

TRANSFORMATION STUDIES IN AlZnMg ALLOYS BY CALORIMETRIC METHODS

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ABSTRACT

The possibilities of calorimetric methods like DSC and heat flow microcalorimetry for transformation studies in Aluminium alloys are demonstrated. The influence of pre-existing nuclei upon decomposition rate at various temperatures is described; unassisted nucleation of equilibrium precipitates seems to be confined to a narrow temperature range.

Equilibrium precipitates of small size are dissolved simultaneously with metastable phases, thereby complicating the interpretation of DSC-curves.

INTRODUCTION

Since the early works of Hirano (ref.1), the use of calorimetric methods for studies in the field of transformation processes in Al-alloys like the age-hardening AlZnMg or AlCu system, has been growing steadily. The commercial availability of advanced instruments of the DSC-type has stimulated the interest of material scientists in calorimetry, as a means for quick information about the precipitation state and the decomposition behaviour of a given alloy (ref.2), (ref.3).

Due to their high resolution (detection threshold better than $10^{-4} \mu\text{W}/\text{mm}^3$) and excellent long time stability, heat flow microcalorimeters of the Tian-Calvet type in isothermal mode have been successfully applied to follow decomposition of Aluminium alloys in a continuous and direct way (ref.4), (ref.5). It should be mentioned that these instruments can also be used in a linear heating mode, with rates up to 8 K/min and a detection threshold of $0,01 \mu\text{W}/\text{mm}^3$ compared to $0,4 \mu\text{W}/\text{mm}^3$ for DSC.

The Al - 5 % Zn - 1 % Mg alloy is the basis for the high strength alloys of the 7xxx series reaching R_m values up to 700 MPa. Strengthening of the soft Al-matrix is caused by the precipitation of coherent Guinier-Preston Zones (GPZ) and metastable Phases (msP) like semicoherent η' ($\approx \text{MgZn}_2$) and coherent R -

their combination, distribution, size etc. can be influenced by alloy composition, processing parameters and thermomechanical treatment.

We have investigated pure and commercial alloys of the 7xxx series by heat flow calorimetry, DSC, transmission electron microscopy (TEM) and other methods (ref.5), (ref.6), (ref.7). We hold that calorimetry is a very powerful tool but necessitates complementation by other techniques in order to take advantage of its potential. It is the purpose of this paper to summarize our latest results and to comment on their implication on the interpretation of DSC-thermograms.

EXPERIMENTAL

The alloy was prepared by the Vereinigte Metallwerke Ranshofen Berndorf AG (VMW) with the composition Al - 5,17 wt % Zn - 1,19 wt % Mg, on the basis of high purity components. After homogenization samples for DSC, TEM and microcalorimetry were machined as it was described in (ref.6) and (ref.7). Solution treatment was performed in air between 400 and 500 °C for at least 30 minutes. The samples were either water quenched or step-quenched in oil at 200 - 250 °C for five minutes; ageing was done in air or in oil, before introduction to the calorimeters samples were stored in liquid nitrogen.

Both in the DSC and in the heat flow calorimeter samples were measured against pure Aluminium as a reference. The base line was established by using pure Aluminium as a sample; in DSC the base line also was found by rapidly cooling the sample after the first scan and performing a rescan, this is particularly useful for higher scanning rates.

The DSC was calibrated with NBS standard sapphire, the heat flow calorimeter by the Joule effect. Each measurement was repeated 2 - 3 times - in general reproducibility was better than 3 %. For further experimental details see (ref.6).

RESULTS AND DISCUSSION

Various authors have found the maximum temperature for GP-Zone formation T_{GPZ} to be ≈ 120 °C for the given alloy composition. Below that temperature GP-Zones are the first decomposition product.

