Original scientific paper

Received: April 12, 2015
Accepted: July 2, 2015

Influence of minor scandium and zirconium additions on the microstructure of Al and Al-5Mg alloy

Vpliv manjših dodatkov skandija in cirkonija na mikrostrukturo Al in zlitine Al-5Mg

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Abstract

The article describes the effect of varying minor scandium and zirconium quantities on the grain refinement of the as-cast alloys Al-Sc, Al-Sc-Zr, and Al-5Mg-Sc-Zr, as well as the distribution of either element in the phases formed during the solidification, homogenisation annealing, and ageing of these alloys. Scandium and zirconium in the Al-Sc-Zr and Al-5Mg-Sc-Zr alloys are present in three metallographic formations: in the solid solution of the aluminium matrix, as primary particles Al_3(Sc, Zr), and as dispersive precipitates. The primary particles Al_3(Sc, Zr), sized between 5 µm and 10 µm, act as crystallisation nuclei during the solidification of the alloys. As the EDS SEM analysis indicates, the primary particles are not homogeneous: the scandium and zirconium contents decrease from centre to edge. Another manifestation of scandium and zirconium in the Al-Sc-Zr and Al-5Mg-Sc-Zr alloys takes the form of secondary precipitates. These precipitates exist in the as-cast, homogenised, and aged alloys. Their sizes range from 5 nm to 60 nm in the as-cast alloys, and from 100 nm to 350 nm in the aged ones. The precipitate number density decreases with the annealing of the alloys.

Key words: aluminium alloys, scandium, zirconium, microstructure

Izvleček

Članek se osredinja na učinek različnih manjših količin skandija in cirkonija na udrobnenje zrn v osnovnih zlitinah Al-Sc, Al-Sc-Zr in Al-5Mg-Sc-Zr in porazdelitev obeh elementov v fazah, ki nastanejo med strjevanjem, homogenizacijskim žarjenjem in staranjem teh zlitin. Skandij in cirkonij v zlitinah Al-Sc-Zr in Al-5Mg-Sc-Zr sta v treh metalografskih oblikah: v trdni raztopini aluminijeve matrice, kot primarni delci Al_3(Sc, Zr) in kot dispergirani izločki. Primarni delci Al_3(Sc, Zr) z velikostjo od 5 µm do 10 µm so kristalizacijske kali med strjevanjem zlitin. Kot je pokazala analiza EDS SEM, primarni delci niso homogeni; vsebnosti skandija in cirkonija se manjšata od sredine k robovom delcev. Drugi način pojavljanja skandija in cirkonija je v obliki sekundarnih izločkov. Izločki se nahajajo v ulitih, homogeniziranih in staranih zlitinah. Velikost izločkov je 5–60 nm v ulitih in 100–350 nm v staranih stanjih zlitin. Gostota izločkov se manjša z žarjenjem zlitin.

Ključne besede: aluminijeve zlitine, skandij, cirkonij, mikrostruktura

Introduction

Scandium (Sc) has a considerable influence on the microstructure and properties of aluminium (Al) and its alloys. There are three main reasons for adding Sc to aluminium alloys (Al-alloys): (i) grain refinement during casting, (ii) precipitation hardening, and (iii) grain structure control [1]. It has been demonstrated that a small Sc addition in Al and Al-alloys produces Al_3Sc precipitates, usually termed dispersoids [1–4]. Al_3Sc dispersoids efficiently impede the movement of grain boundaries, which leads to recrystallisation resistance and to the thermal stability of the crystal grains at higher temperatures [1, 2, 4–6]. Beside the binary Al-Sc alloys, the Sc-containing alloys studied most extensively were the Al-Mg-Sc type alloys [3, 4, 7–9].
The beneficial effects of Sc are enhanced when Sc is added to Al-alloys in combination with zirconium (Zr) [1, 4, 7, 8]. The presence of both elements in the alloy improves its recrystallisation resistance, the stability of its crystal grains during high-temperature annealing, and its mechanical properties [1, 4, 8]. These improvements are due to the formation of very fine and uniformly distributed Al_3(Sc, Zr) precipitates, which pin the grain boundaries [1, 7, 8, 10, 11]. The Al_3(Sc, Zr) precipitates have a core/shell structure with an uneven distribution of Sc and Zr: a Sc-rich core is surrounded by a Zr-rich shell [1, 9, 10–12]. The presence of Zr prompts the grain refinement action at lower concentrations of Sc, starting from the mass fraction of Sc w = 0.18 % [4]. It is for this reason that Sc is introduced into commercial Al-alloys together with Zr [4]. A further advantage of the joint addition of Sc and Zr concerns the superplastic forming of Al-alloys, where a fine-grained and stable microstructure is the basic prerequisite for good superplasticity. Recent researches have shown that the combined additions of Sc and Zr to Al-Mg alloys improve their superplasticity more efficiently than the separate addition of either element does [13–16].
The aim of our experiment was to establish the influence of varying minor Sc and Zr quantities on the cast grain structure and to investigate the distribution of Sc and Zr in the phases formed during the solidification, homogenisation annealing, and ageing of Al and Al-5Mg based alloys.

