EFFECT OF THE PRECIPITATION ON THE THERMOELECTRIC POWER OF Al-Mg-Si ALLOYS : APPLICATION TO THE STUDY OF THE PRECIPITATION KINETICS

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ABSTRACT   The thermoelectric power (TEP) of a 6061 alloy was measured during isothermal ageings performed in the temperature range 100-500°C. A correlation was established between the TEP evolutions and the precipitation kinetics of the various metastable phases, using additional TEM observations and resistivity measurements. It was demonstrated that it is possible to associate with each precipitation sequence a typical TEP evolution, owing to the intrinsic effect of each precipitate and to assess the residual concentration of the alloying elements in the final equilibrium state of the precipitation.

Keywords : *precipitation, thermoelectric power, ageing, Al-Mg-Si alloy*

1. Introduction

The measurement of the thermoelectric power (TEP) is one of the techniques which may be used to follow precipitation kinetics in an alloy. However, this technique is not commonly used, due probably to the difficulties which are sometimes encountered for the interpretation of the observed evolutions. The aim of this paper is to describe the qualitative or quantitative informations which can be brought by this technique in the study of the precipitation in Al-Mg-Si alloys.

2. Materials and experimental procedure

The Al-Mg-Si alloy used in this study is a 6061 alloy (composition : 1 wt% Mg, 0,6 wt% Si, 0,2 wt% Fe, 0,25 wt % Cu and 0,17 wt% Cr). For this alloy, the decomposition of the solid solution obtained after quenching from the solutionizing temperature is generally believed to be as follows : supersaturated solid solution ---> vacancy-rich zones ---> β'' needle-shaped coherent precipitates---> β' rod-shaped semi-coherent precipitates ---> β incoherent precipitates. The age-hardening response of the alloy was studied after a 2 hour solutionizing treatment at 535°C, followed by a rapid water-quench. The ageing temperatures were chosen between 100 and 500°C. The precipitation kinetics were followed by measuring the TEP of the alloy at room temperature after different isothermal ageing times. The principle of the method was described in previous papers [1]. The TEP value of the as-quenched alloy (ΔS_0) being taken as a reference, the kinetics were characterized by the evolution of the difference : $\Delta(\Delta S) = \Delta S_t - \Delta S_0$, where ΔS_t is the TEP value after a time t at the ageing temperature. This evolution is the consequence of two effects : (i) a solute effect resulting from the influence of each alloying element on the TEP, (ii) an intrinsic effect of the metastable precipitates formed during ageing, the magnitude and the sign of which must be determined.

Additional resistivity measurements were also conducted at room temperature with a Sigmatest D 2.068 for comparison.

Lastly, in order to establish a correlation between the TEP evolutions and the microstructural changes occuring during ageing, transmission electron microscopy (TEM) observations were performed on a JEOL-200 CX apparatus.

3. Results

The analysis of the TEP kinetics obtained between 100 and 500°C allowed us to distinguish three temperature domains, to which different precipitation sequences were attributed.

3.1 Precipitation sequence at high temperature (between 325°C and 500°C)

Fig.1.a represents the TEP kinetics obtained in this temperature range. At 450°C and 500°C, these kinetics are characterized by a TEP decrease followed by a stabilization and are associated with the direct precipitation of the β phase. At lower temperature, a two stage decrease is observed before the final stabilization. TEM observations, performed on specimens aged for 2 min and 2 hours at 400°C (Fig.1.b and 1.c), showed that between 350°C and 400°C, the initial TEP decrease reflects the formation of β' precipitates, having a hexagonal structure close to that found by Jacobs [2] and that the final decrease corresponds to the precipitation of the β phase.

Assuming the validity of the Gorter-Nordheim (GN) law (i.e., that (i) the TEP variations are only due to a solid solution effect and (ii) that the phonon-drag component of TEP is negligible, which may be the case in our measurement conditions for an aluminium matrix), we can write :

$$(\rho_0 \Delta S_0 - \rho_t \Delta S_t)_{NG} = \alpha_{Mg}.\Delta S_{Mg}.\Delta C_{Mg} + \alpha_{Si}.\Delta S_{Si}.\Delta C_{Si} \qquad (1)$$

