Influence of composition on natural ageing of Al-Mg-Si alloys

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Abstract

The effect of composition on natural ageing of Al-Mg-Si alloys was studied by the response of hardness HV 30 and electrical conductivity in five alloys (AA6xxx series) containing besides the main solutes Mg and Si (AA6082) also small additions of Cu (AA6262) and Cu with Sn (three variants of AA6023). Simple model concept was adopted to evaluate these responses. The addition of Sn induces an incubation period in both HV 30 and resistivity response that decreases with increasing Mg content. Mg, Si and Cu take part in clustering in Cu and Sn containing alloys.

K e y   w o r d s: aluminium alloys, tin, ageing, hardness, electrical resistivity

1. Introduction

Aluminium alloys containing Mg and Si as major additives belong to industrially used hardenable alloys (6xxx series) and were subjected to several studies in the past years [e.g. 1–5]. The strengthening of AlMgSi alloys is based on the precipitation hardening. The precipitation sequence involves subsequently: α (SSS) $\rightarrow$ GP zones $\rightarrow$ β'' precipitates $\rightarrow$ β' phase $\rightarrow$ β phase [e.g. 6, 7]. α (SSS) is the Supersaturated Solid Solution; the structure of Guinier Preston (GP) zones is not known, they are either spherical- or lath-like clusters. Fine needles of the β'' monoclinic intermediate phase are elongated in $\langle 100 \rangle_{Al}$ directions as are also rod--shaped precipitates of the hexagonal intermediate β' phase. The equilibrium β phase (Mg$_2$Si, FCC structure, $a = 0.639$ nm) precipitates usually as platelets on $\{100\}_{Al}$ planes. When Cu is added, the precipitation sequence changes slightly, Cu induces the Q phase and its metastable forms [8, 9]. The effect of Cu addition changes, most probably, with its concentration: The lath-like intermediate Q$'$ phase either replaces or follows β' phase rods in the sequence mentioned above. Also equilibrium quaternary Q phase is reported to precipitate along with β (Mg$_2$Si) phase.

Solution treated AlMgSi(Cu) alloys undergo natural ageing when kept at room temperature. The formation of small solute clusters was proved by atom probe studies [10] on beginning of this hardening process, which continues by GP zones development. It has been shown, that natural ageing has an adverse effect on artificial ageing of these alloys [11, 12].

Automatic machining of Al alloys is often improved by the presence of a low melting point eutectic constituent in the alloy. Al-Cu and Al-Cu-Mg alloys were designed with the addition of a Pb-Bi eutectic. These low melting point additions are usually fine and dispersed throughout the material and help to form small chips. The elements used have inconsiderable solubility in the matrix. To solve the problem of the Pb--toxicity, Sn is now envisaged as a Pb substitution. Contrary to lead, tin can change the precipitation sequence in Al alloys. The effects of trace additions of Sn on the nucleation of the Θ' phase in Al-Cu alloys were attributed to a lowering of the interfacial energy of the Θ' nuclei by the trace elements [13] or to nucleation at prior formed Sn precipitates [14, 15]. These precipitates strongly bind vacancies that cannot assist the diffusion of Cu in Al. The formation of GP zones is therefore suppressed and the decomposition of supersaturated solid solution starts at higher temperatures directly by the formation of the Θ' phase. According to the recent review [16], both mechanisms are possible, depending on the conditions of thermal treatment. Trace as well as small additions of Sn there-

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Table 1. Chemical composition of alloys investigated (wt.%)

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Pb	Bi	Sn
AA6082	1.080	0.370	0.023	0.444	0.794	0.006	0.030	0.016	0.003	0.000	–
AA6262	0.710	0.450	0.347	0.126	0.971	0.118	0.060	0.025	0.639	0.590	–
AA6023A	1.150	0.190	0.310	0.310	0.58	0.006	0.006	0.031	0.035	0.62	0.72
AA6023B	1.080	0.210	0.390	0.338	0.780	0.009	0.090	0.049	0.034	0.913	0.522
AA6023C	1.10	0.220	0.360	0.340	1.24	0.006	0.030	0.021	0.046	0.78	0.53

fore accelerate and enhance precipitation hardening in Al-Cu alloys [17–20]. A similar suppression of pre--precipitation stages was also observed in Al-Cu-Mg alloys with Sn additions [21].

