CHARACTERIZATION BY ELECTRON MICROSCOPY OF NUCLEATION SITES AND PHASES NUCLEATED DURING QUENCHING OF AN AlZnMgCu ALLOY†

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ABSTRACT A study of the precipitation developed during cooling from the solution treatment temperature to the ambient one has been undertaken by TEM and SEM using an interrupted quenching procedure. Heterogeneous intragranular η precipitation nucleates during high temperature isothermal holdings on dispersoids : semi-coherent non-uniform dispersoids are activated first at very low supersaturation, whereas a higher energy is needed to precipitate on fully coherent uniform dispersoids. The precipitation of the S' (or S) phase has been observed from 300 to 200°C. Intergranular η precipitates are present on grain and subgrain boundaries. Homogeneous η' precipitation has been observed at low temperatures. Results are graphically summed up by plotting a nucleation diagram.

Keywords : *7000 alloys; Precipitation; TEM; Nucleation sites; η phase; S phase*

1. INTRODUCTION

AlMgZnCu alloys are used in aerospace applications, because of their high mechanical properties attributable to finely dispersed precipitates. They undergo a complex thermomecanical treatment sequence : hot rolling, solutionizing, quenching and aging. Quenching is a critical step in this sequence when manufacturing 7xxx thick plates, low cooling rates after solution treatment substantially reducing hardening on aging. This loss of mechanical properties is attributable to non-hardening precipitation formed at high temperatures which reduces the supersaturation of the aluminum matrix and, as a consequence, hardening potential of the alloy during aging [1, 2].

The phases likely to nucleate during cooling from the solutionizing temperature are the $Mg(Zn_2,AlCu)$ η phase, the Al_2CuMg S phase and the $Al_{32}(Mg,Zn)_{49}$ T phase [3]. η is a phase isomorphous to $MgZn_2$ and AlCuMg. η presents several orientation relationships with the matrix [4]. Most frequently encountered in industrial alloys [5] are the coherent precursor phase η', η_2 with the same orientation relationship as η', η_1 and η_4.

In order to characterize and predict the precipitation during quenching of a 7010 alloy, an adequate description of the solid solution decomposition from the solution treatment temperature to the ambient one is needed. The approach adopted in the course of this study and presented in this article is to let the precipitation nucleate from its supersaturated state during precisely controlled isothermal holdings, and to characterize it at room temperature.

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2. EXPERIMENTAL PROCEDURE

The alloy investigated is an industrial 7010 alloy (Al-5,99Zn-2,33Mg-1,73Cu in wt%) which was cast and rolled to a 100 mm thick plate by Pechiney Rhenalu Issoire. Materials samples (10x30 mm plates of 0,8 mm thickness) were taken from quarter-plane along the rolling direction.

The thermal cycles presented figure 1-a were performed using a laboratory designed apparatus. Material samples were solution treated at 475°C for 30 mn and then cooled at a controlled 50°C/s cooling rate between the solutionizing temperature to the isothermal holding one, in order to avoid precipitation. They were then maintained at this temperature for various durations, figure 1-b, so that the precipitation could develop. Samples were then fastly cooled to room temperature.

