Resistance Materials Supporting the Evolution of Electronics

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ABSTRACT Cu-Mn-Ni resistance alloys are important metallic materials which support recent advances in electronics and energy management. In this study, the effects of the addition of Mn and Ni in Cu-Mn-Ni alloys and the impact of the microstructure of metals on the change in resistivity with temperature were investigated. There was a strong positive correlation between the resistivity and the Mn content. We confirmed that in addition to reducing the content of Mn and increasing the content of Ni, coarsening the grain size is effective in reducing the change in resistivity with temperature from 0°C to 150°C. We believe that resistance materials with optimized elements and microstructures will make further contributions to the evolution of electronics in the future.

1. INTRODUCTION

The copper alloy containing 12.0mass% (13.6mol%) of Mn and 2.0mass% (2.1mol%) of Ni was invented by Weston in 1889. Due to its very small temperature dependence on electrical resistance around room temperature, it is still in practical use as a resistance material for more than 130 years after its invention. In recent years, its importance as a material to support the evolution of electronics and energy management has been increasing, and resistors using resistance materials are essential parts for electronic devices such as smartphones, current control of automobiles, and battery sensors, etc. As examples of the use of resistance materials, Figure 1 shows a chip resistor mounted on a printed circuit board, and Figure 2 shows a bus-bar type shunt resistor used in a lead-acid battery state detection sensor (BSS) for automobiles. In these applications, the electric currents, the temperatures in the operating environment and the accuracy of the energy management are increasing. Therefore, resistance materials are required to have stable resistance-temperature characteristics (TCR: temperature coefficient of resistance) with small changes in resistance value compared to the value in normal temperature even in a high-temperature environment of 150°C.

The reason why the temperature dependence of the electrical resistance of Cu-Mn-Ni alloys becomes smaller near room temperature is because the resistivity maximizes around that temperature[1)]. It is known that the temperature at which the resistivity reaches a maximum depends on the Mn content. For Cu–Mn binary alloys, the composition dependence on the change in resistivity with temperature from 0°C to 100°C[2)] has been reported. On the other hand, for Cu-Mn-Ni ternary alloys, although Hirayama reported the composition dependence on resistance-temperature characteristics[3)], the temperature range is narrow, which is from 5°C to 45°C. Therefore, the effect of the addition of Mn or Ni for a wider range of temperature on the resistance-temperature characteristics is not clear. In addition, although it has been reported that the resistance-temperature characteristics change depending on the processing, the annealing temperature, and the grain size[3)], the effect on the resistance-temperature characteristics in a wide range of temperature is also not clear.

Therefore, in this study, we aimed at clarifying the effects of the composition and the microstructure on the

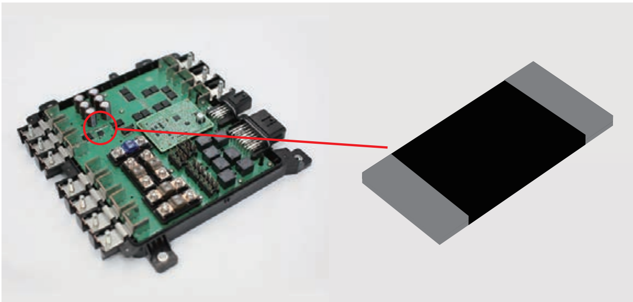

Figure 1 Example of a chip resistor application.

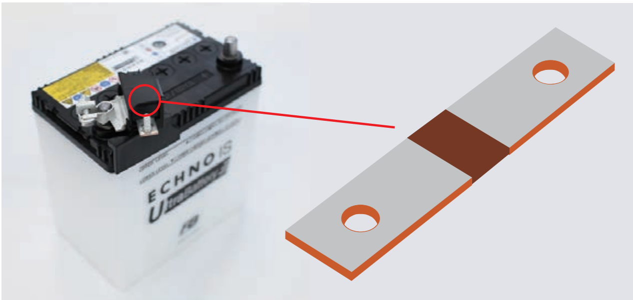

Figure 2 Example of a bus-bar type shunt resistor application.

