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# Crystallization and Electrical Properties of Amorphous Cu-Ag-P Alloys*

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## Synopsis

Amorphous Cu-Ag-P alloys (Cu:79~86, Ag:6~14, P:11~14 wt%) were prepared by melt-quenching technique. The crystallization process of these amorphous alloys was examined by electrical resistivity, X-ray diffraction and differential thermal analysis techniques. The T-T-T diagram of the amorphous Cu-Ag-P alloys could be divided into five distinct regions and the electrical resistivity of these alloys decreased in the order of amorphous → metastable-I → supersaturated metastable → metastable-II → stable state.

Compared with traditional strain gauge materials, the present amorphous alloys exhibited a higher gauge factor (1.8~3.1), lower thermal electromotive force relative to copper (1.07μv/°C), comparable specific resistivity at room temperature (80μΩ·cm) and higher negative temperature coefficient of specific resistivity ($-0.7 \sim -1.2 \times 10^{-4}$/°C). These values showed to be useful as guage materials below the crystallization temperature.

## I. Introduction

In recent years, a number of amorphous alloys have been prepared by using melt-quenching techniques and their crystallization behavior has been studied in detail[1-3]. One of authors (T.M.) have indicated that the amorphous phase (Am) transforms to the stable phase (ST) through the formation of two metastable phases (MS-I and MS-II) on heating. Another metastable phase, a supersaturated solid solution (SS) is formed on prolonged aging at lower temperatures. Thus, the crystallization process of amorphous alloys is generally very complex.

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On the other hand, it has been known that amorphous alloys have essentially high specific resistivity values ($\sim 10^2 \mu\Omega \cdot cm$)[4] and some amorphous alloys show linear change in resistivity below $T_X$ and its temperature coefficient is samall ($\sim 10^{-1} x 10^{-4}/°C$)[4]. Therefore, it may be possible to use them for strain gauges. From this point of view, we have tried to search Cu-based amorphous alloys except Cu-Zr alloy known so far, and found that the amorphous alloys are formed in Cu-Ag-P ternary ststem.

In the present paper, we report the crystallization behavior and the strain gauge characteristics of amorphous Cu-Ag-P alloys. The techniques employed include electrical resistivity, X-ray diffraction and differential thermal analysis.

## II. Experimental

Amorphous Cu-Ag-P alloys were prepared by the single-roller type quenching apparatus in the form of ribbons 1~1.5mm wide and 15~20μm thick. These amorphous ribbons could be prepared only by the iron roller, but not by copper roller for any roll velocity. As the best condition for the formation of amorphous phase, liquid metals (about 800°C) were ejected at $2\sim 5 kg/cm^2$ pressure from the nozzle (0.5~1.0mm diameter) onto the iron roller (20cm diameter) rotating at 2500~5000 r.p.m.. The amorphous nature of the samples was examined by a X-ray monochrometer with Mo-Kα radiation. Structures of crystal phases appeared after heating were analyzed from X-ray diffraction patterns recorded with Mo-Kα radiation. The electrical resistivity was measured by four-point probe method using a potentiometer. The cross-section of the ribbon was estimated from the weight using the specific gravity value of $7.46 g/cm^3$ measured for the amorphous $Cu_{83.5}Ag_{8.9}P_{7.6}$ alloy. The differential thermal analysis was performed at a heating rate of 6°C/min. The electrical resistivity measurement and differential thermal analysis were carried out under argon atmosphere.

## III. Experimental results and discussion

### 1. Confirmation of the amorphous state

The structure factor (S(Q)) was obtained from X-ray diffraction intensity of each amorphous alloy. A sub-peak at about Q=6 $Å^{-1}$ characterized the amorphous alloy. Electron microscopy and electron diffraction pattern also confirmed the amorphous nature of the foil. Hence, we concluded that there were no crystals with grain size greater than