Materials and methods

The experiments were conducted with Al and Al-5Mg alloys containing either a minor addition of Sc or a combination of Sc and Zr. The designation and chemical composition of each alloy is shown in Table 1. The alloys were prepared by laboratory induction melting, using Al99.99 (w/%), Mg99.8, and the master alloys AlSc2.1, AlZr7.5, and AlTi5B1. Three kilograms of Al were melted in a graphite crucible, while the Mg and the master alloys were added to the molten Al at a temperature of (705±5) °C. The melts were repeatedly cast into a wedge-shaped copper mould, where they cooled to ambient temperature at a rate of ≈ 20 K s^{-1}. The shapes of the cut castings are shown in Figure 1. The microstructures of the alloys were examined in their as-cast, homogenised, and aged states. The as-cast alloys without Mg were homogenised for 24 h at 600 °C and those containing Mg for 4 h at 440 °C, followed by 4 h at 460 °C. After the homogenisation annealing, the alloys were aged for 4 h and 24 h at 400 °C.

Table 1: *The chemical composition of the alloys investigated (in mass fractions, w/%)*

Mark	Alloy	Si	Fe	Mn	Mg	Ti	Zr	Sc	Al
A	Al-0.3Sc	0.006	0.002	0.001	0.00	0.002	0.000	0.24	Bal.
B	Al-0.3Sc-0.15Zr	0.008	0.017	0.001	0.00	0.002	0.147	0.28	Bal.
C	Al-5Mg-0.2Sc	0.022	0.048	0.004	5.14	0.016	0.004	0.21	Bal.
D	Al-5Mg-0.2Sc-0.15Zr	0.007	0.013	0.002	5.16	0.011	0.156	0.18	Bal.
E	Al-5Mg-0.35Sc-0.15Zr	0.007	0.016	0.002	4.72	0.012	0.168	0.35	Bal.

The examination methods were light microscopy, scanning electron microscopy SEM (JEOL JSM – 5610 with an EDS detector), and transmission electron microscopy JEOL 3100 (ISIS EDXS with an acceleration voltage of 200 kV). The metallographic investigations were focused on the grain microstructure, the primary phases with Sc and Zr, and the secondary precipitates. The grain microstructure was established by using Baker's reagent. The average crystal grain size was examined with the linear intercept technique. The Sc and Zr contents in the primary phases were checked by SEM EDS, and in the secondary precipitates by the TEM EDXS analysis. The sizes of the secondary precipitates were measured manually, and their density was assessed by a visual count within a set area of bright field TEM (BF TEM) images.

