JOURNAL OF MATERIALS SCIENCE 16 (1981) 2701–2709

The influence of Mg content on the formation and reversion of Guinier-Preston zones in Al-4.5 at% Zn-x Mg alloys

G. HONYEK, I. KOVÁCS, J. LENDVAI, NG-HUY-SINH,* T. UNGÁR
Institute for General Physics, Loránd Eötvös University, Budapest, Hungary

H. LÖFFLER, R. GERLACH
Section of Mathematics and Physics, Pedagogical University, Halle, GDR

The influence of Mg concentrations on the dissolution of Guinier–Preston (GP) zones formed at room temperature (RT) and on the formation of more stable phases has been investigated during continuous heating of Al–4.5 at% Zn–xMg alloys. The Mg content was varied from 0.05 to 3 at%. After different aging periods at RT, calorimetric investigations were carried out at heating rates of 40 and 80° C min^{-1}. In the case of alloys with a lower Mg content ($x \leqslant 0.5$ at%) only the dissolution of GP zones could be observed during the heating, whereas in the case of alloys with a higher Mg content the formation of the η'-phase started before the total dissolution of GP zones and at higher temperatures the formation of the η-phase also took place. These phases were identified by transmission electron microscopy. The heat-of-solution of GP zones shows saturation as a function of RT aging time. The time needed for the saturation increased monotonously with increasing Mg content. The reversion of zones was followed by *in situ* X-ray small angle scattering measurements. The change of the total scattered intensity was measured during continuous heating at a rate of 40° C min^{-1}. These investigations have confirmed the results of the calorimetric measurements which indicate that the total dissolution of zones takes place only in the case of the alloys with a Mg content lower than 0.5 at%. In the case of alloys with a Zn concentration of 4.5 at% studied here, 1 at% Mg is sufficient to initiate the formation of more stable phases during the reversion of zones.

1. Introduction

There are a number of papers which deal with the formation of Guinier–Preston (GP) zones at room temperature (RT) in the Al–Zn–Mg system and with the reversion of these zones at higher temperatures, as well as with the nature of the processes following the reversion [1–14]. Many papers have dealt with the influence of small Mg additions on the zone formation in Al–Zn alloys [15–20]. It has been noted that the addition of even 0.1 at% Mg results in significant hardening compared to the binary Al–Zn alloy [15], but at the same time it slows down the process of decomposition to a considerable extent [16]. By electrical resistivity measurements Suzuki *et al.* [17] also observed the effect of slowing down the decomposition process when only 0.01 at% Mg was added to Al–3 to 5 at% Zn alloys. In their calorimetric investigations on the alloy with 0.012 at% Mg, besides the peak related to the dissolution of the Zn zones in the binary alloy, another peak characteristic only of the ternary alloy also appeared. Ohta and Hishimoto [18] and Tomita *et al.* [19] have also confirmed the co-existence of two types of zones in such alloys.

Polmear [15] and Panseri and Federighi [16] explain the favourable effect of Mg on the amount of zones formed by the fact that Mg increases the

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*On leave from Hanoi University, Vietnam.

0022–2461/81/102701–09$02.90/0

supersaturation at RT. However, according to Ceresara and Fiorini [20] Mg has no effect on the aging processes.

Several models have been proposed explaining the mechanism of precipitation processes following the reversion of zones in this alloy system [4, 6, 8, 9, 11–13]. Based on transmission electron microscopy (TEM) investigations Lorimer and Nicholson [6] proposed that in an Al–5.9 wt% Zn–2.9 wt 5 Mg alloy the particles of η'-phase are formed directly from the large-size GP zones. Kawano *et al.* [4] arrived at a similar conclusion on the basis of X-ray small-angle scattering in the case of an Al–6.5 wt% Zn–1.2 wt% Mg alloy. Dünkeloh *et al.* [9] have found also by X-ray small-angle scattering measurements that GP zones, exceeding a critical size, transform into η'-precipitates if $\text{Zn} + \text{Mg} > 4$ at% and $\text{Zn}/\text{Mg} = 2$. If, however, the concentration of Zn is less than 2.5 at% then the η'-particles nucleate in the areas of concentration fluctuations left behind by the dissoluted zones [12, 13].

In the present paper the effect of Mg concentration and the aging time at RT on the formation of more stable phases is studied by calorimetric, X-ray small-angle scattering and TEM investigations.

2. Experimental procedure

The investigations were carried out on a series of Al–Zn–Mg alloys with a constant Zn concentration of 4.5 at% and with Mg concentrations of 0.05, 0.1, 0.2, 0.5, 1, 1.5, 2, 2.5 and 3 at%, respectively. The alloys were made from 99.99% pure Al, 99.9% Zn and 99.9% Mg. The compositions were determined by spectral analysis. The samples were quenched into RT water after 30 min of solution heat-treatment at 480° C. After quenching, the samples were aged at RT for one day, one week and six months.