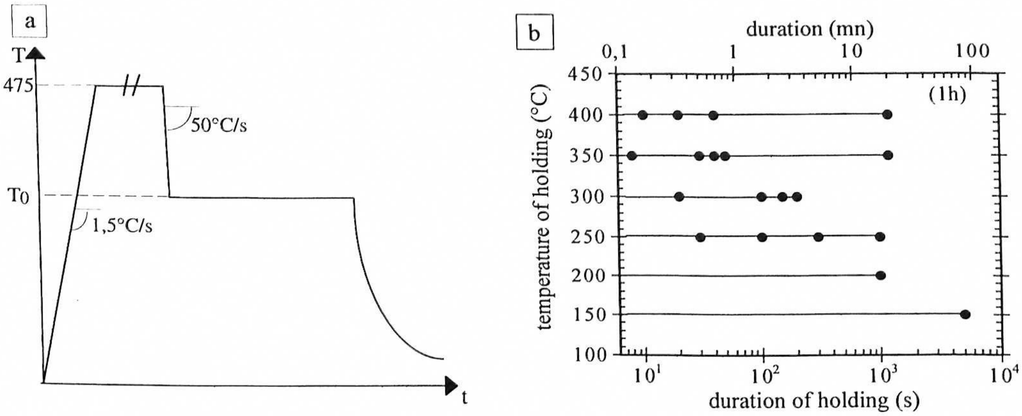

Fig. 1 : Schematic variation of temperature during thermal cycles. Each point at figure 1-b represents a microstructural state investigated at room temperature

Room temperature microstructural observations were performed by transmission electron microscopy (TEM) on a 200kV JEOL 200CX and by scanning electron microscopy (SEM) on a 25kV CAMBRIDGE SCAN 100. Thin foils for TEM were prepared using discs, 3 mm in diameter, which were cut from mechanically ground strips of 0.1 mm thickness. The discs were then electrolytically thinned in a Struers Tenupol jet polishing unit operating at 12 V and -40°C using a Nimet solution (30% nitric acid and 70% methanol by volume). Surfaces for SEM examinations were mechanically polished.

3. RESULTS

3.1 Intragranular heterogeneous precipitation

Nucleation of precipitates is heterogeneous at high temperatures. Preferred intragranular nucleation sites are dispersoids [6, 7], which belong to the Al_3Zr in the 7010 alloy. Most of these dispersoids are finely dispersed round coherent precipitates [8], approximately 20 nm in diameter [9], which inhibits recrystallisation [10] during industrial thermomechanical processing. During holding at a temperature in the range 350-250°C, precipitates nucleate on these dispersoids : figure 2. This uniform precipitation belongs to the η phase. Nucleation is not instantaneous, as the apparent volumic density of precipitates increases with the duration of the holding. Precipitate length as measured on micrographs reaches 550 µm at 350°C and 400 µm at 300°C.

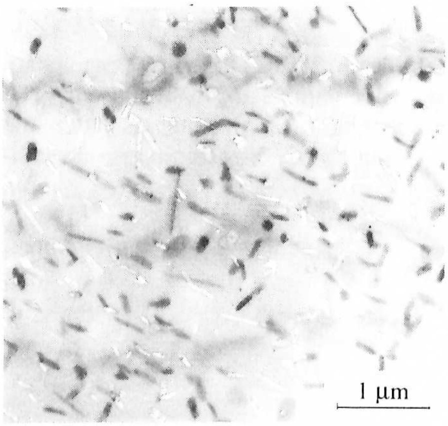

Fig. 2 : uniform heterogeneous precipitation of η after 40 s at 350°C

Long bands of coarse precipitates have been observed at 400 and 350°C : figure 3. There is no orientation relationship between precipitates or bands. Precipitates are plate-shaped, with length up to 650 μm at 400°C and 350 μm at 350°C. They belong to the η phase, η_2 and η_1 essentially. Their nucleation appears to be instantaneous since the apparent density of bands visualized by bright field remains constant during the holdings.

TEM examinations (figure 4) show that Al_3Zr dispersoids are the nucleation sites for this precipitation. These dispersoids present a cubic-like morphology and thus are quite different from the rounded uniformly dispersed β' dispersoids. Nevertheless let us assume that they also belong to the metastable β' phase since their average size is rather low, i.e. 40 nm. The misfit between the coherent β' dispersoid and the aluminum matrix, 0,8±0,1% estimated by [8], leads to a partial loss of coherency for dispersoids bigger than 30 nm. The interface between these cubic-like dispersoids and the matrix is then probably semi-coherent. This partial loss of coherency reduces the activation barrier for η nucleation and allows this nucleation to occur at a lower supersaturation, i.e. at higher temperatures. Those cubic-like dispersoid bands have very likely homogeneously nucleated and then developed with a particular growth path which needs to be further investigated.

