

An Investigation of the Solubility of Scandium in Iron-bearing Constituent Particles in Aluminium Alloys

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Abstract. Twelve different aluminium alloys with constant iron (Fe) and scandium (Sc) contents of 0.5 wt.% and 0.2 wt.%, respectively, were cast and subsequently homogenised. The distribution of Sc in the microstructure was examined by means of Energy Dispersive X-ray Spectroscopy (EDX) in Scanning Electron Microscope (SEM). Emphasis was put on measuring the solubility of Sc in the Fe-bearing phases of the investigated alloys. It was found that the amount of Sc tied up in Fe-bearing phases is so low that it can be regarded as negligible, with the possible exception of α -AlFeMnSi ($\text{Al}_{15}(\text{Fe},\text{Mn})_3\text{Si}_2$) and the π -phase ($\text{Al}_8\text{FeMg}_3\text{Si}_6$). A quaternary AlFeSiSc phase with a composition close to $\text{Al}_{10}\text{Fe}_3\text{Si}_5\text{Sc}_2$ may have been discovered.

Introduction

Iron (Fe) is an inevitable impurity in commercial aluminium alloys[1]. The Al from the electrolysis has a Fe content of typically 0.1 – 0.3 wt.%. In binary Al-Fe alloys the phase that is in equilibrium with α -Al is Al_3Fe or $\text{Al}_{13}\text{Fe}_4$, the latter probably being a more correct stoichiometry[2]. For ternary or higher order alloys a wide range of Fe-bearing phases may form, depending on alloy composition, casting conditions and subsequent heat treatments. The Fe content has little, if any, influence on the functional properties of many wrought aluminium alloys. In some alloys one may seek to keep the Fe content low for the sake of properties such as fracture toughness or corrosion, whereas in other alloys and for other properties there may be a benefit of an increased Fe level.

In the last decade there has been an increasing interest for scandium (Sc) as an alloying element in aluminium alloys. Sc may be used as a grain refiner during casting or welding, as a stabilizer of the grain structure of wrought material, and as a precipitation hardener[3]. All these three effects are due to the formation of the phase Al_3Sc . From an alloy design viewpoint, it is of great interest to know to which extent the various Fe-containing phases solve Sc. Given that a certain Fe-bearing phase solves appreciable amounts of Sc, this Sc is “lost” with respect to subsequent precipitation of Al_3Sc . This should then have some consequences for the alloy design, either by minimizing the Fe level of the alloy in order to minimize the Sc-loss, or to alter the alloy chemistry or processing conditions in such a manner that the Sc-solving Fe-bearing phase is avoided. With this in mind an exploratory investigation of Sc solubility in Fe-bearing phases was carried out for carefully selected alloy compositions, where all the common Fe-bearing phases are represented[4,5].

Experimental Procedure

Twelve different alloys with constant Fe and Sc contents of 0.5 wt.% and 0.2 wt.%, respectively, were prepared for this study. Table 1 shows the composition of the individual alloys (S1-S12) as determined with an optical emission spectrograph except for Sc and Ni, which due to lack of standards were determined by X-ray fluorescence analysis. Small batches of the alloys were melted at 700°C, and subsequently cast as small ingots weighing approx. 70 – 100g. The cooling rate prior to solidification was approx. 0.3 K/s. Material from these ingots was subjected to an isothermal homogenisation heat treatment in laboratory air circulation furnaces for 24h. The chosen homogenisation temperatures depended on the alloy compositions, and are shown in Table 1.

Polished specimens of the homogenised material were examined by energy dispersive X-ray spectrometry (EDX) in scanning electron microscope (SEM). A region approx. midway between the surface and the center of the ingot was examined. First an EDX area scan at low magnification was done in order to make sure that the local Sc content was representative for the specimen. Afterwards some EDX area scans of the interdendritic regions were done, to determine the local Sc content in these regions. At last point analyses of several Fe-bearing particles as well as the Al matrix between the particles were done. For the point analyses, an acceleration voltage of 10kV was used, meaning that the characteristic size of the analyzed volume was in the order of 1 μ m for the Al matrix and somewhat smaller for the heavier particles. The procedure for the SEM investigation is tentatively illustrated in Figure 1.

Table 1 Compositions of the investigated alloys [wt.%], as determined by X-ray fluorescence analysis (Sc and Ni) and optical emission spectrograph (others).

