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# TEM observation of a Cu–Mg age-hardenable alloy

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The precipitation processes in Cu–Be, Cu–Co, Cu–Fe alloys have been thoroughly investigated; however, much less attention has been paid to studying the Cu–Mg system. In this work the decomposition of Cu–3.5 wt% Mg alloy during ageing was investigated by means of transmission electron microscopy (TEM). The microstructure of Cu–3.5 wt% Mg alloy aged at 340° C is characterized by the presence of fine dispersed coherent precipitates. On continued ageing the coherent precipitates disappear and a new transition phase with oblate octahedron morphology grows. At temperatures above 340° C the equilibrium phase is formed by discontinuous precipitation. Ageing of Cu–3.5 wt% Mg alloy at temperatures above 450° C results in the formation of the equilibrium $Cu_2Mg$ phase.

## 1. Introduction

The mechanism by which a supersaturated solid solution decomposes to give GP zones, intermediate and final precipitates was thoroughly investigated for several Cu–alloys (Cu–Be [1], Cu–Co [2], Cu–Fe [3]). Much less attention has been paid to studying the Cu–Mg system [4–6]. Recently Tsubakino and Nozato [7] observed discontinuous precipitation in Cu–Mg alloys. The phase diagram of the Cu–Mg system shows that the Cu–Mg alloys on the Cu-rich side of the system might be suitable for precipitation hardening [8]. Age hardening of Cu–Mg alloys was first observed by Dahl [4].

Usually in age hardenable systems the electrical conductivity was found to decrease during the early stages of precipitation rather than to increase [9]. In contrast to this Dahl [4] has shown that the electrical conductivity accompanying the precipitation process in Cu–3.5 wt % Mg alloy increases simultaneously with the increase in hardness. This feature of the Cu–3.5 wt % Mg alloy makes the investigation of the precipitation process in such a system to be of interest. The Cu–3.5 wt % Mg alloy is beyond the maximum solubility of magnesium in copper [10] and hence it consists of two phases. Nevertheless, it exhibited the highest hardness which did not decrease after extended ageing time [4]. In this paper the electron-microscopic study of precipitation in the Cu–3.5 wt % Mg is reported; the study is related to the processes occurring upon ageing in the solid solution phase only.

## 2. Experimental details

Mg (99.95% purity) and Cu (99.95%+ purity) were used to prepare the Cu–3.5 wt % Mg alloy by melting in a graphite crucible. To minimize the losses of magnesium the copper the magnesium were sliced to discs and then they were arranged alternately in a sandwich form and placed in the crucible.

The melting of the constituents of the alloy in the proper ratio was performed in a vacuum furnace in an ultra high purity argon ambient at or somewhat above atmospheric pressure. Before the melting, the furnace had been repeatedly evacuated to $10^{-5}$ torr and purged with argon. The ingots of 25 mm in diameter and 25 mm long were homogenized for 70 h at 600° C in a protective argon atmosphere and the degree of homogenization was checked by micro-probe analyser. Spectroscopic analysis of the alloy showed traces of Fe and Ni. Chemical analysis confirmed that the composition of the alloy was actually Cu–3.5 wt % Mg. The solution heat treatment of the specimens was performed at 700° C in argon protective atmosphere. Drop quenching into iced brine was achieved by passing electrical current through the wire on which a basket containing the specimens was hung. Ageing of the as-quenched specimens was carried out in evacuated quartz capsules at temperatures in the range from 300 to 550° C.

Specimens for TEM investigation were prepared in a standard TENUPOL-twin jet electropolishing unit containing a solution of 30% nitric acid and 70% methanol chilled to −40° C. In some cases final thinning of the foils was performed by ion milling. A JEOL-200B electron microscope operating at 200 kV was used to examine the structures.

## 3. Results and discussion

In accordance with the structure and morphology of the precipitates observed in the electron microscope it is convenient to arrange the results in the following order of the specimen treatment:

(a) as-quenched specimens
(b) specimens quenched and aged at 340° C
(c) specimens quenched and aged above 340° C in the range of 340°–450° C
(d) specimens quenched and aged above 450° C.