Fig. 3 : band of precipitates observed after a 10 s holding at 400°C

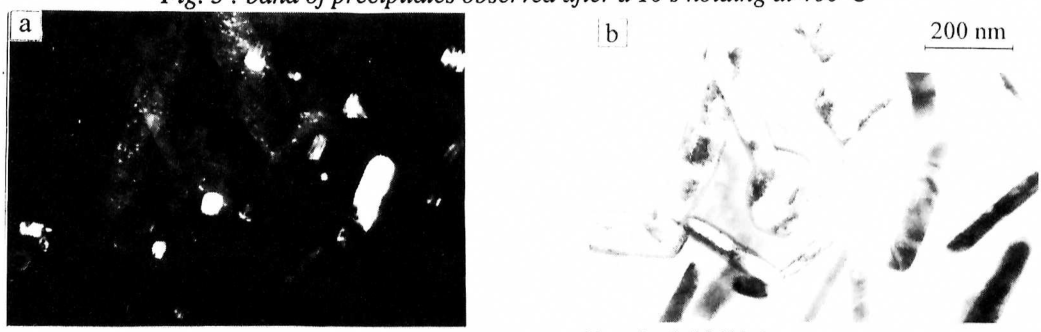

Fig. 4 : dark field on (110) Al_3Zr spot (a) and associated bright field (b) for precipitates in bands. A η_1 precipitate is also visible on the dark field 3-a because its characteristic spot on <112> electron diffraction pattern is close to the (110) β spot

3.2 Other intragranular precipitations

The intragranular precipitation is complex between 300 and 200°C. Various precipitate morphologies have been visualized during isothermal holdings after various incubation times. The Al_2CuMg S' phase, identified on electron diffraction patterns (figure 5-a), appears after the precipitation of η during holdings at a temperature in the range 300-200°C. S' precipitates are lath-shaped and paralled to a cristal direction, probably <100> (figure 5-b). Their apparent volumic density increases with the duration of holdings. Globular precipitates are present at 300 and 250°C. They probably belong to the T phase. The nucleation of both T and S phases is explained when considering phase diagrams. [3] gives an isothermal section of the quaternary system Al-Mg-6wt%Zn-Cu at 360°C : the alloy composition lies in the S+η domain, close to the S+T+η domain. The precipitation of η can moreover introduce a synergetic effect by displacing the solid solution composition, Mg and Zn being dragged out from the solid solution creating a relative excess of Cu.

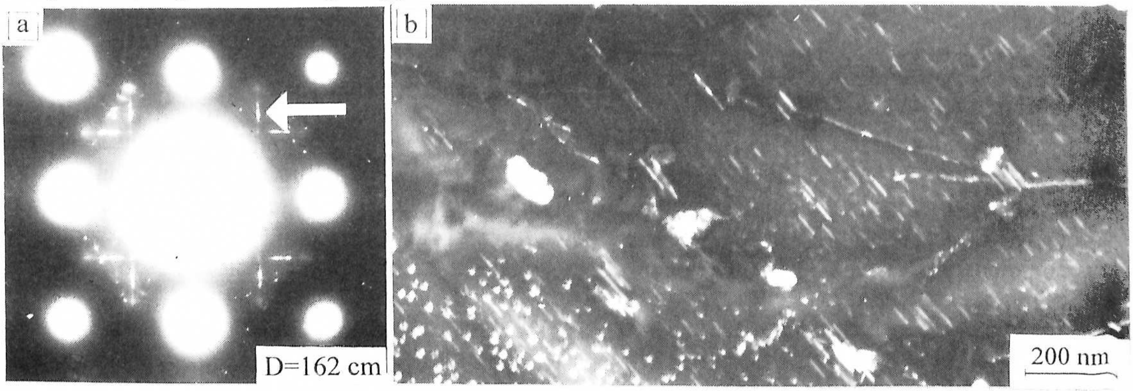

Fig. 5 : <100> diffraction pattern (a) and dark field on the S' streak indicated by the arrow (b)

3.3 Homogeneous precipitation

Homogeneous precipitation has been evidenced for the lowest holding temperatures. At 150°C, the solid solution is retained for times up to 300 s. Then a fine uniform precipitation of η' is observed. At 200°C, a uniform precipitation of the equilibrium phase η is observed with no clear evidence whether it is formed through an heterogeneous nucleation process or not. It is possible that the η' phase nucleated first in an homogeneous way and then rapidly transformed into the observed η phase. In addition, the formation of η phase on cristal defects (subgrain boundaries and dislocations) is clearly visible.

