

# Annealing Effects in Cast Commercial Aluminium Al-Mg-Zn-Cu(-Sc-Zr) Alloys

Martin Vlach<sup>1</sup> · Jakub Čížek<sup>1</sup> · Veronika Kodetová<sup>1</sup> · Tomáš Kekule<sup>1</sup> · František Lukáč<sup>1,2</sup> · Miroslav Cieslar<sup>1</sup> · Hana Kudrnová<sup>1</sup> · Lucia Bajtošová<sup>1</sup> · Michal Leibner<sup>1</sup> · Petr Harcuba<sup>1</sup> · Jaroslav Málek<sup>3</sup> · Volkmar Neubert<sup>4</sup>

Received: 4 August 2019 / Accepted: 4 October 2019 / Published online: 21 October 2019 © The Korean Institute of Metals and Materials 2019

#### Abstract

Precipitation reactions of the cast Al–3.4 at%Mg–2.7 at%Zn–0.80 at%Cu–0.10 at%Fe–0.05 at%Si alloy with and without addition of 0.14 at%Sc and 0.06 at%Zr were characterized by electrical resistometry, electron microscopy, X-ray diffraction, thermal analysis, microhardness testing, and positron annihilation. The AlMgZnCuScZr alloy contains a grain boundary *T*-phase (Mg<sub>32</sub>(Al,Cu,Zn)<sub>49</sub>) with a cubic and/or quasicrystalline structure. The AlMgZnCu alloy contains a mixture of MgZn<sub>2</sub>- and the *T*-phase. Primary multilayer Al<sub>3</sub>(Sc,Zr) particles precipitated during casting and subsequent cooling. The particles have a layered Al<sub>3</sub>(Sc,Zr) +  $\alpha$ -Al+Al<sub>3</sub>(Sc,Zr) structure, i.e. consist of regions enriched with both Sc and Zr. Small atomic Mg,Zn(,Cu)-rich clusters coherent with the matrix were formed during the cooling of both alloys and/or in the course of their storage at ambient temperature. Their dissolution enables precipitation of the transient  $\eta'$ - and/or stable  $\eta$ -phases of the AlZnMgCu system in both investigated alloys. The effective activation energy for the dissolution of the secondary Al<sub>3</sub>(Sc,Zr) particles which cause precipitation hardening and guarantee thermal stability of mechanical properties. Addition of Sc and Zr micro alloying elements resulted in a substantial grain refinement. The grain size remains unchanged up to isochronal annealing at 390 °C.

Keywords 7xxx series  $\cdot$  Clusters  $\cdot$  TEM  $\cdot$  Positron annihilation  $\cdot$  Al<sub>3</sub>(Sc,Zr) particles  $\cdot$  Activation energy

# 1 Introduction

Thanks to the high age hardening response and low density of the commercial Al–Zn–Mg–Cu-based alloys (7xxx series), they are widely used in automotive and aircraft industries as well as in aeronautical applications [1–4]. Nevertheless, the mechanical properties of these alloys of course depend on the chemical composition, especially on Zn and Mg content and on the heat treatment of the

Martin Vlach martin.vlach@mff.cuni.cz

- <sup>1</sup> Faculty of Mathematics and Physics, Charles University, Ke Karlovu 3, 12116 Prague, Czech Republic
- <sup>2</sup> Institute of Plasma Physics, The Czech Academy of Sciences, Za Slovankou 3, 18200 Prague, Czech Republic
- <sup>3</sup> Faculty of Mechanical Engineering, Czech Technical University in Prague, 16636 Prague, Czech Republic
- <sup>4</sup> Institut f
  ür Materialpr
  üfung und Werkstofftechnik, Freiberger Str. 1, Clausthal-Zellerfeld 38678, Germany

