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THE INFLUENCE OF ZIRCONIUM ON DECOMPOSITION IN HIGH STRENGTH ALUMINIUM ALLOYS

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SUMMARY

In high strength Al-Zn-Mg and Al-Zn-Mg-Cu alloys dynamical recrystallization during hot working is successfully suppressed by metastable Al_3Zr precipitates that are formed during the homogenization treatment.

The density, size and distribution of Al_3Zr particles were varied by using different Zirconium concentrations (0 - 0,2 wt % Zn) and homogenization procedures. Two calorimetric methods were used to study the influence of Al_3Zr-particles on the precipitation of GP-Zones during cold ageing and of metastable phases (η', R) during warm ageing respectively.

Cold ageing was found to be retarded whereas warm ageing turned out to be enhanced by Al_3Zr-particles. An explanation is given on the basis of the conservation of dislocations and subgrain boundaries by Al_3Zr-particles.

INTRODUCTION

In most technological applications of high strength AlZnMg and AlZnMgCu alloys (7000 series) the fibrous elongated pancake structure after hot rolling or extruding exhibits superior technical performance with respect to a recrystallized equiaxial grain structure. In order to suppress dynamical recrystallization Chromium and/or Manganese additions in the concentration range 0,1 - 0,2 m % were used to form dispersoids of intermediate size ($\emptyset \approx 100$ nm) which are able to block the movement of dislocations and (sub)grainboundaries. In the last years Chromium and Manganese are increasingly being replaced by Zirconium as the latter results in a much finer and homogenous non-unrecrystallized substructure (1) with a high stress corrosion resistance; furthermore Chromium dispersoids are known to increase the quench sensitivity considerabely (2) (3). After casting metastable Al_3Zr-particles are formed in the course of the homogenization treatment (400 - 500 °C) their size and density depends upon the homogenization procedure (4). According to (5), the precipitation of Zinc and Magnesium is facilitated by Al_3-Zr-particles as these would decrease the nucleation barrier for metastable and/or stable $MgZn_2$-particles. As a part of an extensive project the influence of Al_3Zr-dispersoids upon decomposition processes in the temperature range of Guinier-Preston Zones (GP-Zones) and of metastable phases was investigated - previous work has indicated that cold ageing and warm ageing are affected by Al_3Zr-precipitates in a different manner (6).

EXPERIMENTAL

The investigations were carried out on alloys of the type Al - 5 m%Zn - 1 m%Mg, a typical composition in m% is given below for heat 2218:
0,21% Fe - 0,09% Si - 1,06% Mg - 4,62% Zn - 0,003% Ti - 0,17% Zr.

After casting alloys were homogenized between 450 and 510 °C and extruded to a 25 x 30 mm^2 profile.

Calorimetric measurements were performed with a heatflow microcalorimeter of the Tian Calvet type (isothermal mode) and a Perkin Elmer Power compensated Differential Scanning Calorimeter DSCII (heating rates 10 - 80 K/min), further details are given in (7). The isothermal measurements at room temperature (23 °C) and 140 °C were performed directly after homogenizing and water quenching, pre-aged samples were given an additional solution treatment followed by water quenching; the quenching rate was varied with the help of a motor and gearbox.

The grain- and microstructure of the various material states were characterized by scanning- and transmission electron microscopy.

RESULTS

In a first series of homogenization treatments the formation conditions of Zr-precipitates were varied by

- the heating rate between room temperature and homogenization temperature (>50 K/min; 50 K/h)
- the homogenization temperature (450 - 510 °C).

Samples were water quenched from homogenizing and subsequently aged in the calorimeter at room temperature. The heat evolution as a function of time showed a significant dependence on the homogenization procedure; it was reduced and shifted towards longer ageing times if

- the homogenization temperature was increased
- the heating rate was reduced.

In Figure 1 these two effects are shown for samples that were homogenized by the producer (slow and fast heating rate) solutionized at 400 and 480 °C and subsequently water quenched in the laboratory before introduction into the calorimeter.

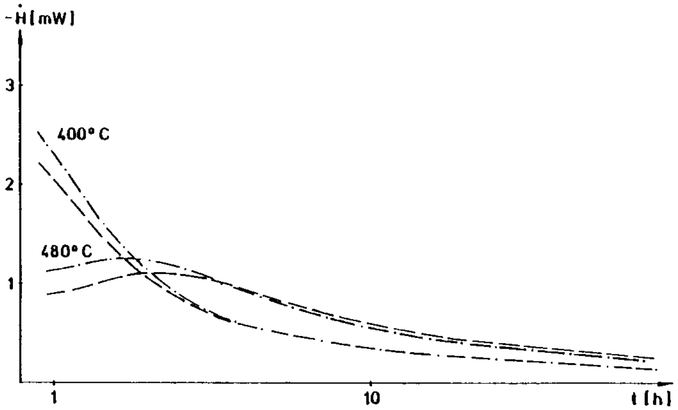

Fig. 1. Room temperature decomposition after water quenching from 400 and 480 °C (slow heating ----, fast heating -.-.-).