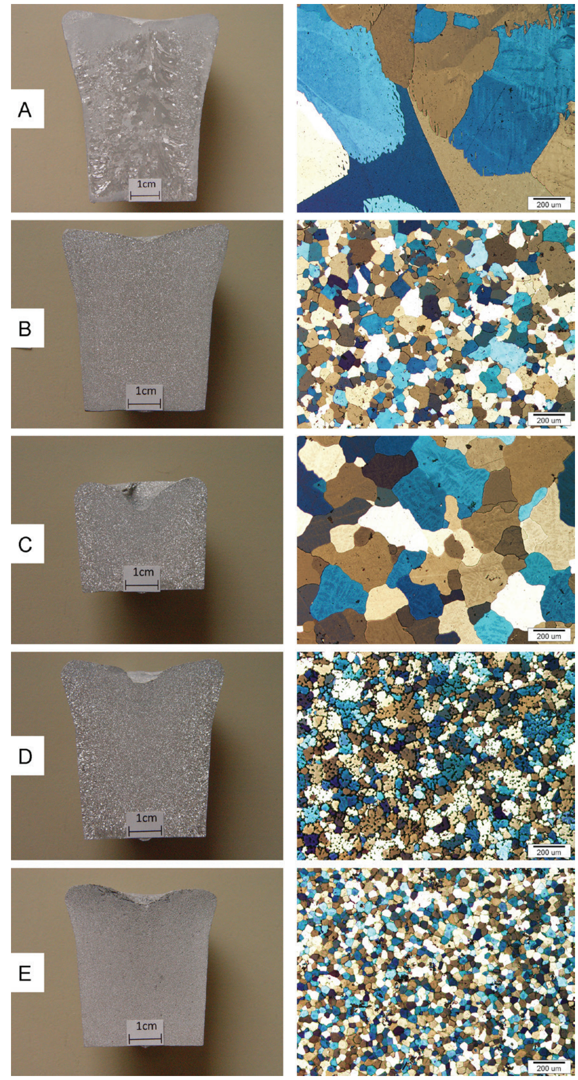

Figure 1: *Macro- and microscopic images of crystal grains in the as-cast A, B, C, D, and E alloys with varying Sc and Zr contents.*

Results and Discussion

Figure 1 shows the macro- and micro-images of crystal grains in as-cast alloys with varying contents of Sc and Zr. The average sizes of the grains are given in Table 2.

Table 2: *The average grain sizes of the alloys investigated*

Alloy	A	B	C	D	E
Grain size (µm)	295	54	190	41.5	33

An addition of less than w(Sc) = 0.3 % does not drastically reduce the grain size of these alloys. The size of the crystal grains is unevenly distributed over the cross-sections of the castings. On the other hand, the simultaneous addition of Sc and Zr refines the grain size of the alloys Al-0.3Sc-0.15Zr, Al-5Mg-0.2Sc-0.15Zr, and Al-5Mg-0.35Sc-0.15Zr to 54, 41.5 µm and 33 µm respectively. All these alloys have an equiaxed, nondendritic grain structure, usually with a uniform grain size within each casting. A minor addition of Zr – about w = 0.15 % in the Al-Sc and Al-5Mg-Sc alloys – has an intensive grain refining effect on the as-cast structure in spite of the low Sc content.

Figure 2 shows the backscattered electron images (BSE images) of a nearly 10 µm square particle within a crystal grain of the as-cast alloy Al-0.3Sc-0.15Zr (a, b), and its composition analysis at spot 1 (c). The particle is composed of Al, Sc, and Zr with its uneven distribution. Figure 4 presents the contents of Sc and Zr at various points of the particle as established by the EDS analysis. The concentration of both elements decreases from centre to edge, but the Zr content is higher at all analysed points. The stoichiometric ratio of Al to (Sc + Zr), expressed in average mass fraction (w), is about 3 : 1. The ratio Zr : Sc in the particle varies from 1.5 to approximately 1.9, with a mean value of 1.65.

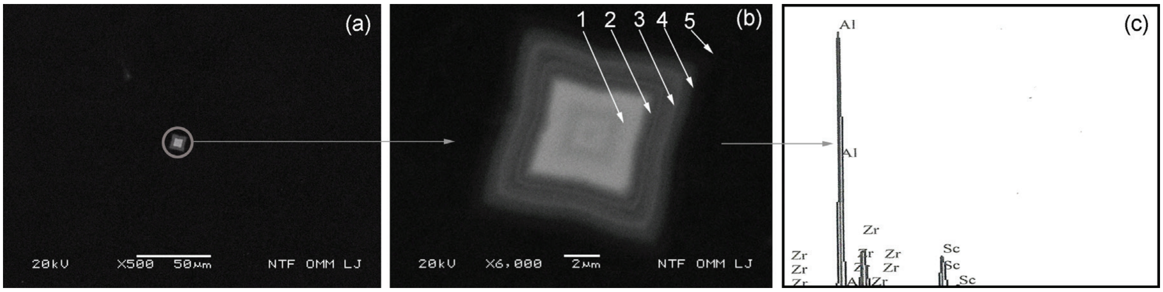

Figure 2: *BSE images of the particle in the as-cast alloy Al-0.3Sc-0.15Zr, with markings of the analysed spots 1–5 (a, b) and a composition analysis of the particle at spot 1 (c).*