In this equation, ρ_0, ρ_t, ΔS_0 and ΔS_t are respectively the initial and current value of the resistivity and of the TEP value; α_{Mg}, α_{Si}, ΔS_{Mg} and ΔS_{Si} are the specific resistivity and thermoelectric power of the magnesium and silicon atoms in the pure solvent at 20°C and ΔC_{Mg} and ΔC_{Si} are the variation of the Mg and Si content in solid solution during ageing (in wt %). Assuming also, in a first approach, that in our 6061 alloy, the solute balance is controlled by the reversible dissolution/precipitation reaction : $2\ Mg(ss) + Si\ (ss) \Leftrightarrow Mg_2Si$ (2) , the difference $(\rho_0 \Delta S_0 - \rho_t \Delta S_t)$ can be directly related to (ΔC_{Mg}), noted as $(\Delta C_{Mg})_{TEP}$. Indeed, relation (2) implies: $\Delta C_{Si} = (\Delta C_{Mg}$ $*M_{Si})/(2*M_{Mg})$ where M_{Mg} and M_{Si} are the atomic weight of Mg and Si. From the experimental evaluation of $(\rho_0 \Delta S_0 - \rho_t \Delta S_t)_{exp}$, $(\Delta C_{Mg})_{TEP}$ can thus be assessed. Furthermore, using the relation between ΔC_{Si} and ΔC_{Mg}, it is also possible to deduce the quantity (ΔC_{Mg}), here noted as $(\Delta C_{Mg})_\rho$ from the resistivity variations $(\Delta\rho)$, since we have the following relation :

$$\Delta\rho = \rho_0 - \rho_t = \alpha_{Mg}.\Delta C_{Mg} + \alpha_{Si}.\Delta C_{Si} - \alpha'_{Mg}.\Delta C_{Mg} - \alpha'_{Si}.\Delta C_{Si}, \qquad (3)$$

, where α'_{Mg} and α'_{Si} are respectively the specific resistivity of the elements (Mg and Si) out of solution at 20°C.

These two different evaluations of ΔC_{Mg} were found to coincide at 450°C at each ageing time and at 400°C, in the final stage of the precipitation (Fig.1.d). As a conclusion, during the whole precipitation kinetic at 450°C and in the last stage of precipitation at 400°C, the coarse β incoherent precipitates which form have no effect on the TEP and GN law is valid. This is confirmed by Fig.1.e where we plotted the evolution of the experimental values of $(\rho_0 \Delta S_0 - \rho_t \Delta S_t)_{exp}$ during an ageing conducted at 450°C and that of the difference $(\rho_0 \Delta S_0 - \rho_t \Delta S_t)_{NG}$ calculated with relation (1) from the values of $(\Delta C_{Mg})_\rho$ deduced from the resistivity measurements, assuming that they give the real variation of the Mg content in solid solution (ΔC_{Mg}). The difference between the two evolutions was attributed to the intrinsic effect of the precipitates on the TEP. At 450°C, this effect is negligible.

To confirm the validity of the GN law when the equilibrium phase precipitates, we calculated from the final TEP values, shown in Fig.1.a and corresponding to the microstructural equilibrium of the alloy, the residual concentration of magnesium in solid solution for all the ageing temperatures considered. As can be seen in Fig.1.f, the obtained values are close to the solubility limit of Mg given in the literature [3]. Thus, when the equilibrium β phase forms, it is possible to derive, from TEP measurements, the residual concentration of elements in solid solution, and subsequently, the volume fraction of precipitates.