Figure 1 shows the decomposition kinetic upon ageing in the heat flow calorimeter at 99 °C for various quenching conditions. Samples were quenched from solution treatment temperature $T_s = 400$ and 500 °C in cold water or quenching was interrupted at 200 and 250 °C (step-quenching), resulting in practically the same curve. Thus the low quench sensitivity that has been found for room temperature ageing persists up to 100 °C, although more stable decomposition products like η_2' (η_1) particles have been found by TEM to be present after 24 hours (ref.7).

Ageing at 140 °C, above T_{GPZ} is shown in Figure 2. Here only a very small decomposition rate is detected upon 5'/200 °C step quenching, whereas water-quenching yields thermal effects about ten times higher, in addition a distinct influence of solution temperature is found yielding higher kinetics for higher T_s .

Samples quenched into water from 400 °C were aged at 110 °C for $t_A = 5, 24$ and 96 hours and then heated in the DSC at a scanning rate of 20 K/min resulting in the thermograms of Figure 3. Compared to the as-quenched sample ($t_A = 0$) ageing at 110 °C shifts the first and second endothermal effect to higher temperatures, their size increases with ageing time. Between 460 and 570 K one or two exothermal effects appear, upon long ageing ($t_A = 24$ and 96 h) the one at about 550 K becomes very sharp and high. The last endothermal peak exhibits only a low increase with ageing time.

After ageing at 120 °C slightly above the limit T_{GPZ} the curves of Figure 4 are obtained. Only two endothermal effects appear, the first one strongly, the second one weakly dependent on ageing time t_A , all three curves exhibit two exothermal peaks between 460 and 570 K.

Much simpler thermograms are found if the scanning rate is increased up to 80 K/min. Figure 5 represents a sample that was water-quenched from 400 °C, linearly heated with 1,25 K/min up to 150 °C and aged for 24 hours. One rather wide endothermal peak is found and no exothermal one; due to the high heating rate small fluctuations are present at higher temperatures. The rescan is taken as base line, it shows no thermal effect except for a small endothermal peak at 390 K.

Like in Figure 2 for isothermal kinetics step-quenching causes drastic changes in DSC-thermograms too. Samples that were aged for various durations at 120 °C after step-quenching from 400 °C are presented in Figure 6. Compared to Figure 4 completely different

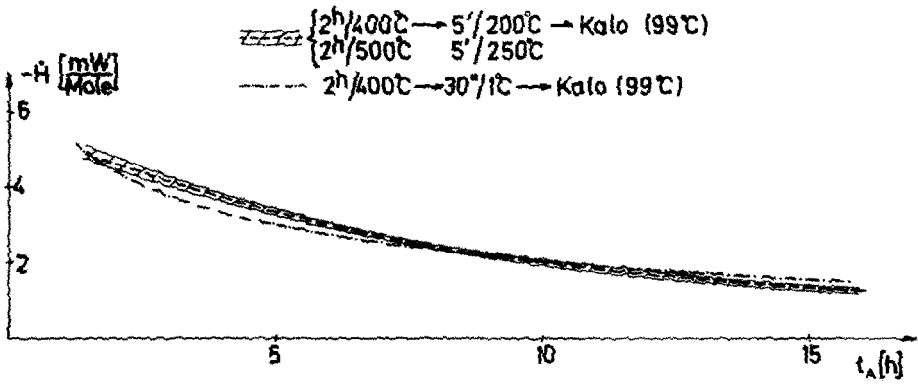


Fig. 1. Isothermal heat flow curves for ageing at 99 °C for various quenching conditions.

