INFLUENCES OF THE THIRD ELEMENTS (Mn,Si,Ge) ON AGING PROCESS IN Al-Cu ALLOY

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Abstract/ Aging processes in binary Al-Cu and Al-Cu alloys with Mn, Si, Ge additions have been investigated by Vickers hardness tests, TEM and DSC measurements. The present work has revealed that G.P.(I) and G.P.(II) (θ"-phase) are independent with each other as far as the thermal stability is concerned. Mn suppresses the formation of G.P.zones and stabilizes the θ'-phase, whereas Si addition does not much modify the aging process. Ge addition alters the process significantly due to formation of other transient phases.

Keywords) Al-Cu alloy, the third elements, precipitation behavior

Introduction

Al-Cu alloy is a well-known precipitation hardening Al-base alloy, and prosperous results have been obtained for the aging process [1-5]. Based on the studies which have been accumulated so far, it has been widely accepted that the sequence of the precipitation follows : supersaturated solid solution → G.P.(I) zone→ G.P.(II) zone (θ"phase) → metastable θ'phase →stable θ phase. The precipitation phenomena have, however, not been fully understood yet, although various modern techniques such as TEM[6], XSAS[7], EXAFS[8], atom probe FIM[9], have been applied to study the phenomena. The sequence and thermal stability of the precipitates is an important problem which is still argued in these days. To settle the argument, it is essentially important not only to consider the structures of the phases but also to examine the thermal stability of the phases thoroughly. Some works presented the experimental results based on the calorimetry [10,11]. But no work has succeeded in presenting the definitive conclusion till now, as far as the calorimetric approaches to the problem are concerned. The present investigation aimed at studying the thermal stability of the metastable/stable phases which are formed in aging process of the Al-Cu alloy and the influences of the third elements in the process, by DSC measurements combining TEM observations and Vickers hardness tests.

Experimental procedure

The compositions of the specimens used in this work are listed in Table 1. The alloy specimens of the binary Al-Cu alloy are noted as C, E, G, H, J, a ternary Al-Cu-Mn alloy as 4AX, an Al-Cu-Si alloy as S1 and an Al-Cu-Ge alloy as G1. All specimens were prepared in a similar fabrication process. Solution treatment was carried out at 843K for 1.08×10^4 s followed by quenching into iced-water. Subsequent isothermal heat treat-

Table 1 Composition of the Al-Cu, Al-Cu-Mn, Al-Cu-Si and Al-Cu-Ge speecipmens

	Cu	Mn	Si	Ge	Al
C	0.56	-	-	-	Bal.
E	1.18	-	-	-	Bal.
G	1.66	-	-	-	Bal.
H	1.94	-	-	-	Bal.
J	2.18	-	-	-	Bal.
4AX	1.50	0.25	-	-	Bal.
S1	1.29	-	0.49	-	Bal.
G1	1.32	-	-	0.49	Bal.

ments were done at 403K, 433K and 463K for various aing periods between 0 to 6.0x10^{5}s using oil-baths. Differential Scanning Calorimetry (DSC) has been carried out using a RIGAKU TAS-8230D with heating rates 0.03, 0.08,0.17 and 0.33K/s. TEM observations were done by JEM100CX operated at 100kV in accelerating voltage. The Vickers hardness tests were conducted by SHIMAZU HV-1000 microhardness tester.

Results and discussion

I. Precipitation behavior in binary Al-Cu alloy

1.Vickers hardness tests

The Vickers hardness is one of the macroscopic properties which is related to the precipitation. Silcox et.al . [5] combined the Vickers hardness and X-ray diffraction data and deduced the phase which was in the majority at several stages of aging. Fig.1 shows the Vickers hardness curves which are obtained in this work. The hardness curves are arranged in order of copper concentration. Depending on the copper concentration, five Hv curves are classified into three groups. The Hv curves corresponding to Al-0.56 (specimen C) and 1.18 at%Cu (E) alloys keep the lowest levels. The curves only rise up a little at the last stage of the annealing. On the other hand, the Hv curves for Al-1.94at% (H) and 2.18at% (J) alloys are close to each other, and the hardness rapidly increases from the early stage of the annealing. The curve for Al-1.66at%Cu alloy, which is an alloy with medium copper concentration, is placed in the middle of the two groups. The increments of the hardness due to copper are not proportional to the concentration. Fig.2 shows the relation between the Vickers hardness and the copper concentration. The curve corresponding to "As quenched" state shows a linear dependence on the copper concentration. It is feasible to regard that the curve shows the effect of copper atoms to the solution hardening, which may be associated with quenched vacancies. It is also noted that the Vickers hardness has an S-shape curve against copper concentration. Up to ~1.2at% in copper concentration, the values of all Hv curves are similar and do not depend on annealing time. The alloys which contain copper more than 1.2at% increase the hardness by isothermal annealing at 433K.

