RESPONSE OF Cu-AL-Mn ALLOYS TO AGEING IN β PHASE

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Abstract. - The effect of isothermal ageing at 300 ºC on the characteristic transformation temperatures and structure changes in Cu-Al-Mn alloys containing 1.5-9 wt% Mn have been studied by differential scanning calorimetry and transmission electron microscopy. Alloys containing 5-6 wt% Mn were least affected by ageing treatment, since changes of M_s were observed only after several hours of ageing. Changes in M_s are attributable to ordering in all the alloys and to matrix composition changes subsequent to formation of γ in low Mn alloys or bainite in high Mn alloys.

1.- Introduction

Cu-Al-Mn alloys over a wide composition range exhibit a martensitic transformation. Characteristic transformation temperatures have been reported by several investigators [1-3] and, in general, show a good agreement. There are very few studies on the influence of ageing treatments on the structure and transformation temperatures. In one such work [3], in alloys containing 1-6.3% Mn (all compositions in wt %), ageing for 30 min at various temperatures showed that the increase of manganese restrains precipitation, while M_s fluctuations are attributable to a matrix composition change due to γ precipitation. The effect of cycling up to 500ºC has been studied in alloys with 4-7% Mn [4], where a significant rise of M_s has been reported on cycling up to 500 ºC, while only insignificant changes occurred below 400 ºC. In another study [5] of alloys containing 10% Mn, ageing at 250 ºC resulted in an increase then a decrease of M_s, while in [6] alloys containing 8% Mn exhibited two stage transformation attributed to the spinodal decomposition reported earlier in [7]. In spite of various compositions investigated the results seem to be contradictory, showing once rise as in [4] and, in other cases, a decrease of M_s during ageing. Moreover, no systematic isothermal ageing experiments have been performed in alloys containing different Mn contents, whose presence in increasing amounts, is supposed to restrain precipitation [3].

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The present work is aimed at such a study, using differential scanning calorimetry (DSC), optical and electron microscopy. The changes of martensitic transformation temperatures, heat of transformation and accompanying structure on isothermal ageing are reported and discussed.

2.- Experimental procedure

Alloys were melted in an induction furnace under protective helium atmosphere from 4N purity Cu and Al and 3N purity Mn. The compositions of the alloys investigated are given in Table 1.

Table 1. Alloys composition and M_S after quenching.

Alloy	Cu	Al	Mn	Ms(ºC)
1	84.8	13.7	1.5	18
2	83.3	13.7	3.0	-59
3	83.0	12.0	5.0	63
4	82.5	11.5	6.0	50
5	81.0	10.0	9.0	5

Alloy 1 was quenched from 920 ºC into water at 55ºC. Other alloys were quenched from 850 ºC either into diethyleneglycol at 160 ºC (alloys 3,4) or into water at room temperature (alloys 2,5). Ageing was performed in a salt bath. Calorimetry was carried out using a DSC-4 Perkin Elmer unit. The temperatures and heat evolution of transformation were recorded at heating/cooling rates of 10ºC/min. Thin foils for TEM investigations were obtained using double jet electropolishing in an electrolyte 1/3 HNO_3, 2/3 CH_3OH at temperatures -5/-60 ºC depending on M_s temperature. The foils were examined using a Hitachi H-600 electron microscope operating at 100 kV.

3.-Results and discussion

The M_s temperatures vs. ageing time at 300 ºC for alloys 1-5 are shown in Fig.1a, and in Fig.1b the average transformation heat (absolute values for cooling/heating) Q vs. ageing time at 300 ºC is presented. It can be seen that M_s changes in a manner similar to Q, i.e. both show an initial increase and then a steady decrease, as in alloys 1 and 5, or both values decrease, as in alloys 2 and 4. The transformation characteristics of alloy 3 remain stable, with insignificant changes in M_s and Q even after a few days of ageing at 300 ºC. Alloy 3 also shows a well defined peak of heat evolution, while other alloys, especially the alloys 1 and 4, show splitting of transformation peak, particularly in the reverse transformation, as can be seen in Fig.2. In the latter figure a set of heating and cooling DSC curves for alloys 1, 3 and 4, after ageing time corresponding to partial decomposition at 300 ºC, are given. Substantial changes in the calorimetric curves after ageing may be observed for alloys 1 and 4, but not for alloy 3, whose thermogram is quite similar to that after quenching. Heat evolution maxima during cooling of alloy 4 show significant oscillations (jerky character) as already observed for hexagonal martensite [8].

