THE EFFECT OF MG-ADDITIONS ON PRECIPITATION BEHAVIOUR OF AL-SI ALLOYS

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Abstract

The addition of magnesium to Al-Si alloys induces a drastic change in nucleation behaviour due to the change of the covalently bonded diamond structure of silicon precipitates into the metallic phase Mg_2Si. Object of this investigation is the transition between the two different precipitation mechanisms as a consequence of variable Mg additions to the binary alloy. Several aspects of precipitation hardening, especially preageing in the clustered condition and different homogenization treatments were studied. This includes increased strength as well as formability, if these alloys are to be used e.g. for automotive sheets. In addition to simple model alloys more complex engineering alloys are considered.

Introduction

Necessity for a better fuel economy gave rise to an increased number of investigation activities in automotive industries. Besides optimizing engine efficiency the most important effect is obtained by a reduction in weight. Here the replacement of rolled products, i.e. car body sheets could contribute to this aim. International research and first applications by both aluminium and automotive industries seem to concentrate on alloys of the age-hardenable/heat treatable Al-Mg-Si type. Because of the complex production process a large number of parameters influences material properties. This becomes even more evident when regarding the high demands on an automotive sheet, i.e. the discrepancy between production and application properties. For an optimum formability the strength has to be low, but buckling strength of the formed and lacquered sheet has to be high.
The fundamental understanding of the structural constituents and their influence on the precipitation process of these alloys could be helpful to optimize process parameters such as heat treatment temperatures or times and to insure constant properties especially in the age-hardened T4 condition. As the relevant alloys show a silicon excess [1], binary Al-Si alloys as well as ternary Al-Mg-Si alloys with a content of alloying elements of not more than 2,5 wt% are investigated. Furthermore the influence of companion elements such as Mn, Fe or Cu is considered. Structure and properties were studied by measurements of hardness, el. conductivity as well as tensile tests, microscopy and DSC analysis.

Al-Si Alloys

The Al-Si system has been object of numerous investigations [2,3] as the covalently bonded dc Si particles seemed to be very effective obstacles to the motion of dislocations. But development of an engineering alloy with low Si content has not been successful because of the extremly high quench sensitivity of these alloys.
Reason for this is the fact that the nucleation of the stable diamond structure is associated with an increased atomic volume. The growth of the clusters prior to nucleation therefore is limited by accumulation of stresses in the cluster-matrix interface. Vacancies can reduce the nucleation barrier by becoming part of the nucleus and thus lowering the interfacial stresses. On the other hand they can increase the diffusion rate of solute atoms. So it is obvious that the hardenability of the alloys -determined by the density of precipitates- is highly dependent on the number of quenched-in vacancies, i.e. on the heat treatment temperature, the quench rate and the quench temperature. But even by rapid quenching a precipitation density of not more than 10^{12} - 10^{14} particles/cm^3 can be achieved [3]. For a sufficient increase in strength in this alloy about 10^{18} particles/cm^3 would be necessary [4].
The quench sensivity of Al-Si alloys can effectively be reduced by ternary additions of Ge. Such ternary alloys obey to the rule that a "successful" precipitation hardening Al alloy contain one element with a larger atomic radius and another with a smaller one (±-rule) [5]. By reducing the interfacial strain energy more clusters achieve the critical size for the coherent fcc structure to collapse into the stable dc structure which stays unchanged (for schematic drawing see [6]). The density of the precipitates of a binary and a ternary alloy, containing the same amount of alloying elements (at%) is shown in figure 1.

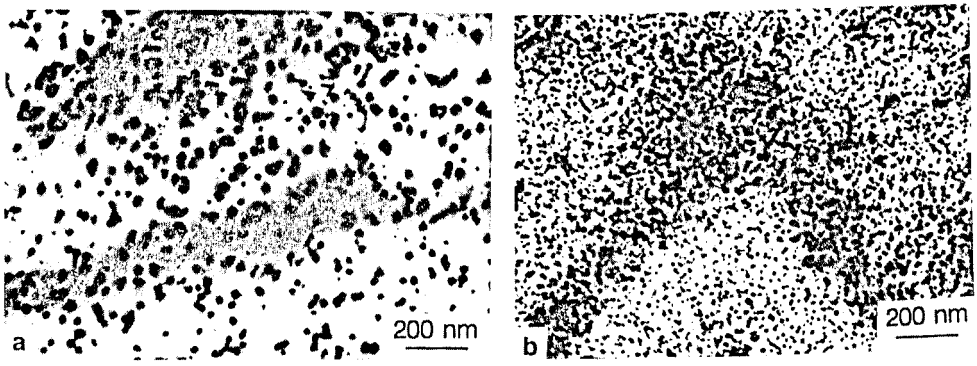

Figure 1a,b. TEM micrograph of a) Al 2 at% Si, b) Al 1 at% Si 1 at% Ge, both homogenized and aged 10 h 160 °C

