A DSC STUDY OF PRECIPITATION IN Al-Cu-Mg ALLOYS

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ABSTRACT The precipitation sequence after solution treatment and quenching has been investigated in two Al-Cu-Mg alloys having a Cu content of 4.5 wt%, a Cu/Mg ratio of about 3 and a different Si content, by Differential Scanning Calorimetry. An interesting effect of the solutioning temperature has been detected. For lower values the typical precipitation sequence $\alpha_{sss} \rightarrow$ GPB $\rightarrow$ S'($CuMgAl_2$) $\rightarrow$ S ($CuMgAl_2$) has been found, while for higher values a strong evidence of the sequence based on the θ' ($CuAl_2$) has also been detected.

keywords: *aluminum alloys, phase transformations, DSC, precipitation kinetics*

1. INTRODUCTION

Age-hardenable aluminum alloys based on the Al-Cu-Mg system having a low Cu/Mg ratio and a copper content of about 4.5 wt%, have been widely used in the past in the aerospace field [1] and are considered until now as a basis for the development of new technical compositions [2].

Their age-hardening is based on the decomposition of a supersatutared solid solution α_{sss} obtained by solution treatment and quenching, and it is generally accepted [3] that the ageing process takes place mainly through the precipitation sequence:

$$\alpha_{sss} \rightarrow \text{GPB} \rightarrow \text{S'}(\text{CuMgAl}_2) \rightarrow \text{S}\ (\text{CuMgAl}_2)$$

where GPB are the Guinier Preston Bagariaskij Zones, and S' is a metastable precursor of the equilibrium S-$CuMgAl_2$ phase.

Even though widely investigated, some aspects concerning the precipitation sequence are still open, and in particular the possible presence of one or more metastable phases owing to the sequence

$$\alpha_{sss} \rightarrow \text{GP} \rightarrow \theta''(\text{CuAl}_2) \rightarrow \theta'(\text{CuAl}_2) \rightarrow \theta\ (\text{CuAl}_2)$$

based on the well known $CuAl_2$ phase typical of both binary Al-Cu and ternary Al-Cu-Mg alloys having a high Cu/Mg ratio.

In this paper we report some results of a Differential Scanning Calorimetry (DSC) investigation relative on the formation of metastable phases in two Al-Cu-Mg alloys having the same Cu content and Cu/Mg ratio of about 3, but different additions of Mn and Si, with the aim to obtain further information about the formation of metastable phases, during a linear temperature scan of a supersaturated solid solution obtained by solution treatment and quenching.

2. MATERIALS AND METHODS

The Al-Cu-Mg alloys were obtained by melting weighted amounts of Al, Cu, Mg, Al-Mn master alloy and Si in a electrical graphite crucible furnace. Molten material was poured into a metallic die having size 100x50x10 mm^3. The chemical composition of the obtained alloys was checked by the wet method; results are shown in tab I. Slices about 1 mm-thick have been obtained by cutting with a refrigerated diamond wheel; the specimens were homogeneized at 490°C for 10 hours and slowly cooled up to r.t.

alloy	Cu	Mg	Mn	Si	Fe	Al
I	4.5	1.6	0.6	0.1	0.17	Bal
II	4.5	1.5	0.001	0.46	0.39	Bal

Tab I – Chemical composition (wt%) of the investigated alloys.

Small discs 6 mm in diameter were punched-out for DSC measurements. They were solution treated at different temperatures ranging between 470 and 520°C, and then quenched in water at 20°C.

Calorimetric scans were performed in a DSC DuPont 990 under argon atmosphere at a scanning rate of 5 K/min on the as-quenched samples; when required, a set of five different scanning rates were used in order to reveal the possible presence of thermally activated reactions. In case, activation energies were calculated according to the Ozawa method [4].

3. RESULTS AND DISCUSSION

Fig.1 shows the DSC traces obtained at 5 K/min for the alloy I quenched from four different solution temperatures in the range 475-520°C. Thermograms show a complex structure of exothermic and endothermic effects that can be interpreted in terms of heat flow due to the precipitation and/or dissolution of the phases involved in the process of decomposition of the α_{sss}. The traces are essentially similar for solutioning temperatures below or equal to 505°C, while a strong effect is noted for the trace corresponding to the quenching temperature of 520°C.

The noticeable effect of the solutioning temperature increase above 505°C can be described as follows:

- the appearance of an exothermal effect **C** at about 290°C;
- the absence of the effect **D**.

It should also be noted that the **D**-peak is not present in the 505°C trace too, and that the endothermal **B** signal is clearly due to more than a single effect in the traces obtained at 520 and 505°C.

