The Development of a Cu-Co-Si Alloy with a High Strength and a High Electrical Conductivity

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ABSTRACT The influence of the amounts of cobalt (Co) on the strengths, the electrical conductivities, the grain sizes and the bending workability of Cu-Co-Si alloys were studied. When the amount of Co is increased, the strength after an aging treatment increases. However, the problem was that the bending workability was deteriorating by the coarsening of the grain sizes of the recrystallization structures because high temperatures are required to dissolve Co and silicon (Si) completely in the solution heat treatments, which is a former process. We have succeeded in achieving both a high strength and a good bending workability by adding a slight amount of chromium (Cr). The mechanism is that a ternary compound of Co-Si-Cr was precipitated on the grain boundary by adding a slight amount of Cr, thereby restraining a coarsening of the grain size.

1. INTRODUCTION

In recent years, the copper alloys for the materials of connectors require a further enhancement of the strength and a superior bending workability because the connectors used in electronic devices and in automobile components are becoming smaller in size, lighter in weight and more precise. In addition, these connectors also require a high electrical conductivity to reduce loss when carrying a large current or to restrain a Joule heat because the trend is that larger electric currents flow in the connectors as a result of the technological innovations such as the quick charge of mobile devices and the next generation automobiles such as plug-in hybrid vehicles (PHV), electric vehicles (EV), etc. In recent years, Cu-Co-Si alloys have been getting attention since they are meeting these required characteristics. The research1) on the strength and the electrical conductivity of the alloys has been reported and the alloys have been being used as materials with a high strength and a high electrical conductivity. The enhancement of the strength and the bending workability are necessary to meet the market demands for the above-mentioned copper alloys for connectors which require high conductivity, and to control the metal structure is effective for fulfilling those requirements.

A Cu-Co-Si alloy is an aging precipitation alloy. It is known to contribute to the strength when the Co and the Si, which were dissolved by a solution heat treatment at a high temperature, form a Co_2Si compound2) when subjected to an aging treatment. Therefore, the increase of the densities of the Co and the Si are effective for improving the strength. However, in such a case, the temperatures at which the Co and the Si dissolve are high. It causes a coarsening of the grains of recrystallized copper matrix, which is generated in the process of the solution heat treatment. As a result, the bending workability and the press workability are deteriorating. We had an in-depth study on the influence of the densities of the Co and the Si in Cu-Co-Si alloys on the electrical conductivities and on the behaviors of the growth of the recrystallized grains at solution heat treatments, and also on the mechanical characteristics and on the electrical conductivities at aging treatments, and thereby identified the composition of a Cu-Co-Si alloy in a good balance of the strength and the electrical conductivity. In addition, we have studied the slight addition of Cr in Cu-Co-Si alloys to restrain a coarsening of the recrystallized grains. That is because, nevertheless the restraint of the growth of recrystallized grains by adding a slight amount of Cr has been reported with Cu-Ni-Si (Corson) alloys3), which are age precipitation alloys just like this Cu-Co-Si alloy, it has not been reported with this alloy yet.

2. EXPERIMENTAL METHOD

The alloys with the compositions shown in Table 1 were melted and casted in an atmosphere furnace, and the hot-rolled plate materials were provided as specimens. The names of the specimens are hereinafter called Alloy-1-8. The Alloy-1-6 are the alloys in which the compositions of the Co and the Si are varied. The Alloy-6-8 are the alloys in which 0.05-0.15 mass% of Cr is added to the Alloy-4. With respect to the composition of the Co

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and the Si, assuming that Co_2Si compounds, which contribute to the strength, are formed, the mass ratio of the added amount of the Si to the added amount of the Co in the range of 0.5-1.4 mass% was set to Co/Si=4.2 (atom ratio Co:Si=2:1). At first, each specimen was formed in a thin plate by cool rolling. Next, they were subjected to heat treatments in a salt bath furnace at 973-1273 K for 30 seconds, then rapidly cooled in water. The electrical conductivity of each heat-treated material was measured by a four-terminal method. The solution temperatures were determined by the temperatures at which the electrical conductivities became permanent, and the solution heat treatments were conducted at the temperatures. After that, aging treatments were performed in a tube furnace, in which argon (Ar) is used as atmosphere gas, at 723-873 K for two hours, then the mechanical characteristics and the electrical conductivities were measured. JIS-13B were used as the size of the specimens for the examination of the mechanical characteristics, and the tensile tests were conducted at 10 mm/min of the crosshead speed. The bending workability was evaluated by 90° W-type bend tests based on the Japan Copper and Brass Association technical standard (JBMA-T307) on the specimens with several widths. The bending direction was in a transversal direction (BW bending), and the ratios of the minimum bendable radius to the thickness (MBR/t) were obtained. In each production process, the microstructures were observed by an optical microscope, a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The grain sizes were measured in compliance with the cutting method of JIS H0501.