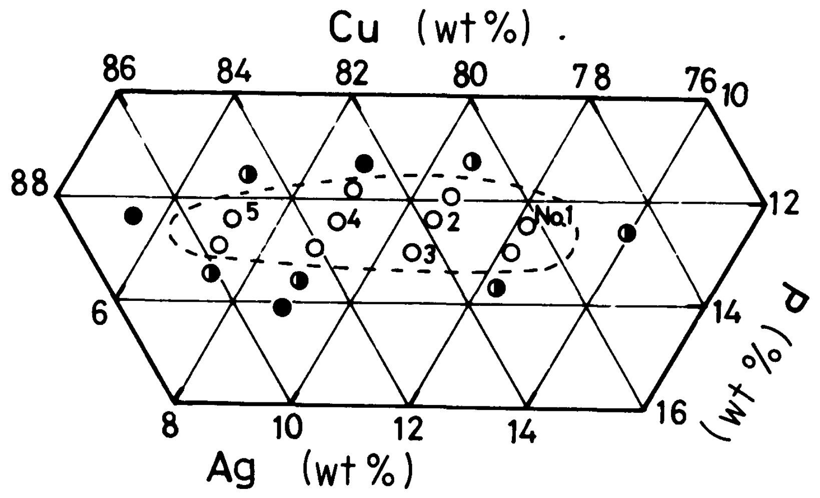


Fig. 1. Composition range of the amorphous Cu-Ag-P alloys.

about 30 Å. The composition range in which the Cu-Ag-P alloys form the amorphous phase is outlined in Fig. 1.

2. Crystallization behavior

Temperature dependence of the electrical resistivity on heating and cooling from liquid nitrogen temperature to 400°C and differential thermal analysis in the temperature range of 20° to 400°C are shown in Fig. 2. Heating rate in both the measurements is 6°C/min. The electrical resistivity curve can be divided into five stages: (1) a linear slight decrease up to about 140°C, (2) drastic decrease (exothermic reaction) between 140~160°C, (3) smooth decrease between 160~200°C, (4) drastic decrease again (exothermic reaction) between 200~220°C, (5) smooth decrease between 220~300°C.

The linear part of first stage below about 120°C is due to no change of amorphous phase (Am). The drastic decrease in the second stage corresponds to the appearance of microcrystals (MS-I) within the amorphous matrix from electron microscopic observation. In the third stage, these microcrystals grow slowly. In the temperature range of the fourth stage, another crystalline phase (MS-II) with X-ray diffraction lines different from those of MS-I phase spreads over all amorphous matrix. In the fifth stage, X-ray diffraction lines became continuosly sharper with increasing aging time and new diffraction lines were not observed. Finally the MS-II phase transfers to stable phases (ST) with a small change in electrical resistivity.

In order to follow the crystallization process in detail, changes

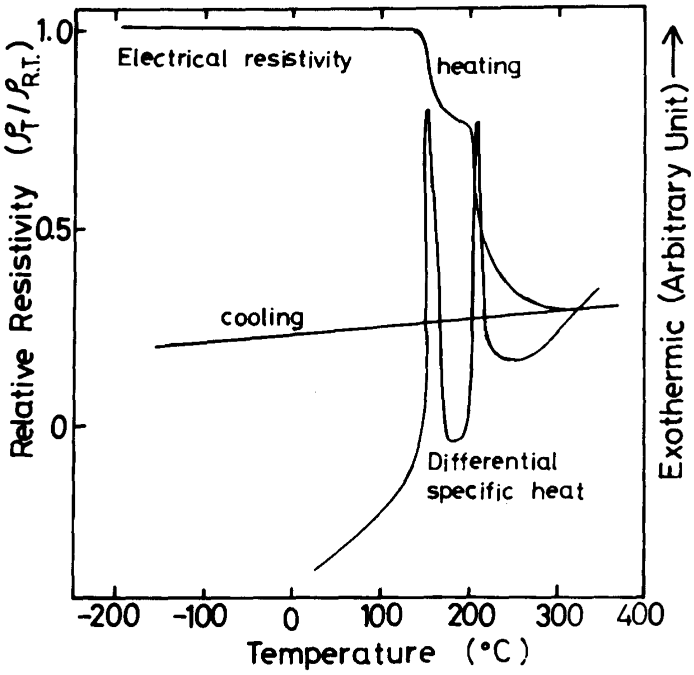


Fig. 2. Curves of relative electrical resistivity and differential thermal analysis at a heating rate of 6°C/min for the amorphous $Cu_{83.5}Ag_{8.9}P_{7.6}$ alloy.

in isothermal electrical resistivity were measured. For example, the aging effect on electrical resistivity at 110, 120, 140, 165 and 290°C is shown in Fig. 3. It is seen in the figure that the values of electrical resistivity in each phase region decreases in the order of Am → MS-I → MS-II → ST. The curve at 120°C shows a slight change in slope at aging time of $10^3$min as shown by an arrow in the figure and the value of electrical resistivity is smaller than that of MS-I phase in the curve at 110°C. As discussed below, this change is due to the appearance of a metastable phase (SS) different from the MS-I.