Alloy	Fe	Sc	Mn	Si	Mg	Cu	Ni	Zn	T _{hom} [°C]
S1	0.48	0.20	-	-	-	-	-	-	600
S2	0.47	0.19	0.91	-	-	-	-	-	600
S3	0.48	0.20	-	0.20	-	-	-	-	600
S4	0.48	0.18	-	0.36	-	-	-	-	600
S5	0.50	0.20	0.44	0.21	-	-	-	-	600
S6	0.51	0.18	-	1.35	0.51	-	-	-	550
S7	0.47	0.18	-	-	-	1.78	-	-	525
S8	0.44	0.16	-	-	-	4.9	-	-	525
S9	0.48	0.19	-	-	-	-	0.42	-	600
S10	0.49	0.18	0.41	1.30	0.47	-	-	-	550
S11	0.41	0.21	0.30	-	0.91	5.0	-	-	450
S12	0.50	0.25	-	-	1.56	1.82	-	6.8	450

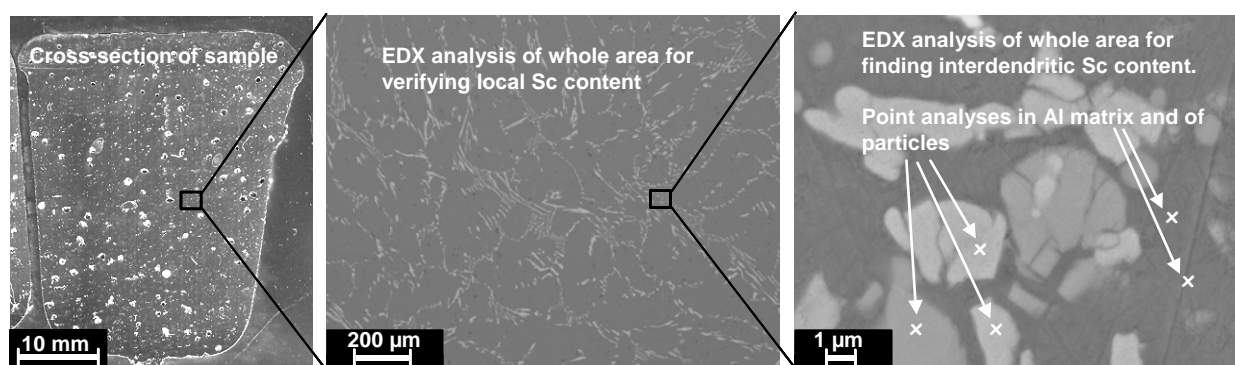


Figure 1 Illustration of the procedure for the SEM-investigation

Results

In the presentation of the results, the measurements of alloying elements in general are reported in wt.% and the compositions of intermetallic particles are given in at.%.

Al-Fe-Sc (S1). The EDX area scans indicated that the interdendritic regions were somewhat enriched in Sc. Point analyses revealed that this was due to a higher Sc content, approx. 0.3 wt.%, in the Al matrix between the Fe-bearing particles. Two types of Fe-bearing phases were found. The first phase had a Fe/Al ratio that matches with Al₁₃Fe₄, which is the phase expected from the equilibrium phase diagram. The second phase had a Fe/Al ratio corresponding to a stoichiometry of Al₅Fe. No measurable amount of Sc was found in any of the analysed Fe-bearing particles.

One large Al_3Sc particle was observed in this sample. The EDX analysis indicated that the particle solves approx. 3 at.% Fe.

Al-Fe-Mn-Sc (S2). The EDX area scans of the interdendritic regions showed that they were depleted in Sc, with an average Sc content in the range 0.10-0.15 wt.%. Point analyses showed that the Al matrix in the interdendritic regions was slightly depleted in Sc. The major reason for the depletion of Sc in the interdendritic regions was, however, the absence of Sc in the intermetallic particles. Two types of intermetallic particles were observed. The most common type was $\text{Al}_6(\text{Fe},\text{Mn})$, which was the expected phase according to phase diagrams[4]. The Fe/Mn ratio in these particles was typically 2/1, but could vary in the range 1/1 – 3/1. $\text{Al}_{13}(\text{Fe},\text{Mn})_4$ particles were also observed. The Mn content of these particles was in the range 1-2 at.%, with an average of 1.7 at.%. No detectable amounts of Sc were found in any of the particles.