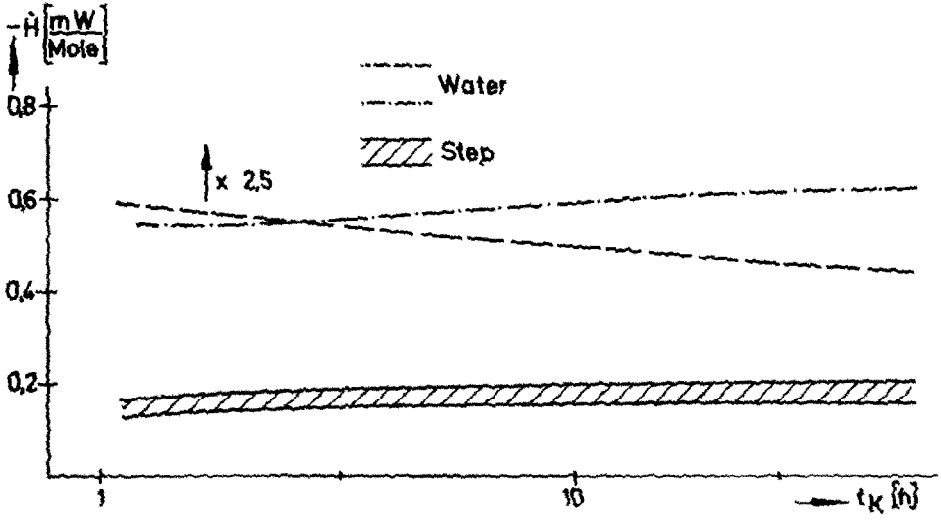


Fig. 2. Isothermal heat flow curves for ageing at 140 °C after water-quenching and step-quenching. Quenching from 400 °C (--- and -.-.-) and from 500 °C (///)

