Determination of solid solution composition in Al alloys by electrical transport properties measurement and XRD method

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Determination of solid solution composition in Al alloys by electrical transport properties measurement and XRD method

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Abstract. The non-heat treatable aluminium alloys usually need homogenization before hot rolling to decrease the inhomogenities. In the process the segregations are dissolving and small precipitations are forming. The progress of the processes strongly depend on the temperature and the duration of the heat treatment. Topic of the research was to describe the dissolution/precipitation processes during the heat treatment. It was carried out by two different methods. Using electrical transport properties (resistance and thermo-power) measurement the percentage of the dissolved elements were calculated, and by X-ray diffraction method the cumulative effect was determined through lattice parameter change. The results of the methods were compared regarding to the heat treatment parameters.

1. Introduction

After casting the non-heat treatable aluminium ingots, during the non-equilibrium crystallization inhomogenities can occur. [1] In this condition the material is not suitable for further forming processes, therefore homogenization is also needed. During this heat treatment process the segregations can dissolve into the solid solution. There are several methods to examine the result, e.g. microstructure analysis. Optical or scanning electron microscopy can be used to investigate the existence, size and shape of the segregations. By microprobe examination the solid solution concentration can be measured, but it can involve the secondary phases also. Using X-ray diffraction (XRD) method this can be avoided. If we know the correlation between the concentration and the lattice parameter changing, approximate calculations can be done. [2] Using the suitable equipment, the lattice parameter definition can be a fast measurement. Also a relatively fast and simple method to measure the resistance and thermo-power of the specimens, and it can provide information about each element in the solid solution. [3] It gives proper result in case of two solute elements, but approximate calculations can be done for multiple alloying elements too.

The goal of the study is to monitor the changing of the alloying elements in different aluminium alloys, after different heat treatment processes. XRD and electrical transport properties (resistance and thermo-power) measurements were carried out, and the results of the two methods were compared.

2. Electrical transport properties measurement

A known method was used to calculate the solute percentage of the elements in the solid solution. [3] It starts from the Matthiessen rule, which says for solid solutions:

$$\rho_{alloy} = \rho_0 + \Delta\rho \tag{1}$$

where

ρ_0 specific resistance of the pure metal (temperature dependent)
$\Delta\rho$ residual resistance of the alloying elements (independent from temperature)

For more alloying elements:

$$\Delta\rho = \sum_i a_i \cdot x_i \tag{2}$$

where

a_i the value characterizing the effect of the ”i” alloying element
x_i the quantity of the ”i” alloying element (wt%)

Normally the specific resistance depends on the sample geometry. But if it is measured on two different temperature, then it can be eliminated:

$$\frac{R_{T1}.\frac{L}{A}}{R_{T2}.\frac{L}{A}} = \frac{\rho_{T1}}{\rho_{T2}} = r \tag{3}$$

where

R_{Tx} the resistance measured on given temperature
L the length of specimen
A the cross-section area of the specimen

If we write Matthiessen rule for an etalon ($\rho_{E(T)}=\rho_{0(T)}+\Delta\rho_E$) and the unknown ($\rho_{x(T)}=\rho_{0(T)}+\Delta\rho_x$) samples, it can be written up:

$$r_x = \frac{\rho_{x(T1)}}{\rho_{x(T2)}} = \frac{\rho_{E(T1)}+\Delta\rho_x-\Delta\rho_E}{\rho_{E(T2)}+\Delta\rho_x-\Delta\rho_E} = \frac{\frac{\rho_{E(T1)}}{\rho_{E(T2)}}+\frac{\Delta\rho_x-\Delta\rho_E}{\rho_{E(T2)}}}{\frac{\rho_{E(T2)}}{\rho_{E(T2)}}+\frac{\Delta\rho_x-\Delta\rho_E}{\rho_{E(T2)}}} \tag{4}$$

