Light Metals 2015
Edited by: Margaret Hyland
TMS (The Minerals, Metals & Materials Society), 2015

Microstructure Evolution of AA3003 Aluminum Alloys Enhanced by Zirconium Addition Studied by Electron Microscopy

Michaela Poková, Mariia Zimina, Miroslav Cieslar

Charles University in Prague, Faculty of Mathematics and Physics, Department of Physics of Materials, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

Keywords: Aluminium alloys, precipitation, transmission electron microscopy

Abstract

Zirconium added to aluminium alloys may under suitable conditions form metastable cubic precipitates Al_3Zr, which pin moving grain boundaries and thus shift recrystallization to higher temperatures. Twin-roll cast AA3003 aluminium alloy cold-rolled to 5 and 1 mm was subjected to several annealing steps in order to find ideal conditions for precipitation of Al_3Zr phase. Mechanical properties were monitored by microhardness measurement and microstructure was observed by light microscope and transmission electron microscope. Annealing to 450 °C with slow heating rate has been used to produce Al_3Zr precipitates. This heat treatment also influenced presence of other phases like cubic α-Al(Mn,Fe)Si. The main mechanisms influencing microhardness were hardening by Al_3Zr precipitates, softening by recovery and recrystallization and depletion of the solid solution from the major alloying elements.

Introduction

Aluminium alloys are widely used in a variety of applications such as automobile, aircraft and food industry. The final mechanical properties of a product are influenced by all thermo-mechanical steps during manufacturing such as casting, homogenization, annealing, rolling and shaping. To meet requirements placed on the final product, manufacturing steps should be carefully studied and understood.

Concerning technological applications of aluminium alloys, prevention of grain coarsening during high temperature treatment is required [1]. This can be achieved by appropriately chosen parameters of processing of the alloy: suitable distribution of second phase particles can provide desired properties. In this line of thoughts, small amount of zirconium added to aluminum alloys and appropriate thermo-mechanical treatment can lead to the formation of metastable coherent Al_3Zr precipitates with $L1_2$ structure with the diameter in the magnitude of 10 nm and cell parameter a=0.408 nm [2]. They pin moving grain boundaries, so they can increase recrystallization temperature and induce a fine grained structure [?].

According to Nes and Slevolden [4], heating rate is crucial for their formation; maximal value has been reported as 5 K/min. If their diameter is in magnitude of 10 nm [5], they can retard recrystallization or increase recrystallization temperature by exerting Zener drag on moving grain boundaries and thus lower the driving force for recrystallization [6]. Clusters of Fe and Si atoms can serve as nucleation sites for Zr particles and accelerate their precipitation kinetics [7]. However, due to microsegregation on the scale of dendrite arms spacing and low diffusion rate of Zr in aluminium, the Al_3Zr precipitates can be inhomogeneously distributed [8] and locations with low density of Al_3Zr are more prone to recrystallization.

Besides Al_3Zr, the main second phase particles occurring in Al-Mn-Fe-Si alloys are cubic or hexagonal α-$Al_{15}(Mn,Fe)_3Si_2$ and tetragonal $Al_6(Mn,Fe)$, which precipitate in temperature range 300-500 °C [9, 10]. Which one is predominant depends mainly on the silicon content. Particles larger than 2 μm can have opposite effect to small Al_3Zr and they can facilitate nucleation of recrystallization nuclei by particle simulated nucleation [5].

This paper is devoted to the search of ideal conditions for Al_3Zr particles formation.

