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A CALORIMETRIC STUDY OF PRECIPITATION PROCESS IN Al-Zn-Mg-Cu ALLOYS

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ABSTRACT

Ageing characteristics in Al-Zn-Mg-Cu alloys containing about 1 at.% Cu were investigated by specific heat measurements to reveal the role of copper. It has been confirmed that the fundamental precipitation process in Al-Zn-Mg alloy is altered significantly by the addition of copper. Two kinds of G.P. zones are formed on ageing at low temperatures: the one is the G.P. zone that is observed in Al-Zn-Mg alloy and the other the G.P.B. zone that is observed in Al-Cu-Mg alloy.

INTRODUCTION

Various metastable precipitate phases are produced in age-hardenable commercial aluminum alloys after ageing treatments. Thermal analysis gives very useful information to clarify the complicated precipitation process.

Al-Zn-Mg-Cu alloy is known as the highest strength commercial aluminum alloy (e.g. A.A 7075 and 7050). However, the role of copper in the Al-Zn-Mg-Cu alloy has not yet completely understood. Most of previous workers have suggested that the addition of copper do not alter fundamentally the precipitation process of Al-Zn-Mg alloy and merely prompt the formation of Guinier-Preston zones (G.P. zones) and intermediate precipitates (η'-phases) characteristic of Al-Zn-Mg alloy, with an increase of the density of G.P. zones and η'-phases. In the present work, the precipitation process in the high purity Al-Zn-Mg-Cu alloys was investigated by specific heat and hardness measurements.

EXPERIMENTAL PROCEDURES

Al-2.38 at.%(5.54 mass%)Zn-2.87 at.%(2.48 mass%)Mg-0.71 at.%(1.62 mass%)Cu alloy (7075 type alloy) and Al-2.64 at.%(6.11 mass%)Zn-2.90 at.%(2.49 mass%)Mg-0.97 at.%(2.22 mass%)Cu alloy (7050 type alloy) were prepared from high purity materials using continuous casting method. Billets, 97 mm in diameter were homogenized and extruded to bars. Specimens for specific heat measurements were

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machined into cylinders, 19 mm in diameter and 25 mm in height. All the specimens were solution heat treated at 738 K for 3 hours and quenched into iced water. The quenched alloys were immediately aged at room temperature, 353, 373, 393, 423 and 473 K. Specific heat versus temperature curve (S-T curve) was obtained using the Nagasaki-Takagi type adiabatic calorimeter at a rate of about 1 K/min during re-heating after quenching and ageing.

RESULTS AND DISCUSSIONS

As simillar results were obtained on both the 7075 and 7050 type alloys, we describe here only the results for 7075 type alloy. Fig. 1 shows the change of hardness for the Al-Zn-Mg-Cu alloys during ageing, compared with that of Al-Zn-Mg alloy (ref.1). The addition of 0.71 at.% Cu increases the maximum hardness and retards the overageing. The ageing times of specific heat measurements are shown by arrow points in Fig. 1.

Fig. 2 shows the S-T curves for the as-quenched and furnace-cooled Al-Zn-Mg-Cu alloys. The S-T curve for the as-quenched Al-Zn-Mg-Cu alloy distinctly differs from that for the as-quenched Al-Zn-Mg alloy (ref.2), clearly indicating that the quartenary alloy has the unique precipitation process. A significant feature of the S-T curve for the as-quenched Al-Zn-Mg-Cu alloy is the fact that the exothermic peak, A, exists at low temperature range that is observed in Al-Cu-Mg alloys (ref.3 and 4). This heat effect is probably attributed to the formation of Guinier-Preston-Bargaryatsky zones (G.P.B. zones) characteristic of Al-Cu-Mg alloy during re-heating from the supersaturated solid solution. Judging from the phase diagram of Al-Zn-Mg-Cu system (ref.5) and the electron microscopic study (ref.6) suggesting the existence of S-phases in Al-Zn-Mg-Cu alloy, it seems that G.P.B. zones, corresponding to the S-phases in Al-Cu-Mg alloy exist also in the Al-Zn-Mg-Cu alloy. On the other hand, the endothermic peak coming from the re-dissolution of G.P.B. zones was not observed, but it may be masked by the three exothermic peaks, B, C and D. Fig. 3 shows the S-T curves for the Al-Zn-Mg-Cu alloys aged at room temperature. Dashed curves in Fig. 3 represent the S-T curves of the as-quenched specimens. After the exothermic peak, A, decreases with ageing time and disappears on ageing for more than 50 hours, the endothermic peak, P, appears in the same temperature range and increases with ageing time. The endothermic peak, P, is caused by the re-dissolution of G.P. zones in Al-Zn-Mg system formed during ageing at room temperature. The same peak has already been reported for the Al-Zn-Mg-Cu alloy aged at longer time at between 298 and 378 K (ref.7). Fig. 4, Fig. 5 and Fig. 6 show the S-T curves of the Al-Zn-Mg-Cu alloys aged at 353, 393 and 423 K, respectively. In the specimens aged at 353 and 393 K, the exothermic peak, A, is entirely absent. The exothermic peak, B, decreases and the exothermic peak,

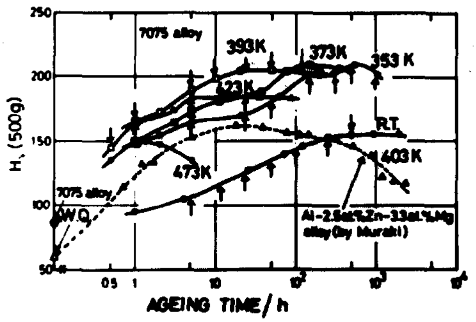

Fig. 1. Change of hardness in Al-2.38 at.% Zn-2.87 at.% Mg-0.71 at.% Cu alloy during ageing at room temperature, 353, 373, 393, 423 and 473 K, along with that in Al-2.5 at.% Zn-3.3 at.% Mg alloy during ageing at 403 K (ref.1).