Addition of Mg to Al-Si alloys

Already small amounts of magnesium lead to a drastic change in the precipitation behaviour of Al-Si alloys [7]. Figure 2 shows TEM micrographs of Al 1 at% Si 1 at% Ge, containing differnt amounts of Mg.

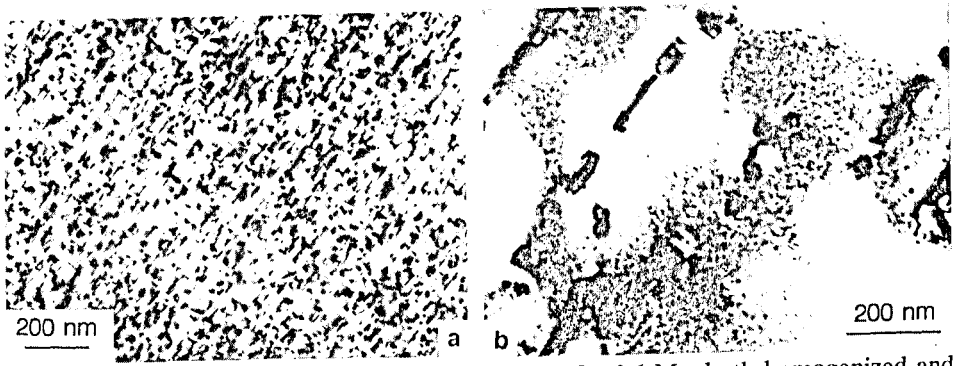

Figure 2a,b. a) Al 1 Si 1 Ge Mg<0,5, b) Al 1 Si 1 Ge 0,6 Mg, both homogenized and aged 10 h 160 °C

The alloy with the low Mg content shows the coexistence of fine Mg_2Si precipitates (dots = needles viewed end on) and coarse dc Si-Ge precipitates, i.e. the refining effect of Ge additions to Al-Si alloys is removed by Mg. Higher amounts lead to a fine Mg_2Si precipitation while very coarse Si only precipitate at heterogenities as dislocation groupings or grain boundaries. Obviously the precipitation hardening effects of both diamond cubic and cubic phase cannot be used simultaneously.
Reason for this is the fact that precipitation hardening of Al-Mg-Si alloys, in accordance with many other aluminium alloys, is connected with a precipitation sequence from the less stable coherent clusters to the stable but incoherent Mg_2Si phase [8]. The sequence will be described by the following terminology:

supersaturated $\alpha \rightarrow$ cluster $\rightarrow$ needle-shaped GP zones $\rightarrow$ rod-shaped ß' $\rightarrow$ Mg_2Si platelets

Peak hardness during artificial ageing is connected with the transition of the needle-shaped coherent GP zones to the less coherent ß' phase (Fig.3).

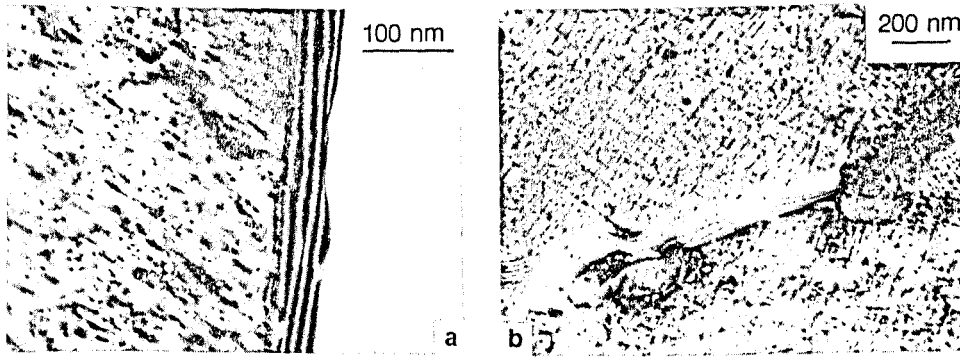

Fig. 3a,b. Al 1,2 Si 0,5 Mg
a) GP zones, under-aged condition (2h 180 °C)
b) Mg_2Si-precipitates after 24 h 180 °C