Table 1　Chemical composition of specimens (mass%).

No.	Co	Si	Cr	Cu
Alloy-1	0.5	0.12	–	Bal.
Alloy-2	0.7	0.17	–	Bal.
Alloy-3	0.9	0.24	–	Bal.
Alloy-4	1.1	0.27	–	Bal.
Alloy-5	1.4	0.35	–	Bal.
Alloy-6	1.1	0.27	0.05	Bal.
Alloy-7	1.1	0.27	0.10	Bal.
Alloy-8	1.1	0.27	0.15	Bal.

3. RESULTS AND STUDIES

3.1 The Electrical Conductivities of the Solution Heat Treated Materials

Figure 1 shows the electrical conductivities after being subjected to the solution heat treatments at 973-1273 K for 30 seconds on the Alloy-1-8. In all the alloys, the electrical conductivities decreased as the temperatures of the heat treatment rose. However, because the electrical conductivities tended to become permanent at certain temperatures and above in each alloy, the temperatures at which the electrical conductivities become permanent were determined to be the solution temperatures. When the added amounts of the Co and the Si increased, the solution temperatures rose. Therefore, the solution temperatures were determined 1048 K in the Alloy-1 (0.5 mass%Co), 1123 K in the Alloy-2 (0.7 mass%Co), 1173 K in the Alloy-3 (0.9 mass%Co) and 1223 K in the Alloy-4 (1.1 mass%Co) and in the Alloy-5 (1.4 mass%Co). No apparent decrease in the electrical conductivities by adding Cr was observed in the Alloy-6-8, which are Cr-added Alloy-4. Therefore, it was assumed that the changing stopped around at 1223 K and the temperature reached the solution temperature.

3.2 The Mechanical Characteristics and the Electrical Conductivities of the Aged Materials

Aging treatments were conducted on the Alloys-1-5 and -8 which were solution heat treated at each solution temperature in advance, and they were provided as specimens. Figure 2 shows the tensile strengths (*TS*) and the electrical conductivities (*EC*) of the specimens at aging temperatures from 723 K to 823 K for two hours. The tensile strengths greatly increased in all the alloys as the aging temperatures rose, and the peak of the strength was 798 K. The electrical conductivities increased in a same pace as the aging temperatures rose, and became permanent in the range of 65-70 %IACS when the temperature reached 848 K and above. Figure 3 shows the influence of the densities of Co on the tensile strengths and on the electrical conductivities in the alloys at 798 K. The strength greatly increased as the density of Co increased, but the increase rate dropped when the Co

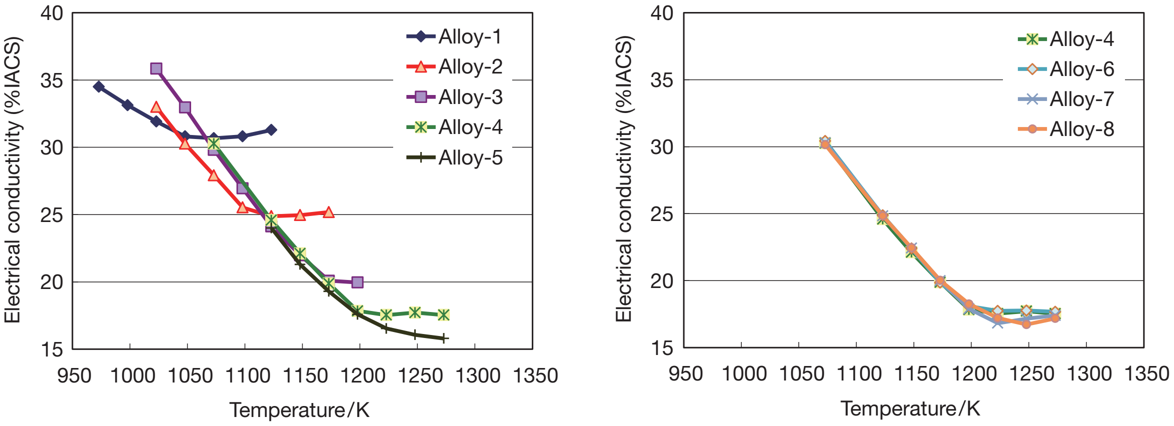

Figure 1　Relationship between increasing solution heat treatment temperature and electrical conductivity of the Cu-Co-Si alloys.