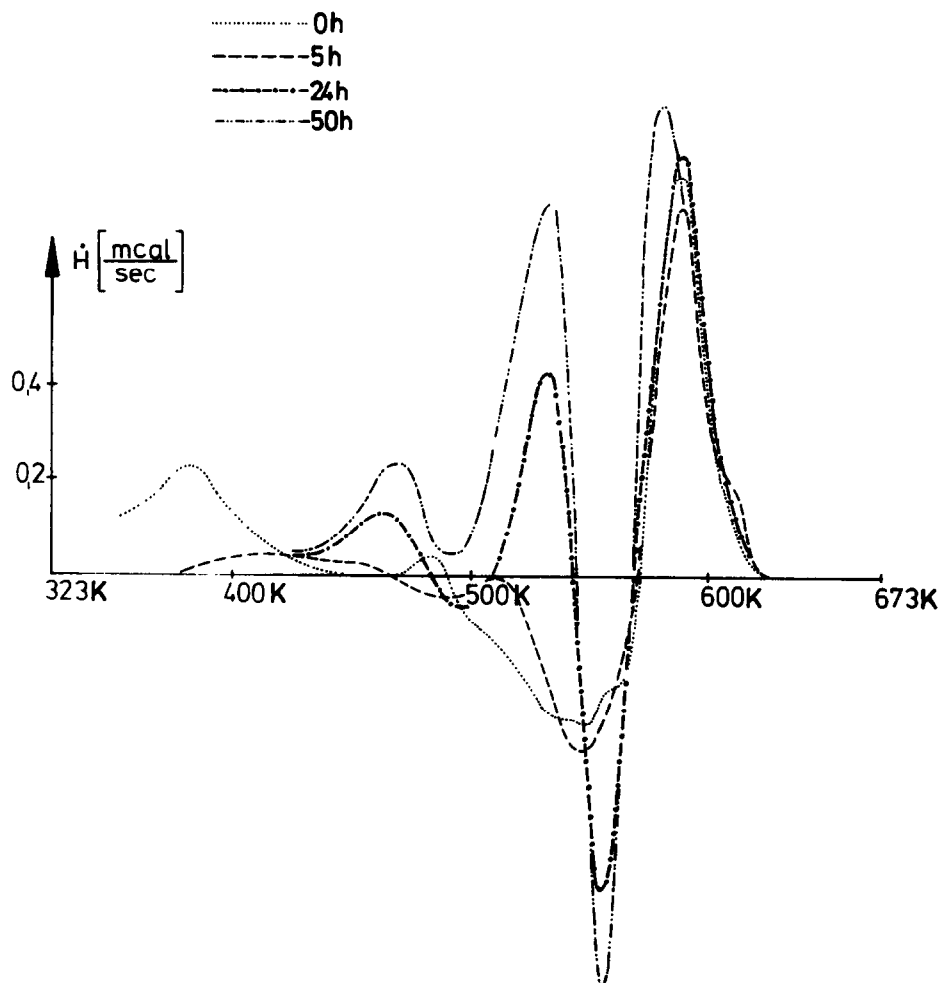


Fig. 3. DSC curves for ageing at 110 °C after water-quenching (scanning rate 20 K/min).

results are obtained. After 5 h/120 °C ageing an exothermal effect starts at ≈ 470 K, it is followed by an endothermal effect of comparable size. Upon increasing ageing time the endothermal peak grows and extends towards lower temperatures, whereas the exothermal one is shifted to lower temperatures and diminished gradually. Samples aged for 24 hours were measured with different heating rates, the exothermal peaks were analyzed according to the methods of Ozawa (ref.8) and Kissinger (ref.9), in both cases the activation energy was found to be $\approx 1,4$ eV/Atom.

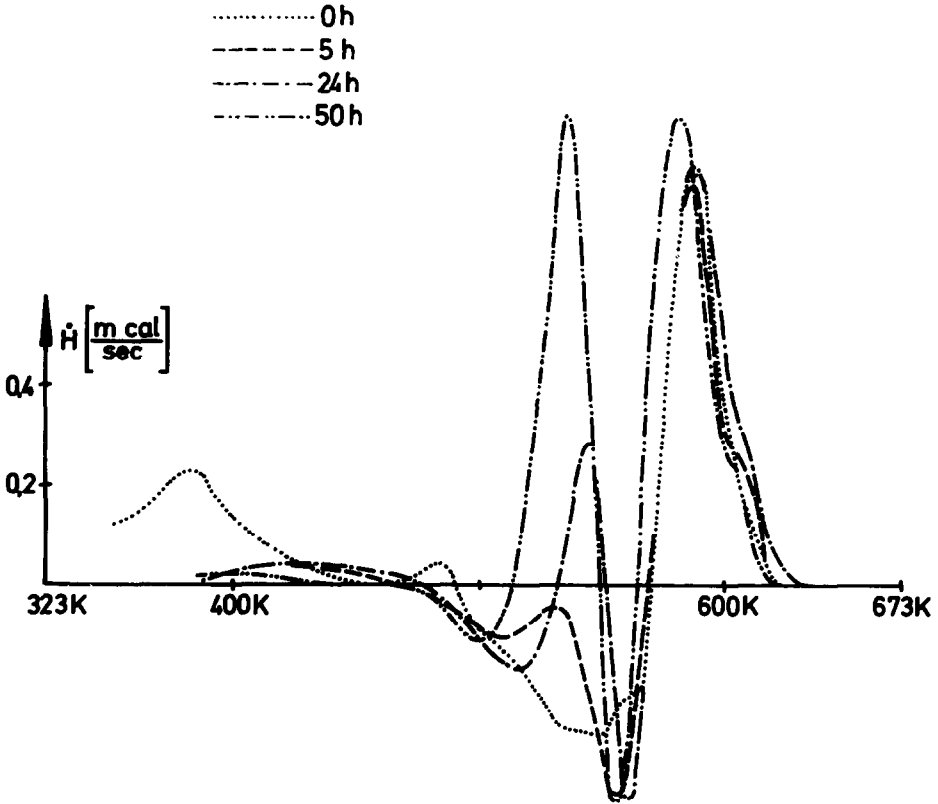


Fig. 4. DSC curves for ageing at 120 °C after water-quenching (scanning rate 20 K/min).