Differential scanning calorimetric (DSC), TEM and X-ray small-angle scattering (XSAS) investigations were carried out. The calorimetric measurements were performed by a Perkin–Elmer DSC-2 calorimeter between 230 and 750 K at heating rates of 40 and 80° C min^{-1}. In order to identify the exothermic peaks in the thermograms TEM investigations were carried out in a Tesla BS 540-type electron microscope. The reversion of GP zones formed during long-term aging at RT was followed by *in situ* XSAS measurements. A modified Kiessig-type XSAS camera was used which measured the total scattered intensity (*TI*) during continuous heating. *TI* was measured from 2.4 to 30 mrad in 2θ by a scintillation counter with an open window of 25 mm and a direct beam stop of 2 mm diameter. CuKα radiation was used with a Ni filter and differential discrimination. Assuming that the distribution of the scattered intensity follows the Guinier approximation it can be shown that the integral intensity, Q and TI are related to each other by the following equation: $Q \simeq 0.244\, TI/R_G$, where R_G is the radius of gyration [13].

3. Results and discussion

The samples were heated up from 230 to 750 K in the calorimeter immediately after quenching and after aging for one day, one week and six months at RT. The initial temperature, 230 K, was applied in order to finish the transient processes before beginning the dissolution of GP zones formed at RT. All thermograms begin with an endothermic process indicating the dissolution of zones even in the case of measurements made immediately after quenching. The thermograms can be divided into two significantly different groups on the basis of the Mg content of the alloys. Within the two groups only small quantitative differences can be observed. The alloys with lower Mg contents (0.05 to 0.5 at% Mg) belong to the first group, in which no heat effect can be observed after the end of the dissolution of the zones. The alloys with a higher Mg content (1 to 3 at% Mg) belong to the other group, in which the dissolution of zones is followed by three well-separated exothermic peaks and a final dissolution process.

Figs 1 and 2 show typical thermograms of alloys with low and high Mg contents at a heating rate of 40° C min^{-1}. It should be noted that thermograms at 80° C min^{-1} show similar characteristics but the superimposed peaks are less distinct than in the case of lower heating rates. From Figs 1 and 2 it can be seen that by increasing the aging time at RT the dissolution of zones starts at higher temperatures and always ends at about 200° C. In the case of low Mg content alloys ($x \leqq 0.5$ at%) no precipitation processes can be observed during continuous heating which means that in these alloys the homogeneous solid solution is the stable state above 200° C, similar to the binary Al–4.5 at% Zn alloy [5, 21].

In the alloys with a low Mg content the dissolution of zones results in two superimposing

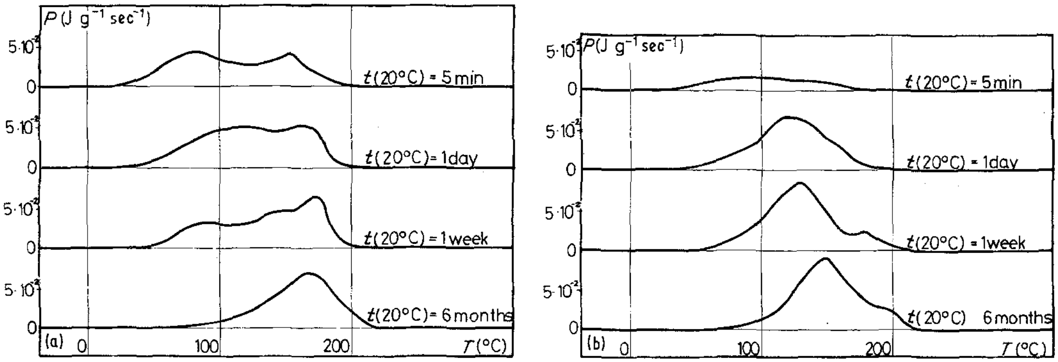


Figure 1 DSC thermograms taken after different aging times at RT at a heating rate of 40° C min^{-1} for the alloys (a) Al–4.5 at % Zn–0.05 at % Mg and (b) Al–4.5 at % Zn–0.5 at % Mg.

peaks, whereas, in the alloys richer in Mg only one exothermic peak can be observed indicating only a single process. On increasing the aging time at RT, the higher temperature peak becomes dominant in the first group at the expense of the lower temperature peak. This indicates that in these alloys two different types of zones are formed during a short time after quenching and only the more stable ones exist after longer aging times at RT. The two dissolution peaks in the alloys containing less than 0.5 at % Mg indicate the formation of two types of zones which are most probably near to the composition of the ones due to the binary Al–Zn and ternary Al–Zn–Mg alloys in accordance with earlier investigations [17–19].

