Tensile properties and conductivities of a precipitation hardened and cold-rolled Cu-0.3Cr-0.1Zr alloy at cryogenic temperature

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Abstract. Cu-0.3Cr-0.1Zr alloy (in mass%) is one of typical precipitation hardened copper-based alloys, and exhibited an excellent combination of high strength and high conductivities at the temperature range of 4 K to 300 K. The tensile properties, electrical resistivity, thermal conductivity and magnetization of precipitation hardened and cold-rolled Cu-0.3Cr-0.1Zr alloy were measures in comparison with oxygen free copper at cryogenic temperatures. The Cu-0.3Cr-0.1Zr showed higher yield ratio (yield strength / tensile strength) and lower the ratio of yield strength to electrical resistivity at cryogenic temperature than oxygen free copper. It exhibited high electrical and thermal conductivities, excellent non-magnetic stability and very low magnetic permeability at 4.2 K.

1. Introduction
The National Research Institute for Metals (NRIM, now National Institute for Materials Science, NIMS) has accumulated physical and mechanical properties at the temperature range of 4 K to 300 K for structural metallic materials since 1980s. Their electrical resistivity, magnetization, thermal conductivity and tensile properties were determined as a part of the work.[1,2] Precipitation hardened copper-based alloys as well as oxygen free copper in the cold-rolled condition were the candidate of a high strength and high conductivity structural material at cryogenic temperature. Since few cryogenic data for those alloys were available [3-5], precipitation hardened copper-based alloys developed as the lead frame in device [6-8] were chosen to evaluate for their cryogenic properties. Figure 1 represents a combination of their tensile strength and electrical conductivity (IACS) in the heavily cold-rolled condition (99% reduction). Cu-0.3Cr-0.1Zr alloy (in mass%) exhibits an excellent combination of high strength (600 MPa) and high electrical conductivity (80% IACS) at room temperature (Figure 1(a)). Furthermore it keeps higher tensile strength among the precipitation hardened copper-based alloys at the both temperatures of 4 K and 77 K (Figure 1(b)), and Cu-Cr-Zr system has no ferrous elements. In the present study, therefore, tensile properties and conductivities of precipitation hardened and cold-rolled Cu-0.3Cr-0.1Zr alloy plates were evaluated in comparison with oxygen free copper at cryogenic temperature, i.e. from 4 K to 77 K.

2. Experimental detail

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2.1. Test materials

Test materials are Cu-0.3Cr-0.1Zr alloy plates and oxygen free copper (OFHC Cu) rods. The nominal composition of Cu-0.3Cr-0.1Zr alloy was Cr: 0.3, Zr: 0.1, Mg: 0.05, Si: 0.02 and Cu: balance (in mass%). The Cu-0.3Cr-0.1Zr plate which ingot was obtained by a vacuum melting was forged, hot-rolled (heated at 1093 K), and solution-treated (at 1223 K, water-quenched). The plate was cold-rolled, aged (at 773 K for 3.6 ks, water-quenched), and finally cold-rolled. The samples with final reduction ratios of 20%, 40% and 60% were provided. Figure 2 represents TEM (transmission electron microscopy) bright field image of Cu-0.3Cr-0.1Zr alloy in the cold-rolled reduction of 99%. The materials were under over aged condition because of grown intermetallic particles, and dislocation cell structure was developed in the matrix as cold-rolling.

The OFHC Cu rod was as received (no annealed) with 4-nine grade, and its specification was JIS H3510 (article: C1011BD-H). Cold-rolling was done with various reduction ratios between 6% and 75%. As a reference, some precipitation hardened copper-based alloy sheets in commercial which were 99% cold-rolled of Cu-0.3Cr-0.1Zr (OMCL1), Cu-0.10Fe-0.034P (KFC-SH), Cu-0.15Fe-0.05P-0.1Sn-0.1Ag-0.1Zn (KLF201), Cu-3.2Ni-0.7Si-1.25Sn-0.3Zn (KLF125) and Cu-1.5Ni-0.3Si-0.03P (PMC102) (in mass%) [6-8] were examined.

![Figure 1](image1.jpg)

**Figure 1.** High strength and high conductivity copper-based alloys developed for the lead frame (a) and their tensile strength at 4 K and 77 K (b).

![Figure 2](image2.jpg)

**Figure 2.** TEM bright field images of Cu-0.3Cr-0.1Zr alloy with the cold-rolled reduction of 99%: (a) precipitates of intermetallic phases and dislocation structure, and (b) dislocations in the matrix. Beam direction is near [011].
2.2. **Measurements**

Tensile test specimen was cut from the plates or rods along the rolling direction. Tensile test (displacement-controlled) was carried out at a strain rate of about 4 x 10^{-4} sec^{-1} using a screw-driven machine. The specimens were immersed in liquid helium (4 K), liquid nitrogen (77 K), and ambient air (293 K), respectively. Yield strength was evaluated by the offset value of 0.2% proof stress using MTS extensometer.

The electrical resistivity was measured using bar-shaped specimens by four-point probe technique between liquid helium temperature (4.2 K) and room temperature (293 K). The thermal conductivities were measured by the steady state heat flow method from 3.5 K to 60 K. Samples were 10 mm x 4 mm x 50 mm strips abrasively polished. The samples were held in a chamber evacuated to 10^{-5} Pa. The temperature gradients along the samples were measured using two calibrated carbon-glass resistors fixed on copper holders. The distance between the thermometers were 20 mm. The sample temperature was defined as the mean value of the two. The sample heater was made of a manganin wire, and the power applied to the sample was measured using the four-probe method.

