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Ductility of Ultra High Purity Copper

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Abstract. The ductility of ultra-high purity copper at elevated temperatures was investigated : purity 99.9999% (6N) and 99.999999% (8N). Tensile tests were conducted at temperatures ranging from 293K to 1073K at strain rates of $4.2 \times 10^{-5} \text{ s}^{-1}$ in a high vacuum. The results are discussed in comparison with those for 99.9% (3N) copper. Ductility at intermediate temperatures was improved by an increase in purity. The temperature at which ductility dropped decreased with increases in purity. Even at the ultra-high purity of 8N, a small ductility drop was observed at 423K. A small number of micro voids were observed on the grain boundaries of 8N specimens after the test at 423K. 6N and 8N copper have nearly same sulphur content of about 0.015 ppm. The intermediate temperature embrittlement of these coppers might be affected not only by sulphur content, but also by total impurity content.

1. INTRODUCTION

Copper has been one of the most popular and important base metals for a long time, because of its excellent electric and thermal conductivity. However, the properties of copper such as electric and thermal conductivity do not reach the levels needed for recent industrial use. In order to improve such properties, copper has been refined. Recently, copper purified to more than 99.9999 % (6N) has been commercially produced by a special purifying process, which combines electrolytic refining, electron beam refining and vacuum melting. The use of high purity copper has been tried recently in highly technical fields, such as superconductors, electron accelerators and interconnections in advanced IC. In these fields, copper with better mechanical properties without the sacrifice of conductivity at high temperatures is also required [1,2]. However, a ductility drop in pure copper and some copper alloys at about 600 to 800K has been reported by many researchers [3-14]. This phenomenon is called intermediate temperature embrittlement due to intergranular failure. Ductility at intermediate temperatures decreases with the decrease in strain rate and with the increase in grain size [5-7,12]. Suzuki and Ito [9] found that reducing the sulphur content in pure copper reduced the effect of intermediate temperature embrittlement at a strain rate of $4.2 \times 10^{-4} \text{ s}^{-1}$. Ito, Kanno, Okamoto and Yamamoto [10] reported that ductility at intermediate temperatures decreased with the increase in sulphur content, and the temperature of the ductility drop decreased with an decrease in sulphur content at a low strain rate of $4.2 \times 10^{-5} \text{ s}^{-1}$. However, they were only interested in sulphur content and not in other impurity elements.

The purposes of the present study are to investigate the ductility of ultra-high purity copper of 6N and 8N from room temperature to elevated temperatures, and to discuss the effect, not only of sulphur content, but also of total impurity content on the intermediate temperature embrittlement of pure copper.

2. EXPERIMENTAL PROCEDURES

The ultra-high purity copper of 6N and 8N used in the present study was purified by the Japan Energy Co., Ltd. Commercial purity copper rod of 99.9 % (3N) purity was used for comparison with the ductility of 6N and 8N copper. Table 1 shows the results of the chemical analysis of the specimens determined by glow

Table 1: Results of chemical analysis of the pure coppers (mass ppm).

Element	3N-Cu	6N-Cu	8N-Cu	Element	3N-Cu	6N-Cu	8N-Cu
C	< 1	< 1	< 1	Co	0.30	0.001	<0.001
S	4.6	0.014	0.015	Ni	2.2	0.063	<0.002
N	< 1	< 1	< 1	Zn	0.28	<0.005	<0.005
O	240	0.8	< 0.1	As	0.40	<0.01	<0.01
H	0.22	0.10	0.03	Cd	<0.005	<0.01	<0.01
Ag	15	0.32	0.011	Sn	10	<0.01	<0.01
Al	0.006	0.14	0.003	Sb	0.43	<0.005	<0.005
Si	0.021	0.068	0.023	Pb	1.4	<0.002	<0.002
P	0.51	0.012	<0.005	Bi	0.069	<0.001	<0.001
Ti	<0.005	0.020	0.004				
Cr	0.009	0.12	<0.002				
Mn	0.19	0.006	<0.002				
Fe	5.5	0.35	0.002				

