

INFLUENCE OF Cu AND Mn CONTENT ON THE PROPERTIES OF Al-Mg4.5-(Mn,Cu) TYPE ALLOY SHEETS

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Abstract

Influence of Cu and Mn content on the grain structure, precipitation effects and mechanical properties of two Al-Mg4.5-(Mn,Cu) type sheets was considered. It was found that a variety of grain size can be obtained in alloy with no Mn after different annealing conditions. In Mn-containing alloy the grain growth was suppressed by Mn-bearing particles and the grain size was not affected by the annealing temperature. The presence of 0.52 % Mn brought an appropriate strength increase ($\Delta YS \leq 30\%$, $\Delta UTS \leq 10\%$), but the ductility was not influenced by Mn content. The electrical resistivity used to follow precipitation/dissolution processes was mostly affected by precipitation or dissolution of Cu-bearing precipitates, which were found dominantly formed during the interstage recrystallization annealing. During final annealing sizeable change of the electrical resistivity was noticed only after high temperature annealing (as 470°C) when intensive dissolution occurs. The ageing response of the tested alloys was effective after ageing treatment at 140°C and 160°C. The high ageing potential of alloy I, with Mn and higher Cu content, was assumed to be due to higher content of Cu/Mg clusters and S'' (Al₂MgCu) phase particles. Since the age hardening effect was effective even at 140°C, this type of alloys becomes suitable for paint baking procedure at lower temperatures than the currently used of 160°-180°C.

Key words: Al-Mg4.5-(Mn,Cu) alloy; grain structure; ageing; tensile properties

Introduction

The application of Al-Mg alloy sheets in car body constructions is complicated in a great deal by applying the paint-baking sequence [1,2], due to the softening of Al-Mg parts at the baking temperatures (usually ranged to 160°-180°C). Using the heat-treatable alloys this problem has been overcome by precipitation hardening effect. The same idea came into play in case of Al-Mg alloys, when a similar precipitation hardening effect is provided by addition of a small amount of copper [3-8]. Such a

“hybrid” alloy, with a low Cu/Mg ratio: 0.1-0.14 in wt.%, designated as AA5030, was supposed to prevent the softening of Al-Mg sheets during the paint baking procedure [9]. The objective of this work was to estimate the influence of Cu and Mn content on the grain structure, precipitation hardening effects and mechanical properties of the Al-Mg4.5-(Mn,Cu) type sheets.

Experimental

Materials

The chemical compositions of the tested sheet materials are given in Table 1. In respect to the detected chemical compositions, they can be designated as Al-Mg4.2-Mn0.52-Cu0.48 (in further text alloy I), and Al-Mg4.7-Cu0.36 type (in further text alloy II), with no manganese ($Mn < 0.05$ wt.%). Alloy I was produced by laboratory casting, while alloy II was supplied in cold rolled condition as 3 mm thick sheet from Impol-Seval Aluminum Rolling Mill.

Table 1. Chemical composition of alloy I (Cu/Mg=0.1) and alloy II (Cu/Mg=0.077)

Alloy/wt.%	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti
I	0.131	0.310	0.48	0.519	4.21	0.136	0.0030	0.069	0.010
II	0.13	0.349	0.356	0.0519	4.66	0.013	0.0025	0.043	0.007

The laboratory produced ingot of alloy I was two-step homogenized at 440°C/8h + 510°C/14h, cooled down to 470°C, held for 2h, and then hot rolled from the initial thickness of ~30 mm to 8 mm. Hot rolled sheets were additionally annealed at 470°C/1h, to ensure fully recrystallized structure, as the hot rolled structures were rather partially recrystallized. The 8 mm thick sheets were cold rolled to 1.0 mm with interstage recrystallization annealing at 350°C/3h after reaching the thickness of 3.48 mm and 2.4 mm. The industrially produced 3 mm thick Al-Mg4.7-Cu0.36 (alloy II) sheets were cold rolled to 2.4 mm, recrystallization annealed at 320°C/3h, and then cold rolled to 1.0 mm. The 1.0 mm thick sheets were finally annealed for 3h at different temperatures (from 220°C to 470°C) in order to produce samples with different structures. The applied thermomechanical treatments (TMTs) were rather close to the industrial manufacturing practice.

