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Low Temperature Age-Hardening of Al-12mass%Zn-0.5mass%Cu Alloy

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Effect of addition of a small amount of copper to Al-12mass%Zn binary alloy on the process of low temperature aging is studied by hardness test and transmission electron microscopy. Age hardening rate after quenching from various temperatures is slowed down by addition of 0.5mass% copper to the binary alloy. The hardness obtained after long aging, however, is increased a little by the addition of copper. The extent of soft surface layer formed by aging in the copper-added alloy is nearly equal to that obtained in the binary alloy.

1. INTRODUCTION

Al-Zn alloy, which is a base binary alloy of ultra-super Duralumin, is a typical age-hardenable alloy and has been studied by many workers, relating to the microscopic structure, on its mechanical and physical properties obtained with various heat treatments. When the alloy is held at around room temperature after quenching from, say, 673K (so-called low temperature aging), many fine GP zones enriched with solute zinc atoms form and contribute to the age hardening. Until recently GP zones had been thought to be formed uniformly in the specimen except for the proximity to grain boundaries. According to the detailed examination by Ohta et al. of the age hardening process at various regions in the specimen, regions near the specimen surface and near the grain boundary in the vicinity of surface remained, even after a long aging, soft compared with the other hardened regions.[1] They later explained the result by use of X-ray small-angle scattering and other methods as follows: Specimen surface and grain boundaries behave as efficient sinks for quenched excess vacancies and the vacancy concentration in the vicinity of them decreases more rapidly than in the other regions, which retards or virtually stops GP zone formation in the region.[2] This region with a little lower hardness near the surface obtained after aging will be called "soft surface layer" hereafter. The present authors performed fatigue test of the Al-Zn alloys with various compositions and heat treatments, paying attention to the effect of this soft surface layer on fatigue, and found that the existence of soft surface layer improved fatigue strength under repeated tensile mode.[3~5]

On the other hand, it is well known in many cases that the formation and growth of GP zones are remarkably influenced by addition of a third element.[6] Addition of silver, for instance, elevates the solvus temperature of GP zones and promotes the formation and growth of the zones, while addition of copper does

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not change the solvus temperature of GP zones.[7,8] In this report, effect of addition of a small amount of copper to Al-12mass%Zn alloy on the age hardening process and on the formation of the soft surface layer is examined.

2. EXPERIMENTAL PROCEDURES

2.1. Specimens

Alloys, nominal compositions of which were Al-12mass%Zn and Al-12mass%Zn-0.5mass%Cu (called hereafter binary alloy and Cu-added alloy, respectively), were made by melting 99.99%Al, 99.999%Zn and 99.999%Cu in the alumina crucible in atmosphere. Chemical analysis of these alloys were shown in Table 1. Ingots obtained were homogenized by annealing at 723K for 180ks, peeled mechanically, and then hot forged and cold rolled with intermediate annealing procedures to a strip of 1.1mm in thickness and a strip of 0.7mm in thickness, from which were prepared the specimens for hardness test and the ones for electron microscopy, respectively. Shapes and dimensions of the specimens were the same as reported previously.[1,3] Crystal grains of the specimen for hardness test were coarsened to about 4mm in diameter by the strain annealing method.

Table 1 Chemical composition of alloys used (mass%)

Alloys	Zn	Cu	Si	Fe	Al
Al-12%Zn	11.3	0.003	0.004	0.003	balance
Al-12%Zn-0.5%Cu	11.2	0.491	0.002	0.001	balance

2.2. Heat Treatments

The sequence of quenching was as follows: The specimen was inserted into the slit of an aluminum block in an electric furnace and was held at 773K for 3.6ks for solution treatment. Then it was cooled in the furnace to the quenching temperature (T_Q), held there for 3.6ks, and finally quenched into iced water.

Aging was carried out at 273K or 293K in an ethanol bath. The sequence of the heat treatment is schematically shown in Fig.1.

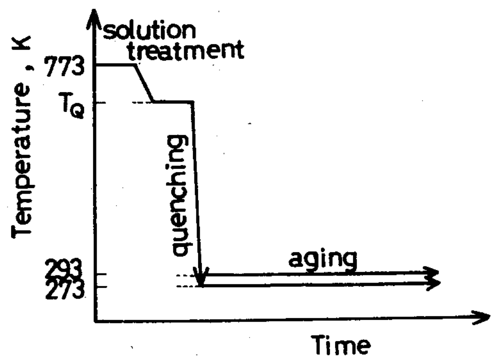

Fig.1 Schematic diagram of the sequence of heat treatment.

2.3. Measurements

Hardness was tested at room temperature using Vickers microhardness tester and ultramicrohardness tester (Akashi Co. Ltd.). Age hardening process was followed at the load of 1.96N, and fully aged state was examined at various penetration loads, 0.01 to 9.8N, at the position more than 200μm apart from the grain boundary before and after each removal of the surface layer about 50 μm in thickness. Surface layer was removed by electropolishing in a perchloric acid-ethanol (1:4) solution.

Microstructure of the aged specimen was observed with a transmission electron microscope, JEM-2000EX, operated at 200kV.

3. RESULTS AND DISCUSSION

Figure 2 shows isothermal age hardening curves of the binary and Cu-added alloys at 293K after quenching from 673K. Average values and standard deviations of more than eight measurements are presented in the figure for the aging time (t_A) equal to or more than 4.8ks, and only average values of four or less measurements are presented for the t_A less than 4.8ks. Hardness increases with increase of t_A and reaches a stationary value in either alloy. The stationary value of Cu-added alloy is a little higher than that of the binary alloy, but the time to reach the value is longer. Baba reported a similar result to the present one for an alloy containing 6%Zn, a comparatively low concentrated alloy.[9] Many spherical GP zones about 6nm in diameter were observed with TEM in either alloy, independent of the copper addition, aged at 293K for 300ks after quenching from 673K.