As-quenched specimens show the presence of fine

  

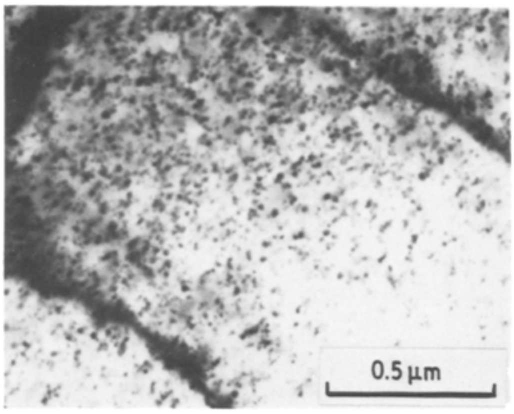


*Figure 1* Bright field electron micrograph of an as-quenched Cu–3.5 wt % Mg alloy showing spherical precipitates.

precipitates (about 12.5 nm in diameter) with spherical morphology, homogeneously distributed in the matrix. Apparently, the quench rate was not sufficient to avoid the emergence of these precipitates. The uniform distribution of these precipitates is shown in Fig. 1. The electron diffraction patterns taken from this area (Figs 2a and b) reveal diffraction spots in addition to the matrix reflections. Dark field imaging experiments have shown that these spots are correlated with the spherical particles seen in Fig. 1. The indexed schematic representation of the diffraction patterns is shown in Fig. 3. The structure of these spherical precipitates was interpreted in terms of hexagonal $DO_{19}$ ordered structure with $a = 0.346$ nm and $c = 0.4214$ nm under the assumption that it corresponds to a hypothetical $Cu_3Mg$ phase. This assumption is supported by calculation of the intensity ratio of the (0 2 . 0) and (0 1 . 0) reflections for $Cu_3Mg$ phase which agrees well with the intensities observed in the diffraction pattern i.e. 0 2 . 0) reflection is much stronger than (0 1 . 0) (Fig. 2). It should be noted that similar intensity ratio for (0 2 . 0) and (0 1 . 0) reflections was observed in the case of the ordered $InTi_3$ phase [11] with $DO_{19}$ structure.

*In situ* heating experiments in the hot-stage of the TEM have shown that the reflections associated with the spherical particles disappear during the heating, suggesting the possibility that these particles represent a metastable condition.

Ageing of quenched specimens at 340° C produced fine-scale clustering of coherent precipitates which are homogeneously distributed through the matrix as seen in Fig. 4. This electron micrograph, taken under two-beam dynamical conditions, exhibits the characteristic strain-field contrast usually associated with coherent particles. In our opinion the character of the contrast in Fig. 4 is such that it might be interpreted as a result of non-spherical strain-field rather than a result of a spherical strain-field. Comparing the image in Fig. 4 to the experimental observations of plate precipitates in the Cu–Be alloy obtained by Phillips and Tanner [12], we suggested that in our case at earlier stages of ageing at 340° C the coherent precipitates have a flat-plate form too. The marked "alignment" of the strain field in [0 2 0] direction (Fig. 4) also indicates that this suggestion is fairly correct. The plate shape of the coherent precipitates is presumably due to the large atomic size difference between Mg (0.16 nm) and Cu (0.128 nm). As it was shown by Thomas [13] in such cases the flat-shaped precipitates provide for the minimization of the strain energy.

