



Article Role of Small Addition of Sc and Zr in Clustering and Precipitation Phenomena Induced in AA7075

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Abstract: A detailed characterization of phase transformations in the heat-treated commercial 7075 aluminum alloys without/with low Sc–Zr addition was carried out. Mechanical and electrical properties, thermal and corrosion behavior were compared to the microstructure development. The eutectic phase consists of four parts: MgZn₂ phase, Al₂CuMg phase (*S*-phase), Al₂Zn₃Mg₃ phase (*T*-phase), and primary λ -Al(Mn,Fe,Si) phase. Strengthening during non-isothermal (isochronal) annealing is caused by a combination of formation of the GP zones, η' -phase, *T*-phase and co-presence of the primary and secondary Al₃(Sc,Zr)-phase particles. Positive influence on corrosion properties is owing to the addition of Sc–Zr. Positron annihilation showed an evolution of solute Zn,Mg-(co-)clusters into (precursors of) the GP zones in the course of natural ageing. The concentration of the (co-)clusters is slightly negatively affected by the low Sc–Zr addition. A combination of both precipitation sequences of the Al–Zn–Mg–Cu-based system was observed. The apparent activation energy values for dissolution/formation of the clusters/GP zones and for formation of the metastable η' -phase, stable *T*-phase and stable η -phase were calculated.

Keywords: 7xxx aluminum series; early precipitation stages; corrosion; Al₃(Sc,Zr) particles; annihilation of positrons; activation energy

1. Introduction

The heat-treated commercial aluminum 7xxx series (Al–Zn–Mg–Cu-based) alloys extensively appear in various applications, including metalworking, automotive, aircraft, and space engineering thanks to their precipitation-hardening reaction and light weight [1–5]. Since aluminum (Al) is commonly used nonferrous metal, the world's consumption of Al increased year by year, mainly driven by the growth in China [2,3]. According to the European Aluminum Association (EAA), massive usage of Al would decrease the CO₂; decreasing the weight of the (hybrid) vehicles by ~100 kg reduces the fuel (energy) consumption ~5 percent [2,3]. Even though aluminum commercial 7xxx-based alloys have been traditionally used especially as a lightweight material for traffic systems, the trends in industry emphasize the improvement and stabilization of the structure and properties of these materials through a careful control of thermo-mechanical processing schedules [4,5].



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Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). The chemical composition of these alloys plays a really big role in their characterization. Many of these useful properties can be influenced and controlled by the appropriate alloying of Mg and Zn [6–11]. However, they are regulated not only by the concentration of solutes, but also by processing and suitable parameters including heat treatment/annealing procedure, rolling/deformation, quenching and/or subsequent ageing [7,10–17]. It enables study to vary the concentration of different types of elements dissolved in Al as well as the size distribution/composition of phases.

The category of transformation line is changed with the content and composition of a particular element; the (non-)isothermal series of annealing steps are usually used [6,8,10,17–23]. Despite having some disagreements and obscurity about the arrangement and the types of the hardening phases in the alloys, the decomposition of supersaturated solid solution is in the consistency with two precipitation sequences, where $\eta'(MgZn_2)$ -phase (hexagonal)/ $\eta(MgZn_2)$ -phase (hexagonal) and $T'(Al_2Zn_3Mg_3)$ -phase (hexagonal)/ $T(Al_2Zn_3Mg_3)$ -phase (cubic) occur [15,19,20]. The precipitation of the semi-coherent η' - and T'-phases usually cause the age-hardening of the materials in contrast to the incoherent η - and T-phases [19,20,22–27]. Many authors use different designations for the early precipitation phases formed during the precipitation; (co-)clusters/Guinier-Preston (GP) zones of different types usually appear during ageing at temperatures lower than ~150 °C [19,20,25,28–33].

One possibility how to improve the potential of traditional commercial aluminum 7075-(Al–Zn–Mg–Cu–Mn–Si–Fe-) based alloys is the addition of rare earth (RE) elements (incl. Sc) and/or the addition of selected transition (TM) metals (e.g., Zr) [1,12–16,19,34–39]. The TM elements diffuse much slower than Sc and a TM-enriched shell behaves as a diffusion barrier preventing the diffusion from the Sc-rich core and this way reduces a coarsening of the core-shell secondary Al₃(Sc,TM)-phase [1]. It enhances the usage of these alloys up to ~400 °C. The addition of Sc (0.05–0.20 at.%) and Zr (0.05–0.50 at.%) is the most effective Sc–Zr combination in aluminum due to the precipitation of the secondary spherical (coherent) coreshell ternary L1₂-structured Sc,Zr-containing phase [1,12,13,20,34,36]. The Sc and Zr content can help to refine and to affect the microstructure and the recrystallization temperature and therefore the materials in a non-recrystallized state improve their mechanical properties and resistance to corrosion [1,15,40–42]. It has recently been found in the commercial Al alloys with low Sc–Zr addition that the inter-metallic particles of primary Al₃(Sc,Zr) phase have a multi-layered structure with many different shapes (dimension about 1–3 μ m) and they appear inside (in the center of) the grains in principle [15,20].

The reason of this work is a detailed characterization of the phase transformation in heat-treated Al-Zn-Mg-Cu-Mn-Si-Fe (-Sc-Zr) alloys and thus contribute to the knowledge of the ongoing processes in the aluminum commercial 7xxx alloys. This work is based on ongoing research, which has partially been recently published in References. [15,19,20,25]. The results of positron annihilation, microhardness and resistivity measurements during the isochronal annealing and subsequent natural ageing, thermal response and corrosion behavior were suitably supplemented with the powder X-ray diffraction and microstructure observations by scanning and transmission electron and atomic force microscopy. The article attempts to enlarge the knowledge about the very early precipitation stages, precipitation mechanism, corrosive characteristics and activation energies for the dissolution/formation of the phases in the Al-based commercial alloys with low Sc-Zr addition. Due to the fact that this is a study of a cast heat-treated ("pseudo-homogenised") aluminum 7075 (-Sc-Zr)-based alloy (i.e., without thermo-mechanical processing such as hot rolling or cold rolling), the research results are relevant to the use of the alloys as shape castings or perhaps more significantly for additive manufacturing although the solidification conditions would be very different.

