

Effect of manganese and exposure to elevated temperature on the corrosion of twin-roll cast Al-Mg alloys

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Abstract

The effect of the addition of manganese and chromium on the corrosion behaviour of AlMg3 and AlMg4.5 twin-roll cast alloys was studied. The influence of Mn and long exposure to elevated temperature on alloy susceptibility to intergranular corrosion was assessed. The presence of Mn in both Al-Mg alloys significantly improves their resistance to intergranular corrosion, especially in the alloy with high Mg content. Exposure to elevated temperatures amplifies the corrosion attack of grain boundaries only in the alloys without Mn and Cr. The presence of Mn facilitates the bonding of Mg atoms in constituent particles and precipitates resulting in reduced amount of Mg available for precipitation on grain boundaries. The lack of β -Al₃Mg₂ precipitation on grain boundaries is the cause of alloys low susceptibility to intergranular corrosion.

Key words: aluminium-magnesium alloys, manganese, corrosion, grain boundaries

1. Introduction

Aluminium-magnesium alloys are nowadays largely used as structural materials for producing lightweight automobiles. Al-Mg alloys are applied in components that require moderate strength, good formability, weldability, and good corrosion resistance. The latter requirement is especially important for automobile skin and under-hood applications in connection with the increased risk of environmental exposure of such structures. Al-Mg alloys are generally known to have good corrosion resistance. However, Al-Mg alloys containing more than 3 wt.% Mg can become susceptible to intergranular corrosion and stress corrosion cracking when they are exposed to temperatures ranging from 50 °C to 200 °C for sufficiently long period of time [1, 2]. This phenomenon is known as "sensitization" and is widely associated with the selective dissolution of the β phase Al₃Mg₂, which can precipitate on grain boundaries during elevated temperature exposure [2].

Al-Mg commercial alloys contain, besides Mg, elements such as Fe and Si (the usual impurities of Al) and Mn or Cr. The role of Fe, Si and Mn on the corrosion resistance of aluminium alloys has been discussed

extensively as reviewed, e.g., in [3]. It is well known [3–7] that the principal corrosion process in aluminium alloys in acid environments is the pitting corrosion due to localized galvanic effects between the second-phase particles, usually present in commercial alloys and the Al matrix. The local galvanic corrosion is enhanced by large differences in the corrosion potentials of the particles and Al matrix (either in the anodic or cathodic direction).

The beneficial effect of Mn on the corrosion behaviour of Al-Mn alloys is well documented [4]. It was demonstrated that the corrosion resistance of hot-rolled Al-Mn alloys can be significantly improved by increasing the Mn/Fe ratio in the alloy. This was assigned to the beneficial effect of Mn in Fe-bearing second-phase particles due to the decreased difference in corrosion potentials of the particles and Al matrix. However, it was shown [5] that the corrosion resistance of Al-Mn alloys can be improved even more effectively by increasing the solid solution concentration of Mn in the Al matrix. It is known that strip casting, and especially twin-roll continuous (TRC) casting, produces materials with high supersaturation of alloying elements in the solid solution. The results presented in

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Table 1. Chemical composition of investigated materials (in wt.%)

Alloy	Sample	Mg	Mn	Fe	Si	Cu	Ti	Cr
AlMg3 (+ Mn)	A1	2.72	0.26	0.24	0.12	0.048	0.021	0.06
AlMg3 (– Mn)	A2	2.68	0.01	0.27	0.10	0.008	< 0.02	< 0.001
AlMg4.5 (+ Mn)	B1	4.18	0.36	0.26	0.13	0.06	0.02	0.14
AlMg4.5 (– Mn)	B2	4.02	0.02	0.28	0.06	0.009	< 0.02	< 0.001

[5] concern Al-Mn alloys issued both from TRC and Direct-chill (DC) casting and prove that the effect of Mn content in solid solution prevails over the effect of Mn in second-phase particles.

In contrast to Al-Mn alloys, the effect of Mn on the corrosion resistance of TRC Al-Mg alloys has been studied at much less extent [6, 7]. The present paper reports the results of an investigation aimed at qualifying the impact of Mn addition on the corrosion resistance of two TRC Al-Mg alloys with an emphasis on their susceptibility to intergranular corrosion. The corrosion properties of AlMg3 and AlMg4.5 sheets were studied both in the as-received soft state and after exposure to elevated temperature.