Testing

Metallographic examinations. The samples were prepared by electrochemical polishing, using perchloric acid and ethanol solution, and etching by Barker’s solution. The average grain size (d_{av}) was determined using the linear intercept method.

Electrical resistivity measurements. Assuming that the precipitation/dissolution processes of the alloying elements is followed with electrical resistivity variations (the precipitation process of Mg, Cu, Mn or Fe is followed by a decrease of electrical resistivity [10,11]), resistivity values were measured after different heat treatments using the Sigmatest D2.068 equipment.

Tensile testing. Tensile tests were performed on an Instron 1332 machine, using the specimens with a gauge length of 50 mm and 12.5 mm width. All the specimens were tested in the rolling direction. The tensile tests were conducted in triplicate per each various heat treated specimens. An applied cross-head rate was 0.75 mm/min, giving an initial true strain rate of $\dot{\epsilon}_1 = 2.5 \times 10^{-4} \text{ s}^{-1}$.

Results

Grain size measurements

Metallographic examination has shown that the structure was not completely recrystallized after annealing at 260°C for 3h. However, after annealing at 280°C recrystallized grain structure was revealed with the average grain diameters of 18-19 μm . In the range of temperatures from 280°C up to 550°C the grain size in the alloy II (with no Mn) was found to increase from $\sim 19 \mu\text{m}$ to $\sim 45 \mu\text{m}$, while in alloy I it was rather unaffected, ranging to 18–19 μm , as it is shown in Fig. 1.

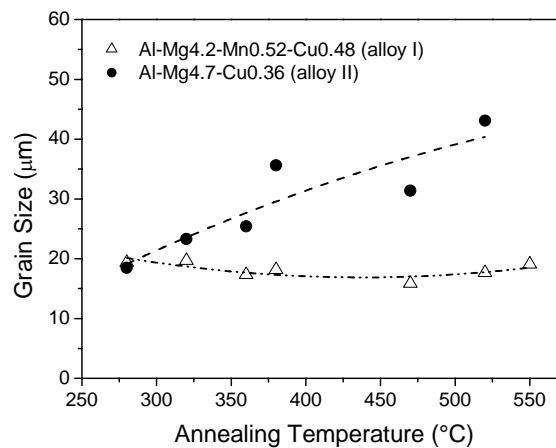


Fig. 1 Influence of the annealing temperature on the grain size variations in 60% cold rolled alloy sheets.

Electrical resistivity variations with different TMTs

Electrical resistivity variation brought by applying different annealing temperatures after recrystallization annealing at 320°/350°C and cold rolling to 60%, for both alloys I and II are shown in Fig. 2. For all final annealing conditions the electrical resistivity of alloy I (with Cu and Mn) was found higher than of alloy II (with no Mn). The resistivity change with annealing temperature was similar for both alloys: low temperature annealing (220°-280°C) brought a resistivity drop in respect to the initial cold rolled condition, but a further temperature increase was followed with an increase of electrical resistivity.

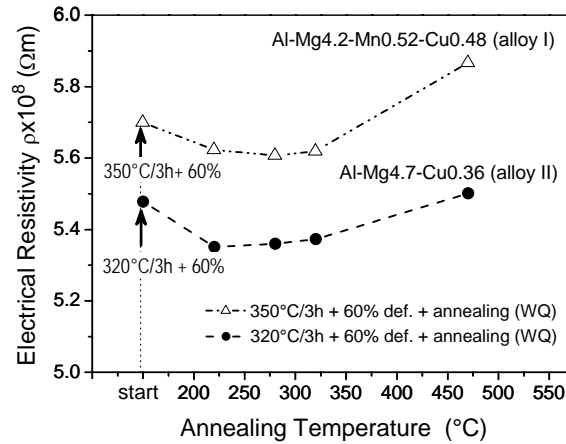


Fig. 2 Influence of the annealing temperature on the electrical resistivity variations in alloy I and alloy II after recrystallization annealing and cold rolling.

Tensile properties

Tensile properties dependence on the annealing temperatures is shown in Fig. 3. After recrystallization annealing (280°-470°C) the yield strength (YS) of alloy I (with Mn) is ranged from 140 to 145 MPa, and it is not affected by an increase of annealing temperature (Fig. 3a).