2. Materials and Methods

Two alloys were studied: Without Sc–Zr addition (labelled as 7075 alloy) and with Sc–Zr addition (labelled as 7075-ScZr alloy). The composition of the alloys is listed in Table 1 (Al is the balance).

Alloy	Mg	Zn	Cu	Mn	Si	Fe	Sc	Zr
7075	3.44	2.76	0.79	0.21	0.22	0.18	-	-
7075-ScZr	3.41	2.72	0.77	0.26	0.24	0.23	0.14	0.06

Table 1. Chemical composition of the alloys investigated (at.%), Al is the balance.

The materials were conventionally prepared by melting of pure Al, Mg, Zn, and Cu (the purity of Al used was more than 99.5%, in case of Mg, Zn, and Cu more than 99%) and commercial-purity master alloys (Al-2Sc and Al-10Zr) in a resistance vacuum furnace (SVÚM, Čelákovice, Czech Republic) at ~ 850 °C. The materials were cast into a cylindrical steel mold with size of ~125 mm \times 20 mm \times 270 mm. The total weight of the ingots was about 1.5 kg; it was therefore an experimental laboratory produced casting. The materials after casting were stored at room temperature (RT) until the measurements. Specimens for characterization of phase development and age hardening were mainly cut parallel to the longitudinal ingot axis. Sampling from the outer ingot part was excluded. The alloys were then subjected to the high temperature annealing at $470 \,^{\circ}$ C in the furnace with a protective Ar-atmosphere. The annealing time at 470 °C was 60 min (or 240 min). After the annealing, the materials were quenched in water at RT. Unless otherwise stated, the state of the alloys after high temperature annealing at $470 \text{ }^{\circ}\text{C}/60$ min is referred to the (heat-treated) HT state. In this view, therefore, the state of the materials after the annealing at 470 °C can be understood as the as-prepared/initial state. The alloys after high temperature annealing at 470 $^{\circ}$ C were also subjected to the subsequent natural ageing at RT. The HT + NA state of the alloys means the alloys in the HT state after 3500 h (~146 days) of natural ageing (NA). The HT + NA15000 state of the alloys means the alloys in the HT state after 15,000 h (~625 days) of natural ageing. Summary of the states of the alloys is given in the Table 2.

Table 2. Summary of the heat treatment conditions (types of the annealing) and the marking of the alloy states.

State of the Alloys	Heat Treatment
HT	470 °C/60 min
470 °C/240 min	470 °C/240 min
HT + NA	470 °C/60 min + natural ageing for 3500 h
HT + NA15000	470 °C/60 min + natural ageing for 15,000 h
470 °C/240 min + NA	470 °C/240 min + natural ageing for 3500 h

The alloys in the different states were further characterized after the step-by-step heat treatment to the different temperatures. The isochronal sequent heat treatment with effective speed of 1 °C/min was performed either in the oil bath (up to 240 °C) or in the furnace (above 240 °C). The immediate cooling into liquid N₂ or water came after the annealing step. The materials were kept in liquid N₂ at 78 K after quenching until measurements or other annealing started to avoid possible NA.

The (relative) electrical resistivity measurements were determined in liquid N₂ bath at 78 K by means of the DC four-point method. The influence of parasitic thermo-electromotive force was suppressed by current reversal with a dummy specimen in series. H-shaped specimens machined to dimensions of ~2 mm × 9 mm × 90 mm were used for the resistivity measurements; the length represents the gauge length. Vickers microhardness (HV0.5) testing (specimens machined to dimensions of ~20 mm × 20 mm × 20 mm) was performed in Wolpert Wilson Micro Vickers 401MVD (Wilson Instruments, Canton, MA, USA) at ~5 °C to avoid possible NA. Detailed information about electrical resistivity and microhardness HV0.5 measurements is described in References. [19,25].

Thermal properties were studied using differential scanning calorimetry (DSC) performed in Netzsch DSC 204 F1 Phoenix apparatus (NETZSCH-Gerätebau, Selb, Germany) at heating rates of 1–20 °C/min up to 400 °C. A material of diameter 2–4 mm and of mass 12–18 mg was placed in Al_2O_3 crucibles and measured in a dynamic nitrogen atmosphere (20 mL/min).

Powder X-ray diffraction (XRD) in symmetric Bragg–Brentano geometry of the HT state of the alloys (surface area of ~4 cm²) was carried out on a vertical powder θ - θ diffractometer D8 Discover (Bruker AXS, Karlsruhe, Germany) using CuK α radiation with a NiK β filter at 40 kV and 40 mA from 15° to 90° (0.02° per step). The measurement was performed at RT.

Positron annihilation spectroscopy (PAS) was employed for positron lifetime (LT) evolution during natural ageing of the HT state of the 7075 and 7075-ScZr alloys (surface area of ~1 cm²). PAS studies were done at -50 °C using a ²²Na positron source (activity of ~1 MBq) sealed between 5 μ m thick Ti foils. One measurement lasted about 2 days. A digital spectrometer with time resolution of 145 ps [43] was employed for LT measurement. Detailed information about LT and XRD measurements is described in References [19,20,44].

Corrosion characteristic were studied by potentiodynamic polarization experiments which were carried out using auto range Wenking M Lab Potentiostat (controlled by a computer, Institut für Materialprüfung und Werkstofftechnik, Clausthal-Zellerfeld, Germany). Fresh surfaces of specimens for corrosion testing were obtained by grinding using 1200 grit SiC papers. Specimen with surface area of ~1 cm² was immersed in 0.1 M NaCl aqueous solution for 15 min prior to polarization, by which time a stable potential (OCP) was obtained. Saturated calomel electrode was used as s reference electrode. Polarization was obtained by scanning from 500 mV more negative than OCP at rate of 20 mV/min. The measurements were performed at RT.