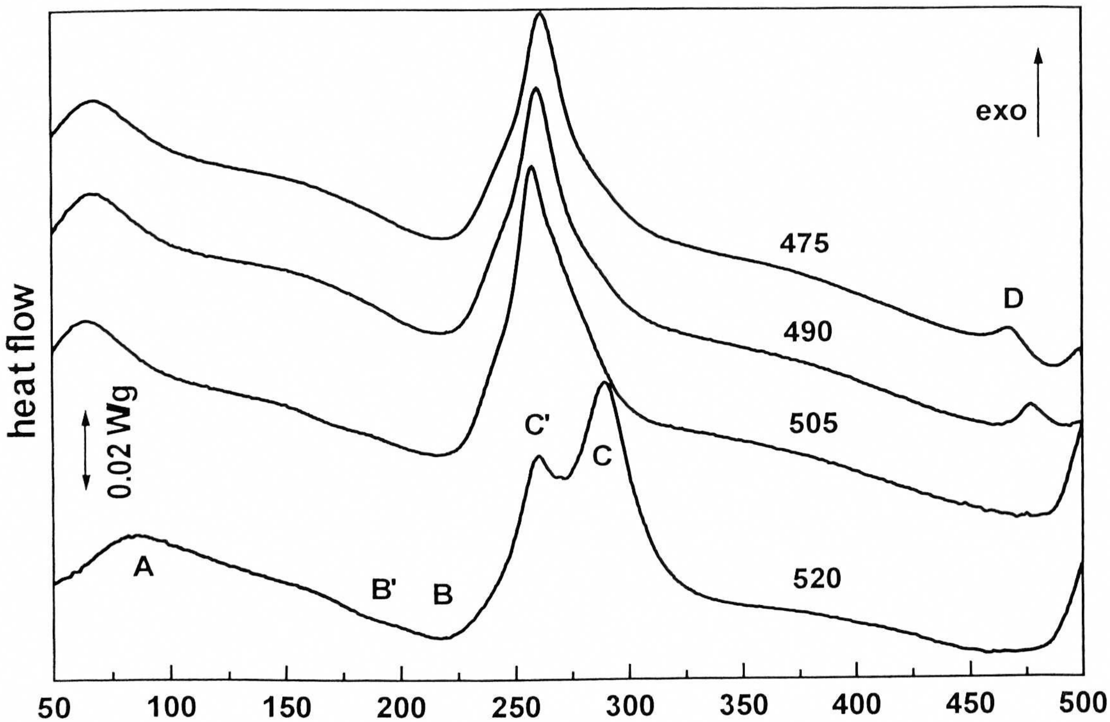

Fig.1 Alloy I. DSC traces for samples solubilized and quenched from the indicated temperatures. Scanning rate: 5 K/min

Measurements performed at different scanning speeds, show that the detected thermal effects are thermally activated; the plot of the logarithm of the scanning rate vs the reciprocal of the peak temperature (Ozawa plot) gives the value of the activation energy without any hypothesis about the transformation mechanism. Obtained results calculated for the traces corresponding to a solutioning temperature of 520°C are reported in tab II

Peak	Alloy I	Alloy II
A	55 ± 6	54 ± 7
B	117 ± 8	114 ± 10
C'	101 ± 5	120 ± 8
C	not detectable	108 ± 11
D	not detectable	not detectable

Tab II Activation energies in kJ/mole obtained by the Ozawa method

A similar result is obtained for the alloy II; in fig 2, the traces obtained at 475 and 520 °C solutioning temperatures are shown for a scanning speed of 50 K/min in order to underline the double-peaked structure of the endothermal effect at temperatures around 200°C.