Experimental

Twin-roll cast aluminium alloy from AA3003 series with nominal composition 1.0 wt.% Mn, 0.2 wt.% Fe, 0.6 wt.% Si and 0.1 wt.% Cu was studied. It was modified by 0.2 wt.% of Zr. This alloy was afterwards cold-rolled to 5 and 1 mm. Materials were heat treated either in an air furnace or in differential scanning calorimeter (DSC). Mechanical properties were tested by microhardness measurement with load 100 g and microstructure evolution was monitored by light optical microscope after electrochemical polish-

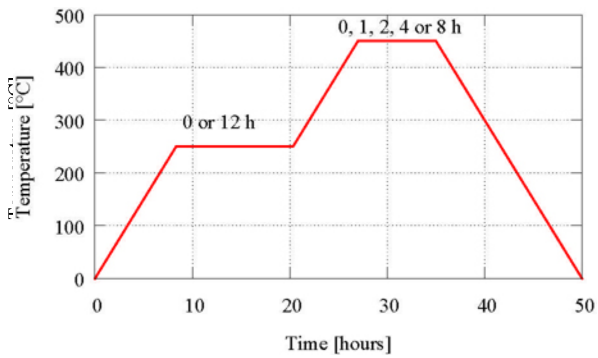


Figure 1: Heating scheme for two-step annealing at 250 °C and 450 °C in DSC.

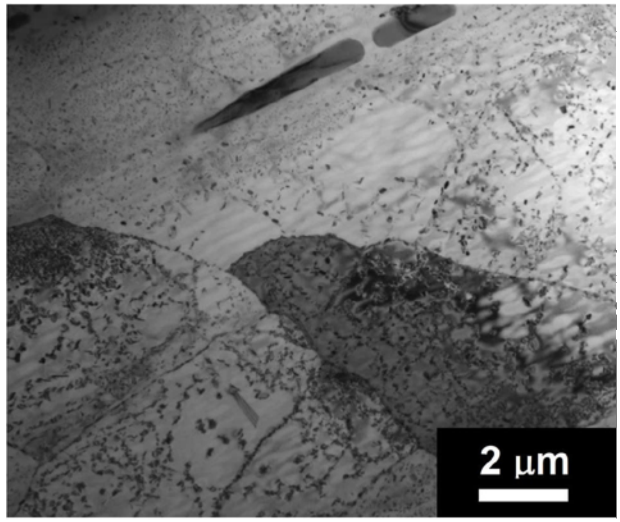


Figure 2: Microstructure of the TRC material after two-step annealing at 12 h/250 °C and 8 h/450 °C with heating rate 0.5 K/min: high number of precipitates, some of them copy subgrain boundaries.

ing by Barker solution and by transmission electron microscope working at 200 kV.

Results

Two-step annealing

Several authors reported that the best results for precipitation of coherent Al_3Zr precipitates were achieved after two-step annealing at 250 °C and 450 °C with slow heating rate (e.g. [11]). Thus two-step annealing was chosen for the first part of investigation.

For examination in TEM two-step annealing in DSC was chosen. 3 mm discs were heated with heating rate 0.5 K/min to 250 °C, held at this temperature for 0 or 12 hours, subsequently heated to 450 °C with the same heating rate, where they remained for 0, 1, 2, 4 or 8 hours. Afterwards they were cooled with rate 0.5 K/min (Figure 1).

After casting materials contained primary particles of α-Al(Mn,Fe)Si in eutectic colonies and some dislocations within the grains. Huge number of α-phase precipitates formed during two step annealing, some of them decorated subgrain boundaries, others were observed in the bulk (Figure 2). They were much smaller in size than primary particles. In more detailed view, tiny precipitates of Al_3Zr phase were found after all annealing steps in as-cast materials. However, their distribution was not uniform, places without these precipitates were found within the material (Figure 3).

After cold-rolling to 5 mm and two-step annealing at 250 °C and 450 °C with heating rate 0.5 K/min, the density of observed Al_3Zr particles was lower than in the non-deformed sheets.

High density of Al_3Zr precipitates was also observed in the step, where the holding at 250 °C was 0 hours. The distribution of Al_3Zr particles was comparable regardless time at 250 °C (see Figure 4) and so one-step annealing at only 450 °C was applied for further study of microstructure and mechanical properties.

