EFFECT OF HEAT TREATMENT ON MECHANICAL, THERMAL AND ELECTRICAL PROPERTIES OF Al-Zn-Mg-Cu(-Sc-Zr) ALLOYS

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Abstract

The as-cast commercial Al-6 wt% Zn-2.5 wt% Mg-1.3 wt% Cu-0.8 wt% Fe, Si, Cr (AA7075) and AA7075-ScZr (0.19 wt% Sc-0.06 wt% Zr) alloys were investigated during isochronal annealing from room temperature up to 450 °C. Precipitation reactions were studied by microhardness, conductivity measurements and differential scanning calorimetry. Microstructure observation by scanning electron microscopy and transmission electron microscopy proved the Zn, Mg, Cu-containing eutectic phase at grain boundaries in the as-cast state of both alloys. The melting of this eutectic phase was observed for both alloys at ~ 480 °C in the DSC curves at heating rate of 20 K/min. The distinct changes in microhardness and conductivity curves as well as in heat flow of the alloys studied are mainly caused by dissolution of GP zones and by formation of the metastable phase particles of the Al-Zn-Mg-Cu system. The hardening effect after isochronal annealing at temperatures above ~ 270 °C reflects the Sc, Zr-addition in the AA7075-ScZr alloy - the secondary $Al_3(Sc,Zr)$ particles precipitation causes a pronounced hardening in the temperature range of 270-450 °C. The eutectic Zn,Mg,Cu-containing phase partly disappeared after the isochronal annealing at 450 °C as it was observed by scanning electron microscopy.

Keywords: AA7xxx series, DSC, SEM, phase transformation, $Al_3(Sc,Zr)$ phase

1. INTRODUCTION

Al- and Mg-based alloys are preferred materials for automotive manufacture to produce lightweight vehicles [1-3]. Sc-addition can effectively improve the strength, refine grains and inhibit recrystallization [1]. A small addition of Sc has a positive impact on mechanical properties of Al-based alloys due to precipitation of dispersed Al_3Sc particles [1]. The high price of Sc is prohibitive for extended commercial applications of Sc-containing aluminium alloys. To reduce the cost Zr is added to reach comparable mechanical properties obtained from the Sc content [1]. The promising results are related to the formation of a dense and homogeneous distribution of the $L1_2$-secondary structured $Al_3(Sc,Zr)$ precipitates, which lead to an efficient control of the microstructure of the alloys [1,4-8]. Commercial Al-Zn-Mg-Cu-based alloys (7xxx series) are widely used in aircraft and automotive industry to produce lightweight vehicles [1-3,9-12]. In terms of precipitation and dissolution of phases, the isothermal sequence of the Al-Zn-Mg-Cu system is commonly used as [9-17]: supersaturated solid solution (SSS) → clusters and/or Guinier-Preston (GP) zones → semicoherent η' phase (hexagonal structure) → incoherent η phase ($MgZn_2$, hexagonal structure). Clusters and/or GP zones are usually formed during ageing at room temperature (RT) or during early stages of artificial ageing [12,13,17].

The aim of the present work was to study the phase transformations in mould-cast Al-Zn-Mg-Cu alloys with and without Sc,Zr-addition. The results of conductivity and microhardness response to the isochronal annealing and thermal changes were compared to the microstructure development.

2. MATERIALS AND METHODS

The as-cast commercial Al-6 wt% Zn-2.6 wt% Mg-1.4 wt% Cu-0.8 wt% Fe,Si,Cr (AA7075) and AA7075-ScZr (0.19 wt% Sc-0.06 wt% Zr) alloys were studied. The chemical composition in wt% is listed in **Table 1**.

Table 1 Chemical composition (in wt%) of the studied alloys

Alloy/Element	Zn	Mg	Cu	Fe	Si	Cr	Mn	Ti	Sc	Zr
AA7075	5.50	2.57	1.35	0.33	0.28	0.20	0.22	-	-	-
AA7075-ScZr	5.88	2.45	1.32	0.37	0.35	0.19	0.17	0.026	0.19	0.06

The temperature ranges of phase transformations in the alloys were determined by electrical conductivity and microhardness measurements (both measured at 295 K) from room temperature (RT) up to 450 °C. The electrical conductivity (eddy current method) measurements were done at RT. Vickers microhardness (HV1) testing was performed in Wolpert Wilson Micro Vickers 401MVD at ~ 10 °C. The measurement of the microhardness values started no longer than 60 s after the quenching.

The annealing was carried out in an oil bath (up to 240 °C) or in a furnace with protective atmosphere (at higher temperatures); each annealing step was finished by a quenching. Samples of the alloys for conductivity and microhardness measurements were studied during the isochronal annealing procedure (steps of 30 K / 30 min) which was performed exactly in the same way as described in Refs. [3,17]. The samples were kept in liquid nitrogen between measurements to preserve the microstructure developed during the annealing.