Some characteristic temperatures of the peaks in the thermograms obtained after six months RT aging are shown in Fig. 3 as a function of Mg concentration with heating rates of 40 and 80° C min^{-1}. It can be seen that these temperatures characteristic of the zone dissolution and of the three consecutive formation processes are essentially independent of the Mg concentration. The formation processes taking place during heating

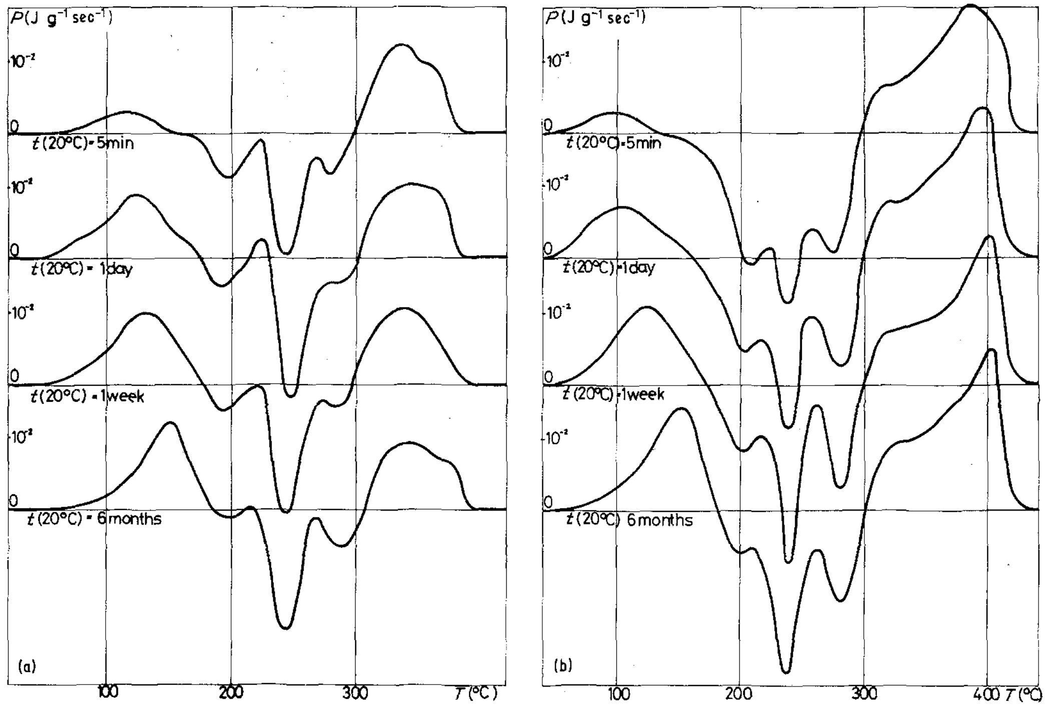


Figure 2 DSC thermograms taken after different aging times at RT at a heating rate of 40° C min^{-1} for the alloys (a) Al–4.5 at % Zn–1 at % Mg and (b) Al–4.5 at % Zn–2 at % Mg.

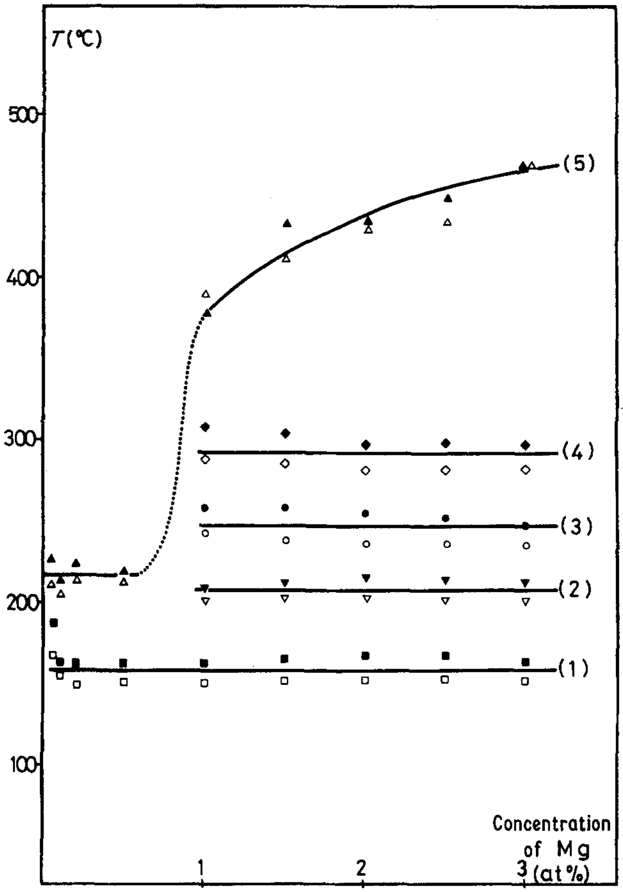


Figure 3 Characteristic temperatures of thermograms taken after aging for six months at RT against Mg concentration; (1) peak temperature of zone dissolution, (2) η'-phase formation by homogeneous nucleation, (3) η'-phase formation by heterogeneous nucleation, (4) η-phase formation and (5) the minimum temperature of total dissolution (the open points are the characteristic temperatures of thermograms taken at a heating rate of 40° C min^{-1}, the full points are those at a rate of 80° C min^{-1}.

do not depend on the pre-history of the samples as well, since the three formation processes proceed in the same way after different periods of pre-aging. It is interesting to note, however, that in the alloys with low Mg concent, where there are two dissolution peaks, the temperature belonging to the first dissolution process agrees to a good approximation with the temperature of the single dissolution peak in the alloys containing more than 1 at% Mg.