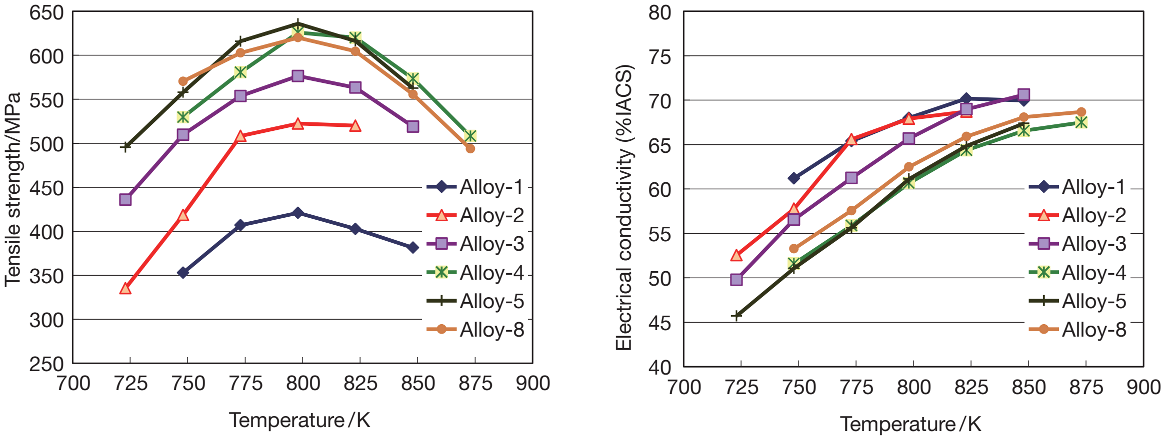

Figure 2 Relationship between increasing aging temperature and tensile strength, electrical conductivity of the Cu-Co-Si alloys.

density was 1.1 mass% and over. The electrical conductivity decreased in the range of 0.7-1.1 mass%, but there was almost no change when the Co was less than 0.7% and was 1.1 mass% and above. An addition of Cr slightly shifted the aging curve of the tensile strength and the electrical conductivity to the side of the low temperature, but almost had no influence on the peak strength and on the electrical conductivity. Therefore, taking a balance between the strength and the electrical conductivity into consideration, the density of the Co is appropriate to be within 0.7-1.1 mass%. Figure 4 shows the TEM blight field image of the Alloy-4 aged at 798 K (*TS*=620 MPa, *EC*=61%) as an example of the aged structures. A clear contrast of the precipitates, which is estimated to be Co_2Si, was observed, and these precipitates are considered to contribute to the strengths of the alloys.

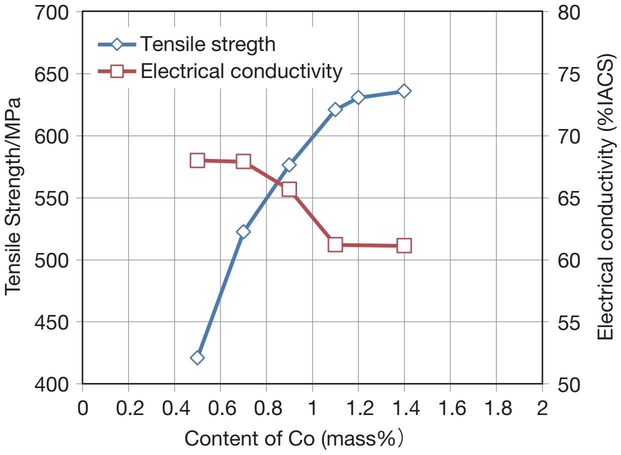

Figure 3 Relationship between content of Co and tensile strength, electrical conductivity in aged Cu-Co-Si alloys (at 798 K, for 2 hr aging).