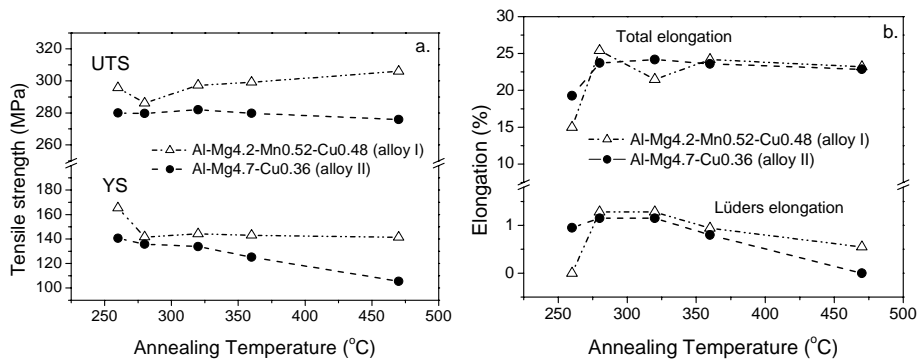


Fig. 3 Tensile properties of the tested alloys after different annealing conditions.

In case of alloy II the YS was decreased by increasing the annealing temperature from ~ 135 MPa (after annealing at 280°C) to ~ 105 MPa (after annealing at 470°C). Within the applied range of annealing temperatures the YS values for the two alloys differ less than $\leq 30\%$ (in the low temperature range, $t < 320^\circ\text{C}$, it is $\leq 10\%$). The ultimate tensile strength (UTS) is higher in alloy I, and it seems as it slightly increases by the annealing temperature from 290 MPa to 320 MPa, while in alloy II it is less changeable. The difference in UTS values for the two alloys is ranged up to 10 %).

The total elongation was increased in the range of transition from recovered (~260°C) to recrystallized structure (~280°C) reaching ~25 %, and after that it is rather constant (Fig. 3b). The Lüders elongations were quite similar in both alloys, attaining the maximum value of ~1 % in samples annealed at 280°C and 320°C. After high temperature annealing (at 470°C) the Lüders elongation is decreased to ~0.5 % in alloy I, while it is suppressed to ~0 % in alloy II (with no Mn).

Thus, the total effect of the annealing temperature on the tensile properties of the tested alloys is not very pronounced, especially in case of Mn containing alloy I. This alloy shows somewhat higher strength parameters, but the uniaxial ductility was the same for both alloys.

Ageing response

In order to evaluate the ageing potential of the tested alloys the ageing treatment was performed at 140°C, 160°C and 180°C for 30 minutes. The samples were annealed at 280°C and stretched with 5 % deformation before ageing. The thermal exposure at 280°C was selected according to the results of previous examinations which show the highest formability level after annealing at 280°C [12,13].

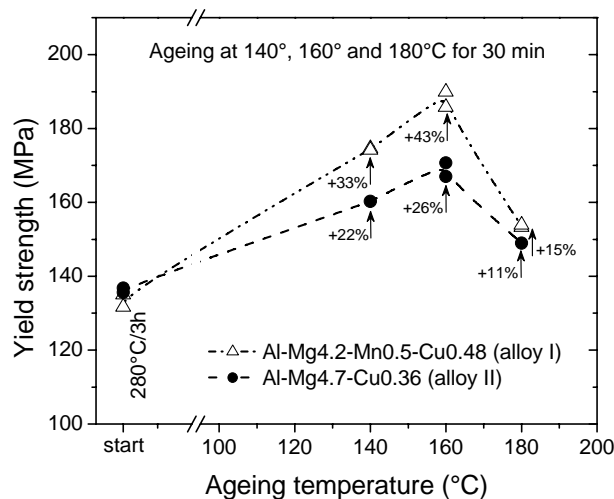


Fig. 4 Influence of the ageing temperature on the yield strength of the tested Al-Mg-(Mn,Cu) alloys.

After ageing at 140°C, 160°C and 180°C, the YS of alloy I in the annealed condition is increased from ~135 MPa to ~170 MPa (33%), ~190 MPa (43%), and to ~155 MPa (15%), respectively (Fig. 4). In case of alloy II the YS is changed to ~165 MPa (22%), ~170 MPa (26%) and ~150 MPa (11%) after the same ageing sequences. Thus, the age hardening effect was similar for both alloys with a maximum level attained after ageing at 160°C, but the ageing response was more intensive in alloy I, especially at 140°C and 160°C. After ageing at 180°C the ageing response was

obviously weaker for both alloys (Fig. 4), as the YS appeared to be lower than after ageing at 160°C or even 140°C.