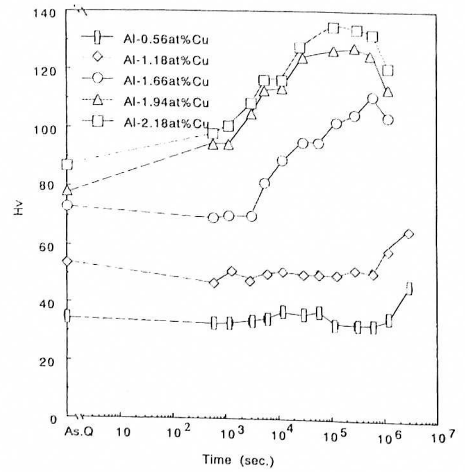


Fig.1 Vickers hardness curves of binary Al-Cu alloys aged at 433K

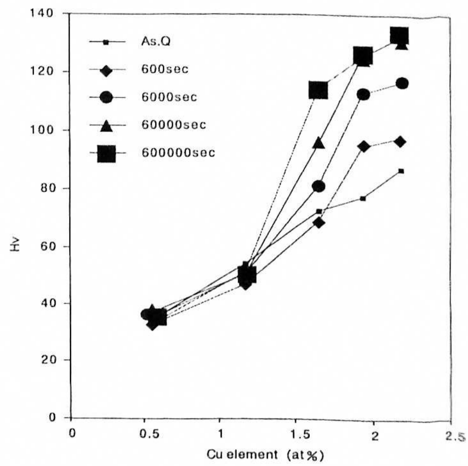
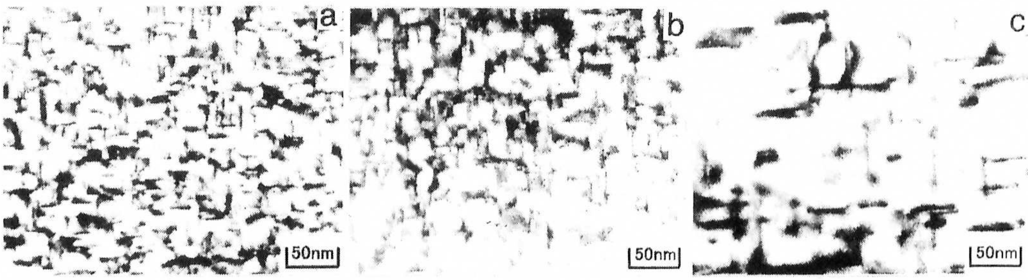


Fig.2 Compositional dependence of Vickers hardness in Al-Cu alloys

This leads to the conclusion that the copper concentration (~1.2at%) is corresponding to the solution limit of copper at 433K. The alloy with copper concentration more than 1.9at% shows a gentle slope in the hardness measurements. This feature suggests that excess copper atoms over 1.9at% do not effectively work for precipitation hardening. The reason of the saturation is not clear, but it may be related to the quenched vacancies which help the solute clustering as carriers or nucleation sites.

2.TEM observation

TEM observation gives us the information of the sizes and distributions of precipitated particles. Fig.3 shows bright field TEM images taken for the Al-1.7at%Cu aged at 433K for 1.2, 3.0 and 6.0×10^5sec. In Al-0.56 and 1.18at%Cu alloys, much large precipitates are sparsely distributed at the last stage of the annealing, whilst fine and much dense precipitates are formed at the early and subsequent stage of the annealing in the alloy comprising copper atoms with higher concentrations, although the microstructures of the alloys with high copper concentrations become similar to those of the dilute alloys at the late



1.2×10^5sec 3.0×10^5sec 6.0×10^5sec

Fig.3 Bright field TEM images of binary Al-Cu alloys aged at 433K

stage of the annealing. The TEM observation suggests that the precipitation process in Al-Cu alloy containing high copper concentration is different from that of Al-Cu alloy with low copper concentration. The hardness curves show small increase after long annealing. This may be due to the large precipitates which are also found in Fig.3(c). But the increment of the hardness in the alloy with low solute concentration is much smaller than that of the alloys with high copper concentration. The major effect of the increase in the Hv curve is, therefore, caused by small precipitates which are formed at the early stage of the annealing.