2. Experimental

Twin-roll continuously cast AlMg3 (AA5754) and AlMg4.5 (AA5182) alloys were studied (Table 1). Two variants of each alloy, differing in Mn content, were prepared using almost identical industrial processing routes. Sheets were manufactured from strips TRC cast at thickness of approximately 6 mm by cold rolling, homogenization, additional cold rolling and recrystallization annealing at the final thickness of 1 mm. Microstructure examinations were performed by light microscopy on samples cut in the plane parallel to the normal and rolling directions after grinding and polishing in a conventional manner. Grain structure was examined on samples anodized in Barkers reagent (4% solution of fluoroborid acid in water) using crossed polarizers. Special attention has been paid to the examination of specimens subjected to corrosion tests. Thin foils for transmission electron microscopy (TEM) were prepared by electropolishing in a 30% HNO₃ in methanol solution at –17°C using Tenupol twin jet device. Microstructure investigation, in particular the morphology of precipitates and particles, and the presence of tiny precipitates were performed using a TEM Philips CM 100 operated at the 200 kV.

The open circuit potentials E_{corr} of the sheets were measured according to [8] using a standard saturated calomel electrode (SCE) and NaCl water solution (58.5 g/l of NaCl), pH adjusted with H₂O₂ (9 ml/l of 30% H₂O₂). The susceptibility to intergranular corrosion of the alloys was tested by the Nitric Acid Mass

Loss Test (NAMLT) [9]. The test consists of two steps: first the test specimens are immersed in concentrated nitric acid and kept at the constant temperature of 30°C for 24 h; and then the mass loss per unit area is determined. Water-free nitric acid of specific gravity ranging from 1.413 to 1.422 (concentration 70–72 wt.%) was used. Each specimen was tested separately, using every time a fresh reagent. In order to assess the effect of long-term exposure to elevated temperatures, both as-received specimens and specimens subjected to annealing at 75°C for 48 hours (sensitized) were tested.

3. Results

3.1. Microstructure of as-received and sensitized specimens

Details on the as-cast microstructures of all alloys and the transformations during thermo-mechanical treatment are presented in [10]. The microstructure of 1 mm sheets is described in [10] and will be only briefly presented here. The second phase in the sheets is in the form of uniformly dispersed particles. EDAX analyses in TEM indicated that in the alloys A2 and B2 (without Mn) the particles are of two types: either they contain only Al and Fe or they contain Al, Fe and Si. In the alloys A1 and B1 the phases contain also Mn. Previous investigations of the authors [10] have shown, in agreement with [6, 7], that Al₆(Fe,Mn) and α -Al₁₂(Fe,Mn)₃Si particles are present in the Mn-rich alloys and Al₆Fe or β -AlFeSi in the alloys without Mn. Isolated particles of pure Si were also observed in both samples of alloy B2. The second-phase (constituent) particles form at casting and they transform during the high temperature homogenization. Coarse precipitates of the above mentioned phases form and coarsen either during homogenization or during the recrystallization annealing applied at final sheet thickness. These precipitates are observed mainly in grain interiors, in contrast to the coarse primary particles that were found preferentially on grain boundaries or on triple junctions. High bulk density of precipitates was observed by light microscopy in alloys A1 and B1 containing Mn but not in alloys A2 and B2 without Mn. Careful examination of specimens B1 and B2 by