Expressing δ like:

$$\delta = \frac{\Delta\rho_x-\Delta\rho_E}{\rho_{E(T2)}} \tag{5}$$

From Eq. (4) and (5):

$$r_x = \frac{r_E+\delta}{1+\delta} \tag{6}$$

$$\delta = \frac{r_x-r_E}{1-r_x} \tag{7}$$

By transforming the relationship:

$$\frac{\delta}{1+\delta} = \frac{\Delta\rho_x}{\rho_{0(T2)}+\Delta\rho_x} \tag{8}$$

where
$\rho_{0(T2)}$ specific resistance of the pure metal on T_2 temperature

Therefore a characteristic value can be determined, where no need to measure the exact geometrical sizes by measuring on two temperatures. The δ value has linear correlation with the solute alloying element percentage, and ”δ/(1+δ)” is linear to the thermopower of the material, as known from the Nordheim-Gorter relationship (Figure 1). [4]

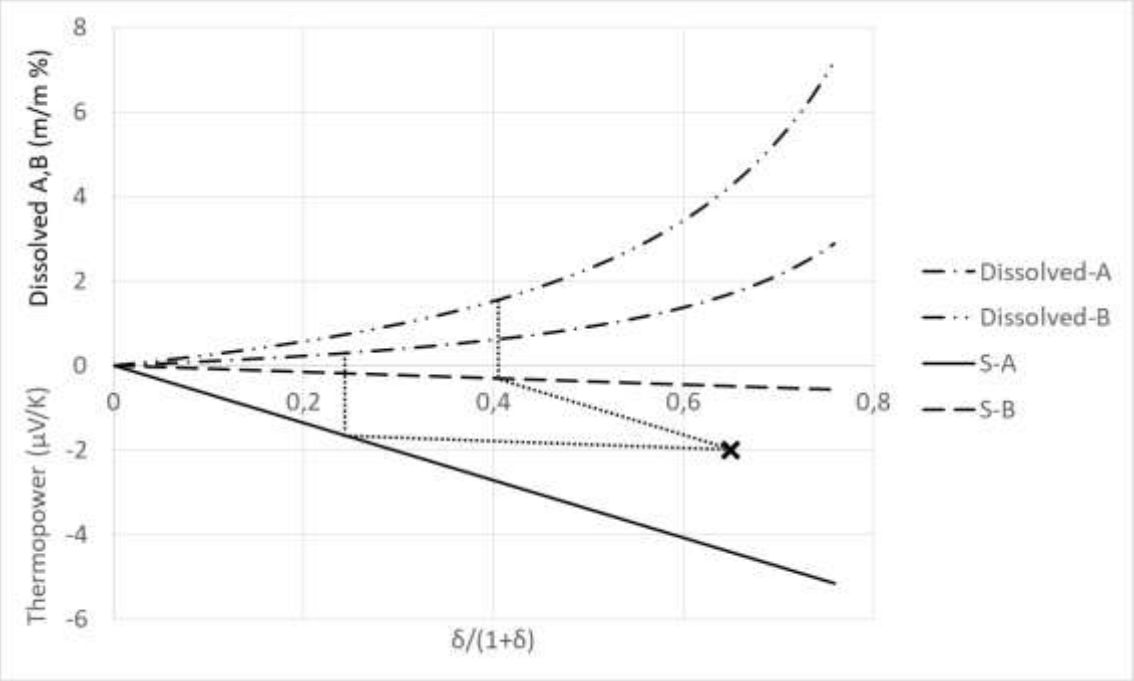

Figure 1. Calculation of solute content in case of two dissolved elements (S – thermopower)

3. Lattice parameter determination by XRD method

The dissolved elements change not only the electrical resistance, but also the lattice parameter. The Figure 2 shows how the alloying elements change the lattice parameter in binary systems of aluminium [2].

In multicomponent systems the influence of each element is separable with cross correlation calculations if enough measurement results are available. The lattice parameter determination is feasible with techniques based on diffraction (TEM, SEM, XRD, neutron diffraction). The precision lattice constant determination by XRD have been used for decades to examine the lattice parameter and perhaps this is still the most suitable method to investigate it, especially for powder specimens. The precision lattice parameter determination, the full pattern refinement, Rietveld analysis or any kind of method require a smooth diffractogram to determine the lattice parameter [5, 6]. It is possible to determine numerically the effect of each alloying element to the lattice parameter and electrical resistance if enough literary data are available. Conversely, the dissolved alloying elements concentration is predictable according to the change in the electrical resistance and lattice parameter.