The surface topography of the HT state of the alloys (surface area of ~4 cm²) was gauged employing an Atomic Force Microscopy (AFM) Solver Pro-M (NT-MDT, Moscow, Russia) in the semi-contact mode. Microstructure pictures were recorded with the frequency of 0.7 Hz and the resolution 256×256 pixels. The measurements were realized using high-resolution etalon PHA_NC type cantilevers (Au coating, cone angle less than 22° ; resonant frequency 140 kHz and force constant 3.5 N/m). Microstructure observations of the materials were observed by disposing transmission electron microscopy (TEM), JEOL JEM-2000FX microscope (JEOL, Tokyo, Japan), and scanning electron microscopy (SEM), MIRA I Schottky FE-SEMH microscope (TESCAN ORSAY HOLDING, Brno-Kohoutovice, Czech Republic). The analysis of precipitates was carried out by energy-dispersive spectroscopy (EDS) using an X-ray BRUKER microanalyzer (Bruker AXS, Karlsruhe, Germany). The specimens for TEM and SEM were annealed by the same procedure (isochronal sequent annealing with effective speed of 1 °C/min) as the specimens for electrical resistivity and microhardness HV0.5 measurements.

3. Results and Discussion

3.1. Heat-Treated (Initial) State of the Alloys

Characterization of the microstructure of the heat-treated (initial) state of the materials is very complex, as it is presented below. The HT alloys contain eutectic phases at grain boundaries; eutectic volume fraction was observed comparable for both alloys—an overview is shown in Figure 1. Figure 2 presents TEM picture of the eutectic phase(s) and the Mn,Fe,Si-containing particle at grain boundary of the 7075-ScZr alloy. Eutectic boundary phases and their composition in the alloy containing Sc–Zr addition were determined by EDS match as the MgZn₂ phase and *S*-phase (Al₂CuMg). Although electron diffraction (ED) was not sufficiently conclusive, it can be assumed in the light of our previous research in the hot-deformed 7075(-ScZr) alloys (see References [15,20]) that the Mn,Fe,Si-containing particle is very likely the primary cubic λ -Al(Mn,Fe,Si) phase. The presence (indirectly also the composition) of the eutectic phases was confirmed by XRD, see Figure 3. In these measurements another phase was proved: *T*-phase (the phase belongs to the Al₂Zn₃Mg₃ or Mg₃₂(Al,Cu,Zn)₄₉ structural type of phases). The same eutectic phase in the as-cast and hot-deformed state of the Al–Zn–Mg–Cu-based alloys was observed—see References [15,19,20]. With respect to the TEM and EDS results, it can be assumed that the MgZn₂ phase is also

distinguishable in the XRD results, although the peaks of this phase are very weak and may be affected by the background. In view of results obtained by XRD, it can be said that the content of primary Mn,Fe,Si-containing particles observed by TEM may be relatively small and inhomogeneous.

The Sc,Zr-containing particles that correspond to the primary phase were also revealed in the 7075-Sc,Zr alloy in the HT state in several grains (Figures 1 and 4). Although the structure of the Sc(Zr)-containing particles is greatly dependent on the composition (and heat treatment routes), very similar structure (square and polygonal shapes) of the primary Sc,Zr-containing particles was detected in the Al-Mg-Sc-based [45-47] and Al-Zn-Mg-Sc-based alloys [15,19,20,48]. Figure 4 shows an AFM image according to the EDS observation of a selected primary Al₃(Sc,Zr)-phase particle in the 7075-ScZr material. In contrary to the primary Al₃Sc particles (References [45-47]), where a deep hole in the center surrounded by an area of several shell-like layers characterized by variant depths was proved, the incoherent Sc,Zr-containing particles detected here have heights falling in the interval of about 200–300 nm. Thus it can be concluded that significant altitude difference of the layers of the primary Sc-containing particles (References [45–47]), the inner central pothole, the less deep profound interlayer, the same profound of the inner convex layer around the pothole, and the marginal layer can be induced by different resistance of various layers of the primary particles to the electro-polishing before AFM observation. The surface of specimens for AFM observations was prepared only by a standard metallographic mechanical polishing and no electro-polishing was applied. It is therefore questionable whether electro-polishing connected with possible selected erosion in the sample preparation for the characterization of the Al-based materials with Sc-Zr addition by AFM should be avoided. However, this conclusion would require a more detailed examination which is not the subject of this work.

Formation of the coherent secondary $Al_3(Sc,Zr)$ particles (L1₂/cP4 structure) with the size of 10–50 nm predominantly situated in grain interiors and denuded zones created along boundaries of the grains were also revealed in the heat-treated 7075-ScZr alloy (Figure 5). The particle dispersion shows a typical contrast of "the coffee bean". ED pattern of the L1₂-structured precipitates is shown as inset in Figure 5. No precipitates other than the Al₃(Sc,Zr) were observed inside grains by TEM, which means that other phases (if any) inside grains have very low volume fraction. Compared to the as-cast state of the alloys (see Reference [19]), it means that the high-temperature annealing (isothermal annealing at 470 °C/60 min) is sufficient to dissolve the precipitates from the Al–Zn–Mg–Cu system inside grains, but at the same time the particles from the Al–Sc–Zr system can precipitate.



Figure 1. Microstructure overview (SEM images) of the HT state: (**a**) The 7075 alloy; (**b**) the 7075-ScZr alloy.



Figure 2. TEM image of the heat-treated 7075-ScZr alloy: (**a**) Eutectic phase(s); (**b**) coarse Mn,Fe,Si-containing particle.