3.DSC measurements

To investigate the thermal stability of the metastable/stable precipitates which are formed in the aging process, the present work employed the DSC measurements. In the DSC thermograms, a formation of metastable/stable phase gives rise to an exothermic peak, and the dissolution of the phase to an endothermic peak. The sequential formation and dissolution of the phases can be detected by examining the DSC thermograms for the Al-Cu alloys. It is essential to take into account that the difference of the calorimetric result and the reaction undergoing in isothermal aging. Because of the difference, the DSC measurements in the present work were carried with both as-quenched and pre-aged Al-Cu alloy specimens. Fig.4 shows the DSC curves which are obtained for the as-quenched Al-Cu alloy specimens. Three large exothermic peaks are explicitly observed in the DSC curves for the specimens with high copper concentration, whilst the first exothermic peaks are scarcely observed in the curves for the alloy specimens with low copper concentration.

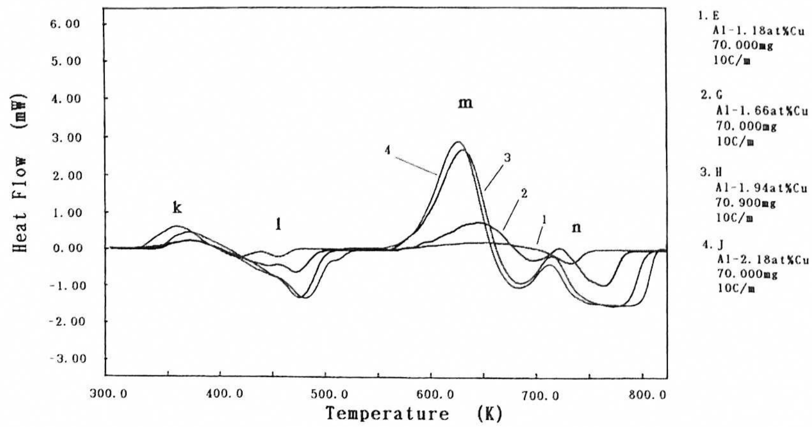


Fig.4 DSC curves of as-quenched Al-Cu alloys

Looking into the curves for the as-quenched specimens carefully, a small exothermic peak appears at ~440K. They are relatively small compared with other exothermic peaks. If four metastable/stable phases are formed in the annealing as mentioned above, the peak k, l, m and n are corresponding to the formation of G.P.(I), G.P.(II), θ' and θ phases, respectively. Based on the results shown in Fig.4, the reaction of the G.P.(II) formation which appears at ~420K, is outstandingly separated from that of G.P.(I) with changing copper concentration. This feature of the DSC curve is also explicitly seen in the DSC curves for the Al-Cu alloys pre-aged at 433K for 600s, which correspond to the condition forming small precipitates with high density as shown in TEM observation (c.f.,Fig.3(b)). The sequence of the G.P.(I) and G.P.(II) have been argued for long years. But the present DSC measurements leads to the conclusion that the G.P.(I) and G.P.(II) are independent with each other as far as the thermal stability is concerned.

II.Precipitation behavior in Al-Cu-X (X=Mn,Si,Ge) alloys

1.Vickers hardness tests

Fig.5 shows the Vickers hardness for the ternary Al-Cu-X(X=Mn,Si,Ge) alloys which are isothermally annealed at 433K with that of Al-1.66at%Cu as reference. The Al-Cu-Mn alloy keeps almost same level just before peak position, whilst the Hv curves of Al-Cu-Si and Al-Cu-Ge alloys gradually increase their hardness with annealing time.

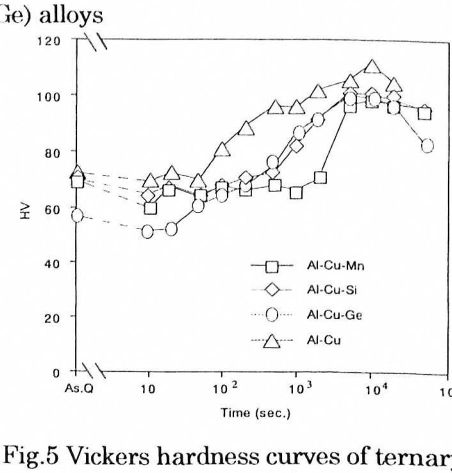
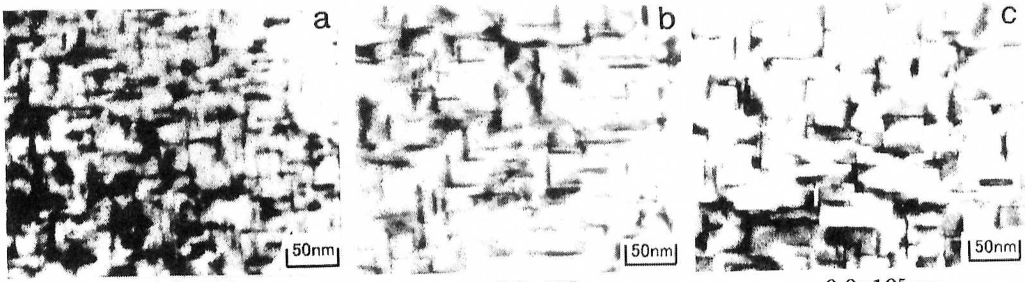