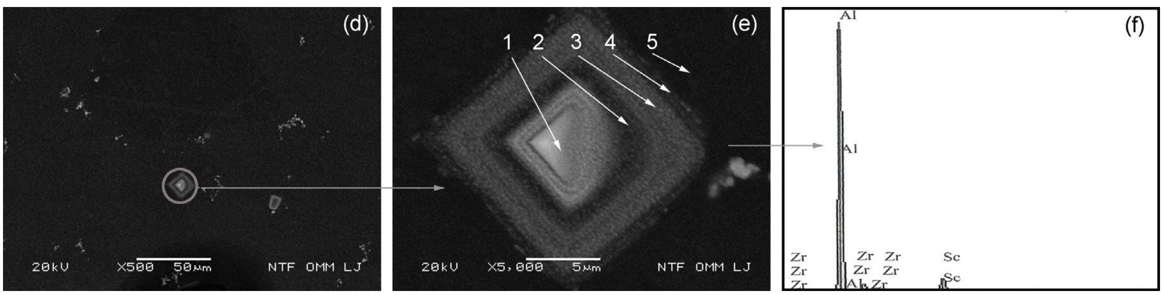

Figure 3: *BSE images of the particle in the homogenised alloy Al-0.3Sc-0.15Zr, with markings of the analysed spots 1–5 (d, e) and a composition analysis of the particle at spot 1 (f).*

Figure 3 shows the BSE images (d, e) of the particle with the composition (c), taken after the homogenisation annealing of the Al-0.3Sc-0.15Zr alloy at 600 °C for 24 h. The concentrations of Sc and Zr are reduced in comparison with the as-cast state of the alloy (Figure 4). The contents of both elements are nearly equal at all analysed spots, decreasing from centre to edge. The decomposition of the particle changes the stoichiometric ratio Al : (Sc + Zr). The contour of the particle does not disappear despite the long-continued homogenisation annealing at a relatively high temperature.

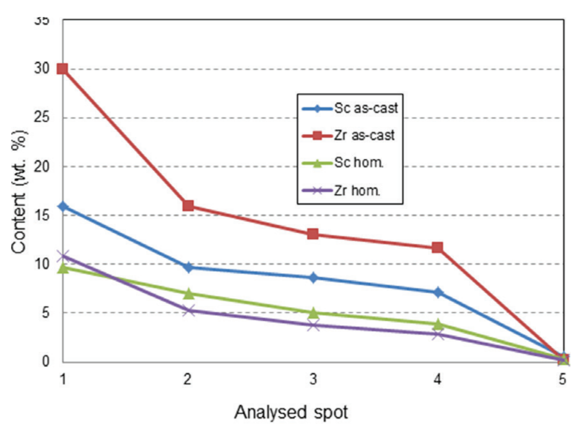

Figure 4: *The Sc and Zr contents in the particles presented in Figures 2 and 3, belonging to the as-cast and homogenised alloy Al-0.3Sc-0.15Zr.*

When, on the other hand, Sc and Zr have been added simultaneously, the Al-Sc-Zr and Al-5Mg-Sc-Zr alloys in as-cast, homogenised, and aged states contain not only large particles but also nm-size precipitates. These precipitates, shown in BF TEM and BSE SEM micrographs (Figure 5), consist of Al, Sc and Zr. The average quantitative composition of the precipitate, determined by the EDS TEM analysis, is displayed in Table 3. The average chemical composition of the precipitates in the aged alloy is similar in all states analysed and does not depend on the ageing time. The distribution of Sc and Zr in the precipitates is not evident from the BF TEM micrographs. The Al-matrix close to the precipitates does not contain Sc or Zr, and the average stoichiometric ratio Al : (Sc + Zr) in the precipitates is nearly 3 : 1. In addition, the EDS SEM analysis reveals that the bright points in the BSE image (Figure 5h) contain more Sc and Zr than the surrounding Al-matrix does. These results are in agreement with the data found in literature: it has been reported by a number of researchers that dispersive precipitates

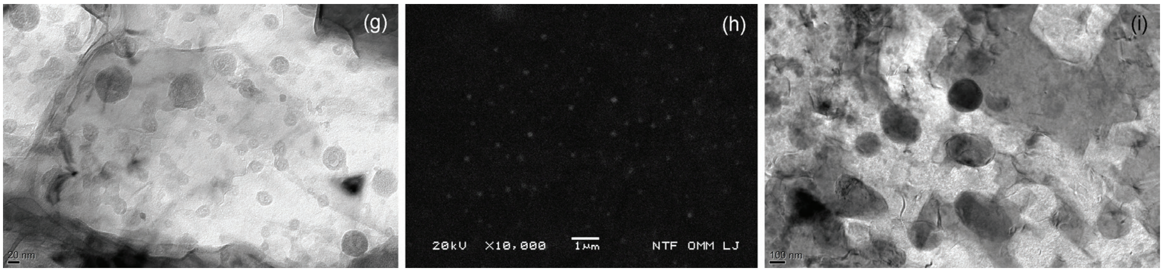

Figure 5: *The BF TEM image of Al_3(Sc, Zr) precipitates in the as-cast alloy Al-0.3Sc-0.15Zr (g); BSE (h) and BF TEM (i) images of Al_3(Sc, Zr) precipitates in the Al-0.3Sc-0.15 Zr alloy, aged for* 4 h *at* 400 °C.

in alloys of the Al-Sc-Zr type consist of Al, Sc, and Zr with random distribution. The chemical formula of the composed precipitates can be noted as Al_3(Sc, Zr) or, more correctly, as $Al_3(Sc_{1-x}, Zr_x)$ [1, 8–10].

