RESPONSE OF AS-CAST Al-Zn-Mg-Cu ALLOY WITH Sc, Zr-ADDITION TO ANNEALING WITH CONSTANT HEATING RATE

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Abstract

The as-cast Al-Zn-Mg-Cu-based alloy with and without Sc,Zr-addition was studied during isochronal annealing from room temperature up to 480 °C. Precipitation reactions were studied by differential scanning calorimetry and microhardness measurements. These measurements were compared to microstructure development that was observed by scanning electron microscopy. Microstructure observation proved eutectic phase at grain boundaries in the as-cast state of both alloys. The measurements of positron lifetime (LT) spectroscopy confirmed the presence of Guinier-Preston (GP) zones in the initial state of both studied alloys. Neither structure nor volume fraction of eutectic phase shows changes after annealing up to 480 °C. The distinct changes in microhardness curves as well as in heat flow of the alloys studied are mainly caused by dissolution of GP zones and by formation of the particles of the Al-Zn-Mg-Cu system. The apparent activation energy values of the thermal processes were calculated. The hardening effect after isochronal annealing at temperatures above ~ 300 °C reflects the Sc,Zr-addition.

Keywords: Differential scanning calorimetry, hardness Vickers, Al-Zn-Mg-Cu system, $Al_3(Sc,Zr)$ phase

1. INTRODUCTION

Commercial Al-Zn-Mg-Cu based alloys (7xxx series) are widely used in aircraft and automotive manufacture to produce lightweight vehicles [1-3]. Important properties that must be considered for these applications are strength, ductility, or corrosion and damage tolerance [4].

The precipitation sequence of Al-Zn-Mg-Cu based alloys could be described as: a) supersaturated solid solution (SSS) → GP zones → metastable η' → stable η ($MgZn_2$); b) SSS → GP zones → *T´* phase → *T* phase ($Al_2Zn_3Mg_3$) [5]. GP zones are generally formed during room temperature (RT) ageing or the early stages of artificial ageing. It is accepted that there are two types of GP zones, i.e., GPI and GPII [6]. Generally, GPI and GPII zones can serve as nucleation sites for the metastable η' phase [6]. Metastable η' phase, instead of stable η phase ($MgZn_2$), is believed to be responsible for the peak hardening of Al-Zn-Mg-Cu alloys [6]. Therefore, the η' phase is widely studied in composition and crystal structure [6]. Precipitation sequence mainly depends on ratio of Zn and Mg addition [7,8], if Mg content is higher than Zn content then *T* phase is main hardenable phase [7,8].

Generally, the addition of Sc to the material can effectively improve strength, refine grains and inhibit recrystallization. The improvements of these properties are owing to the formation of Al_3Sc dispersoids [9]. However, the high cost of Sc limits the developing of Al-Zn-Mg-Cu-Sc alloys. To reduce the cost, Zr is added with Sc to reach the equivalent mechanical properties obtained from a high Sc content [9]. In fact, recent work has shown that ternary complex $Al_3(Sc,Zr)$ precipitates produced by additions of Sc and Zr are more stable, and promoting effect in inhibiting recrystallization is more remarkable [9].

2. MATERIALS AND METHODS

The as-cast Al-5.3 wt.% Zn-3.2 wt.% Mg-1.5 wt.% Cu (AlZnMgCu) and Al-5.3 wt.% Zn-3.2 wt.% Mg-1.5 wt.% Cu-0.25 wt.% Sc-0.15 wt.% Zr (AlZnMgCuScZr) alloys were studied. The temperature ranges of phase transformations in the alloys were determined by Vickers microhardness (HV0.5) measurements (measured at RT) during the isochronal annealing with steps of 30 K / 30 min from RT up to 480 °C. The annealing was carried out in an oil bath (up to 240 °C) or in a furnace with protective gas atmosphere (at higher temperatures) and each annealing step was finished by a quenching in water or liquid nitrogen. The thermal characteristics of the alloys studied were measured by differential scanning calorimetry (DSC) performed at heating rates of 1, 2, 5, 10 and 20 $K \cdot min^{-1}$ in the Netzsch DSC 204 F1 Phoenix apparatus. A specimen of mass between 10-20 mg was placed in Al_2O_3 crucibles. Measurements were performed without a reference specimen. Nitrogen flowed at the rate of 40 ml / min as a protective atmosphere.

The measurements were compared to microstructure development observed by scanning electron microscopy (SEM) microscopy. SEM observations were carried out in MIRA I Schottky FE-SEMH microscope to determine the microstructure of the as-cast alloys. The analysis of precipitated phases was complemented by energy-dispersive spectroscopy (EDS) performed by X-ray BRUKER microanalyser. Positron annihilation spectroscopy (PAS) was employed for measurement of positron lifetime (LT). The measurements were performed using ^{22}Na positron source sealed in titanium foil. Detailed information about LT measurements is described in Ref. [10].

3. RESULTS AND DISCUSSION

Microstructure observations proved the eutectic phase at grain boundaries in the as-cast state of the AlZnMgCu and AlZnMgCuScZr alloys. The volume fraction of this phase was very close for both alloys. **Figure 1** shows SEM image of the AlZnMgCuScZr alloy in the initial state. Approximate composition of the eutectic phase (Mg_2ZnCu) was found using EDS for both studied alloys, these results are in agreement with Refs. [11,12].