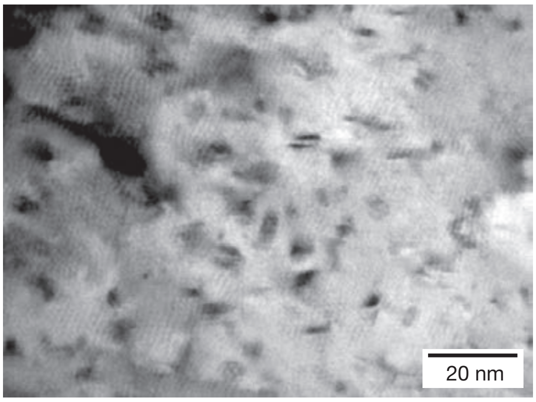

Figure 4 TEM blight field images of Alloy-4 aged at 798 K for 2 hr.

3.3 The Influence of the Solution Heat Treatment Temperatures on the Grain Sizes and on the Mechanical Characteristics

Next, we show the results of the studies on the grain sizes and the bending workability of the alloys with 1.1 mass% of the Co density. Figure 5 shows the influence of the solution temperatures on the grain size after the solution heat treatments and on the tensile strength after aging treatments in the Alloy-4. The aging condition was set at 798 K (2 hr), at which the peal strength was achieved. The tensile strength after the aging treatment increased in a same pace as the solution heat treatment temperature rose, but decreased when the temperature was over 1273 K. On the other hand, the grain size almost did not change until the temperature reached 1173 K, but greatly grew when the temperature was over 1173 K. The Alloy-4 was subjected to the solution heat treatments at 1173 K and at 1223 K, and then aged at 798 K for two hours to be taken as specimens for comparing the mechanical strengths before and after the grain size greatly grew. Table 2 shows the grain sizes and the mechanical strengths of the specimens. The tensile strength was higher by 40 MPa when the solution heat treatment was conducted at a high temperature, but the bending workability was deteriorating due to the enlargement of the minimum bendable radius (MBR). The deterioration of the bending workability is assumed to have occurred because shear zones develop in a single grain due to the concentration of the stress when the grains size is large. That is, the grain size is required to be kept small to achieve a good bending workability, and the solution heat treatment is required to be conducted at a low temperature. On the other hand, Co and Si are required to be fully dissolved at the solution temperatures and above to achieve a high strength. That is, a method of restraining a grain growth at a solution temperature and above is required to be developed to achieve both a strength and a bending workability. To restrain a coarsening of the grain size at a solution heat treatment, the method of restraining a grain boundary migration by the Zener pinning effect4) after precipitating a second phase (intermetallic compound) which stably exists at the solution temperature and above instead of a Co_2Si compound which is dissolved at the solution temperature is promising. We studied the possibilities of the application of the method by adding Cr, and the results are stated in the following section.

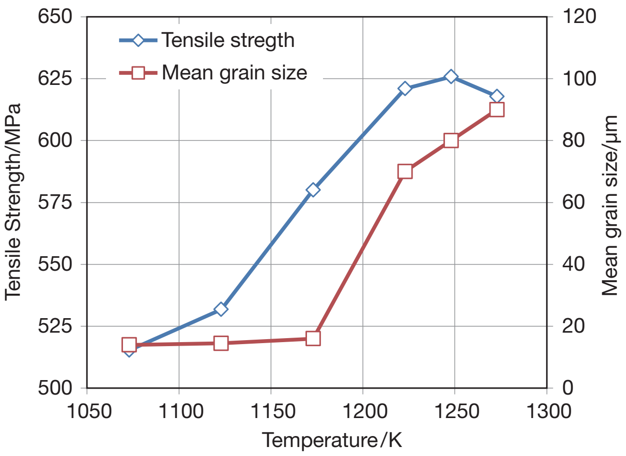

Figure 5 Relationship between temperature and tensile strength, mean grain size in aged Alloys-4 (at 798 K, for 2 hr aging).

Table 2 Mechanical properties and mean grain size of Alloy-4 (solution treated at 1173 K and 1223 K) aged at 748 K for 2 hr.