Figure 3. XRD diffraction patterns of the heat-treated 7075 and 7075-ScZr alloys with identified phases.



Figure 4. AFM images of the incoherent primary Sc,Zr-containing particle: (**a**,**b**) 3D topography; (**c**) phase shift image and (**d**) the height profile in the middle section of the particle (cross-section).



Figure 5. Microstructure image (TEM, [110]_{Al} orientation) of the coherent secondary Al₃(Sc,Zr) particles and denuded zones in the 7075-ScZr alloy, ED pattern in the inset.

3.2. Natural Ageing of the Heat-Treated Alloys

Time evolution of the mean LT of positrons and microhardness Δ HV0.5 values of the alloys during natural ageing is shown in Figure 6. The mean LT behavior (Figure 6a) is comparable for both alloys. It can be divided into three individual stages: Up to 500 min an LT increase (stage I), then from 500 min up to ~1980 min (33 h) a roughly constant values of the LT (stage II), and above ~33 h a decrease of the LT (stage III). It can be also seen that the LT values for the 7075-ScZr alloy are higher than those for the 7075 alloy without Sc–Zr addition. Microhardness HV0.5 values (Figure 6b) increase immediately from the beginning of the natural ageing. The initial absolute HV0.5 value of the 7075 alloy (HV0.5 \approx 70) is significantly lower than the 7075-ScZr alloy (HV0.5 \approx 95). The microhardness values of the alloys reflect the Sc–Zr addition. This can be also seen from Table 3, where the microhardness HV0.5 values and absolute electrical resistivity ρ values (measured at temperature of liquid N_2 —78 K) after different heat treatment are given: The state after heat treatment at 470 °C/240 min and the HT state (470 °C/60 min); and both states after the subsequent natural ageing (33,450 and 3500 h). Presence of the secondary phase from the Al–Sc–Zr-based alloys caused typical hardening effect as $\Delta HV \approx 20$ –40, see References [15,19,20,25]. Comparable strengthening caused by co-presence of the primary incoherent and secondary coherent Sc,Zr-containing particles was observed in the deformed Al–Zn–Mg–Cu-based alloys with Sc–Zr addition [15,19,20]. Thus the presence of these Sc,Zr-containing particles is a probable reason for higher microhardness HV0.5 of the studied 7075-ScZr alloy. Table 3 also confirmations that no significant differences are between the values for the comparable states (cf. the state after annealing at 470 °C/240 min and the HT state). A difference in microhardness Δ HV0.5 values and resistivity $\Delta \rho$ values between the 7075 and 7075-ScZr alloys is similar within the error through the natural ageing regardless of the annealing time at 470 °C. According to the microstructure observation of the alloys (see above), this also justifies the claim that the heat treatment at 470 °C/60 min is sufficient for the Al–Zn–Mg–Cu system.



Figure 6. The evolution during natural ageing of the 7075 and 7075-ScZr alloys: (**a**) Mean LT values; (**b**) microhardness changes Δ HV. Vertical dashed lines indicate individual stages I–III.

Table 3. Values of microhardness HV0.5 and electrical resistivity ρ in the different state of the 7075 and 7075-ScZr alloys after different heat treatment and during subsequent natural ageing (NA) after 33, 450, and 3500 h.

Aller	Heat Treatment –	HV0.5			$ ho$ (n Ω ·m)			
Alloy		Initial State	NA 33 h	NA 450 h	NA 3500 h	Initial State	NA 33 h	NA 3500 h
7075	HT state	70 ± 3	117 ± 2	134 ± 3	145 ± 2	27 ± 1	35 ± 1	36 ± 1
7075-ScZr	HT state	86 ± 6 95 ± 4	113 ± 2 139 ± 5	$\frac{134 \pm 2}{155 \pm 6}$	144 ± 4 168 ± 3	26 ± 1	33 ± 1	-34 ± 1
7075-ScZr	470 °C/240 min	94 ± 4	138 ± 5	154 ± 4	167 ± 2	-	-	-

By two exponential components the LT spectra of all samples studied can be well described. Lifetimes τ_1 and τ_2 of the constituents and relative intensity I_2 of the longer constituent are plotted in Figure 7a,b, respectively. The shorter constituent with the lifetime τ_1 comes from free positrons (not captured in defects). The longer constituent with $\tau_2 \approx 220$ ps can be ascribed to the positrons captured at solute (co-)clusters in the alloys [20]. The lifetime τ_2 is comparable in both 7075 and 7075-ScZr alloys. This indicates that both alloys contain similar type of solute (co-)clusters. Note that LT component with similar lifetime τ_2 was observed also in these alloys subjected to hot deformation [20]. Our previous CDB investigations revealed that these clusters contain mainly Mg and Zn solutes [20]. It also has to be mentioned that coherent secondary as well as primary Al₃(Sc,Zr) particles do not trap positrons [19,20] but the Sc–Zr addition in the alloys can affect the development of the other phases (e.g., non-eutectic phases of the Al–Zn–Mg-based system [20]).

Positron annihilation spectroscopy (PAS) investigations of the Al–Zn–Mg-based alloys indicated that the interaction between solute atoms and vacancies has an influence on (co-)clusters/GP zones [19,20,25]. Parallel to PAS observations in the Al–Mg–Si-based [49–51] and Al–Zn–Mg–Cu-based alloys [19,20] one can conclude that immediately after high temperature treatment (solution treatment) the studied alloys contain vacancies associated with single and/or multiple Zn- or Mg-solutes and/or Zn,Mg(-co)-clusters developed during quenching. These solute (co-)clusters further evolve in the course of natural ageing. Owing to the strengthening effect of the (co-)clusters, the microhardness HV0.5 of the 7075 and 7075-ScZr alloys increases continuously during ageing at RT which is probably due to growing and development of these solute (co-)clusters in analogy with Al–Zn–Mg-based alloys (e.g., References [25,52,53]).