Different from the Al-Si alloys, an age-hardening process starts immediately after a solution treatment with subsequent rapid quenching, resulting in an increase in hardness and strength (Fig. 4a). This natural ageing effect is ascribed to the formation of clusters, circular and disordered, as they can be observed neither by electron image nor by electron diffraction. Positive evidence is the anomalous decrease of electrical conductivity during artifical ageing (Fig. 4b). Additional to [8] the clusters have to be regarded as a seperate precipitation stage. This becomes obvious by DSC curves of age hardened samples which show an endothermic peak before the exothermic reaction which can be ascribed to the precipitation of the GP zones.

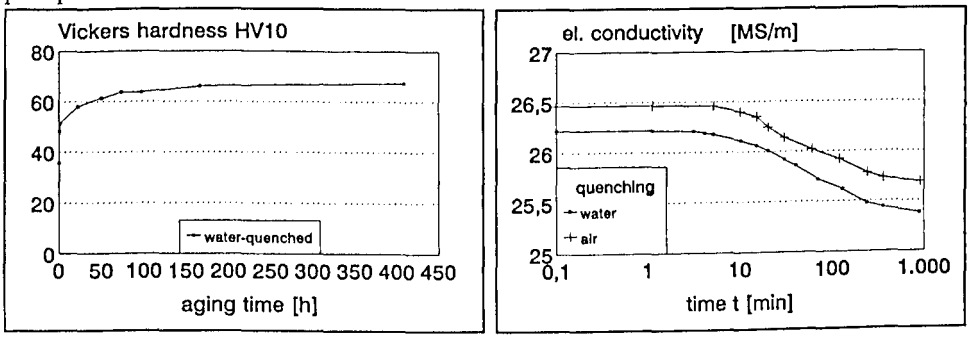

Fig. 4a,b. Al 1,2 Si 0,4 Mg
a) Vickers hardness and b) el. conductivity versus natural ageing time

The clusters are assumed to consist of a ternary Mg,Si-rich solid solution with Al atoms. In the binary Al - Si system Al-free clusters have to form because of the low interaction energy between these two elements. Both, Mg - Si and Mg - Al have a higher interaction energy, indicated by the formation of compounds. So Mg atoms make possible a zone of all the three elements. Due to the ±-rule mentioned above the interfacial stresses of such zones are relatively low so that they can grow. Al-free clusters, i.e. the nucleation of dc is inhibited. Nucleation of the dc phase is restricted to inhomogenities as dislocations or grain boundaries, which locally lower the activation energy (see Fig. 2b). For a change to a more stable Mg_2Si precipitate the Al atoms have to be rejected from the ternary zones. Al-free parts of a zone form ordered needles. Al-rich parts have to dissolve, causing the endothermic peak in the DSC curve. A schematic drawing of the nucleation-/precipitation process is given in Fig.5.

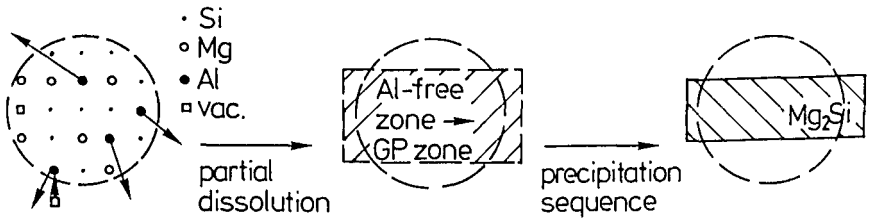

Fig. 5. Schematic drawing of cluster and GP zone formation in an AlMgSi-alloys

Although the precipitation of the dc phase is inhibited by Mg, a Si excess severely influences the ageing characteristic of the ternary alloy. Table I gives yield stresses of several AlMgSi-alloys with different Mg_2Si contents and Si excesses. All alloys contain the same amount of companion elements (Fe 0,17-0,20wt%, Cu 0,25 wt%, Mn 0,25 wt%).

Table I. Influence of Mg_2Si content and Si excess on yield stress $Rp_{0,2}$ in the T4 and T6 condition (1h 180°C), homogenization 540°C, water quenched. Experimental results from VAW, Bonn, Germany, to be published.

