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A STUDY OF THE STRUCTURAL PRECIPITATION IN THE Al-Mg-Si-Cu SYSTEM

L. Sagalowicz[1], G. Hug[1], D. Bechet[2], P. Sainfort[2], G. Lapasset[3].
1. LEM, ONERA, B.P.72, 92322 Châtillon CEDEX
2. PECHINEY C.R.V., B.P.27, 38340 Voreppe
3. ONERA B.P.72, 92322 Châtillon CEDEX

Abstract

The structural precipitation taking place within three 6xxx alloys was studied by Transmission Electron Microscopy. These alloys were aged to peak strength or to an overaged condition. At peak strength, two main types of precipitates are present. The first one exhibits a needle shape with its length lying along $<001>_{Al}$. Its structure appears to be compatible with a monoclinic structure. This precipitate, which is present in the three alloys, is likely to be β'', a precursor of β-Mg_2Si stable phase. The second type has a lath shape; it is observed only in the alloys containing copper. This precipitate may be a precursor of the λ (or Q) quaternary phase. After prolonged ageing, the density of the β'' precipitates significantly decreases while other precipitates may appear; the nature of these precipitates depends on the alloy composition. At the same time, precipitates of the second type grow slightly and their morphology remain unchanged.

Introduction

The 6xxx Al alloys are industrially used in a very broad range of industrial applications (earth transportation, building application) and some of them may be candidates for use in the aeronautical industry. These alloys are strengthened by structural precipitation. Thus the final thermal treatment consists in a solution heat treatment followed by a quench and an artificial ageing at a temperature close to 450 K. It is known that during ageing treatment of Al-Mg_2Si balanced alloys, the following sequence of precipitation takes place [1,2] :

$$\beta''_{\text{needle}} \text{-->} \beta'_{\text{rods}} \text{-->} \beta_{\text{Mg2Si}}$$

The equilibrium phase β has a face centred cubic structure with a=0.642 nm. The structure of the β' as determined by electron diffraction [2,3] would be hexagonal with a=0.705 nm, c=0.405 nm and the following orientation relationship : $[0001]_p // [001]_{Al}$ and $[2\bar{1}\bar{1}0]_p // [110]_{Al}$. The same crystal structure was also observed by high resolution electron microscopy [4], but various orientation relationships were present. The composition of the β' phase was determined by X-ray emission spectroscopy to be $Mg_{0.44}Si$ [3]. All these observations were made for overaged conditions. Two monoclinic structures were proposed for β" with the following lattice parameters: a=b=0.616 nm, c=0.71 nm, γ=82° [5,6]; and a=0.3 nm, b=0.33 nm, c=0.405 nm, γ=70° [3].

Compared to the balanced alloy, the alloys containing an excess of Si are known to have better mechanical properties. The effect of Si is attributed to the earlier formation of Si rich clusters [3,7]. For overaged alloys, the microstructure of precipitation is very different since precipitates having three different crystal structures were identified [8].

An addition of copper leads also to a strong hardening. Tamizifar and Lorimer [9] observed in overaged alloys that the precipitate cross section is rectangular when copper is added while it is circular without. They would contain copper and the total volume fraction of precipitates is increased. Sakuraï and Eto [10] proposed that the addition of copper results in the formation of the θ' phase (Al_2Cu), although the β' or β" phase is still present; furthermore, the increase of density of the last one would be responsible for better mechanical properties.

To summarize, it is now well known that Si or Cu additions to the quasi-binary Al-Mg_2Si alloys are beneficial for mechanical properties, but the microstructural changes involved in the corresponding hardening mechanism are not well understood. This study is aimed at a better understanding of these phenomena, especially for peak-aged alloys.