alloys [2, 5-8]. Within the last couple of years, the effects of the core elements (Mg, Zn and Cu) on the strength and toughness of the alloys were studied intensively, e.g. Refs. [4, 9-16]. The type of precipitation sequence varies with the alloy composition despite the existence of controversies and ambiguities about the structures and the species of the hardening precipitates, the sequence is commonly used as (e.g. Refs. [4–7, 10–15]): supersaturated solid solution (SSS)  $\rightarrow$  Guinier–Preston (GP) zones and/ or coherent clusters  $\rightarrow$  semi-coherent  $\eta'$ -phase (hexagonal structure)  $\rightarrow$  incoherent  $\eta$ -phase (hexagonal structure). Vice a stable  $\eta$ -phase, the formation of the GP zones/ coherent clusters, and  $\eta'$ -phase are proved to be responsible for the peak strength of the alloys [4, 5, 8, 11, 16]. The formation of the GP zones/coherent clusters, and  $\eta'$ phase precipitates yet depends on the alloy composition, artificial ageing temperature, ageing time, heat treatment etc. [6-8, 15], the decomposition sequence should also contain metastable semi-coherent T'-phase (hexagonal structure) and equilibrium *T*-phase (cubic structure) [8,

9, 16]. Recently, Montage and Tillard [17] proved that the  $Mg_{32}Al_{12}Zn_{37}$  single crystal structure can be disordered and belongs to the well-known approximant structural type commonly called  $Mg_{32}(Al_{1-x}Zn_x)_{49}$  or *T*-phase. In this family,  $Mg_{32}Al_{12}Zn_{37}$  is a new member remarkable for its very special composition. To emphasize the great adaptability of the *T*-phase through atom disorder, the authors (see Ref. [17]) also discussed its structural features in comparison with literature data.

Low additions of Sc (~0.15 at%) and Zr (~0.1 at%) to aluminium and its alloys can significantly improve their mechanical and technological properties [1, 18–23]. A large improvement of aluminium alloys due to the Sc and Zr addition has been frequently reported to be the formation of secondary spherical (coherent) Al<sub>3</sub>(Sc,Zr)-phase precipitates  $(L1_2 \text{ structure})$  [1, 18–21]. Then again, for the cast ingots, the presence of inter-metallic particles of primary Al<sub>3</sub>Sc phase also helps refine the microstructure with Sc addition and reaches eutectic composition, which improves both the strength and formability [24–33]. Primary Al<sub>3</sub>Sc particles have been investigated in a few recent studies (e.g. Refs. [25-28, 34-40]) out of which the majority have observed square or triangle morphological features of primary particles. These particles mostly appeared at the grain inside and grain boundaries with a cusped cubic morphology [34, 39, 40] and in some cases they exhibit an apparent internal cellular structure and/or observed quasi-cubic morphological features of Al<sub>3</sub>Sc particles with an interfacial feature of rounded corners and concave faces [39]. However, primary particles have been identified recently as some eutectic structure consisting of a multilayer of  $Al_3Sc + \alpha - Al + Al_3Sc$ +... with a cellular-dendritic mode of growth. When Sc and Zr is added to the alloys, the structure consists of a layer of  $Al_3Sc + \alpha - Al + Al_3Zr + \alpha - Al + Al_3Sc + \alpha - Al + \cdots [34-37]$ .

The aim of the present work was to study the phase transformations in cast commercial Al–Mg–Zn–Cu alloy with and without Sc and Zr content during non-isothermal annealing as an unintended technological non-isothermal onset of annealing can undesirably influence the final structure and is not always taken into account. To provoke a complexity of phase transformations for the study isochronal annealing was used. It is well known that the history of a material determines effects developed at higher annealing temperatures. Therefore we applied positron annihilation study of the cast alloys together with microstructure description by TEM, SEM and EBSD to detect a possible cluster formation or other very early decomposition species in the initial state of alloys before the annealing.

The results of positron annihilation, relative resistivity changes, and microhardness response to the isochronal annealing and thermal changes were compared to the electron backscattered diffraction, powder X-ray diffraction methods, and to the microstructure development.

#### 2 Materials and Methods

The commercial Al–3.4 at%Mg–2.7 at%Zn–0.80 at%Cu–0. 10 at%Fe–0.05 at%Si (AlMgZnCu) alloys with and without addition of 0.14 at%Sc and 0.06 at%Zr (AlMgZnCuScZr) were studied. The alloys were conventionally prepared by melting of pure Al, Mg, Zn and Cu (the purity of Al used was ~99.9% and Mg, Zn and Cu were of purity ~99.5%) and commercial-purity master alloys (Al-2Sc and Al-10Zr) in a resistance vacuum furnace at ~850 °C. The alloys were cast into a cylindrical steel mould. Some specimens were cut parallel to the longitudinal ingot axis, some of them perpendicular to the axis. Sampling from the outer ingot part was excluded.