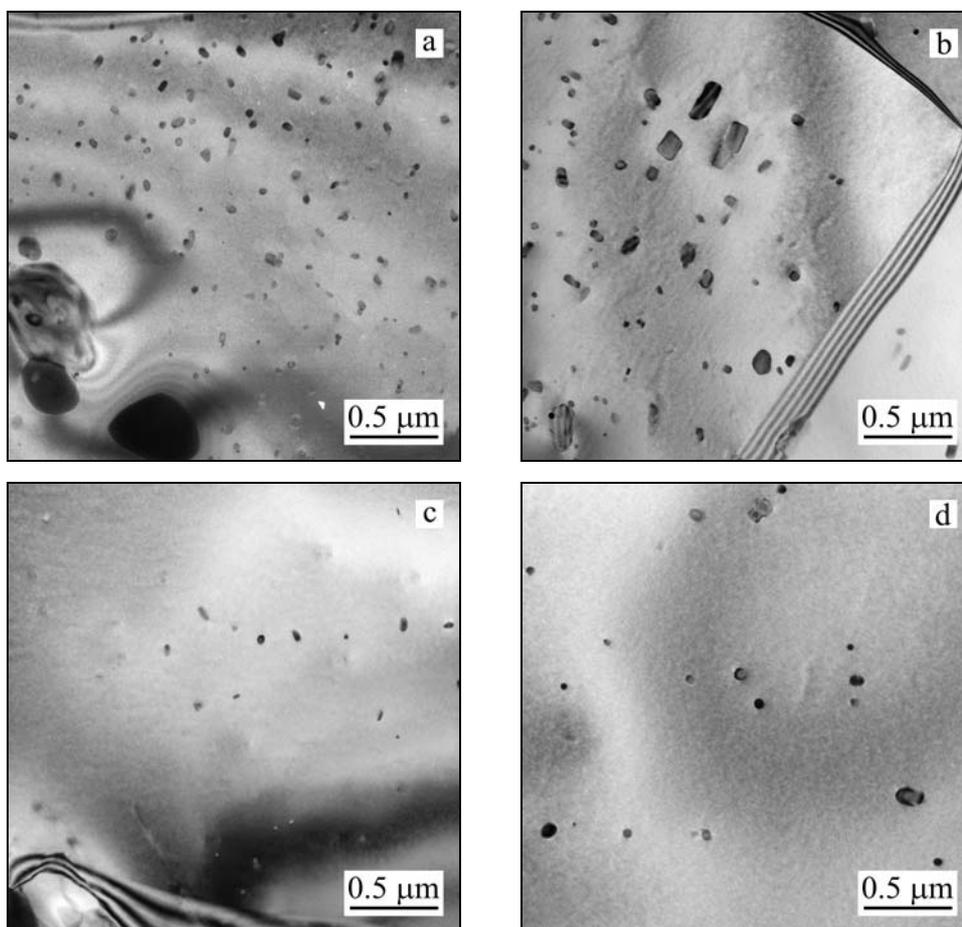


Fig. 1. TEM micrographs comparing the size and bulk density of precipitates in alloys B1 and B2: a), c) as-received specimens, b), d) specimens sensitized by annealing at 75°C/48 h.

TEM (Fig. 1a,b) indicated that the latter also contains precipitates which are much smaller and less numerous than in B1. Similar difference in precipitate density was observed also in specimens A1 and A2. The coarse particles and precipitates in alloys A1 and B1 contain also Cr, i.e., the phase composition corresponds to $\text{Al}_6(\text{Fe},\text{Mn},\text{Cr})$ and $\alpha\text{-Al}_{12}(\text{Fe},\text{Mn},\text{Cr})_3\text{Si}$ phases. The presence of Mg was detected by EDAX analyses in the constituent particles and precipitates of alloy B1 (containing Mn) but not in the alloy B2 without Mn.

TEM analyses of sensitized specimens indicated that their microstructure does not significantly differ from that of non-sensitized specimens. The size and bulk density of precipitates and coarse particles are comparable in both specimens. The only difference observed between sensitized and non-sensitized specimens of alloy B2 was the presence of tiny precipitates of 20 nm in diameter on grain boundaries (Fig. 2). Owing to their extremely small size, the chemical analysis of the tiny precipitates by EDAX was not feasible. However, it is highly probable that these are $\beta\text{-Al}_3\text{Mg}_2$ particles known to precipitate on grain boundaries in

