The correlation between microstructure and thermomechanical properties studied on AlCuMg-based alloys

U. SCHMIDT and R. UNGER

Martin Luther University of Halle-Wittenberg, Department of Physics, 06099 Halle, Germany

Abstract: This paper deals with the description of the structure and precipitation sequence of AlCu4.5 alloys with a content of Mg between those of binary AlCu and quasi-binary AlCuMg alloys. For alloys with a small Mg content (0.23 wt%) these are the coherent Cu-like GP zones and the incoherent Θ' and Θ phases with the adequate content of dissolved Mg, so the precipitation sequence can be essentially realized without any difficulties. In the case of higher Mg concentration a re-orientation occurs because it requires both time and energy. An undisturbed transition to the Θ (Mg) phase is impossible. The phase structure becomes more similar to that of the S phase but it is not safe to say that it is already a quasi-binary structure. The different size developments between the AlCu4.5 and AlCuMg0.98 alloys are discussed.

1. Introduction

Since many years the binary AlCu alloy has been investigated in the whole sequence range. As a result a variety of forms of the Guinier-Preston (GP) zones was found [1].

The stability of the GP zones and the metastable phases depends on the preageing conditions. This result could be confirmed by extensive investigations of the partial and total reversion.

In many production processes magnesium (Mg) is added to the AlCu alloys because magnesium improves the room-temperature (RT) hardening of technical AlCu alloys. But up to now the exact mechanism of the formation of the CuMg complexes is not completely known.

Above all the question is in the dark whether different types of GP zones do exist for AlCuMg-alloys.

The investigations of one-step ageing show a different influence depending on the Mg concentration.

Reversion experiments give special information on the stability of the metastable precipitates.

The TTU diagram as a summary result of the one-step ageing (see Fig.1):

- Magnesium accelerates the decomposition.
- The possibility of heterogeneous nucleation of semicoherent precipitates in needle form on helical dislocations and dislocation loops accelerate the decomposition of the AlCuMg-alloys [2].

- Dislocations in Al alloys are not favoured in the usual $a/2$ [110] direction but in the $a/2$ [001] direction.
- Investigations of the earlier states of decomposition in AlCu4.5MgX support the occurrence of greater precipitation density and more fine-disperse precipitates as compared to the binary AlCu alloy.
- The form multiplicity of GP zones, which is characteristic of the binary AlCu alloys, is missing in AlCuMg alloys since the thickening is important to the size growth (in AlCu alloys the precipitates have a disk form whereas those of the AlCuMg alloys are cylindrical).
- It is unintelligible in the frame of the acceleration and continuous insertion of Mg in the Cu-GP zones that stable phase lines, homogeneity, solvus, and liquid lines and the eutectical temperature occur, and that these lines abruptly transform into those of the quasi-binary alloys (see Fig.2).

2. Experimental

Positron-annihilation lifetime technique, differential thermoanalysis, and scanning electron-microscopy complete the set of methods such as Vicker's hardness, neutron small-angle scattering and transmission electron-microscopy because they are expedient to follow up the decomposition kinetics at higher temperatures (Table 1).

Four alloys were investigated with almost equal Cu but varying Mg contents between 0 and 0.98 wt% produced from material of 4N purity (Table 2). The samples were homogenized at 500 °C for 8 h, then IQ-quenched into water, and isothermally or isochronally aged at the annealing temperature T_a for a time t_a .

3. Results and Discussion

3.1 Thermal Analysis

The A0.0 alloy (Fig.3) essentially shows the complete precipitation sequence, ie, both formation and dissolution. The next stable phase can only be formed after the dissolution of the previous phase. In particular, in the case of the GP-zone interval, the dissolution takes place in a fixed small region. This is in conformity with former results which describe that a definite state (type and size of a GP zone, precipitated Cu content) possesses a definite solvus temperature. In contrast to that, the formation and dissolution of Θ'' and Θ' phases take place in a wide temperature interval. The Θ phase is already formed during the partial dissolution of the Θ' phase.