In the alloys of higher concentration the final dissolution temperature increases monotonically with the increase of Mg concentration and is basically independent of the pre-aging time. The temperatures determined in this way give the solid solubility limit of these alloys at the given heating rate. On increasing the heating rate the characteristic temperatures increase only by a few degrees.

In Fig. 4 the values of the solution heats of GP zones (calculated from the' areas under the first endothermic peaks in the thermograms) are shown as a function of aging time. In all the alloys saturation-type kinetics were observed. The saturation value of the solution heat increases from 8 to 12.5 J g^{-1} with increasing Mg content. Under 0.2 at% Mg and above 2 at% Mg concentration the solution heats of zones do not depend on the Mg concentration. In the alloys of very low Mg content the solution heat attains the value of saturation immediately after quenching. This

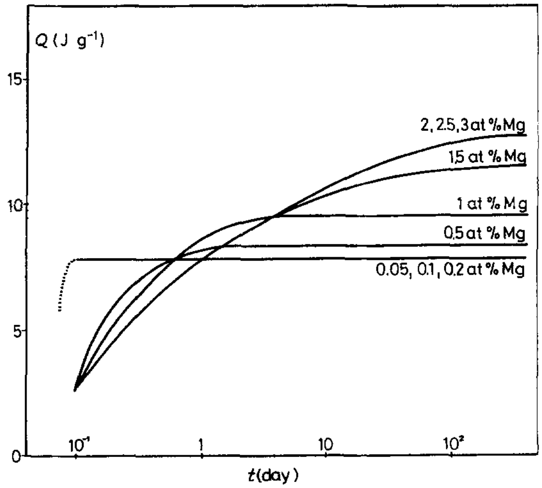


Figure 4 Solution heat of zones as a function of aging time at RT for samples of different Mg concentrations.

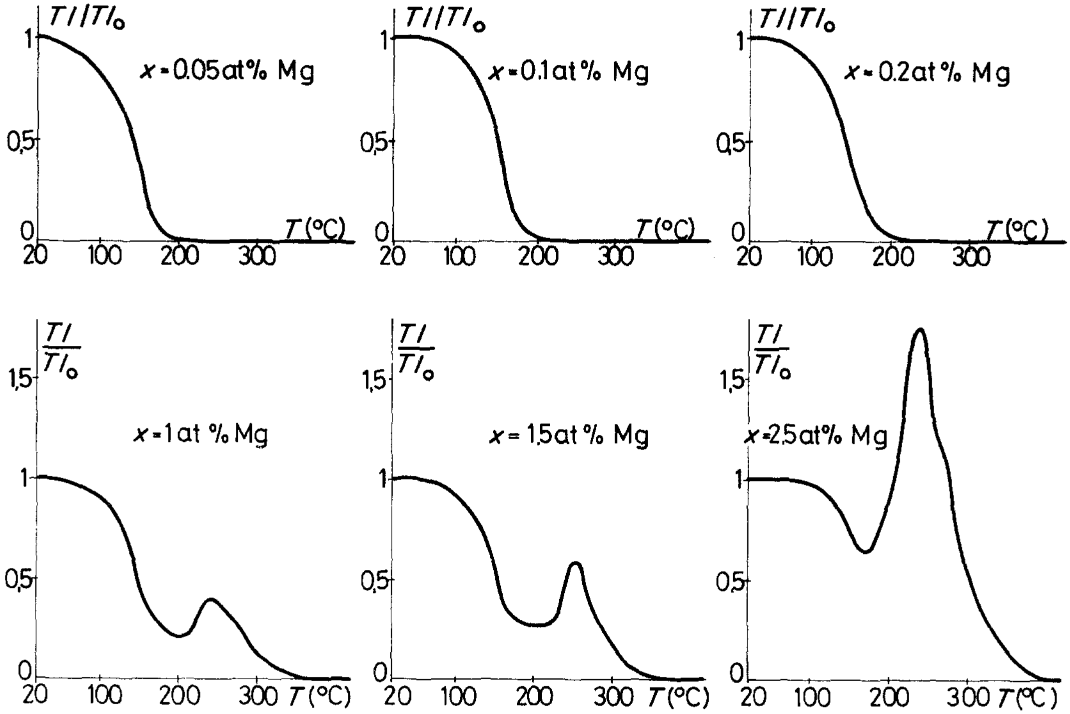


Figure 5 Changes of the total scattered intensity after long-term aging at RT during continuous heating at a rate of 40° C min^{-1} for alloys of different Mg contents (*TI* was normalized with its initial value, TI_0).

means that a few minutes aging time difference just after quenching has no effect on the quantity of the dissolving zones. In alloys with a higher Mg content the time needed for saturation increases with increasing Mg content up to about 1.5 at% Mg. Consequently Mg appears to slow down the formation of GP zones at RT increasingly up to about 1.5 at% concentration and its effect does not increase further in the Mg content range between 1.5 to 3 at% Mg.