Experimental Procedure

Three alloys of different compositions are studied : 0.65% Si - 1% Mg - 0.25% Cu (alloy A), 1.1% Si - 1% Mg - 0.01% Cu (alloy B), and 0.65% Si - 0.87% Mg - 1% Cu (alloy C). The first one corresponds to a balanced Al-Mg_2Si alloy with a small Cu addition, the second one contains an excess of Si, the third one is close to the first one but it has a higher Cu content. These alloys were cast and processed by PECHINEY CRV. Finally they were solutionized, water-quenched and then aged at 458 K for 6 hours (peak-aged temper) and 600 hours (overaged temper). Thin foils were examined in a Philips CM20 equipped with twin lenses (Cs=2.8mm, point resolution 3.3Å) and operating at 160 kV. The techniques used were: high resolution transmission electron microscopy (HRTEM) and conventional transmission electron microscopy in the bright field and dark field modes and in the selected area electron diffraction (SAED) mode.

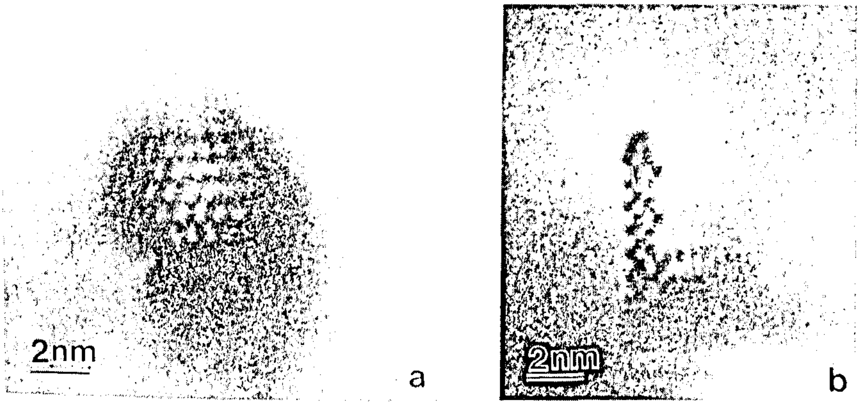

Figure 1: High resolution images of precipitates at peak-strength
a : precipitate β'' present in all the alloys (image obtained in the alloy A)
b : precipitate L present in the alloys containing copper (image obtained in the alloy C)

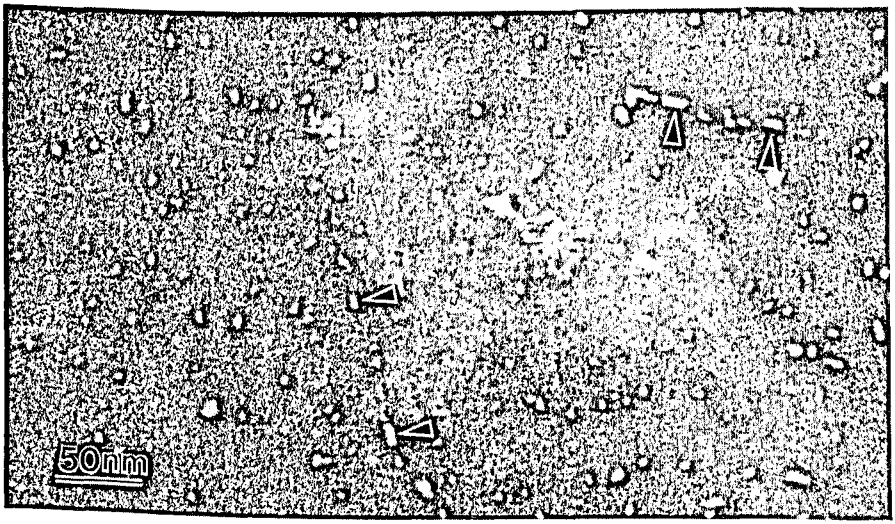

Figure 2 : Dark field image of the alloy B at peak strength. The objective aperture was centered on the 110 forbidden reflection of aluminium. The precipitate β''_d is present on dislocations and is arrowed.

