.25Fe-0.30Zr alloy heat-treated at 180 °C for 11 h

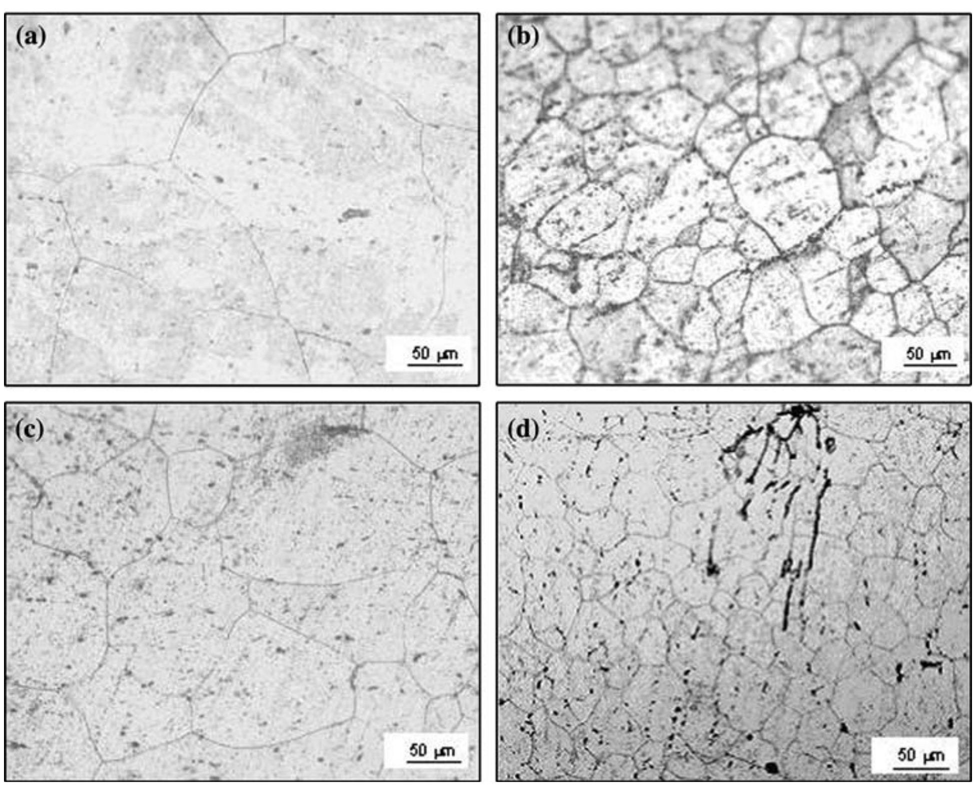

Fig. 4 Microstructures of Al-1.2Si-0.5Mg-0.25Fe alloys with and without Zr heat-treated at 180 °C for 30 min: (a) without Zr, (b) with 0.30 Zr and 11 h (c) without Zr and (d) with 0.30 Zr

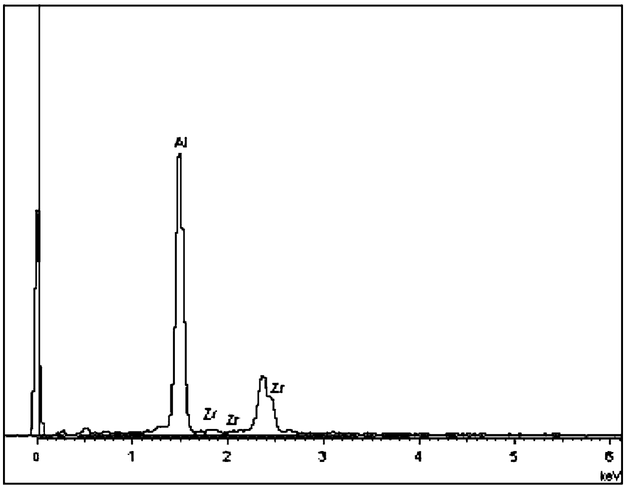

Fig. 6 EDX spectrum on precipitates as seen in microstructure of Al-1.2Si-0.5Mg-0.25Fe-0.30Zr heat-treated at 180 °C for 11 h

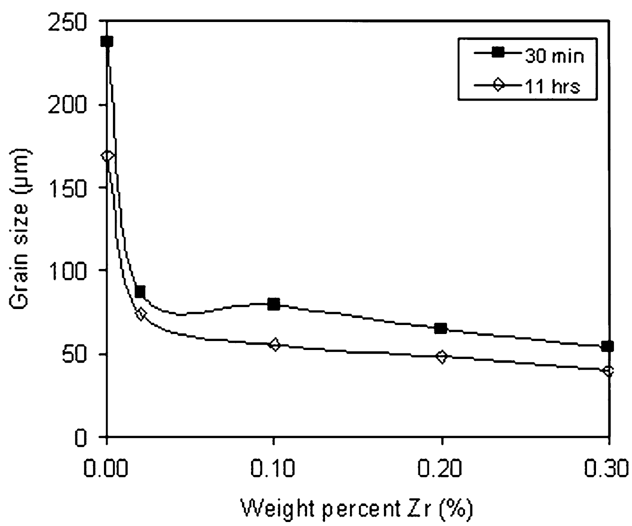

Fig. 7 Variation in grain sizes of Al-1.2Si-0.5Mg-0.25Fe-*x*Zr (*x* = 0-0.30) alloys heat-treated at 180 °C for 30 min and 11 h

The precipitates of an Al-0.18wt.%Zr alloy were found to be of the metastable cubic Al_3Zr with a misfit of $0.8 \pm 0.1\%$ (Ref 20) while Ryum (Ref 14) reported that equilibrium Al_3Zr were found after annealing for several hours at 640 °C. The slight misfit between these particles and the matrix will give rise to stress fields which hinder the movement of dislocations, ultimately causing the increase in hardness of the alloy.

4. Conclusions

Microhardness and ultimate tensile strength of Al-1.2Si-0.5Mg-0.25Fe alloy was increased through additions of Zr, with higher Zr contents giving more superior mechanical properties. Additions of 0.15 wt.% Zr and above to Al-1.2Si-0.5Mg-0.25Fe for the 30 min heat-treatment gave higher values of microhardness and ultimate tensile strength compared to Al-1.2Si-0.5Mg-0.25Fe without Zr additions heat-treated for 11 h. The age-hardening response improvement for the 30 min heat-treatment is attributed to the formation of Zr-containing precipitates and grain refinement in the alloy. The precipitates are believed to have caused the pinning effect on grain boundary and dislocations movements, thus effectively hardening the alloy.

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