For step-quenched samples a series was made with ageing times 5, 24, 48 and 96 hours at ageing temperatures between 100 and 200 °C. In Figure 7 the curves for $t_A = 96$ h at 120, 130, 140 and 170 °C are given. Ageing at 130 °C yields thermograms like in Figure 6, with a distinct exothermal effect even for long ageing times, whereas at $T_A = 140$ °C and above no exothermal effects are detected and there is only one rather small endothermal peak at about 600 K, the size of which is a minimum upon ageing at 140 °C.

Owing to the high binding energy between Mg-atoms and vacancies a high excess vacancy concentration persists at low temperatures, practically for any quenching path. Therefore GP-Zones, having a low nucleation barrier, form with the aid of the excess vacancies and make the alloy rather quench insensitive.

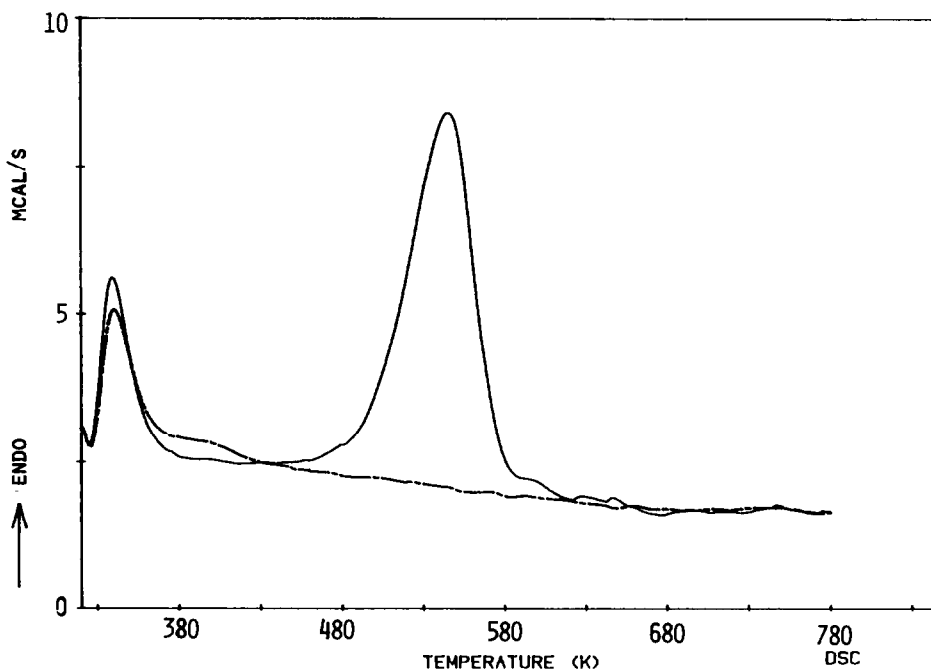


Fig. 5. DSC curves of water-quenched samples slowly heated (1,25 K/min) up to 150 °C and aged for 24 hours (scanning rate 80 K/min).

Above T_{GPZ} , GPZ-formation is no longer a means to reduce the free energy and decomposition starts with the formation of metastable phases. As demonstrated by Ryum (ref.10) and confirmed by calorimetric investigations (ref.6) metastable phases nucleate on vacancy-rich-clusters (VRC) which form during rapid quenching (ref.11). The density of VRC's is dependent on solution treatment temperature and quenching rate, their formation is suppressed, if during step-quenching the excess vacancies are annealed out; their size was estimated to be below 2 nm in diameter (ref.12).

Figure 2 reflects decomposition via VRC's, with a higher VRC density after quenching from 500 °C, and shows in the absence of VRC's that homogeneous nucleation at 140 °C is very difficult. If GP-Zones are present, like in Figure 1, they govern formation of more stable precipitates, and the VRC's become less important.

