RESPONSE OF HOT ROLLED Al-Zn-Mg-Cu-(Sc-Zr) ALLOYS TO ANNEALING WITH CONSTANT HEATING RATE

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Abstract

In the present work hot rolled AlZnMgCu alloys with and without Sc,Zr addition were studied. First, the temperature and time of annealing of hot rolling was looking for. Then, precipitation reactions of hot rolled alloys were studied by differential scanning calorimetry and microhardness measurements during annealing from room temperature up to 450 °C. These measurements were compared to microstructure development that was observed by scanning electron microscope and by electron backscattered diffraction. The grain size was ~ 20 μm in the AlZnMgCuScZr and ~ 1000 μm in the AlZnMgCu alloy. Microstructure observation proved eutectic phase at (sub)grain boundaries. Primary multilayer $Al_3(Sc,Zr)$ particles also precipitated during casting and subsequent cooling in the alloy with Sc,Zr addition. These particles were observed in the alloy with Sc,Zr addition after annealing up to 450 °C, too. In the DSC curves the exothermic process at ~ 200 °C was observed. Activation energy of the process was calculated. There were observed constant values of microhardness (in accuracy of measurements) during annealing up to 450 °C. Higher microhardness values were measured in the alloy with Sc,Zr addition.

Keywords: Al-based alloys, hot rolling, differential scanning calorimetry, SEM, primary $Al_3(Sc,Zr)$

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]. Most of these properties can be controlled through appropriate alloying, processing, or a combination of both. 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 ($Al_2Zn_3Mg_3$) [5-7]. 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 [8]. Generally, GPI and GPII zones can serve as nucleation sites for the metastable η' phase [8]. 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 [8]. Precipitation sequence mainly depends on ratio of Zn and Mg addition [6,9].

Generally, the addition of Sc and/or Zr to the material can effectively improve strength, refine grains and inhibit recrystallization. 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 [1,10]. For the cast ingots, the particles of primary $Al_3(Sc,Zr)$ phase occurs [11-14]. Primary $Al_3(Sc,Zr)$ particles have been investigated in a numerous studies and most of them observed the square or triangle morphological features of primary particles [11-14]. Primary particles were identified as some eutectic structure consisting of a multilayer of Al_3Sc + α-Al + Al_3Sc + ... with a cellural-dendritic mode of growth or consists of Al_3Sc + α-Al + Al_3Zr + α-Al + Al_3Sc + α-Al + Al_3Zr + ... layer [13,14].

2. MATERIALS AND METHODS

Two Al-6.6 wt% Zn-3.0 wt% Mg-1.9 wt% Cu-0.2 wt% Fe (AlZnMgCu) and Al-6.2 wt% Zn-2.9 wt% Mg-1.8 wt% Cu-0.2 wt% Fe-0.23 wt% Sc-0.19 wt% Zr (AlZnMgCuScZr) alloys were studied. The mould cast (MC) samples were annealed at temperature 300 °C for 30, 60 or 120 min and at temperature 350 °C for 30, 60 or 120 min and then hot rolled. Hot rolling was finished by quenching into water at room temperature (RT).

Alloys studied were isochronally annealed (in steps of 30 K/30 min) up to 450 °C. The influence of the annealing on mechanical properties was studied using the Vickers microhardness (HV0.5) measured at RT. Between the measurements the samples were kept in liquid nitrogen to preserve the microstructure developed during the annealing. The thermal behaviour of the alloys was studied using differential scanning calorimetry (DSC) performed at heating rates of 1, 2, 5, 10 and 20 K/min up to 450 °C in the Netzsch DSC 204 F1 Phoenix apparatus. A specimen of mass between 10 - 20 mg was placed in Al_2O_3 crucibles in a dynamic nitrogen atmosphere (40 ml/min).