The alloys were characterized in the as-cast state and after annealing to various temperatures. The isochronal step-by-step annealing (30 K/30 min) was undertaken either in the oil bath (up to 240 °C) or in the furnace (above 240 °C) with a protective argon atmosphere. The annealing step was followed by the immediate cooling into liquid N<sub>2</sub> or water, respectively. Between the measurements the sample was kept in liquid N<sub>2</sub> to preserve the microstructure developed during the annealing.

The H-shaped specimens machined parallel to the longitudinal cross section to dimensions of ~2×9×70 mm<sup>2</sup> were used for electrical resistivity measurements (RESI). The value of the length (70 mm) represents the gauge length for electrical resistivity. Relative resistivity changes  $\Delta \rho / \rho_0$  were measured at 78 K within an accuracy of 10<sup>-4</sup> by means of the DC four-point method with a dummy specimen in series. The influence of parasitic thermo-electromotive force was suppressed by current reversal. The deformation of electrical field in the vicinity of contacts was estimated yielding the measured resistance accuracy better than ~4% [41].

Mechanical properties were evaluated by Vickers microhardness (HV) testing during the isochronal annealing in Wolpert Wilson Micro Vickers 401MVD at ~ 10 °C. The measurement of the HV values started no longer than 60 s after immediate cooling of the sample.

Thermal behaviour of the alloys was studied using differential scanning calorimetry (DSC) performed in Netzsch DSC 204 F1 Phoenix apparatus at heating rates of 1, 2, 5, 20 and 30 K/min up to 350 °C and at heating rate 10 K/min up to 500 °C. A specimen of mass between 10 and 20 mg was placed in  $Al_2O_3$  crucibles and measured in a dynamic nitrogen atmosphere (20 ml/min).

Defect characterization of the as-cast state was performed using positron annihilation spectroscopy (PAS) [42]. It involves positron lifetime (LT) spectroscopy [43] which enables to identify the type of defects present as well as coincidence Doppler broadening (CDB) [44] which carries information about the local chemical environment of defects. PAS studies were performed at -40 °C using a <sup>22</sup>Na positron source (activity of ~ 1 MBq) sealed between 5 µm thick Ti foils. A digital spectrometer with time resolution of 145 ps [45] was employed for LT measurement. CDB investigations were carried out using a digital spectrometer [46] equipped with the HPGe detectors.

Powder X-ray diffraction (XRD) methods were carried out on a vertical powder  $\theta$ - $\theta$  diffractometer D8 Discover (Bruker AXS) using Cu $K_{\alpha}$  radiation with a Ni $K_{\beta}$  filter. The diffracted beam was detected by a 1D detector Lynx Eye. The XRD measurements were performed in the Bragg–Brentano geometry with 0.5° fixed divergent slit in the primary beam. The penetration depth of the Cu $K_{\alpha}$  radiation into the alloys studied the amounts of 60 µm for perpendicular incident angle.

The microstructure development was studied employing transmission electron microscopy (TEM) utilizing a JEM 2000FX microscope and scanning electron microscopy (SEM) performed on MIRA I Schottky FE-SEMH and FEI Quanta 200FEG microscopes, respectively. The analysis of precipitates was carried out by energy-dispersive spectroscopy (EDS) using an X-ray BRUKER microanalyser. Electron backscatter diffraction (EBSD) was made to determine the grain structure of the alloys studied disposing a JEOL JSM 7600F scanning electron microscope at 20 kV fitted with a Nordly EBSD detector. The EBSD data were processed by HKL Channel 5 software equipment. The specimens for TEM, SEM and EBSD were annealed by the same procedure as those for RESI and HV investigations.

