RESPONSE OF AS-CAST Al-Zn-Mg ALLOY WITH AND WITHOUT Sc, Zr ADDITION TO ANNEALING WITH CONSTANT HEATING RATE

KODETOVÁ Veronika[1], VLACH Martin[1], SMOLA Bohumil[1], MÁLEK Jaroslav[2], KEKULE Tomáš[1], KUDRNOVÁ Hana[1]

[1]Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic, EU, veronika.kodetova@seznam.cz

[2]Czech Technical University in Prague, Faculty of Mechanical Engineering, Prague, Czech Republic, EU

Abstract

The as-cast Al-Zn-Mg-based alloy with and without Sc, Zr-addition was investigated during isochronal annealing from room temperature up to 480 °C. Precipitation reactions were studied by electrical resistometry, microhardness measurements and differential scanning calorimetry. These measurements were compared to microstructure development that was observed by optical microscopy and transmission and scanning electron microscopy. Microstructure observation proved the Zn, Mg-containing eutectic phase at grain boundaries in the as-cast state of both alloys. It was also observed that the Sc, Zr-content is not homogeneously distributed but concentrated in randomly localized matrix regions and together with Zn and Mg in the particles at grain boundaries. The distinct changes in resistivity and microhardness curves as well as in heat flow of the alloys studied are mainly caused by dissolution of the Zn, Mg-containing Guinier-Preston (GP) zones and subsequent precipitation of the metastable particles from the Al-Zn-Mg system. The hardening effect after isochronal annealing at temperatures above ~ 280 °C reflects the Sc, Zr-addition. The eutectic Zn, Mg-containing phase partly disappeared during the isochronal annealing above this temperature. Precipitation of the Mn,Fe-contaning particles was also observed in the alloys. The apparent activation energy values were calculated regardless of Sc, Zr- addition as: dissolution of the GP zones (~ 100 kJ/mol) and formation of the metastable Zn, Mg-containing particles (~ 100 kJ/mol). Melting of the eutectic phase was observed by differential scanning calorimetry at ~ 475 °C.

Keywords: Electrical resistivity, DSC, TEM, early precipitation stages, $Al_3(Sc,Zr)$ phase

1. INTRODUCTION

Al- and Mg-based alloys are very preferred for automotive manufacture to produce lightweight vehicles [1-3]. 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]. An attractive and veritable advantage is that the phase does not change the material density and it is unusually stable with respect to coarsening [1]. After designing Al-Sc-Zr-based alloys, typically ~ 0.2 wt.% Sc, ~ 0.1 wt.% Zr, an effort was put into investigation of the effect of Sc and Zr addition to commercial Al hardenable alloys [1, 4]. A simultaneous addition of Sc and Zr is probably the most effective element combination having an antirecrystallization impact in Al due to precipitation of the $Al_3(Sc,Zr)$ phase with $L1_2$ structure [1, 4]. The formation of the $Al_3(Sc,Zr)$ nano-precipitates in Al-based alloys have been studied in several recent articles using conventional and high-resolution transmission electron microscopy (e.g. Ref. [5]). Mechanical properties of the commercial Al-based alloys (AA7xxx series) logically depend on chemical composition, mainly on Zn and Mg content and on the heat treatment of the studied alloys [6-9]. Decomposition sequence of the Al-Zn-Mg system is known as [6-9]: solid solution → Guinier-Preston (GP) zones → η' phase → η ($MgZn_2$). Generally, GP zones can be formed as precursors to the metastable η' phase. The η'-phase precipitates play major role on the strengthening effect in the Al-Zn-Mg-based alloy. But the formation of the η' precipitates depends on the alloy composition, artificial ageing temperature, ageing time, heat treatment etc. [6, 7]. Despite the fact that the AA7xxx series alloys are some of the most extensively used Al-based alloys

[1, 2], relatively few studies have investigated the mechanical and thermal properties of the Al-Mg-Zn-based alloys with Sc, Zr-addition. A tailoring of the material with required properties is very difficult without the detailed knowledge of precipitation processes and the role of Sc and Zr in microstructure development.