Electron backscatter diffraction (EBSD) was carried out to determine the recrystallization of the alloy using a JEOL JSM 7600F scanning electron microscope at 20 kV equipped with a Nordly EBSD detector. The samples were polished in an "ELYANA 230" electrolytic polisher by using a 5 vol% $HClO_4$ and 1.5 vol.% HNO_3 solution in C_2H_5OH. The results were processed by HKL Channel 5 software equipment. Microstructure development was observed by scanning electron microscopy (SEM). SEM observations were carried out in JOEL JEM 2000FX, FEI Quanta 200FEG and MIRA I Schottky FE-SEMH microscopes to determine the microstructure of the alloys, respectively. The analysis of precipitated phases was complemented by energy-dispersive spectroscopy (EDS) performed by X-ray BRUKER microanalyser.

3. RESULTS AND DISCUSSION

The mould cast AlZnMgCuScZr alloys were isothermally annealed at 300 °C for 30, 60 and 120 min and at 350 °C for 30, 60 and 120 min. After that, samples were hot rolled with reduction 10 %. Hot rolling was finished by quenching into water at RT. Temperature of isothermal annealing was chosen on the base of previous research of the alloys with Sc,Zr addition [15,16]. In the initial state of the AlZnMgCu(ScZr) alloys annealed at 300 °C/60 min and subsequently annealed at 460 °C/45 min Sc-rich regions and particles of Al-Zn-Mg system were observed [15]. As with AlZnMg(ScZr) alloys we assume precipitation of particles of Al-Zn-Mg-Cu system after isochronal annealing at 300 °C/30 min and/or 350 °C/30 min in the AlZnMgCu(ScZr) alloys.

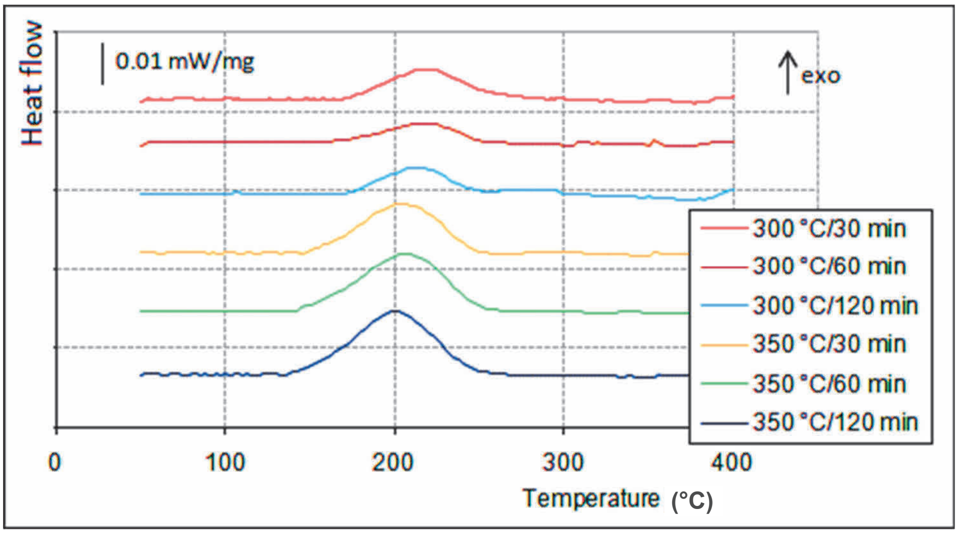

Figure 1 DSC curves of AlZnMgCuScZr alloy isothermally annealed at 300 °C and 350 °C at heating rate of 5 K/min

All hot rolled samples were measured by differential scanning calorimetry at heating rate 5 K/min from RT up to 400 °C (see **Figure 1**). DSC curves of hot rolled materials were compared to each other. In the DSC curves of HR alloys was observed only one exothermic process with maximum at 205 °C - 220 °C. On the base of DSC results, procedure of annealing at 300 °C for 60 min and then hot rolling with reduction 10 % finished by quenching into water at RT was chosen for detailed analysis. This procedure of preparation will be here labelled as HR10.

The grain size of the AlZnMgCu(ScZr) alloys in the initial state was determined by EBSD measurements. The average grain size of the AlZnMgCu mould cast alloy was ~1000 μm and ~20 μm in the AlZnMgCuScZr alloy - see **Figure 2** [17]. It was found that Sc,Zr addition hugely refine grains. SEM and EBSD observation showed that hot rolling of the alloys has no influence on the average grain size in both studied alloys.