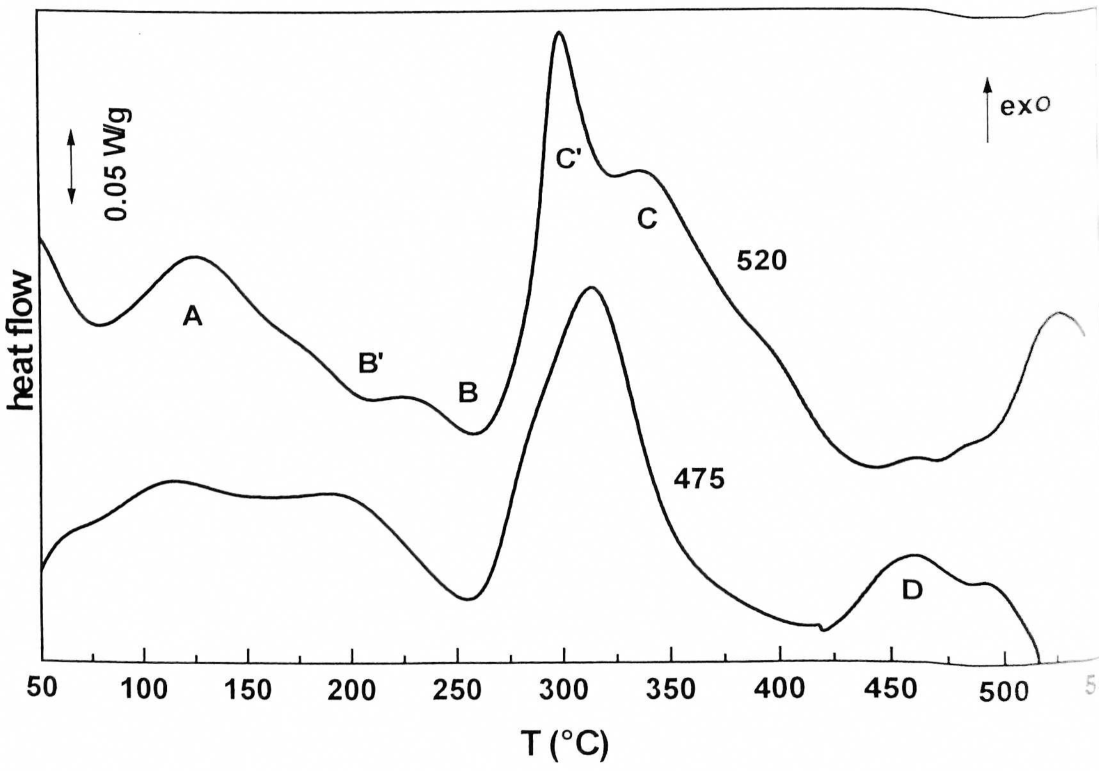

Fig.2 - Alloy II. DSC traces at 50 K/min obtained after different solutioning temperatures

A discussion of the obtained results can be started from the analysis of the traces obtained at the lowest quenching temperatures of 475 °C. On the basis of literature data [5], and taking into account the Cu/Mg ratio, the thermal effects marked **A**, **B**, and **C'** can be easily attributed to GPBZ formation, GPBZ dissolution, and S' formation respectively.

The additional peak **C** appearing when the solutioning temperature is increased should be therefore attributed to the precipitation of the θ' phase. The double-peaked exothermic path falling in the range 250÷350°C is in fact well described in literature [6,7] since it has been studied in Al-Cu-Mg alloys having a similar Cu content and higher Cu/Mg ratio. The exothermal effects evidenced in this range of temperature have been linked out to the formation of S' and θ'on the basis of a joint DSC/TEM investigation, even though a precise attribution of each peak to a given phase was not possible.

In the present investigation the possibility to have a single sequence based on the S phase for lower quenching temperatures, allows to discriminate between the two thermal effects when they appear together.

A further remark should be devoted to the high-temperature peak **D**. It is the indication of a high temperature precipitation superimposed to the endothermal dissolution signal starting at about 350°C. Since it disappears when the peak **C** is present, we could argue that the **D** effect should be attributed to heterogeneous $CuAl_2$ precipitation, as already suggested [7]. Its absence can be therefore linked out to the homogeneous precipitation of θ' dragging out Cu atoms not more available for a successive precipitation at higher temperatures.

The increased Si addition has the remarkable effect of increasing to a value of 120 kJ/mole the activation energy of 108 obtained for the precipitation of the phase S' associated with the peak **C'**. This should be attributed to the stabilization effect of the Si atoms onto the GPB zones which has been already investigated in Al-Cu-Mg alloys [9] with similar results.

About the double peaked **B** structure, the DSC is not able to suggest an attribution, since the appearance of the **B'** effect could be due to both the S and θ sequences. Further work, in particular TEM examinations, have been planned.

4. CONCLUSIONS

A DSC investigation performed on two high-copper Al-Cu-Mg alloys having a low Cu/Mg ratio has shown that both the $\alpha_{SSS} \rightarrow$ S-$CuMgAl_2$ and $\alpha_{SSS} \rightarrow$ θ-$CuAl_2$ precipitation sequences can be present during the decomposition of the supersaturated α_{SSS} obtained by solution treatment and quenching, provided that the solutioning temperature is sufficiently high

The possibility of obtaining the $\alpha_{sss} \rightarrow$ S-$CuMgAl_2$ sequence alone for lower solutioning temperatures, has allowed to give a precise attribution to the precipitation peaks owing to the S' and θ' phases, and this was not possible in alloys having the same Cu content but a higher Cu/Mg ratio.

The stabilization effect onto the GPB zones induced by the presence of Si atoms has been also confirmed by an increase of the activation energy for the precipitation of the S' phase.

5. REFERENCES

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