The size and distribution of the precipitates in the as-cast and aged alloy Al-0.3Sc-0.15Zr were measured with the help of BF TEM micrographs. The results are shown in Table 4. The smallest precipitates with the highest density are found in the as-cast alloy. The aged alloy, by contrast, contains larger precipitates with a much lower density. While the duration of the ageing time has no considerable influence on their density, longer ageing does slightly increase their size. The size and density of the precipitates in the TEM images are comparable with those in the BSE images.

The microstructures of the quaternary Al-Mg-Sc-Zr (D and E) alloys were investigated in the same way as the Mg-less B alloy. The microstructures of these alloys were found to be very similar to the Al-0.3Sc-0.15Zr (B) alloy, with relatively large primary particles composed of Al, Sc, Zr, and dispersive Al_3(Sc, Zr) precipitates. Figure 6 shows the BSE images of primary particles in the as-cast (j, k) and homogenised (l) Al-5Mg-0.35Sc-0.15Zr (E) alloy. In shape, size, and composition, they equal the particles in the Al-0.3Sc-0.15Zr (B) alloy. The secondary Al_3(Sc, Zr) precipitates are present in D and E alloys – as-cast, homogenised, and aged – and their characteristics are similar to the precipitates in the Mg-less Al-0.3Sc-0.15Zr (B) alloy.

The average grain sizes of the investigated as-cast alloys Al-0.3Sc (A) and Al-5Mg-0.2Sc (C) are 295 μm and 190 μm respectively. Alloys with less than w(Sc) = 0.3 % show no grain refinement effect. According to the Al-Sc phase diagram, the eutectic point occurs at approximately

Table 3: *The average composition of the precipitates and of the Al-matrix in the aged Al-0.3Sc-0.15Zr alloy (in mass, w/%, and amount fractions, x/%)*

Place	State	w/%			x/%		
		Al	Sc	Zr	Al	Sc	Zr
Precipitate	4 h, 400 °C	76.72	14.26	9.02	87.23	9.73	3.03
Precipitate	24 h, 400 °C	73.76	15.01	11.23	85.68	10.46	3.86
Al-matrix	24 h, 400 °C	99.97	0.04	0.01	99.98	0.02	0.00

Table 4: *The average size and density of the precipitates in the as-cast and aged alloy Al-0.3Sc-0.15Zr*

State	Precipitate size	Precipitate density
As-cast	5–60 nm	≈ 320 precipitates/1 μm^2
Aged 4 h, 400 °C	100–300 nm	≈ 5–6 precipitates/1 μm^2
Aged 24 h, 400 °C	150–350 nm	≈ 6 precipitates/1 μm^2

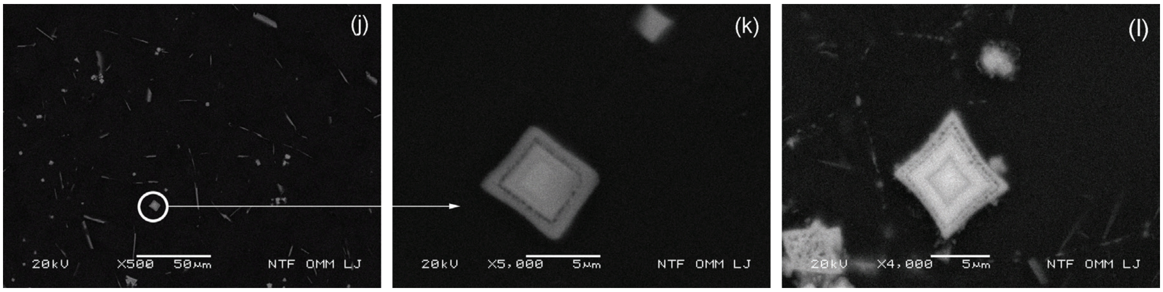

Figure 6: *BSE images of the primary particles in the as-cast (j, k) and homogenised (l) alloy Al-5Mg-0.35Sc-0.15Zr (the E alloy).*