On continued ageing at 340° C the strain field contrast eventually disappears and a new structure grows having an oblate octahedron morphology (Fig. 5). Indexed selected area diffraction patterns taken from a region in Fig. 5 are shown in Figs 6a and b. The symbols "M" and "p" in Fig. 6 are related to matrix and precipitate reflections, respectively. The symbol "d" in Fig. 6b is associated with reflections caused by double diffraction. Indexing of the precipitate's reflections was made in terms of orthorhombic unit cell with parameters $a = 0.404$ nm, $b = 0.4215$ nm and $c = 0.3105$ nm. The precipitates could not be identified neither with equilibrium phases existing in the Cu–Mg system nor with magnesium oxide (which possibly might occur if internal oxidation takes place). Therefore, it might be that these precipitates represent a transition phase obtained at low temperature ageing. At higher ageing temperatures in the range of 340 to 450° C discontinuous and continuous precipitation was observed (Fig. 7). Discontinuous precipitation nucleates at twin and grain boundaries and grows into the grain interiors as long plates with a regular distance between them. This observation is in accordance with results of Tsubakino *et al.* [7] and Böhm [5].

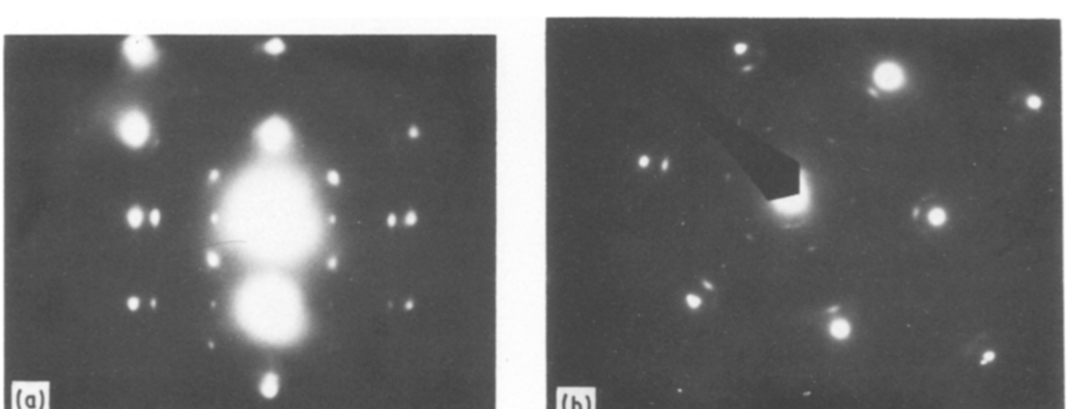


*Figure 2* Selected area diffraction patterns taken from the area in Fig. 1 (a) matrix zone axis [1 1 1] (b) matrix zone axis [$\bar{1}$ 1 2].

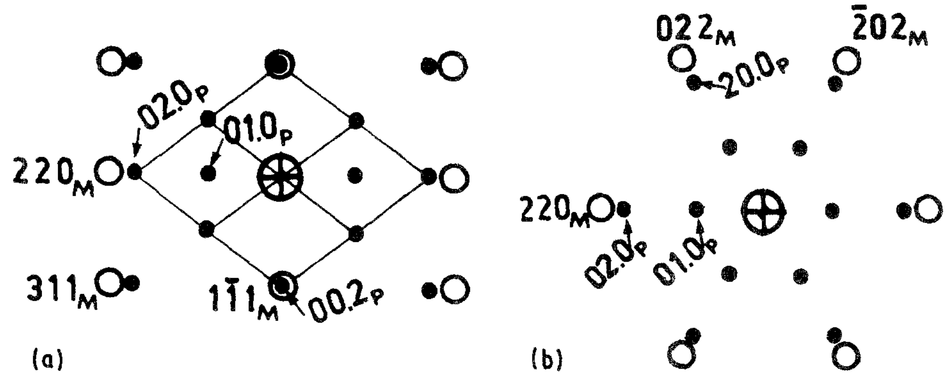


*Figure 3* Indexed schematic diagram for the electron diffraction patterns represented (a) in Fig. 2a (b) in Fig. 2b. ○ – matrix, ● – precipitate. Reflections marked by "M" and "p" are related to the matrix and the precipitate, respectively.