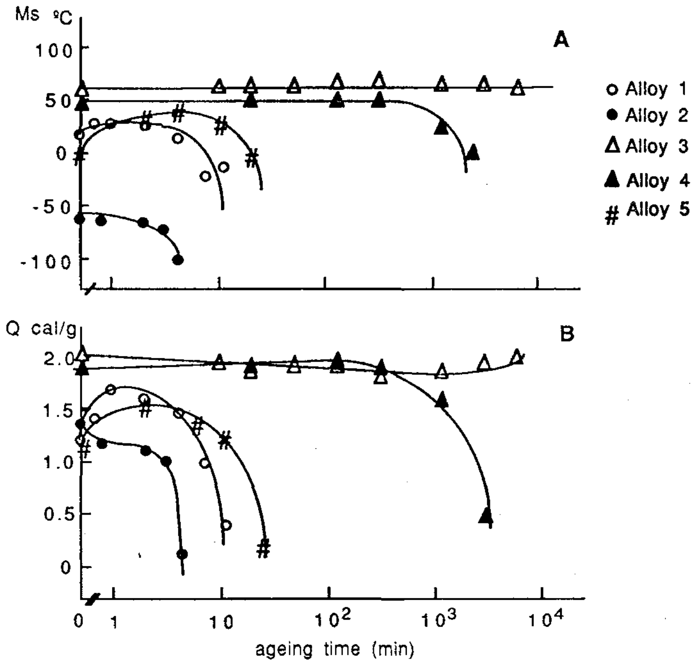

Figure 1. Relationship of M_S (a) and heat of transformation Q (b) vs. ageing time at 300 °C for alloys 1 - 5 .

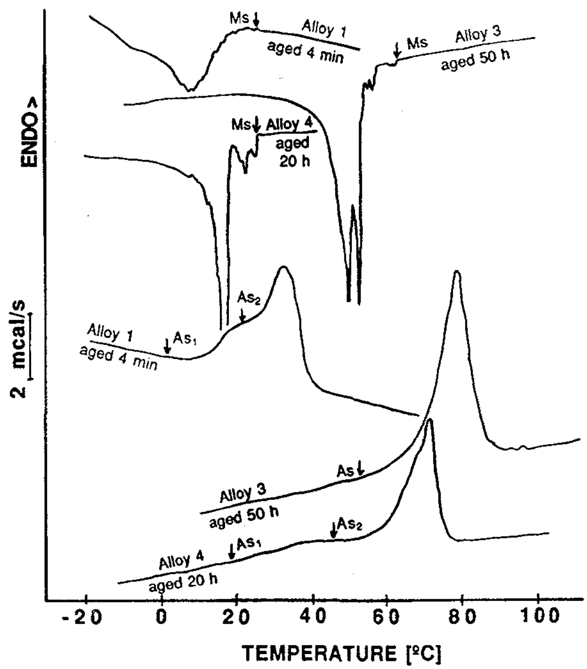

Figure 2. DSC curves for alloys 1, 3 and 4 aged at 300 °C for 4 min, 50 h and 20 h respectively.

TEM studies indicated that martensite in all alloys investigated was of the 2H type, except for alloy 4, where a small amount of 18R martensite was detected. Existence of two martensites in alloy 4, aged 10 min at 300 ºC is presented in figure 3. The 2H martensite has a variable stacking fault density, as can be seen in Fig. 3a, low in one of the twin plates and high in the other, causing substantial streaking in the diffraction pattern. The 18R martensite was always found to contain very high density of stacking faults, suggesting that it has formed in the later stages of the transformation under stress (related to the second peak observed in DSC curves). This was confirmed during in situ heating experiments, where 18R needles retransformed first.