	Solution heat treatment temperature K	Mean grain size µm	Tensile strength MPa	0.2% proof stress MPa	MBR BW
Alloy-4	1173	16	580	463	0
	1223	70	620	496	>1

3.4 The Influence of the Addition of Cr on the Grain Sizes After Recrystallization

The relationships between the solution heat treatment temperatures and the grain sizes of the Alloy-4 and the Alloy-6-8 (0.05-0.15 mass% of Cr is added to the Alloy-4) are shown in Figure 6 to study the influence of the addition of Cr on the grain growth at heat treatments. The crystal grains started to grow greatly from the neighborhood of 1173 K in the Alloy-4 without the addition of Cr, which is stated in 3.3. On the other hand, the more the Cr was added, the less the coarsening of the grain sizes occurred. The Alloy-8, in which 0.15 mass% of Cr was added, did not become coarse until 1248 K. Judging from Figure 1, the solution temperatures of the Alloy-4 and the Alloy-6-8 are considered 1223 K, and the structures were subjected to the solution heat treatments at 1223 K are shown in Figure 7. Figure 8 shows the relationships between the amounts of the addition of Cr and the grain sizes. It was confirmed by those results that the restraint of the grain growth becomes doable with 0.10 mass% and above of the addition of Cr at the solution temperature of 1223 K. To investigate the cause of the restraint of the grain growth at a solution heat treatment by adding Cr, the structures of the Alloy-8 in Figure 7, in which the grain growth was restrained, were observed with a TEM. Figure 9 shows the TEM image and the results of the energy dispersive X-ray spectrometry (EDX) of the submicronsized precipitates and the matrix on the grain boundaries indicated by arrows. By the comparison of the EDX peaks of the precipitates and the matrix, the precipitates on the grain boundaries were confirmed to be the compounds mainly consisting of Co, Cr and Si. That, is the Co-Si-Cr ternary compounds were not dissolved at the temperature. Therefore, it is considered that the pinning effect of the ternary compounds restrains the grain growth. Figure 10 shows the influence of the solution heat treatment temperatures on the grain size after solution heat treatments and the tensile strength after aging treatments in the Alloy-8. Compared with the Alloy-4 without Cr in Figure 5, the grain growth was restrained without changing the tensile strengths after aging. The alloy-8 was conducted with a solution heat treatment at 1223 K, then conducted with an aging treatment at 748 K for two hours to be taken as a specimen. Table 3 shows the mechanical characteristics of the specimen. The grain size was about 15 µm. The strength of the Alloy-8 was almost equivalent to that of the Alloy-5 conducted with a heat treatment at 1223 K as shown in Table 2, but the bending workability was almost equivalent to the Alloy-5 conducted with a heat treatment at 1173 K. It means the strength and the bending workability can be achieved simultaneously.

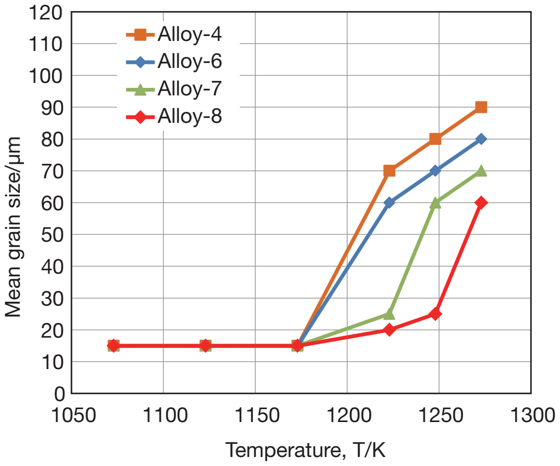

Figure 6 Relationship between temperature and mean grain size in solution heat treated Alloys-4, 6-8.

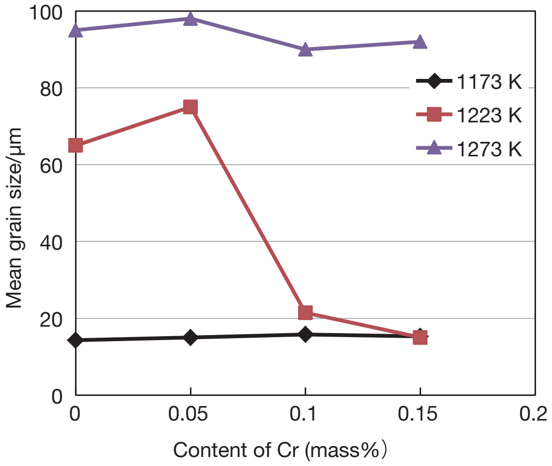

Figure 8 Relationship between content of Cr and mean grain size in solution heat treated Cu-1.1Co-0.27Si alloys.