When longer aging times are applied for alloys of higher Mg concentration (above 0.5 at Mg) the zone dissolution and the subsequent formation processes cannot be separated in the thermograms (Fig. 2), i.e. the formation processes of more stable phases start before the total dissolution of zones. Thus, in these cases the thermograms show curves of superimposing endothermic and exothermic processes, therefore, the heat due to the total dissolution of GP zones formed during RT aging cannot be determined exactly.

The conclusions drawn for the reversion of GP zones are supported by XSAS investigations as well. After long-term aging (at least two months) at RT the alloys were heated up from RT to 480° C at a heating rate of 40° C min^{-1} and the total scattered intensity was measured *in situ*. When the zones are dissolving *TI* decreases and therefore this method is suitable for detecting the reversion. *TI* was always normalized with the initial scattered intensity (TI_0). In Fig. 5 TI/TI_0 is plotted against the temperature for six different alloys. Fig. 5 reveals that in the alloys containing less than 1 at% Mg the total dissolution of zones is finished at approximately 210° C. Above this temperature no *TI* increase was observed indicating no further formation of precipitates. The behaviour of the alloys containing more than 1 at% Mg is quite different. The formation of more stable precipitates starts before the total dissolution of zones which means that in these alloys there is no complete reversion. The higher the Mg content of the alloy, the less complete the reversion of zones before considerable further precipitation takes place.

The finer details of the simultaneous dissolution and precipitation processes (the superimposing parts of the peaks in the thermograms) cannot be observed by *TI* measurements. Nevertheless, in several significant features (e.g. the end of zone dissolution, the start of the formation of more stable phases) there is a highly satisfactory corre-

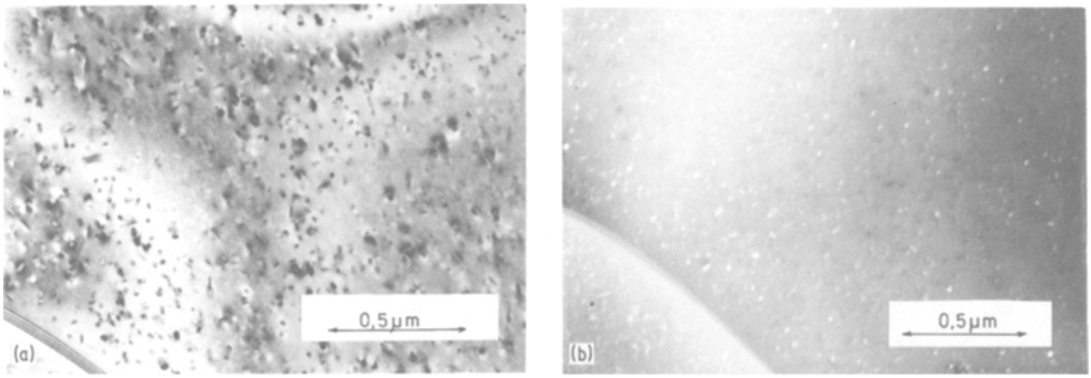


Figure 6 (a) Bright-field and (b) dark-field micrographs of an Al–4.5 at % Zn–2 at % Mg alloy heated up to 210° C at 40° C min^{-1} after quenching and one week RT aging.

spondence between the DSC and XSAS measurements. At the same time, XSAS measurements prove directly that if the Mg concentration is 1 at % or more, the new phase formation starts before the total dissolution of zones.

In order to identify the types of phases formed during heating TEM investigations were carried out on the Al–4.5 at % Zn–2 at % Mg alloy. Thermograms of this alloy are shown in Fig. 2b. The heat treatment of the samples investigated was selected according to the calorimetric heating circumstances. After aging at RT for a week after quenching, the samples were heated up to a given temperature at a heating rate of 40° C min^{-1}. When the required temperature was reached the samples were quenched into RT water. Only one RT aging period was applied because the DSC thermograms showed that pre-history of the samples has little influence on the formation processes taking place during heating. On the basis of the DSC measurements the following maximum heating up temperatures were chosen: 210, 230, 260, 290, 310, 330 and 380° C. In each case bright- and dark-field images and diffraction patterns were obtained in the electron microscope. The most important results of the TEM investigations are demonstrated in Figs 6 to 9.

