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Effects of grain boundaries on electrical property of copper wires[①]

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Abstract: By means of annealing at different temperatures, the copper wires with various numbers of grain boundaries were achieved. And the resistivity of copper wires was measured. The results show that with increasing the number of grain boundaries, the resistivity of copper wires increases, the relationship between the number of grain boundaries and the resistivity of cooper wires can be expressed as $y = 1.86\times 10^{-8} e^{-0.90/x}$. Unlike dislocation and lattice vacant sites, the curve of the grain boundary vs the resistivity is not linear. Grain boundary controls the general trend of the curve, but the type and the quantity of impurity controls the details of the curve.

Key words: copper wire; grain boundary; resistivity
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1 INTRODUCTION

To prevent the nucleation of crystals on the mould wall, a heated mould that can maintain at a certain temperature was used instead of the conventional cold mould[1-4]. This is the principle of Onho Continuous Casting (OCC) method. With the method, it is possible to obtain a long and thin single crystal copper wire. Recently, in the world particularly in Japan, Korea, American, Canada, and so on, the manufacture of single crystal copper wire becomes a very attractive aspect[5-7], because the single crystal copper wire has a good future in the marketplace.

It is reported that grain boundaries(GB), in particular, which is perpendicular to the direction of signal transmission, have an evident effect on the signal distortion and attenuation[8]. Since there is no grain boundary in single crystal copper wire, the quality of signal transmission is excellent. The effects of grain boundaries on the electrical property of copper wires by measuring the resistivity of copper wires with various numbers of grain boundaries are investigated in this paper.

2 EXPERIMENTAL

In present work there are two types of samples. One is the current highly pure copper wires named as T1 with dimension of d 1.12 mm × 1 000 mm, the other is the copper wires with dimension of d1 mm × 1 000 mm pulled from single crystal copper wires with 6 mm in diameter which are produced by OCC method and named as T2. Two types of copper wires are annealed at different temperatures for 2 h, The annealing temperatures of sample T1 are 500, 600, 700, 800 and 900 ℃, respectively, and those of sample T2 are 400, 600, 800 and 900 ℃, respectively. Then, the copper wires with various numbers of grain boundaries can be achieved. Pure copper, particularly at high temperature, can be oxidized easily. Therefore, when they are annealed, the samples must be protected with anti-oxidation coating.

After the distorted copper wires are annealed at various temperatures, there are different grain boundaries in the copper wires. Based on Heyn method and the metallographs from present work (as shown in Fig. 1 and Fig. 2), the number of grain boundaries in the copper wires can be calculated.

Because Cu is a good conductive material and the effect of grain boundaries on the resistivity of copper wires is not so evident, the precision of apparatus for measuring the resistivity of copper wires needs relatively high. In this research, the resistance meter YY2513 with precision of 1×10^{-6} Ω was chosen. Method of four-end measure was used in order to avoid the contact resistance. The measure was carried out at 27 ℃. The resistivity ρ can be worked out by the following equation:

$$\rho = RS/L \quad (1)$$

where R is the resistance of the copper wires; S is the cross section area of the copper wires and L is the distance of two voltage ends.