Figure 7. The evolution of: (a) The lifetimes τ_1 and τ_2 ; (b) the intensity I_2 of the HT state of the alloys subjected to natural ageing.

The intensity I_2 in the 7075-ScZr sample is lower than in the 7075 alloy. It indicates that the Sc–Zr addition has a slight negative influence on the concentration of solute (co-)clusters. Si, Cu or Mg solutes are most probably bound to Sc and Zr solutes and/or to the (secondary) Al₃Sc(Zr) particles. This presumed conclusion is further supported by the fact that the 7075-ScZr sample, i.e., the alloy with lower concentration of solute (co-)clusters, also exhibits slightly lower changes in microhardness HV0.5, see Figure 6b. However, it is also not possible to eliminate mutually different supersaturation in the solid solution.

The majority of positrons is trapped in solute (co-)clusters ($I_2 > 80\%$) already after the heat treatment at ~470 °C. It means that solute (co-)clusters were formed already during quenching of the sample. In the course of natural ageing the concentration of solute clusters increases in the stage I. This is reflected by an increase of I_2 in the stage I which reaches maximum in the stage II. A long term natural ageing (stage III) leads to a decrease of I_2 due to agglomeration of solute (co-)clusters into bigger objects ((precursors of the) GP zones). This results in an increase of the mean distance between clusters and thereby a decrease of their density.

Taking into account the behavior of the constituent (especially Zn, Mg, and Cu) at temperatures from RT to ~80 °C [20] and the calculated contribution of the solute concentration to the resistivity of Al (e.g., References [1,54,55]), the resistivity development during natural ageing is mainly associated with the change of Zn and Mg concentrations in the Al matrix. In the first approximation it can be assumed that the (co-)clusters/GP zones are composed of Zn and Mg atoms in a ratio of: (a) 1:1; (b) 1:2, see e.g., References [10,15,17,19–33,56–58]. If we assume this, then the resistivity $\Delta \rho$ changes in the HT + NA state (after natural ageing

up to 3500 h), $\Delta \rho \approx 8 \ n\Omega \cdot m$, see Table 3, would correspond to the decrement of Zn- and Mg-concentration in the matrix: (a) $\Delta C_{Zn,Mg} \approx 0.7 \pm 0.1$ at.%; (b) $\Delta C_{Zn} \approx 0.8 \pm 0.2$ at.% and $\Delta C_{Mg} \approx 0.4 \pm 0.1$ at.%. This decrement reasonably implicates that the changes in resistivity, microhardness and PAS characteristics can be attributed to the process of the formation/coarsening of the (co-)clusters/GP zones. These conclusions suitably complement the findings obtained through PAS.

In addition to microstructural characterization during the natural ageing, the corrosion characteristics of the alloys in the HT + NA state (natural ageing after 3500 h) were studied. The results of the potentiodynamic polarization are shown in Table 4 and Figure 8. The 7075-ScZr alloy has a higher corrosion potential $E_{\rm corr}$ than the 7075 alloy without Sc–Zr addition. A comparable difference of the $\Delta E_{corr} \approx 28$ mV caused by the Sc–Zr addition was measured in our previous study in the hot-rolled alloys with the comparable composition, see Reference [15]. In the studied 7075 and 7075-ScZr alloys the passivation region, where the corrosion current kept almost the same value ΔE_{corr} (see Table 4), was observed, which means that passive films were formed on the surfaces. A lower value of corrosion current density $I_{\rm corr}$ in the 7075-ScZr alloy (2.23 μ A/cm²) indicates a better corrosion resistance and a slower corrosion rate (~0.0243 mm/a) than for the 7075 alloy $(2.96 \ \mu A/cm^2 and \sim 0.0322 mm/a)$. For the studied alloys it can be concluded that the positive influence on corrosion properties is (probably) mainly caused by the Sc-Zr addition. Although corrosion measurement results can be found on many Al-based alloys, there are really very few detailed electrochemical measurements on the Al(-Sc)-Zr-based alloys (e.g., References [41,42,59-62]) and even less on the alloys of this type (7xxx series) with Sc and Zr elements in the available literature. In addition to our previous study in the hot-rolled alloys with comparable composition [15], the observed results are in agreement with Reference [62] where better corrosion resistance (especially slower corrosion rate and lower corrosion current density) was measured by electrochemical measurements for the AlZnMgCuScZr alloy than for the AlZnMgCu alloy in the EXCO testing solution.

Table 4. Corrosion characteristics of the HT + NA (3500 h) alloys obtained by potentiodynamic polarization measurements (measured at RT) in the 0.1 M NaCl solution. WL represents weight loss, CR corrosion rate, I_{corr} corrosion current density and E_{corr} corrosion potential.

Alloy	$I_{\rm corr}$ (μ A/cm ²)	WL (g/m ² /d)	CR (mm/a)	$E_{\rm corr}$ (mV)
7075	2.96	~0.238	~0.0322	-1154
7075-ScZr	2.23	~0.180	~0.0243	-1125



Figure 8. Potentiodynamic polarization diagram (measured at RT) in the 0.1 M NaCl solution.

3.3. Phase Development during Isochronal Annealing

The ageing processes in the Al–Zn–Mg–Cu-based alloys are complex and the decomposition of supersaturated solid solutions obtained by quenching takes place in several formation steps [15,19,20,24,63,64]. Typically, the precipitation of the (co-)clusters, precursors of the GP zones, and coherent GP zones precedes the formation of the semicoherent intermediate precipitates and incoherent equilibrium precipitates during isochronal annealing [15,19,20,25,65–67]. The early precipitation stages in these alloys are abundant and can have a significant influence the resistivity and (micro)hardness development during the natural ageing and/or the beginning of the annealing [25,30,49,52,53]. Isochronal resistivity $(\Delta \rho / \rho_0)$ and microhardness annealing curves of the HT alloys are presented in Figure 9. Electrical resistivity decrease in two stages (1-stage up to ~140 °C and 2-stage between 140 °C and 280 °C). Then the electrical resistivity is nearly constant (3-stage) and after annealing at temperatures higher than ~360 °C (4-stage) increases insignificantly. 1- and 2-stages of the resistivity decrease are connected with a maximum hardening HV0.5 after annealing up to 180–220 °C (Figure 9). The higher HV0.5 values of the 7075-ScZr in the HT state is probably caused by the secondary/primary Al₃(Sc,Zr)-phase particles (already existed in the HT state—see Figures 4 and 5). The comparable effect on HV0.5 values due to the presence of these particles is observed during natural ageing of the alloys (see Table 3).