Al-Fe-Si-Sc (S3 and S4). Even though the only difference between these two alloys is rather small adjustment of the Si level, they show opposite segregation patterns of Sc in the interdendritic regions as found by EDX area scans.

In alloy S3 with the lowest Si content the interdendritic regions were enriched in Sc, approx. 0.35 wt.%. Point analyses of the Al matrix showed only a slight increase in the Sc content as compared to the average value, indicating that some of the Sc may be in the form of particles. Two different types of Fe-bearing particles were found: $\text{Al}_{13}(\text{Fe},\text{Si})_4$ particles with a Si content of typically 1 at.%, and $\text{Al}_m(\text{Fe},\text{Si})$ particles with a Si content of approx. 0.5 at.%. The value of m ranged from 5 to 9, but most frequently with $m = 5$. Some of these particles were found to solve approx. 0.1 at.% Sc.

The interdendritic regions in alloy S4 were slightly depleted in Sc. The matrix point analyses did not indicate any lower Sc content than the average, indicating that the depletion was due to less Sc in the intermetallic particles. The majority of the particles were of the type described in the literature as $\text{Al}_8\text{Fe}_2\text{Si}$ [4]. The Fe/Si ratio of the present particles did not quite match a value of 2, but rather a value close to 7/3. No solubility of Sc in the $\text{Al}_8\text{Fe}_2\text{Si}$ phase was detected. $\text{Al}_{13}(\text{Fe},\text{Si})_4$ with a Si content of approx. 2 at.% was also found, but without Sc. One large Al_3Sc particle was analysed, and found to have a Si content of approx. 0.5 at.%.

Al-Fe-Mn-Si-Sc (S5). A strong depletion of Sc from the interdendritic regions was found by the EDX area scans, with a Sc content in the range 0.08 – 0.12 wt.%. The matrix concentration of Sc in the interdendritic region was typically 0.12-0.17 wt.%, accounting for the majority of the depletion. Most of the observed particles are of the phase commonly referred to as $\alpha\text{-AlFeMnSi}$, and with a reported stoichiometry of $\text{Al}_{15}(\text{Fe},\text{Mn})_3\text{Si}_2$ [4]. However the (Fe+Mn)/Si ratio of the observed particles was often found to be 3 rather than 3/2, and the Fe:Mn:Si ratio was almost invariably close to 2:1:1. A few of these particles were found to contain 0.05 – 0.2 at.% Sc. Two other Fe-containing particle types were observed. The first one was $\text{Al}_{13}(\text{Fe},\text{Mn},\text{Si})_4$ with typically 2.5 at.% Mn and 1 at.% Si. One of these particles was also found to contain 0.3 at.% Sc. The other phase was $\text{Al}_6(\text{Fe},\text{Mn})$ with typically 4 at.% Mn and without measurable Sc content.

Al-Fe-Si-Mg-Sc (S6). A strong segregation of Sc, up to 1.5 wt.%, to the interdendritic regions was found by the EDX area scans. The Sc content in the interdendritic Al-matrix was low, meaning that Sc-containing particles account for the segregation. Two Fe-bearing phases were identified. The phase commonly referred to as $\beta\text{-AlFeSi}$ was dominating. The stoichiometry of this phase is often given as Al_5FeSi [4]. However, the measured contents of Al, Fe and Si were in the range 67-69 at.%, 13-16 at.% and 16-20 at.% Si, respectively, which does not quite match this stoichiometry but which nevertheless is in accordance with other findings[6]. No solubility of Sc in the Al_5FeSi phase was detected. The second type of detected Fe-containing particles was a small amount of the phase commonly referred to as the π -phase, with a stoichiometry of $\text{Al}_8\text{FeMg}_3\text{Si}_6$ [4]. The measured composition matches this stoichiometry well. A solubility of Sc in the π -phase of approx. 0.6 at.% was measured.

One did also observe a tiny amount of something which might be a hitherto undiscovered phase containing Al, Fe, Si and Sc. Three particles were analyzed, and the composition of Al, Fe, Si and Sc was in the range 48-58 at.%, 13-15 at.%, 19-25 at.% and 8-12 at.%, respectively. In the Al-Si-Sc system the existence of a ternary phase AlSc_2Si_2 , nominated V-phase, is reported[7], and one cannot exclude the possibility that the present observed particles contain a mixture of the V-phase with the $\beta\text{-AlFeSi}$ phase, which would match the measured composition fairly well. No separation into different phases could be observed in the SEM, and there was a good consistency in composition between the analyzed particles, but a closer examination is needed before one can determine whether this is a newly discovered phase.