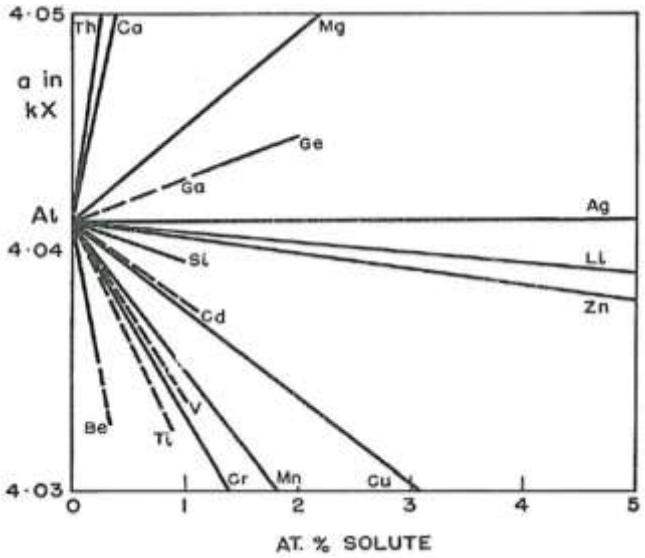

Figure 2. The influence of the alloying element to the lattice parameter in the binary systems of aluminium [2]

4. Experimental

Homogenizing heat treatments were carried out following six different processes. The first three occurred on lower temperature (LT) at 510°C for 1-5-10 hours. The rest were annealed first at higher temperature (HT), at 540°C for 4 hours, then the same 510°C, 1-5-10 hours long heat treatment were applied. The size of the specimens for electrical transport properties measurement were 1×4×120 mm, for XRD examinations it was 17×20×60 mm.

The composition of the investigated aluminium alloys (alloy A, B, C) are shown in Table 1. It is assumed, that Fe is segregated during solidification and the amount does not change because of the low solubility [7], therefore only the other two main elements were taken into account in every case (highlighted in the table).

Table 1. Composition of the examined alloys (m%)

	Al	Si	Mn	Fe	Mg	Zn	Pb	Cu	Cr	Ti	Cd	Ni	Zr
A	97,985	***0,23***	***1,1***	0,53	0,016	0,023	0,001	0,057	0,004	0,022	0,0005	-	-
B	96,89	***0,12***	0,08	0,26	***2,41***	0,01	0,002	0,044	0,16	0,012	-	-	-
C	97,97	0,06	***1,09***	0,2	0,006	0,02	0,01	***0,52***	0,001	0,125	0	0,003	0,003

4.1. Electrical transport properties measurement

The electrical resistance measurements were performed at -196°C (liquid nitrogen) and at 0°C (melting ice). The thermo-power measurements were carried out four times on each sample: twice (with different current direction) during "cooling" and twice during "heating". One side of the specimen was always at room temperature, while the other was at 0°C (melting ice) or ~45°C (hot water). Naturally during a given measurement the temperature difference was fixed.

During evaluation in some cases correction was necessary because the calculated values exceeded the maximum limit, which is impossible. It is caused by the segregations, which have effect on the resistivity but not on the thermo-power, therefore the "δ/(1+δ)" values were decreased by empirical amount. It is less precise, but it still gives a very good view on the progress of the process.

4.2. XRD method

Unfortunately, the conventional lattice parameter determination by XRD (Bruker D8 Advance with Euler cradle) was not applicable to our bulk casted specimens because of the diffraction pattern split due to the strong texture and very large grain size. Longer exposure time and rotation oscillation was also performed but there was not significant improvement in the quality of the results in an acceptable time range. The Figure 3 shows the diffractograms measured by the conventional XRD technique.

