HARDENING PRECIPITATES AND THEIR PRECURSORS IN 7XXX ALLOYS

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Abstract. Precipitation in an industrial Al-Zn-Mg alloy after conventional two-step heat treatment at 100°C and 150°C has been studied. Transmission electron microscopy (TEM) investigation revealed presence of two types of clusters, GP I and II, in the material after the first step of heat treatment. In the T6 condition η'-precipitates and retained particles of type II were observed. Analysis of the composition of the precipitates after two-step aging, was performed using atom probe field ion microscopy. Distribution of alloying elements in the precipitates and in the surrounding matrix is discussed.

Keywords: Al-Zn-Mg alloy, precipitates, transmission electron microscopy, atom probe field ion microscopy, composition.

1. Introduction

The precipitation process in Al-Zn-Mg based alloys relies upon the available quenched in excess vacancies [1,2]. Most investigators agree that there are two types of precipitate nuclei: solute rich clusters that form during low temperature aging, and vacancy rich clusters that form during quenching. The solute rich clusters dissolve partially or completely during artificial aging, depending upon temperature [3]. The vacancy rich clusters, on the other hand, are stable and act as the nucleation sites for the η' phase and T phase at appropriate aging temperatures [1,4]. The strong age hardening of the alloys is in most cases associated with the disperse precipitation of the metastable η' phase. However, despite extensive research concerning precipitation in these alloys, neither precipitation sequence nor the structure and composition of the different phases are completely clear.

The goal of this investigation was to study precipitation in an industrial Al-Zn-Mg alloy after conventional two-step heat treatment at 100°C and 150°C using transmission electron microscopy (TEM) and atom probe field ion microscopy (APFIM) techniques. Extremely fine precipitates can be difficult to characterize using conventional analytical techniques such as TEM alone. Even if the structure of precipitates can be in this way identified their composition can not be easily obtained. APFIM technique has the ability to determine elemental composition on an extremely fine scale and thus, is ideally suited to problems of this nature. The APFIM analysis is performed by tearing ions off a needle-shaped specimen by applying a high electric field on the specimen surface. The surface atoms of the needle tip are removed and ionized, and the mass-to-charge ratio of the ions is determined by mass spectrometry [5].

The report concerns results from studies of the structures and compositions of the precipitates developed during the applied heat treatment.

2. Experimental

The material was supplied in the as extruded condition by Hydro Raufoss Research Centre. It was solution heat treated at 480°C for 30 min., annealed first at 100°C for 5 h and then at 150 for 6 h. The composition of the material was (wt%): 92.94 Al - 5.40Zn - 1.20Mg - 0.16Zr, with Cu, Fe, Mn, and Si as the remainder.

Thin-foil specimens for TEM were prepared by electropolishing in solution of 10% perchloric acid in 20% glycerol and 70% methanol at -20°C using jet polisher. TEM investigations were performed using JEM 200CX and Zeiss 912 equipped with an omega energy filter.

The sharp needle-shaped specimens for APFIM analysis were produced from 0.5 x 0.5 x 10 mm rods by electropolishing in two steps. In the first step the rods were necked by electropolishing in a 2 mm thick layer of 10% perchloric acid-20% glycerol-70% methanol solution (floating on trichloroethylene), using 20V DC voltage at room temperature. Then the final shape of the specimen was obtained using electropolishing in a 2% perchloric acid in butoxyethanol solution, using 15 V DC at room temperature, until the neck was polished through.

The atom probe instrument used has been described in detail elsewhere [6]. The specimen temperature during experiment was 30 K and the pulsed voltage 20% higher than the applied DC voltage. Concentration profiles were derived from atoms collected from a cylinder of material approximately 20Å in diameter. The profiles were plotted by dividing the data into groups of 50, 75 and 100 ions, obtaining the numbers of solute atoms in each group, and then plotting these numbers versus the total number of atoms collected. APFIM investigation concerns only the material that received two-step heat treatment.