2. MATERIALS AND METHODS

The as-cast Al-5.3 wt.% Zn-3.2 wt.% Mg (AlZnMg) and Al-5.3 wt.% Zn-3.2 wt.% Mg-0.2 wt.% Sc-0.1 wt.% Zr (AlZnMgScZr) alloys were studied. The temperature ranges of phase transformations in the alloys were determined by electrical resistivity and microhardness (HV1) measurements during the isochronal annealing with steps of 30 K/30 min from room temperature (RT) up to 480 °C. The annealing was carried out in an oil bath (up to 240 °C) or in a furnace with protective atmosphere (at higher temperatures) and each annealing step was finished by quenching into liquid nitrogen or water, respectively. The sample was kept in liquid nitrogen between measurements to preserve the microstructure developed during the annealing.

Relative electrical resistivity changes $\Delta\rho/\rho_0$ were obtained to within an accuracy of 10^{-4} (ρ_0 is the value of resistivity in the initial state). Resistivity was measured by the DC four-point method with a dummy specimen in series. The influence of parasitic thermoelectromotive force was suppressed by current reversal. The influence of isochronal annealing on mechanical properties was studied using Vickers microhardness measurements following the same annealing procedure as in the resistivity measurements. The thermal behaviour of the alloys was studied using by differential scanning calorimetry (DSC) performed at heating rates of 1, 2, 5, 10, 20 and 30 $K\cdot min^{-1}$ in the Netzsch DSC 204 F1 Phoenix apparatus. The temperature range of the measurements was from RT up to 480 °C at heating rate of 20 K/min and up to 460 °C at the other heating rates. 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 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 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 electrical resistivity.

3. RESULTS AND DISCUSSION

The response of the relative resistivity changes $\Delta\rho/\rho_0$ and microhardness HV1 measurements to step-by-step isochronal annealing in the AlZnMg(ScZr) alloys are shown in **Figure 1**. The initial values of relative resistivity were calculated as ~ 27 nΩ·m for the AlZnMg alloy and ~ 30 nΩ·m for the AlZnMgScZr alloy, respectively. Higher initial value of the resistivity is probably caused by the Sc and Zr addition and also by higher content of the Mn and Fe in the AlZnMgScZr alloy (as detected by EDS). The electrical resistivity curves show significant decrease of the $\Delta\rho/\rho_0$ to a minimum at ~ 300 °C. Then the electrical resistivity increases for both alloys. One can see a small warp (at ~ 360 °C) which is followed by rapid increase of the relative resistivity up to the initial values. The initial microhardness values of the AlZnMg(ScZr) are comparable for both studied alloys HV1 ≈ 125 - see **Figure 1**. At first, the HV1 values slowly decrease to a local minimum at 120 °C. After that the microhardness HV1 increases to a maximum at ~ 200 °C. The temperature range of the hardening peak (at ~ 200 °C) corresponds to the temperature of the fastest decrease of relative resistivity changes. It can be seen that the Sc, Zr-addition has almost no effect on microhardness changes up to 270 °C. But after that the HV1 values of the alloy without the Sc,Zr-addition continually decrease up to 360 °C in contrast to the AlZnMgScZr alloy. Difference between AlZnMg and AlZnMgScZr alloy is nearly of the ΔHV1 ≈ 22. The microhardness HV1 values of the AlZnMgScZr alloy are almost constant at temperatures after the annealing above ~ 330 °C.