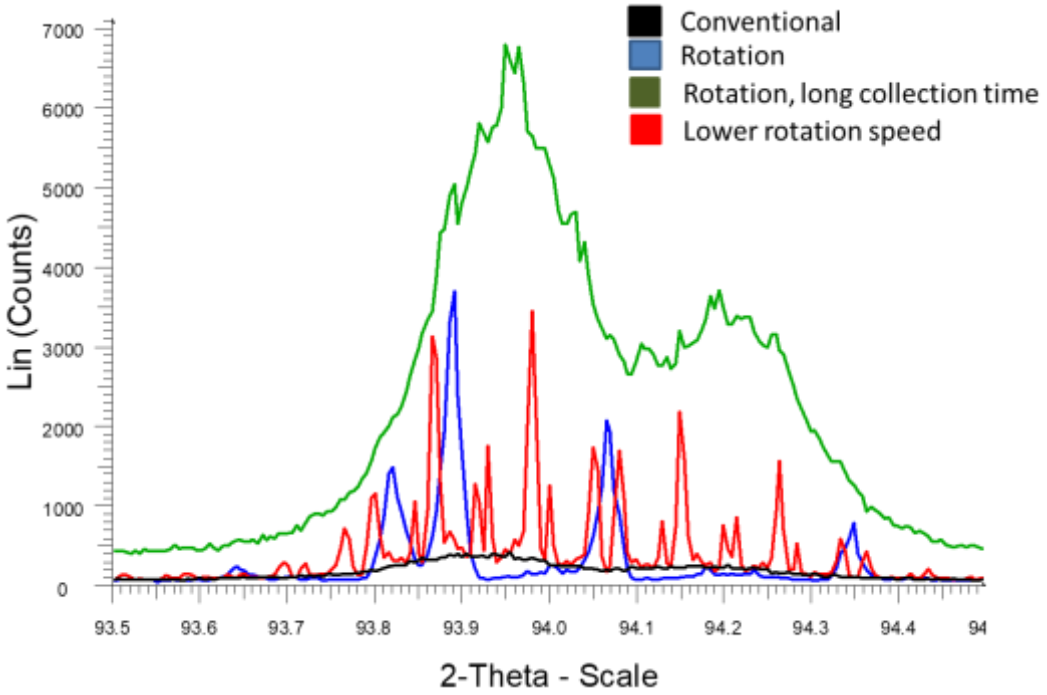

Figure 3. Split peaks measured by conventional technique

After several attempts it became clear the cause of the split is the texture and the grain size. To eliminate this peak splitting it was necessary to irradiate the largest area during one exposure, and collect the diffracted beam from as much direction as possible (from the same plane series). This problem was solved by nationally unique centreless X-ray diffractometer, the Stresstech G3R, in the Institute of Physical Metallurgy, Metalforming and Nanotechnology. There were several advantages to use this diffractometer. These devices produced for measuring residual stress, so they can measure the lattice distance changing very accurately and quickly. Two line detector collect the diffracted beams at the same time, which reduce the measuring time to 5 minutes (compared to the 16 hours measuring time with the conventional method). Since it is a centreless diffractometer, it is possible to use any kind of sample holder, in this case a modified high-speed rotation table was used as the Figure 4 shows. Applying this high-speed rotation table and linear oscillation the number of the grains fulfilled the Bragg diffraction requirements were increased, so it behaves just like a powder sample. The signals of the two detectors during one exposure were similar, so it confirms that the texture and the grain size effect was eliminated (Figure 5.). The details of the measurements were: Cr radiation source, 60 s exposure time, 28 kV accelerating voltage, 8 mA currents, ±4 mm linear oscillation, rotation speed of the table ~600 rpm. Details of the applied calculation: Peak fit with Pearson VII function, $K\alpha_2$ stripping for the signal of both detectors.