Then, the temperature dependence of electrical resistivity at different heating rates (5, 20, 40, 50, 70, 120 and 190°C/hr) was measured and the result is shown in Fig. 4. The electrical resistivity curves show the transformation of Am → MS-I → MS-II → ST for high heating rates(120 and 190°C/hr), the transformation of MS-I → SS at point shown by arrows (indicating a change in the temperature coefficient) for intermediate heating rates (40, 50 and 70°C/hr) and the transformation of Am → SS → MS-I → MS-II → ST for low heating rates

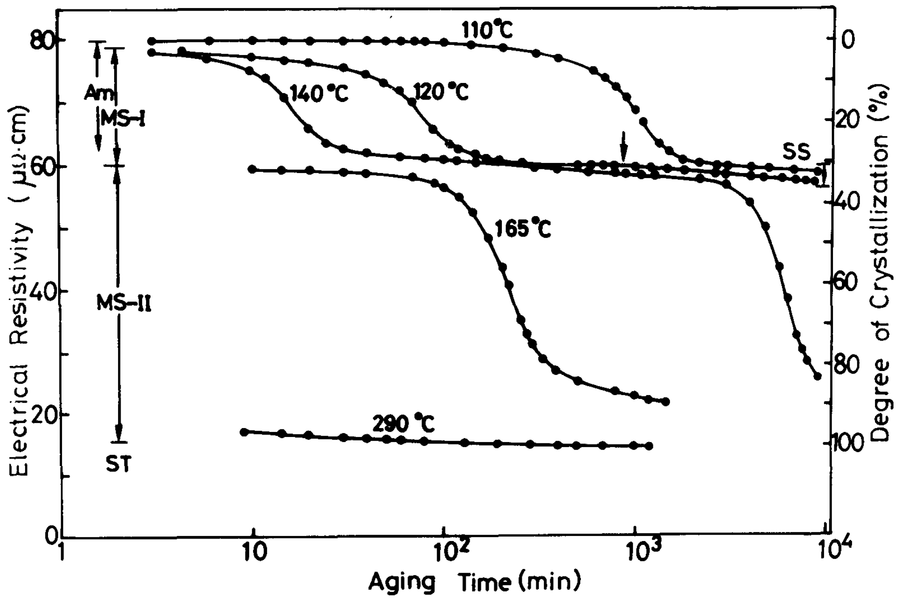


Fig. 3. Changes in electrical resistivity of the amorphous $Cu_{83.5}$-$Ag_{8.9}P_{7.6}$ alloy during aging at 110, 120, 140, 165 and 290°C.