In Fig. 6 the micrographs were taken of samples heated up to 210° C. The bright-field image (Fig. 6a) shows homogeneously distributed η' precipitates within the grain. The dark-field micrograph (DFM) taken with the (10.2) reflection of the η'-phase (Fig. 6b) shows that the particles are really η' precipitates. The position of the $(10.2)_{\eta'}$ reflection was calculated using the data of de Ardo and Simensen [22]. In Fig. 7 the micrographs taken after heating to 230° C are shown. These particles are also η' precipitates (see the DFM in Fig. 7b) heterogeneously nucleated on dislocations. In the diffraction pattern taken in these two decomposition states there was no indication of the presence of the η-phase. On the basis

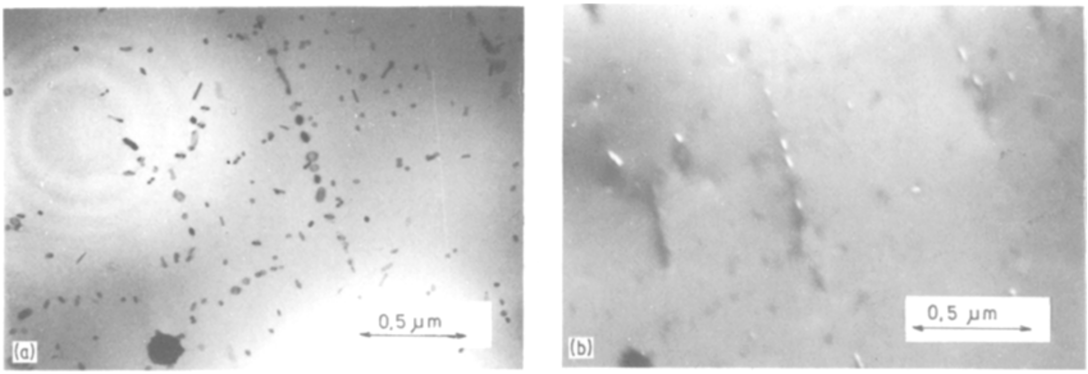


Figure 7 The same as Fig. 6 but heating up to 230° C.

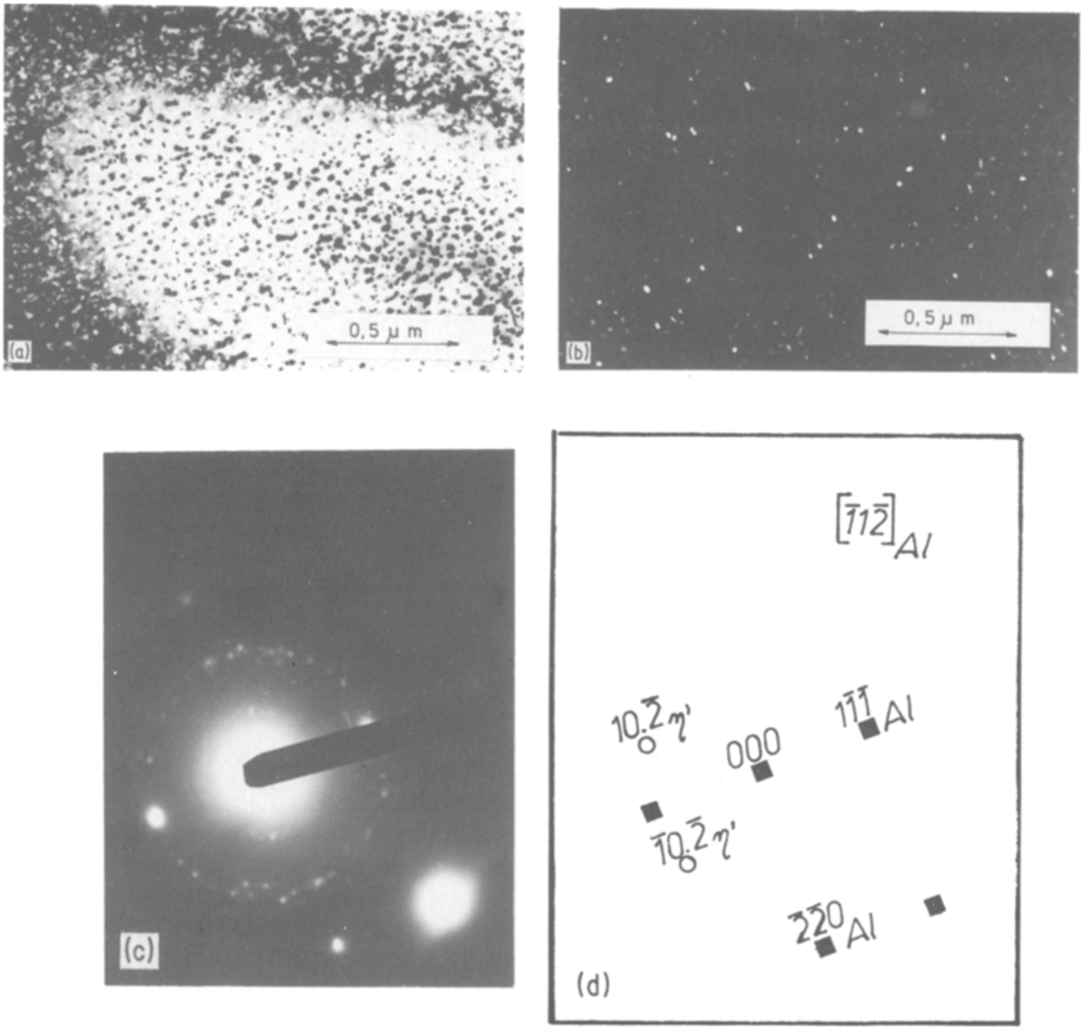


Figure 8 (a) Bright-field, (b) dark-field micrographs and (c) and (d) diffraction pattern after heating up to 260° C.