Figure 4. Centreless X-ray diffractometer with high speed rotation table

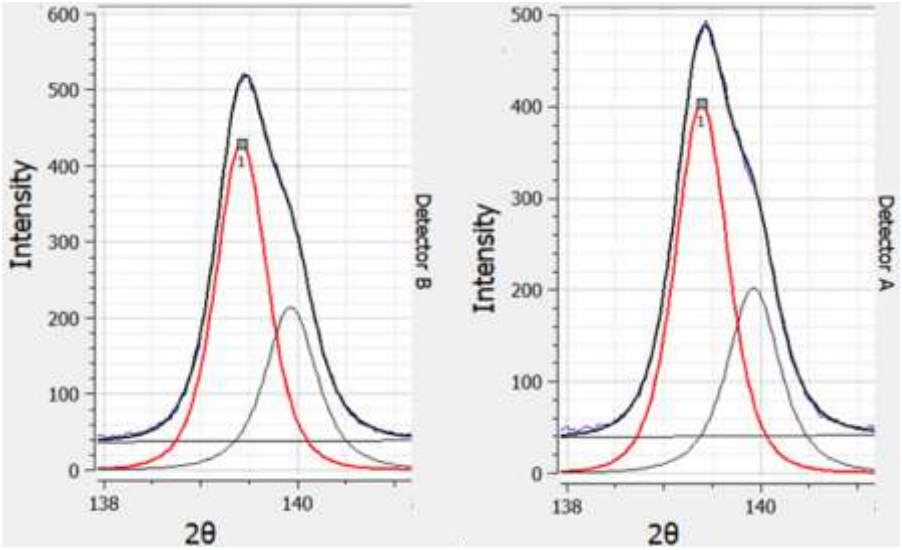

Figure 5. Spitless peaks measured by Stresstech G3R centreless diffractometer, {311**}** reflection on the two detectors

5. Results and discussion

The calculated values are shown on Figure 6. If we look first on diagrams on the left, it is clear, that the solute Mn amount decreases, because it forms segregations. This is visible on the microstructure, as Figure 7 shows. This segregation formation has no difference in the examined 1-10 hour range. The lattice parameter changing verifies this theory, but in some cases with higher fluctuation of the values.

The Mn-free alloy B has no big changes in the solute content except some Mg segregation and minor Si dissolution, which can cause the small lattice deformation measured by XRD.

The alloy C behaves like the alloy A in case of Mn segregations. But here some differences can be seen between the two heat treatment processes, if we look on the calculated Cu values. On lower temperature the amount decreases, some segregations can be formed. In contrast, on higher temperature the amount barely changes. There is no segregation process or they are dissolving during the heat treatment.