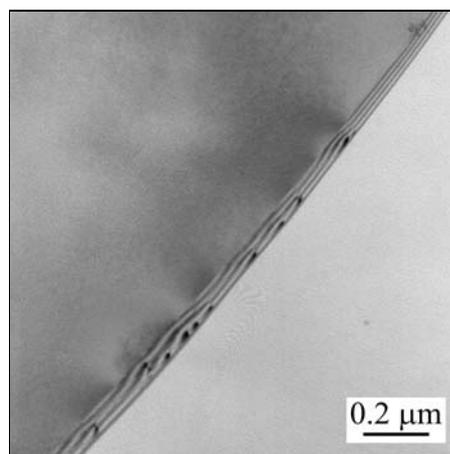


Fig. 2. TEM micrograph showing tiny precipitates on a grain boundary in the sensitized specimen of alloy B2.

high Mg aluminium alloys during elevated temperature exposure [2]. No tiny precipitates were observed in the sensitized specimen of alloy B1.

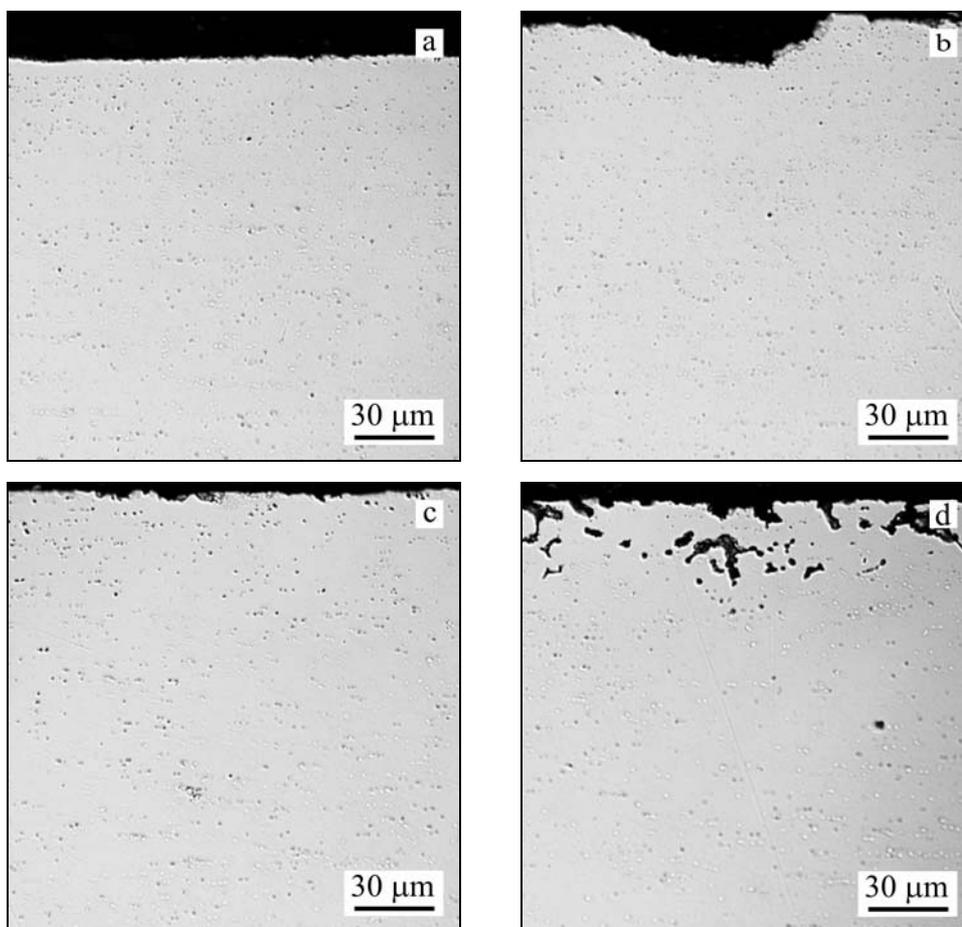


Fig. 3. Micrographs of the cross section at the surface of specimens of alloys A1 (a, b) and A2 (c, d) after the NAMLT test: a), c) non-sensitized specimens, b), d) specimens sensitized by annealing at 75°C/48 h.