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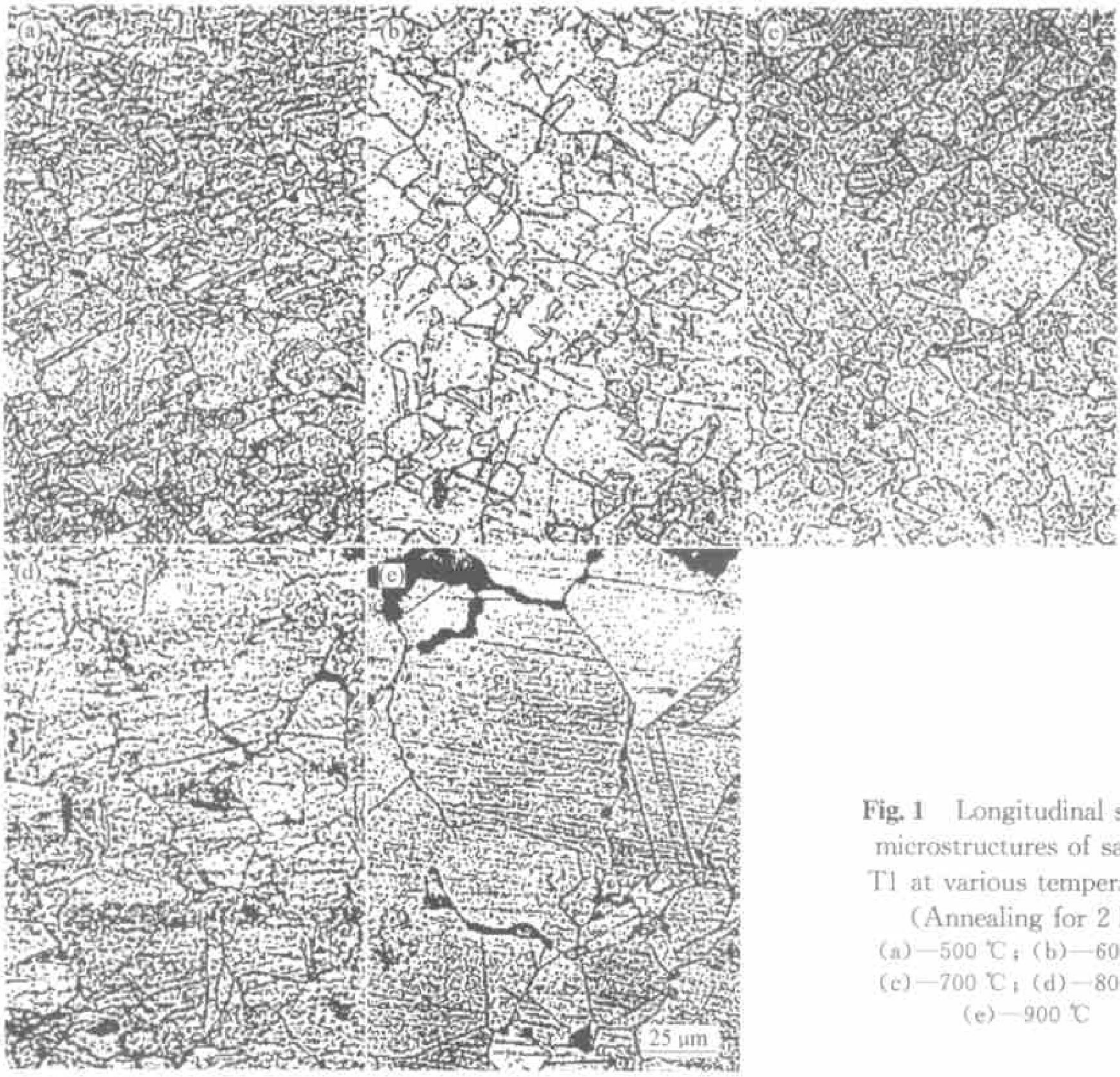

Fig. 1 Longitudinal section microstructures of sample T1 at various temperatures (Annealing for 2 h)
(a)—500 ℃; (b)—600 ℃; (c)—700 ℃; (d)—800 ℃; (e)—900 ℃

3 RESULTS AND ANALYSIS

The experimental results are listed in Tables 1 and 2. It is observed that with increasing the annealing temperature, the number of grain boundaries and the resistivity of the copper wires decrease. The relationship between the number of grain boundaries and the resistivity of the copper wire is shown in Fig. 3, indicating that the resistivity of the copper wires increases with increasing the number of grain boundaries. Unlike dislocation and lattice vacant sites, the effects of the grain boundaries on the resistivity are not linear. When the number of grain boundaries is small, the resistivity rapidly increases with increasing the number of grain boundaries. After the grain boundaries number reaches some amount, however, the increase of resistivity becomes slow, which is exactly the same as the effect of grain boundaries on the resistivity of aluminum wires[9]. When the increase of resistivity becomes slow, the number of grain boundaries for sample T1 is more than 22, but that of sample T2 is less than 22. The relationship between the number of grain boundaries and the resistivity of the copper wires can be expressed as

$$y = a e^{b/x} \quad (2)$$

where x stands for the number of grain boundaries, y is the resistivity of copper wires. By regressing the data from Tables 1 and 2 the average value for a is about 1.86×10^{-8}, and b is about -0.90. Then, Eqn. (2) can be expressed as:

$$y = 1.86 \times 10^{-8} e^{-0.90/x} \quad (3)$$

4 DISCUSSION

4.1 Electrical resistivity of metal

In a perfect crystal, the crystal lattice is

Table 1 Data of number of grain boundaries along longitudinal section, annealing temperature and resistivity of sample T1