In the case of the A0.23 alloy the formation of the Θ (Mg) phase provides the partial dissolution of the Θ' (Mg) phase. The formation of the semicoherent Θ' (Mg) phase is more intensive than in an AlCu alloy. The plot of the A0.56 alloy shows a further intensification of the formation of the Θ' phase and a decrease in its dissolution before the transition to the stable Θ (Mg) phase.

The evolution of the dissolution peak at $T = 227$ °C is noteworthy. The heat flow of the dissolution peak is very great for the A0.98 alloy. The subsequent formation enthalpy at $T = 295$ °C exceeds all enthalpies realized. A wide dissolution interval follows, which shows the transition to the homogeneous dissolution.

The cooling trace show a formation maximum at 210 °C which can already be taken from the plot of the A0.56 alloy. The cause of this formation process can only be Cu and Mg atoms dissolved, respectively, which could

not be completely precipitated because of the high cooling rate. With respect to the precipitation sequence the formation of GP zones should be essential. This result supports the fact that the transition to semicoherent and incoherent precipitates, respectively, is more difficult on the way of homogeneous nucleation.

3.2 Hardness measurements

3.2.1 Hardening curves after isothermal annealing

In the case of the A0.98 alloy in the interval from 130 to 300 °C, the isothermal hardening shows the transition to the semicoherent phase at 190 °C which is indicated by the HV-hardness maximum. The shift of this maximum at higher temperatures to shorter times is connected with the acceleration of the hardening process at higher temperatures (see Fig. 4).

The HV-hardness maximum is missing for all alloys in the annealing temperature interval from 350 to 410 °C. The indirect state quenched in at T_a directly approaches a plateau with almost the same value for all alloys. Differences can only be taken from the length of this plateau. Only in the AlCu alloy such a plateau could not be found which shows a transition to the θ phase. This differentiation becomes more distinct at the annealing temperature $T_a = 410$ °C.

The comparison of these results with those of SEM investigations indirectly confirms this statement. Within the plateau essential transition processes take place that cannot be characterized as θ phase in the A0.98 alloy at 350 °C. In the A0.0 alloy the HV hardness continuously decreases which supports the assumption that the transition to the θ phase takes place without any nucleation hindrances.

3.2.2 Hardening curves after isochronal annealing

The isochronal HV-hardness measurements that were parallelly performed with the positron-annihilation lifetime measurements show no essential differences from expectations up to $T_a = 200$ °C (The procedures for both techniques were the same: the samples were heated step by step, see also Fig. 5). The HV maximum is insignificantly shifted to higher values with increasing Mg content which is connected with the higher thermal stability of Mg-containing GP zones and θ'' precipitates already mentioned. The HV decrease for T_a greater than 200 °C is a typical indication of the coarsening and coherence break of the precipitates.

However, the HV courses above $T_a = 350$ °C are important.

The indicated plateau in the A0.0 alloy (small hardness contribution) should originate from the transformation of the θ'' precipitates. The copper is precipitated in relatively small incoherent phases. The decrease in the HV hardness to the as-quenched state and the re-increase are caused by coarse incoherent θ phases (Al₂Cu) and the beginning homogenization (dissolution of copper in the matrix) and starting decomposition after the quenching into water.

The Mg-containing AlCu alloys show a quick HV-hardness decrease with rising temperature up to 350 °C, too. After an intermediate weak reversion a new HV-hardness increase follows, which is more distinct in case of the higher Mg content. After fast reaching the as-quenched state the homogenization and re-hardening (increase of HV-hardness) start then, too.

3.3 Positron-lifetime measurements

The results of positron-lifetime measurements are shown in Fig. 6. The results can be interpreted as follows, starting from the simplified statement that the decrease in the lifetime characterizes a coarsening or

a dissolution process and that the increase in lifetime is caused by a formation process.

At first for all alloys a coarsening process of the GP zones takes place. The lifetimes decrease to values that correspond to the complete reversion of the GP zones. The estimated average lifetimes for the complete solubility of the A0.98 alloy ($\tau = 164$ ps) do not essentially differ from that of the binary A0.0 alloy ($\tau = 165$ ps). If the vacancy foreign-atom mechanism is used, for the binary AlCu alloy a lifetime of $\tau = 210$ ps and for the quasi-binary AlCuMg alloy a lifetime of $\tau = 221$ ps can be calculated.