The thermal behaviour of the alloys was studied by differential scanning calorimetry (DSC) performed at heating rate of 20 $K \cdot min^{-1}$ up to 510 °C in the Netzsch DSC 204 F1 Phoenix apparatus. A specimen of mass between 10-20 mg was placed in Al_2O_3 crucibles. Nitrogen flowed at the rate of 40 ml/min as a protective atmosphere.

The measurements mentioned above were compared to microstructure development observed by optical microscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM and SEM observations were carried out in JOEL JEM 2000FX and MIRA I Schottky FE-SEMH microscopes to determine the microstructure of the as-cast alloys, respectively. The structure of the alloys was studied by metallographic microscope Jena Metaval 85618 (OM). Samples were prepared by polishing in “Flick Etch Solution” (1.3 vol% HCl and 0.87 vol% HF solution in distilled water).The analysis of precipitated phases was complemented by energy-dispersive spectroscopy (EDS) performed by X-ray BRUKER microanalyser. The specimens for TEM and SEM were annealed by the same procedure as those for the conductivity and microhardness measurements.

3. RESULTS AND DISSCUSION

The response of the electrical conductivity and microhardness HV1 changes to step-by-step isochronal annealing in the AA7075 and AA7075-ScZr alloys are shown in **Figure 1** and **Figure 2**, respectively. The initial values of absolute conductivity values were measured as ~ 15.1 $mS \cdot m^{-1}$ for the AA7075 alloy and ~ 14.3 $mS \cdot m^{-1}$ for the AA7075-ScZr alloy, respectively. Higher initial conductivity value is probably caused by a lower content of the solutes in the AA7075 alloy. The different initial values of microhardness HV1 of the AA7075-ScZr alloy compared to the alloy without Sc, Zr-addition probably reflect also an effect of solutes content.

The electrical conductivity curve for both alloys exhibits three stages. A slight increase of conductivity in the I-stage in the temperature range up to 150 °C is followed by a sharper increase in the II-stage reaching a maximum at ~ 300 °C. Above 300 °C (III-stage) the conductivity annealing curves continuously decrease up to the end of the annealing. The microhardness annealing curves decrease in the I-stage to a local minimum at 150 °C. The hardening peak between temperatures 150 °C and 210 °C corresponds to the increase of conductivity in the **II**-stage. Above 240 °C the HV values of the AA7075 alloy decrease significantly in comparison to only a slight decrease of the HV values of the AA7075-ScZr alloy. The difference in microhardness between the alloys isochronally annealed up to 360 °C is ∆HV1 ~ 35.

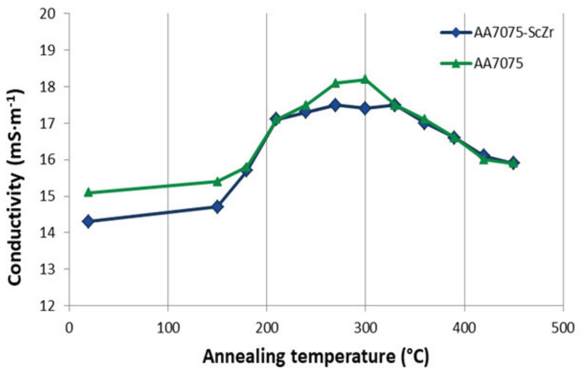

Figure 1 Isochronal annealing curves of electrical conductivity (measured at 295 K) of the AA7075 and AA7075-ScZr alloys

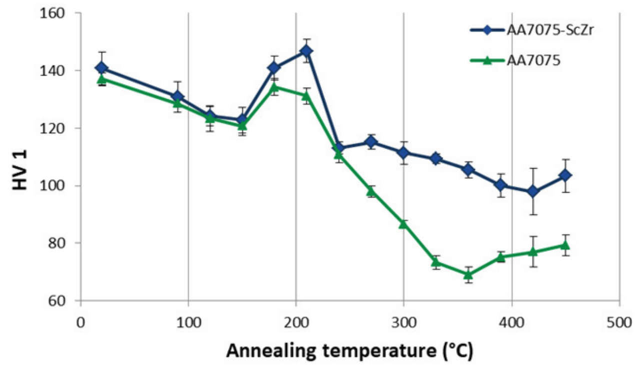

Figure 2 Isochronal annealing curves of microhardness HV 1 (measured at RT) of the alloys studied