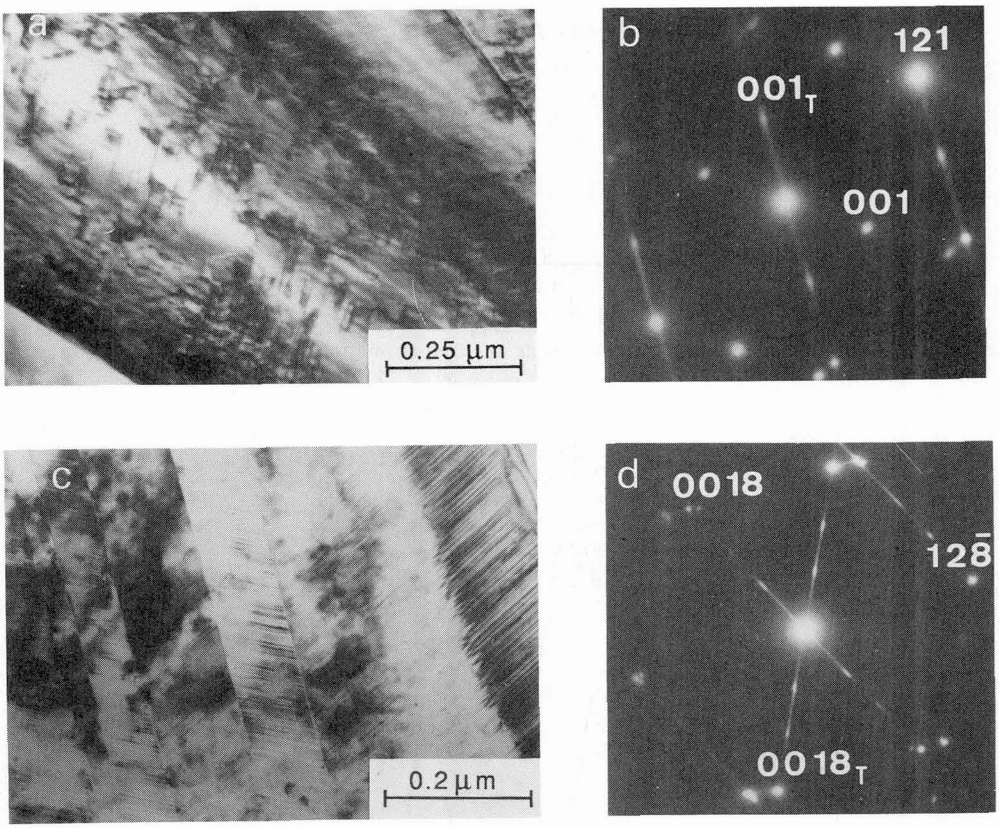

Figure 3. Transmission electron microstructures of alloy 4 aged 10 min at 300 ºC (a,c) and the corresponding selected area diffraction patterns (SADP) at [210] zone axis orientation (b,d)

After a longer ageing time in alloys 4 and 5 (with a higher Mn content) bainitic needles were found, as shown in the optical micrograph of Fig.4. The presence of this bainite is responsible for changes in martensitic transformation temperatures. Much larger martensitic plates formed at room temperature can also be seen in the same micrograph.

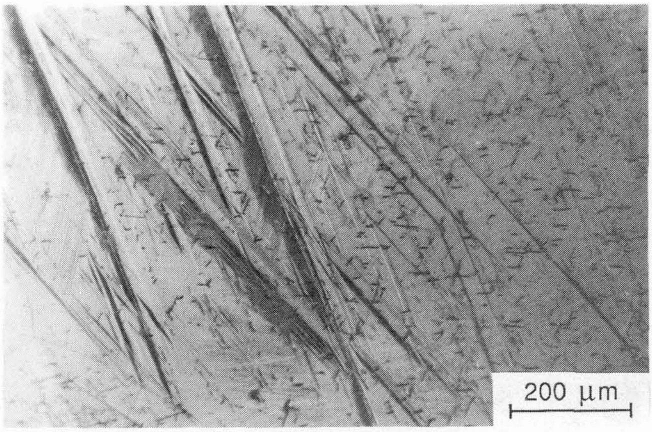

Figure 4. Bainitic and martensitic plates in alloy 5 aged for 10 min at 300 ºC .