The magnetization measurements at 4.2 K were made using a computerized PAR-EG&G vibrating-sample magnetometer. Point-by-point measurements were taken in stepped fields between -3 and 3 MA/m provided by a superconducting solenoid. The typical sample was a 3 mm-diameter cylinder. The shearing correction by demagnetizing factor, N=0.27, was made.[9]

3. **Results and discussion**

3.1. **Tensile properties**

Figure 3 shows the load displacement curves of the 20% cold-rolled Cu-0.3Cr-0.1Zr material at low temperatures. As the test temperature decreased from 293 K to 4 K, both strength and elongation increased. Especially, the higher homogeneous elongation and work hardening rate were, the lower the temperature was. Both ultimate tensile strength and 0.2% proof stress were higher as the increase of

![Figure 3. Stress-strain curves of Cu-0.3Cr-0.1Zr 20% cold-rolled material at cryogenic temperatures.](image)
**Figure 4.** Effects of cold-rolling on tensile properties of (a) Cu-0.3Cr-0.1Zr alloy and (b) OFHC Cu at cryogenic temperatures.
cold-rolled ratio from 20% to 60%, although the elongation was almost the same without the cold-rolled ratios at each temperature (Figure 4(a)). These tensile properties’ dependence on test temperature was similar to that of OFHC copper. Figure 4(b) summarized the tensile properties of cold-rolled OFHC Cu with the reduction from 0% to 75%. Both ultimate tensile strength and 0.2% proof stress were higher as the increase of cold-rolled ratio, although the elongation was lowered. The yield ratio (yield strength / tensile strength) of Cu-0.3Cr-0.1Zr, however, was higher than that of OFHC Cu at lower temperature as shown in Figure 5, since both precipitation strengthen and dislocation strengthen may introduce high yield strength with less temperature dependence. The precipitation behavior and the dislocation structure developed on Cu-Cr-Zr and Cu-Fe-P alloys have been evaluated and discussed with their mechanical property in the references [10-12].

3.2. Conductivities

The electrical resistivity of Cu-0.3Cr-0.1Zr alloy and OFHC Cu was summarized in Figure 6(a). The residual resistivity ratio (RRR) of each material was also interpolated in the figure. The resistivity of materials is increased as the increase of cold-rolled ratio for each alloy. The RRR in Cu-0.3Cr-0.1Zr alloy is roughly from 4 to 5, although the RRR in OFHC Cu is much higher than that in Cu-0.3Cr-0.1Zr alloy and strongly depend on the cold-rolled ratio. Slight solid solubility in copper may affect the high resistivity in the precipitate strengthen alloys,[12] although the resistivity of OFHC Cu is rapidly decreased at around several ten degrees [1,4]. Then the ratio of yield strength to electrical resistivity was plotted at test temperatures in Figure 6(b). The ratio in OFHC Cu is much higher than that in Cu-0.3Cr-0.1Zr alloy especially at lower temperature.

The thermal conductivity of Cu-0.3Cr-0.1Zr alloy is about one tenth of heavily cold-rolled OFHC Cu at cryogenic temperature as shown in Figure 7. However, it was twice as high as that of phosphorous-deoxidized copper [1,4]. Thus Cu-0.3Cr-0.1Zr alloy exhibited high electrical and thermal conductivities as well as the excellent combination with high strength in the cooper alloys at cryogenic temperature.
Figure 6. Electrical resistivity (a) and the ratio of yield strength to resistivity (b) for Cu-0.3Cr-0.1Zr alloy and OFHC Cu at cryogenic temperatures.
Figure 7. Thermal conductivity of cold-rolled Cu-0.3Cr-0.1Zr and OFHC Cu at cryogenic temperatures.

3.3. Magnetization

Figure 8 represents the variation of d.c. magnetization with applied field at 4.2 K for Cu-0.3Cr-0.1Zr and Cu-0.15Fe-0.05P-0.1Sn-0.1Ag-0.1Zn materials cold-rolled with 99%. The Cu-0.3Cr-0.1Zr exhibits paramagnetism at 4.2 K, since its magnetization is directly proportional to the applied field in Figure 8(a). On the other hand, the plots of Cu-0.15Fe-0.05P-0.1Sn-0.1Ag-0.1Zn develop a saturation shown in Figure 8(b). But the magnetization of the alloy at 3 MA/m is about 0.25 kA/m. Thus the alloy exhibits very low magnetization and susceptibility under high fields, although it has higher permeability in the tested alloys. All tested alloys exhibited excellent non-magnetic stability up to high fields and very low magnetic permeability.

Figure 8. Magnetization curve of heavily cold-rolled sheets of (a) Cu-0.3Cr-0.1Zr and (b) Cu-0.15Fe-0.05P-0.1Sn-0.1Ag-0.1Zn at 4.2 K.
4. Conclusions
The tensile properties, electrical resistivity, thermal conductivity and magnetization were determined at cryogenic temperature for precipitation hardened and cold-rolled Cu-0.3Cr-0.1Zr alloy in comparison with OFHC Cu. The Cu-0.3Cr-0.1Zr alloy exhibited an excellent combination of high strength and high conductivities at the temperature range of 4 K to 300 K. Major results are summarized as follows:
The Cu-0.3Cr-0.1Zr showed higher yield ratio and lower the ratio of yield strength to electrical resistivity at cryogenic temperature than OFHC Cu. The Cu-0.3Cr-0.1Zr alloy exhibited high electrical and thermal conductivities, excellent non-magnetic stability and very low magnetic permeability at 4.2 K, although its slight solid solubility in copper resulted in the higher resistivity and lower thermal conductivity than OFHC Cu.

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