Table 2. Corrosion potentials E_{corr} of investigated sheets

Sample	Mn (wt.%)	Cr (wt.%)	E_{corr} (V)
A1	0.26	0.06	-0.758
A2	0.01	< 0.001	-0.767
B1	0.36	0.14	-0.759
B2	0.02	< 0.001	-0.774

3.2. Corrosion potentials

The values of the corrosion potential E_{corr} of all alloys in the as-received (non-sensitized) state are given in Table 2. The alloys A1 and B1 have practically the same corrosion potentials, whereas both alloys without Mn and Cr exhibit more negative (anodic) values of E_{corr} .

3.3. Susceptibility to intergranular corrosion

Figures 3 and 4 show the cross sections through

the surface of non-sensitized and sensitized specimens after the NAMLT test. It can be seen that the surface of the specimens with Mn (and Cr) is much less attacked as compared to their counterpart specimens of the alloys without Mn and Cr. The most significant corrosion attack is observed in the alloy B2 with high Mg and very low Mn contents, followed by the alloy B1 with high Mg and Mn (Cr). The sensitized specimens of alloys A2 and B2 exhibit deeper corrosion penetration than their non-sensitized counterparts. Only shallow corrosion pits were revealed on the surface of Mn (Cr) containing alloys, whereas intergranular corrosion (Fig. 5) is the typical propagation mechanism in the alloys without Mn and Cr.

Figure 6 shows the results of NAMLT tests in a column graph comparing the mass losses per unit area of all tested specimens. It is obvious from Fig. 6 that the mass losses of the specimens resulting from the corrosion attack of nitric acid depend on alloy composition and are affected by the exposure to elevated temperature. The alloys with higher Mg content B1 and B2 suffer from larger mass losses than their counterparts of the alloys A1 and A2. A peculiar result is that the mass losses of the specimens annealed at