3.4 Intergranular heterogeneous precipitation

Precipitation on grain boundaries has been viewed by SEM using backscattered electrons. This precipitation is present at 400°C, with a low density. At 350°C (figure 6-a), a rapid and copious precipitation is observed. Precipitation on subgrain boundaries is present in the temperature range 300-200°C (figure 6-b). Even at 250°C where the diffusion is slow, the nucleation of this precipitation is instantaneous.

4. DISCUSSION

Nucleation sites in the investigated alloy are numerous and various. They were characterized in this study by a temperature domain of activation, figure 7. The η solvus line has been determined in the course of this study by differential calorimetry [11] as being 440°C.

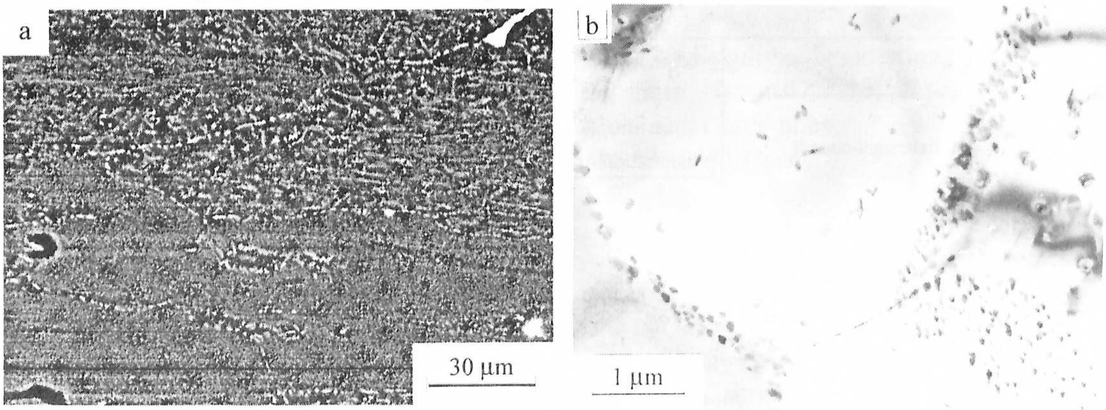

Fig. 6 : intergranular heterogeneous precipitation a) on grain boundaries after 20 mn at 350°C and b) on subgrain boundaries after 20 s at 300°C

This study demonstrated that different phases could nucleate during cooling. Those informations are reported on a nucleation diagram, figure 8. η is coarse and incoherent at high temperatures. At intermediate temperatures, S' can appear on isothermal holdings. Its incubation time has been roughly determined by looking for extra S' spots on electron diffraction patterns for various holding times between 300 and 200°C. At 200 and 150°C, η' nucleates after an incubation period, function of the holding temperature, during which the solid solution remains supersaturated. The sequence of decomposition η' → η has been added on figure 8 to recall that at temperatures higher than 150°C, η' rapidly transforms into η. As we did not investigate temperatures lower than 150°C, no information is available on GP zone nucleation.