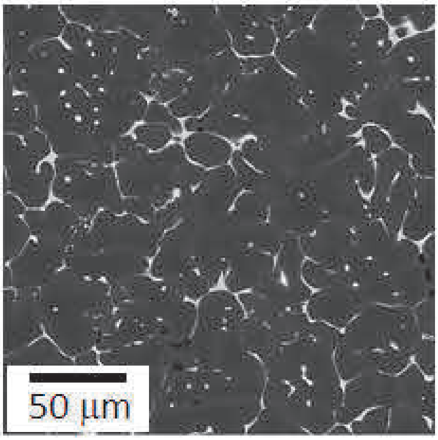

Figure 1 SEM image of the AlZnMgCuScZr alloy in the initial state

The response of microhardness HV0.5 to isochronal step-by-step annealing of the AlZnMgCu and AlZnMgCuScZr alloys are shown in **Figure 2**. The initial values of microhardness are higher for AlZnMgCuScZr (HV0.5 ≈ 128) alloy than for AlZnMgCu alloy (HV0.5 ≈ 117) alloy. The difference is probably caused by higher content of addition in the solution and/or by presence of Sc, Zr-containing particles. At first, the HV0.5 values slowly decrease to a local minimum at ~ 120 °C in both studied alloys. After that the microhardness increases to a maximum at ~ 180 °C in the AlZnMgCu and ~ 210 °C in the AlZnMgCuScZr alloy. After annealing above temperatures 300 °C it can be seen that Sc,Zr-addition has a hardenable effect. HV0.5 values of the alloy without Sc,Zr addition continually decrease up to 480 °C in contrast to the

AlZnMgCuScZr alloy. The microhardness HV0.5 values of the AlZnMgCuScZr alloy are almost constant in the temperature interval 300 °C - 480 °C. Difference between final microhardness values (after annealing up to 480 °C) of AlZnMgCu and AlZnMgCuScZr is nearly of the ΔHV0.5 ≈ 30.

Figure 3 shows the DSC curves of the AlZnMgCu(ScZr) alloys at heating rate of 5 K/min up to 270 °C. One can see two and three thermal processes in these curves, respectively. In the AlZnMgCu alloy the first significant endothermic effect (process I) with minimum at ~ 120 °C is followed by two exothermic effects (process II and process III) with maxima at ~ 200 °C and ~ 230 °C. In the AlZnMgCuScZr alloy the minimum of the endothermic effect (process I) is shifted to higher temperatures than in AlZnMgCu alloy (Δ*t* ~ 20 °C) and this process is followed just by one exothermic effect (process III) with maximum at ~ 230 °C. There were no thermal changes in the DSC curves after annealing up to 270 °C in both alloys.

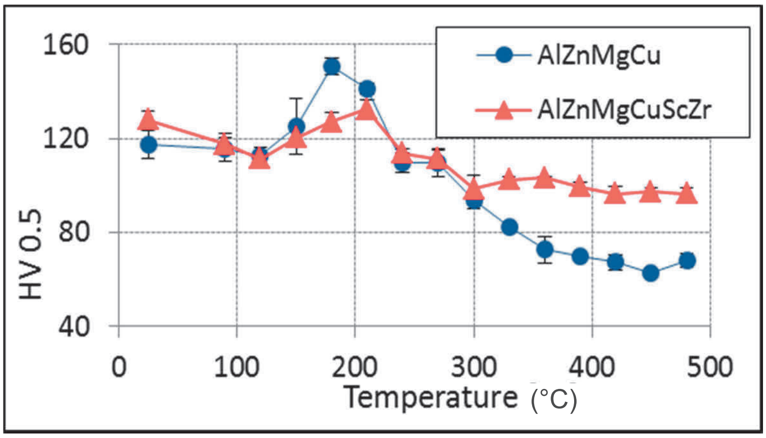

Figure 2 Isochronal annealing curves of hardness ΔHV0.5 changes (measured at RT) of the alloys studied

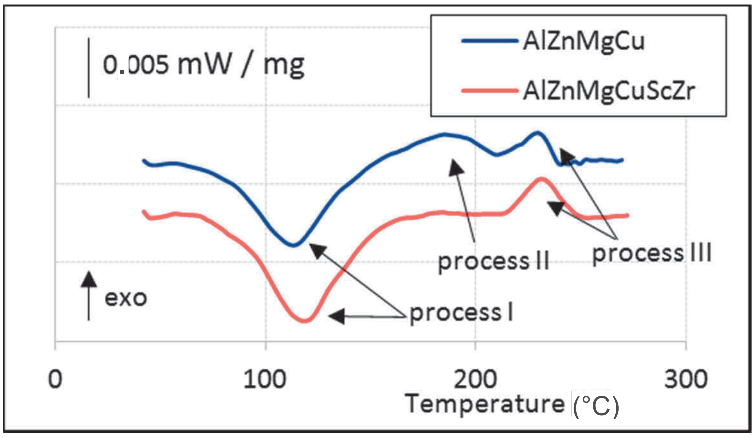

Figure 3 DSC curves in linear heating rate of 5 K/min of the alloys studied up to 270 °C