For both the slowly and rapidly heated material, the heat evolution rate for quenching from 400 °C is highest at low ageing times whereas quenching from 480 °C shifts the maximum towards longer ageing times. It should be noted that after approximately 16 hours the total heat is equal for both solution treatments. An increase in the heating rate up to the homogenization temperature leads to a comparatively small but however significant enhancement of the heat evolution rate.

The influence of the Zr-content is reflected in DSC-thermogrammes of figure 2 for a Zr-free material VLA5 and VLA8 containing 0,17% Zr. After quenching from 480 °C and ageing at room temperature for 2 and 5 hours the endothermal dissolution peak for Zr-free material around 380 K is approximately twice as large in the VLA8 (0,2% Zr). Isothermal microcalorimetry shows that room temperature ageing is considerabely retarded by the addition of Zr up to ≈ 0,20% (8).

After describing the influence of the homogenization procedure (including the heating rate) and the Zr-concentration the effect of the quenching rate is demonstrated in figure 3. Samples homo-

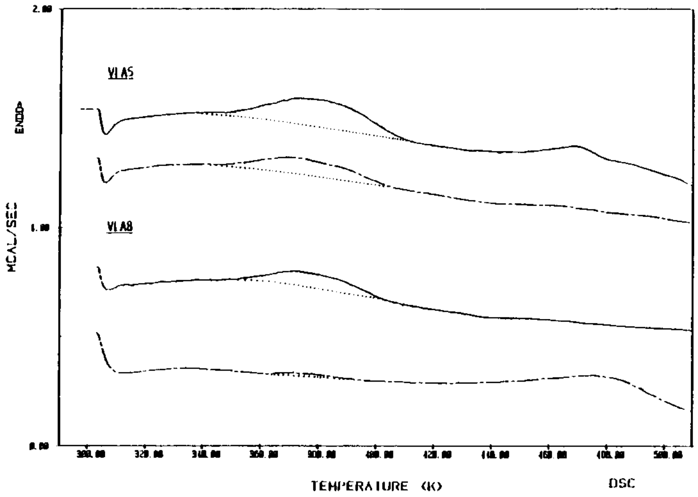

Fig. 2. DSC-curves (10 K/min) of Zr-free material VLA5 and VLA8 material containing 0,17% Zr after water quenching from 480 °C and ageing at room temperature for 2 h (-.-.-) and 5 h (———).

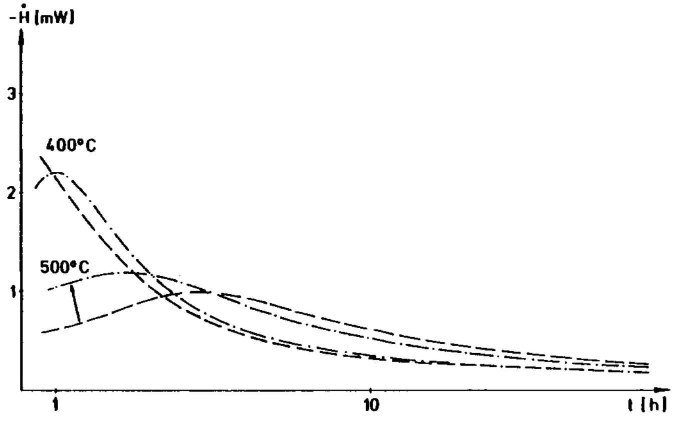

Fig. 3. Room temperature decomposition of Zr-containing material after water quenching (----) and retarded cooling (-.-.-) from 400 and 500 °C.

genized as before were solutionized at 400 and 500 °C, and then quenched in water as usual or cooled with an average cooling rate of 1,5 °C/sec before being immersed in the water at temperatures between 250 and 290 °C. As can be seen from the resulting thermogrammes there is a distinct shift towards shorter ageing times for samples that were given a controlled quench from 500 °C, whereas only a minute shift towards longer ageing times is observed for quenching from 400 °C.

The effect of warm ageing at 140 °C was studied isothermally in the microcalorimeter. Extruded material with 0 and 0,2% Zr was solutionized at 400, 450 and 500 °C water quenched and subsequently aged in the calorimeter - a series of measurements is given in figure 4. A very strong increase of the overall decomposition rate is the result of higher solution treatment temperatures; the addition of 0,2% Zr yields a further enhancement compared to the Zr-free material. If a 1 h/600 °C treatment is given to the samples a minute increase in reaction rate is found for 0% Zr whereas a drastical reduction occurs for the Zr-containing material. In a similar series after 1 h/600 °C the curves were practically identical for 0 and 0,2% Zr.