of these observations the first two exothermic processes in the thermograms are caused by the formation of η' precipitates by two different nucleation mechanisms. In the first process the particles are formed most probably on GP zones retained after reversion, this explains the homogeneous distribution of the particles. In the second process the nucleation takes place mostly on dislocations.

After heating the samples up to 260° C (Fig. 8) both η' and η precipitates can be observed. The presence of the η'-phase is proved by the DFM taken with the $(10.\bar{2})_{\eta'}$ reflection (Fig. 8b) and by the $\{10.2\}_{\eta'}$ spots in the diffraction pattern (Fig. 8c). The appearance of the η-phase is indicated by the spot clusters around the $(2/3)\langle 2\,2\,0\rangle_{\mathrm{Al}}$ direction containing spots of the η'-, η_1-, η_2- and η_4-phases. The TEM investigations after heating up to 290° C gave similar results, the only difference being that the amount of the η-phase was increased.

Increasing the heating temperature to 310° C the third decomposition process (see Fig. 2b) is finished. In agreement with the result the micrographs in Fig. 9, show fairly large plates of η-phase and very distinct spots of the η-phase in the diffraction pattern. No indications of the presence of η'-phase could be found.

The micrographs taken after heating the alloy up to 330° C show further coarsening of the η particles and those taken at 380° C show a homogenized alloy.

4. Conclusions

The results of our investigations can be summarized as follows:

(1) The zone formation process taking place after quenching is slowed down by the increase of Mg concentration. In the alloys containing less than 0.5 at % Mg the total amount of the dissolving zones does not change after a few minutes of RT aging. In the alloys containing 2, 2.5 and 3 at % Mg the zone formation processes are identical.

(2) In the alloys with less than 0.5 at % Mg two types of GP zones are formed at the beginning. During long-term aging the less stable zones transform into the more stable ones. To give a closer description of this transformation as well as of the two types of zones further investigations are needed.

(3) The stability of zones also increases with aging in the case of alloys containing more than 0.5 at % Mg, which is indicated by the fact that the peak temperature of the zone dissolution process increases with aging time in the period investigated. If the aging time is fixed this temperature is constant for all the alloys, i.e. it does not depend on the Mg concentration.

(4) For alloys with Mg less than 0.5 at % the GP zones are completely dissolved during heating up to about 210° C. In these alloys no other phase formation process was observed during heating. In the alloys containing more than 1 at % Mg new precipitation processes start before the total dissolution of zones thus in these alloys there is no complete reversion. The temperature of solid solubility limit of the second phases in these alloys increases by a large extent (about 150° C) in the range 0.5 to 1 at % Mg.

(5) In the alloys where the reversion is not complete three different precipitation processes

