Effect of Si and Fe on the Recrystallization Response of Al–Mn Alloys with Zr Addition

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Al–Mn alloys are often used for the production of automotive heat exchanger fins. Recently, the thickness of fins was reduced below 0.1 mm. At this very low thickness, the fin has to maintain its mechanical strength to avoid collapse [1], and at the same time the material should resist recrystallization to keep its strength after brazing at about 600 °C. Therefore, the alloy should contain a dense distribution of second phase particles to exert a drag force (the Zener drag) on moving subgrain and grain boundaries [2]. The best anti-recrystallization addition is scandium, leading to the formation of Al13Sc dispersoids [3]. However, scandium is very expensive and its commercial use is thus limited. Consequently, Zr addition, resulting in the formation of the Al13Zr phase, should be used [4–6].

The decomposition of the supersaturated solid solution in pure Al–Mn binary alloys is very slow [7, 8]. The commercial aluminium alloys contain Si and Fe, and these elements can in some cases deteriorate or improve their properties. Additions of iron and silicon decrease the solubility of Mn and speed up the precipitation of Mn-bearing dispersoids, Al12(Fe,Mn) or α-Al12(Mn,Fe)3Si [7–10]. Furthermore, in Zr-containing alloys Fe and Si support the formation of Al13Zr particles, because Al13Zr dispersoids usually precipitate on Si and Fe atom clusters [4]. In addition, Si has also a positive effect on Al13Zr stability. It substitutes Al in the DO22 compound (Al12Si20)3Zr which is more stable than DO23 or L12 crystal structures [11]. A problem of using Zr as anti-recrystallization addition is that Zr is usually heterogeneously distributed due to the segregation during casting and its low diffusivity [6]. A more homogeneous distribution of Al13Zr particles could be achieved by two-step precipitation annealing [5, 12]. The size and distribution of dispersoids have a fundamental role also in the regulation of the microstructure of Al-Mn alloys during downstream processing.

Besides small Al13Zr particles and large primary constituent phases formed during solidification, Al-Mn alloys contain medium sized dispersoids precipitated during heat treatment. These Mn-containing second phase particles (Al12(Fe,Mn) or α-Al12(Mn,Fe)3Si) can either stimulate or impede grain growth during thermomechanical treatment. Coarse particles (> 1.5 μm) stimulate recrystallization by particle stimulated nucleation (PSN) mechanism [3], smaller particles (< 0.5 μm) assist Al13Zr dispersoid in impeding the movement of subgrain and grain boundaries [2].

The paper reviews main results of the studies of the influence of Si and Fe on the size and formation of dispersoids and recrystallization behaviour of Al–Mn–Zr alloys prepared by direct-chill (DC) casting in the laboratory conditions [13] and also by twin-roll casting (TRC) in the industrial conditions [14].

2. Experimental details

2.1. DC-cast alloys

The experimental alloys were produced using an Al–1.43 wt% Mn base alloy by DC casting to billets of the dimensions of 20 mm × 55 mm × 100 mm. The results of the chemical analysis are given in Table. The billets were cold rolled with 89% reduction (equivalent strain ε ≈ 2.5) to the thickness of 2 mm. One-step and two-step annealing were applied after cold rolling in order to compare the final microstructure, particularly the homogeneity of the distribution and the density of secondary phase particles. Heating to 450°C, soaking for
12 h at this temperature, and cooling (50 °C/h) were applied during one-step annealing. Two-step annealing involved holding the samples for 10 h at the temperature of 250 °C, heating to 450 °C and soaking for 12 h followed by cooling down at the same rate as in the case of one-step annealing.

<table>
<thead>
<tr>
<th>Chemical composition of studied alloys (wt%)</th>
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<tr>
<td><strong>Alloys</strong></td>
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<tr>
<td>DC-cast</td>
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<tr>
<td>Al-Mn-Zr</td>
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<tr>
<td>Al-Mn-Zr-Fe</td>
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<tr>
<td>Al-Mn-Zr-Si</td>
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<tr>
<td>Al-Mn-Zr-Si-Fe</td>
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<tr>
<td>Twin-roll cast</td>
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<td>B (Si)</td>
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2.2. *Twin-roll cast alloys*

Two industrially twin-roll cast strips, 8.5 mm in thickness, were processed in laboratory conditions. The alloy A (Fe) had higher amount of iron (0.32 wt%) while the alloy B (Si) contained higher amount of silicon. The content of other elements was nearly the same (Table). After cold rolling with 39% reduction to 5.2 mm thickness (equivalent strain \( \varepsilon \approx 0.56 \)), the samples were subjected to the two-step precipitation annealing mentioned above. Annealed samples were cold rolled with 94% reduction to 0.3 mm thickness (equivalent strain \( \varepsilon \approx 3.3 \)) then recrystallization annealing took 3 h at 550 °C, and cold rolled to the final gauge of 0.065 mm (reduction 78%, equivalent strain \( \varepsilon \approx 1.76 \)). These samples were subjected to isochronal annealing for 6 h in the temperature range from 260 to 400 °C. The recrystallization response was monitored on the values of 0.2% proof stress obtained in the tensile test.