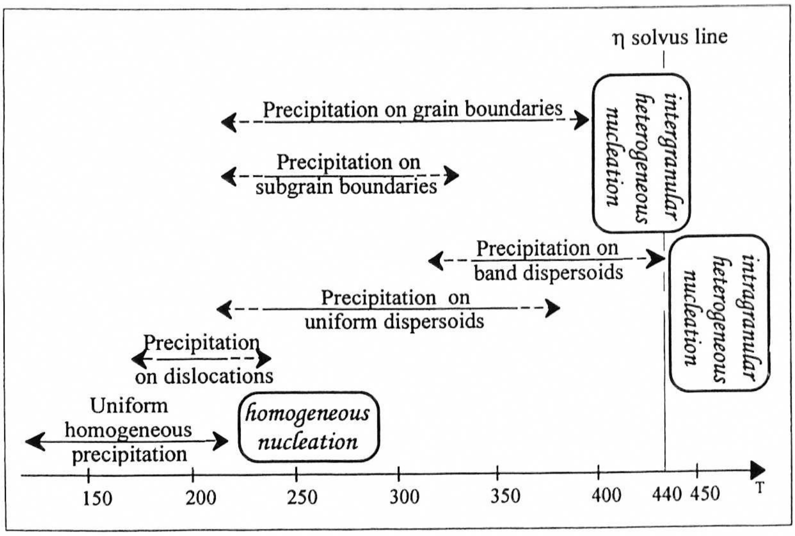

Fig. 7 : nucleation sites activated as a function of temperature for the investigated 7010 alloy

This diagram is specific to the family of the investigated alloy. Ryum [12] showed an equivalent diagram for a ternary Al-Mg-Zn alloy without zirconium. The sequences of decomposition are totally different, because no dispersoids are present in the matrix, and no copper in the solid solution. In this case, he observed the precipitation of the T phase in addition to the η phase.

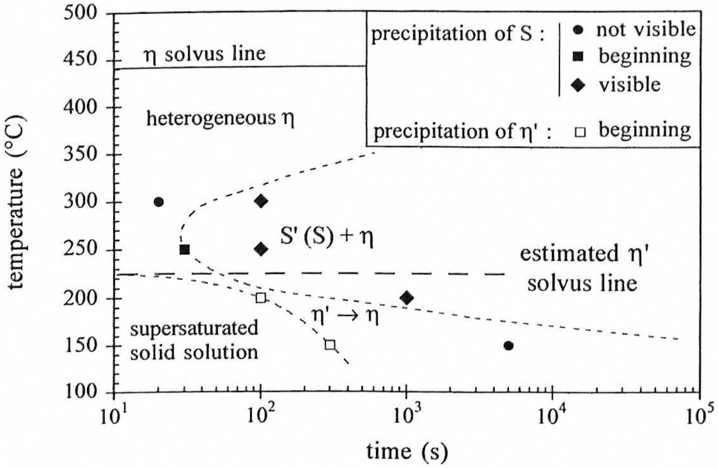

Fig. 8 : nucleation diagram deduced from this microstructural study for the investigated 7010 alloy

5. CONCLUSION

This study pointed out the complexity of the solid solution decomposition during cooling from the solutionizing temperature. The interrupted quenching procedure adopted here allowed to precisely characterize the different nucleation sites and phases nucleated as a function of temperature and duration of isothermal holdings. Caution should be however exerted when transposing figure 8 to continuous cooling. In this case the solid solution is no more supersaturated at a given temperature and decomposition sequences may change.

REFERENCES

[1] J.W. CAHN: Acta Met, 4(1956), 572.

[2] J.W. EVANCHO and J.T. STALEY: Met Trans, 5(1974), 43.

[3] D.J. STRAWBRIDGE, W. HUME-ROTHERY and A.T. LITTLE: J Inst Metals, 74(1948), 191.

[4] J. GJONNES and C.J. SIMENSEN: Acta Met, 18(1970), 881.

[5] B. DUBOST and J. BOUVAIST: Journées d'Automne SF2M, (1976).

[6] M. CONSERVA, E. DI RUSSO and O. CALONI: Met Trans, 2(1971), 1227.

[7] P. ARCHAMBAULT: Thèse d'état INP Lorraine (1985).

[8] E. NES: Acta Met, 20(1972), 499.

[9] K. RANGANATHAN, H.R. LAST and T.H. SANDERS: ICAA3, (1992), 15.

[10] NES, RYUM and HUNDERI: Acta Met, 33(1985), 11.

[11] D. GODARD and P. ARCHAMBAULT, to be published.

[12] N. RYUM: Z Mettalkde, 66(1975), 338.