Al-Fe-Cu-Sc (S7 and S8). The segregation pattern of Sc was found to be similar in these alloys, but with larger scatter in the S8 alloy. Both alloys had a segregation of Sc to the interdendritic regions, the EDX area scans indicated 0.20-0.35 wt.% in alloy S7 and 0.10-0.60 wt.% in alloy S8. The matrix content of the interdendritic regions was 0.15-0.30 wt.% in S7 and varied from 0.0 to 0.50 wt.% in the S8 alloy. Two types of Fe-bearing particles were observed in the S7 alloy, $\text{Al}_{23}\text{CuFe}_4$ [5] and $\text{Al}_7\text{Cu}_2\text{Fe}$ [4,5]. A few particles of both types were found to dissolve up to 0.1 at.% Sc. In the S8 alloy the only Fe-bearing phase found was the $\text{Al}_7\text{Cu}_2\text{Fe}$ phase. Only one of the investigated $\text{Al}_7\text{Cu}_2\text{Fe}$ particles in this alloy contained any Sc, at an amount of 0.2 at.%. One noted that the measured composition of the $\text{Al}_7\text{Cu}_2\text{Fe}$ particles differed somewhat between the alloys, in alloy S7 these particles contained 70-80 at.% Al whereas in alloy S8 they contained 60-66 at.% Al.

One investigated a few Al_2Cu particles in the S8 alloy. These were found to contain appreciable amounts of Sc, 3.9 at.% on average, as well as approx. 0.5 at.% Fe. From the measured compositions it seems like Sc substitutes for Al in the particles.

Al-Fe-Ni-Sc (S9). The interdendritic regions of this alloy seemed to be neither enriched nor diluted in Sc. Only one type of Fe-bearing particles was found, Al_9FeNi [4]. Approx. half of the investigated particles contained measurable amounts of Sc, up to 0.2 at.%.

Al-Fe-Mn-Mg-Si-Sc (S10). The Sc content in the interdendritic regions varied from 0.1 wt.% (depletion) to 1.5 wt.% (strong segregation) in the EDX area scans. Likewise there was a large scatter in the Sc content of the Al matrix in these regions, from 0 to 0.5 wt.% Sc. The dominating Fe-bearing phase in this alloy is $\alpha\text{-AlFeMnSi}$ ($\text{Al}_{15}(\text{Fe,Mn})_3\text{Si}_2$). The measured compositions of the particles match well with this stoichiometry. A few of the $\alpha\text{-AlFeMnSi}$ particles contained some Sc,

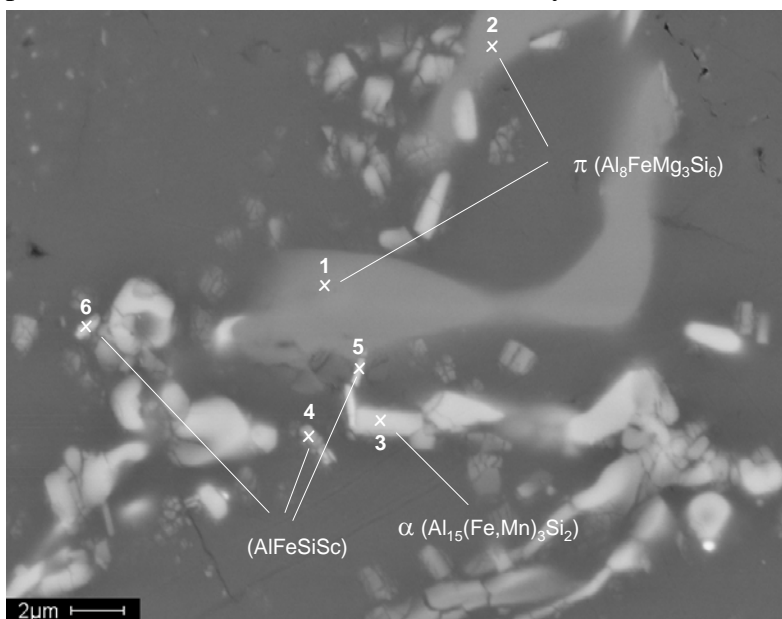


Figure 2 SEM backscatter electron micrograph of an interdendritic region in alloy S10 with several Sc-containing Fe-bearing particles.

up to 2 at.%, but the majority of the particles contained no measurable amount of Sc. The π -phase ($\text{Al}_8\text{FeMg}_3\text{Si}_6$) was also found in some regions, and with a composition that matches this stoichiometry well. The π -phase was invariably found to contain some Sc, up to 2.5 at.%.