Annealing temperature/ ℃	Number of GB/ mm^{-1}	Resistivity/ (10^{-8} Ω·m)
500	51.15	1.858 2
600	42.12	1.848 6
700	33.04	1.846 0
800	22.46	1.834 7
900	12.31	1.757 0

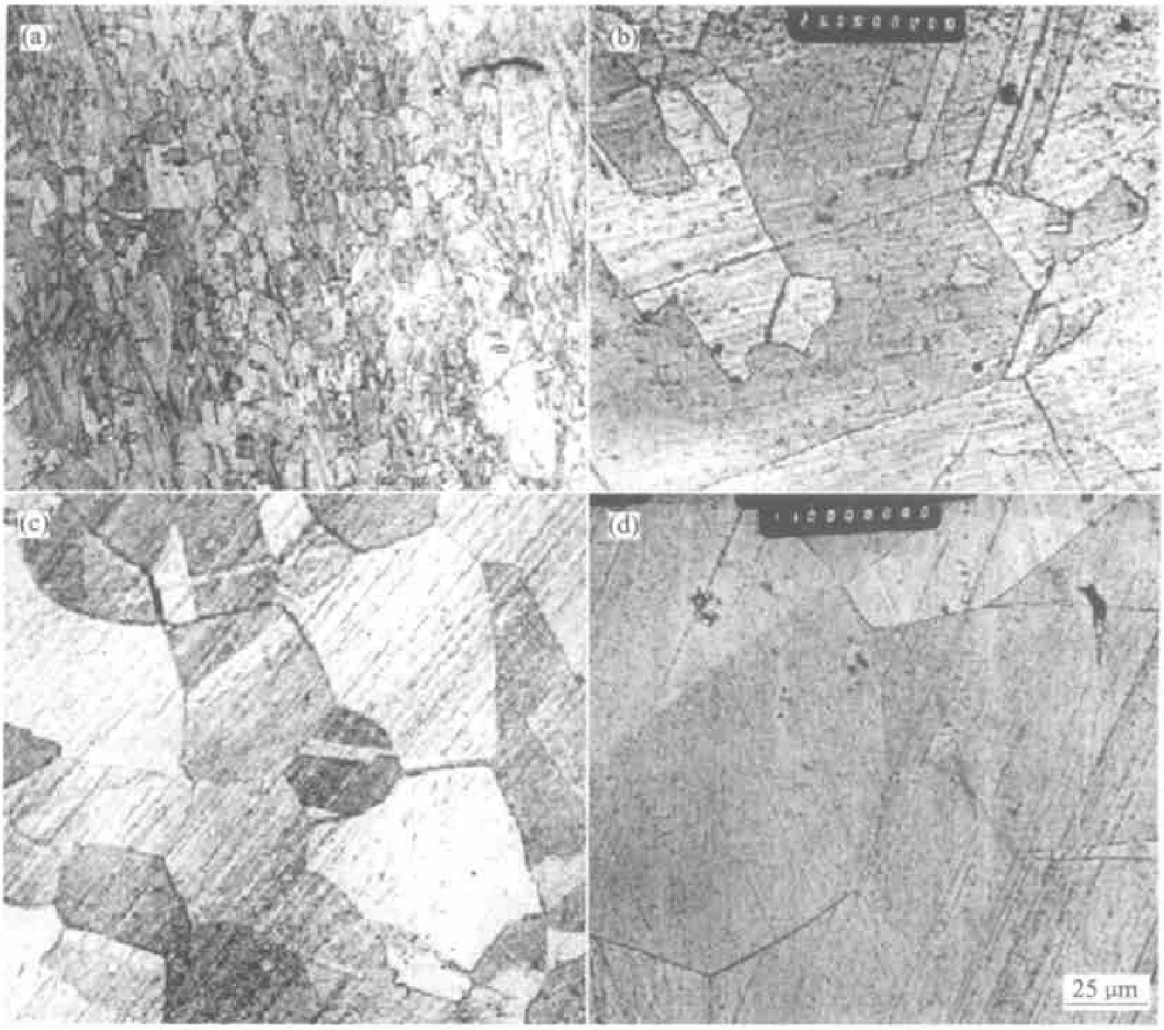

Fig. 2 Longitudinal section microstructures of samples T2 at various temperatures (Annealing for 2 h)
(a) —400 ℃; (b) —600 ℃; (c) —800 ℃; (d) —900 ℃