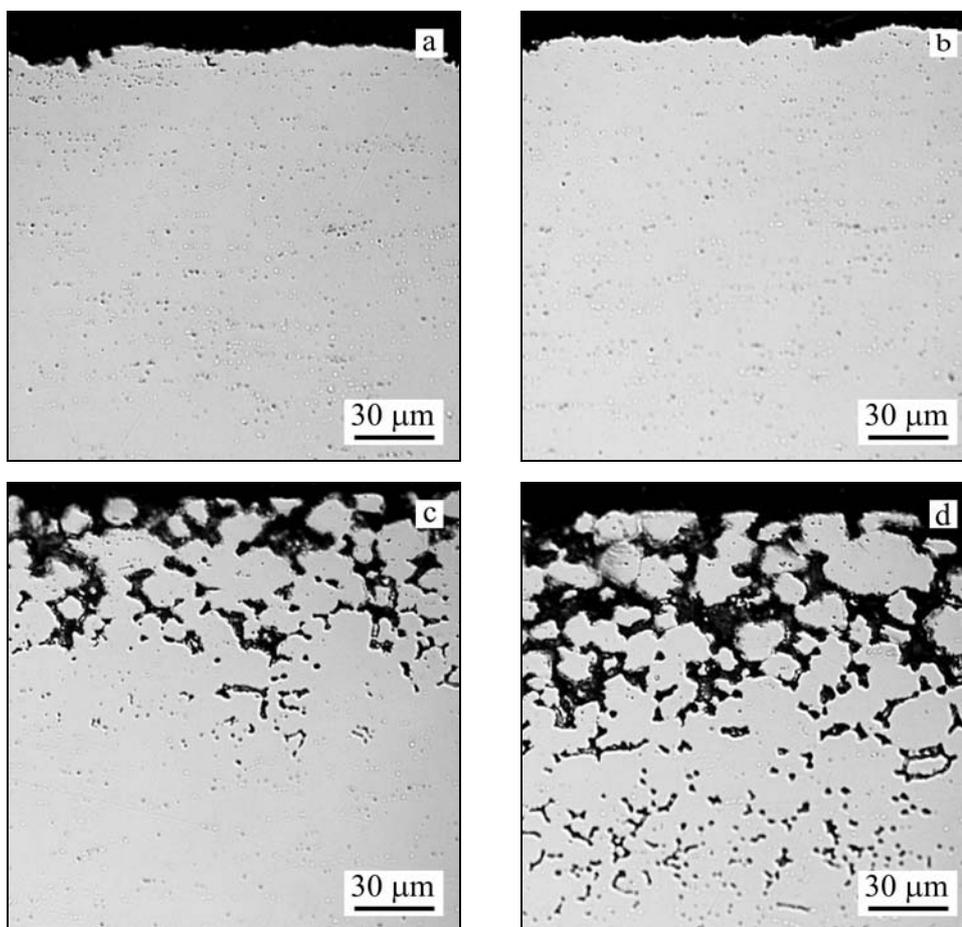


Fig. 4. Micrographs of the cross section at the surface of specimens of alloys B1 (a, b) and B2 (c, d) after the NAMLT test: a), c) non-sensitized specimens, b), d) specimens sensitized by annealing at 75°C/48 h.

75°C/48 h are in all cases higher than these of the as-received specimens. The difference induced by elevated temperature sensitization is more significant in the specimens of the alloys without Mn and Cr.

SEM examinations of the surface of NAMLT tested specimens [12] showed that the corrosion pits were small, shallow and uniformly distributed, except for both specimens of alloy B2. Sporadically, larger shallow pits were observed. The number of larger pits was higher in the sensitized samples. The corroded surfaces of both specimens of alloy B2 had very deep pits forming a continuous network depicting surface grains. The deep pits are obviously the result of an intensive dissolution of Al matrix along the grain boundaries. Some pits in grain interiors were also observed but they were also very shallow.

4. Discussion

As already mentioned, the principal corrosion process in aluminium alloys is the pitting corrosion due to localized galvanic effects between second-phase particles and the aluminium matrix. It is obvious that

the size and the depth of corrosion pits would increase with increasing particle size. Moreover, it depends on the difference of potentials of the particular phases and Al matrix. In addition, Al-Mg alloys with Mg content higher than 3 wt.% are known to be susceptible to intergranular corrosion.

It was ascertained that the alloys A2 and B2 without Mn and Cr exhibit more negative (anodic) corrosion potentials than the alloys containing Mn and Cr. The difference in corrosion potentials indicates that the alloys would probably exhibit different corrosion resistance when exposed to environments containing chloride ions. The alloys A2 and B2 whose potentials are more negative (active) are expected to corrode more easily than alloys A1 and B1. This result is in agreement with the results reported in [6, 7] stating that Mn in solid solution shifts E_{corr} slightly in positive direction whereas Mg in solid solution makes the alloy electrochemically less positive (more active). In spite of the fact that high temperature annealing was applied during sheet processing, we can assume, in accordance with more recent results of the authors [13], that a fraction of the total Mn content in alloys A1 and B1 has remained in solid solution. The dif-