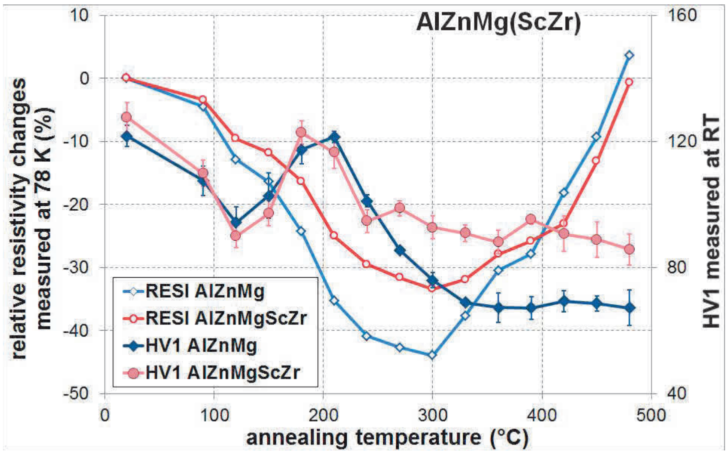

Figure 1 Isochronal annealing curves of relative resistivity changes (measured at 78 K) and microhardness HV1 changes (measured at RT) with standard deviation

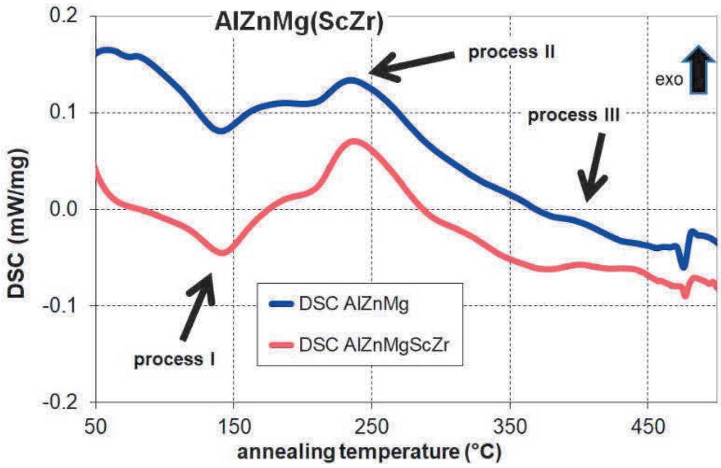

Figure 2 DSC curves in linear heating rate 20 K/min of the AlZnMg(ScZr) alloys up to 480 °C

Figure 2 shows DSC curves of the AlZnMg(ScZr) alloy at heating rate of 20 K/min up to 480 °C. Both curves show similar trend. The first endothermic effect (process I) at ~ 140 °C is followed by significant exothermic effect (process II) in the temperature range 200-270 °C. One can see the insignificant exothermic process (labelled as III) at ~ 400 °C.

SEM proved the Zn,Mg-containing eutectic phase at grain boundaries in the as-cast state of both alloys. The melting of this eutectic phase was observed at ~ 475 °C in both alloys (see **Figure 2**). It was also observed in the initial state that the Sc,Zr-content in the AlZnMgScZr alloy is not homogeneously distributed but concentrated in randomly localized matrix regions and together with Zn and Mg in the particles at grain boundaries.

Generally, ageing processes in the Al alloys of the Al-Zn-Mg-based system are complex and the decomposition of saturated solid solutions obtained by quenching takes place in several stages [6-9]. Typically, coherent Guinier-Preston (GP) zones and clusters formation precede the formation of the semicoherent intermediate precipitates and incoherent equilibrium precipitates. In general, early precipitation stages can be universally abundant in Al-based alloys and are known to affect the resistivity and microhardness [1]. Many authors have attempted to explain changes of electrical resistivity and microhardness at the beginning of the precipitation kinetics in the Al-based alloys due to the formation of the GP zones. From comparison of the isochronal annealing and DSC curves up to ~ 150 °C (see **Figure 2**) it can be concluded that the GP zones are dissolved first. Dissolution of the GP zones leads to the resistivity and microhardness decrease as well as to the endothermic effect (labelled as thermal process I). The formation of the GP zones was probably done during the cooling of material after casting. The Sc,Zr-addition does not significantly influence the formation of GP zones considering small concentration of the Sc,Zr disolved in the matrix (because of the large amount of these additions is in the Zn,Mg-rich particles around grain boundaries).