However, during the beginning of the precipitation sequence at 400°C, when the β' metastable phase forms, GN law is not valid. This can be attributed to an intrinsic effect of the β' precipitates on the TEP, which disappears during the $\beta' \to \beta$ transition.
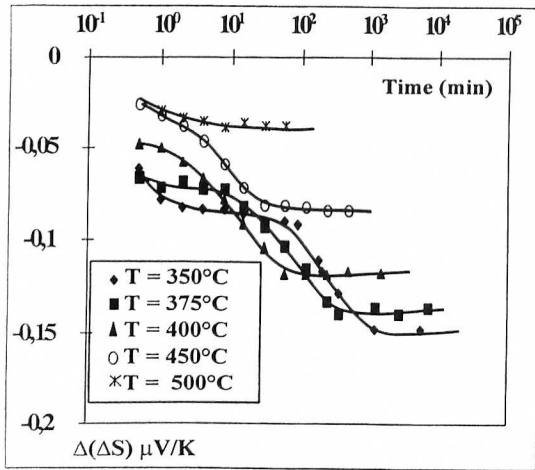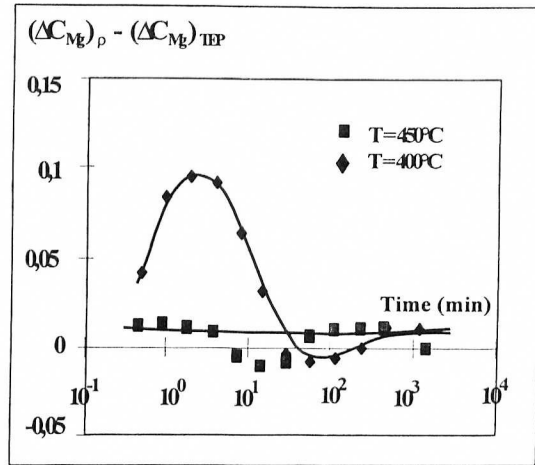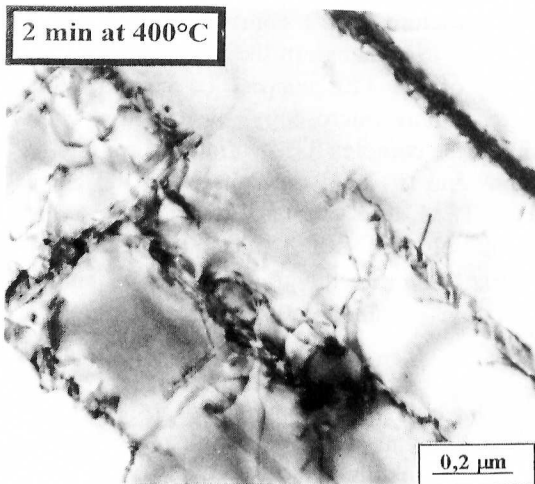
Figure 1.a
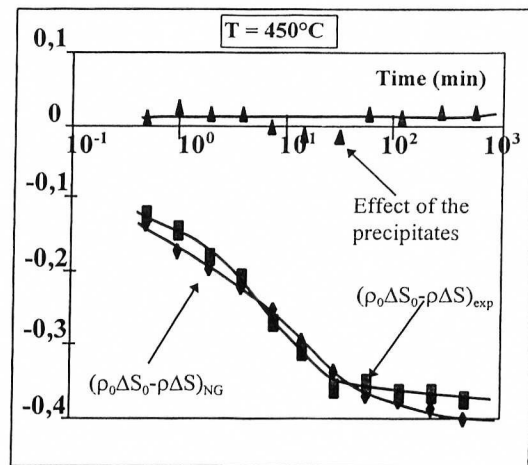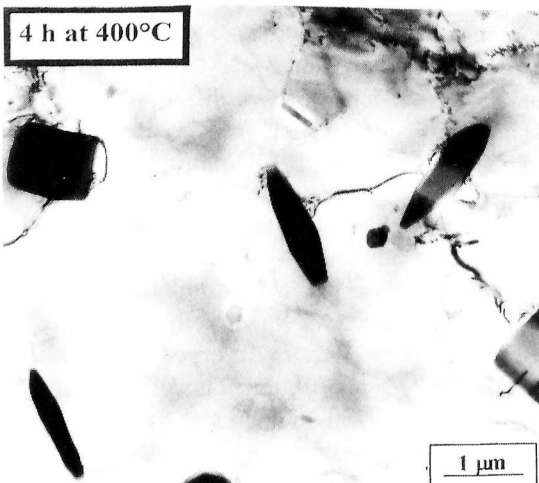

Figure 1.d

Figure 1.b : β' precipitates

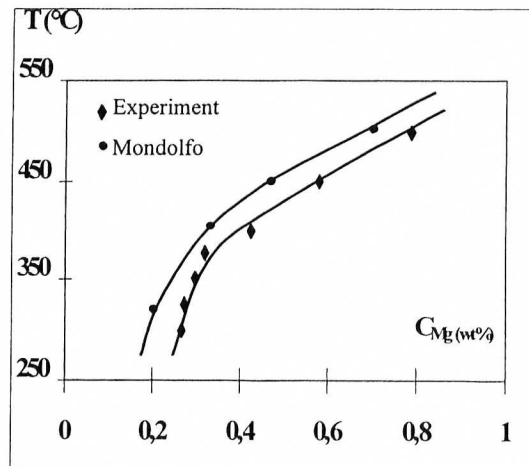Figure 1.e

Figure 1.c : β precipitates

Figure 1.f

3.2 Precipitation sequence between 200°C and 325°C

The TEP curves obtained in this temperature range are presented in Fig. 2.a. Their general aspect appears in Fig. 2.b where the TEP variations measured during an ageing at 300°C were reported. For comparison, the resistivity evolution was also plotted. While the resistivity gradually decreases, the TEP evolution is more complex. After an initial decrease, the TEP reaches a minimum and then increases, before passing a sort of maximum. At the end of the precipitation, the TEP stabilizes indicating that the microstructural equilibrium of the alloy is reached.