	Mg_2Si [wt%]	Mg [wt%]	Si excess [wt%]	$Rp_{0,2}$ T4 [MPa]	$Rp_{0,2}$ T6 [MPa]
1	0,46	0,29	0,42	94	132
2	0,47	0,3	1,03	128	200
3	0,65	0,41	0,96	150	218
4	0,77	0,49	0,45	140	215
5	0,93	0,59	0,45	157	233
6	0,93	0,59	0,85	176	262
7	1,25	0,79	0,52	170	239
8	1,28	0,81	0,74	176	260
9	1,56	0,99	0,63	170	253

The strength increases with increasing Mg_2Si content (1,4,7). A Si excess enhances both natural and artificial ageing (compare 1,2/5,6/7,8). This might be due to the fact that Mg atoms allow the formation of more finer clusters the larger the number of Si atoms is. During subsequent heat treatment these clusters can act as nucleation sites and lead to a finer dispersion of the GP zones. The alloy composition therefore should follow a compromise between necessary formability in the T4 condition and desired strength in the T6 condition (constant ageing time and temperature). At solution treatment temperature all the Si should be solved. Otherwise artificial ageing process is retarded and peak hardness is lowered.

Technical Al-Mg-Si alloys

In contrast to the ideal model alloys an engineering alloy contains further companion elements which influence the precipitation behaviour in different manners. The microstructure of such an alloy can be described as follows. In addition to the hardening precipitates we find constituent particles with a size up to several μm: They form during solidification. As their solubility in aluminium is poor they cannot be dissolved during subsequent heat treatments. It's only possible to influence their form by a homogenization treatment. Their influence in both the T4 and the T6 condition is the same. The larger those particles are and the higher their volume fraction is, the worse becomes the fracture behaviour and toughness of the sheet. As all the constituent types contain silicon ($Al_{12}Fe/Mn_3Si$, $Al_{15}Fe/Mn_3Si_2$ or Fe_2SiAl_8), they lower the silicon excess and may even reduce maximum hardenability.
The same is true for the the dispersoids. Their size ranges from 0,1-0,5μm. They form by a solid-state reaction and -for the same reason as the constituents- cannot be redissolved.

On the one hand such particles are desired, because they reduce grain coarsening and induce a homogeneous slip behaviour. On the other hand they lead to an increased quench sensitivity of the alloys due to the precipitation of coarse Mg_2Si particles at low quench rates. As in alloys with silicon excess hardenability depends on the Mg content maximum hardenability cannot be achieved (Fig. 7) and adjacent to the rods there is a particle free zone after subsequent heat treatment (T6) to be found (Fig. 6).

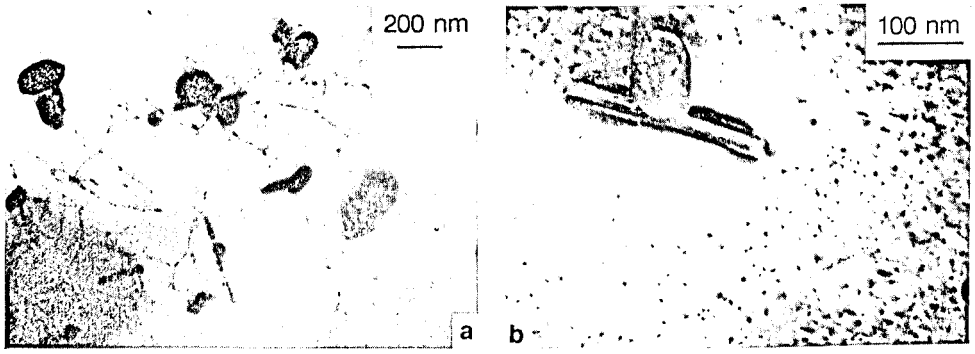

Fig. 6. Precipitation of ß'-rods at dispersoids (TEM BF) a) T4 b) T6
AlSi1,2Mg0,4Cu0,13Fe0,15Mn0,12, hom. 540°C, air-quenched, 30 min 180°C