Experimental Results

Precipitation in the peak aged alloys (6 hours at 458 K)

The first type of precipitate is present in all the alloys examined in this study. It has a needle shape with its length along $<001>_{Al}$, the section normal to the needle axis is almost circular (Figure 1a). The mean diameter is 2.5 nm and while its length varies between 10 and 50 nm. When the beam direction is parallel to $[001]_{Al}$, the motif evidenced on the lattice image may be interpreted as monoclinic with $a \approx 0.65$ nm, $b \approx 0.76$ nm and $\gamma \approx 70°$ (Figure 1a).This precipitate is likely to be β", a precursor of β–Mg_2Si. Most of the precipitates were found to have $[100]_{\beta''}$ lying at 10° from $<100]_{Al}$, and the intersections between the interface and the $(001)_{Al}$ plane are: $[100]_{\beta''}$, $[010]_{\beta''}$, and $[110]_{\beta''}$. On the [001] zone axis SAED, streaks parallel to [100] and [010] directions and distant of 0.405 nm^{-1} are present. This would indicate that the third axis is equal to c=0.405 nm which is the same parameter as that of aluminium. The needles lying perpendicular to the beam direction exhibit a contrast arising from coherency strains.

The second type of precipitates is present in the alloys containing copper (Figure 1b); it is referred as the L precipitate. Its density is higher in the alloy C than in the alloy A indicating that it is very likely to contain copper. This precipitate has a morphology of a lath with its sides parallel to the <001> directions of the matrix ; its dimensions are about : 0.8 x 5x 50 nm. When the length of the lath is parallel to the beam (Figure 1b), a rectangular centred arrangement is visible with $a \approx 0.8$ nm and $b \approx 0.7$ nm. The orientation relationship is as follows : $[100]_L$ // $[100]_{Al}$ and $[010]_L$//$[010]_{Al}$.

Another type of precipitates with a different shape from β" is observed in the alloy B and mainly on dislocations (Figure 2). It is referred to as β''_d and it precipitates with a lath morphology (Figure 2). This lath has its length parallel to $<001>_{Al}$. In the $(001)_{Al}$ plane, the two sides of laths parallel to the electron beam are at 12° from $<100>_{Al}$. It was not possible to obtain lattice images from this type of precipitates.

Precipitation in the overaged alloys (600 hours at 458 K)

In alloy A, a precipitate is observed which is referred to as β'. It has a rod-like morphology with its length along $<001>_{Al}$; perpendicular to its length, its cross section looks like an ellipse with its long axis along $<110>_{Al}$. Its mean diameter is about 10 nm. On the high resolution image (Figure 3a), the motif is hexagonal with $a \approx 0.7$ nm and $[11\bar{2}0]_{\beta'}$ (short axis of the ellipse) // $<110>_{Al}$. This is consistent with the structure proposed by Jacobs [2] in his electron diffraction study. This author as well as Matsuda et al. [4] have observed this phase in Al-Mg_2Si balanced alloys without copper.

In alloy B, a precipitate referred to as M is present. It has a lath morphology with its length along $<001>_{Al}$. On the high resolution image of the Figure 3b, the motif appears to be

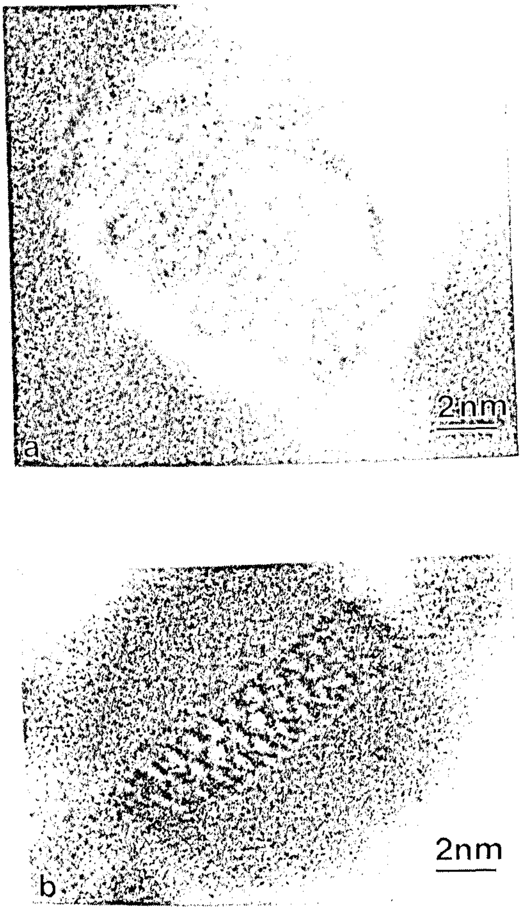

Figure 3: High resolution images of precipitates present in the overaged alloys
a : precipitate β' present in the alloy A
b : precipitate M present in the alloy B