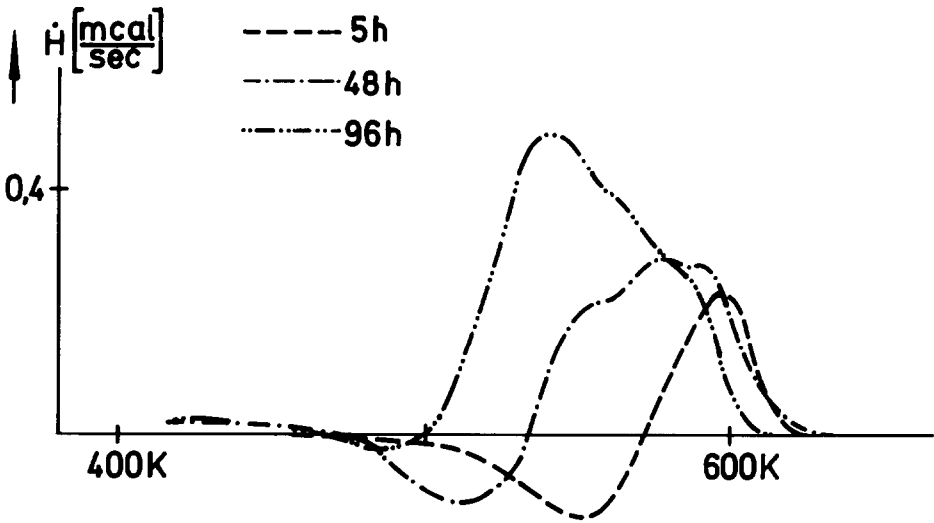


Fig. 6. DSC curves of step-quenched samples for ageing at 120 °C (scanning rate 20 K/min).

Water-quenched samples therefore always contain a high density of VRC's, which, in DSC-runs at low and medium heating rates, give rise to cupious precipitation of equilibrium phases $\eta(\text{MgZn}_2)$, resulting in the exothermal peak for the as-quenched samples in Figure 3 and 4. At lower temperatures GP-Zones and metastable phases are reverted, at about 600 K the stable phases (sP) are dissolved too, thus producing three individual endothermal effects.

As to the small exothermal peaks around 500 K, they sometimes are thought to reflect the transformation from GP-Zones to metastable precipitates. If this were correct, one would expect these peaks to increase with GP-Zone size or ageing time, and not to appear in the absence of GP-Zones, both of which is not the case as can be seen from the relevant curves in Figure 3 and 4. In our opinion there exists only one wide exothermal effect due to VRC-assisted formation of equilibrium particles, whose dissolution is reflected by the last endothermal peak; if less stable precipitates like η' are dissolved simultaneously, two exothermal peaks can appear by superimposition. Referring to the as-quenched curve as a rough base line, the endothermal msP-dissolution peak at about 520 K can be seen to grow with increasing ageing times