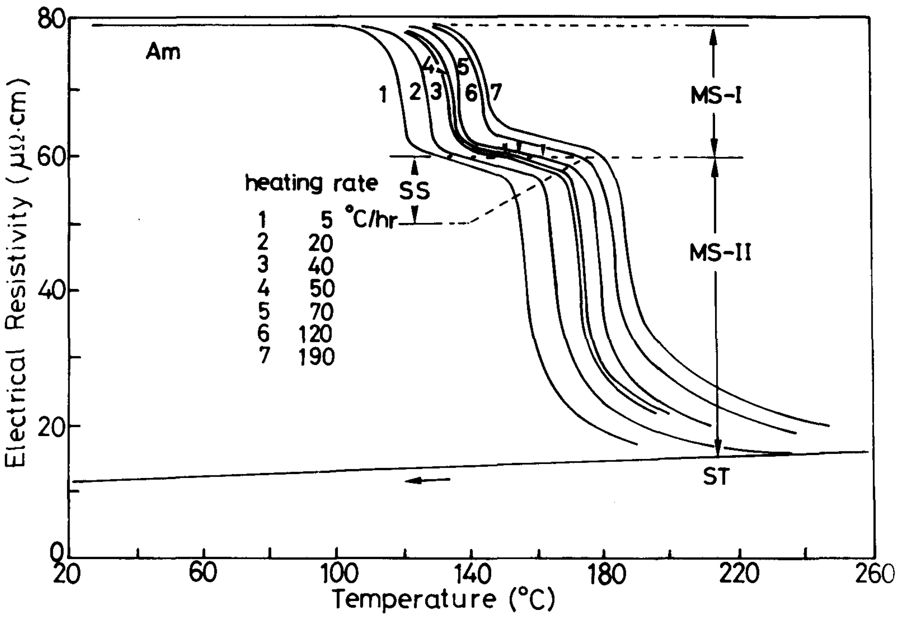


Fig. 4. Changes in electrical resistivity of the amorphous $Cu_{83.5}$-$Ag_{8.9}P_{7.6}$ alloy during heating at the rates of 5, 20, 40, 50, 70, 120 and 190°C/hr.

Table 1. Analysis of X-ray patterns (aged for 1100min at 140°C or 700min at 122°C) showing the presence of metastable phase I (MS-I).

| number of line | $d_{obs.}$(Å) | f.c.c. hkl | f.c.c. $d_{cal.}$(Å) | f.c.c. hkl | f.c.c. $d_{cal.}$(Å) |
|---|---|---|---|---|---|
| 1 | 2.363 | | | 111 | 2.361 |
| 2 | 2.098 | 111 | 2.090 | | |
| 3 | | | | 200 | 2.045 |
| 4 | 1.821 | 200 | 1.810 | | |
| 5 | 1.446 | | | 220 | 1.446 |
| 6 | 1.284 | 220 | 1.280 | | |
| 7 | 1.238 | | | 311 | 1.233 |
| 8 | 1.177 | | | 222 | 1.181 |
| 9 | 1.095 | 311 | 1.091 | | |
| | | a=3.62 Å | | a=4.09 Å | |

Table 2. Analysis of X-ray diffraction patterns (aged for 6700min at 140°C) showing metastable phase II (MS-II).

| number of line | $d_{obs.}$(Å) | hexagonal hkl | f.c.c.(a) hkl | f.c.c.(b) hkl |
|---|---|---|---|---|
| 1 | 3.14 | 111 | | |
| 2 | 5.51 | 112 | | |
| 3 | 3.37~2.32 (B) | 202 | 111 | |
| 4 | 2.19 | 211 | | |
| 5 | 2.15 | | | 111 |
| 6 | 2.03 | 300 | 200 | |
| 7 | 1.98~1.94 (B) | 113,212 | | |
| 8 | 1.82 | | | 200 |
| 9 | 1.76~1.73 (B) | 302,104 | | |
| 10 | 1.46 (B) | 311 | | |
| 11 | 1.57 | 222 | | |
| 12 | 1.52 | non index | | |
| 13 | 1.45 | | 220 | |
| 14 | 1.41 | 223 | | |
| 15 | 1.37 | 321 | | |
| 16 | 1.33 | 115 | | |
| 17 | 1.30~1.29 (B) | 322 | | 220 |
| 18 | 1.23~1.22 (B) | 311 | | |
| 19 | 1.19~1.15 (B) | 323,350,413 | 222 | |
| 20 | 1.13 (B) | 421 | | |
| 21 | 1.11~1.09 (B) | 206 | | 311 |
| 22 | 1.07~1.05 (B) | 422 | | 222 |

B; broad line

(5 and 20°C/hr).