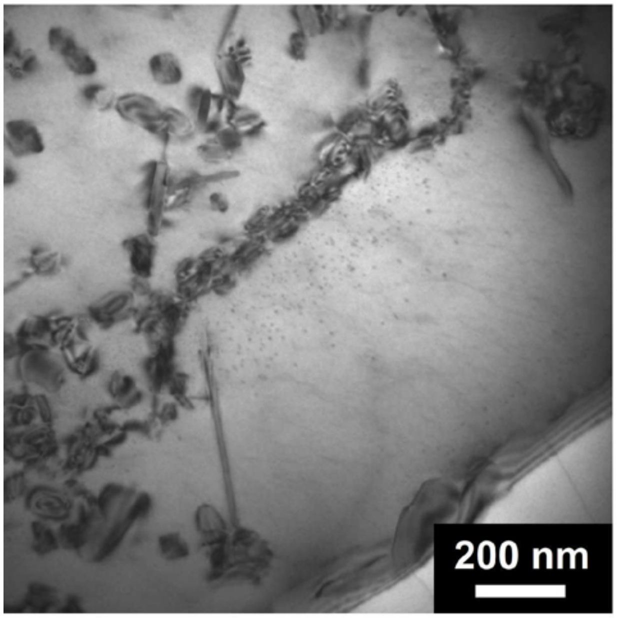
One-step annealing

In further step materials were subjected to annealing to 450 °C in an air furnace with heating rate 0.5 K/min and holding at 450 °C, followed by water quenching. The mechanical properties and microstructure were studied with regard to the time of holding at 450 °C – from 0 to 16 hours.

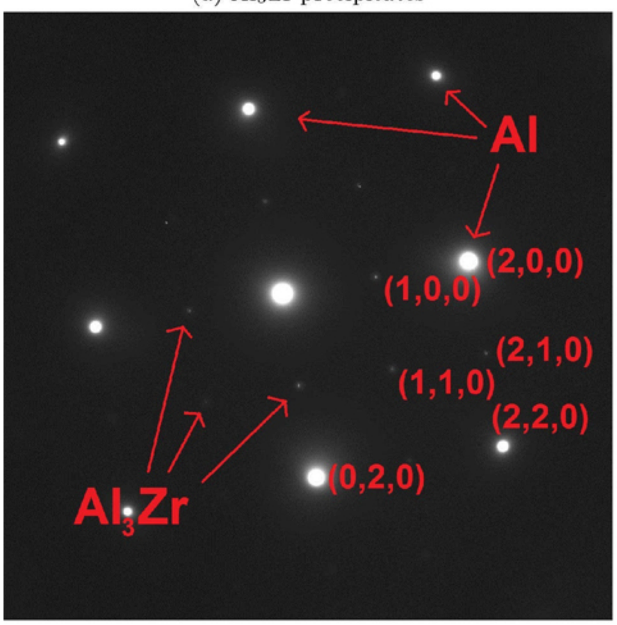
Mechanical properties

The evolution of Vickers microhardness during annealing at 450 °C is displayed in Figure 5. Moreover, the values of microhardness of the as-cast states and cold-rolled state before annealing are plotted. After heating to 450 °C, microhardness of the as-cast material increased and during holding at 450 °C it decreased moderately.

The microhardness drop in sheets cold-rolled to 5 mm was fluent, maintaining the same slope of the decrease up to 16 hours of annealing.