The main resistivity decreases and microhardness increases in both studied alloys (see **Figure 1**) in the temperature range of 150-300 °C is due to precipitation of the metastable η'-phase particles. In the Al-Zn-Mg(-Cu) alloys the metastable η' phase is typical hardening phase [6-9]. **Figure 3** shows TEM image of the AlZnMg alloy isochronally annealed up to 220 °C. Therefore, the significant exothermic effect (process II) in DSC curves (see **Figure 2**) is connected with this process.

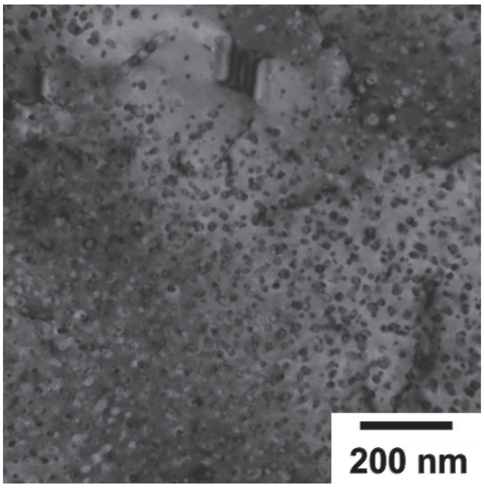

Figure 3 TEM image of the AlZnMg alloy isochronally annealed up to 220 °C. See particles of the η´ phase

After annealing up to 360 °C microstructure observation proved presence of particles of the stable η phase in both studied alloys. Moreover, particles with Mn,Fe-content were observed in the AlZnMgScZr alloy. The presence of these particles is probably connected with higher content of Mn and Fe addition in the alloy than in the AlZnMg alloy. It can be mentioned that the Mn and Fe addition are traditionally contained in commercial alloys of the AA7xxx series. Precipitation of the both mentioned phases does not lead to the hardening [6-9]. Thus, the hardening effect after isochronal annealing in the AlZnMgScZr alloy at temperatures above ~ 280 °C probably reflects the Sc,Zr-addition which is typical for the Al-Sc-Zr-based alloys [1, 4, 5]. The particle precipitation of the stable η and Mn,Fe-containing particles is probably the reason of the undulating of the resistivity curves (**Figure 1**) and the existence of the process III in the DSC curves (see **Figure 2**) at these temperatures. But this process can be also affected by a weak additional precipitation of the Al_3(Sc,Zr) particles in the AlZnMgScZr alloy. Annealing above 390 °C also led to the dissolution of the particles from the Al-Zn-Mg system. Furthermore, the eutectic Zn,Mg-containing phase partly disappeared during the isochronal annealing above this temperature (as it was observed by SEM). It is mainly connected with the resistivity increase above ~ 360 °C.

The DSC measurements were done in the alloys in addition to resistometry and microhardness measurements. One endothermic effect (process I) and two exothermic effects (process II and III) were detected in the samples. The characteristic temperatures T_f of the minimum and maximum heat flow of the process I and II for the heating rate of 1 K/min was observed at ~ 115 °C and ~ 185 °C, respectively. The characteristic temperature T_f of maximum heat flow of the process III was observed at ~ 370 °C for the alloys at heating rate of 2 K/min. This peak was observed at heating rates of 2-20 K/min only. Generally, the thermal response of this process was very weak. One can see that the DSC peaks of the process I and II correspond to the resistivity decrease during annealing up to 300 °C - compare **Figures 1** and **2**. The temperatures T_f shifted to higher temperatures with increasing heating rate. On the basis of the obtained results, the apparent activation energy for individual processes (**Figure 4**) by the Kissinger method [10] can be determined: Q_I = (105 ± 20) kJ·mol^{-1}, Q_{II} = (107 ± 10) kJ·mol^{-1} and Q_{III} = (150 ± 30) kJ·mol^{-1} for the processes **I-III**, respectively.