Figure 9. Isochronal annealing curves of relative resistivity changes and microhardness HV0.5 changes with standard deviation of the HT alloys.

The microhardness isochronal curves for the HT + NA (natural ageing for 3500 h) alloys and the 7075-ScZr alloy heat treated at 470 °C/240 min after natural ageing (NA) for 3500 h are given in Figure 10. The microhardness values of the 7075-ScZr alloys are comparable for both alloys (heat treatment at 470 °C/60 min and 470 °C/240 min) after natural ageing. This indicates that the annealing at 470 °C/60 min is sufficient for the Al–Zn–Mg–Cu system, as stated above. The initial microhardness HV0.5 values of the HT + NA alloys in comparison with the HT alloys without NA (compare Figures 9 and 10) reflects the presence of the (co-)clusters/precursors of the GP zones developed during natural ageing. The HV0.5 values decrease to a local minimum at ~90 °C. The temperature range of the hardening peak can be observed at 150–210 °C. It is seen that the Sc–Zr addition has almost no effect on microhardness changes at 210–330 °C. But after that the HV values of the alloy with the Sc–Zr addition after only a slight decrease reach constant course in contrast to the continual decrease of the 7075 alloy. The Δ HV0.5 difference between 7075 and 7075-ScZr alloys at the end of annealing is nearly HV0.5 \approx 20 microhardness development of the alloys studied reflects the Sc–Zr addition, again.

190

170

150





Figure 10. Isochronal annealing curves of microhardness HV0.5 changes with standard deviation of the HT + NA alloys and 7075-ScZr alloy heat treated at 470 °C/240 min after natural ageing for 3500 h.

Out of the comparison of the microhardness and electrical resistivity changes annealing curves of the studied materials up to ~140 °C (Figures 9 and 10) it could be assumed that the precursors of the GP zones and/or GP zones are formed in the HT alloys during the isochronal annealing. This process is connected with microhardness and electrical resistivity increase at the 1-stage. Despite this fact, the precursors of the GP zones and/or GP zones are dissolved first in the HT + NA alloys. This dissolution leads to the microhardness decrease (up to ~100 °C). The results are in an agreement with the measurements of the Al–Zn–Mg(–Sc–Zr) alloys in our previous study (see Reference [25]).

Figure 11 shows microstructure of the 7075-ScZr alloy in the HT state (without NA) after isochronal heat treatment up to 220 °C, where the dense particle dispersion can be seen. Thus the main resistivity decrease (2-stage) and microhardness increase (140–220 °C) in the alloys studied are due to the precipitation of these particles. According to the literature (e.g., References [15,19,20,31-33]), the following phases in this temperature range come into consideration: (a) Metastable η' -phase (hexagonal, a = 0.496 nm, c = 0.935 nm or bcc, a = 1.422 nm, MgZn₂) [19,20,25,32,33]), (b) non-eutectic stable *T*-phase (bcc, a = 1.435 nm, $Al_2Zn_3Mg_3$ and/or $Mg_{32}(Al_{1-x}Zn_x)_{49})$ [20,25,31], (c) GP zones (hexagonal, *a* = 0.496 nm, c = 0.935 nm or bcc, a = 1.422 nm) [19,20,25,31,32]. Figure 12 shows the diffraction patterns from different grains of the 7075-ScZr alloy after isochronal heat treatment up to 220 °C taken near: (a) $[110]_{A1}$ and (b) $[111]_{A1}$ orientations. Figure 12a contains weak spots assigned to the secondary $Al_3(Sc,Zr)$ -phase particles, GP zones and non-eutectic T-phase particles. This is in conformity with recently published results, see References [19,20,31,32,58]. On the contrary, Figure 12b also shows weak spots which can be assigned to metastable η' -phase particles (see References [25,32,33]) and to the GP zones and secondary Al₃(Sc,Zr)-phase particles [19,25,57,67]. Although the presence of the GP zones, T-, η' - and Al₃(Sc,Zr)-phase particles has been demonstrated in electron diffraction (Figure 12), the individual types of the particles could not be easily recognized in conventional TEM image thanks to the high density of the particles (Figure 11). One can therefore mention that the phase composition is different in different places of the samples even after heat treatment.



Figure 11. Microstructure (TEM) of the 7075-ScZr alloy (near [110]_{Al} orientation) annealed up to 220 °C.



Figure 12. SAED pattern of the 7075-ScZr alloy after isochronal heat treatment up to 220 °C: (**a**) Near $[110]_{Al}$ orientation with weak spots from the GP zones, *T*-phase and Al₃(Sc,Zr) phase; (**b**) near $[111]_{Al}$ orientation with weak spots from the GP zones, η' -phase and Al₃(Sc,Zr) phase.

