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INVESTIGATIONS OF THE DECOMPOSITION OF AlCu4.5Mn(x) ALLOYS

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Abstract

Experimental results show a strong effect of rapid quenching on the structure of multi-component aluminium alloys containing conventional age-hardening elements (Cu) and transition elements (Mn). Such effects like grain refinement, increase of the solid solubility and many structure and lattice defects influence the thermo-mechanical properties of AlCuMn alloys.

Introduction

In the aluminium production new properties like the improvement of the creep resistance are of an essential interest besides already existent advantages of aluminium (low density, good continue manufacture and recycling).

The requirements for suitable alloying elements can be derived from the following facts:

- The element alloyed (T) must be an effective former of intermetallic phases (IMP) (Al_nT with n values as large as possible).
- The IMP formed must be thermally stable. At high temperatures, a sufficient diffusion rate is necessary, too.
- An easy solution in the Al melt and the sufficient supersaturation also at low quenching rates are required.

Under these aspects, transition elements are suitable for such a quench-in of the relatively high solubility of the molten state is successful.

From several rapid-quench (RQ) procedures, the melt spinning was chosen. The investigations were carried out on AlCu4.5wt% and AlCu7wt% alloys that were alloyed with the transition element manganese (Mn) (< 5 wt%). Although the transition element Mn does not play an important role in the most papers, it seems to be suitable in AlCu alloys as it will be shown on the hand of the following results.

For rapid-quenched Al alloys Mn is favourable since a large saturation at relatively low cooling rates can be reached (10^3 to 10^4 K/s) [1, 2].

Unfortunately, only a few papers on Al alloys with transition metals and conventional elements like Cu, Mg, Zn are available [3].

The structure of AlCuMn alloys

Before the description of the ternary alloy system the important properties of the binary AlCu and AlMn alloy systems are pointed out:

1. AlMn alloys

In the AlMn system several metastable phases are found. The maximum aluminium concentration in these compounds is relatively large (Al_6Mn). The Mn solubility in the liquid phase is the highest of all transition elements. The eutectic temperature is near the melting point of Al so that a very small crystallization interval arise (a tenth K).

In RQ Al alloys a high metastable manganese saturation (13 wt% at 10^7 K/s) can be reached as well at relatively low cooling rates [1, 2], too.

The supersaturated solid solution has a high thermal stability and decomposes by the formation of disperse intermetallic phases. No clear evidence exists how extensive the decomposition is performed by forming Guinier-Preston zones (GPZ) [3].

2. AlCu alloys

The complex decomposition sequence of the binary AlCu system has been investigated in the last years. There are a lot of results (see for instance refs 4 and 5). In this paper only the information is of interest which influence has a possible interaction between Cu and Mn atoms. It seems to be possible that a change of the lattice constant, of the thermal stability, and of metastable phases take place.

The authors suppose that mainly Cu is not available for the decomposition process because of its binding in AlCuMn phase.

The mechanism of the decomposition from the strong saturated solid solution of a rapid quenched AlCu alloy changed barely compared with conventional quenched alloys. The forming of zones slow down [6]. The temperature of phase composition decreases with increasing Cu content [7].

3. The solidification structure of the ternary AlCuMn alloys

Regarding the effect of a third component on the AlCu structure especially after rapid quenching, we can expect that the solid solubility of Mn is increased and the forming of the ternary $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ is oppressed at the beginning [8, 9]. The phase diagram contains a greater region of the ternary solid solution [10].

Micro-analysis investigations for conventional quenched $\text{Cu}4.5\text{Mn}(1,3,5)\text{wt}\%$ and $\text{AlCu}7\text{Mn}(1,3,5)\text{wt}\%$ alloys show that the copper solubility in the matrix is decreased from a maximum value of 5.2wt% to 2.5wt%. The remaining is decomposed starting with the $\text{AlCu}4.5\text{Mn}3$ alloy in form of $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$. For $\text{AlCu}4.5\text{Mn}5$ Al_6Mn precipitates could pointed out after a heat treatment, too.

Unfortunately, there is a lack of information on the forming conditions of the $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ in literature.

Investigations are performed depending on the cooling rate due to the different solubility of Cu and Mn.

The solidification is caused by sufficient high quenching rate so the process of nucleation and following growth of the phases cannot proceed. As a result the supersaturated solid solution or different IMP can be formed which cannot be achieved under conditions of stability.

The one-phase solidification structure with enrichments of dendritic arms (cell boundaries, concentration segregation) is substituted by homogeneous and heterogeneous non-equilibrium solidification to a two-phase structure (with primary crystallization) [11].

In the case of rapid solidification the forming of deformation dislocations and inner tensions should be mentioned which can serve as vacancies together with the dense network of dislocations at cell boundaries. They can explain the partly contradictory result of the forming of vacancy-free zones.

In contrast to the AlCu system the structure of the degenerated eutectics changes in AlCuMn alloys. The dendritic structure is formed from Al₆Mn.

In RQ materials a really regular Cu and Mn distribution is achieved. The structures are one-phased with many concentration variations.