The Mg contents of the A0.23 and A0.56 alloys shift the solvus lines somewhat to higher temperatures. The formation of the Θ'' precipitates follows. A higher Mg content accelerates this process and the process starts at lower temperatures. The coarsening of the Θ'' precipitates is characterized by the decrease in the average lifetime, again. The second minimum is differentiated. An increasing Mg content shifts this minimum to lower temperatures.

From the course of the average lifetime can be learned that the vacancies anneal out at a high rate.

The smaller decrease of the average lifetime for the A0.98 alloy in the region of the minima is connected with the higher thermal stability of vacancy loops. This result is an indication of a changed decomposition behaviour in the A0.98 alloy, too. It is not unambiguous if a change in the decomposition mechanism occurs.

3.4 Scanning electron-microscopy (SEM) investigations

Scanning electron-microscopic photographs confirm the continuous growth of inhomogeneous precipitates between 300 and 450 °C. At a temperature of 300 °C no analysable precipitates could be found because of the low SEM contrast. Only when the phases have distinct incoherent structures, then they can be displayed by SEM.

Fig.7 shows the evolution of the diameter and the particle density. There is a high precipitation density for the A0.0 alloy at $T_a = 350$ °C. In the A0.98 alloy a reversion minimum can be found at $T_a = 350$ °C and $t_a = 50$ min. No precipitates are evident. The formation of Θ starts at $t_a = 100$ min and is in full progress at $T_a = 410$ °C.

The decomposition can be described by three stages: nucleation, growth, and Ostwald ripening. In particular, the growth and Ostwald ripening are important to the investigated temperature and time region. For the "classical" description the LSW (Lifshitz, Slyozov, Wagner) theory is used predominantly.

Now the present experimental results are analyzed with respect to the phase growth (see Figure).

In the A0.0 alloy the size growth can be described using a d^3 law. At the temperature $T_a = 410$ °C the validity of the d^3 law is restricted to the beginning. Beginning from $t_a = 200$ min it seems that only Ostwald ripening occurs. The decrease in the precipitation density for $T_a = 350$ °C means a growth on the basis of the destruction of smaller precipitates (thermodynamic process). The strong decrease in the particle density at $T_a = 410$ °C is unintelligible at first glance. Considering the small size change, this decrease can only be understood as the transition to the Θ phase and the considerable increase in the Cu solubility in the Al matrix (increase to 1.5 wt%).

The Mg has an influence on the growth behaviour, too. At $T_a = 350$ °C the growth actually belongs to the d^3 law, but the Mg distinctly influences the growth in the case of annealing at $T_a = 410$ °C.

Considering the A0.23 alloy, the Ostwald ripening is shifted to smaller

annealing times (at $T_a = 410^\circ\text{C}$ and $t_a = 50$ min). This result agrees with the hardness course (HV-hardness decrease above 50 min as compared to the A0.0 alloy with the beginning at $t_a = 200$ min).

In the case of the A0.56 alloy, the d^3 relationship is valid in effect for $T_a = 410^\circ\text{C}$ but higher d values are observed as compared to $T_a = 350^\circ\text{C}$. We can take the continuity of the nucleation as the basis.

The d^3 law is valid for the A0.98 alloy at $T_a = 350^\circ\text{C}$, too. The particle density increases very fast. The formation is distinct. First of all, at $T_a = 410^\circ\text{C}$ a growth occurs at shorter times, too, but slower as compared to the d^3 relation. The decrease in the particle density refers to a growth at the expense of the smaller particles.

But it is necessary to consider the temperature-dependent solubility of Cu and Mg in the Al matrix. That is to say that the Mg decreases the Cu solubility in the Al matrix at 350°C from 0,85 wt% to 0.7 wt% and at 410°C from 1.5 wt% to 1 wt%, respectively. That means that more Cu is proportionally available in the precipitates. The precipitation density slowly decreases or keeps constant. This fact is valid for both the A0.23 and A0.56 alloys. Only in case of the A0.98 alloy the process begins to reverse since the precipitates coarsen considerably faster.