SEM and TEM observation of the 7075-ScZr alloy in the HT state after isochronal heat treatment up to 440 °C proved a coarsened secondary Sc,Zr-containing phase particles—see Figure 13. A volume fraction and composition of the eutectic grain boundary phase stay unmodified and the grain size does not vary in comparison to the initial HT state of the alloys (see above Chapter 3.1.). Furthermore, the Zn,Mg-containing (co-)clusters/GP zones and other phases (*T*-phase, η'/η -phase) disappeared during the isochronal annealing up to this temperature. The dissolution of these phases is mainly connected with the resistivity increase above ~360 °C (see Figure 9). At temperatures above ~240 °C, particle precipitation of the η -phase and *S*-phase was proved in the Al–Zn–Mg–Cu-based systems, e.g., see References [20,25]. This precipitation is a probable explanation of the undulating of the electrical resistivity curves in the 3-stage (Figure 9) and microhardness HV0.5 curves (Figures 9 and 10) at a temperature range of 250–350 °C. One can also conclude that the annealing is sufficient for homogenization of the Al–Zn–Mg–Cu-based system, but it is insufficient for the Al–Sc–Zr-based system, again. Microhardness development of the all

alloys studied (Figures 9 and 10) reflects the Sc–Zr addition at temperatures above ~300 °C. Assuming the presence of the primary and secondary $Al_3(Sc,Zr)$ -phase particles it can be also concluded that the yield strength cannot be captured as a linear superposition of several strength contributions. This conclusion is in an agreement with other observations in commercial 2xxx, 6xxx and 7xxx alloys, see References [20,25,65,67–69].



Figure 13. Microstructure (TEM) of the 7075-ScZr alloy after isochronal annealing up to 440 °C: Particles of the secondary Sc,Zr-containing phase with $L1_2$ structure (ED pattern of $[100]_{A1}$ zone in the inset).

3.4. Thermal Properties of the Alloys

Due to the acquired additional characteristics about the kinetics of phase development in the 7075(-ScZr) alloys in the different states, the apparent activation energy of the thermal processes by using DSC were calculated. The following states of the 7075 and 7075-ScZr alloys were used for the thermal study: HT, HT + NA (3500 h at RT) and HT + NA15000 (15,000 h at RT). Figure 14 shows, for clarity only, selected DSC thermographs up to 400 °C for one heating rate (5 °C/min). The curves mainly differ due to natural ageing (the HT state vs. HT + NA state and HT + NA15000 state). One endothermic effect marked B and five exothermic effects marked A, C–F (see Figure 14) are shown in the DSC curves of the samples.



Figure 14. Selected DSC curves (5 $^{\circ}$ C/min) of the 7075 alloy in the HT state and the 7075-ScZr alloy in the HT, HT + NA, and HT + NA15000 state.

Table 5 shows characteristic temperatures $T_{\rm m}$ of a DSC peak of maxima/minima of the thermal effects A–E in the alloys studied in the HT and HT + NA state. The exothermic effect C in the HT + NA state and the effect F in all the alloys studied were very often too weak to be analyzed through the materials studied, so they are not listed in Table 5.

Table 5. Characteristic temperatures $T_{\rm m}$ of a DSC peak of maxima/minima of the thermal effects A–E of the 7075 and 7075-ScZr alloys in the HT and HT + NA state.

Effect/Alloy	1 °C/min	2 °C/min	5 °C/min	10 °C/min	20 °C/min
Effect A (7075 HT)	58	63	72	83	90
Effect A (7075-ScZr HT)	58	63	72	84	91
Effect B (7075 HT + NA)	106	110	118	126	141
Effect B (7075-ScZr HT + NA)	104	110	118	127	142
Effect C (7075 HT)	165	177	191	201	209
Effect C (7075-ScZr HT)	165	178	189	198	-
Effect D (7075 HT)	208	219	231	239	255
Effect D (7075-ScZr HT)	207	219	230	241	255
Effect D (7075 HT + NA)	207	217	231	242	249
Effect D (7075-ScZr HT + NA)	208	216	229	239	250
Effect E (7075 HT)	237	255	263	277	295
Effect E (7075-ScZr HT)	237	254	265	276	294
Effect E (7075 HT + NA)	240	254	267	277	298
Effect E (7075-ScZr HT + NA)	238	256	265	277	292

The apparent activation energies Q of the observed effects A–E (see Table 6) were determined by the Kissinger method [24,70] based on the data obtained from the DSC curves (Table 5) and the knowledge that the characteristic temperatures T_m correspond to the maxima (minima) of the observed process and maximum process speed of the observed effect, respectively. Then the activation energies Q for the individual thermal effects are determined by a linear regression, i.e., $\ln(\delta/T_m^2)$ plotted vs. $1/T_m$, where δ is the heating rate. Some activation energies were not calculated as a consequence of a low markedness of the maximum heat flow (e.g., effect C for the HT + NA alloys).

Table 6. Activation energies *Q* of the thermal effects A–E determined by the Kissinger analysis of DSC data.

Sample	Effect (Process)	Activation Energy Q (kJ/mol)		
	A (GP zones formation)	84 ± 6		
	C (η' -phase precipitation)	111 ± 6		
7075 HI	D (<i>T</i> -phase precipitation)	130 ± 11		
	E (η -phase precipitation)	122 ± 9		
	A (GP zones formation)	81 ± 5		
	C (η' -phase precipitation)	113 ± 10		
7075-ScZr H1	D (<i>T</i> -phase precipitation)	127 ± 10		
	E (η -phase precipitation)	124 ± 10		
	B (GP zones dissolution)	103 ± 13		
7075 HT + NA	D (T-phase precipitation)	136 ± 5		
	E (η -phase precipitation)	122 ± 12		
	B (GP zones dissolution)	100 ± 11		
7075-ScZr HT + NA	D (T-phase precipitation)	137 ± 5		
	E (η -phase precipitation)	130 ± 12		

The exothermic effect A corresponds well to the hardening and resistivity decrease (1-stage) up to ~140 °C of the HT alloys, see Figure 9. The endothermic effect B corresponds well to the softening up to ~120 °C of the HT + NA alloys (Figure 10). The effect A obviously corresponds to the production of (the precursors of) the GP zones, effect B to their dissolu-

tion, respectively. Given the available experimental options, it is not possible to distinguish between coarsening of the precursors of the GP zones ((co-)clusters) and the GP zones. The activation apparent energy values of the effect B (~102 kJ/mol) are in a good agreement for the dissolution of the GP zones, those reported in References [25,71–73]. The temperature range of the dissolution is logically higher and activation energy values are logically also higher than the values for the effect A (~82 kJ/mol)—the formation of the (co-)clusters/GP zones [25,52,63]. The temperature range of the effect B (i.e., (co-)clusters/GP zones dissolution) is slightly influenced by the natural ageing time, cf. HT + NA state and HT + NA15000 state in Figure 14. However, measurements on the HT + NA15000 sample were made only once (at one heating rate only).