This article is a re-edition of a paper published in the Journal of Japan Institute of Copper (Volume 60, No. 1, 2021).

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Research & Development Div.

resistance-temperature characteristics over a wide range of temperature from 0°C to 150°C in Cu-Mn-Ni alloys, and obtaining a design guideline for resistance materials with stable resistance-temperature characteristics over a wider range of temperature.

2. EXPERIMENTAL METHOD

Alloys with the compositions shown in Table 1 were melted and cast in an atmospheric furnace, and ingots with a width of 25 mm and a thickness of 25 mm were manufactured. The obtained ingots were homogenized and heat-treated at 900°C for 3.6×10^3 s, hot rolled at the same temperature to a thickness of about 10 mm, and water-cooled. They were cold-rolled to a thickness of 1 mm, then heat-treated at 600°C for 60 s in an Ar atmosphere, recrystallized, and finally cold-rolled to a thickness of 0.3 mm. The effect of the composition was investigated with a specimen which was heat-treated at 600°C for 30 s in an Ar atmosphere, and the effect of the microstructure was investigated with a cold-rolled specimen of 0.3 mm thickness after being heat-tread at 600°C in Ar atmosphere for 30 s, 3.6×10^3 s, and 2.6×10^5 s. In addition, a specimen which was heat-treated at 600°C for 30 s was cold-worked to a thickness of 0.2 mm, and its processed structure was investigated.

Table 1 Chemical compositions of the specimens.

	Composition (mol%)		
	Mn	Ni	Cu
Alloy-1	12.5	2.6	Bal.
Alloy-2	12.8	3.8	Bal.
Alloy-3	12.0	3.8	Bal.
Alloy-4	12.9	1.6	Bal.

The resistivity of the specimens at 20°C were measured with the four-terminal measurement method. And the changes in resistivity with temperature were evaluated by lowering the temperature from 150°C to 0°C at an atmosphere at a rate of 8.3×10^{-3}°C/s. For microscopic observation, cross sections parallel to the rolling direction were subjected to acid etching after mechanical polishing and observed with a metallurgical microscope. The average grain sizes were determined with the cutting method from the picture of each structure.

3. EXPERIMENTAL RESULTS AND STUDY

3.1 Effect of the Composition on the Resistance-temperature Characteristics

Alloy-1 to 4 annealed at 600°C for 30 s all had the equivalent grain size, and Figure 3 shows the metal microstructure of Alloy-1 as a representative example. The average grain size was 4 μm, and from the state diagram[4], all compositions are considered to be a single-phase at 600°C. Figure 4 shows the change in resistivity with temperature of Alloy-1 to -4. The resistivities at 20°C were 42.4 μΩ·cm for Alloy-1, 44.1 μΩ·cm for Alloy-2, 41.6 μΩ·cm for Alloy-3, and 44.0 μΩ·cm for Alloy-4. Figure 5 (a) shows the relationship between the Mn content and the resistivity of Cu-xMn-3.8Ni from a comparison of Alloy-2 and -3. Figure 5 (b) shows the relationship between the Ni content and the resistivity in Cu-12.8Mn-yNi from a comparison of Alloy-2 and -4. And in both (a) and (b), the values calculated by Linde's rule[5] are shown. From the slopes between the two points, the effect on the resistivity was estimated to be 3.1 μΩ·cm / mol%Mn and 0.05 μΩ·cm / mol%Ni. Although the effect of Mn corresponds to the report by Linde[5], the effect of Ni was significantly smaller than that. Therefore, the amount of Ni addition in this alloy system does not follow Linde's rule. In the Cu-Mn system, the s-d interaction between the conduction electrons and the spins has a large effect, and the resistivity is affected by the magnetism[6]. It is suggested that this may be the reason why the usual correlation between the amount of Ni addition and the resistivity was no longer observed. In addition, Figure 4 shows that the resistivity of all alloys changed with a maximum value at about 40°C, but the changes were very small, indicating that these alloys are excellent as resistance materials.