In order to obtain further information on this type of evolution, we plotted in Fig. 2.c the difference between the experimental and calculated values of $\rho_0 \Delta S_0 - \rho_t \Delta S_t$ at 300°C. The effect of the precipitates deduced from this curve (Fig. 2.c) shows that the initial precipitates have an increasing negative effect on the TEP. Then, this negative effect decreases, becomes sligthly positive and vanishes, indicating the formation of β equilibrium precipitates, which have no effect on the TEP. TEM observations conducted on specimens aged at 300°C showed the presence of : (i) β precipitates with an hexagonal structure, after 5 min and 1 hour (before and after the minimum of the TEP curves) (Fig. 2.d and 2.e) and (ii) β incoherent platelets after two weeks (Fig. 2.f).

In order to interpret the complex TEP evolutions obtained in this temperature range, two main hypothesis can be advanced. The first is that the structure or the composition of the β' precipitates evolves during the precipitation sequence, leading to a change in the intrinsic effect of these precipitates on the TEP and thus to the minimum of the TEP curves. To confirm this assumption, a more detailed study based on high resolution microscopy observations and nanoanalyses is undertaken. The second hypothesis is that these complex TEP variations are due to a duplex precipitation : (i) of β' precipitates in the grains and (ii) of β precipitates in the grain boundaries surrounded by a precipitated free zone (PFZ). TEM observations showed us that this PFZ increased in size with the ageing time, owing to the dissolution of the β' phase in this region. The co-precipitation of β' and β, followed by the β' → β transition near the grain boundaries and in the grains at high ageing times, could explain the TEP variations obtained in this domain.

3.3 Precipitation sequence between 100°C and 200°C

In this temperature range, the TEP curves (Fig.3.a) have the same general aspect. However, due to thermal activation, the curves are shifted to lower times as the temperature is increased. Fig.3.b allows us to compare the TEP and resistivity evolutions obtained at 200°C. The resistivity curve shows a monotonic decrease, while the TEP evolution is characterized by an initial decrease, followed by a stabilization and by a further increase observed in the scale of time investigated ($t < 10^4$ min) only at 200°C. This type of TEP evolution cannot be explained by the only effect of the decrease in the Mg and Si content in solid solution, as this effect would lead to a continuous TEP decrease. This behaviour can thus only correspond to the existence of two different types of precipitates on both sides of the minimum of the TEP curve. To confirm such an hypothesis, TEM observations were carried out on specimens aged 15 min and 24 hours at 200°C. On the specimen aged 15 min at 200°C (Fig. 3.c), a fine precipitation mainly visible owing its coherency contrast was detected. High resolution microscopy observations showed that these needle-shaped precipitates having a monoclinic structure compatible with that proposed by Edwards [4], corresponded to the β'' phase. After 24 hours at 200°C (Fig. 3.d), β'' and β' precipitates were observed simultaneously.