w(Sc) = 0.55 % and at a temperature of 659 °C [1, 4, 6, 17]. The maximum solubility of Sc in Al in the solid state is *w*(Sc) = 0.35 % [4]. When an aluminium melt with a hyper-eutectic content of Sc is slowly cooled, the first phase in the melt will be Al_3Sc [1, 2, 5, 6, 8]. The Al_3Sc phases, fcc with a lattice parameter of 0.4105 μm, act as potential nucleation sites for aluminium crystal grains [5, 6]. The investigated Al-0.3Sc and Al-5Mg-0.25Sc alloys reveal no Al_3Sc particles: this agrees with the data that it is only Sc additions greater than the eutectic composition (*w*(Sc) ≈ 0.55 %) that act as grain refiners of aluminium castings, due to the formation of primary particles during solidification [1, 2, 4–6, 8, 17].

The minimum Sc level required for grain refinement can be reduced by the simultaneous addition of a minor Zr content to the alloys. In the alloys investigated – Al-Sc-Zr and Al-5Mg-Sc-Zr – Sc and Zr are present in three forms: in a solid solution of Al, as primary phases in the form of square or rectangular particles sized between 5 μm and 10 μm, and as fine dispersive precipitates.

The composition of the primary particles is not homogeneous: the Sc and Zr contents decrease from centre to edge. The average ratio Al : (Sc + Zr) is nearly 3 : 1, which is in accordance with the chemical formula Al_3(Sc, Zr) [1, 4]. The Al_3(Sc, Zr) particles are the first to form in the melt, thus serving as effective crystallisation nuclei during the solidification of the residual melt, which results in a fine-grained microstructure. This is demonstrated by the BSE images of the as-cast alloy Al-5Mg-0.35Sc-0.15Zr, which reveal the presence of Al_3(Sc, Zr) particles within some crystal grains (Figure 7). The reason why such particles are not evident in all grains is the variety of their orientation and of their cross-sections, resulting from the preparation of the metallographic samples.

As indicated by the EDS SEM analysis, the Zr content in the centre of the primary particles is higher than the Sc content. On the basis of the Al-Zr and Al-Sc phase diagrams [8, 18–20] as references for the Al-Sc-Zr type alloys, it is believed that Al_3Zr precipitates first form from the melt

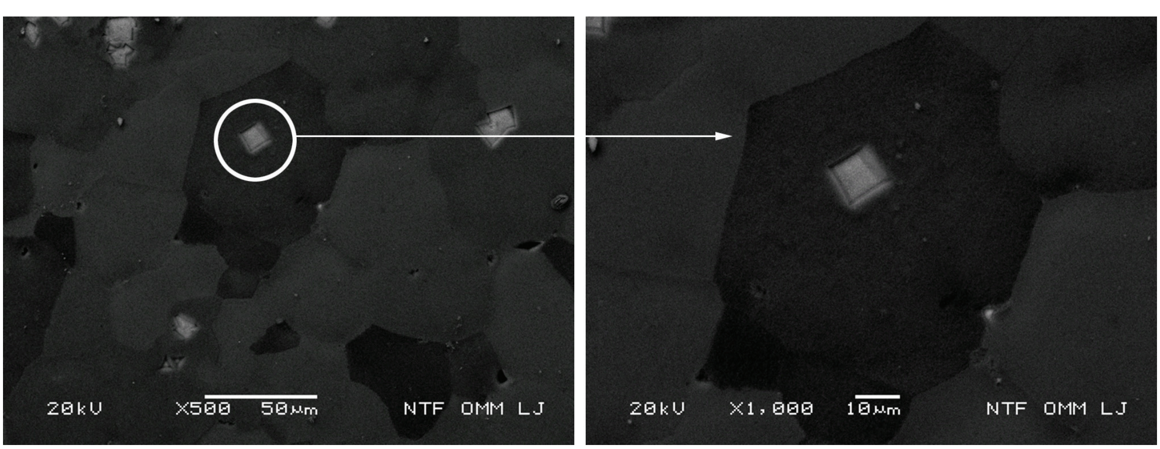

Figure 7: *BSE images of the as-cast alloy Al-5Mg-0.35Sc-0.15Zr containing Al_3(Sc, Zr) particles.*

by peritectic reaction at about w(Zr) = 0.1 %. This is followed by the precipitation of Al_3Sc on the Al_3Zr [4, 8, 21]. The uneven distribution of Sc and Zr in the particles is due to the further diffusion of both elements during the cooling of the alloy after solidification. In the newly formed composed particles Al_3(Sc, Zr), Zr replaces a part of the Sc content required for achieving the critical size of Al_3Sc as a crystallisation nucleus [4, 8]. Thus the addition of about w(Sc) = 0.2 % and w(Zr) = 0.1 % significantly refines the grain sizes of Al and Al-Mg type alloys at a much lower content of the costly Sc [8], and therefore Sc is introduced into commercial aluminium alloys together with Zr [4]. However, the mechanism by which the primary particles containing Sc and Zr are formed in Al and Al-alloys is still not entirely explained.