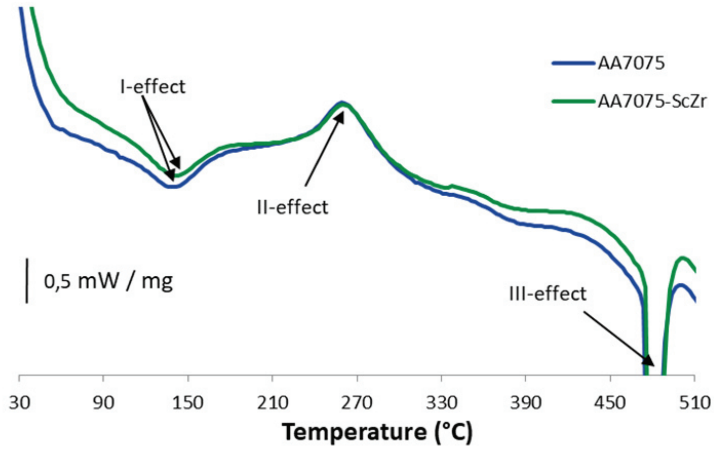

Figure 3 DSC curves in linear heating rate of 20 K/min of the AA7075 and AA7075-ScZr alloys

The DSC measurements in heating rate of 20 K/min were done in the alloys in addition to conductivity and microhardness HV1 measurements. Three processes in both alloys were detected: an endothermic process (labelled as **I**-effect) followed by an exothermic process (**II**-effect) and the melting (**III**-effect), see **Figure 3**. The maximum heat flow was observed at characteristic temperatures T_f equal to ~ 139 °C, ~ 260 °C and ~ 479 °C for the AA7075 alloy and ~ 140 °C, ~ 260 °C and ~ 482 °C for the AA7075-ScZr alloy, respectively. It is good to notice that the temperature of the **I**-effect corresponds to the increase of conductivity and decrease of microhardness in the **I**-stage. Also the temperature of the **II**-effect corresponds to the increase of conductivity and the HV values in the **II**-stage.

SEM and EDS proved the Zn, Mg, Cu-containing eutectic phase at grain boundaries in the as-cast state of the both alloys. An overview of the alloys in the as-cast state is shown in **Figures 4, 5** and **6**. The melting (**III**-effect) of this eutectic phase was observed at ~ 480 °C (see **Figure 3**). Only small density of dislocations in grain interiors in the as-cast state of the alloys was observed by TEM. No other phases and/or particles (except the mentioned eutectic phase) were detected.

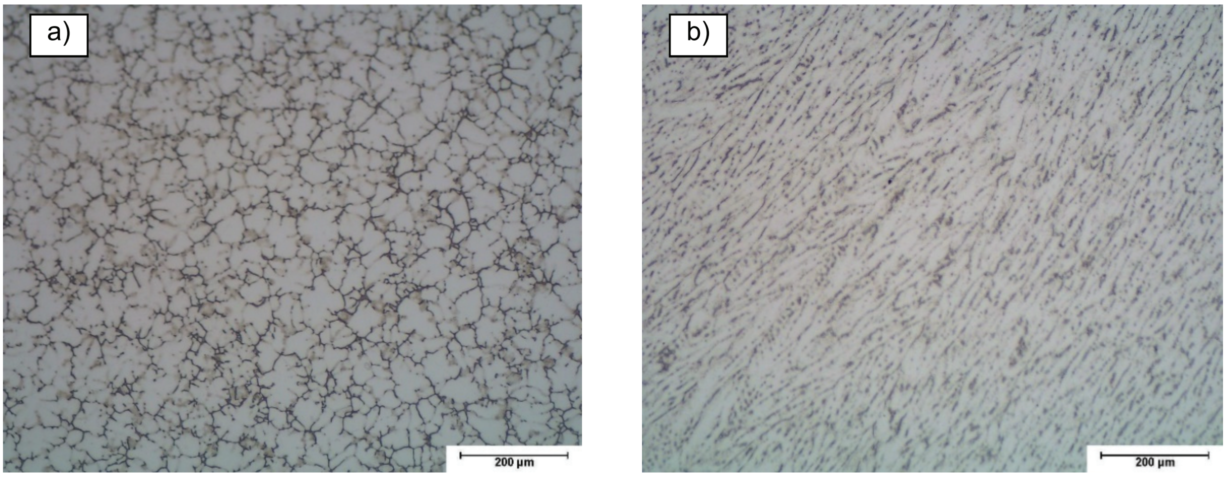

Figure 4 OM image of the a) AA7075 alloy and b) AA7075-ScZr alloy in the as-cast state