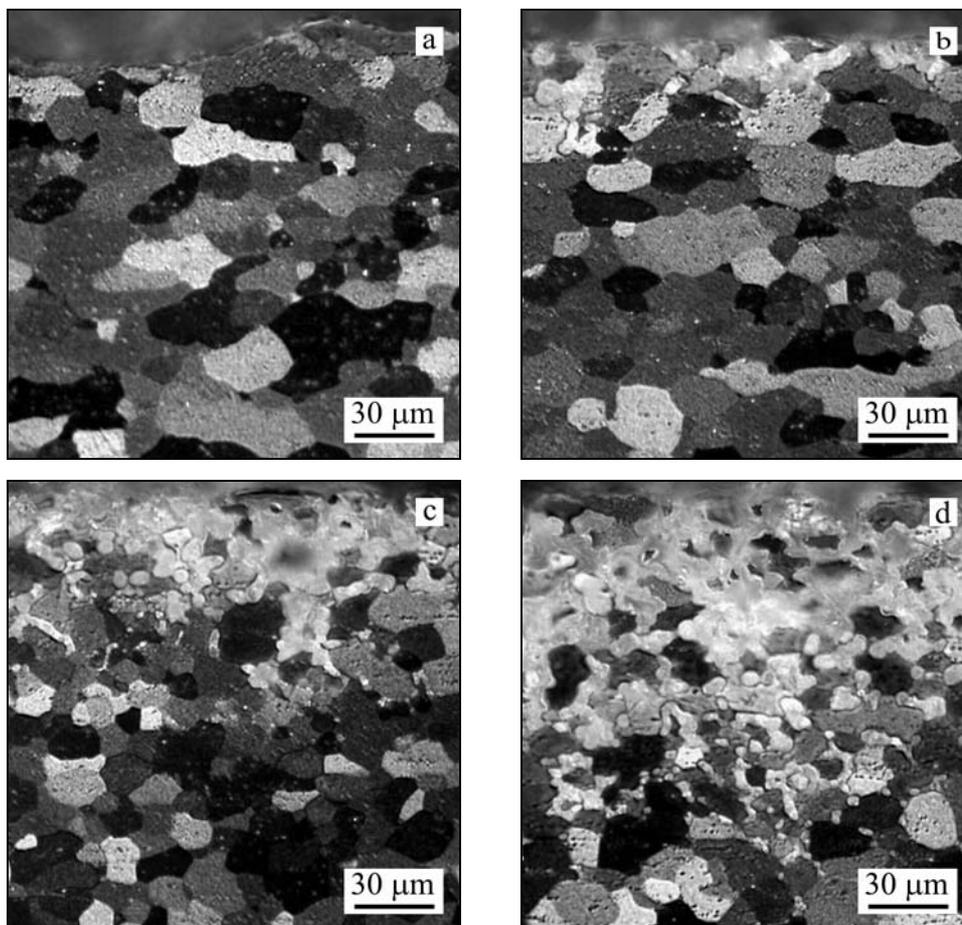


Fig. 5. Polarized light micrographs of the alloys A2 (a, b) and B2 (c, d) after the NAMLT test: a), c) non-sensitized specimens, b), d) specimens sensitized by annealing at 75°C/48 h.

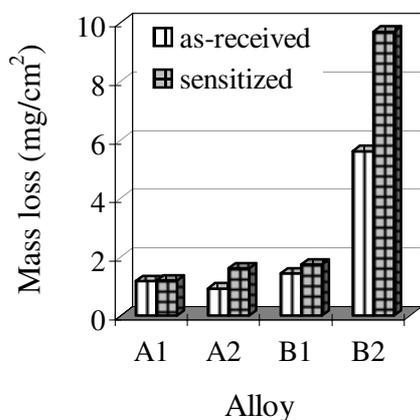


Fig. 6. Mass loss per unit area of as-received specimens and sensitized specimens.

ference in Mn solid solution content may be therefore the reason for the less negative values of E_{corr} in the alloys A1 and B1.

In all alloys under investigation, the constituent particles were often observed on grain boundaries or

on triple junctions. Coarse second-phase particles are known to act either as nucleation sites for particle stimulated nucleation of recrystallized grains or as obstacles to the boundaries of growing recrystallized grains. These particle effects on recrystallization may explain their observed preferred location on grain boundaries. Therefore, pitting corrosion is also expected to attack preferentially grain boundaries. It is to note, however, that the alloys under investigation were produced via TRC casting technology. As a consequence, their constituent particles are smaller than these in DC-cast alloys. Therefore, TRC-cast alloys are expected to be much less sensitive to intergranular corrosion than DC-cast alloys. Nevertheless, our results indicate that significant differences in the corrosion resistance of the investigated TRC alloys are observed and may be related to their different Mg, Mn and Cr contents.

In alloys A1 and B1, high density of relatively coarse precipitates, mainly in grain interiors, was observed. Tiny precipitates located on grain boundaries were found only in the sensitized specimen of alloy B2. The composition of these precipitates was not identi-

fied but it is highly probable that these are β -Al₃Mg₂ particles known to precipitate on grain boundaries in high Mg aluminium alloys during elevated temperature exposure [2]. No such precipitates were observed in the sensitized specimen of alloy B1. On the other hand, magnesium was detected in some of the coarser precipitates and constituent particles in alloy B1. This result indicates that the presence of Mn in Al-Mg alloys suppresses the selective precipitation of Mg on grain boundaries when the alloy is subjected to long exposures to elevated temperatures. In accordance with our TEM and EDAX observations, the effect of Mn can be ascribed to the fact that Mg is bonded in the Mn bearing constituent particles formed either during casting or during subsequent annealing procedures. When Mn is not present, Mg is less effectively bonded in constituent particles and can precipitate on grain boundaries. Mn additions to Al-Mg alloys with high Mg content thus prevents the corrosive weakening of boundaries by the highly anodic phase Al₃Mg₂ (the potentials of Al₃Mg₂ and alloy B1 are -1.24 V and -0.87 V, respectively [14]).