Another manifestation of Sc and Zr in the Al-Sc-Zr and Al-5Mg-Sc-Zr alloys takes the form of fine secondary precipitates. According to the literature on the subject, these dispersive precipitates have a core/shell structure where the composition of the core differs from that of the surrounding shell. These precipitates, designated as Al_3(Sc, Zr), are coherent with the matrix [1, 8, 10–12]. They consist of a core containing Al and Sc (Al_3Sc) and surrounded by a Zr-rich shell (Al_3Zr) [10]. The distribution of Sc, Zr and Al in the secondary precipitates differs from that in the primary Al_3(Sc, Zr) particles, which is due to the different diffusion rates of Sc and Zr during solidification and in the solid solution [11, 21]. The precipitation in the secondary precipitates starts with the nucleation of nearly pure Al_3Sc, whereas Zr precipitates on Al_3Sc nuclei at a later stage [1]. The Al_3(Sc, Zr) precipitates were found in all three forms of the Al-Sc-Zr and Al-5Mg-Sc-Zr alloys: homogenised, aged, and as-cast. This can be explained with the short incubation period (≈ 102 s) of the Al_3Sc nuclei [8, 21, 22]. Evidently, dispersive Al_3(Sc, Zr) precipitates form in the Al-solid solution even while the castings are still cooling after solidification. These dispersive precipitates are effective in pinning the dislocations and in impeding the movement of high-angle boundaries, thus causing resistance to recrystallisation and improving the thermal stability of the fine-grained microstructure at higher temperatures [7, 8, 10].

Conclusions

The article describes the effect of varying minor scandium and zirconium quantities on the microstructure of the alloys Al-Sc, Al-Sc-Zr, Al-5Mg-Sc, and Al-5Mg-Sc-Zr. The findings of the research include the following:

— Scandium and zirconium are present in the investigated alloys Al-Sc-Zr and Al-5Mg-Sc-Zr in three metallographic formations: (i) in solid solution, (ii) as primary particles Al_3(Sc, Zr), and (iii) as dispersive precipitates.
— There is no grain-refining effect in as-cast alloys Al-Sc and Al-5Mg-Sc with less than w(Sc) = 0.3 %. The addition of about w(Zr) = 0.15 % significantly refines the grain sizes of the Al-0.3Sc and Al-5Mg-0.2Sc alloys.
— The primary particles Al_3(Sc, Zr), sized between 5 µm and 10 µm, act as crystallisation nuclei during the solidification of the alloys. The composition of the primary particles is not homogeneous: the Sc and Zr contents decrease from the centre to the border areas, with the Zr content exceeding that of the Sc. The presence of Mg in the alloys does not alter the formation of primary particles.
— Another manifestation of Sc and Zr in the Al-Sc-Zr and Al-5Mg-Sc-Zr alloys takes the form of secondary precipitates. They are found in as-cast, homogenised and aged alloys. The size of the precipitates ranges from 5 nm to 60 nm in as-cast alloys, and from 100 nm to 350 nm in aged alloys.

Acknowledgements

The authors wish to thank dr. Goran Dražić, Nika Breskvar, Tomaž Martinčič, Božo Skela and Samo Smolej for their help with the experimental work. This study was partly supported by the Slovenian Research Agency (ARRS), Government of the Republic of Slovenia, through Project L2-4183.

References

[1] Röyset, J. (2007): Scandium in aluminium alloys overview: physical metallurgy, properties and applications. *Metallurgical Science and technology*, 25, pp. 11–21.

[2] Röyset, J., Ryum, N. (2005): Kinetics and Mechanisms of precipitation in an Al-0.2 *w*t. % Sc. *Material Science and Engineering A*, 396, pp. 409–422.

[3] Sawtell, R. R., Jensen, C. L. (1990): Mechanical properties and microstructures of Al-Mg-Sc alloys. *Metallurgical Transactions A*, 21 A, pp. 421–430.