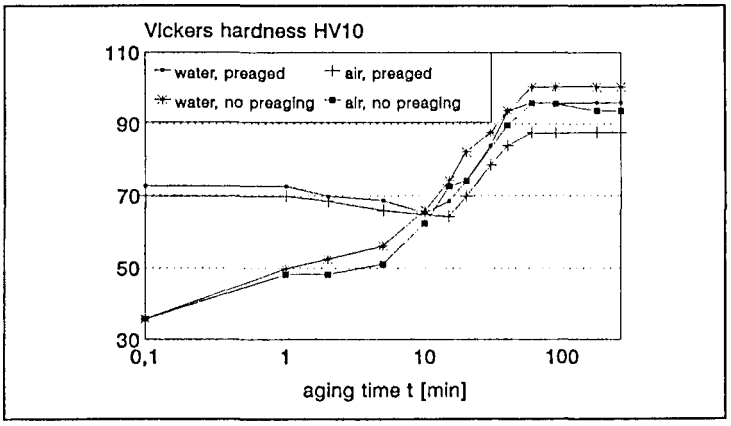

Fig. 7. Influence of quench rate and preageing at room temperature on artificial ageing, alloy: see Fig. 6

In Fig. 7 besides the quench sensitivity the negative influence of preageing at room temperature becomes obvious. Due to the formation of the clusters the initial hardness of the preaged samples is higher, but the dissolution of the clusters retards artificial ageing. Some larger clusters act as nucleation sites for the GP zones. TEM investigations show a coarser dispersion compared to samples without preageing. Thus peak hardness must be lower.

The preageing effect can be reduced by interrupted quenching to a temperature where GP zones but no clusters form and subsequent water quenching. The cluster state now is limited to the solubility difference between quenching temperature and room temperature. But the lowered number of quenched in vacancies simultaneously leads to a retardation of artifical ageing (Fig. 8).

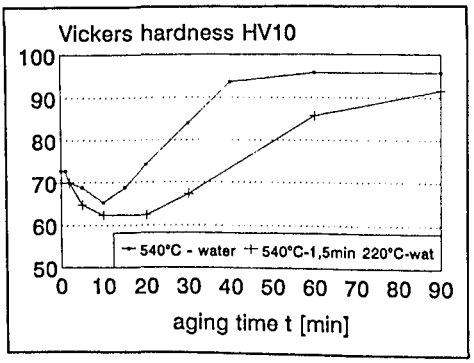

Fig. 8. Influence of interrupted quenching on artificial ageing, AlSi1,2Mg0,4, hom. 540 °C, preageing at room temperature, artificial ageing at 180 °C

Conclusions

1. The interaction energies of several combinations of Al, Si und Mg atoms can be ordered as follows (c covalent, m metallic):
   $(Si\text{-}Si)_c > (Si\text{-}Mg)_m > (Al\text{-}Mg)_m > (AL\text{-}Mg\text{-}Si)_m > (Al\text{-}Si)_m > (Si\text{-}Ge)_m > (Si\text{-}Si)_m$
   According to this sequence the formation of Si clusters in binary Al-Si alloys requires Al-free clusters. Prerequisite for the growth of such clusters to the critical size for collapse into the stable covalently bonded dc structure are vacancies. They reduce the interfacial strain energies but leading to an undesired quench sensitivity.
2. Ge atoms may help to reduce quench sensivity. Because of their atomic size they lower the strain energy of Al-free $(Si\text{-}Ge)_m$ clusters and lead to a fine distribution of dc Al-Si particles. The application as an engineering alloy is restricted by the high price of Ge.
3. Additions of Mg induce a drastic change in precipitation behaviour. Because of the interaction energies between Mg and Si respectively Mg and Al the formation of ternary Al-Mg-Si clusters becomes possible. The differences in atomic size allow these clusters to grow (just as Si-Ge clusters). The formation of more stable precipitates requires the emission of Al atoms i.e. partial dissolution of the clusters. Growth of the clusters and the fcc - Mg_2Si transition are enhanced by vacancies.
4. A fine distribition of the dc phase is inhibited by Mg additions. An alloy combining the precipitation hardening contributions of both of cubic Mg_2Si and dc Si does not exist. Nevertheless a Si excess enhances both natural ageing and artificial ageing. Good formability in the T4 condition and acceptable strength in the T6 condition require a compromise in alloy composition.
5. This is also true for the effect of companion elements which lead to an increased solid solution hardening (T4 and T6). By the formation of dispersoids quench sensivity is increased but grain growth is limited.

6. Due to our present understanding of the precipitation sequence and the influence of supersaturation and number of quenched-in vacancies different heat treatments permit an exact control of production and application properties. But always the strong influence of small deviations of composition, time, temperatures and quench rate and their interdependence have to be kept in mind.

Acknowledgement

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