# 3 Results

#### 3.1 Microstructure of the Cast Alloys

Properties development during thermal treatments is predetermined by the initial microstructure of investigated alloys. The studied AlMgZnCu alloy has a typical cast structure with elongated grains longer than 1000 µm in longitudinal ingot cross section and minimally ~ 100 µm in transversal cross section (see Fig. 1a). The grain size is considerably smaller in the transversal cut in both alloys. The Sc and Zr addition refines grains (see Fig. 1b) several times. Dislocation density in grain interiors observed by TEM (Fig. 2) and estimated by linear intersection point method is lower than  $10^{13}$  m<sup>-2</sup>. The eutectic grain boundary phase in the AlMgZnCuScZr alloy surrounds grains with a mean size of ~ 25  $\mu$ m in the transversal cross section and despite the different grain size; its volume fraction was very similar in both alloys. This boundary phase in the AlMgZnCuScZr alloy has a cubic structure with a lattice parameter a = 1.41(1) nm (see the diffraction



**Fig. 1 a** EBSD map of the as-cast AlMgZnCu alloy in longitudinal ingot cross section with grains > 1000  $\mu$ m long and minimally ~ 100  $\mu$ m in diameter, **b** SEM image of the as-cast AlMgZnCuScZr alloy in transversal ingot cross section with equiaxed grains ~ 25  $\mu$ m (linear intersection point method)



**Fig. 2** TEM image of the AlMgZnCuScZr alloy in the as-cast state, inset shows ED reflections of the *T*-phase (orientation [3 1 4]<sub>*T*-phase</sub>)

pattern in inset of Fig. 2). The phase belongs to the structural type commonly called *T*-phase or Mg<sub>32</sub>(Al,Cu,Zn)<sub>49</sub> phase. Recently, this phase has been also identified as a crystalline approximant (Mg<sub>32</sub>Al<sub>12</sub>Zn<sub>37</sub> single cubic crystal) of the quasicrystalline structure in the Mg–Al–Zn system (see Ref. [17]). The XRD investigations do not exclude the quasicrystalline structure (see Fig. 3) in the as-cast alloy. The Rietveld refinement of the XRD pattern yielded the *T*-phase lattice parameter a=1.409(9) nm. The composition of the eutectic boundary phase in the



Fig. 3 XRD diffraction patterns of as-cast AlMgZnCu and AlMgZnCuScZr alloys with identified phases

AlMgZnCuScZr alloy is determined by EDS match of the  $Mg_{32}(Al,Cu,Zn)_{49}$  phase.

Unlike the AlMgZnCuScZr alloy with only one observed eutectic phase the EDS analysis of the AlMgZnCu alloy shows a mixture of predominant  $MgZn_2$ -phase and a minor fraction of the above mentioned cubic and/or quasicrystalline *T*-phase in the grain boundary regions. The XRD measurements (Fig. 3) confirm this fact.

Layered primary Al<sub>3</sub>(Sc,Zr) particles were observed in the AlMgZnCuScZr alloy (see Figs. 1, 4 and 5). The correlated enrichment of the core in Al<sub>3</sub>(Sc,Zr) particles and the surrounding layers rich in both Sc and Zr is distinctive and can be identified as "Al<sub>3</sub>(Sc,Zr) +  $\alpha$ -Al + Al<sub>3</sub>(Sc,Zr)" layered structure. Particles with a core enriched solely with Sc or with Zr are usually reported in literature (see Refs. [34–37]). Even in the secondary  $Al_3(Sc,Zr)$ -phase particles solutes, Sc and Zr together were not observed in the particle centre (core) [18, 23]. Zhou et al. [34–36] suggested that the first phase forming during solidification is either the primary  $Al_3Sc$ - or the  $Al_3Zr$ -phase which nucleate at preexisting oxide particles in the melt. Although the resolution of SEM we used is limited, the Sc- and/or Zr-oxide does not probably exist in the middle of the  $Al_3(Sc,Zr)$  particles. It seems that both Sc and Zr comprise an integral part of the primary  $Al_3(Sc,Zr)$  particles already in their centre. It indicates a different partitioning behaviour during solidification of the primary  $Al_3(Sc,Zr)$  particles from the melt as well as a different mechanism of precipitation of the secondary  $Al_3(Sc,Zr)$  precipitates controlled by a long range diffusion of Sc and Zr in the solid Al matrix. It is also probable that



**Fig. 4** SEM images and EDS line profiles of the primary Al<sub>3</sub>(Sc,Zr) phase particles in the as-cast AlMgZnCuScZr alloy







Fig.6 Isochronal annealing curves of RESI and HV of the cast AlMgZnCu and AlMgZnCuScZr alloy

Mg and Cu alloying elements enhanced nucleation of the primary Al<sub>3</sub>(Sc,Zr) particles.