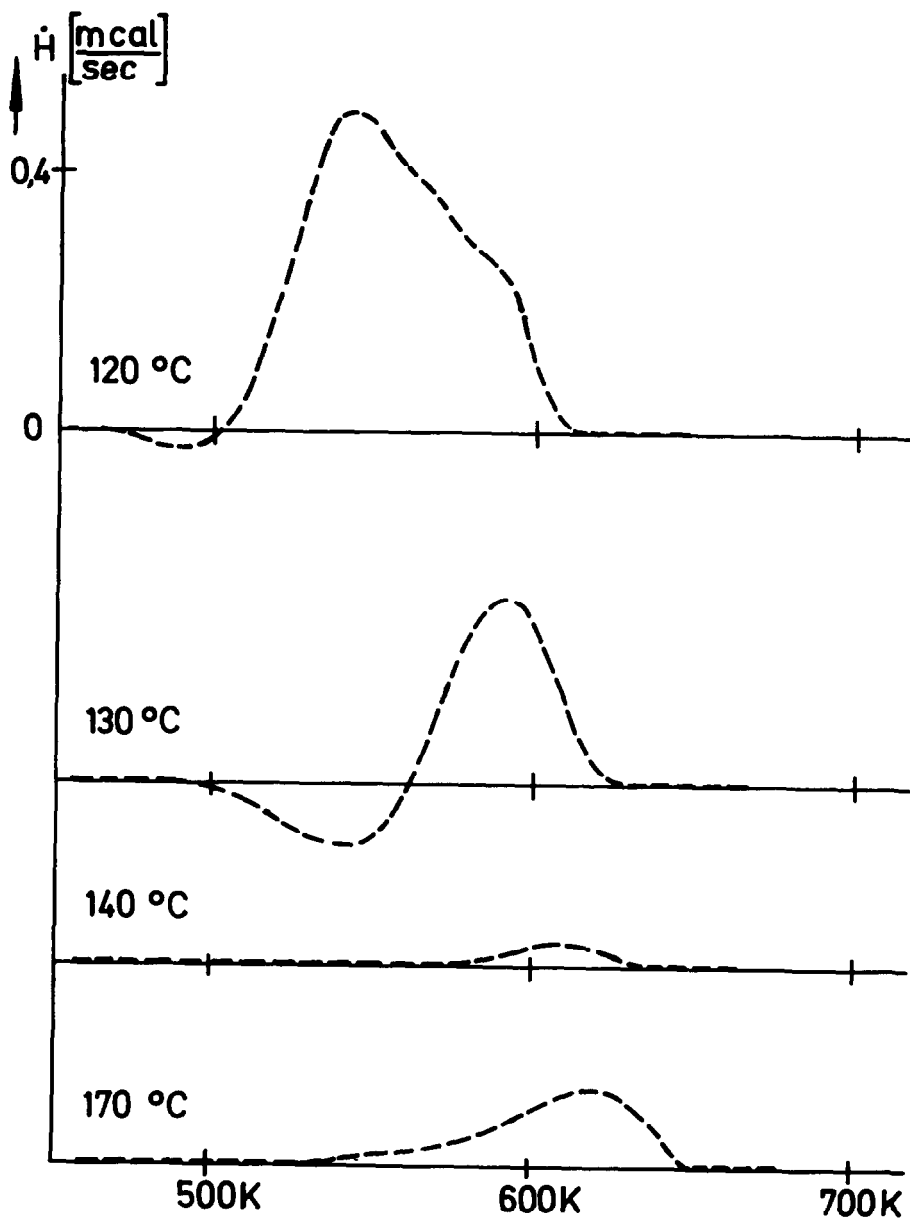


Fig. 7. DSC curves of step-quenched samples for 96 h ageing at various ageing temperatures (scanning rate 20 K/min).

5, 24 and 96 hours. The sharp exothermal peak of Figure 3 indicates that sP-formation rate is highly accelerated when, due to msP-dissolution, the solute concentration is increased. As can be deduced from the last endothermal effect a substantial msP \rightarrow sP transformation only occurs if large msP are present after long ageing times.

As mentioned before, equivalent amounts of msP (η') and sP (η_1) had been detected by TEM in water-quenched samples aged at 110 °C and higher (see Figure 7 in (ref.7)). According to the literature one would expect these sP-precipitates to be dissolved in the course of the last endothermal peak, which is in contradiction with the fact that this peak describes the dissolution of sP, precipitated in the DSC. According to TEM (ref.7) slow heating up to 150 °C and 24 h-ageing produces η'_1 , η_1 and η_2 besides some metastable R_2 . DSC-runs with 20 K/min have resulted in two endothermal peaks (Figure 5 in (ref.12)), whereas for 80 K/min the present work Figure 5 exhibits only one endothermal peak which seems to correspond to the msP-dissolution peaks in Figure 3 and 4. Thus the sP-precipitates of the η_1 -type detected after ageing ($T_A = 110$ °C, 120 °C) are dissolved in the same temperature range as the msP, in spite of their different crystallographic structure. This unexpected result might be put down to the low solute concentration in the matrix and to the small size of semicoherent η_1 -precipitates (< 10 nm) formed at 110 and 120 °C making it impossible for them to grow as fast as the critical size of a stable nucleus. Coherency does not seem to be important, as can be seen from Figure 5 for semicoherent η_1 and incoherent η_2 . It should be mentioned that η_1 and η_2 particles, if they are allowed to grow up to 50 nm and more are dissolved at about 600 K in the temperature range of the last endothermal peak (ref.13). From a practical point of view these findings could be summarized by stating that the second so called metastable dissolution peak in DSC-analyses reflects the amount of metastable and stable precipitates of small size and high density which both would contribute to the strengthening mechanism of the soft Al-matrix.