X-ray diffraction analysis of samples aged for 1100min at 140°C or 700min 122°C is shown in Table 1. This result shows that MS-I phase is a mixture of amorphous and two types of f.c.c. phase (a=3.62 and 4.09Å) and these f.c.c. phases correspond to metallic Cu and Ag respectively. Therefore, the MS-I phase is microcrystals of each metallic element (Cu and Ag), similar to other amorphous alloys. X-ray analysis of the specimen aged for 6700min at 140°C is shown in Table 2, wherein the diffraction lines can be indexed by two different f.c.c. lattices and hexagonal lattice. Table 3. also shows X-ray

Table 3. Analysis of X-ray patterns (aged for 800min at 300°C) showing the presence of stable phase (ST)

| number of line | $d_{obs.}$(Å) | $Cu_3P$ | | Cu | | Ag | |
|---|---|---|---|---|---|---|---|
| | | hkl | $d_{cal.}$(Å) | hkl | $d_{cal.}$(Å) | hkl | $d_{cal.}$(Å) |
| 1 | 3.128 | 111 | 3.1268 | | | | |
| 2 | 2.487 | 112 | 2.4924 | | | | |
| 3 | 2.363 | | | | | 111 | 2.3637 |
| 4 | 2.293 | 202 | 2.3029 | | | | |
| 5 | 2.169 | 211 | 2.1689 | | | | |
| 6 | 2.082 | | | 111 | 2.0831 | | |
| 7 | 2.049 | | | | | 200 | 2.0470 |
| 8 | 2.008 | 300 | 2.0074 | | | | |
| 9 | 1.961 | 113 | 1.9657 | | | | |
| 10 | 1.926 | 212 | 1.9200 | | | | |
| 11 | 1.803 | | | 200 | 1.8040 | | |
| 12 | 1.748 | 302 | 1.7503 | | | | |
| 13 | 1.709 | 104 | 1.7134 | | | | |
| 14 | 1.629 | 311 | 1.6265 | | | | |
| 15 | 1.564 | 222 | 1.5634 | | | | |
| 16 | 1.441 | | | | | 220 | 1.4474 |
| 17 | 1.406 | 223 | 1.4045 | | | | |
| 18 | 1.359 | 321 | 1.3565 | | | | |
| 19 | 1.317 | 115 | 1.3142 | | | | |
| 20 | 1.291 | 322 | 1.2887 | | | | |
| 21 | 1.276 | | | 220 | 1.2756 | | |
| 22 | 1.234 | | | | | 311 | 1.2344 |
| 23 | 1.220 | 314 | 1.2203 | | | | |
| 24 | 1.189 | 323 | 1.1915 | | | | |
| 25 | 1.177 | | | | | 222 | 1.1818 |
| 26 | 1.162 | 305 | 1.1645 | | | | |
| 27 | 1.151 | 413 | 1.1515 | | | | |
| 28 | 1.126 | 421 | 1.1271 | | | | |
| 29 | 1.104 | 206 | 1.1079 | | | | |
| 30 | 1.089 | | | 311 | 1.0878 | | |
| 31 | 1.071 | 422 | 1.0862 | | | | |
| 32 | 1.042 | | | 222 | 1.0415 | | |
| | | a=6.954 Å c=7.149 Å | | a=3.608 Å | | a=4.089 Å | |

analysis of sample aged for 800min at 300°C. This result shows the presence of 3 phases of Cu, Ag and $Cu_3B$ compound. The result of X-ray analysis for the sample aged for 19700min (2weeks) at 75°C showed to consist of two type of f.c.c. phase, but these diffraction lines were broad. Therefore, the lattice constants of two phases could not be accurately determined. Each phase is in a metastable state supersaturated with phosphorus and appears only for low heating rates or aging at low temperatures.

Based on results of these electrical resistivity and X-ray diffraction analysis, the time-temperature-transformation diagram for amorphous $Cu_{83.5}Ag_{8.9}P_{7.6}$ alloys can be constructed as shown in Fig. 5.