As a conclusion, between 100°C and 200°C, the β'' phase grows directly from the solid solution. The beginning of the β''---> β' transition is detected by the minimum observed on the TEP curves, as the intrinsic effect of the β'' and β' precipitates on the TEP is different. This effect is such that the β''---> β' transition leads to a TEP increase, the magnitude of which is greater than the TEP decrease associated with the weakening of the solid solution in magnesium and silicon. It can only be explained by a negative intrinsic effect of β'' on the TEP stronger than the negative effect of the β' precipitates.
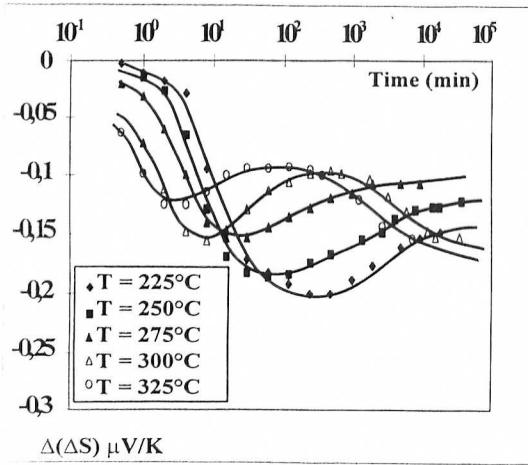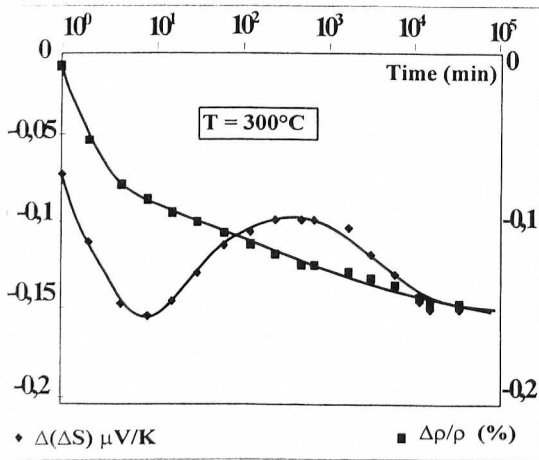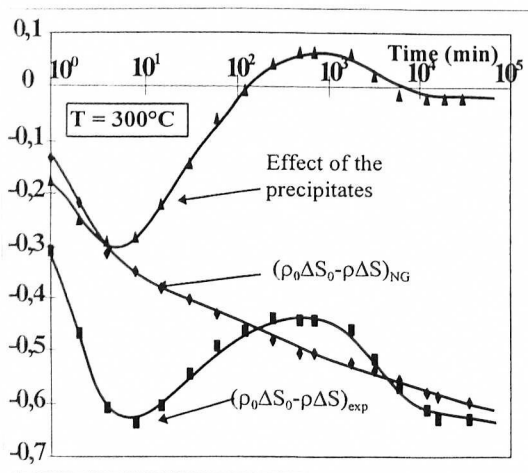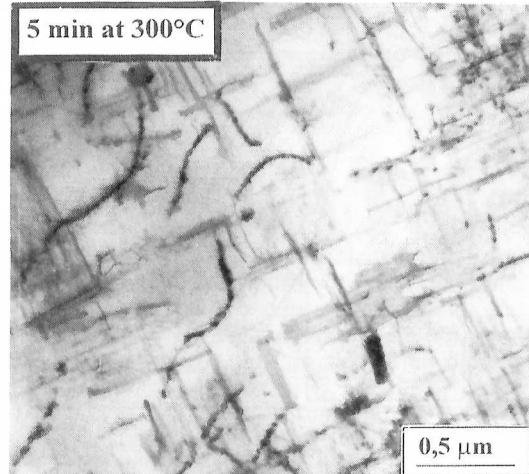
Figure 2.a

Figure 2.d : β' precipitates (z.a. : [001])
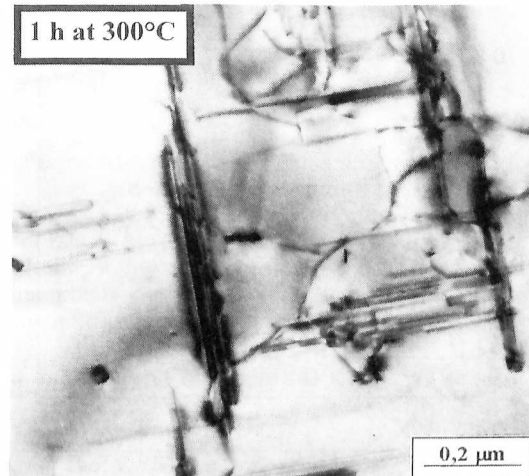

Figure 2.b

Figure 2.e : β' precipitates (z.a. : [001])