2.3. *Materials characterization*

The Vickers hardness measurements with 10 kg load (HV10) were carried out in order to determine approximately the onset and the progress of the softening processes, recovery and recrystallization, of DC-cast alloys. The precipitation reactions during annealing and the changes in the solid solution concentrations were monitored by electrical conductivity measurements performed using the Foester Sigmastest device. The microstructure of all samples was studied by Nikon Epiphot 300 metallographic microscope equipped with the camera Hitachi-HBC 20A. The second phase particles were revealed using a 0.5% solution of hydrofluoric acid in water. The grain structure was visualized in the polarized light after anodizing in the Barker reagent. The precipitate size and density of DC-cast alloys were determined on light micrographs, while for TRC alloys electron micrographs were used. The scanning electron microscope (SEM) FEI Quanta 200 F equipped with the Schottky type field-emission gun (FEG) was operated at 5 kV in the backscattered electron (BSE) signal. From each sample, 20 micrographs at the magnification 5000×, and 20 micrographs at the magnification 50000× were recorded to examine coarse and fine phase particles, respectively. This number of micrographs enabled to analyse more than 3000 particles at each condition to have a statistically sufficient data set [15]. All sets of micrographs were first normalized to have a constant mean value and standard deviation of brightness and then processed by the software written in Matlab [16], using toolboxes Image Processing and Statistics. Coarse particles in the precipitation annealed samples were analyzed by energy dispersive X-ray spectroscopy (EDXS), and also by electron backscattering diffraction (EBSD) phase analysis according to their crystallographic structure.

3. *Results*

3.1. *Hardness and electrical conductivity of DC-cast alloys*

On the sheets cold rolled to 2 mm, hardness and electrical conductivity were measured in the initial condition, and on other samples taken at different points of the annealing curve. The differences between the hardness and the conductivity of the samples subjected to one- and two-step annealing were surprisingly only very small, within the range of the experimental scatter [13].

Therefore, only the results obtained after two-step annealing are presented in Fig. 1 showing the evolution of hardness and electrical conductivity of all five DC-cast alloys as a function of time. For the sake of clarity, the corresponding temperature course is also plotted. For all five alloys, the most important drop of hardness accompanied by a steep increase of electrical conductivity arises during heating up from 250 to 450 °C. In this period, most of the precipitates are formed, and the matrix depletes of the solute atoms. In the following 12 h soaking period, the conductivity slightly increases and the hardness somewhat decreases. If we compare the values in the initial condition, the hardness values are in the order of the amount of alloying elements in the solid solution, i.e., the lowest hardness is for the binary alloy Al–Mn (63 HV10), followed by the ternary one Al–Mn–Zr (67 HV10), quaternary Al–Mn–Zr–Fe (69 HV10), and Al–Mn–Zr–Si (78 HV10), and finally Al–Mn–Zr–Si–Fe (80 HV10) (see also Table). If we take into account only
quaternary alloys, the hardening effect of Si in the solid solution is higher than that of Fe, as expected, because of higher Si solubility.

![Figure 1](image1.png)

**Fig. 1.** Evolution of hardness (a) and electrical conductivity (b) of DC-cast alloys subjected to two-step annealing procedure. For the sake of clarity, the corresponding temperature course is also plotted.

Throughout annealing at 250°C, the hardness decreases due to recovery, the important drop of hardness in the middle of the annealing period is due to recrystallization. In the final annealing condition, the hardness of the Al-Mn, Al-Mn-Zr-Fe, and Al-Mn-Zr-Fe-Si is comparable (34 HV10), while the Al-Mn-Zr-Si alloy shows only a small increase (36 HV10) indicating that silicon has a small positive effect on precipitate formation. The highest hardness values not only in the final condition (42 HV10), but also during the whole soaking period, were measured for the Al-Mn-Zr alloy (Fig. 1a). As for the values of the conductivity, the differences between individual alloys are not so important. The values range from 13 to 14 MS m⁻¹, and from 29 to 30.5 MS m⁻¹ in the initial and final condition, respectively. More important differences are only in the middle of the annealing period, where the dispersoids precipitate (Fig. 1b).