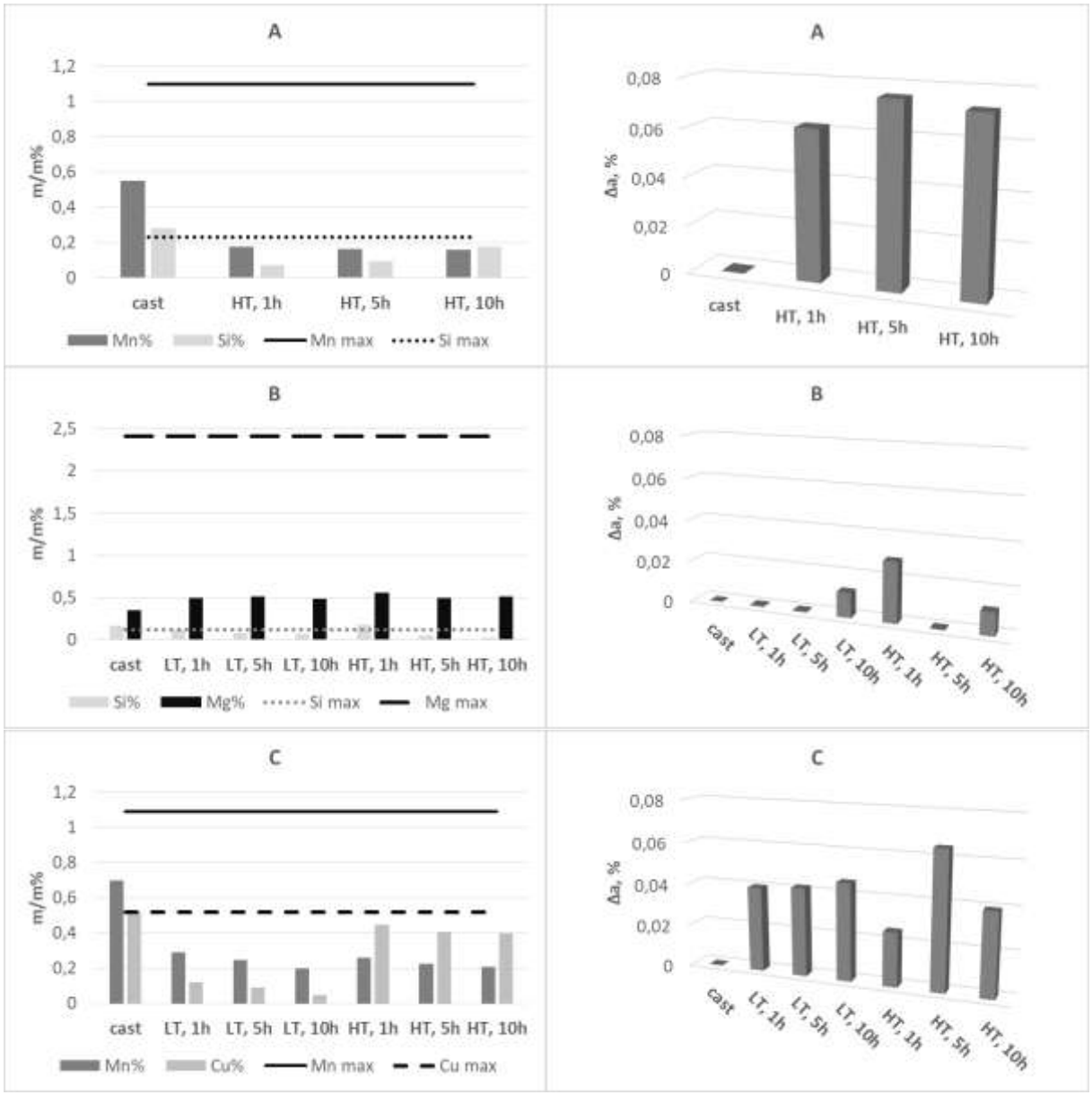

Figure 6. Calculated results in case of the different alloys
(left column: by electrical transport properties measurements, right column: by XRD method)

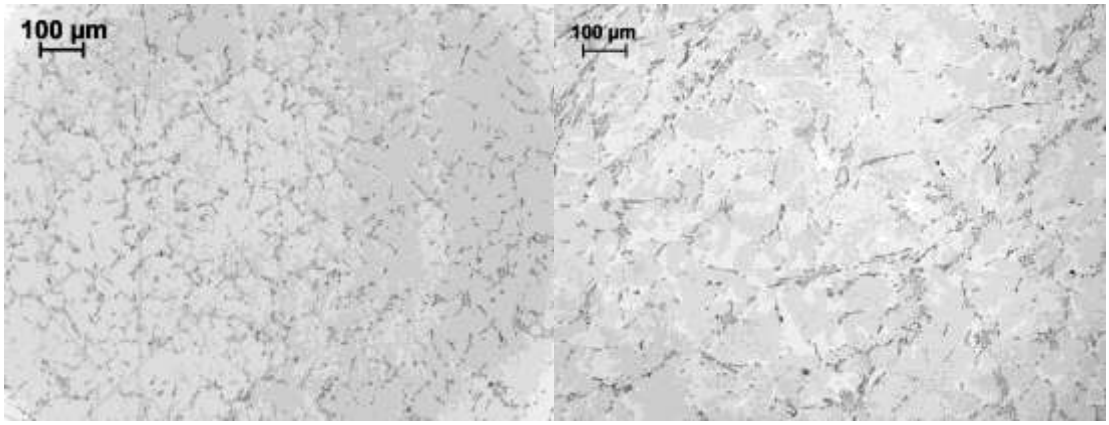

Figure 7. Microstructure of alloy A (left: as cast, right: after 10 h heat treatment)

6. Summary

Two different examination methods were carried out on Al alloys. The specimens were different materials, with various heat treated state. Electrical resistance measurements were carried out at -196°C (liquid nitrogen) and at 0°C (melting ice), then thermo-power examination on the same samples. Using the Matthiessen's rule and the Nordheim-Gorter relationship the alloying element content in the solid solution can be determined, therefore the homogenization process can be evaluated. The samples after the same processes were measured by X-ray diffraction method. From the peak positions the lattice parameters were calculated. During a 540°C annealing followed by a 510°C process the percentage of the manganese segregation can be detected. It was observed, that the homogenizing time in 1-10 h range has no effect on the dissolved manganese content, in Al-Mn + Si/Cu alloys. In case of Cu the segregation can be seen only after the process without the 540°C annealing. The used heat treatment parameters had only minor effect on the dissolved Mg-Si content in the alloy B. The previous observations were confirmed by the XRD examinations. Therefore the lattice parameter change calculation (beside the electrical transport properties measurement) can be a suitable method to follow the homogenizing heat treatment process, by determining this way the cumulative effect of the alloying elements.

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