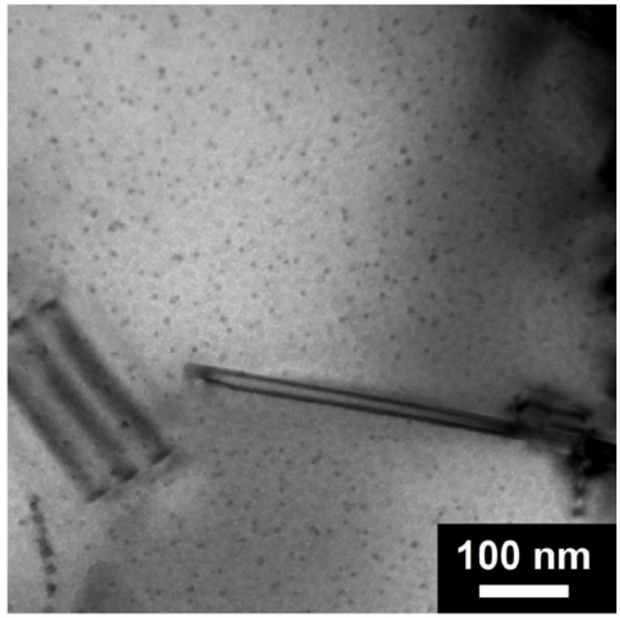


(a) Al_3Zr precipitates

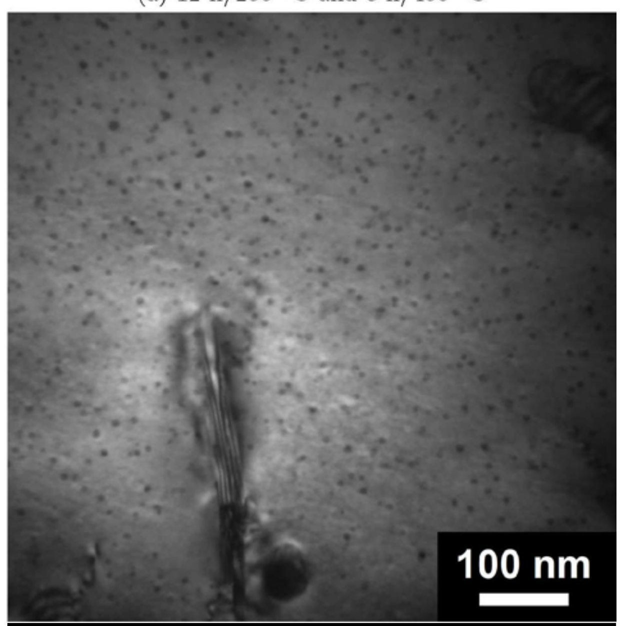


(b) Diffraction pattern

Figure 3: (a) Microstructure of TRC material after two-step annealing 12 h/250 °C and 0 h/450 °C with heating rate 0.5 K/min; inhomogeneous distribution of Al_3Zr in the central part of the micrograph. (b) Corresponding diffraction pattern of $L1_2$ phase of Al_3Zr precipitates.



(a) 12 h/250 °C and 8 h/450 °C



(b) 8 h/450 °C

Figure 4: Microstructure of C471 material after annealing at 8 h/450 °C with and without annealing step at 250 °C.

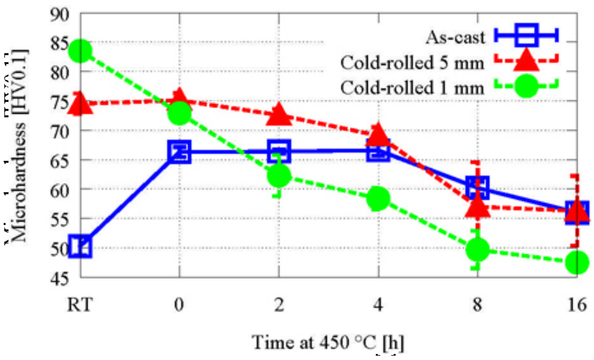


Figure 5: The evolution of Vickers microhardness during annealing at 450 °C for as-cast and cold-rolled materials.

Concerning sheets cold-rolled to 1 mm, microhardness values decreased during annealing to 450 °C and this trend continued also during holding at 450 °C. Most of this drop was completed after 8 hours of holding at 450 °C.

Concerning the tensile tests at room temperature, annealing for 8 hours at 450 °C caused reduction in ductility by ~30 % and slight increase in yield strength.

Microstructure

The evolution of grain structure was monitored by light optical microscopy. Holding at 450 °C for 16 hours did not impact the grain size of the as-cast sheets substantially.