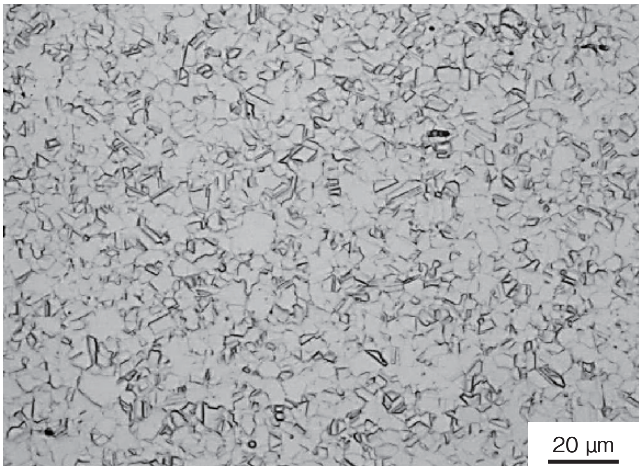

Figure 3 Microsyructure of Alloy-1 annealed for 30 s.

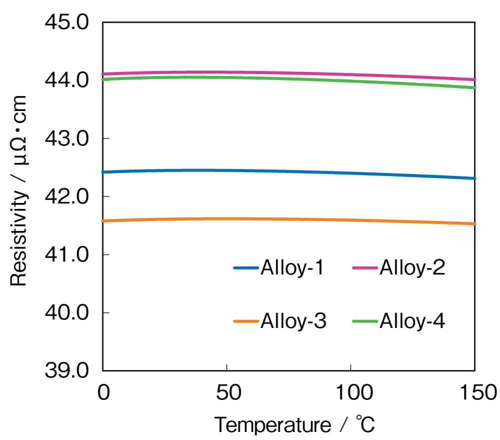

Figure 4 Relationship between the resistivity and the temperature of each alloy.

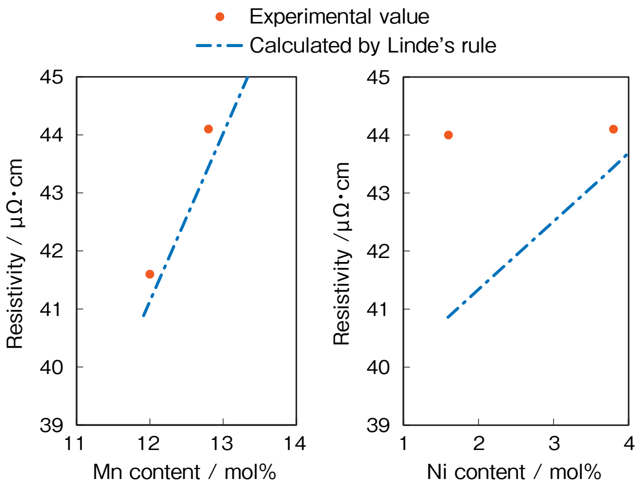

Figure 5 Relationship between the resistivity and (a) Mn content in Cu-xMn-3.8Ni alloy, (b) Ni content in Cu-12.8Mn-yNi alloy.

In order to compare the resistance-temperature characteristics of each alloy in detail, Figure 6 shows the values obtained by standardizing the resistivity at each temperature with the resistivity at 0°C in Figure 4. In all alloys, the changes in resistivity with temperature were parabolic, and the resistivities decreased monotonically from 100°C to 150°C. The temperatures at which the resistivity was maximum were precisely 36°C for Alloy-4, 39°C for Alloy-1, 42°C for Alloy-2, and 50°C for Alloy-3. The rate of change in the resistivity at 150°C asymptotically approached 1 as the temperature at which the resistivity reached its maximum increased.This means that the higher the temperature at which the resistivity is maximized, the smaller the change with temperature between 0°C and 150°C, and the better the resistance-temperature characteristics.