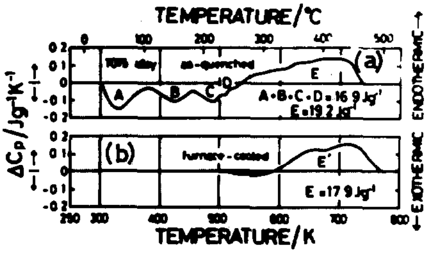

Fig. 2. Specific heat vs. temperature curves of Al-2.38 at.% Zn-2.87 at.% Mg-0.71 at.% Cu alloy (a) as-quenched and (b) furnace-cooled.

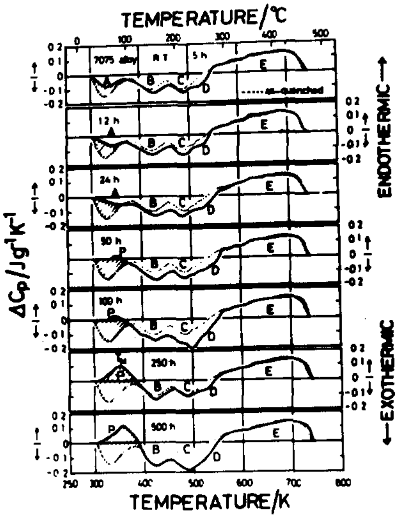

Fig. 3. Specific heat vs. temperature curves of Al-2.38at.%Zn-2.87at.%Mg-0.71at.%Cu alloy aged at room temperature, ageing time being from 5 hours till 500 hours.

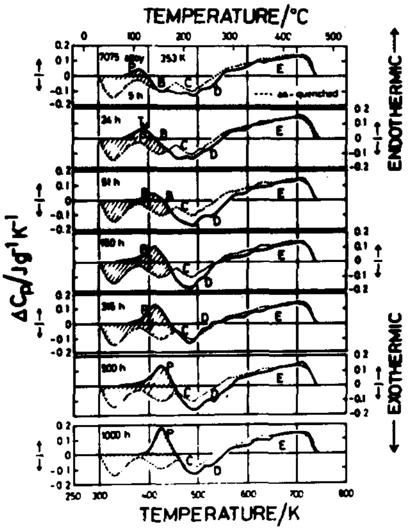

Fig. 4. Specific heat vs. temperature curves of Al-2.38at.%Zn-2.87at.%Mg-0.71 at.%Cu alloy aged at 353 K, ageing time being from 5 hours till 1000 hours.

P, increases with ageing time. The exothermic peak, B, may be responsible for the formation of intermediate S'-phases in Al-Cu-Mg system during re-heating. As shown in Fig. 6, in the specimen aged at 423 K the two exothemic peaks, A and B, are not observed. Then, the endothermic peak, P, increases and the exothermic

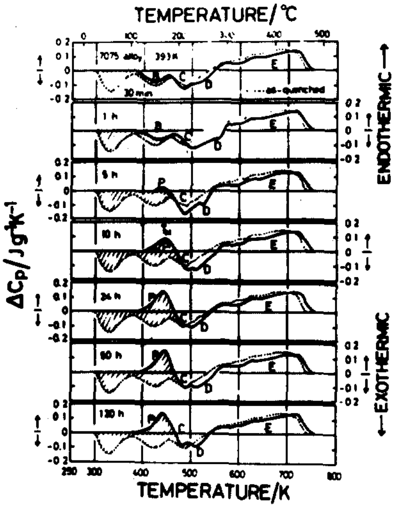

Fig. 5. Specific heat vs. temperature curves of Al-2.38at.%Zn-2.87 at.%Mg-0.71at.%Cu alloy aged at 393 K, ageing time being from 30 minutes till 120 hours.

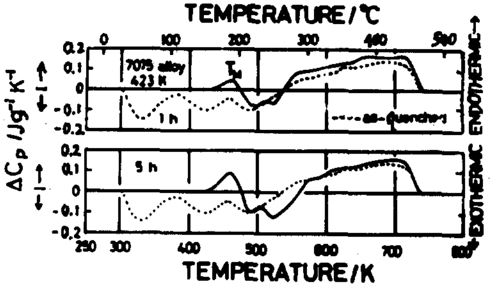

Fig. 6. Specific heat vs. temperature curves of Al-2.38at.%Zn-2.87at.%Mg-0.71at.%Cu alloy aged at 423 K for 1 and 5 hours.

peak, C, decreases with ageing time. The exothermic peak, C, may be due to the formation of intermediate η'-phases in Al-Zn-Mg system during re-heating.

In conclusion, complicated ageing behavior suggested from the S-T curves for the Al-Zn-Mg-Cu alloys containing about 1 at.% Cu can not be explained alone in view of the precipitation process observed in Al-Zn-Mg alloy. From our extensive studies, it is expected that the two kinds of precipitation processes that observed in both Al-Zn-Mg and Al-Cu-Mg alloys occur simultaneously in the Al-Zn-Mg-Cu alloy: supersaturated solid solution → G.P. zones → intermediate η'-phases → stable η -phases → stable T-phases, and supersaturated solid solution → G.P.B. zones → intermediate S'-phases → stable S-phases. The enhanced age-hardening by the addition of copper in Al-Zn-Mg alloy is attributed to the contribution of G.P.B. zones and intermediate S'-phases.

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