The size distribution was analyzed to check this statement.

- The higher the concentration the narrower the size distribution.
 - The higher the temperature the earlier the precipitation begins.
- These statements are valid for the A0.0, A0.23, and A0.56 alloys. The A0.98 alloy is an exception to the rule, too.

The investigations of the decomposition behaviour of Al-Cu4.5Mg-Mg(X) up to the homogenization region show:

- Mg influences the precipitation sequence.
- There could not be found any indications of different coexisting precipitation structures like Mg-containing and Mg-free precipitations in the case of the Cu-Mg ratio $>2:1$.
- The decomposition behaviour of the A0.56 and A0.98 alloys distinctly differs from that of the binary AlCu alloys in the region of the θ' and θ phases. The A0.98 alloy most distinctly shows this influence. A strong phase reformation above 300°C occurs depending on the decomposition rate (thermal analysis, isochronal hardness traces, positron lifetimes). The formation of the stable phase starts only above 350°C in the case of the A0.98 alloy (SEM).

4. Conclusions

Alloys with a content of Mg which diverge from those of the quasi-binary composition have structures between those of binary AlCu and quasi-binary AlCuMg alloys. They take the energetically favourable structures.

For alloys with a small Mg content (A0.23 alloy) these are the coherent Cu-like GP zones and the incoherent θ' and θ phases with the adequate content of dissolved Mg, so the precipitation sequence can be essentially realized without any difficulties. In the case of the higher Mg concentration a re-orientation occurs according to the results of this paper. This re-orientation requires both time and energy. An undisturbed transition to the $\theta(\text{Mg})$ phase is impossible. The phase structure becomes more similar to that of the S phase. It is not safe to say that it is already a quasi-binary structure. Further investigations are necessary. The different size developments between the A0.0 and A0.98 alloys and the strong reversion and reformation in the range above 300°C can be interpreted in this way.

5. References

- [1] SCHÜLBE R., SCHMIDT U., *phys. stat. sol. (a)* **103** (1987) 29,
- [2] PRATSCHLER H.-CH., SCHMIDT U., SCHÜLBE R., SIEBERT P., *phys. stat. sol. (a)* **125** (1991) 417.

6. Tables

Table 1: Measurement Methods

Method	Device	Measurement	Remarks
Calorimetry	DSC 7 (Perkin Elmer Corp)	Heating and cooling rates 20 and 40 K/min	uncertainty 0.3 K, sample weight 20 -25mg
Positronen-lifetime measurement	EG&G ORTEC	conventional fast-slow coincidence	time resolution 230 ps
Scanning electron-microscopy	BS 300, Tesla, Picture analysis system BAS-Robotron	characteristic size distribution and particle size	diameter of a circle equal in size and statistic size distribution
HV-Measurement	Neophot II, Hanemann mikrohårdness	HV measurment, isothermal and isochronal annealing	Power: 0.102 N, measurement at room temperature

Tab. 2 : Cu- and Mg-Contents of the AlCuMg-Alloys

Alloy	c_{Cu} / wt%	c_{Mg} /wt%
A0.0	4.5	-
A0.23	4.5	.23
A0.56	4.5	.56
A0.67	4.5	.67
A0.98	4.5	.98

7. Figure Captions

Fig.1: TTU diagram of one-step ageing (T_a : ageing temperature, t_p : ageing time at the plateau beginning)

Fig.2: The stable phase lines of AlCu4.5Mg alloys depending on the Mg concentration

Fig.3: DSC heating traces after water quenching from $T_q = 500^\circ\text{C}$, $t_q = 8\text{ h}$

Fig.4: Vickers' hardness after isothermal annealing of the A0.98 alloy between $T_a = 130^{\circ}\text{C}$ and 350°C

Fig.5: Vickers' hardness after isochronal annealing of AlCuMg alloys

Fig.6: Positron-lifetime measurements of AlCuMg alloys after water quenching and isochronal heating, $t_a = 200$ min in steps of 30 K

Fig.7: Evolution of the mean diameter and particle density