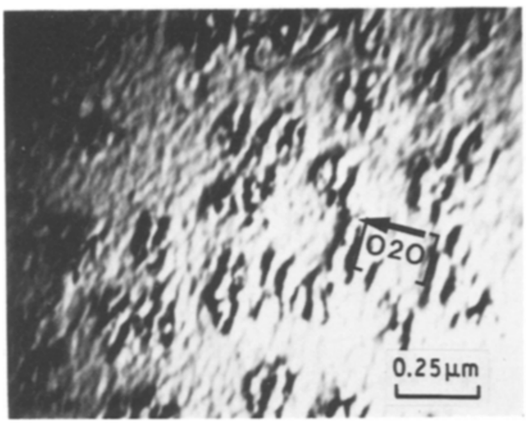


*Figure 4* Electron micrograph demonstrating appearance of coherent precipitates. Alloy aged at 340° C for 8 h.

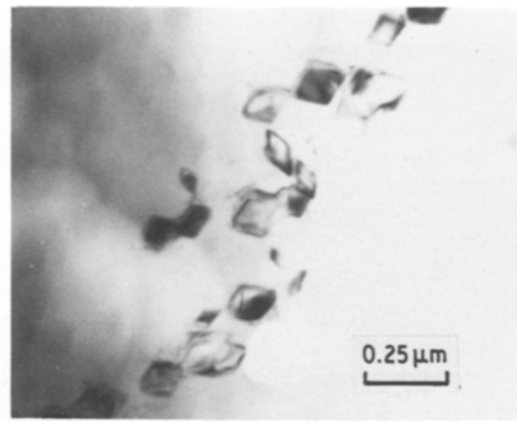


*Figure 5* Oblate octahedron-like precipitates obtained at relatively low ageing temperatures (340° C, 122 h).

Ageing at temperatures above 450° C results in the appearance of the equilibrium FCC-phase of $Cu_2Mg$ ($a$ = 0.704 nm). Depending on duration of ageing two different morphologies of the equilibrium precipitates have been observed: plate-shaped precipitates (Fig. 8) formed after a relatively short period of ageing and thick particles of hexagonal shape (Fig. 9) which grew in the matrix as ageing proceeded. The orientation relationships between the matrix (M) and $Cu_2Mg$ precipitate (p) determined from analysing the electron diffraction pattern were:

$$(1\,1\,\bar{1})_M \parallel (1\,1\,1)_p \quad [1\,\bar{1}\,0] \parallel [\bar{1}\,1\,0]_p$$

(for the plate shape precipitates)

and

$$(0\,0\,1)_M \parallel (\bar{2}\,1\,2)_p \quad [0\,1\,0]_M \parallel [\bar{1}\,2\,\bar{2}]_p$$

(for the hexagonal shape precipitates)

## 4. Conclusions

1. Fine metastable precipitates with $DO_{19}$-type structure ($a$ = 0.346 nm, $c$ = 0.4214 nm) are formed in the as-quenched Cu–3.5 wt % Mg alloy. These precipitates vanish during heating.

2. Ageing of Cu–3.5 wt % Mg alloy at 340° C results in fine-scale clustering of coherent precipitates with flat-plate form. On continued ageing at 340° C these coherent particles disappear and a new