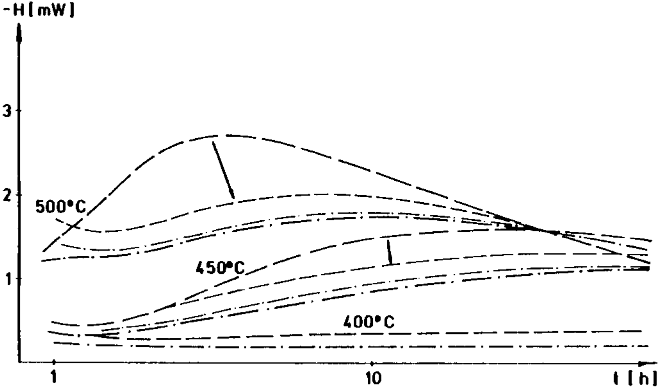

Fig. 4. Decomposition at 140 °C of Zr-containing material (----) and Zr-free material (-.-.-) after water quenching from 400, 450 and 500 °C (this lines were obtained after a 1 h/600 ° treatment).

In figure 5 DSC-thermogrammes are shown for material containing 0 and 0,2% Zr both with an ascast and an extrusion microstructure; all samples have been homogenized after slow heating before undergoing a 24 h/140 ageing treatment.

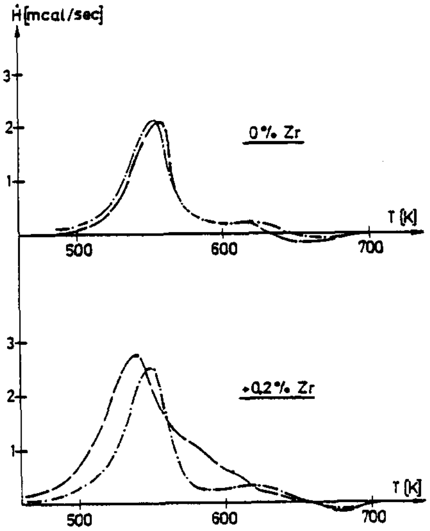

Fig. 5. DSC-curves (40 K/min) after water quenching and 24 h/140 °C ageing for underformed (-.-.-) and extruded (----) material.

For the Zr-free material there is practically no difference with respect to the strong endothermal dissolution peak between 500 and 600 K. The material containing 0,2% Zr exhibits a considerably stronger endothermal effect in comparison to 0% Zr; furthermore the extruded samples yield an effect which is about 30% larger in area. This difference in the 0,2% Zr-material disappears after a 1 h/600 °C treatment.

DISCUSSION

Microstructural investigations (TEM, REM) have shown (4), (8) that a finer and more homogeneous distribution of Al_3Zr-precipitates is attained by slow heating up to the homogenization temperature. An increase in the homogenization temperature results in a small reduction of density and increase in size.

The experiments shown in figures 1 - 3 exhibit the following features

a) a finer $AlZr_3$ precipitation retards decomposition at room temperature, when quenched from the same temperature

b) in spite of a less fine Al_3Zr distribution quenching from higher solution treatment temperatures slows down room temperature decomposition too

c) decomposition at room temperature is fastest for Zr-free material

d) Slow cooling from high solution treatment temperatures yields a higher room temperature decomposition rate.

From all these observations it was concluded that during fast quenching from high temperatures thermal stresses produce dislocations which are mostly annealed out in the absence of dispersoids like Al_3Zr-particles. If the latter are present, they can conserve dislocations thereby increasing the density of sinks for vacancies and possible solute atoms - a finer and denser distribution of Al_3Zr would increase the dislocation density. Consequently the decomposition rate would decrease because of a reduction of vacancy and solute supersaturation. Higher homogenization temperatures produce a less dense Al_3Zr-distribution, however this effect is overcompensated by higher thermal stresses that are created during rapid quenching. This model derived solely from calorimetric measurements was confirmed by transmission electron microscopy (8).

The strong effect of Zr upon 140 °C-ageing can be explained unambiguously by the presence of subgrain boundaries within the elongated grains after extrusion. As can be seen from numerous publications the coverage of subgrain boundaries by metastable and/or stable precipitates ($MgZn_2$) is rather high (9).

As smaller subgrains and thus a larger area of subgrain boundaries are attained only in the presence of Zr-dispersoids which are able to pin dislocations, the higher decomposition rate observed in extruded material with 0,2% Zr reflects the precipitation of Zn and Mg on subgrain boundaries. A semiquantitative evaluation shows that up to 30% of the $MgZn_2$ precipitates are formed on subgrain boundaries. If the subgrain boundary structure is destroyed by a 1 h/600 °C treatment, the Zr-effect on the precipitation of Mg and Zn dissappears. The large increase of the formation rate with higher solution treatment temperatures reflects the precipitation on vacancy rich clusters (10); recently these clusters have been claimed to be quenched-in dislocation loops (11).

CONCLUSIONS

Based on mainly calorimetric and complementary electron metallogrpahic work it was found that Zr-dispersoids can exercise a distinct influence on the decomposition behaviour of AlZnMg(Cu)-alloys.

In the case of cold ageing Zr-dispersoids in combination with rapid quenching conditions may retard the age hardening kinetics for the first hours. This effect can be reduced by lowering the homogenization or solutionizing temperature and/or the quenching rate.

The effect of Zr-dispersoids upon warm ageing is a more apparent one, because the additional precipitates in the subgrain boundary regions do not contribute to the actual age hardening substantially however they might have some beneficial effect on toughness and stress corrosion performance.

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