Each copper rod of different purity was cold swaged from 8.0 mm to 6.5 mm in diameter. Specimens for the tensile tests of 20 mm gauge length and 3 mm diameter were machined from the round rods of 6.5 mm diameter. Every specimen was annealed for 1.8 ks at 573K at a high vacuum of 1.3×10^{-2} Pa. The average grain size was 30 μm for 3N, 50 μm for 6N and 100 μm for 8N after annealing. Tensile tests were carried out at the initial strain rate of $4.2 \times 10^{-5} \text{ s}^{-1}$ between 293K and 1073K at a high vacuum of 7×10^{-4} Pa. The reduction in area (RA) after tensile test was used as the indicator of ductility. Scanning electron microscopy (SEM) of the fractured surfaces was carried out on several specimens after the tensile tests. The microstructure near the fracture surface after the tensile tests was observed to confirm the formation of cavities on grain boundaries and dynamic recrystallization by deformation.

3. RESULTS

3.1 Ductility at Room Temperature

Figure 1 shows stress-strain curves of different purity coppers tested at room temperature. Yield stress and maximum stress of ultra-high purity copper of 6N and 8N are lower than those of 3N copper. The RA of ultra-high purity copper, 91% for 6N and 96 % for 8N, is higher than that of commercial copper, 82 % for 3N. However, the elongation of 8N copper is slightly lower than that of 6N copper. This phenomenon might be caused by the effect of grain size. The ductility of pure copper at room temperature increases with the decrease in impurities. The significant difference between 3N copper and 6N, 8N copper is especially recognizable.

Figure 1 Stress-strain curves of pure copper at room temperature under the strain rate of 4.2×10^{-5} .

3.2 Ductility at Elevated Temperatures

Figures 2 and 3 show the stress-strain curves of 6N and 8N copper at elevated temperatures at a strain rate of $4.2 \times 10^{-5} \text{ s}^{-1}$. Above 473K for 6N copper and above 523K for 8N copper, the stress-strain curves show the typical shape of dynamic recrystallization [15-21]. After work hardening, the stress decreases, then increases slightly, and some peaks of stress are observed. The number of stress peaks increases with an increase in test temperature.

On the other hand, the stress-strain curves of 6N and 8N coppers at 873K and 1073K become different from those accompanying typical dynamic recrystallization. At these temperature ranges, decrease of stress after work hardening is very fast. Then, the curves look like saw teeth. The same behaviour cannot be observed in 3N copper, because of its low ductility at elevated temperatures, as described below. In ultra-high purity 6N and 8N coppers, the velocities of dynamic recrystallization might be very fast, due to the rapid rearrangement of dislocations accumulated by deformation.

The work hardening rate is very high at 423K for 6N copper and 373K for 8N copper. The total elongation of these coppers is small at each temperature. This phenomenon might be related to ductility drop, as described below.

Figure 4 shows the effect of test temperature on RA at temperatures ranging from 273K to 1073K. The RA of 3N copper drops remarkably above 473K. The RA of 3N copper above 673K falls lower than 20 %. Although these ductility drops are caused by intermediate temperature embrittlement, no recovery of RA in 3N copper at a temperature of 1073K is observed. The RA drop is observed in 6N copper from 423 to 523K, and in 8N copper from 373 to 473K. However, RA of the 6N and 8N coppers is quite high, almost 100 % above 523K and 473K, respectively. In these temperature ranges, chisel point fracture is observed in 6N and 8N coppers. The ductility drop is improved by an increase in purity. The temperature of the ductility drop decreases with the increase in purity.

Figure 5 shows the microstructures of fractured surfaces after the tensile test at RA drop temperature at a strain rate of $4.2 \times 10^{-5} \text{ s}^{-1}$; the test temperatures were 873K for 3N copper, 473K for 6N copper and 423K for 8N copper.

The fractured surface of 3N copper tested at 873K shows intergranular fracture. A lot of small dimples on the grain boundaries can be observed. A lot of intergranular failures can be also observed in the microstructure of 3N copper in (d). The cavities nucleated on the grain boundaries at first. They grew and chained together during deformation.

Figure 2 Stress-strain curves of 6N copper at elevated temperature.