It is supposed that in Al-Mg-Si-(Cu) alloys a large amount of Mg-Si-(Cu)-vacancy clusters acting as nucleation sites for GP zones develop. It happens with the excess of Si over the stoichiometric composition of Mg_2Si during natural ageing [22] as the binding energies of Mg-vacancy (17.3 kJ/mol) and Si-vacancy (27 kJ/mol) are positive and relatively high [23]. A modification of natural ageing can be expected in Al--Mg-Si-(Cu) alloys with Sn additions due to the very high binding energy between Sn atom and vacancy (38.6 kJ/mol [15]). The influence of Sn addition on natural ageing of Al-Mg-Si-(Cu) alloys with Si-excess over the stoichiometric Mg_2Si composition is therefore introduced in this work.

2. Experimental details

Three types of Al alloys, AA6082, AA6262 and AA6023 were die extruded to the rods with diameter equal to 18.85 mm at 500–520 °C and quenched by water spray directly behind the die. Their composition is given in Table 1. Three various contents of Mg were chosen in the AA6023 alloy. The alloys AA6082 and AA6023 were homogenized before extrusion (510 °C/1 h + 500 °C/8 h for AA6082 and 530 °C/3 h + 545 °C/5.5 h for AA6023).

Hardness HV 30 and electrical conductivity at room temperature were measured during natural ageing. Förster Sigmatest was used for the conductivity measurement. The absolute accuracy is ± 0.2 MS/m, the statistical standard deviation of several measurements was about 0.5 %. The mean diagonal value of 6 indentations in both directions was determined for HV 30. Specimens were solution treated at 540 °C for 0.5 h and water quenched immediately before the investigation of natural ageing started. The measurements of the initial values started not longer than 0.1 h after the quenching. Natural ageing was monitored at one specimen for each alloy to omit scattering.

Results for the AA6023 alloy were compared to those of AA6082 and AA6262 alloys. The commercial AA6082 alloy has a Si-excess over the stoichiometric

composition of Mg_2Si and contains Mn for its anti--recrystallization effect. The content of Mg and Si is balanced in the commercial AA6262 alloy and a small amount of Cu (~ 0.3 wt.%) and Cr (~ 0.1 wt.%) is added there. The AA6023 alloys differ from the AA6082 alloy mainly by Sn and Cu content.

3. Results and discussion

The developments of hardness HV 30 and electrical conductivity during natural ageing are shown in Figs. 1 and 2. The initial hardness of the AA6082 alloy is larger than of the AA6262 and AA6023 alloys most probably due to the presence of Mn and Fe, eventually Si containing particles. In the AA6082 and AA6262 alloys hardness increases immediately with natural ageing while a relatively long time is needed before HV 30 starts to increase in the AA6023 alloy containing Sn. This time depends distinctively on the Mg content (cf. A, B and C variants). After 1000 h
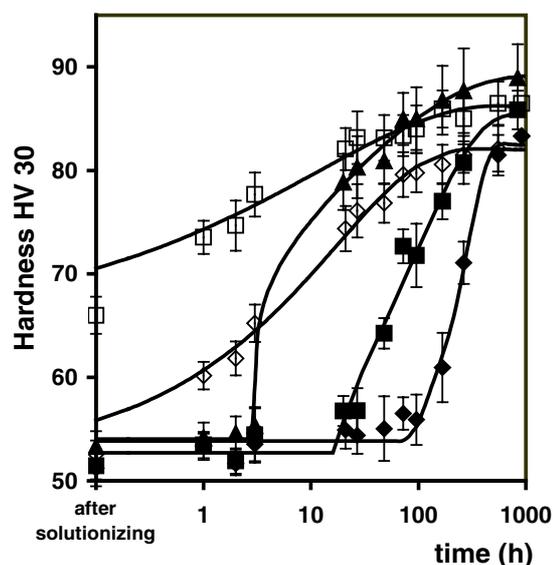