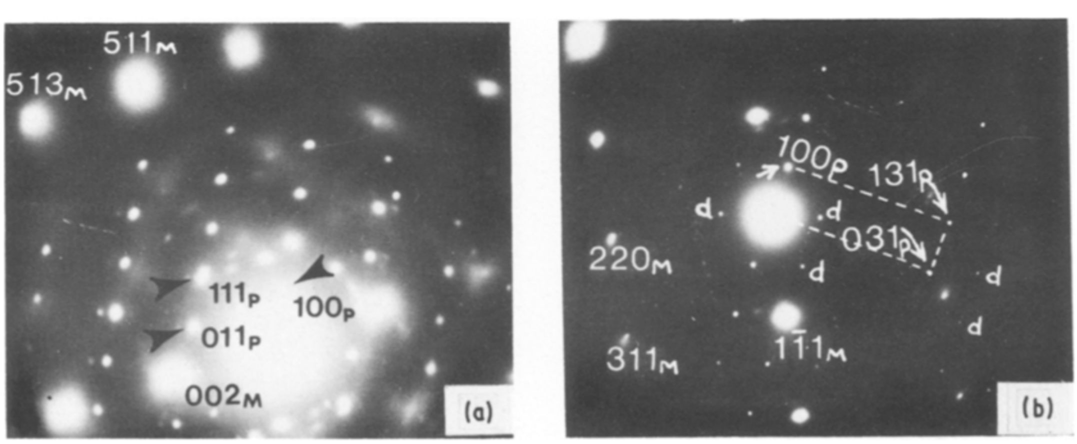


*Figure 6* Indexed selected area diffraction patterns taken from the region in Fig. 5. (a) Zone axis [1 $\bar{5}$ 0], (b) zone axis [$\bar{1}$ 1 2]. The symbols "M" and "p" are related to the matrix and the precipitate reflections, respectively. The symbol "d" is associated with reflections caused by double diffraction.

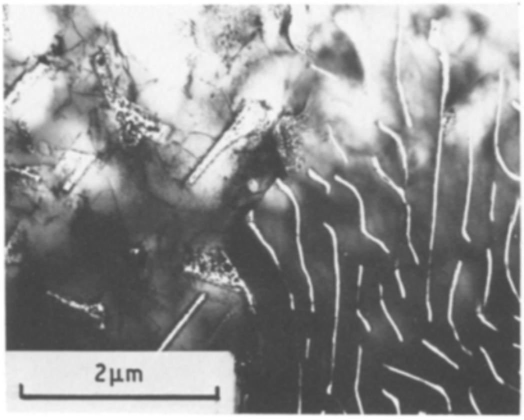


*Figure 7* Discontinuous precipitation in a specimen aged at 450° C for 8 h.

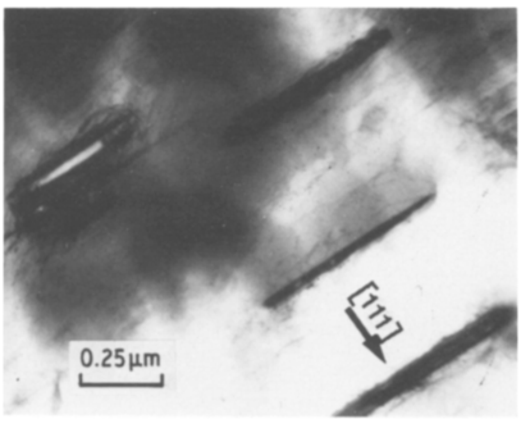


*Figure 8* Plate-shaped equilibrium precipitates in Cu–3.5 wt % Mg alloy.

intermediate phase with orthorhombic structure ($a$ = 0.404 nm, $b$ = 0.4215 nm, $c$ = 0.3105 nm) grows.

3. Ageing of Cu–3.5 wt % Mg alloy at temperature above 450° C results in the formation of the equilibrium $Cu_2Mg$-phase.

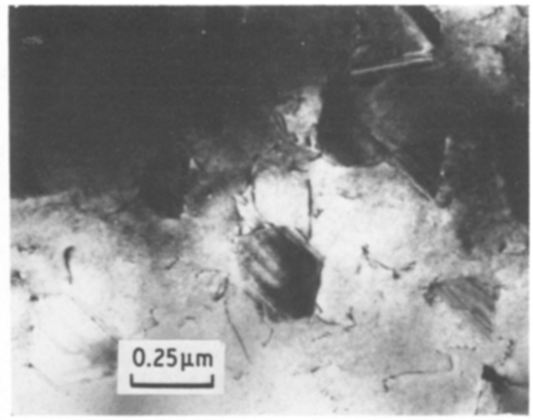


*Figure 9* Thick equilibrium particles of hexagonal shape (the alloy was aged at 550° C for 30 min).

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