In the vicinity of the π -phase particles one could some places find small particles of what is possibly a new phase as described in the section of alloy S6. Figure 2 shows an interdendritic region in alloy S10 where this phase was found co-located with the π -phase. Table 2 shows the measured compositions of the particles indicated in Figure 2. From the size

of the particles 4-6 one should expect some contribution from the surroundings to the overall analysis. Thus, the actual Al content of these particles may be somewhat lower than indicated in Table 2. Again, one cannot exclude the possibility that the particles 4-6 contain a mixture of previously described phases. However, if one treats this as a new phase and tries to find a stoichiometry that best matches the present measurements (of both alloy S6 and S10), a proposal of $\text{Al}_{10}\text{Fe}_3\text{Si}_5\text{Sc}_2$ would not be too far off.

A particle that probably is of the V-phase (AlSc_2Si_2) was also found in the vicinity of a π -phase particle in this alloy. However, the composition of this particle was found to be Al_2ScSi , which is not in accordance with the phase diagram[7].

Table 2 EDX point analyses [at.%] of the positions indicated in Fig. 2.

Particle no.	Al	Fe	Si	Mn	Mg	Sc	Others
1	46.64	4.84	29.15	-	15.40	1.30	-
2	48.86	4.97	28.76	-	14.83	2.58	-
3	72.13	14.72	11.04	1.68	0.43	-	-
4	78.26	8.14	9.89	-	0.53	3.18	-
5	50.56	12.07	27.58	-	2.27	6.35	1.17 Ca
6	56.03	13.56	20.42	-	1.21	8.78	-

Al-Fe-Cu-Mg-Mn-Sc (S11). The Sc content of the interdendritic regions varied from 0.1 to 1.3 wt.% in the EDX area scans, whereas the Sc content of the Al matrix in these regions varied from 0.05 to 0.6 wt.%. The only Fe-bearing particle type found was probably of the $\text{Al}_7\text{Cu}_2\text{Fe}$ phase, even though the measured Al content was higher and the Cu and in particular the Fe contents lower than expected from the stoichiometry. No Sc solubility in these particles was detected.

Several types of intermetallic particles without Fe were also detected. Some had a composition corresponding approx. to $\text{Al}_6\text{Mg}_3\text{Cu}_2$, which are probably of the S-phase (Al_2CuMg)[5] and were found to dissolve up to 0.05 at.% Sc. Another class of particles with Al, Cu and Mg contents of 65-70 at.%, 24-27 at.% and 2-6 at.%, respectively, was also found. No such phase is found to be described in available phase diagram handbooks, and it is speculated that this is Al_2Cu particles with a high solubility of Mg, i.e. $\text{Al}_2(\text{Cu},\text{Mg})$. The $\text{Al}_2(\text{Cu},\text{Mg})$ particles invariably solved a significant amount of Sc (1.8 – 3.3 at.%, with an average of 2.4 at.%). In addition, an Al_xCu phase with x in the range 3-5 was observed. These particles differed from the $\text{Al}_2(\text{Cu},\text{Mg})$ in that they contained little Mg (0.3 – 0.9 at.%) and practically no Sc (0.03 at.% was found in one particle).

Al-Fe-Zn-Mg-Cu-Sc (S12). Both depletion and enrichment of Sc in the interdendritic regions was found by the EDX area scans, as the Sc content in these regions ranged from 0.1 to 0.5 wt.%. The matrix Sc concentrations in the same regions varied from 0 to 0.2 wt.%. Two types of Fe-bearing particles were found, $\text{Al}_{13}(\text{Fe},\text{Cu})_4$ with a Cu content of typically 1.5 – 3 at.%, and $\text{Al}_7\text{Cu}_2\text{Fe}$. Both phases were occasionally found to solve up to 0.3 at.%Sc, but for most particles no detectable level of Sc was found. Besides the Fe-bearing phases one also found the S-phase (Al_2CuMg) and the phase thought to be a Mg-containing Al_2Cu phase (see the results from alloy S11). The latter phase contained 1.3 at.% Sc.