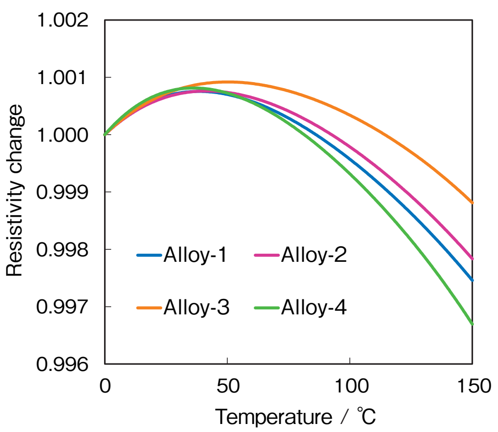

Figure 6 Relationship between the resistivity change and the temperature in each alloy.

Comparing Alloy-2 and -3 in Figure 6, the maximum value shifted to the low temperature side as the Mn content increased. That is, the addition of Mn has the effect of increasing the change in resistivity. It should be noted that the higher the Mn content, the greater the decrease in the resistivity at 50°C or higher, which is in good correspondence with the report on the Cu-Mn binary system[2).

On the other hand, when comparing Alloy-2 and -4, which have the same Mn content, the higher the Ni content, the maximum value shifted to higher temperatures, and the change between 0°C and 150°C was small. From the above, it was found that the addition of Ni has the opposite effect of the addition of Mn with respect to the change in resistivity with temperature.

These results indicate that the addition of Ni to a Cu–Mn–Ni alloy reduces the temperature dependence of the resistivity, although the effect on the absolute value of the resistivity is negligible. It has been pointed out that the addition of Ni may affect the suppression of the Kondo effect[2)], and it was confirmed experimentally. Therefore, Ni is considered to be a suitable element for controlling the change in resistivity with temperature in Cu-Mn alloys. In Alloy-3, which had the smallest change in resistivity with temperature, it was suggested that reducing the Mn content and increasing the Ni content would be effective in further reducing the change in resistivity with temperature.

3.2 Effect of the Grain Size on the Resistance-temperature Characteristics

Figure 7 shows the metal microstructures of alloy-1 specimens after being heat-treated at 600°C for 3.6×10^3 s and 2.6×10^5 s. Comparing to Figure 3, the grains grew as the heat treatment time increased, and the average grain sizes were 18 μm for 3.6×10^3 s and 49 μm for 2.6×10^5 s. Figure 8 shows the relationship between the heat treatment time and the resistivity at 20°C after being heat-treated at 600°C for 30 s, 3.6×10^3 s, and 2.6×10^5 s. No clear relationship was observed between the heat treatment time and the resistivity, and the resistivity was constant regardless of the grain size. Figure 9 shows the

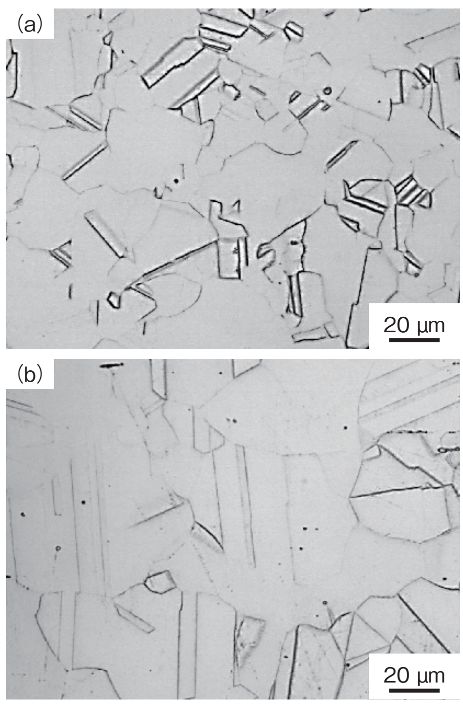

Figure 7 Microstructures of Alloy-1 annealed for (a) 3.6×10^3 s, (b) 2.6×10^5 s.