Table 2 Data of number of grain boundaries along longitudinal section, annealing temperature and resistivity of sample T2

Annealing temperature/ ℃	Number of GB/ mm^{-1}	Resistivity/ (10^{-8} Ω•m)
400	57.15	1.818 4
600	23.30	1.788 4
800	16.30	1.763 5
900	13.81	1.722 6

periodic, and the conduction electrons can freely move. When the period of crystal lattice is destroyed, the distorted crystal lattice scatters the conductive electrons and becomes an obstacle to the movement of conductive electrons. This is the essence of electrical resistivity. In 1960, Matthiessen's rule[10] was brought forward and the resistivity ρ consists of three parts:

$$\rho = \rho_{therm} + \rho_{chem} + \rho_{phys} \tag{4}$$

where ρ_{therm} is resulted from lattice vibration, ρ_{phys} is due to crystal imperfects, and ρ_{chem} is caused by the impurity of metals. Since the chemical composition and measurement condition are exactly same for one set of samples, which means that ρ_{therm} and ρ_{chem} are not changed, the only difference is the number of grain boundaries. With increasing the number of grain boundary, the electrical resistivity increases.

4.2 Characteristic distribution of grain boundaries

There are two kinds of grain boundaries, one is high-angle grain boundary and the other is low-angle grain boundary. The former includes low-energy and high-energy grain boundaries. It has been proved[11] that the amount of low-energy grain boundary increases with decreasing the grain size. And it is also pointed out[11] that when the grain size is smaller than 20 μm, the proportion of low-energy grain boundary reaches 50%, and when the grain size is smaller than 2 μm the proportion of low-energy grain boundary reaches 100%. The energy of grain boundaries reflects the degree of crystal distortion caused by grain boundaries. After the number of grain boundaries reaches some amount, with increasing the grain boundaries, the proportion of low-energy boundaries increases, and the differential coefficient between the general distortion and the number of grain boundaries lessens. Crystal distortion causes conductive electrons to scatter, which is the essence of resistance. Then, the effect of grain boundaries on the resistivity is not linear. When the number of grain boundaries is small, the effect of grain boundaries on the resistivity of copper wires is notable, but when the number of grain boundaries is large, the effect is not evident. In present work, the relationship between the number of grain boundaries and copper wires resistivity is $y = ae^{b/x}$. However, the relationship between the number of dislocation or lattice vacant sites and resistivity is linear[5]. The reason is that, while the number of dislocation or lattice vacant sites increase, the crystal distortion caused by each dislocation and lattice vacant sites is invariable.

4.3 Influence of impurity on resistivity

Fig. 3 shows that the curve trend of the influence of grain boundaries on the resistivity of copper wires T1 is the same as that of copper wires T2. But, there are some differences in the two curves. For example, when the increase of resistivity becomes slow, the number of sample T1 is more than 22, but that of sample T2 is less than 22. When the number is the same, the resistivity of sample T1 is higher than that of sample T2. The only difference between samples T1 and T2 is the type and quantity of impurity. The analysis of X-ray energy spectrum shows that there is about 0.4% Cr in sample T1, and the only impurity in sample T2 is Fe with amount of 0.01%. It is reported[12] that the crystal constant of Cr is less than the mean free path of conductive electrons in Cu-Cr alloy. Then, although the impurity can not change the trend of curve between the number of grain boundaries and the resistivity, it can control the details of curve, such as the number of grain boundaries when the resistivity increases. Impurity can not only result in the increase of the wires resistivity, but also influences the signal transmission[8]. The resistivity of grain boundary is greater than that of internal crystals. The grain boundary can act as resistance and capacitance. When there is impurity, particularly oxygen at grain boundary, the resistance and capacitance of grain boundary increase. Then the grain boundary makes the signal distorted and attenuated.