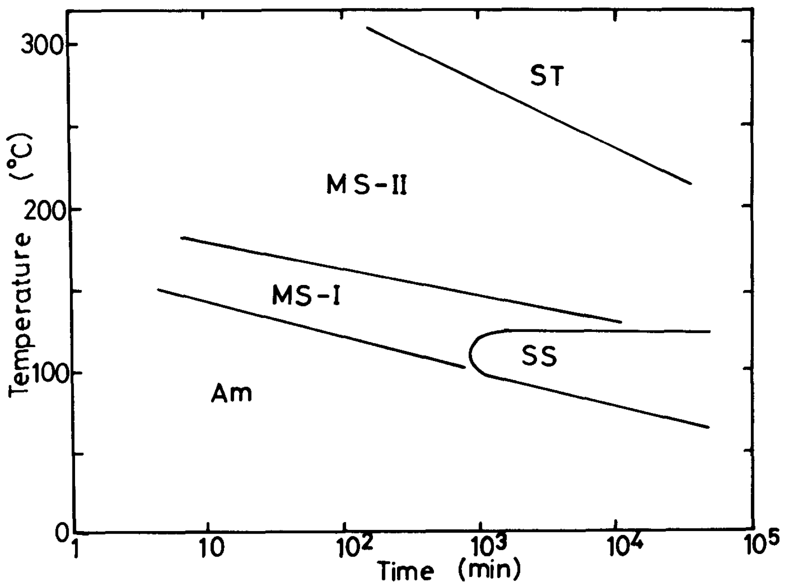


Fig. 5. Time-temperature-transformation diagram of the amorphous $Cu_{83.5}Ag_{8.9}P_{7.6}$ alloy.

3. Electrical properties of the amorphous Cu-Ag-P alloys

In order to evaluated the usefulness of the amorphous alloys as strain gauge materials, their electrical characteristics were measured for five samples of No.1 to No.5 in Fig. 1. Generally, the factors required for good strain gauge materials are (1) high gauge factor (K), (2) low thermo electromotive force relative to copper (e.m.f.), (3) high specific resistivity ($\rho$) and (4) small temperature coefficient of specific resistivity ($1/\rho(d\rho/dT)$).

Measured values of the above-mentioned four parameters are summarized in Table 4, together with those of traditional strain gauge materials. The $1/\rho(d\rho/dT)$ from room temperature to 100°C is -0.7 ~

Table 4. The values of crystallization temperature, strain gauge factor and electrical properties for five Cu-Ag-P amorphous alloys and two traditional strain gauge alloys.

| Alloy No. | Composition (Wt%) | | | $T_x$ (°C) | K | ρ(20°C) (μΩ·cm) | $C_f$(0~40°C) ($\times10^{-4}$/°C) | $E_{mf}$(0~40°C) (μv/°C) |
|---|---|---|---|---|---|---|---|---|
| | Cu | Ag | P | | | | | |
| 1 | 80.3 | 12.2 | 7.5 | 111 | 3.1 | 135.6 | -1.23 | 1.02 |
| 2 | 81.9 | 10.5 | 7.6 | 115 | 2.5 | 137.6 | -0.97 | 1.07 |
| 3 | 82.5 | 10.5 | 7.0 | 125 | 1.8 | 136.9 | -0.90 | 1.07 |
| 4 | 83.5 | 8.9 | 7.6 | 120 | 2.4 | 147.5 | -0.67 | 1.07 |
| 5 | 85.2 | 7.1 | 7.7 | 104 | 2.8 | 254.3 | -1.00 | 1.07 |
| $Cu_{55\sim60}Ni_{40\sim45}Mn_{0\sim1}$ | | | | | 2.04 ~ 2.12 | 45 ~ 50 | 0.2 | -45 |
| $Ni_{80\sim85}Cr_{15\sim20}$ | | | | | 2.1 ~ 2.65 | 100 ~ 120 | 0.2 | -4 |

$-1.2\times10^{-4}$/°C higher than for traditional strain gauge materials, but the specific resistivity of 80μΩcm at room temperature is comparable. As shown Fig. 6, the e.m.f. value of 1.07μv/°C from 0°C to 100°C is very small and is independent of composition.

Next, we obtain the gauge factor K. Generally, electrical resistance R is written as

$$R = \rho(L/S), \quad (1)$$

where L is length, S the cross-section of sample and ρ the specific resistivity. Electrical resistance changes with temperature T and stran ε:

$$dR/R = (dR/R)_T + (dR/R)_\varepsilon \;. \quad (2)$$

At constant temperature,

$$dR/R = (dL/L) - (dS/S) + (d\rho/\rho) \quad (3)$$

Since the cross-section changes due to expansion or contraction in one direction by Poisson's ratio ν,

$$dS/S = -2\nu(dL/L). \quad (4)$$

Hence,

$$(dR/R)/(dL/L) = (1 + 2\nu) + (d\rho/\rho)/(dL/L), \quad (5)$$

where (dR/R)/(dL/L) is guage factor, K. In amorphous alloys, fracture surface lies at 45~50 deg. to the tensile axis in the direction of thickness and is perpendicular to direction of the width[5]. Hence, it is thought that ν is about 1/3. Therefore, the first term of equation (5) becomes about 1.7, and then, the values of K for amorphous alloys are expected to be higher than 1.7 from equation (5).