[4] Zakharov, V. V. (2003): Effect of scandium on the structure and properties of aluminium alloys. *Metal Science and Heat Treatment*, 45, pp. 246–253.

[5] Blake, N., Hopkins, M. A. (1985): Constitution and age hardening of Al-Sc alloys. *Journal of Material Science*, 20, pp. 2861–2867.

[6] Hyde, K. B., Norman, A. F., Prangnell, P. B. (2001): The effect of cooling rate on the morphology of primary Al_3Sc intermetallic particles in Al-Sc alloys. *Acta Materialia*, 49, pp. 1327–1337.

[7] Peng, Y., Yin, Z., Nie, B., Zhong, L. (2007): Effect of minor Sc and Zr on superplasticity of Al-Mg-Mn alloys. *Transactions of Nonferrous Metals Society of China*, 17, pp. 744–750.

[8] Yin. Z., Pan, Q., Zhang, Y., Jiang, F. (2000): Effect of minor Sc and Zr on the microstructure and mechanical properties of Al-Mg alloys. *Material Science and Engineering A*, 280, pp. 151–155.

[9] Johansen, A., Bauger, Ø., Emburg, J. D., Ryum, N. (2006): Alloy development in the Al-Mg alloy system. Part I, Part II, *Aluminium*, 82, pp. 868–879, pp. 980–985.

[10] Tolley, A., Radmilović, V., Dahmen, U. (2005): Segregation in Al_3(Sc, Zr) precipitates in Al-Sc-Zr alloys. *Scripta Materialia*, 52, pp. 621–625.

[11] Radmilović, V., Tolley, A., Lee, Z., Dahmen, U. (2006): Core-shell structures and precipitation kinetics of Al_3(Sc, Zr) Li_2 intermetallic phase in Al-rich alloy. *MJoM-Metalurgija-Journal of Metallurgy*, 12, pp. 309–314.

[12] Lefebrvre, W., Danoix, F., Hallem, H., Forbord, A., Bostel, A., Mathinsen, K. (2009): Precipitation kinetic of Al_3(Sc, Zr) dispersoits in aluminium. *Journal of Alloys and Compounds*, 470, pp. 107–110.

[13] Lee, S., Utsunomiya, A., Akamatsu, H., Neishi, K., Furukawa, M., Horita, Z., Langdon, T. G. (2002): Influence of scandium and zirconium on stability and superplastic ductilities in ultrafine-grained Al-Mg alloys. *Acta Materialia*, 50, pp. 553–564.

[14] Avtokratova, E., Sitdikov, O., Markushev, M., Mulyukov, R. (2012): Extraordinary high-strain rate superplasticity of severely deformed Al-Mg-Sc-Zr alloy. *Material Science and Engineering A*, 538, pp. 386–390.

[15] Smolej, A., Klobčar, D., Skaza, B., Nagode, A., Slaček, E., Dragojević, V., Smolej, S. (2014): The superplasticity of friction stir processed Al-5Mg alloy with additions of scandium and zirconium. *International Journal of Materials Research (formerly Zeitschrift für Metallkunde)*, 105, pp. 1218–1226.

[16] Smolej, A., Klobčar, D., Skaza, B., Nagode, A., Slaček, E., Dragojević, V., Smolej, S. (2014): Superplasticity of rolled and friction stir processed Al-4.5Mg-0.35Sc-0.15Zr alloy. *Material Science and Engineering A*, 590, pp. 239–245.

[17] Norman, A. F., Prangnell, R. B., McEvan, R. S. (1998): Solidification behaviour of dilute aluminium-scandium alloys. *Acta Materialia*, 46, pp. 5712–5732.

[18] Janghorban, A., Antoni-Zdiziobek, A., Lomello-Tafin, M., Antion, C., Mazingue, Th., Pish, A., (2013): Phase equilibria in aluminium rich side of Al-Zr system. *Journal of Thermal Analysis and Calometry*, 14, pp. 1015–1020.

[19] Okomoto. H. (1993): Al-Zr (Aluminium-Zirconium). *Journal of Phase Equilibria*, 14, pp. 259–260.

[20] Murray, J.L. (1998): The Al-Sc (Aluminium-Scandium) system. *Journal of Phase Equilibria*, 19, pp. 380–384.

[21] Song, M., He, Y. H. (2011): Investigation of primary Al_3(Sc, Zr) particles in Al-Sc-Zr alloys. *Material Science and Technology*, 27, pp.431–433.

[22] Blake, N., Hopkins, M. A. (1985): Constitution and age hardening of Al-Sc alloys. *Journal of Materials Science*, 20, pp. 2861–2867.