### 3.2 Response of Electrical, Thermal and Mechanical Properties to Thermal Treatment

The thermal stability of microstructure can be very easily investigated by changes in electrical resistivity term caused by lattice defects scattering of electrons or by heat amount necessary to keep a certain temperature of a specimen. Microstructure changes also considerably influence mechanical properties such as hardness. Electrical resistivity changes measured at very low and well defined temperature (78 K in liquid N<sub>2</sub>) after a certain heat treatment which finished by quenching reflect microstructure changes that occurred during the step-by-step isochronal annealing. Relative resistivity changes  $\Delta \rho / \rho_0$  together with the HV response are shown in Fig. 6. Relative resistivity changes decrease in two stages (I-stage up to ~ 150 °C and II-stage between 150 and 300 °C) then the resistivity increases insignificantly after annealing at temperatures higher than 300 °C. I-stage of the RESI decrease is connected with a decrease in the microhardness annealing curve with a maximum softening after annealing up to 120 °C. The effect is very poor only in the alloy without Sc and Zr addition. Hardening accompanies the second resistivity decrease (II-stage) in both alloys and after annealing up to 240 °C it falls approximately to its initial HV value. Further annealing leads to a considerable softening in the AlMgZnCu alloy while HV values remain almost constant in the AlMgZnCuScZr within the annealing temperature range 300–390 °C. The difference in HV between both alloys is nearly 30 after annealing up to 390 °C.

Figure 7a shows DSC curves of both cast alloys measured with the heating rate of 1 K/min up to 300 °C. They differ very insignificantly from each other; only a slight temperature shift appears in the alloy with Sc and Zr addition. The endothermic effect (labelled as process A) with a minimum heat flow at ~ 100 °C is followed by an exothermic effect (process B) with maximum ~ 208 °C. The endothermic process A corresponds well to the softening with a local minimum at ~ 120 °C and the RESI decrease in the I-stage (cf. Figures 6 and 7). Similarly, II-stage and process B connected with hardening at annealing temperatures 150–240 °C coincide and the fastest decrease of the RESI changes corresponds to the maximum heat flow of the exothermic process B.

Melting (processes C and D) was observed at ~481 and 488 °C (see inset of the Fig. 7) in the DSC curve of the AlMg-ZnCu alloy. Only one process at ~489 °C was observed in the AlMgZnCuScZr alloy (not shown). It agrees excellently with the observation of a mixture of two eutectic phases (MgZn<sub>2</sub> phase and *T*-phase) in the cast AlMgZnCu alloy and only one



Fig. 7 a Linearized DSC annealing curves (1 K/min, inset detail of an endothermic peaks measured using the heating rate of 10 K/min up to 500 °C) of the AlMgZnCu and AlMgZnCuScZr alloy, **b** Kissinger plot constructed from series of DSC measurements with various heating rates

eutectic phase (*T*-phase) in the cast AlMgZnCuScZr alloy (see Figs. 1, 2 and 3). The sharp endothermic process C which appeared in the AlMgZnCu alloy can be ascribed to the melting of the MgZn<sub>2</sub> phase and the indistinctive endothermic process D which appeared in both alloys can be ascribed to melting of the *T*-phase.

Kissinger plot [47], i.e.  $\ln(\beta/T_f^2)$  plotted versus  $1/T_f$ , where  $\beta$  is the heating rate and  $T_f$  is the temperature corresponding to the maximum heat flow in DSC, is usually used for determination of the activation energies Q for the individual thermal processes. Figure 7b shows the plot for the processes A and B. Both are of Arrhenius type and the effective activation energies were calculated by linear regression of the experimental data as ~ 103 kJ/mol and ~ 143 kJ/mol for A and B processes, respectively. The determined activation energy values do not differ within experimental uncertainties, see Fig. 7b.