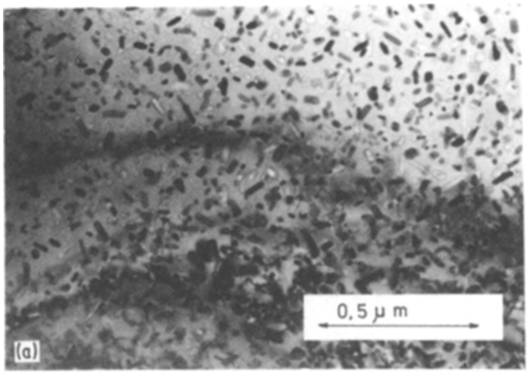
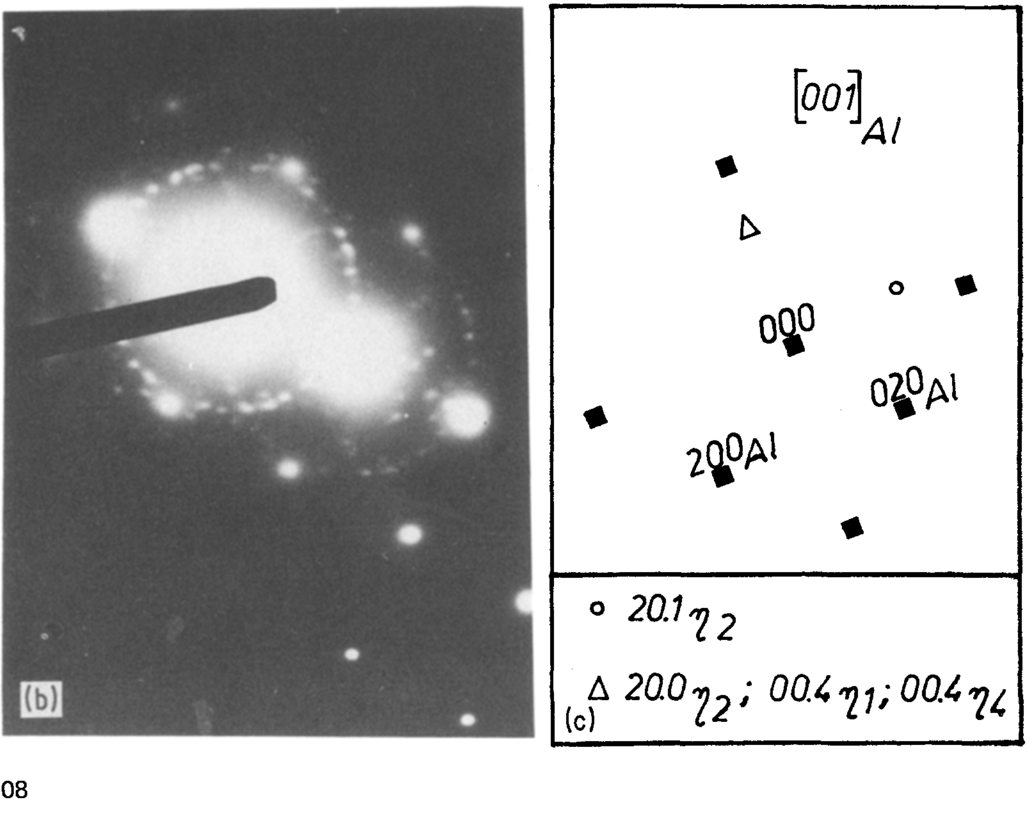


Figure 9 (a) Bright-field micrograph, (b) and (c) diffraction pattern after heating up to 310° C.



take place during heating. The first two are the formations of η' precipitates homogeneously distributed in the matrix and heterogeneously formed at dislocations, respectively. The third process is the formation of the η-phase.

(6) The peak temperatures of the three consecutive and superimposing formation processes are the same in all the alloys, i.e. the nature of the precipitates is independent of Mg concentration between 1 and 3 at %.

References

1. R. GRAF, *Compt. Rend.* **242** (1956) 1311.
2. *Idem, ibid.* **244** (1957) 337.
3. H. SCHMALZRIED and V. GEROLD, *Z. Metallkde.* **49** (1958) 291.
4. O. KAWANO, Y. MURAKAMI, T. NAKAZAWA and K. S. LIU, *Trans. Japan Inst. Met.* **11** (1970) 12.
5. L. F. MONDOLFO, *Met. Rev.* **153** (1971) 95.
6. G. W. LORIMER and R. B. NICHOLSON, *Acta Met.* **14** (1966) 1009.
7. P. A. THACKERY, *J. Inst. Met.* **96** (1968) 228.
8. N. RYUM, *Z. Metallkde.* **66** (1975) 338.
9. K. M. DÜNKELOH, G. KRALIK and V. GEROLD, *ibid.* **65** (1974) 291.
10. P. E. MARTH, H. I. AARONSON, G. W. LORIMER, T. L. BARTEL and K. C. RUSSELL, *Met. Trans.* **7A** (1976) 1519.
11. G. GROMA and E. KOVÁCS-CSETÉNYI, *Phil. Mag.* **32** (1975) 869.
12. T. UNGÁR, J. LENDVAI, I. KOVÁCS, G. GROMA and E. KOVÁCS-CSETÉNYI, *Z. Metallkde.* **67** (1976) 683
13. T. UNGÁR, J. LENDVAI and I. KOVÁCS, *Aluminium* **55** (1979) 663.
14. M. RADOMSKY, O. KABISCH, H. LÖFFLER, J. LENDVAI, T. UNGÁR, I. KOVÁCS and G. HONYEK, *J. Mater. Sci.* **14** (1979) 2906.
15. I. J. POLMEAR, *J. Inst. Met.* **86** (1957) 113.
16. C. PANSERI and T. FEDERIGHI, *Acta Met.* **11** (1963) 575.
17. H. SUZUKI, M. KANNO and K. FUKUNAGA, *J. Jap. Inst. Light Met.* **22** (1972) 286.
18. M. OHTA and F. HASHIMOTO, *J. Phys. Soc. Jap.* **19** (1964) 130.
19. Y. TOMITA, K. S. LIU, Y. MURAKAMI and M. MORINAGA, *Trans. JIM* **15** (1974) 99.
20. S. CERESARA and P. FIORINI, *Mater. Sci. Eng.* **10** (1972) 205.
21. M. HANSEN and K. ANDERKO, "Constitution of Binary Alloys" (McGraw-Hill, New York, 1958) p. 149.
22. A. J. DE ARDO and C. J. SIMENSEN, *Metall. Trans.* **A4** (1973) 2413.

Received 13 October 1980 and accepted 26 March 1981.