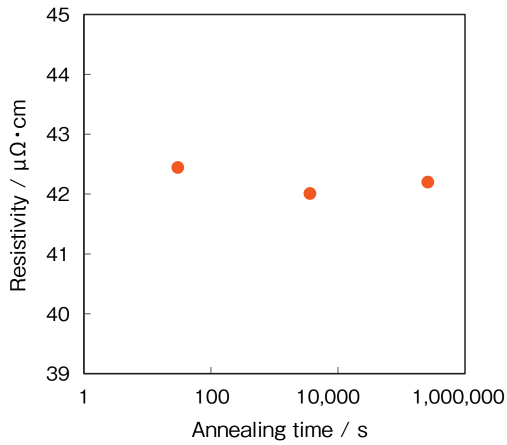

Figure 8 **Relationship between the resistivity at 20°C and the annealing time at 600°C in Alloy-1.**

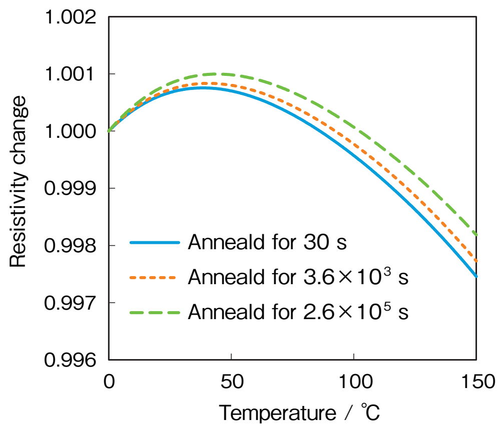

Figure 9 **Relationship between the resistivity change and the temperature in Alloy-1 annealed for each time.**

resistance-temperature characteristics standardized by the resistivity at 0°C. It was found that the grain size did not affect the resistivity, but did affect the temperature dependence. After being heat-treated for 30 s, 3.6×10^3 s, and 2.6×10^5 s, the temperatures at which the resistivity was maximized were 39°C, 41°C, and 45°C, respectively. Similar to the effect of composition, the higher the temperature of the maximum resistivity, the smaller the change in resistivity between 0°C and 150°C. It was found that the longer the heat treatment time, the coarser the grain size and the shift of the maximum point of resistivity to a higher temperature, resulting in the smaller changes in the resistivity between 0°C and 150°C . In addition, the finer the grain size, the lower the resistivity at high temperatures, and the results of this experiment were in accordance with the previous study[3] which shows that the finer the grain size, the lower the temperature coefficient of resistance.

3.3 Effect of the Processing Strain on the Resistance-temperature Characteristics

Figure 10 shows the metal microstructure of the specimen (thickness = 0.3 mm) in Figure 3, which was further cold-rolled to a thickness of 0.2 mm. Comparing to Figure 3, it can be confirmed that the grains were stretched in the rolling direction and strain was applied.