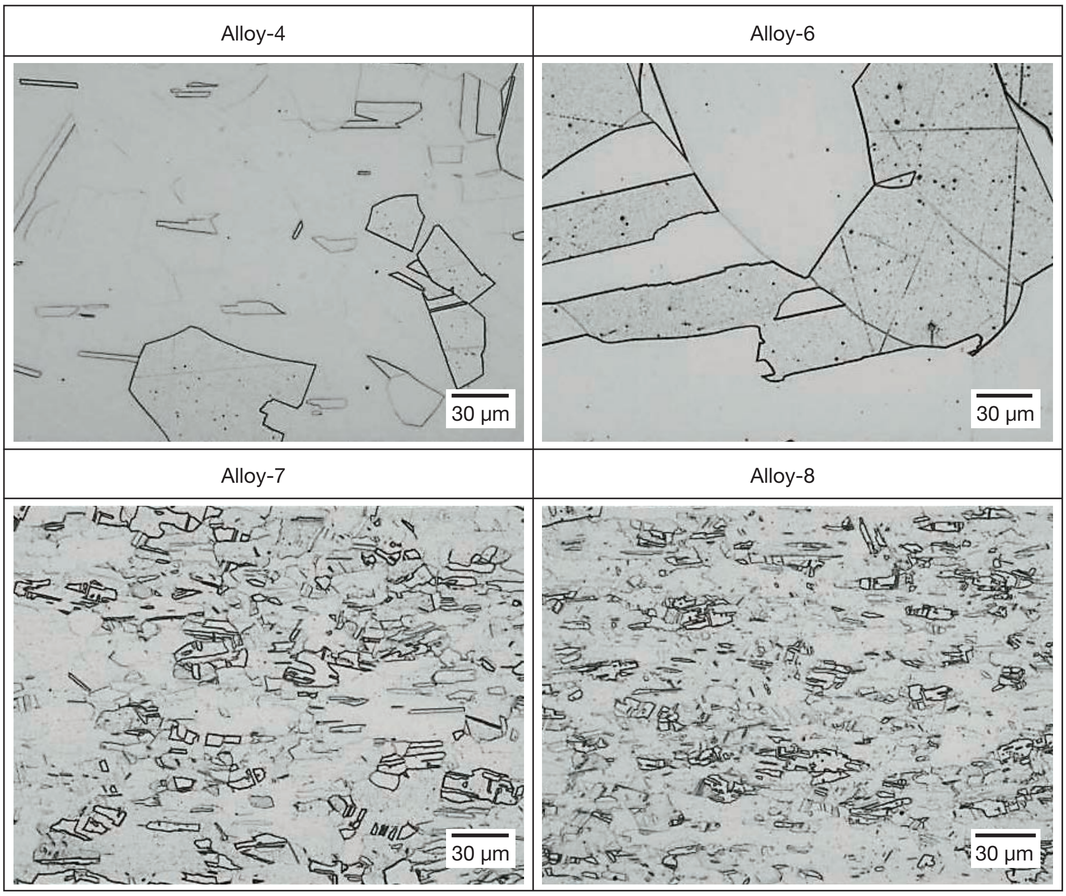

Figure 7 Optical micrographs of specimens after solution heat treatment.