Figure 2.c

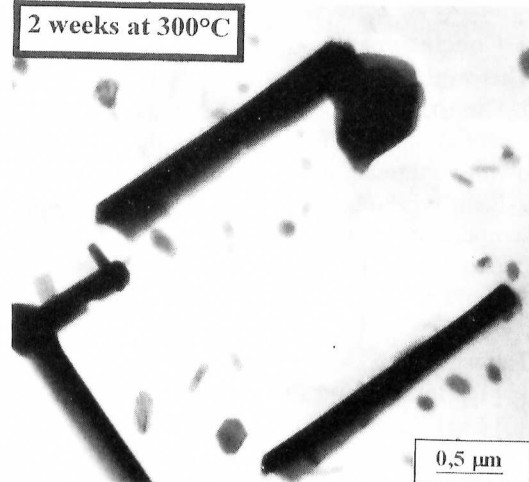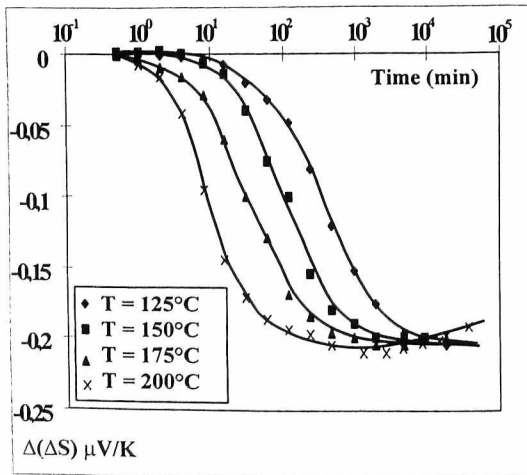

Figure 2.f : β precipitates (z.a. : [001])
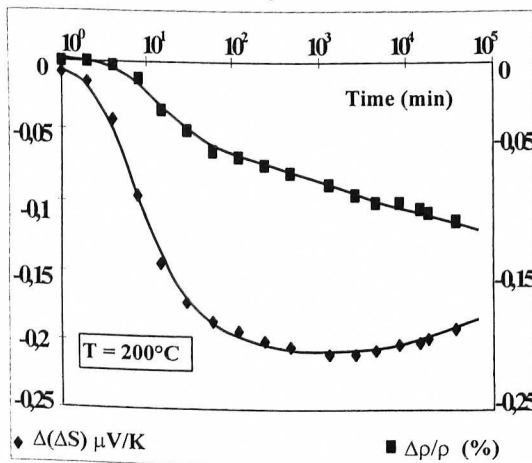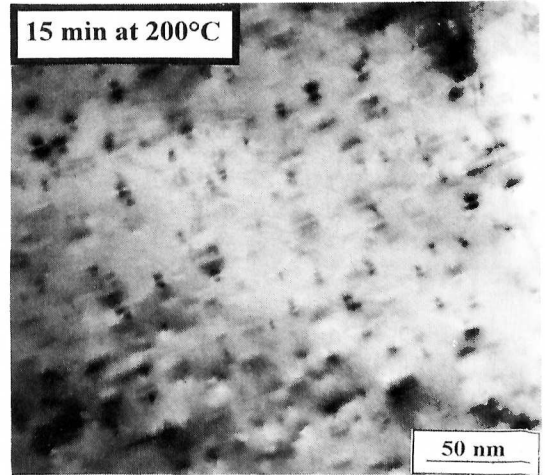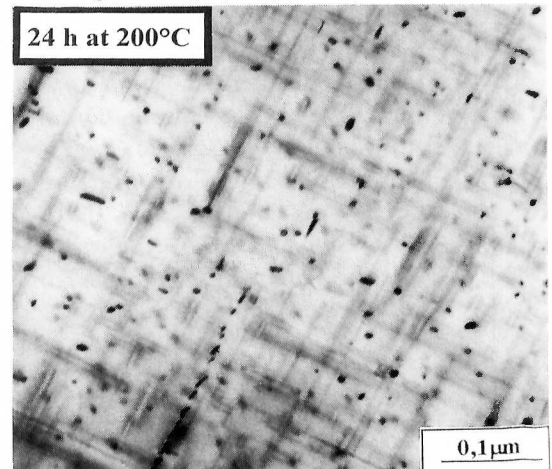
Figure 3.a

Figure 3.c : β'' precipitates (z.a : [001])

Figure 3.b

Figure 3.d : β'' and β' precipitates (z.a.:[001])

4. Conclusions

This work showed that the TEP can bring informations on the precipitation of Al-Mg-Si alloys :

1-The transition between two phases and complex microstructural evolutions can be more easily detected on the TEP evolutions than with other techniques, as electrical resistivity measurements, owing to the fact that metastable precipitates have an strong intrinsic effect on the TEP.

2-Each type of precipitation sequence being associated with a typical TEP evolution, the critical temperatures corresponding to a change of precipitation sequence can be easily determined.

3-At the end of the precipitation, Gorter- Nordheim law is valid and the residual concentration of Mg and Si in solid solution can be assessed, using complementary resistivity measurements.

References

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