The exothermic processes C and D correspond well to the hardening with a maximum at ~180 $^{\circ}$ C of the alloys in the HT and HT + NA state as well as the resistivity decrease in the 2-stage (cf. Figure 9, Figure 10, and Figure 14). As the microscopy observation by TEM at 220 °C is shown in Figures 11 and 12, these effects C and D can be assumed to be associated with metastable η' -phase and non-eutectic stable *T*-phase particle precipitation. The activation energy of the effects C and D were calculated as ~112 kJ/mol and ~133 kJ/mol, respectively. The calculated value for the precipitation of the η' -phase particles in the studied alloys excellently agrees with the values for the precipitation of the η' -phase determined in the Al–Zn–Mg-based alloys [25,72]. Although the data in literature for the *T*-phase precipitation are usually not available, in our previous study [25] we calculated the activation energy in the alloys with comparable composition without Cu for this precipitation in the range of 128–168 kJ/mol. But the result was based only on a few experimental points. Given the direct evidence using TEM (Figure 12) in this study, it can be concluded that the effect D is very probably connected with the T-phase precipitation. From the obtained results it can also be deduced that the formation of the η' -phase particles is affected by natural ageing at RT similarly to the formation/dissolution of the (co-)clusters/GP zones, while the *T*-phase precipitation is not affected by natural ageing.

The activation energy for the effect E is calculated as ~125 kJ/mol. The energy value could not be determined for the effect F because a weak thermal process was detected only for some heating rates. The calculated value of the effect E is in an agreement with literature for the precipitation of the stable η -phase: 118–142 kJ/mol, see References [25,71–73]. Although there is no direct microscopic evidence, the temperature region of the effect F corresponds very well to the temperature range (240–300 °C) of the precipitation of irregular shape S-phase particles [20,25,58,74,75]. Conversely, formation of the η -phase particles can occur below ~240 °C in the Al-based alloys [19,20]. Although the data in the literature for this precipitation are insufficient, the calculated values indicate that precipitation of the *T*-phase takes place by a different mechanism than the precipitation of the stable η -phase. One can also conclude that Sc–Zr addition has a little effect on the ongoing transformation processes, probably due to the fact that these elements are not in solid solution, but in the Al₃(Sc,Zr)-phase particles.

4. Conclusions

A detailed characterization of the phase development and age hardening of the heattreated commercial aluminum 7075(Al–Zn–Mg–Cu–Mn–Si–Fe(–Sc–Zr))-based alloys can be stated in the following points:

- The microstructure of the initial (heat-treated) state of the alloys is very complex. The observation proved that the eutectic phases consist of four types at ones: MgZn₂ phase, Al₂CuMg phase (*S*-phase), Al₂Zn₃Mg₃/Mg₃₂(Al,Cu,Zn)₄₉ phase (*T*-phase) and primary cubic λ-Al(Mn,Fe,Si) phase. In addition, two types of non-eutectic particles in the alloys with Sc–Zr addition are present: Primary incoherent Al₃(Sc,Zr) particles. with square and polygonal shapes and secondary coherent Al₃(Sc,Zr) particles.
- The Sc,Zr-containing alloys cannot be completely homogenized due to these elements. However, for the 7xxx-based system, a heat treatment above ~440 °C is sufficient (unless eutectic phase is considered). It is not even possible to observe the differ-

ence in characterization of the properties after the high-temperature annealing at $470 \degree C/60$ min and $470 \degree C/240$ min, respectively.

- Microhardness values reflect the Sc–Zr addition in the 7075-ScZr alloy. Strengthening is caused by the presence of the primary/secondary Al₃(Sc,Zr)-phase particles. Positive influence on corrosion properties is also caused by the Sc–Zr addition.
- Single and/or multiple Zn- or Mg-solutes and/or Zn,Mg(-co)-clusters developed during quenching immediately after high temperature treatment in the alloys. These solute (co-)clusters further evolve in the course of natural ageing. This process causes a significant increase in microhardness and electrical resistivity values. A long term natural ageing leads to a coarsening of the solute (co-)clusters into bigger objects (probably precursors of the GP zones).
- Addition of Sc and Zr has a slight negative influence on the concentration of solute (co-)clusters. Si, Cu or Mg solutes are most probably bound to Sc and Zr solutes and/or to the Al₃Sc(Zr)-phase particles. However, in general it can be said that the co-presence of the Sc- and Zr- elements have only a little effect on the phase transformations of the Al–Zn–Mg–Cu system.
- Formation of the η'/η -phase is slightly suppressed in the alloys after natural ageing. The dissolution of the precursors of the GP zones/GP zones is shifted to higher temperatures depending on the time of natural ageing.
- The apparent activation energy values of the observed thermal processes were calculated as: Formation of the precursors of the GP zones/GP zones: ~82 kJ/mol, dissolution of the (co-)clusters/GP zones: ~102 kJ/mol, formation of the metastable η'-phase: ~112 kJ/mol, formation of the stable *T*-phase: ~133 kJ/mol, formation of the stable η-phase: ~125 kJ/mol.
- A combination of both precipitation sequences of the Al–Zn–Mg–Cu-based system was observed in the studied alloys.

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