THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

IMPROVEMENT OF THE THERMOMECHANICAL PROPERTIES OF ALUMINIUM-CASTING ALLOYS

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Abstract

The improvement of the properties of technical aluminium-casting alloys can be done on different ways. One of the mean problems is the improvement of the grain structure. A second one is the thermal stability at high temperatures and a third one is the process improvement of the recycling of aluminium casting scraps. All these questions are connected with the problem of the solution of the alloying elements and impurities in the materials. The aim of this paper is the investigation of different factors and methods.

Metal-physics base of the decomposition process:

(i) Selection of suitable alloys under the point of view:
- the mobility of the elements in the Al-matrix,
- the solubility of the elements,
- the solidification by suitable technology,

(ii) Production of the rapid-quenched (RQ) ribbons
- Laboratory plant: rotating copper disk
- estimating of the solidification rate

(iii) Selected results will give for the
- AlMn system
- AlSi system
- AlCuMg system.

Introduction

In the past age-hardened aluminium alloys on the base of AlZn, AlZnMg, AlSiMg, AlCu, and AlCuMg were investigated.

The aim is the investigation of strength and kinetics of the growth process of the supersaturated Al solid solution by forming coherent Guinier-Preston (GP) zones or semicoherent precipitates. But the disadvantage is that the strength strongly decreases at relatively low temperatures

($\leq$ 200°C) by the increase of the decomposition structure (Oswald ripening). The way out of this disadvantage is the bringing-in of fine particles into the Al-matrix as a contribution to the strength in form of dispersion hardening.

The problem: The small particles (<50nm) of this thermal stable, hard intermetalic phases like Al_3Ti, Al_3Fe, Al_4C_3, or ceramic phases like SiC, Al_2O_3 in sufficient concentration (10at%) must be regularly distributed in aluminium or in Al alloys.

Methods: **- The rapid solidification from the melt by melt spinning,**
- the combination of special elements for the casting alloys.

Microstructure Development

Mobility of the elements

- The mobility of the alloying elements is only possible by vacancies (single vacancies or foreign-atom vacancy pairs).
- The total vacancy concentration in the thermodynamical equilibrium can be estimated from the forming and binding energy.
- For non-transition elements this value is relatively known.
- For transition elements the theoretical estimation and experimental results are not so sure because of the small solubility and the trend of clustering.

Solubility of the elements

Sufficient hardening in aluminium can be reached only if the solubility maximum of the alloying elements is large enough (> 2at%).
Results: Elements with a high mobility have a high solubility, too. They have a good effect of agehardening, but on the other side a quick overageing (HV-hardness decrease) is the consequence.
Way out: The higher solubility of the elements in the melt must be transferred to the solid state.

Work-hardening by special technologies

The strength of an alloy is caused by the trouble of the crystal. Irregularities in the lattice decrease the movability of dislocations.
A sufficient great effect of work-hardening is reached if

- the volume fraction of the precipitates is great,
- the mean radius of the precipitates (dispersion of the inter-metallic phase (IMP)) is small as possible.
- A very fine grain gives an extra hardness at the grain boundary (in respect to the Hall-Petch relation proportional to $1/d^{1/2}$ (d diameter of the grain)) without an essential change of the ductility.

These results are valid the method of the rapid quenching from the melt.

Application

The aim of aluminium-scrap recycling

The aluminium recycling is a energy-saving technique. From both kinds of aluminium scraps (primary and secondary) the secondary scrap is of important interest because aluminium or Al alloys with a high Al fraction must be added to the melt. The main problem is the inexact knowledge of the alloy composition.

Casting alloys of the type of AlSi, AlCuMg, AlMg have many impurities of different elements like Fe, Mn in the scrap materials.

In the case of conventional recycling techniques a change to worse materials is the result of the recycled aluminium. Thus, the recycling of aluminium scraps is seriously hindered because conventional refinery techniques are not available or economical.
New processes and technologies are in need for the recycling of the aluminium scraps for the production of standard alloys.

The method of the melt spinning is a suitable way. This method is suited for investigation of the alloyed contents, too, which can be higher than that of usual standard elements.

The employment of the rapid-quench technique for the recycling of the aluminium scraps

The rapid-quench technique will be increasingly accepted as a possibility of the materials production with improved qualities.
New for this idea is the application of this technology for the recycling of aluminium scraps (a parallel employment took place at the Technical Universities of Delft and Eindhoven in the Netherlands).