Experimental

The used experimental methods are shown in the following summary (see Table I).

Table I: Measurement Methods

Method	Devis	Measurment	Remarks
Calorimetry	DSC 7 (Perkin Elmer Corp)	Heating and cooling rates 20 K/min	uncert. 0.3 K, sample weight 20 - 25 mg
Electron-beam micro-analyzer	EMX-SM 120000 Anadex Instr.	energy-dispersive method	
HV - Measurement	BUEHLERMET II	HV measurement, isothermal, isochronal annealing	Power: 0.25 N, measurement at RT
Light microscopy	Olympus PMG3, Quantimet 500	Grain and cellular distributions	application of Normaski DIC, polarisation
Positron-lifetime measurement	EG&G ORTEC	conventional fast-slow coincidence	time resolution 300 ps
Small-angle neutron scattering	spectrometer IBR-2, JINR (Dubna)	radii of gyration, size distribution	correction of double Bragg scattering

Results and Discussion

1. Structure of the alloys

The structure of the alloys is cellular. The cell dimensions depend on the composition of the alloys and the cooling rates (see Table II).

The first value characterizes the AlCu_{4.5}Mn(x) (x = 5wt%) (1) alloys whereas the second value do it for AlCu₇Mn(x) (x = 5wt%) (2) alloys

Table II: Typical values of the AlCuMn alloys after different cooling methods

solidification state	T (K/s)	Characterizat. of the state	d _z (μm)		d _k (μm)	
			(1)	(2)	(1)	(2)
conventional solidification	<30	n = 0.25, A = 18-45	12	20	420	
flat chill	200-300	n = 0.39 A = 41	8	4.3	12	10.5
RQ material	5*10 ⁴ *	n = 0.28 A = 48	0.63	0.45	2.5	1.8

The cooling rates were determined by the measurement of the thickness of the ribbon $x = 200-40 \mu\text{m}$ ($dT/dt = B/x^2$, $B = 10^4 \text{ mm}^2\text{K/s}$). The distance of the dendritic arms were calculated by $d_z * T_c^n = A$ where the constants n and A were from experimental results.

All alloys show a cell structure which is the typical sign for heterogeneous solidification. The rapid quenched alloys show only a small dependence on the cell structure from the composition referring to the cell dimension. This result can be interpreted as a consequence of a non-equilibrium state. The heterogeneous nucleation does not take place and the numbers of nuclei only depend from the size of supercooling. With increasing Mn content the dispersion of the cell structure increases at low cooling rates, too.

We can conclude from DSC experiments, HV measurements, and micro-analysis that the Cu and Mn atoms in the rapid quenched AlCu_{4.5}Mn1-5Gwe% alloys are solved in the quenched state whereas in the chill and conventional alloys precipitations at 5 wt% do exist. For the AlCu₇Mn(1-5wt%) alloys a small part of decomposed elements is shown in the initial state.

2. The decomposition process in AlCuMn alloys between RT and 530°C.

2.1. Isothermal ageing without heat treatment. We will get information on the decomposition process from the comparison of the course of isothermal ageing with and without homogenization at T_q , expecting, that a part of Cu and Mn already metastably supersaturate in solution during the solidification.

The initial state: The HV-hardness increase restores with increasing Mn content because the number of dispersoids and dislocation increase.

$T_a = RT$ ageing, 100 and 180 °C: The HV hardness compared with the as-quenched state is attributed to the decomposition of the complete Cu.

However, the forming of zones and the hardening slow. Suzuki et al. [12] deny the occurrence of GPZ II. This fact could explain the absence of the second HV-hardness increase.

We conclude from the similarities of the HV-hardness courses of the alloys that the hardening is caused by the decomposition of Cu in the lower temperature region [4].

$T_a = 200 - 300$ °C: Mn favours the semi- and incoherent copper precipitates by heterogeneous nucleation.

$T_a > 300$ °C: Two reverse processes take place: (i) dissolution of a part of copper in the solid solution and (ii) the start of precipitation of Mn.

After a short ageing time a small HV-hardness decay takes place that can be interpreted as enlargement of the Cu precipitates. The following HV-hardness increase can be attributed to the begin of Mn precipitations. The relatively strong HV-hardness increase for a relatively large period leaves on a homogeneous growth process. But it cannot be decided in this paper whether Mn diffuse into Cu precipitates or forms independent precipitates.

Polesia et al. [9] give the temperature for the begin of the precipitation as 340°C. Regarding the results of this paper the process of decomposition should begin earlier.

2.2. Isothermal ageing after heat treatment at T_q for t_q . The initial state after heat treatment is different from the non-heat treatment because an essential larger quantity of Cu and Mn are solved.

RT ageing: Lower HV-hardness values at the begin and the HV-hardness increase were found as compared to non-treated samples. This means that the solution of Cu and Mn is more intensive.

The hardening is accelerated in comparison to the direct ageing (DQ) what means a more rapid forming of zones. The authors are of the opinion that this effect is caused by dislocations and vacancy agglomeration (indicated by positron-annihilation experiments).