## **4** Discussion

To identify the nature of the observed property changes we started from the processes at low annealing temperatures—Figs. 6 and 7a. A decrease of the RESI defect term always means less scattering for the electrons. It is usually therefore a manifestation of precipitation processes as they diminish solute atoms concentration in the alloy matrix. An exception represents dissolution of tiny GP zones and/or small clusters because they can scatter more effectively than individual solutes. Precipitation usually causes hardening; softening can be observed during dissolution of very early decomposition objects. In general, the early precipitation stages can be abundant in Al-based alloys and are known to affect the resistivity and (micro) hardness development [29, 48–51]. Many authors have attempted to explain changes of RESI and HV at the beginning of the precipitation kinetics in the Al-based alloys by the formation of the GP zones and/or coherent clusters [14, 29, 49–51]. Solute clusters formed during cooling in the casting procedure and/or during its storage at ambient temperature are too small to be visible by TEM [52]. We therefore applied positron annihilation study of the cast alloys to reveal that the clusters or other very early decomposition species exist in the alloys in the initial state before annealing and they can dissolute.

The positron annihilation LT spectrum of the as-cast AlMgZnCu alloy consists of two components: a shorter component with a lifetime  $\tau_1 = 60(10)$  ps and intensity  $I_1 = 12(1)\%$  comes from free positrons (not trapped at defects); a longer component with a lifetime  $\tau_2 = 224(3)$  ps and intensity  $I_2 = 88(1)\%$  represents a contribution of positrons trapped at defects. The lifetime  $\tau_2$  is shorter than the value for vacancies in Al [53] and it is comparable with the value reported for positrons trapped at solute clusters [54]. We attribute the component  $\tau_2$  to positrons confined inside GP zones and/or small clusters of alloying elements formed during cooling and/or storage at ambient temperature. No precipitation effects were confirmed by TEM.

Comparable positron lifetime values were evaluated for the as-cast AlMgZnCuScZr alloy:  $\tau_1 = 80(10)$  ps,  $\tau_2 = 221(2)$  ps and corresponding intensities  $I_1 = 18(3)\%$ ,  $I_2 = 82(3)\%$ . Lower  $I_2$  value means a slightly lower concentration of GP zones and/or clusters in the AlMgZnCuScZr than in the AlMgZnCu alloy.

The CDB spectroscopy enables to identify elements forming the GP zones and/or coherent clusters. Figure 8a shows the CDB ratio curves (related to well annealed pure Al) of the as-cast AlMgZnCu and AlMgZnCuScZr alloys. We compared the CDB ratio curves to the curves measured for reference specimens of pure elements Mg, Cu, Zn, Sc, Zr in the Fig. 8b. The ratio curve for the as-cast AlMgZnCu alloy shows that positrons are annihilated in the vicinity of Al (63%), Mg (16%), Zn (16%) and Cu (5%) atoms and it indicates a composition of the GP zones and/ or clusters. The fractions of positrons annihilated in the vicinity of Mg, Zn and Cu atoms are significantly higher than the concentrations of these elements in the alloy and



**Fig.8** CDB ratio curves with respect to well annealed pure Al for: **a** as-cast AlMgZnCu and AlMgZnCuScZr alloys, **b** the ratio curves for as-cast AlMgZnCu and AlMgZnCuScZr alloys compared with the ratio curves for pure Mg, Zn, Cu, Sc and Zr reference samples

it means that the local chemical environment of positron traps is enriched with Mg, Zn and Cu.

The CDB ratio curve introduced in the Fig. 8a for the as-cast AlMgZnCuScZr alloy is very similar to that one of the AlMgZnCu alloy and therefore the fraction of positrons annihilated in the vicinity of Sc and Zr atoms is negligible in the studied as-cast AlMgZnCuScZr alloy. It has been recently shown (Ref. [29]) that the Al<sub>3</sub>(Sc,Zr) particles do not represent trapping sites for positrons either. The assessment of element ratio for positron annihilation in the AlMgZnCuScZr alloy slightly differs from the one in the alloy without Sc and Zr: Al (54%), Mg (25%), Zn (18%) and Cu (3%). Hence, the fraction of positrons annihilated in the locality of Mg and Zn was enhanced in the AlMgZnCuScZr alloy at the expense of those ones annihilated in the vicinity of Al and Cu.