### 3.2. Dispersoids in DC-cast alloys

The size and the distribution of the particles during annealing were examined by light microscopy. The micrographs of the particles, corresponding to the surface regions of Al-Mn-Zr, Al-Mn-Zr-Fe, Al-Mn-Zr-Si, and Al-Mn-Zr-Si-Fe sheets in the final condition after two-step annealing and cooling are presented in Fig. 2. The binary alloy is not included since its micrographs were almost the same as those of the Al-Mn-Zr alloy showing a homogeneous distribution of fine particles (Fig. 2a) through the whole cross-section of the sheet. The addition of Si (Fig. 2b) leads to distinctly coarser particles having a less homogeneous distribution. The alloys with Fe addition (Fig. 2c, d) show coarse primary phases. In the vicinity of these coarse particles, fine secondary precipitate is often absent. The addition of Si and Fe (Fig. 2d) leads to coarse primary phase formation and also to the coarsening of the secondary precipitate. Depleted regions, where fine secondary particles are absent, can be seen not only along the primary phases, but also in other regions at the surface as well as in the middle of the sheet [13].

A quantitative comparison of the particle density in the middle region of the cross-section of the sheets at the final condition for both one- and two-step annealing procedures is in Fig. 3. The density of these relatively coarse (> 0.4 μm) particles decreases with the amount of alloying elements. Another comparison is possible between the one- and two-step annealing. It follows that the two-step annealing yields a higher density of particles in the middle of the sheets, except for the Al-Mn-Zr-Fe alloy (Fig. 3). From the alloys containing Fe, Si or both these elements, the alloy Al-Mn-Zr-Si subjected
3.3. Twin-roll cast alloys

Both alloys showed a similar grain structure, typical for twin-roll casting. The grains, 200 to 500 μm long, were inclined from the rolls to the centre of the strip. Besides large blocks (> 30 μm) or needles (> 100 μm long) of the primary Al12Zr phase present in both alloys, EDXS and EBSD analysis revealed cubic α-Al12(Mn,Fe)2Si and orthorhombic Al6(Mn,Fe) primary phase in the alloy A (Fe), while in the alloy B (Si) there was a mixture of cubic α-Al12(Mn,Fe)2Si and hexagonal α-Al13(Mn,Fe)2Si2 primary phases.

A comparison of the microstructure of the alloys at 0.3 mm thickness after intermediate heat treatment for 3 h at 550°C is in Fig. 4. Both alloys are fully recrystallized, but their grain structure and particle dispersion are distinctly different. The alloy A (Fe) shows very fine grains, 50 to 100 μm long in the centre of the strip, and up to 200 to 300 μm on its surface, while the grains in the alloy B (Si) are very coarse, several hundreds of micrometres long. This difference is due to particle stimulated nucleation in alloy A (Fe), containing a dense distribution of coarse particles, as it can be noticed on the results of the particle analysis (Fig. 5b). On the other hand, the alloy B (Si) contains much lower density of coarse particles which could provoke particle stimulated nucleation. As for fine particles (30 to 200 nm), important for blocking of the movement of subgrain and grain boundaries (the Zener drag), the situation is opposite — their density in...
the alloy A (Fe) is much lower than in the alloy B (Si) (Fig. 5a).

FEG-SEM micrographs of the sheets at the final gauge 0.065 mm are in Fig. 6. There is again a distinct difference in the size and distribution of intermetallic particles — they are coarser in the alloy A (Fe) (Fig. 5b, Fig. 6a) and more densely distributed in alloy B (Si) (Fig. 5a, Fig. 6d). The resistance of such microstructures to recrystallization was checked on the evolution of 0.2% proof stress after isochronal annealing for 6 h at the temperature range 200 to 400 °C (Fig. 7). From the sharp decrease in the plots it can be seen that recrystallization of the alloy A (Fe) at these conditions starts at temperatures over 250 °C, while the onset of recrystallization for the alloy B (Si) is shifted to temperatures beyond 350 °C.

4. Discussion

From the results it follows that all alloys containing more than 0.2 wt% Fe (Al-Mn-Zr-Fe, Al-Mn-Zr-Si-Fe and A (Fe) alloys), regardless if they are DC-cast or twin-roll cast, exhibit a higher density of coarser particles (Fig. 2c,d, Fig. 5b, Fig. 6), in whose vicinity the fine secondary precipitate is often absent. In DC-cast alloys, the depleted regions, where fine secondary particles were absent, could be seen not only along the coarsest primary phases, but also in other regions at the surface as well as in the middle of the sheet [13]. On the other hand, the alloys containing more silicon than iron (Al-Mn-Zr-Si, and B (Si)) show lower density of coarse particles (Fig. 2b), and much higher density of fine particles exerting the Zener drag (Fig. 5a). This difference can be attributed to higher silicon content in the solid solution of these alloys, having lower electrical conductivity in the first stages of annealing those Fe-containing alloys (Fig. 1b). As the nucleation of Al12Zr particles is easier at clusters of Si [4, 11, 18, 19], the higher density of small particles in the alloy B (Si) could be also caused by an increased number of Al12Zr precipitates more easily nucleated due to a higher silicon concentration in the solid solution of this alloy.