hexagonal with a≈1.0 nm . Such a motif has already been observed in an alloy containing also an excess of silicon by means of HRTEM and microbeam electron diffraction [8].

Finally the precipitate L is observed in the alloys A and C. It keeps the same morphology than the one observed in the peak aged alloys. But it has become larger and its dimensions are now: 2 x8 x50 nm.

Evolution of the precipitation

In the peak-aged alloy A, the phases β" and L are present . The density of β" is approximately ten times higher than the density of L. During overaging, it seems that the density of L precipitates increases while β" disappears and β' forms.

In alloy B at peak strength, the phases β" and β''_d are present . The density of β" is much higher than that of β''_d. After a prolonged ageing, only the precipitate M is present.

In alloy C at peak strength, the phases β" and L are present (Figure 4). The density of β" is about three times higher than that of L. After a prolonged ageing, only the L precipitate remains visible (Figure 5).

Discussion

In the present study, precipitates exhibiting various morphologies were evidenced. But this discussion will concern the two main types of precipitates present at peak strength: the so-called β" and L phases.

It should be pointed out that the lattice image interpretation must be done with great care. First, since the atomic structure is not known, no image simulation can be performed. Secondly, because of the small size of these precipitates (less than 3 nm in diameter) some artefacts are possible. The precipitates may be elastically strained. It may also happen that during preparation of the foil, the edge and the centre of the precipitates are not thinned in the same way. This last effect would result in changing the position of the bright dots seen on high resolution images.

We have called β" the phase which appears in all the alloys at peak strength, since in the balanced alloy A, it is present in the process of precipitation before β'. Moreover, the monoclinic motif visible on a high resolution image (a≈0.65nm, b≈0.76nm, γ=70°) looks like a distorted motif of the hexagonal phase β' (a=7Å). It must also be added that if the angle γ remains constant when going from one precipitate to another, the a and b lattice parameters can vary broadly (a≈0.65±0.04nm, b≈0.76±0.02nm). Despite the low accuracy of length measurements, these variations are thought to be partly due to strain within the precipitates.

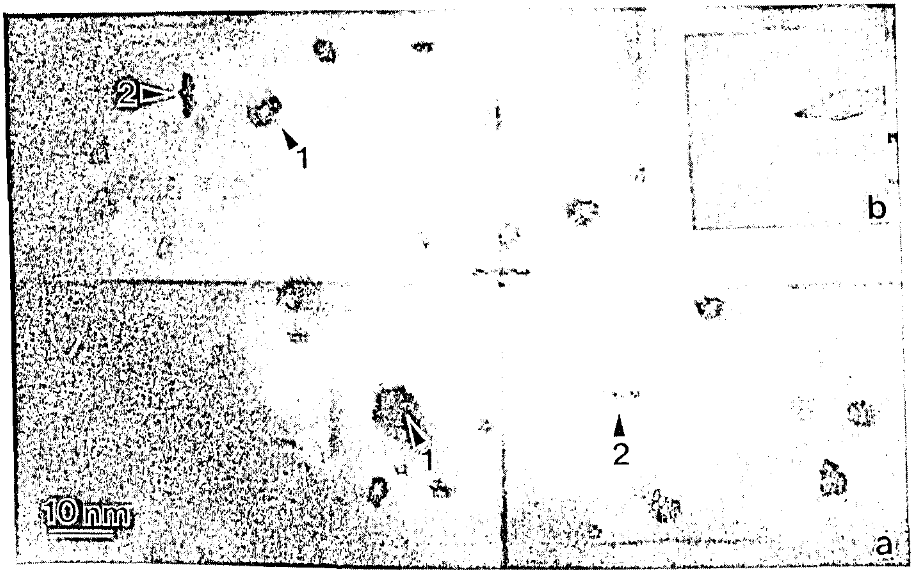

Figure 4 : alloy C at peak strength

a : High resolution image, precipitates β" are labelled 1 and precipitates L are labelled 2