Now, the relation between dR/R and dL/L was measured. As shown in Fig. 7, dR/R changes linear with dL/L until the point of tensile fracture of the amorphous alloy. From the slopes of the straight lines, the gauge factors are obtained. The values of K are in the range of 1.8 to 3.1 as shown in Table 4. It is a little higher than for traditional strain gauge materials. From these properties, it appears possible that these amorphous alloys are used as strain gauge materials below their crystallization temperatures.

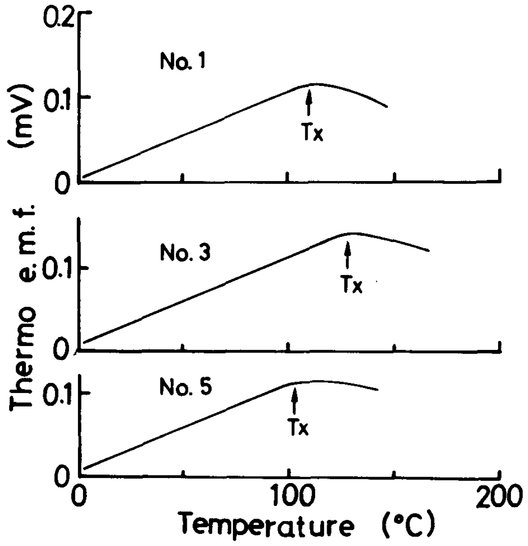


Fig. 6

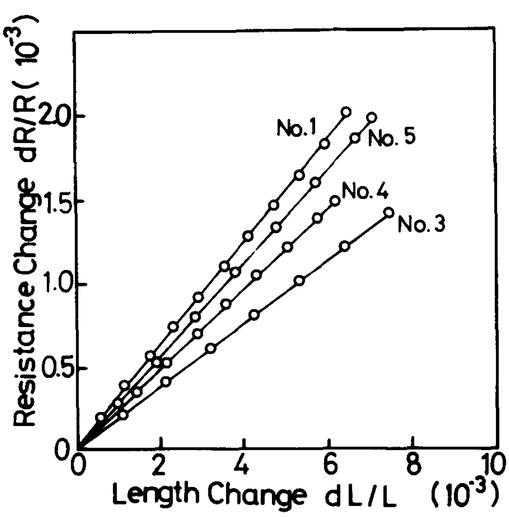


Fig. 7

Fig. 6. Thermo electromotive force against copper for Kinds of amorphous Cu-Ag-P alloys.

Fig. 7. Relation between the change of resistance and the length at room temperature for 4 kinds of amorphous Cu-Ag-P alloys.

## Summary

Crystallization process and electrical preperties of amorphous Cu-Ag-P alloys prepared by the single-roller quenching method were examined using X-ray diffraction, differential thermal analysis and electrical resistivity. The results are summarized as follows:

(1) Crystallization process is divided into 5 stages. With increasing temperature, the amorphous phase (Am) is crystallized in the sequence of amorphous and two f.c.c. phases (MS-I) → two f.c.c. and hexagonal phases (MS-II) → Cu, Ag and $Cu_3P$ compound (ST). On the other hand by long aging at lower temperatures, two phases of Cu and Ag supersaturated with P are obtained.

(2) The electrical resistivity changes linearly with strain until the

point of tensile fracture.

(3) Compared with traditional strain gauge materials, specific resistivity is a little higher ($-0.7\sim-1.2\times10^{-4}$/°C), thermo e.m.f. is lower (1.0μv/°C), resistivity is comparable (80μΩcm) and K is little higher (1.8~3.1) for amorphous Cu-Ag-P alloys. These amorphous alloys may be used for strain gauges at low temperatures.

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