Fig. 1. Hardness HV 30 development during natural ageing. Experimental data: □ AA6082, ◇ AA6262, ◆ AA6023A, ■ AA6023B, ▲ AA6023C. Full lines are model fits of corresponding experimental data.
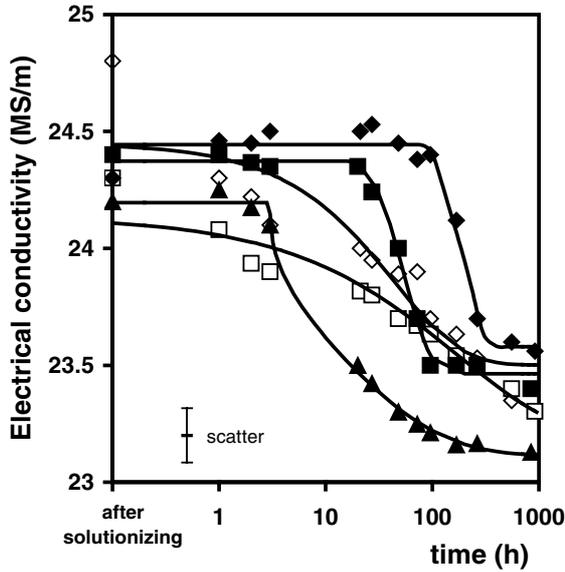
Fig. 2. Response of electrical conductivity (measured at room temperature) on natural ageing. Experimental data: □ AA6082, ◇ AA6262, ◆ AA6023A, ■ AA6023B, ▲ AA6023C. Full lines are model fits of corresponding experimental data.

Fig. 3. Dependence of HV 30 on the yield tensile stress $R_p0.2$ measured at room temperature. □ AA6082, ◇ AA6262, ▲ AA6023.

the hardening is almost finished in all alloys studied.

Electrical conductivity decreases with time of natural ageing for all alloys studied. The incubation periods similar to those in the hardness development were observed in AA6023 alloys and their values correspond very well together. This behaviour can be ascribed to a clustering of solutes in the investigated specimens. The three-dimensional atom probe data [24] indicate the forming of Cu clusters in the very early stages of natural ageing in the Al-Cu-Mg-Mn (Al-1.2%Cu-1.2%Mg-0.2%Mn and Al--1.9%Cu-1.6%Mg-0.2%Mn (at.%)) alloys, which become enriched in Mg as the time of natural ageing increases. The same experimental method proved solute atoms clusters during natural ageing of Al-Mg-Si-(Cu) alloys [10]. It is well known that small clusters of solute atoms scatter conduction electrons more than individual atoms, if their radius does not overcome a certain value [25, 26]. With an increasing concentration of clusters (or GP zones) electrical resistivity increases and consequently a decrease in electrical conductivity is observed [25, 26]. A similar behaviour of electrical resistivity was observed during natural ageing of AA6111 alloy [27]. Simultaneously mechanical properties as proof stress or hardness are improved due to a clustering.

Both types of the dependences show that the kinetics of natural ageing varies with the alloy composition. To describe the observed kinetics the influence of solutes and clusters on the electrical resistivity and on the yield tensile stress was considered. Figure 3
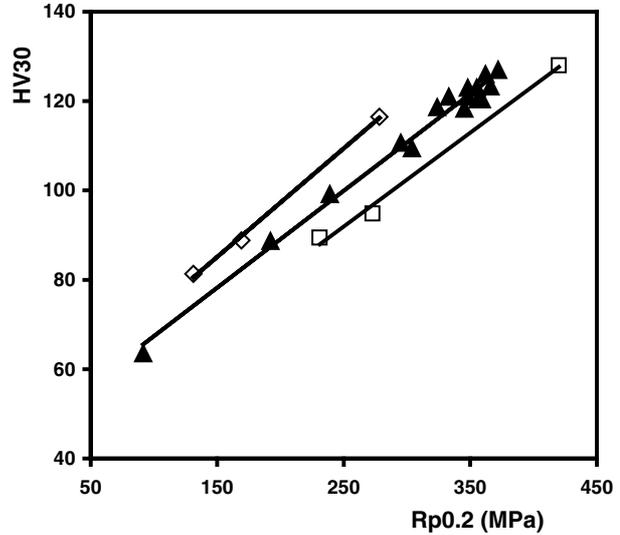
shows that HV 30 is proportional to the proof stress $R_p0.2$ at room temperature for alloys investigated and so a concept developed for the yield tensile stress was transformed to the HV 30 values. The values were obtained after various thermo-mechanical treatments.