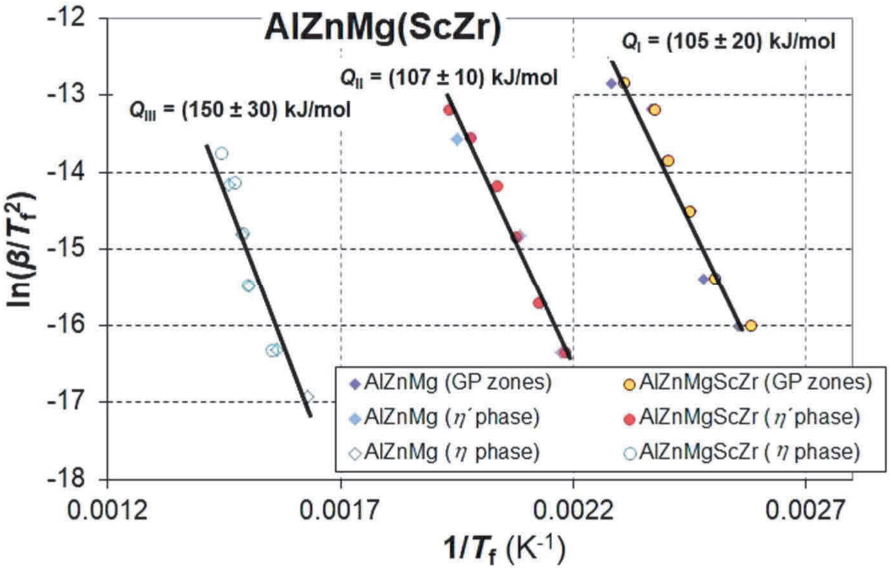

Figure 4 Kissinger plot in the coordinate system of [ln(β/T_f^2); 1/T_f] of the heat effects in the AlZnMg(ScZr) alloys, β is the linear heating rate [K·s^{-1}] ; T_f is the peak temperature of DSC trace for particular heat effects

The calculated range of the activation energy of the dissolution of the GP zones in our work (85 - 125 kJ·mol^{-1}) is higher than that for the GP zones formation (~ 60 kJ·mol^{-1} [7]) in the Al-Mg-Zn-based alloys. The obtained value is comparable to the diffusion activation energies of both Zn and Mg in Al of ~ 120 kJ·mol^{-1} [7]. The obtained average activation energy of η'-phase precipitation calculated as ~ 107 kJ·mol^{-1} is lower than the diffusion energies of both Zn and Mg in Al. The value agrees within accuracy with the apparent activation energy for precipitation of the η'-phase (80-100 kJ·mol^{-1}) determined in the Al-Zn-Mg-based alloys after ageing at various temperatures [7]. The activation energy of the process III was obtained as (150 ± 30) kJ·mol^{-1}. The determined activation energy Q_{III} is close to the activation energies associated with η-phase particles precipitation reported for this precipitation (~ 113 kJ·mol^{-1} and/or ~ 138 kJ·mol^{-1}) [7]. The calculated activation energy of the process III is encumbered by a big scatter due to the small thermal response. The observed slight exothermic effect can also correspond successively to concurrence of several processes. Unfortunately, the activation energy must be identified with individual nucleation and growth steps in a transformation. Owing to the developed overlapped peaks, the exact positions of the beginning and end of the peaks cannot be precisely determined. Thus, the analysis of the activation energy of the process III in the studied alloys becomes uncertain.

4. CONCLUSIONS

Results of characterization of the Al-Zn-Mg and of the Al-Zn-Mg-Sc-Zr alloys by electrical resistometry, thermal analysis, microhardness testing and electron microscopy, can be summarized in the following points:

- Microstructure observation proved the Zn, Mg-containing eutectic phase at grain boundaries in the as-cast state of both alloys. The eutectic phase partly dissolved during the isochronal annealing above ~ 400 °C. Melting of the eutectic phase was observed by differential scanning calorimetry at ~ 475 °C.