It can be concluded that Mg,Zn(,Cu)-rich clusters dissolve first during the step-by-step non-isothermal annealing. The dissolution of the clusters is responsible for RESI and HV decrease in the I-stage (Fig. 6). Precipitation of the hardening phase in the solution treated commercial 7xxx series Al alloys with compositions similar to the investigated alloy without Sc and Zr is realized usually at 120 °C [1]. Even though this aging temperature is within the temperature range of the softening observed during the isochronal annealing, it does not contradict our results. The clusters developed during the solution procedure of a 7xxx series alloy dissolve at shorter times at 120 °C. It eliminates to a certain degree a material history and ensures maximum of alloying elements in the solid solution for continuing thermal exposure at 120 °C. Unlike the isothermal annealing, higher annealing temperatures are necessary for hardening in the isochronal process as the annealing time is strictly limited in the isochronal annealing. The endothermic process A occurring in both alloys in the temperature range 75-150 °C agrees with this dissolution, too. Similar results were obtained in the DSC measurements of the AA7012 (Al-Zn-Mg-Cu-Zr) alloy (see Ref. [50]) where the first endothermic process proceeds at temperatures ranging from 90 to 140 °C depending on the scanning rate; it was explained by dissolution of a pre-precipitated phase (GP zones and/or small clusters) developed during natural ageing. It also indicates that this dissolution is thermally activated. The calculated range of the activation energy O for the dissolution (~103 kJ/mol, see Fig. 7b) is higher than the one for the GP zones formation (~60 kJ/mol [50, 51, 55, 56]) in the AlZnMg(Cu)-based alloys and very well agrees with the value  $(106 \pm 15)$  kJ/mol determined in the cast and coldrolled AlZnMg(ScZr) alloys with similar contents of Zn and Mg [51]. Activation energies for the GP zones and/or clusters dissolution reported in literature vary in a large range from 65 to 120 kJ/mol [6, 50, 51, 56] and do not doubt GP zones/coherent clusters dissolving in the investigated alloys in the I-stage. The DSC measurements found in the literature also support our results because they reveal clustering of solutes and/or formation of the GP zones in solution-treated Al-Zn-Mg-based alloys at low temperatures 30-110 °C [6, 49, 57] manifested by a weak exothermic effect.

The explanation of the II-stage in the annealing curves is supported by TEM. The dissolved small clusters (and/or GP zones) in the I-stage enabled that the particles of secondary phase(s) precipitated in the AlMgZnCuScZr alloy isochronally annealed up to 360 °C-see Fig. 9. Diffraction patterns of [001] Al zone in the AlMgZnCuScZr alloy (inset in Fig. 9) are very close to those in Refs. [51, 58, 59] and confirm the presence of transient  $\eta'$ - and/or stable  $\eta$ -phases of the Al-Zn-Mg-Cu system. Microhardness increases and is followed by a decrease due to particle growth and decreasing particle number density. The same phase(s) precipitated in the cold-rolled AlZnMgScZr alloy at 180-360 °C (e.g. Ref. [51]) and also cause(s) electrical resistivity decrease and hardening. The slight increase of the electrical resistivity after annealing at temperatures higher than 300 °C indicates that solid solution concentrations in both alloys increase as solubility of the solutes increases.



**Fig.9** Bright field TEM image of AlMgZnCuScZr alloy isochronally annealed up to 360 °C. Weak diffraction spots in  $[001]_{A1}$  zone diffractogram mainly from the  $\eta$ '- and/or  $\eta$ -phase and the secondary Al<sub>3</sub>(Sc,Zr)-phase particles with Ll<sub>2</sub> structure

The precipitation is also the reason of the observed calorimetric effect (the process B in Fig. 7a). The temperature position corresponds very well to observations published in literature introducing the precipitation of the metastable  $\eta'$ -phase immediately followed by the precipitation of the  $\eta$ -phase; the similar temperature range was also referred to the development of the simulated fraction of these phases in the Al–Zn–Mg-based alloy during a DSC run [3, 14, 51]. We obtained the value of activation energy as  $Q_{\rm B} = (143 \pm 6)$ kJ/mol. Neither temperature position of the peak maxima in the DSC curves nor the calculated activation energies are influenced by the Sc and Zr addition in the studied cast alloys. The values of (80-140) kJ/mol were published as activation energies of the  $\eta'$ -phase precipitation determined in the Al-Zn-Mg-based alloys after ageing at various temperatures [15, 51, 55]. The activation energy for the  $\eta$ -phase formation in the Al–Zn–Mg–Cu–Zr (AA7012) alloy was determined as 115-160 kJ/mol [15, 50, 51, 55]. Unfortunately, the activation energy must be identified with individual nucleation and growth steps in a transformation. Concerning the possibility of the overlapped peaks corresponding to the precipitation of the  $\eta'$ - and  $\eta$ -phase particles, the exact positions of the peak beginning and peak completing cannot be determined. Thus, the analysis of the activation energy of the effect B in the studied alloys from the Kissinger analysis probably corresponds to an effective value for the formation of a mixture of  $\eta$ - and  $\eta'$ -phase particles.