4.4 Relationship between number of grain boundary and resistivity

From above analysis, the relationship between number of grain boundary and the resistivity of copper wires is in good agreement with Eqn. (3). Based on experimental data in Fig. 4[9], it is found that the relationship between the number of grain boundary and the resistivity of aluminum is expressed as:

$$y = 3.04 \times 10^{-8} e^{-0.18/x} \tag{5}$$

From Eqns. (3) and (5), it is evident that the values of the parameters a, b in Eqn. (2) are of

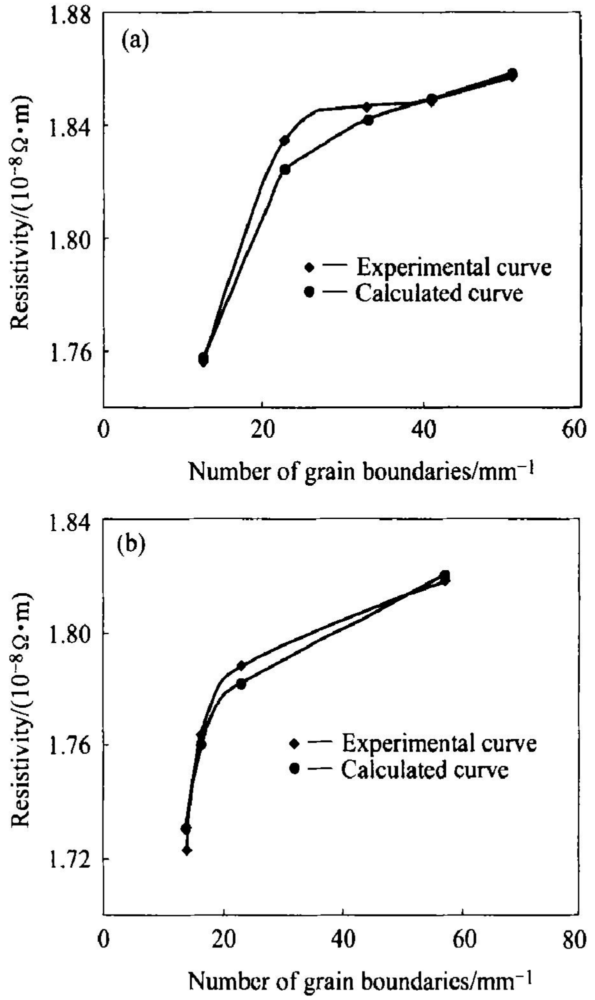

Fig. 3 Effects of grain boundary on resistivity of copper wires
(a) —Sample T1; (b) —Sample T2

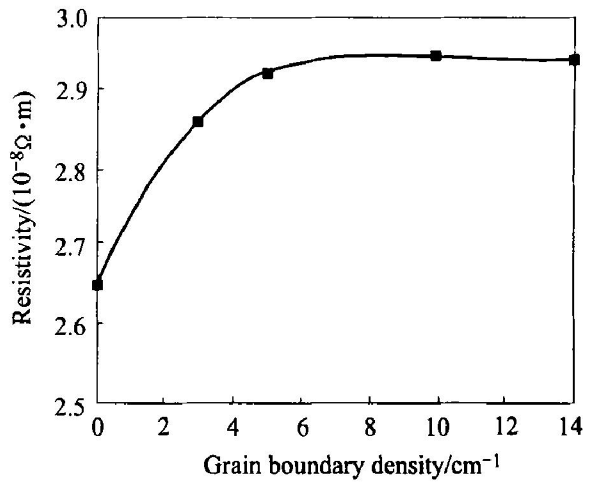

Fig. 4 Influence of grain boundary density on resistivity[9]

great difference for copper and aluminum. The crystal structure for both copper and aluminum is exactly the same, and only difference between them is the lattice constant (Cu: 0.404 96 nm, Al: 0.361 47 nm) and the amount of conductive electrons (Cu: 2, Al: 3). The values of parameters a, b, therefore, are likely controlled by the lattice constant and the number of conductive electrons. For copper wires, the value of parameter a varies between 1.850×10^{-8} and 1.892×10^{-8}, and b between -0.887 and -0.925 for samples T1 and T2, respectively. It can be concluded that the fluctuation is controlled by the type and the quantity of impurity. It should be pointed out that Eqns. (3) and (5) have the limitation that both equations are not used in single crystal.

5 CONCLUSIONS

1) With increasing the number of grain boundaries, the resistivity of copper wires increases.

2) Unlike dislocation and lattice vacant sites, the effects of the grain boundaries on the resistivity are not linear, and relationship between the grain boundaries and the resistivity of copper wires is expressed as $y = 1.86 \times 10^{-8} e^{-0.90/x}$.

3) Although impurity can not change the general trend of curve between the number of grain boundaries and the resistivity of copper wires, it can control the details of curve, and make the values of the parameters a, b fluctuate.

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