The yield stress σ can be, in the first approximation, described as:

$$\sigma = \sigma_p + \sigma_{ss} + \sigma_{cl}, \tag{1}$$

where σ_p is a contribution from matrix, σ_{ss} is a contribution from solid solution hardening and σ_{cl} comes from clusters.

If the actual relative volume fraction of clusters is f_r, then [28]

$$\sigma_{ss} \sim (1 - f_r)^{2/3}$$

and

$$\sigma_{cl} \sim f_r^{1/2}.$$

Note that f_r equals zero at the beginning and approaches 1 if all possible clusters are developed. Then

$$\sigma = \sigma_p + S_{ss} \cdot (1 - f_r)^{2/3} + S_{cl} \cdot f_r^{1/2}, \tag{2}$$

where S_{ss} and S_{cl} are coefficients of proportionality. As the absolute volume fraction should be proportional to the real concentration of solutes involved in the clustering, S_{ss} and S_{cl} depend not only on a type of solutes and clusters, respectively, but also on the concentration of those solutes before natural ageing.

T a b l e 2. Fitted parameters from hardness response to natural ageing

Alloy	k (h^{-1})	n	HV_1	HV_2	t_0 (h)
AA6082	$(5.46 \pm 0.01) \times 10^{-3}$	0.470 ± 0.005	18.090 ± 0.003	37.620 ± 0.008	–
AA6262	$(21.3 \pm 0.1) \times 10^{-3}$	0.706 ± 0.001	6.021 ± 0.001	36.22 ± 0.01	–
AA6023A	$(3.27 \pm 0.02) \times 10^{-3}$	2.5 ± 0.3	6.0 ± 0.6	35 ± 1	72.0 ± 0.1
AA6023B	$(4.9 \pm 0.9) \times 10^{-3}$	1.1 ± 0.2	4.880 ± 0.001	37.55 ± 0.01	18 ± 3
AA6023C	$(15 \pm 1) \times 10^{-3}$	0.47 ± 0.04	6.191 ± 0.001	41.27 ± 0.01	3.0 ± 0.1

T a b l e 3. Fitted parameters from electrical resistivity response to natural ageing

Alloy	k (h^{-1})	n	ρ_0 (nΩm)	ρ_1 (nΩm)	ρ_2 (nΩm)	t_0 (h)
AA6082	5.46×10^{-3}	0.47	29 ± 9	12 ± 9	14 ± 9	–
AA6262	21.3×10^{-3}	0.706	29 ± 13	12 ± 13	13 ± 13	–
AA6023A	$(7.15 \pm 0.08) \times 10^{-3}$	2.0 ± 0.6	28 ± 12	14 ± 12	13 ± 12	72
AA6023B	$(23 \pm 2) \times 10^{-3}$	1.5 ± 0.3	28 ± 8	13 ± 8	14 ± 8	18
AA6023C	$(70.9 \pm 0.2) \times 10^{-3}$	0.43 ± 0.8	29 ± 8	12 ± 8	15 ± 8	3

Adapting Eq. (2) for hardness, one obtains

$$HV = HV_0 + HV_1 \cdot (1 - f_r)^{2/3} + HV_2 \cdot f_r^{1/2}. \quad (3)$$

Supposing that clusters develop with time t during isothermal annealing according to a model of nucleation, growth and impingement of diffusion fields and that the number of nucleation sites is limited and all the sites are used for nucleation very early in the transformation (so called "site saturation"), then

$$f_r = 1 - \exp\left(-\left(k\left(T\right)t\right)^n\right), \quad (4)$$

where $k(T)$ is the kinetics rate at a constant temperature T and n is the kinetics exponent [4, 29–32].

Time dependence of the hardness HV during natural ageing can be then written as

$$HV = HV_0 + HV_1 \cdot \left(\exp\left(-k\left(T\right)t\right)^n\right)^{2/3} + \\ + HV_2 \cdot \left(1 - \exp\left(-k\left(T\right)t\right)^n\right)^{1/2} \quad (5)$$

and from the measured isothermal curves of HV 30 during natural ageing HV_0, HV_1, HV_2, k and n parameters can be fitted. If an incubation period t_0 is observed, t is substituted by the term $(t - t_0)$ and so t_0 can be fitted, too. To restrict the number of parameters HV_0 was estimated using the observed dependences of HV 30 on $R_p0.2$ and the $R_p0.2$ of pure Al equal to 10 MPa as it was used in modelling of precipitation hardening in pre-aged Al-Mg-Si-(Cu) alloys [4].