- The distinct changes in resistivity and microhardness curves as well as in heat flow of the alloys studied are mainly caused by dissolution of the Zn,Mg-containing Guiner-Preston (GP) zones and subsequent precipitation of the metastable particles from the Al-Zn-Mg system.
- The hardening effect after isochronal annealing at temperatures above ~ 280 °C reflects the Sc,Zr-addition. Precipitation of the Mn,Fe-contaning particles was also observed in the AlZnMgScZr alloy.
- The apparent activation energy values were calculated regardless of Sc,Zr-addition as: dissolution of the GP zones (105 ± 20 kJ·mol^{-1}) and formation of the metastable Zn, Mg-containing particles (107 ± 10 kJ·mol^{-1}).

ACKNOWLEDGEMENTS

The work (MV) is a part of activities of the Charles University Research Centre "Physics of Condensed Matter and Functional Materials". This work was also supported by The Czech Science Foundation (GACR, project no. 17-17139S) and by the Ministry of Education, Youth and Sport of the Czech Republic (Program NPU1, project no. LO1207). VK acknowledges support by the grant SVV-2017-260449 (Specific Academic Research Projects).

REFERENCES

[1] TOROPOVA, L. S., ESKIN, D. G., KHARAKTEROVA, M. L., DOBATKINA, T. V. *Advanced Aluminum Alloys Containing Scandium - Structure and Properties*. Amsterdam: Gordon and Breach Science Publisher, 1998. ISBN 90-5699-089-6.

[2] MICHNA, Š., LUKÁČ, I., OČENÁŠEK, V., KOŘENÝ, R., DRÁPALA, J., SCHNEIDER, H., MIŠKUFOVÁ, A. a KOL. *Encyklopedie hliníku*. Prešov: Adin s.r.o., 2005. ISBN 80-89041-88-4.

[3] ČÍŽEK, J; PROCHÁZKA, I; SMOLA, B. et al. Precipitation effects in ultra-fine-grained Mg-RE alloys. *International Journal of Materials Research*, 2009, vol. 100, no. 6, pp. 780-784. DOI: 10.3139/146.110103.

[4] VLACH, M., STULÍKOVÁ, I., SMOLA, B. et al. Annealing effects in hot-deformed Al-Mn-Sc-Zr alloys. *Kovové Materiály-Metallic Materials*, 2015, vol. 53, no. 5, pp. 295-304. DOI: 10.4149/km_2015_5_295.

[5] VO, N. Q., DUNAND, D. C., SEIDMAN, D. N. Role of silicon in the precipitation kinetics of dilute Al-Sc-Er-Zr alloys. *Materials Science and Engineering: A*, 2016, vol. 677, pp. 485-495. DOI: 10.1016/j.msea.2016.09.065.

[6] PRASANTA, K. R., GHOSH, M. M, GHOSH, K. S. Microstructural, mechanical and electrochemical behaviour of a 7017 Al-Zn-Mg alloy of different tempers. *Materials Characterization*, 2015, vol. 104, pp. 49-60. DOI: 10.1016/j.matchar.2015.03.025.

[7] AFIFY, N., GABER A., ABBADY G. Fine scale precipitates in Al-Mg-Zn alloys after various aging temperatures. *Materials Sciences and Applications*, 2011, vol. 2, no. 5, pp. 427-434. DOI: 10.4236/msa.2011.25056.

[8] GHOSH, K. S., GAO, N., STARINK, M. J. Characterization of high pressure torsion processed 7150 Al-Zn-Mg-Cu alloy. *Materials Science and Engineering: A*, 2012, vol. 552, pp. 164-171. DOI: 10.1016/j.msea.2012.05.026.

[9] GHOSH, K. S., GAO, N. Determination of kinetic parameters from calorimetric study of solid state reactions in 7150 Al-Zn-Mg alloy. *Transactions of Nonferrous Metals Society of China*, 2011, vol. 21, no. 6, pp. 1199-1209. DOI: 10.1016/S1003-6326(11)60843-1.

[10] STARINK, M. J. The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. *Thermochimica Acta*, 2003, vol. 404, no. 1-2, pp. 163-176. DOI: 10.1016/S0040-6031(03)00144-8.