b : Selected area diffraction pattern

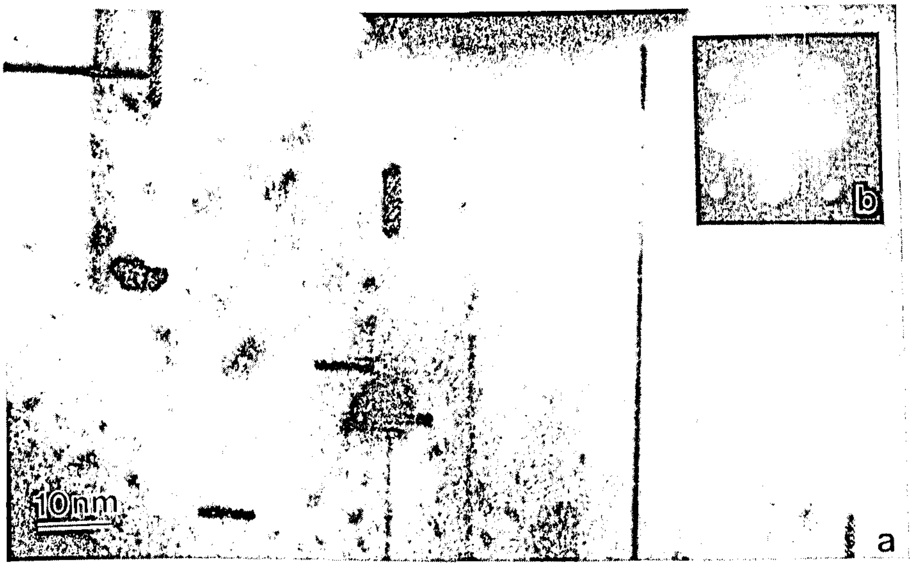

Figure 5 : alloy C in an overaged condition

a : High resolution image, notice that only L precipitates are present

b : Selected area diffraction pattern

Several authors [9,10] have reported the presence of another kind of precipitates when copper is present in the alloy. Sakuraï and Eto [10] suggested that the phase θ' (Al_2Cu) is present. But a quaternary phase (called λ or Q) belonging to the Al-Mg-Si-Cu system has been shown to be stable at 733 K [11] ; its approximate composition is : $Al_5Cu_2Mg_8Si_7$ (which is not the case for θ) for compositions close to the one of the alloy C. It has also been observed in an alloy annealed at 673 K [12], and in alloy 2214 (similar composition to alloy C but with a copper content closed to 4%) at peak strength [13]. In alloy C, the comparison of the precipitation between the peak-aged temper and the overaged temper indicates that the L precipitates seem to have grown at the expense of the β" phase. This strongly suggests that the L precipitate contains Mg and Si. On the other hand, the density of this precipitate, as estimated in the three alloys of this study, increases with the Cu content of the alloy. Therefore the L phase is very likely to be a precursor of λ. Chemical Analysis of this precipitate is still lacking to confirm this assumption.

Conclusion

In this study, for the two conditions of ageing, at least five different kinds of precipitates were identified. At peak strength, two main types of precipitates were observed. The first one is present with a large density in all the alloys and exhibits a needle shape with its length lying along $<001>_{Al}$. On a high resolution image, its structure appears to be monoclinic and is proposed to be β", a precursor of Mg_2Si-β . The second one is present only in the alloy containing copper and is likely to be a precursor of the quaternary phase (Al, Mg, Si and Cu) λ. This last precipitate has a lath morphology. After long ageing, its proportion strongly increases at the expense of β' type phase.

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