Fig.5 Vickers hardness curves of ternary Al-Cu-X alloys aged at 433K

2. TEM observation

Fig.6 shows the microstructures of the Al-Cu alloy containing Mn (4AX). The sizes of the precipitates are slightly larger than those of the binary Al-Cu alloy after annealing at 433K for 1.2×10^3s. At this stage of annealing, the precipitates are a little more densely distributed in the binary alloy. However, the coarsening of the precipitates occurs much faster in the



1.2x10^5sec 3.0x10^5sec 6.0x10^5sec

Fig.6 Bright field TEM images of ternary Al-Cu-X alloys

binary Al-Cu alloy than in the ternary Al-Cu-Mn alloy. The peak position of the size distribution shifts faster in the Al-Cu alloy, whereas the precipitates grow slowly in the Al-Cu-Mn alloy. The TEM image of the Al-Cu-Si alloy looks almost similar to that of the binary alloy, whereas the image of the Al-Cu-Ge alloy shows that the alloy has precipitates which are different from those observed in the binary Al-Cu alloy.

3.DSC measurements

The DSC curves for Al-Cu-Mn, Al-Cu-Si and Al-Cu-Ge alloys are shown in Fig.8 together with the Al-Cu alloy as reference. The DSC curve for the Al-Cu-Mn alloy shows a relatively large exothermic peak at ~630 K, although the initial exothermic peak which explicitly appear in the Al-Cu alloy, is almost disappeared. The curve for the Al-Cu-Si alloy is similar to that for the reference specimen.

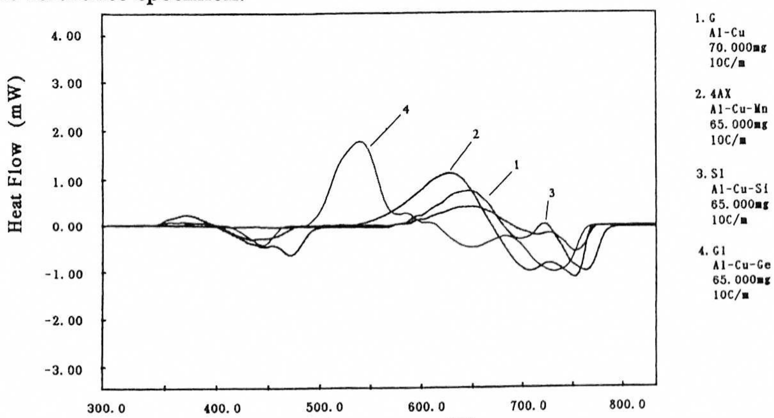


Fig.7 DSC curves for binary Al-Cu, Al-Cu-Mn, Al-Cu-Si and Al-Cu-Ge alloys

Exothermic peaks which are observed in the DSC curve for the reference are all appeared in the Al-Cu-Si alloy. The DSC curve for the Al-Cu-Ge alloy shows the profile with small exothermic and endothermic peaks, which is different from that for the reference.

The different influences of the third elements may be interpreted as follows. The formations of the G.P.zones and other precipitates are subject to the diffusions of copper and the third element atoms. If the third element atom has a strong chemical affinity and migrates with low mobility like Mn, the solute segregation can not use vacancy diffusion and the secondary defects of vacancy effectively. Therefore, G.P. zones are hardly observed in Al-

Cu alloy containing Mn addition. On the other hand, if the element which has a weak interaction to the solute atoms or the mobility comparable with the solute atoms is added, the precipitation behavior does not change much (AL-Cu-Si alloy) or sometimes the third elements form precipitates consisting of the own element in Al-Cu alloy (Al-Cu-Ge alloy).

Summary

The present investigation revealed that precipitation hardening is caused in Al-Cu alloy which contains more than 1.2at% copper. G.P.(I) zone and G.P.(II) zone are independent with each other in Al-Cu alloy, as far as the thermal stability is concerned. Manganese addition makes G.P. zones unstable and accordingly stabilizes the θ' phase. Silicon addition does not change the precipitation phenomena much, whilst Germanium alters the precipitation behavior significantly due to formation of other transient phases.

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