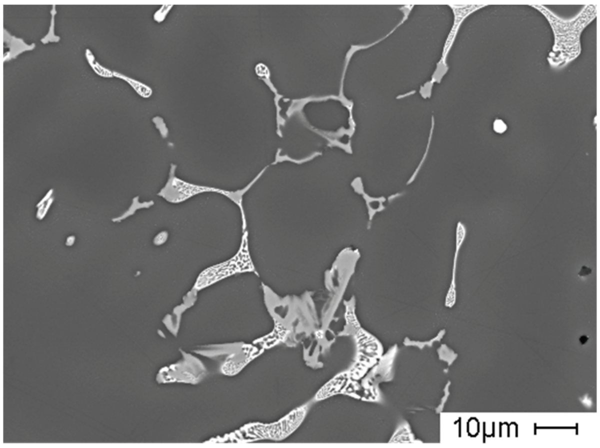

Figure 5 SEM image of the AA7075 alloy in the as-cast state

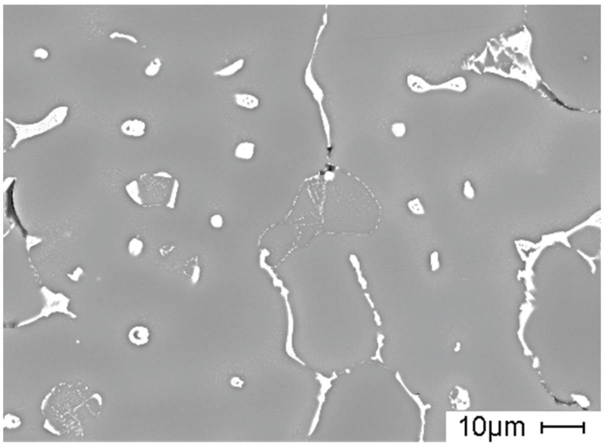

Figure 6 SEM image of the AA7075-ScZr alloy in the as-cast state

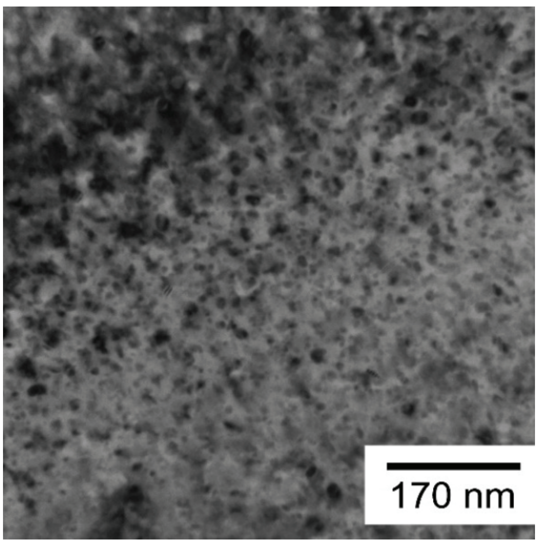

Figure 7 Particles of the Al-Zn-Mg-Cu system (AA7075 alloy annealed up to 220 °C)

Based on our previous study [17], it can be assumed that clusters and/or GP zones are being formed during cooling after casting and subsequent natural aging of the materials studied and subsequently dissolved during isochronal annealing. This is apparently the reason for the slight increase of conductivity and simultaneous decrease of microhardness observed within the temperature range of I-stage and corresponding heat I-effect. The hardening peak observed during the II-stage of isochronal annealing was probably caused by metastable η' phase precipitation, which is typical hardening phase in Al-Zn-Mg(-Cu)-based alloys [14,16,17]. TEM image of the AA7075 alloy isochronally annealed up to 220 °C is shown in **Figure 7** where a dense dispersion of the particles can be observed.

Thus, the pronounced exothermal II-effect in DSC curves (see **Figure 3**) can be imputed to supposed precipitation of particles of the η' phase. Hence, the decrease of the HV values of the AA7075 alloy during annealing above 300 °C is probably caused by coarsening and subsequent dissolution of these particles. The comparison of the HV annealing curves (see **Figure 2**) indicates a favourable effect of the Sc, Zr-addition on hardening character. A very probable explanation is that during annealing at temperatures above ~ 330 °C precipitate $Al_3(Sc,Zr)$ particles, as it was shown in case of alloys of the Al-Zn-Mg-Sc-Zr system [17]. The eutectic Zn, Mg, Cu-containing phase partly disappeared after the isochronal annealing at 450 °C as it was observed by scanning electron microscopy.

4. CONCLUSIONS

Results of characterization of the commercial AA7075 alloy with Sc, Zr-addition studied by electrical conductivity, thermal analysis, microhardness testing and electron microscopy, can be summarized in the following points:

- Zn, Mg, Cu-containing eutectic phase at grain boundaries in the as-cast state of both alloys was observed, a melting of this eutectic phase was observed for both alloys at ~ 480 °C.
- Changes in microhardness and conductivity curves as well as in heat flow of the alloys studied are mainly caused by dissolution of GP zones and by formation of the metastable phase particles of the Al-Zn-Mg-Cu system.
- The hardening peak observed in temperature of 150-210 °C very probably stems from precipitation of the metastable η' phase particles.
- The hardening effect after isochronal annealing at temperatures above ~ 270 °C reflects the Sc, Zr-addition in the AA7075-ScZr alloy.

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