It is generally known that the solute clusters and/or GP zones are formed in early stages of decomposition of solid solution in Al-based alloys [13]. Ordinarily, these formations affect microhardness changes and heat flow observed by DSC measurements [13, 14]. From comparison of the isochronal annealing curves up to ~ 120 °C (see **Figure 2**) it can be concluded that the GP zones are probably dissolved first. The first endothermic thermal effect (labeled as process I) with maximum at ~120 °C corresponds to the dissolution of GP zones [13, 14]. GP zones were probably formed during the cooling of material after casting [15]. In AlZnMgCu alloy positrons annihilate at traps associated with GP zones and characterized by a positron lifetime of 0.213 ns. This measured value is in a good agreement with the results in [16] and corresponds to the positrons annihilations from GP zones.

The main microhardness increases in both studied alloys are in the temperature interval 120 °C - 240 °C. Higher hardening was observed in the AlZnMgCu alloy (see **Figure 2**). The thermal effects (process II and III in the AlZnMgCu alloy and process III in the AlZnMgCuScZr alloy) are probably connected with hardening in the temperature interval 150 °C - 250 °C. The HV0.5 values of the alloy without the Sc,Zr-addition continually decrease up to 480 °C in contrast to the AlZnMgCuScZr alloy. Microhardness of the AlZnMgCuScZr shows almost no changes in the temperature interval 300 °C - 480 °C. From comparison of isochronal annealing curves of microhardness changes above 300 °C it can be concluded that the Sc,Zr-addition has a significant hardenable effect. The same results were obtained on Al-Zn-Mg(-Sc-Zr) alloys in the temperature range 320 °C - 480 °C [15] - the Sc,Zr-containing particles precipitate in this temperature range in the AlZnMgScZr alloys [15]. The most likely explanation is (similarly like in the AlZnMgScZr alloys), that coherent $Al_3(Sc,Zr)$ particles precipitate after annealing above 300 °C in the AlZnMgCuScZr alloys. However, these conclusions are necessary to be verified by further microscopic observations. Neither volume fraction nor composition of the eutectic phase was changed after annealing up to 480 °C in both studied alloys.

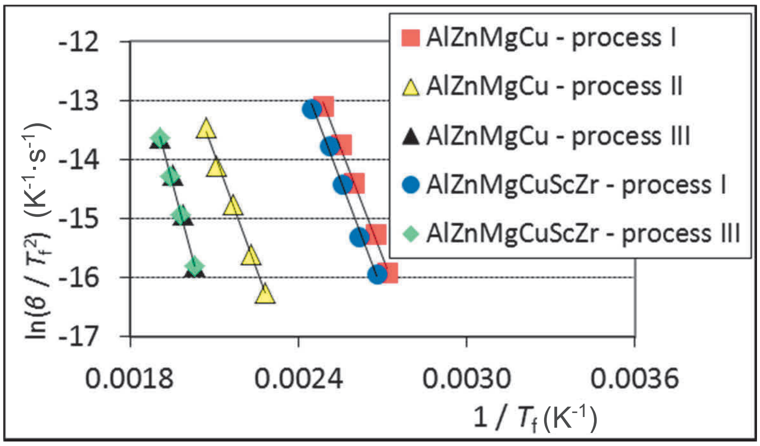

Figure 4 Kissinger plot in the coordinate system of [ln(β / T_f^2); 1 / T_f] of the heat effects in the AlZnMgCu(ScZr) alloys, β is the linear heating rate; T_f is the peak temperature of DSC trace for particular heat effects

On the basis of the obtained results from DSC curves, the apparent activation energy for individual processes (**Figure 4**) can be determined by the Kissinger method [17] as: $Q_I \approx 100$ kJ·mol^{-1}, $Q_{II} \approx 108$ kJ·mol^{-1} and $Q_{III} \approx 150$ kJ·mol^{-1} for the processes I-III, respectively. The values of the activation energy of dissolution of GP zones and the process III are in agreement those reported in [15]. The temperature interval of the dissolution of GP zones is probably slightly influenced by the Sc,Zr-addition. The temperature interval of the process III is connected with the highest hardening in the alloys. There are no changes of this process in the alloy with Sc, Zr-addition.

4. CONCLUSIONS

Results of characterization of the AlZnMgCu and of the AlZnMgCuScZr alloys by microhardness, thermal analysis and microscopy observation can be summarized in the following points:

a) the slight difference in the initial values of microhardness is caused by higher concentration of solutes and/or by presence of Sc,Zr-containing particles,

b) after annealing above temperatures 300 °C the Sc,Zr-addition has hardenable effect,

c) the hardening and thermal changes in the alloys during the annealing are caused by the dissolution of GP zones and precipitation of particles of the Al-Zn-Mg-Cu system,

d) apparent activation energies of the dissolution on GP zones and precipitation processes (exothermic process II and III) were calculated in the alloys studied.

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