Owing to cold-rolling, 1 mm thick sheets contained narrow grains elongated in rolling direction. Thickness of the grains was higher in the center of the sheets. After heating to 450 °C, the structure remained deformed(Figure 6a); partial recrystallization was apparent after holding for 2 hours at 450 °C. Recrystallization started probably near the surface, as the deformed structure was observed only in the central part of the sheet (Figure 6b). The recrystallization was completed after 8 hours of annealing. Though, the rolling direction was still apparent. The structure was very inhomogeneous, ranging from several tiny equiaxed grains with the size of 10 μm in the bulk to the grains at the surface with length of several mm.

High number of α-Al(Mn,Fe)Si particles formed in the course of annealing. During holding at 450 °C their average diameter slightly increased, volume fraction decreased and primary particles spheroidized.

In cold-rolled materials the α-Al(Mn,Fe)Si precipitates were homogeneously distributed inside the material.

Regarding precipitation of Al_3Zr particles in TRC alloy, first precipitates were observed in the alloy just after heating up to 450 °C. However, their number density was very low. It increased significantly during holding for 2 hours at 450 °C (Figure 7). They were identified as metastable coherent phase with cubic $L1_2$ structure with diameter around of 5 nm. Their distribution was not uniform within the material and their size only slightly raised during further annealing.

No Al_3Z precipitates were detected by TEM in the material which was cold-rolled to 1 mm and subsequently annealed to 450 °C.

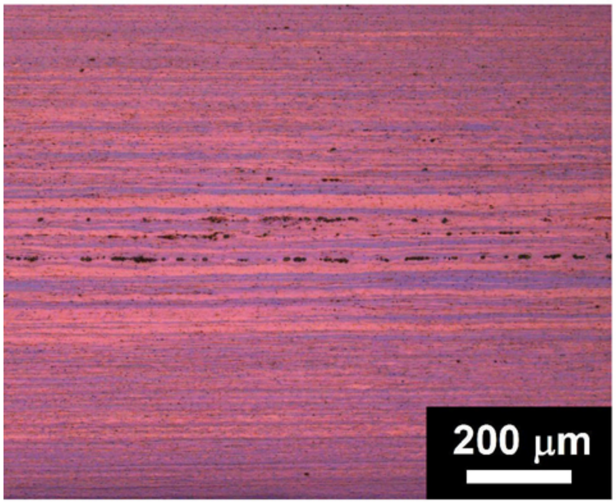
Discussion

All alloys were subjected to annealing at 250 °C and 450 °C in order to find out suitable conditions for precipitation of Al_3Zr particles. It was shown that coherent precipitates of Al_3Zr phase were present in as-cast material even after 12 h/250 °C + 0 h/450 °C or 0 h/250 °C + 8 h/450 °C annealing steps. Annealing at 250 °C was thus shown unnecessary for their formation and only annealing at 450 °C was studied further. Volume fraction of Al_3Zr precipitates increased with the annealing time. However, their distribution remained inhomogeneous.

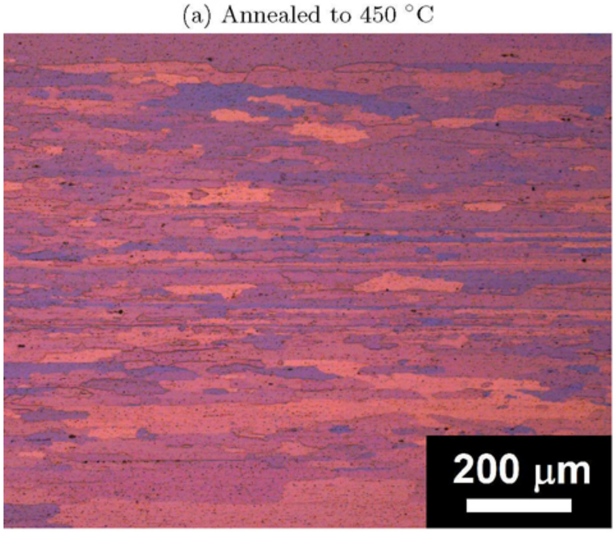
Distribution of both Al_3Zr and α-Al(Mn,Fe)Si precipitates was comparable regardless the way of annealing – either in DSC with slow cooling rate or in an air furnace with water quenching from 450 °C.