Materials-science investigations of the alloys

Main emphasis:

1. Investigation of RQ alloys, firstly binary systems of the type of AlMn, AlFe, AlSi, AlCu and AlMg;
2. Combination of the binary alloys to ternary, quaternary alloys and so on;
3. Characterization of important microscopical properties of these alloys and the determination of thermomechanical characteristics.
4. Investigation of ingot scraps.
5. Processing of a few of selected RQ alloys to semi-finished materials.

Experimental

Production of RQ ribbons

Labor equipment [1]

Substrate: revolved, polished copper disk with variable rotation velocity between 100 and 5000 min^{-1}, free-chosen inclination to the melt jet,
solidification rates: 500 up to 50,000 K/s.
Lower solidification rates: flat chill (100 to 500 K/s)
As-quenched state: conventional casting ($dT/dt = 1$ to 3 K/s).

Thermal treatment and experimental methods

Heat treatment: $T = RT - T_q$, $t > 0h - 24h$, mechanical, electrolytic or chemical surface treatment for microscopical or hardness investigations.

Experimental methods

The used experimental investigation methods are shown in Table I.

Table I: Measurement Methods

Method	Devise	Measurement	Remarks
Electron-beam microanalyzer	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, polarization
Positron-lifetime measurement	EG&G ORTEC	conventional fast-slow coincidence	time resolution of 300 ps
Small-angle neutron scattering	spectrometer IBR-2, JINR (Dubna)	radii of gyration, size distributions	correction of double Bragg scattering
Transmission electron microscopy	TESLA BS 540	phase distribution	structure investigations

Results

1. The system AlMn

Structure and decomposition in RQ AlMn-alloys

Non-equilibrium phase diagram:

- Shift of the eutectic point [2]
- The region of the solid solution is broadened.
- Forming of Al_4Mn phases instead of Al_6Mn (peritectical reaction).

Structure of the supersaturated solid-solution crystal:

- degenerated eutectics with Al_6Mn,
- non-equilibrium eutectics with Al_4Mn,
- primary crystals Al_6Mn or Al_4Mn,
- metastable precipitates.

Properties of the supersaturated AlMn solid solution:

- Thermal stable,
- the decomposition process starts at higher temperatures (300 °C),
- instable precipitates in the range T<500°C, t>1h

Precipitation sequence: GP zones (coherent), G phase (structure similar to $Al_{12}Mn$), Al_6Mn (ortho-rhombic lattice, stable)

Result for RQ alloys

RQ AlMn2wt% ribbon, as-quenched state:

Precipitation bands are formed at dislocations. Small coarse precipitates (diameter 30 to 100 nm) heterogeneously nucleated at dislocation loops. Theses dislocations are surrounded by dislocations tangles. The grain boundaries are free of precipitates.

Heating 300 °C, 1h

We suppose that within the grain are GP zones. The dislocation tangles are dissolved. 'The sub and small-angle grain boundaries are formed by glide and climb processes. The small Al_6Mn precipitates within the grains serve as pinning points. Precipitates are formed in the small-angle grain boundaries, in particular at the subgrain corners because of the higher defect density.

Heating 500 °C, 1h

In the grain, thin plates of the Al_6Mn phase and precipitates of isometric form $Al_{12}Mn$ are formed. The Al_6Mn is surrounded by dislocations. An explanation for this fact is the great volume misfit. The dislocations favour the formation of small precipitations by pipe diffusion. These precipitates in the grain boundaries cause precipitate-free zones at grain boundaries.

RQ AlMn5wt% ribbon

As-quenched state

Cellular structure, there are in the spherical and square Al_6Mn particles and plates in the grains. Both of the precipitates are surround by dislocation loops.

Heating 300 °C, 1h

The cellular grains begin to solve. The greatest cellular boundaries are formed by spherodization lines if Al_6Mn precipitates.
In the grains, heterogeneous nucleation of small precipitates take place at the dislocation tangle around the Al_6Mn precipitates. The nucleation and difficult formation of the Al_6Mn phase can be explained from the high supersaturation of manganese after RQ. The high density of the small precipitates initiates the HV-hardness increase.

Heating 500 °C, 1h

The precipitates are enlarged, and a second phase is arises (semicoherent, cylindrical precipitates). The interface between the phase and solid solution shows many adapted dislocations. This phase could be the hexagonal metastable Al_4Mn phase.

RQ AlMn10wt% ribbon:

As-quenched state

The Al_6Mn and Al_4Mn eutectics is degenerated. In the eutectics small precipitates are found.