Discussion

Structure features

Grain size. Results shown in Fig. 1 indicate that the grain size control is dependent in a great deal on the presence of manganese. It seems that the Mn – bearing particles (Al_6Mn or $Al_6(Mn,Fe)$) are very strong obstacles for grain growth, thus limiting the grain size to the unchangeable value close to $\sim 20\ \mu m$ in alloy I, independently on the applied annealing temperature. This effect was also recognized earlier [14], and seems to be partly overcome in cases when coarse grained structure is needed, by applying a very slow heating up rate in the annealing sequence [15,16]. In Fig. 1 it is obvious that in alloy II with no Mn the grain size variation by annealing temperature change is very effective.

Processing influenced dissolution/precipitation

During recrystallization annealing at 320°/350°C (Fig. 2) S' type (Al_2CuMg) particles should be present in both alloys (S' phase precipitates at 280°C-350°C [5]). Those precipitates dissolve into Al-matrix in the temperature range of 360°-430°C.

The higher resistivity level detected for alloy I can be attributed to the higher content of alloying elements, especially Mn and Cu, as well as other alloying elements, such as Ti and Cr (Table 1), which affect the resistivity in a same manner [10].

The detected resistivity variation with final annealing is not so pronounced as the precipitation processes were already active during recrystallization annealing at 320°/350°C and the developed structure could not be affected in a great deal by further low temperature annealing. After annealing at 470°C the electrical resistivity was considerably higher due to the dissolution of S' phase particles. It should be noted that at temperatures over 350°C the precipitation of Mn-bearing particles (Al_6Mn or $Al_6(Fe,Mn)$ type) is the only or even dominant process [9,15], but the resistivity drop due to the Mn-bearing particles precipitation is obviously overlapped by the S' dissolution effect and an increase of the alloying elements in the solid solution.

Mechanical properties

The strength parameters appeared to be somewhat higher in alloy I that contains Mn ($\Delta YS \leq 30\%$ and $\Delta UTS \leq 10\%$), as shown in Fig. 3. The final annealing temperature didn't bring any change of these parameters in case of alloy I, while in alloy II the gradual drop of YS is assumed to be due to the grain size increase brought by an increase of annealing temperature of this alloy (Fig. 1).

The ductility is rather the same for both alloys with the maximum value attained after recrystallization at 280°C (Fig. 3b), but it was not influenced by annealing temperature. Even the coarse-grained structure in alloy II did not bring higher elongations.

The highest Lüders elongations appeared in both alloys with fine grained structure obtained after annealing at 280°-320°C. It was decreased up to 0.5 % in alloy I, and completely suppressed in coarse-grained structure of alloy II after annealing at 470°C.

Low temperature ageing effects

Age hardening effect was detected in both alloys after 5 % stretching and all applied ageing treatments (Fig. 4). The more intensive ageing in alloy I with Cu and Mn was assumed to be due to the higher Cu content, i.e. the higher retained Cu content in the solid solution after the S' precipitation in the previous processing route.

The low temperature ageing effect in these alloys is related to the complex process of GPB (Guinier-Preston-Bagaryatsky) zones and S'' (Al₂MgCu) phase precipitation. It was established [6,7] that in such a low Cu/Mg ratio alloys two concurrent processes become active: (i) heterogeneous S'' precipitate at dislocations and (ii) homogenous precipitation in the matrix of Cu/Mg clusters (GPB zones) and S'' particles. The contribution of these two phase types to the total age hardening was estimated [6] to be dependent on the cooling rate from the solid solution range before ageing.

Besides the highest ageing effect attained at 160°C (43% in alloy I and 26% in alloy II), it is worth noting that the hardening effect at 140°C is also sizeable (33% and 22% for alloys I and II, respectively). Namely, the paint baking process currently occurs in the temperature range of 160°-180°C, but the recent intentions [5,17], about the introduction of ecologically more acceptable water based colors, will probably need a lower baking temperatures around 140°-160°C.