Alloys 1 and 2 with the lowest Mn content show a different mode of decomposition at 300 ºC, i.e. precipitation of small γ particles already after a short ageing time. It contributes together with $L2_1$ ordering changes to M_s evolution. Fig. 5 shows an electron microstructure of alloy 1 aged for 2 min/300 ºC. Two martensite morphologies can be clearly seen (as confirmed also using optical microscopy); one consisting of large twinned plates of [1$\bar{2}$0] orientation with (121) twinning plane as evidenced in the SADP (Fig. 5b). The second type of martensite consists of very fine twinned plates with a high density of dislocations. Its reflections indicating [0$\bar{1}$2] orientation with ($\bar{1}$21) twinning plane are diffused along Debye-Scherrer rings, as can be seen in SADP in Fig. 5c. Weak reflections of γ phase can be indexed as belonging to [111] zone axis orientation. Appearance of two types of martensites in alloy 1 can be noticed in the heat evolution curves shown in Fig. 2 .

4.- Conclusions.

1. In all alloys investigated containing 1.5-9 % Mn, 2H martensite was found. In alloy containing 6 % Mn, additionally a small fraction of heavily faulted 18R martensite was observed. It caused splitting of transformation peak as detected in DSC curves.

2. Alloys with Mn content around 5-6% posses the highest resistance to degradation of martensitic transformation after ageing. Alloys of lower and higher Mn content decompose earlier at 300 ºC.

3. In alloys containing up to 3% Mn small γ-phase precipitates form during ageing. In this case two martensite morphologies appear, i.e. large plates with twins and heavily dislocated fine plates.

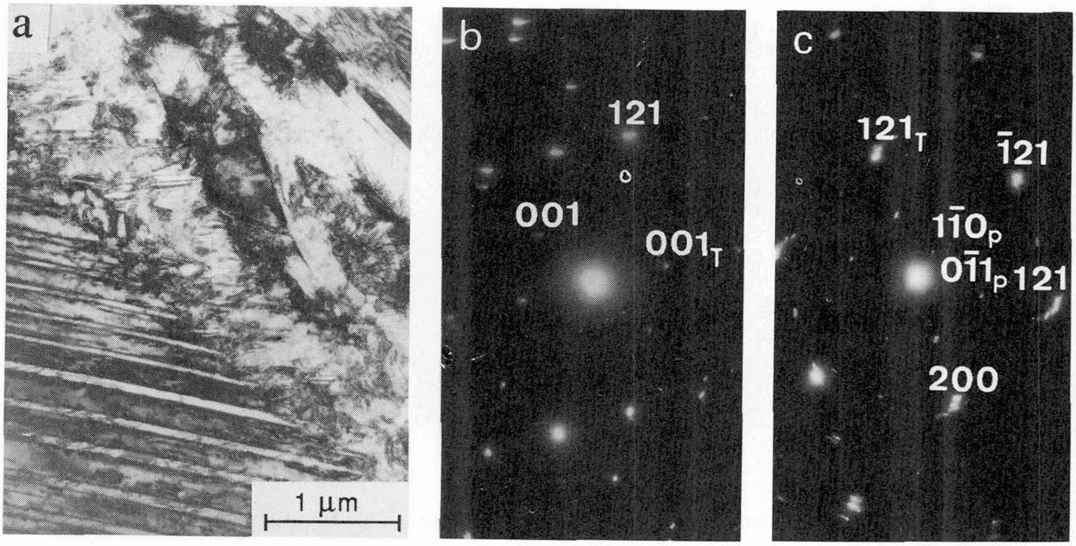

Figure 5. Alloy 1 aged 2min at 300 °C. (a) Transmission electron micrograph, (b) SADP taken from a large twinned plate in the lower left corner, (c) SADP taken from a fine plate area in the upper part.

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