The result of the same experiment as Fig.2 but of a higher T_Q, 773K, is shown in Fig.3. Similar behavior to Fig.2 was obtained for this higher T_Q. Time to reach the stationary value, however, is shorter than that of Fig.2 for either alloy, which is considered to be due to faster diffusion of solute atoms with higher concentration of vacancies quenched from higher temperature.

Difference in the age hardening process between the two alloys shown in Figs.2 and 3 is considered to be explained by the copper atom-vacancy binding energy which is a little larger than the zinc atom-vacancy

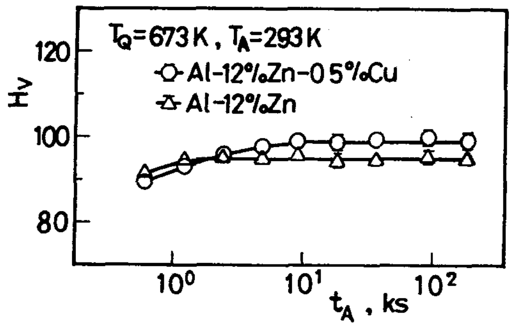

Fig.2 Isothermal age hardening curves of the Al-12 mass%Zn binary alloy and Cu-added alloy aged at 293K after quenching from 673K.

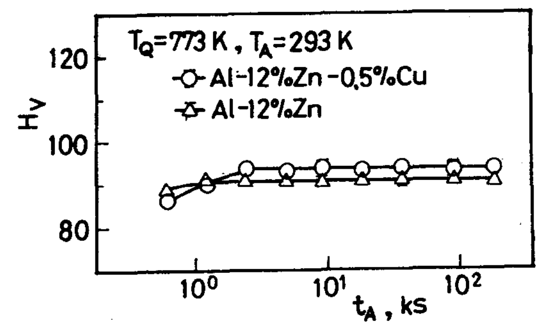

Fig.3 Isothermal age-hardening curves of the Al-12 mass%Zn binary alloy and Cu-added alloy aged at 293K after quenching from 773K.

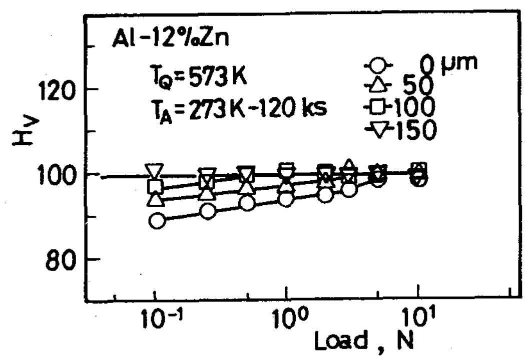

Fig.4 Dependence of hardness on the indentation load for the binary alloy specimen just aged at 273K for 120ks after quenching from 573K and the ones aged and electropolished to remove the surface layers.

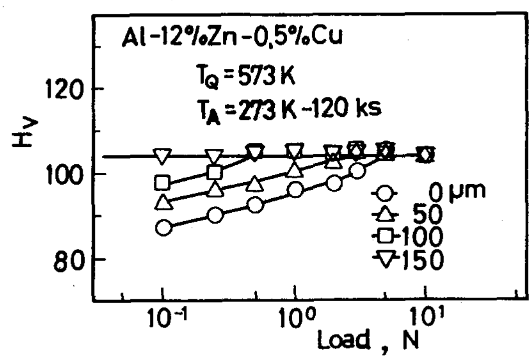

Fig.5 Dependence of hardness on the indentation load for the Cu-added alloy specimen just aged at 273K for 120ks after quenching from 573K and the ones aged and electropolished to remove the surface layers.

binding energy, and by the formation of a kind of copper atom clusters in addition to the GP zone formation proper to the binary alloy.

Figures 4 and 5 show the variation along the depth from the surface of the hardness of the fully aged specimens of binary alloy and Cu-added alloy, respectively. Open circles represent the result of the hardness test carried out at various penetration loads, 0.01 to 9.8N, of the specimen just aged at 273K for 120ks after quenching from 573K. The fact that hardness decreases with decrease of the load indicates that hardness near the surface is lower than that of the interior. Hardness of the Cu-added alloy is slightly lower than that of the binary alloy when measured at smaller loads, but they coincide with each other when measured at 4.9N or more of the load. Surface layers of 50μm in thickness were removed successively and hardness was measured after each removal (△,□,▽). Removal of the layer more than 100μm in thickness was required in either alloy to obtain the hardness independent of the load. It may be considered therefore that the thickness of the soft surface layer in this case has 100μm or more for either alloy. Similar result was obtained for the specimen quenched from different temperatures. Addition of a small amount of copper (0.5%) did not alter the thickness of the soft surface layer. The average grain size of the Cu-added alloy specimen was almost the same as that of the binary alloy specimen. Taking account of the previously reported fact that addition of a small amount of silver to Al-Zn alloys, which elevates the solvus temperature of GP zones, suppress the formation of the soft surface layer,[10] the result that change was hardly observed in the thickness of the soft surface layer by the addition of copper is considered to be due to little change in solvus temperature by the addition.

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