Heating 300 °C, 1h

Great plates with semicoherent interfaces to the matrix and small precipitates are probably formed by accelerated pipe diffusion at dislocations. The strong tensions of the aluminium matrix near the precipitates can be explained from the great differences of the atomic radii. These are the Al_4Mn or Al_6Mn phases. Single precipitates are $Al_{12}Mn$ which can be interpreted from a TEM diffraction picture. The adjacent grain boundaries have semicoherent interfaces. The grain boundary is so shifted by thermal activation at 300 °C, that it can surround a particle and can be favourably adapted.
The matrix background (tension) under the picture conditions let us assume the presence of GP zones. The HV-hardness increase is a second hint for this fact.

Heating 500 °C, 1h

The precipitates are identified as $Al_{12}Mn$ and, particularly, as Al_6Mn.

2. The AlSi system

Different alloys were prepared in the home-made melt-spinning equipment. After the melting at temperatures between 820 and 920°C samples of 20 g blow out. The ribbons have been investigated.

The ribbons are cut to pieces (parts of mm order), after that compacted, 15 min preheated and at temperatures of 450°C pressed to get semi-finished materials. The extrusion relation amounts 35:1. The extrusion product is a ribbon or a form part. Such profiles can be directly used for constructions or as materials for forming processes.

Melt-spinning ribbon

A fine-grain region without structure is on the substrate side of the ribbon. Stretched structures similar to Stengel crystals are in the middle part. A small structure region remains on the upper side. Pronounced phases are not seen. Only at strong overheating T > 450°C, clear accumulation in the Si distribution is seen (micro-analysis measurements)

Structure of pressed materials

- Grain boundaries are not or only very difficultly detectable. This fact can be interpreted as a good extrusion process.
- Structure morphology is more globular than in the ingot state.
- Precipitates (phases) are small still (TEM measurements). A magnification of the Si precipitates occurs at temperatures $T_a = 300°C$, $t_a > 20h$.

Course of the mechanical properties in dependence on the ageing

- HV-hardness measurements: Ageing in the region of the standard T6 ageing leads only to a small HV-hardness decrease at long times ($t_a > 400$ h).
- Two-steps ageing at $T_a = 300°C$ after $T_{Preageing}$, $t_{Preageing}$ a HV-hardness decrease to a nearly constant value after $t_a = 20h$. (HV-decrease due to an increase of the Si decomposites).
- For aged alloys, the hardness slowerly decreases because of the overageing in the first step of the ageing process.
- The microstructure of the RQ alloys is different from the conventional molten alloys:
  - A fine disperse structure. The mean grain size is smaller by a factor of 100,
  - The mechanical properties measured as hardness are better and stable at high temperatures.
- Strength and ductility of these alloys are in the order of the conventional high-strength alloys.

3. The AlCuMgMn system

- The presence of Mn in the AlCu alloys retards the GPZ formation at room temperature.
- At $T_a > 150°C$ Mn favours the decomposition of the supersaturated solid solution and the formation of the semicoherent θ' and stable θ phase.
- comprehensive heterogeneous nucleation at Mn presence.
- Magnesium accelerates this effect and improves the dispersion.
- At $T_a > 340°C$ a coincidence of two different processes take place in the RQ material:

1. Beginning dissolution of a part of the copper in the solid solution.
2. Decomposition of manganese.

---> Formation of a ternary Al-Cu-Mn phase, the stable form is the T phase ($Al_{20}Cu_2Mn_3$) [3].
---> Alloy with high creep-resistance and hardness.

Magnesium is added to AlCu alloys because of the two following causes:

- Mg increases the hardening rate,
- Mg allows the RT hardening at higher concentrations of impurity elements, for instance Fe.

For the casting of AlCuMg alloys, the heterogeneous nucleation plays a greater role than in AlCu alloys (higher number of vacancies and dislocations). In the RQ material this effect clearly appears as fine-disperse precipitates in the as-quenched state. We find the maximum hardness at room temperature.

Addition of manganese to AlCuMg alloys

The RQ AlCuMn alloys clearly show in the temperature region from 300 to 380 °C the decomposition of manganese from the solid solution (hardness measurements and SANS).

The hardness increase in technical ingot alloys with Fe contents is similar to that of the AlCuFe alloys. But the influence of the cooling rate is strong.
The thermal stability in the temperature region between 300 - 400 °C is different for Mn-containing and Mn-free alloys. The cause can be seen from TEM photographs.

Results

The results confirm that manganese is highly soluted in the aluminium matrix in RQ ribbons. The decomposition process begins at lower temperatures as it was supposed till now (positron-annihilation measurements and SANS). That means that GP zones are present.
With increasing temperature (higher 500 °C) AlMn type decomposites rapidly grow, precipitations take place at grain boundaries with precipitate-free zones that leads to worse mechanical properties.

References

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