At the cast and intermediate 5.2 mm thickness, the difference in the iron and silicon content of twin-roll cast alloys (alloy A (Fe) 0.32 wt% Fe, 0.13 wt% Si; alloy B (Si) 0.18 wt% Fe, 0.49 wt% Si) had only a negligible influence on the grain size and morphology of the strips. At the cast thickness of 8.5 mm, the coarse particle distribution was also nearly the same (Fig. 5b) (fine particles were not quantified). However, an important difference was in the composition of constituent phases. The alloy A (Fe) with more Fe than Si contained orthorhombic A15(Mn,Fe) and cubic α-Al12(Mn,Fe)2Si phases, while in the alloy B (Si) containing more Si, there was a mixture of cubic α-Al12(Mn,Fe)2Si and hexagonal α-Al15(Mn,Fe)5Si2 phases. This observation corresponds with the results of Westermann [20], Cama et al. [21], Slámová et al. [22], and Cieslar et al. [23].

During the second step of the precipitation annealing at 450 °C at 5.2 mm thickness, some of the α-Al15(Mn,Fe)

phase transformed to the cubic alpha phase (6-to-α transformation [17, 24]), but the transformation was not complete and the phase difference between the alloys persisted. This constituent phase difference and higher silicon content in the alloy B (Si) were at the origin of the differentiation of the microstructure and properties during further downstream processing of the alloys.

From the plots in Fig. 5a it follows that the density of small particles after cold rolling from 5.2 to 0.3 mm and annealing 550 °C/3 h in the alloy A (Fe) was substantially reduced, while in the alloy B (Si) it remained almost constant. Therefore, there were several simultaneous processes acting at the same time during this annealing: (i) nucleation of new dispersoids (observed up to the temperature of 300 °C [25]), (ii) 6-to-α transformation and coarsening of dispersoids, and (iii) partial particle dissolution and re-enchirishment of the solid solution in Mn and Si [23]. It seems that the dissolution rate and nucleation rate became equal in the alloy B (Si) and so the density of small particles after intermediate annealing 550 °C/3 h remained almost unchanged, while the density of coarse particles increased. On the other hand, in the alloy A (Fe) the coarse particles further coarsened on the expense of the dissolution of the small ones, and there were almost no or much less new dispersoids nucleated.

![Fig. 7. Evolution of 0.2% proof stress of twin-roll cast foils 0.065 mm thick after annealing for 6 h at given temperature.](image-url)
ing an effective dragging force on moving subgrain and grain boundaries. In consequence, the recrystallization resistance of the alloy $B$ (Si) was much higher (Fig. 7).

5. Conclusions

The influence of Si and Fe on the secondary phase particle distribution and recrystallization response of five DC-cast and two industrially twin-roll cast Al–Mn alloys with Zr addition was studied. The main results can be summarized as follows:

1. The density of precipitates in all five DC-cast alloys after one- and two-step annealing was higher in the middle of the 2 mm sheets than in the surface regions. The coarsest primary phases formed in the alloys Al–Mn–Zr–Fe, Al–Mn–Zr–Si–Fe. Close to these coarse particles, fine dispersions are often absent.

2. The type of the annealing (one-step vs. two-step) practically did not influence the evolution of hardness and electrical conductivity in DC-cast alloys — the differences were only very small. Except for the Al–Mn–Zr–Fe alloy, the two-step annealing procedure led to a higher density of dispersions in the middle of the sheets than one-step annealing.

3. In the twin-roll cast alloy $A$ (Fe) with excess of iron, the constituent phases were $\text{Al}_6(\text{Fe}, \text{Mn})$ and cubic $\alpha$-$\text{Al}_{12}(\text{Mn}, \text{Fe})_3\text{Si}$, while in the alloy $B$ (Si) with higher Si content a mixture of cubic $\alpha$-$\text{Al}_{12}(\text{Mn}, \text{Fe})_3\text{Si}$ and hexagonal $\alpha$-$\text{Al}_{15}(\text{Mn}, \text{Fe})_3\text{Si}_2$ phases were found. Very coarse blocks or needles of primary $\text{Al}_3\text{Zr}$ phase were found in both alloys.

4. In the twin-roll cast alloy $A$ (Fe), the density of coarse particles ($> 1.5 \mu m$) steadily increased during processing, and at the same time, the density of small precipitates (30 to 100 nm) reduced in an important manner. $A$ (Fe) alloy thus recrystallized easily due to particle stimulated mechanism and insufficient dragging force.

5. On the other hand, in the twin-roll cast alloy $B$ (Si) the distribution of coarse particles did not change significantly, and simultaneously, a high density of fine particles produced by precipitation annealing remained almost constant down to the intermediate thickness of 0.3 mm and reduced to a smaller extent at the final gauge. In consequence, the alloy $B$ (Si) showed much higher recrystallization resistance.

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