3. Results and discussion

Electron micrographs and diffraction patterns were taken at different stages of the two-step artificial aging treatment. The energy filtered patterns are seen to be very well suited for revealing weak precipitate spots. Two different types of diffraction patterns Fig. 1a-c were obtained from specimens aged for 5 h at 100°C. One kind, which is prominent in the [001] matrix orientation , is interpreted as ordered GP(I) zones on {100} planes. The other type (II) is characterised by a few strong spots, frequently of irregular shape, as seen in Fig. 1 b and c taken along [112] and [111] axes. The strong spots near (311)/2 and (422)/3 Al-positions are close to expected positions of 11.1 and 11.0 reflections from the metastable precipitate phase η' [7] - and also to the strongest reflections from the T'-phase [8] During the subsequent aging at 150°C η' -precipitates with diameter 2-4 nm appears, as revealed by diffraction patterns, and dark field micrographs from the

T6 condition, Fig 2 a-c. Streaks and extra spot indicate considerable disorder in this phase. Spots that indicate some remaining type (II) particles are also seen.

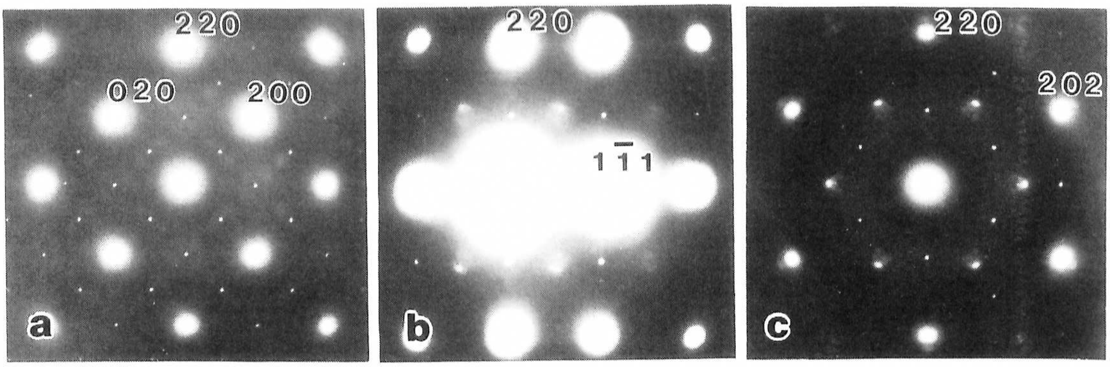

Fig. 1. Electron diffraction patterns after aging at 100°°C for 5h. a: [001], b: [112], c: [111] matrix orientation.

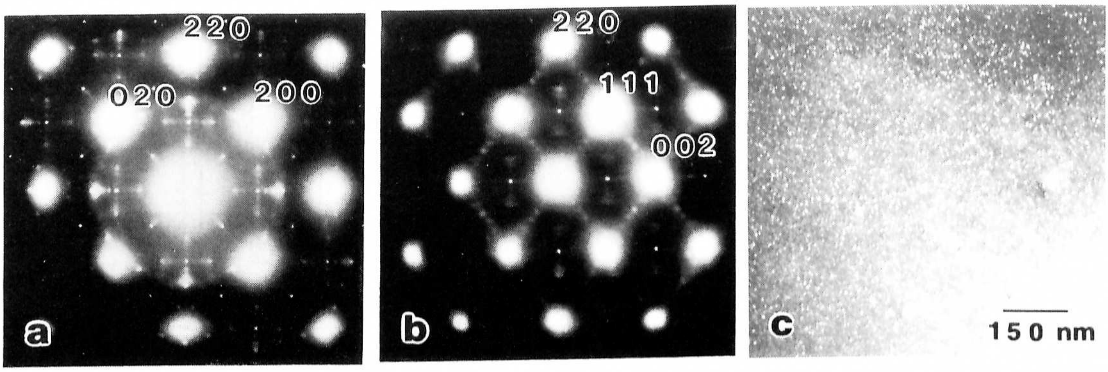

Fig. 2. Diffraction patterns and dark field image after T6-aging (5h at 100°C + 6h at 150°C) .
a : [001], b: [011] , c: dark field in 1/3 (422)