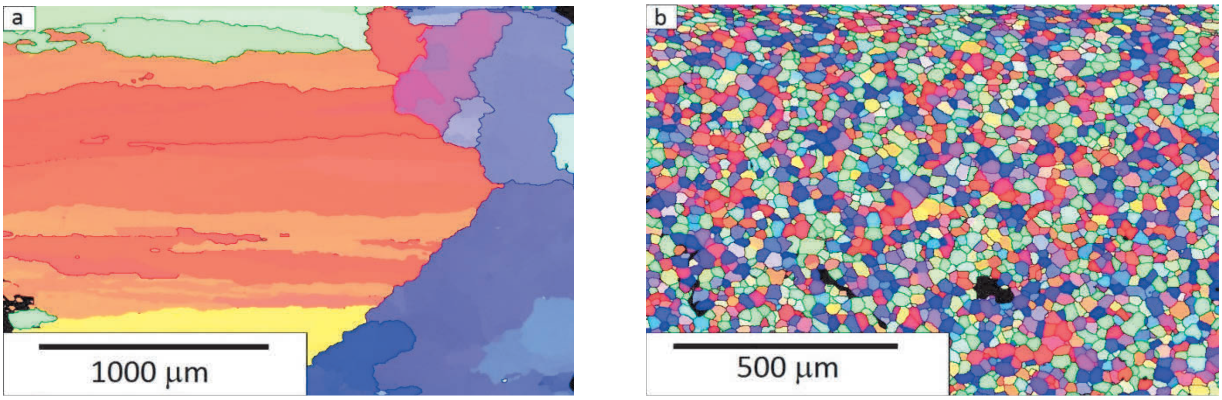

Figure 2 EBSD image of the a) AlZnMgCu, b) AlZnMgCuScZr mould cast alloys

Microstructure observations proved the eutectic phase at grain boundaries in the MC and HR10 AlZnMgCuScZr alloys and the eutectic phase at subgrain boundaries in the MC and HR10 AlZnMgCu alloys. The volume fraction of this phase was very close for both studied alloys. Primary $Al_3(Sc,Zr)$ particles also precipitated inside grains/on the grain boundaries in the MC and HR10 AlZnMgCuScZr alloy. The average size of these particles was observed as ~ 2 μm. There were observed primary rectangular and/or triangular $Al_3(Sc,Zr)$ particles consists of layers both in Sc and Zr in the alloy by SEM and EDS. In contrast to Refs. [13,14] it can be concluded that shell-like layers of primary $Al_3(ScZr)$ particles in the MC and HR10 AlZnMgCuScZr alloys can be probably identified as: $Al_3(Sc,Zr)$ + α-Al + $Al_3(Sc,Zr)$ + α-Al + ...

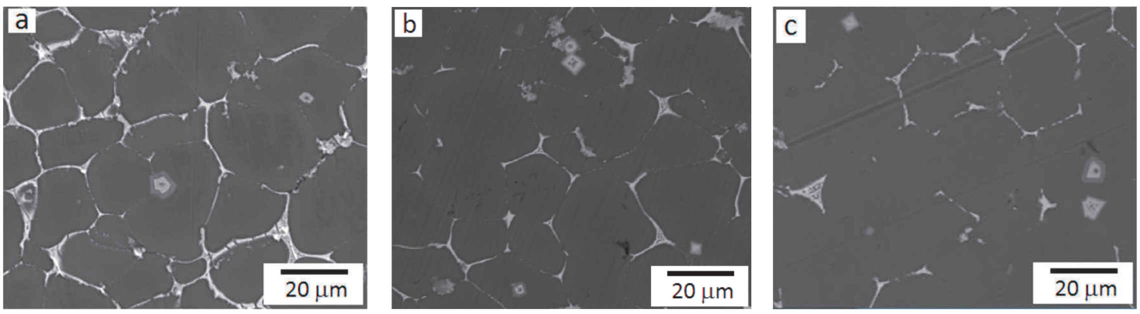

Figure 3 SEM images of AlZnMgCuScZr HR10 a) in the initial state, b) after isochronal annealing up to 210 °C, c) after isochronal annealing up to 450 °C