The addition of zirconium positively influenced mechanical properties of the studied alloys. This was monitored by the evolution of Vickers microhardness, which was higher in comparison with material without Zr addition [12].

In the as-cast state zirconium atoms were dissolved in the solid solution of aluminium. After heat treatment HV moderately raised due to the precipitation hardening from α-phase precipitates. However, thanks to the nucleation of Al_3Z particles, which strengthen the matrix, the increase was much higher in the Zr-containing alloys [12]. During holding at 450 °C the slight decrease of HV was caused by depletion of the solid solution from Mn and Si atoms. This decrease was compensated by further formation of Al_3Z precipitates at short annealing times - up

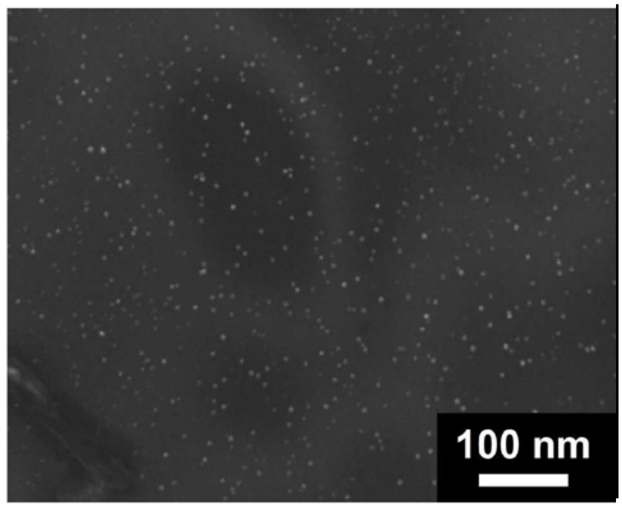


(a) Annealed to 450 °C

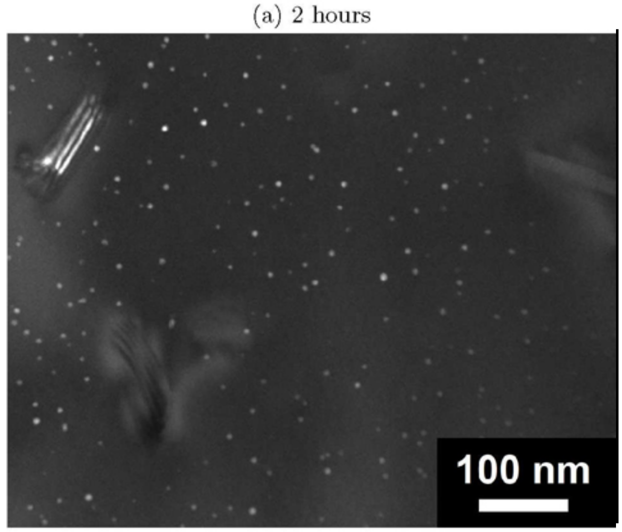


(b) 4 hours at 450 °C

Figure 6: Grain structure of material cold-rolled to 1 mm after annealing to 450 °C with heating rate 0.5 K/min and holding for 4 hours at this temperature.



(a) 2 hours



(b) 8 hours

Figure 7: Dark field TEM image of Al_3Zr precipitates in TRC alloy after annealing to 450 °C with heating rate 0.5 K/min and holding for 2 and 8 hours at this temperature.

to 4 hours at 450 °C. Owing to the high number of Al_3Z, the final value of HV after long-time exposure to 450 °C remained higher than in the Zr-free alloy [12].

Cold-rolling resulted in formation of elongated grains in all materials and to deformation hardening with significant increase of HV. The deformed substructure recovered and new grains formed during recrystallization; this process was considerably affected by the presence of Zr. Materials cold-rolled to 1 mm fully recrystallized after 8 hours of holding at 450 °C. Which is considerably higher recrystallization resistance than in alloys without Zr.