In addition to the beneficial effect of Mn in preventing Mg precipitation on grain boundaries, further causes of the improved corrosion resistance of Mn and Cr containing alloys can be identified in the investigated alloys. Recent unpublished results [13] have demonstrated that the presence of Mn in TRC AlMg3 and AlMg4.5 type alloys significantly improves also their resistance to galvanic surface corrosion in acid environments containing Cl ions (SWAAT test).

As mentioned above, the susceptibility to pitting corrosion of Al alloys is strongly affected by the corrosion potentials of constituent particles [4–7]. The corrosion potentials of Fe-bearing constituent particles Al₃Fe (-0.56 V), β -AlFeSi and Si (-0.26 V) are very cathodic [14] (less negative) with respect to the matrix of all alloys under investigation (-0.86 and -0.87 V according to [14]). The difference is even larger for the alloys A2 and B2 (see Table 2, the differences between the values reported in [14] are probably due to differences in test conditions, i.e., in NaCl solution concentration). On the other hand, Mn-containing phases such as Al₆Mn and α -AlMnSi have corrosion potentials very similar to these of alloys A1 and B1 (-0.85 V for Al₆Mn versus -0.86 and -0.87 V for alloy A1 and B1, respectively [14]). Therefore, Mn-bearing particles do not deteriorate the resistance to pitting corrosion of Al alloys. Furthermore, it has been demonstrated in [5–7] that Fe-bearing particles act as catalyzers for the local cathodic reaction (resulting in Al dissolution). The presence of Mn in these particles has been shown to suppress the catalyzing activity of Fe. Lunder et al. [7] have shown that the presence of even very small amount of Fe in Al₆Mn and α -AlMnSi particles significantly accelerates the cathodic reaction (i.e., Al dissolution). In addition to the Fe-bearing particles in

the alloys A2 and B2, the particles of Si with their very cathodic potential with respect to the Al-matrix may also contribute to the inferior corrosion resistance of these alloys with respect to their Mn and Cr containing counterparts.

5. Conclusions

The effect of the addition of manganese and chromium on the corrosion behaviour of aluminium-magnesium alloys with medium (AlMg3) and high (AlMg4.5) magnesium content was studied. The main efforts were focussed on the assessment of the influence of Mn on alloy susceptibility to intergranular corrosion. The results of the investigation can be summarized as follows:

1. High susceptibility to intergranular corrosion was observed only in the high-Mg alloy AlMg4.5 not containing Mn and Cr. Only the heat sensitized specimen of the alloy AlMg3 without Mn exhibits a weak intergranular corrosion attack. The alloys containing Mn and Cr do not exhibit intergranular corrosion.

2. Alloy sensitization to intergranular corrosion by long exposure at elevated temperature contributes to the increase in the depth and intensity of corrosion attack, especially in the alloys without Mn and Cr. The most pronounced effect is observed in the alloy AlMg4.5Mn having high Mg content.

3. It can be concluded that the presence of Mn in the studied Al-Mg alloys significantly improves their resistance to intergranular corrosion, especially in the alloy AlMg4.5.

4. The effect of Mn can be ascribed to the fact that Mg solute atoms are bonded in the Mn-bearing constituent particles and precipitates and not bonded in Fe-rich particles without Mn. The amount of Mg available for precipitation of the β -Al₃Mg₂ phase on grain boundaries is significantly reduced in Mn-rich alloys that results in substantial decrease in their susceptibility to intergranular corrosion.

5. The beneficial effect of Mn on the pitting corrosion of Al-Mg alloys was also documented by measurements of alloy corrosion potentials in chloride ions containing water solutions and the mechanisms of this effect have been discussed.

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