The evolution of primary particles was observed in the AlZnMgCuScZr HR10 by SEM during the isochronal annealing. AlZnMgCuScZr samples were prepared in four different states: HR10 in the initial state, HR10 after isochronal annealing up to 210 °C, HR10 after isochronal annealing up to 360 °C and HR10 after isochronal annealing up to 450 °C. It was found that the isochronal annealing has no apparent influence neither on amount, size and shape of particles nor on composition of layers of primary $Al_3(Sc,Zr)$ particles. The SEM images of the HR10 AlZnMgCuScZr alloys are shown in **Figure 3**. One can see primary particles of the HR10 alloy, after isochronal annealing up to 210 °C and 450 °C. It can be seen that the eutectic phase at (sub)grain boundary partly dissolved after isochronal annealing up to 450 °C.

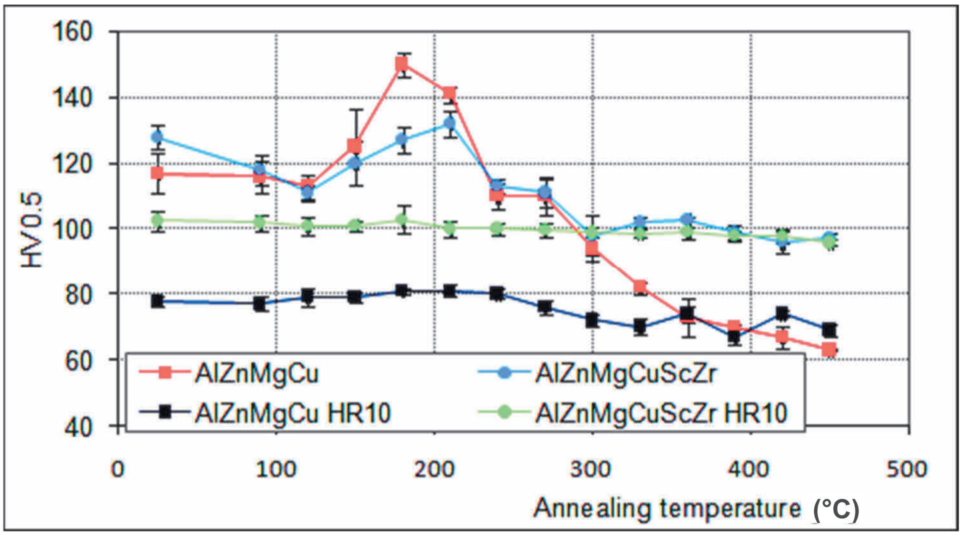

Figure 4 Isochronal annealing curves of microhardness HC0.5 changes measured at RT of the MC and HR10 AlZnMgCu(ScZr) alloys