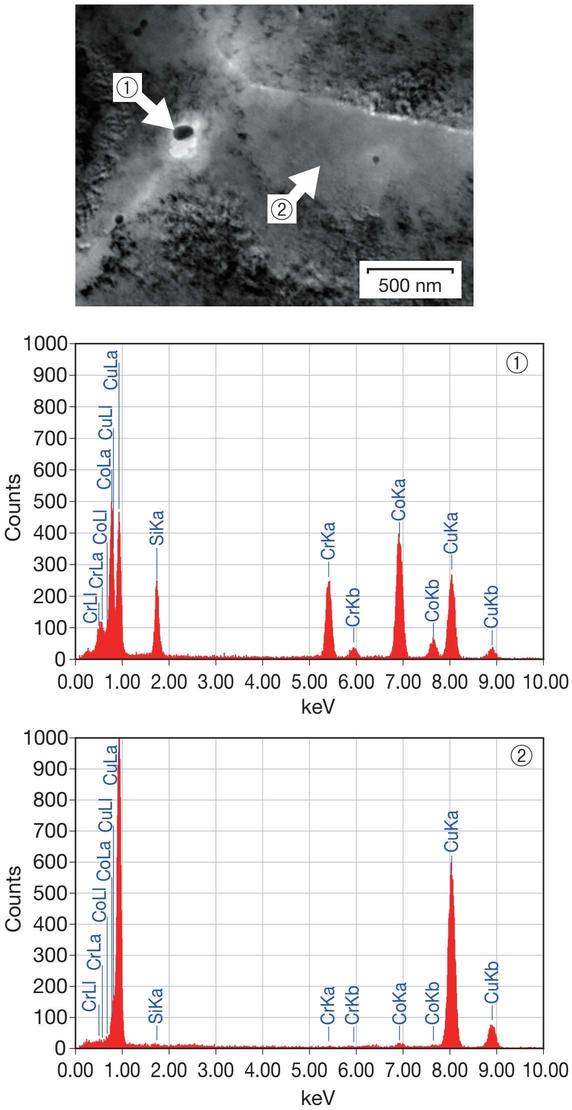

Figure 9 TEM bright field image of Alloy-8 solution treated at 1223 K, and EDX spectrum of a compound on grain boundary (allowed as ① and ②) ① Co-Si-Cr compound and ② Cu mother phase.

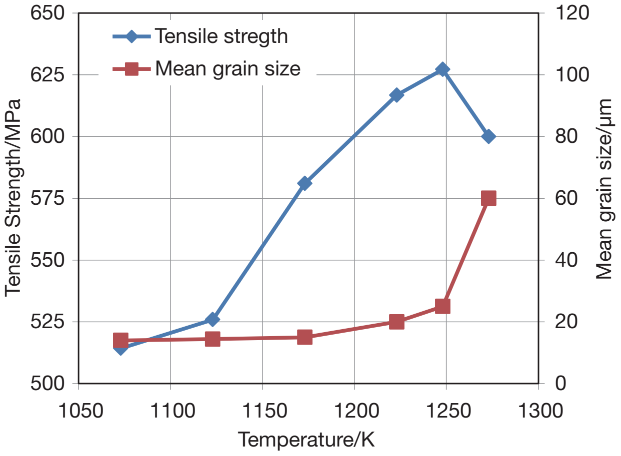

Figure 10 Relationship between temperature and tensile strength, mean grain size in aged Alloy-8 (at 798 K, for 2 hr aging).

Table 3 Mechanical properties and mean grain size of Alloy-8 aged at 798 K for 2 hr.

	Mean grain size μm	Tensile strength MPa	0.2% proof stress MPa	MBR BW
Alloy-8	15	616	495	0

4. CONCLUSION

The influence of the Co densities on the solution temperatures, on the strengths and on the electrical conductivities in the Cu-Co-Si alloys are studied. Also, alloys added with Cr were prepared to study the influence of the addition of Cr on the grain growth and on the bending workability at solution heat treatments. The conclusions are stated below.

(1) With respect to the Cu-Co-Si alloys with a mass ratio of Co/Si=4.2, it was determined that the solution temperatures at which the solution of Co and Si are saturated in the solution heat treatments are 1048 K in 0.5 mass%Co, 1123 K in 0.7mass%Co, 1173 K in 0.9mass%Co and 1223 K in 1.1 mass%Co and in 1.4 mass%Co.

(2) The strength after the aging treatment increases as the Co density increases, but it is saturating at 1.1 mass%Co and above.

(3) In 1.1mass%Co, the bending workability is deteriorated by the coarsening of the grain size when the temperature of the solution heat treatment is raised to the solution temperature. On the other hand, when the solution heat treatment is conducted at the solution temperature and less, the solution amounts of the Co and the Si are not enough, thus a sufficient strength is not achieved at the aging treatment.

(4) The coarsening of the crystal grains at a heat treatment is restrained by the addition of Cr. That is because the ternary compounds of Co-Si-Cr, which exist at a higher temperature than the solution temperature, are precipitated and pin the grain boundaries.

(5) An alloy with Cu-1.1 mass%Co-0.27 mass%Si-0.15 mass%Cr was manufactured and it showed the values of *TS*=616 MPa, *EC*=61 %IACS and *MBR* (BW)=0, which indicate that a high strength, a high electrical conductivity and a superior bending workability are achieved.

REFERENCE

1) R. Matsuo, K. Hirose and T. Eguchi: J. JRICu, 49 (2010) 153-156. (in Japanese)
2) H. Takeuchi and T. Toda: J. Japan Inst. Metal, 26 (1962) 570-575. (in Japanese)
3) K. Hirose: Furukawa Denko Jiho, 121 (2008) 23-27. (in Japanese)
4) C. Zener, quoted by C. S. Smith: Trans. AIME 175 (1948) 15–51.