Discussion and Conclusions

Several different Al alloys containing Fe and Sc have been investigated, and the Sc contents of a wide range of Fe-bearing particles have been measured. The range of Fe-bearing particles represents the vast majority of those found in commercial wrought Al alloys and thus it is possible to draw some conclusions on the interactions between Sc and Fe in wrought Al alloys in general.

From the available phase diagram[8], the formation of ternary AlFeSc phases is not expected in Al alloys. This is substantiated by the lack of such phases in this study. When it comes to the

solubility of Sc in the Fe-bearing phases, one finds that for most of the investigated Fe-bearing phases, $\text{Al}_{13}\text{Fe}_4$, Al_mFe , $\text{Al}_6(\text{Fe},\text{Mn})$, $\text{Al}_8\text{Fe}_2\text{Si}$, Al_5FeSi , $\text{Al}_{23}\text{CuFe}_4$, $\text{Al}_7\text{Cu}_2\text{Fe}$ and Al_9FeNi , only a fraction of the observed particles contained measurable amounts of Sc and when Sc was found the level would be below 0.2-0.3 at.%. There seems to be a trend that when a certain phase solves some additional alloying elements, such as $\text{Al}_{13}\text{Fe}_4$ solving Mn, Si and Cu in alloy S5 and S12, then there is also an increasing tendency to solving Sc. However, the amount of Sc solved does not indicate that any of the phases listed above need to be avoided in the design of Sc-containing Al alloys.

The α -AlFeMnSi phase ($\text{Al}_{15}(\text{Fe},\text{Mn})_3\text{Si}_2$) was found to solve up to 0.2 at.% Sc in alloy S5, but up to 2 at.% Sc in alloy S10. Only a small fraction of the α -AlFeMnSi particles was found to contain Sc, and the depletion of Sc from the Al matrix due to dissolving in α -AlFeMnSi is probably negligible even in alloy S10. However, one should examine a wider range of alloys with the α -AlFeMnSi phase before one can state whether the α -AlFeMnSi should be avoided or not.

The π -phase ($\text{Al}_8\text{FeMg}_3\text{Si}_6$) was invariably found to contain some Sc, from 0.6 at.% in alloy S6 to up to 2.5 at.% in alloy S10. The volume fraction of the π -phase is normally found to be low in the Al-Mg-Si alloys, and therefore the solubility of Sc in this phase is in general of little concern. However, it is advisable to avoid alloy compositions or thermal treatments that are expected to lead to extensive formation of the π -phase.

Some Fe-bearing particles with high Sc content were found in alloy S6 and S10. It is possible that this is a phase not described earlier, and the composition appears to be close to $\text{Al}_{10}\text{Fe}_3\text{Si}_5\text{Sc}_2$. Obviously, if this phase would account for a considerable part of the Fe-bearing particles then it would tie up large amounts of Sc. However, only very few and quite small particles were found and the amount of Sc tied up in them is therefore negligible.

The general conclusion from this investigation is that the solubility of Sc in Fe-bearing phases is so low that it can be regarded as negligible, with the possible exception of α -AlFeMnSi and the π -phase.

References

- [1] N.A. Belov, A.A. Aksenov and D.G. Eskin: *Iron in Aluminum Alloys* (Taylor & Francis, London, UK 2002).
- [2] A.L. Dons: *Z. Metallkde.* Vol. 75 (1984) p.170
- [3] J. Røyset and N. Ryum: *Int. Mater. Rev.* Vol. 50 (2005) p.19
- [4] L.F. Mondolfo: *Aluminum Alloys: Structure and Properties* (Butterworths, London, UK 1976).
- [5] G. Petzow and G. Effenberg: *Ternary Alloys* (VCH Verlagsgesellschaft mbH, Germany, 1990).
- [6] W. Khalifa, F.H. Samuel and J.E. Gruzleski: *Metall. Mater. Trans.* Vol. 34A (2003), p. 807
- [7] A.T. Tyvanchuk, T.I. Yanson, B.Ya. Kotur, O.S. Zarechnyuk and M.L. Kharakterova: *Russ. Metall.*, (1988) No.4 p.190
- [8] L.S. Toropova, D.G. Eskin, M.L. Kharakterova and T.V. Dobatkina: *Advanced Aluminum Alloys Containing Scandium* (Gordon and Breach Science Publishers, The Netherlands 1998).