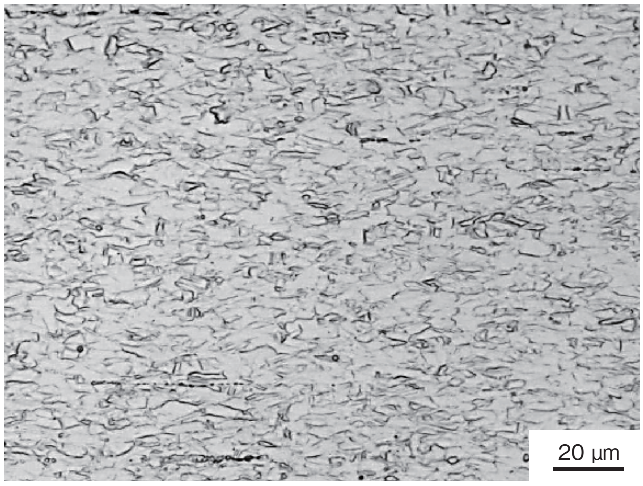

Figure 10 **Microstructure of the cold-worked Alloy-1.**

Figure 11 shows the resistance-temperature characteristics of the recrystallized material in Figure 3 and the rolled material in Figure 10. In addition, since the cold-worked material recovers during the resistance measurement at 150°C and the resistivity fluctuates, it was annealed at 300°C before the resistance measurement for convenience for the purpose of suppressing it. The resistivities at 20°C of the recrystallized material and the rolled material were 42.4 μm·cm and 42.5 μm·cm, respectively, which were of equivalent values. On the other hand, the maximum point was 33°C in the rolled material, which shifted to a lower temperature from 39°C in the recrystallized material. That is, the change in the resistivity between 0°C and 150°C was large as before. This result is in accordance with Hirayama's report[3].

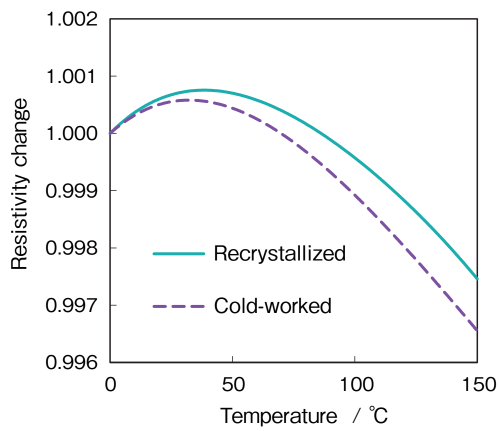

Figure 11 **Relationship between the resistivity change and the temperature in the recrystallized and the cold-worked Alloy-1.**

From the above results, it was found that the finer the grain size and the higher the strain, the lower the temperature at which the maximum resistivity occurs, and the greater the change in resistivity. This means that lattice defects such as grain boundaries and dislocations provide the same effect as the addition of Mn, but the reason for this is not clear. Industrially, by reducing the lattice defects in Cu-Mn-Ni alloys, it is possible to control the change in resistivity with temperature from 0°C to 150°C to be small without changing the resistivity. Therefore, it is considered to be a useful discovery for material design.

Table 2 summarizes the effects of Mn and Ni addition amounts and metal microstructures on the change in resistivity with temperature. From these results, in the range of this alloy composition, when the change in resistivity with temperature from 0°C to 150°C needs to be smaller, reducing the Mn content, increasing the Ni content and coarsening the grain size were confirmed to be effective. Reviewing the composition of elements and controlling the microstructure enables the alloy design with more stable resistance-temperature characteristics, and we believed that this material can make a further contribution to the evolution of electronics in the future.

Table 2 Effects of Mn and Ni additions and the microstructure on the change in resistivity with temperature respectively in Cu-12.5mol%Mn-2.6mol%Ni alloy.

	Resistivity	Resistivity change (from 0℃ to 150℃)
Mn addition	increase	decrease
Ni addition	small effect	increase
Fine-grain structure	small effect	decrease

4. CONCLUSION

We investigated the effect of the composition and the microstructure on the resistivity and on the resistance-temperature characteristics from 0°C to 150°C for Cu-12~12.9mol%Mn-1.6~3.8mol%Ni alloy, and obtained the following results.

(1) We found that the amount of Mn addition to the resistivity of this alloy follows Linde's rule, but the amount of Ni addition does not.

(2) In this alloy, the change in resistivity with temperature from 0°C to 150°C follows a convex parabola, and the higher the temperature at which the resistivity is maximized, the smaller the change in resistivity. In addition, we confirmed that the change in resistivity with temperature becomes large with the addition of Mn, but it becomes small with the addition of Ni.

(3) In this alloy, the finer the grains and the more the cold-rolling strain is applied, the more the resistivity peak shifts to a lower temperature, and the change in resistivity with temperature increases.

(4) In this study, we found that reducing the Mn content, increasing the Ni content, and coarsening the grain size are effective in reducing the change in resistivity with temperature within the range of these alloy compositions.

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