Table 1. Composition of the matrix between the precipitates

	(at%)
Al	98.98±0.06
Mg	0.49±0.04
Si	0.05±0.01
Zn	0.45±0.04
Zr	0.04±0.01
Cu	-

Table 2. Composition of precipitates rich in Zn and Mg

	Zn/Mg=1.58	Zn/Mg=0.94
Al	76.90±0.57	84.82±0.87
Mg	8.84±0.39	7.15±0.63
Si	0.20±0.06	0.41±0.16
Zn	13.96±0.47	7.56±0.64
Zr	0.07±0.04	-
Cu	0.02±0.02	0.06±0.06

APFIM investigation of the material after the two-stage heat treatment revealed existence of small, dark appearing precipitates. The obtained average material composition agreed well with the nominal composition, from which it was concluded that the conditions for APFIM analysis were optimized. The composition of the matrix between the precipitates is presented in Table 1 and shows substantial depletion of Zn and Mg from the matrix.

Fig.3 shows one of the composition profiles containing four precipitates rich in Mg and Zn. The precipitates could be divided into two groups according to their Zn /Mg ratios, being 0.94 and 1.58 respectively. The average number of ions collected from the precipitates with the higher Zn/Mg ratio was 1084, corresponding to the average diameter of 4.5 nm, while only 564 ions were collected from the precipitates with the lower Zn content. The compositions of these two groups of precipitates are presented in Table 2. It should be pointed out that the recorded Al content in the precipitates is higher than the real value. The reason for this is some contribution from the surrounding matrix. APFIM studies indicated also an inhomogenous distribution of the precipitates. The observed number density of precipitates obtained from similar volumes in different specimens was found to vary by an order of magnitude, between $5x10^{24}m^{-3}$ and $2x10^{25}m^{-3}$.

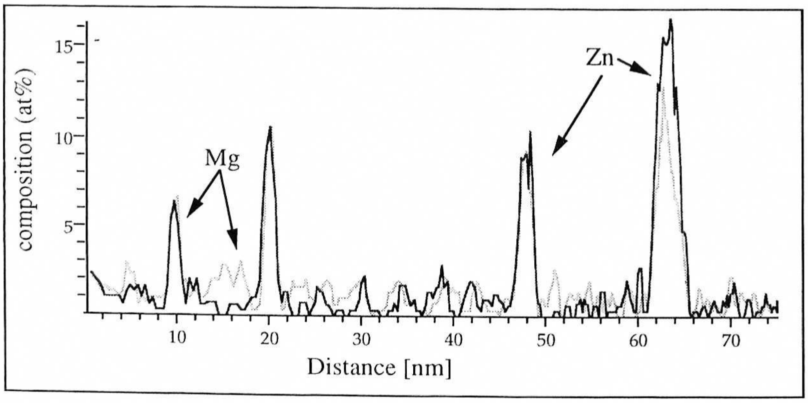

Fig. 3. Composition profile showing presence of four precipitates rich in Zn and Mg.

The two different Zn/Mg contents suggest two different kinds of precipitates or different stages in precipitate development. In the TEM investigations we observed both η' and type II zones at this stage; the diffraction spots indicate that II may be a precursor for the η ' precipitates. The large particles with the higher Zn/Mg rate is therefore assumed to be the fully developed η' phase.

Other atoms were also detected in the precipitates, notably Si, Zr and Cu. The amount Si is significantly higher than in the surrounding matrix, which indicates this element to participate actively in the precipitation (see fig 4). Small amounts of Zr and Cu were incorporated in some precipitates. Zirconium is introduced in the alloy as a grain refiner and recrystalization inhibitor through precipitation at high temperature of the metastable cubic dispersoid Al_3Zr [9,10], prior to the aging treatment. Recent studies have shown that zirconium influences early stages of aging in

Al-Zn-Mg alloys [11] by slowing down the nucleation and growth of GP zones. A possible explanation for this effect is that Zr remaining in solid solution decreases the free vacancy supersaturation during quenching. The amount of Zr found in the precipitates is not significantly higher than in the matrix (Table 1) indicating that Zr is not readily incorporated into the precipitates.