One more phase was detected in the diffraction pattern of the AlMgZnCuScZr alloy isochronally annealed up to  $360 \,^{\circ}\text{C}$ —the secondary Al<sub>3</sub>(Sc,Zr)-phase. It has the L1<sub>2</sub> structure and its diffraction feature is seen in Fig. 9, too. It is inherent to the annealed specimens, only large primary Al<sub>3</sub>(Sc,Zr) particles were observed in the cast alloy. Precipitation of the particles in the alloy with Sc and Zr addition and the corresponding hardening compensates the



Fig. 10 EBSD map of the AlMgZnCuScZr alloy isochronally annealed up to 390  $^{\circ}\mathrm{C}$ 

loss of mechanical properties observed in the AlMgZnCu alloy in annealing higher than 300 °C and explains the significantly better thermal stability of the AlMgZnCuScZr alloy, see Fig. 6b. A similar hardening effect due to the secondary Al<sub>3</sub>(Sc,Zr)-phase precipitation was observed in the AlZnMg(Cu)ScZr alloy (see Refs. [15, 51]) at similar annealing temperatures 300–390 °C. The temperature stability of the AlMgZnCuScZr alloy is not connected with any grain structure changes, primary Al<sub>3</sub>(Sc,Zr) particles and/or the grain boundary phase development. Volume fraction of the eutectic grain boundary phase remains almost unchanged and the grain size does not change as it can be seen in Fig. 10. It shows the EBSD map of the AlMgZnCuScZr alloy annealed up to 390 °C, up to the highest annealing temperature of our investigation.

# 5 Conclusions

The characterization of the Al–Mg–Zn–Cu alloy with and without the addition of Sc and Zr by electrical resistometry, microhardness testing, thermal analysis, positron annihilation spectroscopy, electron microscopy, and X-ray diffraction can be summarized in the following points:

- The as-cast AlMgZnCuScZr alloy contains a grain boundary *T*-phase with a cubic and/or quasicrystalline structure. The AlMgZnCu alloy contains a mixture of MgZn<sub>2</sub> and the *T*-phase.
- (2) Small atomic clusters coherent with the matrix were formed during the cooling of the cast alloys and/or in the course of their storage at ambient temperature. These clusters were formed predominantly by Mg and Zn alloying elements. Their dissolution enables precipitation of the transient  $\eta'$  and/or stable  $\eta$ -phases of the AlZnMgCu system in both investigated alloys. The effective activation energy for the dissolution of the clusters was calculated as ~ 103 kJ/mol.

- (3) Primary Al<sub>3</sub>(Sc,Zr) particles in the as-cast AlMgZn CuScZr alloy have a layered Al<sub>3</sub>(Sc,Zr) +  $\alpha$ -Al + Al<sub>3</sub> (Sc,Zr) structure, i.e. consist of regions enriched with both Sc and Zr.
- (4) Annealing of the AlMgZnCuScZr alloy above 300 °C leads to a formation of the secondary Al<sub>3</sub>(Sc,Zr) particles which cause precipitation hardening and guarantee thermal stability of mechanical properties.
- (5) Addition of Sc and Zr micro alloying elements resulted in a grain refinement. The grain size remains unchanged up to isochronal annealing at 390 °C.

Acknowledgements This work was supported by The Czech Science Foundation (GACR), Project 17-17139S. The authors are also grateful to Ivana Stulíková, Tamara Čučková and Bohumil Smola for their help. PH acknowledges support by ERDF under the project CZ.02.1.01/0.0 /0.0/15\_003/0000485.

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