Figure 3 Stress-strain curves of 8N copper at elevated temperature.

Figure 4 Effect of test temperature on reduction in area under the strain rate of 4.2×10^{-5} .

Figure 5 Fractured surfaces and microstructures after the tensile tests at (a) (d) 873K for 3N copper, (b) (e) 473K for 6N copper and (c) (f) 423K for 8N copper.

Finally, intergranular failure occurred at intermediate temperatures. The fracture surfaces of ultra-high purity copper of 6N tested at 473K and 8N at 423K show ductile fractures. No intergranular surfaces can be observed. However, in the microstructure of 6N copper tested at 473K, intergranular failures can be observed. In the microstructure of 8N copper tested at 423K, only a few cavities can be observed. These

cavities are located on the grain boundaries. Although the number of intergranular failures decreases with the increase in purity, fracture at intermediate temperatures is caused in every case by the cavities nucleated at grain boundaries.

4. DISCUSSION

In the present research, no recovery of RA in 3N copper at a temperature of 1073K is observed. This result is different from the results in some former reports [4-14]. There are two reasons to explain this phenomenon. One is the lower purity of 3N copper used in the present research, and the other is the lower strain rate in present research. In the most of the former reports, copper of purity greater than 4N was used, and strain rates over 10^{-3} s^{-1} were chosen. In our view, the ductility drop of 3N copper above 473K in the present research is caused by intermediate temperature embrittlement, although no recovery of RA to temperature of 1073K is recognized. Generally, the intermediate temperature embrittlement of pure copper and copper alloys is caused by intergranular failure due to cavities nucleated on the grain boundaries. It is thought that the nucleation of cavities on the grain boundaries is caused by boundary sliding and piling-up of the dislocations on the grain boundaries through the slip line in the grains [3, 22-24]. Boundary sliding and the diffusion of the defects to the grain boundaries occur more easily with increasing temperature. On the other hand, dynamic recrystallizations also occur more easily with increasing temperature. Dynamic recrystallization along the grain boundaries occurs more easily than in the grains. So ductility improves at higher temperatures due to dynamic recrystallization.

Kanno and Ito [12] found that decreasing sulphur content in pure copper made recrystallization temperatures lower. That made the ductility of pure copper at intermediate temperatures higher and caused the temperature of the ductility drop to fall. In the present research, ductility at intermediate temperatures was improved by an increase in purity. The temperature of the ductility drop decreased with the increase in purity. However, the sulphur content of ultra-high purity copper of 6N and 8N is nearly same. Although sulphur is one of the most important elements in recrystallization behaviour, the improvement in intermediate temperature embrittlement is caused not only by sulphur content, but also by total impurity content through the decreasing dynamic recrystallization temperature. Figure 6 shows the static recrystallization behaviour of pure coppers after being cold deformed 83% in area. The static recrystallization temperature is about 400K for 8N copper, 420K for 6N copper and 500K for 3N copper. The static recrystallization temperature decreases with the increase in purity. Although dynamic recrystallization behaviour is not quite the same as static recrystallization behaviour, the dynamic recrystallization temperature of ultra-high purity coppers must be lower than that of coppers of industrial purity. In fact, the stress-strain curve of 6N copper at 473K suggests the dynamic recrystallization in Figure 2. Although the stress-strain curve of 8N copper at 423K does not suggest the dynamic recrystallization in Figure 3, some dynamically recrystallized small grains are observed along the grain boundaries near the fractured surface of 8N copper tested at 423K in Figure 5 (f).

Figure 6 Static recrystallization behavior of pure coppers annealed for 30 min after cold deformed 83 % in area.

5. CONCLUSIONS

- (1) The ductility of ultra-high purity copper of 6N and 8N is much better than that of conventional copper of 3N at room temperature.
- (2) The ductility drop caused by intermediate temperature embrittlement is improved by an increase in purity because of decreasing dynamic recrystallization temperatures.
- (3) The temperature of the ductility drop decreases with the increase in purity because of decreasing dynamic recrystallization temperatures.
- (4) Intermediate temperature embrittlement is not affected only by sulphur content, but also by the total impurity content of pure copper.

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