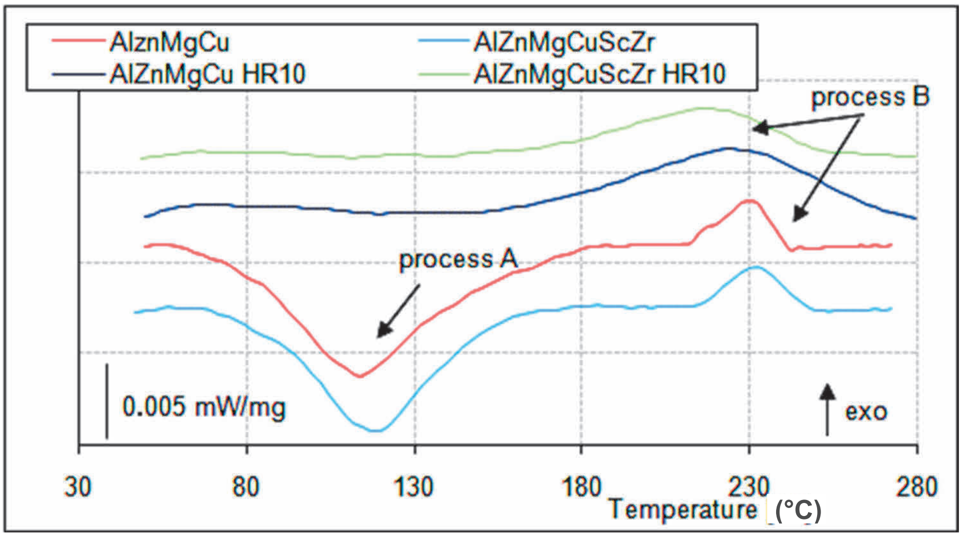

Figure 5 DSC curves at linear heating rate of 5 K/min of the mould cast and HR10 AlZnMgCu(ScZr) alloys

The response of microhardness HV0.5 to isochronal step-by-step annealing of the AlZnMgCu(ScZr) HR10 alloys is shown in **Figure 4**. Higher initial values in the AlZnMgCuScZr HR10 alloy (HV0.5 ≈ 100) than in AlZnMgCu HR10 (HV0.5 ≈ 80) are probably caused by presence of Sc,Zr-containing particles and/or by higher content of addition in the AlZnMgCuScZr alloy. Hot rolling has significant influence on microhardness values during isochronal annealing up to 450 °C. There were observed no changes of microhardness values (in accuracy of measurement) from RT up to 450 °C in HR10 alloys. In the mould cast AlZnMgCuScZr alloy the hardening effect observed after annealing up to 360 °C is caused by the precipitation of secondary $Al_3(Sc,Zr)$ particles [17]. We assume that these secondary particles and/or some particles of Al-Zn-Mg-Cu system precipitated during isothermal annealing at 300 °C/60 min and hot rolling in the alloys studies. The unchanging microhardness values from RT up to 450 °C in HR10 alloys are probably due to the presence of these particles. However, further deeply microstructure research (using transmission electron microscopy) is needed to verify these assumptions.

Figure 5 shows DSC curves of the AlZnMgCu(ScZr) HR10 alloys at heating rate of 5 K/min up to 270 °C. Endothermic process A observed in the mould cast alloys [17] was not observed after hot rolling. This process is connected with the dissolution of the GP zones and/or clusters [17]. Dissolution of the GP zones and/or clusters was probably done during annealing at 300 °C/60 min and subsequent hot rolling. In the DSC curves of HR10 alloys only the exothermic process (process B) was observed. The maximum of this process was at ~218 °C in AlZnMgCuScZr HR10 and at ~225 °C in the AlZnMgCu HR10 at heating rate of 5 K/min. The activation energy of the process B was calculated using Kissinger method as ~150 kJ/mol. Due to the temperature interval of the process B, maxima values and value of activation energy we assume, that process B in the HR10 alloys is caused by precipitation the same particles (particles of Al-Zn-Mg-Cu system [17]) as in mould cast alloys. For verifying the assumption the further research is needed.

4. CONCLUSIONS

Results of the characterization of the hot rolled alloys can be summarizes in the following points:

a) Using EBSD was determined grain size as ~ 1000 μm in the AlZnMgCu HR10 and as ~20 μm in the AlZnMgCuScZr HR10 alloy.

b) The eutectic phase was observed at (sub)grain boundary in the MC and HR10 alloys.

c) Primary multilayer Al_3(Sc,Zr) particles were observed in the AlZnMgCuScZr MC and HR10 alloy. Isochronal annealing up to 450 °C has no influence on these particles.

d) There were observed no changes in microhardness values of the HR10 alloys from RT up to 450 °C. Higher microhardness values were observed in the AlZnMgCuScZr HR10 alloy probably due to presence of Sc and Zr particles and/or higher content of addition in this alloy.

e) One exothermic process with maximum at ~218 °C in the AlZnMgCuScZr HR10 and ~225 °C in the AlZnMgCu HR10 alloy at heating rate of 5 K/min was observed. This process is probably caused by precipitation of particles of Al-Zn-Mg-Cu system.

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