In addition to the Mg-Zn precipitates, some small clusters of just a few Mg -atoms were observed, Fig. 5. Magnesium is known to have high binding energy with vacancies. Resistivity measurements of Al-Mg alloys indicate clustering of Mg at low temperatures (-30°C) [12]. Besides, thermal analysis of these alloys reveals an endothermic peak at about 70°C that has been attributed to the dissolution of the clusters of Mg atoms [13]. It is therefore interesting to note that this type of clusters is existing in Al-Zn-Mg material even after prolonged heat treatment at 150°C.

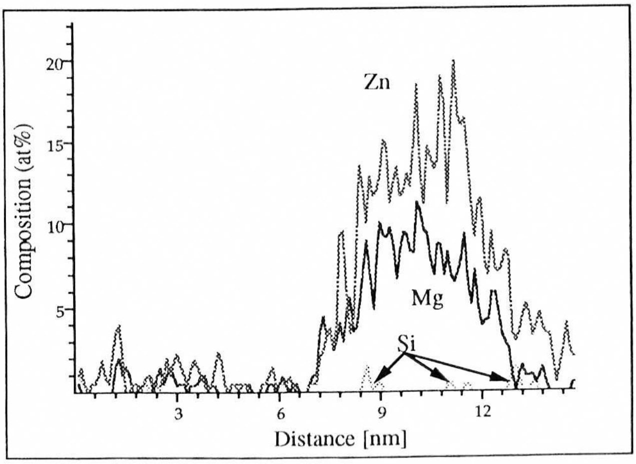

Fig. 4. Composition profile through one precipitate. Si is incorporated to the Zn- and Mg-rich phase.

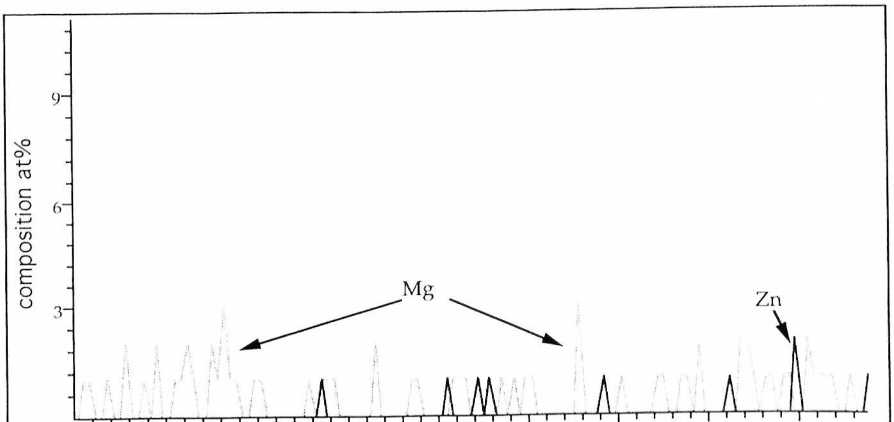

Fig. 5. Concentration profile revealing existence of small Mg clusters.

4. Conclusions

- Two types of clusters, GP(I) and GP(II), were present in the material after the first step of heat treatment .
- After conventional two-step aging treatment, TEM investigation reveals presence of η'-precipitates and retained particles of type II .
- APFIM studies confirm result obtained by TEM after two-step aging treatment and show that the precipitates can be divided into two groups depending on their composition : one with Zn/Mg ratio of 0.94 and the other with Zn/Mg ratio of 1.58.
- Si is incorporated to the precipitates.
- Mg clusters were also found in the material.

5. References

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