If Matthiessen's rule is valid the contributions of matrix ρ_0, solutes ρ_{ss} and clusters ρ_{cl} to electrical resistivity at a constant temperature are additive and ρ_{ss} and ρ_{cl} are proportional to the concentration of solutes and clusters, respectively.

Then

$$\rho = \rho_0 + \rho_1 \cdot \exp\left(-k\left(T\right)t\right)^n + \\ + \rho_2 \cdot \left(1 - \exp\left(-k\left(T\right)t\right)^n\right), \quad (6)$$

where ρ_0, ρ_1 and ρ_2 are parameters depending on material and temperature. In the case of an incubation period t_0, t will be substituted by the term $(t-t_0)$ again.

From the measured values of electrical conductivity the time dependence of electrical resistivity during natural ageing can be derived and parameters ρ_0, ρ_{ss}, ρ_{cl}, k and n (eventually also t_0) can be fitted.

The fitted parameters from hardness and electrical resistivity response to natural ageing are summarized in Table 2 and 3, respectively. The method of least squares was used.

If the parameters k and n for the AA6082 and AA6262 alloys in the fitting procedure of electrical resistivity response are adopted from the hardness response fitting, the fitted values of ρ_0, despite of their large deviations, are very close to electrical resistivity value for pure Al (26.5 nΩm at 20 °C). Using the values of incubation period t_0 from hardness responses of the AA6023 alloys the fitted values of the parameter n in electrical resistivity responses correspond very well to those in hardness response. The fitted values of parameter ρ_0 match well the value for pure Al again.

The parameter HV_2 depends on the square root of a real concentration of solutes (cf. Eq. (3)) and for various alloys also on the type of clusters. Comparing values obtained for the AA6023 alloy – Fig. 4, it seems that all Mg, Si and Cu take part in the clustering process, because a linear dependence of HV_2 on the square root of total concentration of Mg, Si and Cu in the alloy can be drawn. The HV_2 value for the
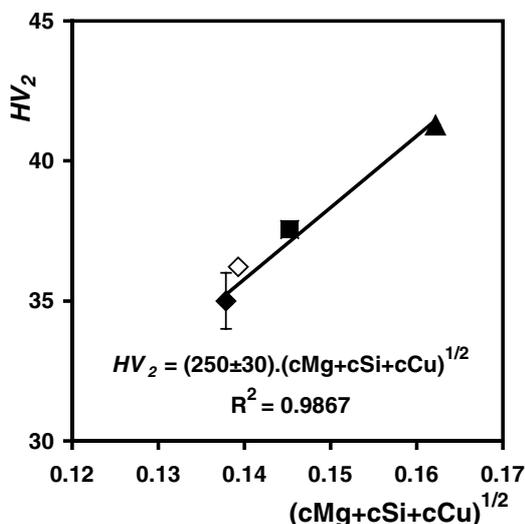
Fig. 4. Dependence of HV_2 parameter on the sum of Mg, Si and Cu concentrations in the AA6023 and AA6262 alloys. ◆ AA6023A, ■ AA6023B, ▲ AA6023C, ◇ AA6262.

AA6262 alloy, which also contains Cu, matches the dependence in Fig. 4, too. One can suggest that the clusters in the AA6023 alloys with the Sn addition are of the same nature as those in the AA6262 alloy. These clusters develop further to Q' and Q phase precipitates during annealing of all Cu containing alloys at elevated temperatures.

4. Conclusions

Results on the natural ageing of Al alloys (AA6xxx) containing Mg, Si, Cu and small addition of Sn can be summarized as follows:

– Sn solutes induce the incubation period in natural ageing due to the strong bond of vacancies to the Sn atoms;

– Incubation period decreases with increasing Mg content;

– Effect of cluster development on hardness and conductivity can be described by simple model concept;

– Magnesium, silicon and copper atoms take part in the clustering during natural ageing;

– Similar hardness and electrical resistivity response on natural ageing in AA6023 and AA6262 alloys manifest similar nature of clusters in these alloys.

Acknowledgements

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