$T_a = 100$ to 300°C: Starting at $T_a = 100$ °C, the HV-hardness values for the isothermal ageing after heat treatment are below that of the hardening without heat treatment.

In comparison to the binary AlCu alloy shows:

- the hardening is slowed,
- the typical variety of the GP forms from AlCu alloys is reduced (results from DTA measurements),
- the second rise is absent at $T_a = 100$ °C,
- the overageing, enlargement of the Θ' phase at $T_a > 200$ °C is clear recognizable.

There are precipitates which were identified from several authors as $Al_{20}Cu_2Mn_3$ [3]. That means that Cu is extracted from the matrix to form of this phase.

The HV-hardness increase up to $T_a > 100^\circ\text{C}$ (for large ageing times) indicates a metastable phase.

The role of the heterogeneous nucleation at vacancies and dislocation is probably dominant for this process of the thermal ageing without heat treatment.

After RQ a high dislocation density $10^8 - 10^9 \text{ cm}^{-2}$ is available. The circle of vacancies has a diameter of 15 - 25 nm at a concentration of 10^8 cm^{-2} . Vacancy concentrations of 10^{-6} cm^{-2} were measured in binary AlCu alloys [13].

A part of the vacancies are placed on dislocations, grain boundaries, and subgrain boundaries. Less vacancies are available at decompositions. Therefore the decomposition rate decreases at RT (thermal activation of the vacancies only at higher temperatures).

For the RQ materials the curves come in the same way so that we can speak about the same mechanism of hardness. For the chosen alloys SANS measurements were carried out.

AlCuMn: The Guinier radius shows at low temperatures and ageing times only slight differences in dependence of the Mn concentration. The utilization of a R_d description [14] and the attempt of a growth kinetics from [15] show a different behaviour in dependence of the Mn concentration. From $T_a = 170^\circ\text{C}$, $t_a = 3\text{h}$ the thickness increases. The deceleration of the growth at Mn-free Cu alloys can be attributed to missing vacancies while the decomposition at high temperatures. These vacancies are already cured.

Decomposition process between 300 and 550°C : All curves are characterized by a HV-hardness increase after a weak minimum. But the hardening shows yet a clear effect of overageing up to $T_a = 400^\circ\text{C}$ (shift of the maximum to slower values and t_a times).

Please note that the HV-hardness increase is reached after a weak minimum at $T_a = 300^\circ\text{C}$, $t_a = 300\text{h}$ and is quickly shifted then to smaller t_a as compared to $T_a = 200^\circ\text{C}$.

Investigations with EMPA result that the Cu content in the solid solution clearly degrade itself.

Table III: Cu contents in the solid solution of AlCu4.5 and AlCu4.5Mn3.5 wt% different temperatures

350 °C	400°C	450 °C	notes
0.4	0.6	1	AlCu4,5Mn3wt%
0.9	1.4	2.7	AlCu4.5wt%/15/

3. The decomposition mechanism in rapid quenched AlCuMn alloys

The stable ternary phase in AlCuMn alloys is the T phase ($\text{Al}_{20}\text{Cu}_2\text{Mn}_3$).

Starting from the fact, that the diffusion takes place, you could keep on estimating the form of this phase if the diffusion coefficients of the ternary system are known.

You can recognize by the comparison with the binary system, that $D_{\text{Cu}} \gg D_{\text{Mn}}$ (10^5 at $T_a = 300^\circ\text{C}$, 10^3 at 500°C). That means that there are long times in need for overcoming the diffusion distances to form of the T phase because of the small diffusion ability of Mn.

At $T_a < 300^\circ\text{C}$ the mobility of the Mn is reduced so that the formation of the T phase cannot take place.

For example: law of diffusion $D = D_0 \exp(-Q/kT)$

$$D_0 (\text{Mn}) = 104 \text{ cm}^2/\text{s}, Q (\text{Mn}) = 2.19 \text{ eV}$$

$$D_0 (\text{Cu}) = 0.15 \text{ cm}^2/\text{s}, Q (\text{Cu}) = 1.37 \text{ eV}$$

The diffusion distance is $x_t = (D^*t)^{1/2}$.

For RQ samples grain and cell boundaries must additionally taken into account for the diffusion.

That means that the phase-forming rate strongly depends on the concentration difference of the precipitates. The smaller the difference of the concentration between Cu and Mn the faster the precipitation take place. In RQ samples the part of solved Cu is very high. Mn importantly influences this process.

High solved Mn concentration are placed within the dendritic structure. That Mn homogeneously precipitates due to absent nuclei. On this way it can be understood why fine disperse and small AlCuMn precipitates can be expected without the formation of the stable T phase.

Within the dendrites a region remains with a small Mn concentration in the solid solution.

Corresponding to the ternary equilibrium the stable phase of the alloys is the solid solution and the $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ phase. Electron and X-ray diffraction give a proof of the presence of these phases after the HV-hardness maximum. The particles of this ortho-rhombic phase have the form of crosses or ellipsoids. The distribution is irregular because of the micro-segregation. They are growing very slowly. This result from REM photographs is in coincidence with SANS measurements.

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