After step-quenching, for ageing at 120 °C and above, easy nucleation on GP-Zones and VRC is no longer possible; decomposition rates in isothermal microcalorimetry become very small (see Figure 2 and Figure 6 in (ref.14)). At $T_A = 120$ °C however rather

stable nuclei are formed which can grow in the DSC due to a high solute supersaturation. Growth kinetics is controlled by diffusion, as shown by the activation energy $\approx 1,4$ eV/atom, which corresponds well to the values for Zn diffusion in AlZnMg of Beke (ref. 15) and Fujikawa (ref.16). Upon ageing for 96 hours these nuclei result in a rather large precipitate volume fraction; their dissolution starts at lower temperatures as, due to the low solute concentration, the critical size is diminished. After 96 h-ageing at 130 °C precipitation is appreciably reduced (it is represented by the difference of the exo- and endothermal effect), it is a minimum after 96 h/140 °C ageing.

TEM-investigations on air-cooled samples, which gave the same DSC-curves as 24 h/140 °C ageing after step-quenching, had shown that precipitation in the absence of GP-Zones and VRC only takes place on heterogenous nuclei like grain boundaries, dislocations or impurity constituents. Predominantly η_4 -needles were found near vacancy sinks, whereas the pure matrix regions were empty. In water-quenched samples η_4 appeared only for ageing temperatures $T_A > 140$ °C.

As preliminary interpretation - TEM-results for ageing at 120 and 130 °C are on the way - one might conclude that between 120 and 140 °C the critical size for a stable nucleus $r_c = - 2\gamma / \Delta G_v$ (γ interfacial energy, ΔG_v volume free energy gain) is increasing rather rapidly. This may be caused to some extent by a gradual reduction of ΔG_v , but more dramatical changes would occur if a drop of coherency caused higher interfacial energies γ ; coherent interfaces have values between 25 - 200 erg/cm², whereas energies of incoherent boundaries fall in the range 500 - 1000 erg/cm² (ref.17). Thus during ageing at 120 and 130 °C in the absence of GPZ and VRC, nuclei which are to some extent coherent form homogeneously within the matrix (e. g. small η_2' and or η_1). At 140 °C and above however this type of nuclei is no longer stable and precipitation is confined to heterogeneous nuclei of low density. Due to higher diffusion rates the growth kinetics at higher ageing temperatures increases slowly.

CONCLUSIONS

By combination of calorimetric methods and transmission electron microscopy it was shown that for water quenched Al - 5 % Zn - 1 % Mg, in the course of a DSC-analysis with heating rates bet-

ween 10 - 40 K/min equilibrium phases are formed. Simultaneously, precipitates which had been produced by ageing at medium temperatures, are dissolved giving rise to the so called metastable dissolution peak. It was shown that η_1 and η_2 particles, although having the crystallographic structure of the stable equilibrium phase MgZn_2 can be dissolved in the same temperature range as the metastable phases η'_2 , R_2 .

Interpretation of DSC-curves has therefore to distinguish between stable precipitates formed during an ageing treatment and formed in the DSC.

In the absence of GP-Zones and vacancy rich clusters homogeneous nucleation of equilibrium precipitates MgZn_2 seems to be possible up to 140 °C. From this temperature onwards decomposition takes place predominantly via heterogeneous nuclei.

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