Such shift in recrystallization resistance could be attributed to Zener pinning of Al_3Z precipitates. However, no such particles were detected by TEM in the sheets cold-rolled to 1 mm. In foils of thickness of 5 mm their number density was lower than in the as-cast sheets. This is in contradiction with Nes and Slevolden [4] who claim that deformation should facilitate nucleation of Al_3Z as dislocations can serve as nucleation sites and, in addition, accelerate diffusion. It is therefore probable that the Al_3Z precipitates in the cold-rolled material were too small to be detected by transmission electron microscopy.

The impact of other phases on microhardness in the cold-rolled materials was compensated by recrystallization.

Conclusion

High number of coherent Al_3Zr precipitates formed both during one-step annealing at 450 °C and two-step annealing at 250 °C + 450 °C. As the density of Al_3Zr was comparable for both annealing schemes, heating step at 250 °C was shown to be unnecessary.

Cold-rolling to 5 and 1 mm suppressed formation of Al_3Zr precipitates.

Acknowledgement

The financial supports of grants GAUK 1428213 and GAČR P107-12-0921 are gratefully acknowledged by the authors.

References

[1] M. Cieslar, M. Slámová, J. Uhlíř, C. Coupeau, and J. Bonneville, "Effect of composition and work hardening on solid solution decomposition in twin-roll cast Al-Mn sheets," *Kovové Materiály*, vol. 45, pp. 91–98, 2007.

[2] K. S. Vecchio and D. B. Williams, "Convergent beam electron diffraction study of Al_3Zr in Al-Zr and Al-Li-Zr alloys," *Acta Metallurgica*, vol. 35, pp. 2959–2970, 1987.

[3] E. Nes and H. Billdal, "Non-equilibrium solidification of hyperperitectic Al-Zr alloys," *Acta Metallurgica*, vol. 25, pp. 1031–1037, 1977.

[4] E. Nes and S. Slevolden, "Mechanical properties of new strip-cast AlMnZr alloys," *Aluminium*, vol. 55, pp. 398–400, 1979.

[5] Z. Jia, G. Hu, B. Forbord, and J. K. Solberg, "Effect of homogenization and alloying elements on recrystallization resistance of Al-Zr-Mn alloys," *Materials Science and Engineering A*, vol. 444, pp. 284–290, 2007.

[6] K. E. Knipling, D. C. Dunand, and D. N. Seidman, "Precipitation evolution in Al-Zr and Al-Zr-Ti alloys during aging at 450-600 °C," *Acta Materialia*, vol. 56, pp. 1182–1195, 2008.

[7] M. Karlík, T. Mánik, and H. Lauschman, "Influence of Si and Fe on the distribution of intermetallic compounds in twin-roll cast Al-Mn-Zr alloys," *Journal of Alloys and Compounds*, vol. 515, pp. 108–113, 2012.

[8] N. Ryum, "Precipitation and Recrystallization in an Al-0.5 wt.% Zr-Alloy," *Acta Metallurgica*, vol. 17, pp. 269–278, 1969.

[9] M. Karlík, M. Slámová, and T. Mánik, "Influence of Fe and Si on the microstructure of the Al-Mn alloy with Zr addition," *Kovové Materiály*, vol. 47, pp. 139–146, 2009.

[10] M. Poková, M. Cieslar, and J. Lacaze, "The Influence of Silicon Content on Recrystallization of Twin-Roll Cast Aluminum Alloys for Heat Exchangers," *Acta Physica Polonica A*, vol. 122, pp. 625–629, 2012.

[11] Z. Jia, G. Hu, B. Forbod, and J. K. Solberg, "Enhancement of recrystallization resistance of Al-Zr-Mn by two-step precipitation annealing," *Materials Science and Engineering A*, vol. 483-484, pp. 195–198, 2008.

[12] M. Poková, M. Cieslar, and J. Lacaze, "The Influence of Pre-deformation on Minority Phases Precipitation in Modified AW-3003 Aluminium," in *Metal 2012 Conference Proceedings*, Brno, 2012, pp. 73–78.