Conclusions

Two Al-Mg4.5-(Mn,Cu) type alloys with different Cu and Mn contents (0.52% Mn, 0.48% Cu - alloy I, and 0.36% Cu - alloy II) were tested.

It was found that the grain size is stabilized in Mn containing alloy I, due to inhibition of grain growth probably by Mn-bearing particles. In case of alloy II (with no Mn) the grain growth was not inhibited and a variety of grain structures can be obtained after different annealing conditions. The presence of 0.52% Mn brought an appropriate strength increase ($\Delta YS \leq 30\%$, $\Delta UTS \leq 10\%$), but the ductility was not influenced by Mn content. The Lüders elongations were ranged up to 1% in fine-grained structure for both alloys and were completely suppressed in coarse-grained structure of alloy II.

Electrical resistivity variations have shown that the precipitation of Cu-bearing particles already occurred during the interstage recrystallization annealing at 320°/350°C in the processing route. During the final annealing it is less affected except at higher temperatures (470°C) when intensive dissolution occurs. Higher resistivity level for alloy I can be attributed to the presence of Mn-bearing particles, while the resistivity variation in the whole range of temperatures was mostly affected by precipitation/dissolution of Cu-bearing precipitates.

The ageing response of the tested alloys was found very effective after ageing treatment at 140°C and 160°C. The high ageing potential of alloy I, with Mn and higher

Cu content, was assumed to be due to higher content of Cu/Mg clusters and S'' (Al₂MgCu) phase particles precipitated primarily heterogeneously at dislocations. The highest hardening effect was detected at 160°C, but the ageing response was effective even at 140°C, thus making these type of alloys suitable for paint baking procedure at lower temperatures than the currently used of 160°-180°C.

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References

- [1] G.B. Burger, A.K. Gupta, P.W. Jeffrey, D.J. Lloyd, *Mater. Characterization*, 35 (1995) 23.
- [2] J. Hirsch, *Mater. Sci. Forum*, 242 (1997) 33.
- [3] T. Fujita, K. Hasegawa, M. Suga: European Patent no.0616044 A2, (1994).
- [4] Y. Suzuki, M. Matsuo, M. Saga, M. Kikuchi, *Mater. Sci. Forum*, 217-222 (1996) 1789.
- [5] P. Ratchev, B.Verlinden, P. De Smet, P. Van Houtte, *Mater. Trans., JIM*, No1, 40 (1999) 34.
- [6] P. Ratchev, B. Verlinden, P. De Smet, P. Van Houtte, *Acta mater.*, 46 (1998) 3523.
- [7] P. Ratchev, B. Verlinden, P. De Smet, P. Van Houtte, *Proc. of ICAA6: Aluminium Alloys*, vol.2, 1998, p.757.
- [8] B. Verlinden, P. Ratchev, P. De Smet, P. Van Houtte, *Proc. of ICAA6: Aluminium Alloys*, vol.2, 1998, p.1075.
- [9] J.M. Story, G.W. Jarvis, H.R. Zonker, S.J. Murtha, *SAE Paper No.930277* (1993) 320.
- [10] M. Popović, E. Romhanji, *Mat. Sci. Eng*, A492 (2008) 460.
- [11] S.I. Vooijs, S.B. Davenport, I. Todd, S. van der Zwaag, *Philosophical Mag.*, A81 (2001) 2059.
- [12] E. Romhanji, M. Popović, D. Glišić, R. Dodok, D. Jovanović, *J. of Mat. Proc.Tech.*, vol.177 (2006) 386.
- [13] E. Romhanji, M. Popović, D. Glišić, R. Dodok, D. Jovanović, *Journal of Metallurgy (Metalurgija)*, vol.11, No.4 (2005) 267.
- [14] H. Watanabe, K. Oori, Y. Takeuchi, *Trans. ISIJ*, 27 (1987) 730.
- [15] Lj. Radović, M. Nikačević, M. Popović, E. Romhanji, *Journal of Metallurgy (Metalurgija)*, vol.13, No.1 (2007) 83.
- [16] Lj. Radović, M. Nikačević, M. Popović, E. Romhanji, *Journal of Metallurgy (Metalurgija)*, vol.13, No.4 (2007) 259.
- [17] K.R. Brown, M.S. Venie, R.A. Woods, *JOM*, 47 (1995) 20.