Development of a High Stress Relaxation Resistance Cu-Co-Si Alloy

Shunta Akiya[*1], *Shoichi Danjo*[*1], *Takemi Isomatsu*[*2], *Ryosuke Matsuo*[*1], *Tatsuhiko Eguchi*[*1]

ABSTRACT The electrical contact materials such as connectors have been required to have a higher strength and a higher electrical conductivity because of the advance of the increase in current and the size reduction of electronic devices. In this study, we have researched the influence of the concentrations of Co and Si and the addition of Sn and Mg to the strength, the electrical conductivity and the stress relaxation property of Cu-Co-Si alloys for the development of an alloy with balanced properties including a stress relaxation property which is important for connector materials. We have improved the balance of various properties by increasing the concentrations of Co and Si and simultaneously adding Sn and Mg, thereby developed a Cu-Co-Si based alloy with an excellent strength, electrical conductivity and stress relaxation property.

1. INTRODUCTION

In recent years, the electric circuits in automobiles and in electronic devices have been requiring an increase in voltage and in current with a back ground where the reduction in size and in thickness of the connectors for automobiles and electronic devices has been rapidly advancing and also where the quick charge technology of hybrid vehicles and electric vehicles has been spreading and progress. Therefore, the copper alloys for connectors highly require both high mechanical and high electric properties in terms of the connection reliability and the suppression of resistance heating.

In the past, Cu-Ni-Si alloys, i.e. Corson alloys have been used because they have an excellent balance of mechanical and electrical properties. However, especially in the next generation connectors, the requirements for the improvement of the electrical conductivity especially based on the uses are nearly exceeding the performance of the Corson alloys. To meet such requirements, we have committed in improving the balance among the electrical conductivity, the strength and the bending workability, etc. by focusing on Cu-Co-Si alloys which are the promising copper alloys with a high strength and a high electrical conductivity[1), 2)].

However, the strength of the alloys has not exceeded the Corson alloys and need further improvements. To improve the strength, an increase in the concentrations of Co and Si are expected to be efficient based the prior research[3)]. In addition, although a stress relaxation property is important in the operation of connectors, improvements in the stress relaxation property has not been attempted in the research of the Cu-Co-Si alloys. On the other hand, while the stress relaxation properties improve in phosphor bronze and Corson alloys when the grains become coarse[4), 5)], it is reported that the simultaneous achievement of the bending workability is difficult in Cu-Co-Si alloys[2)]. In the case of Corson alloys, the prior studies show that the stress relaxation property improves with the increase in the NiSi compound dispersed as a second phase in the copper matrix or the addition of a small amount of Sn or Mg[5), 6)].

Given the above, in order to develop a Cu-Co-Si based alloy excellent in a stress relaxation property (development target: tensile strength≧700 MPa, in electrical conductivity≧50%IACS and in stress relaxation rate (120 °C ×1000 hrs.) ≦10%), we have clarified the influence of the Co and Si concentrations and the addition of a small amount of Si and Mg on various properties, and developed a copper alloy with an excellent balance of the properties, so we are reporting on these.

[*1] Automotive Products & Electronics Laboratories, R&D Division.
[*2] Electronics Component Material Division, Copper & High Performance Material Production Division

2. EXPERIMENTAL PROCEDURE

First, copper alloys with the compositions shown in Table 1 were melted in the atmosphere using a high frequency furnace and casted with a metallic mold. Next, they were subjected to homogenization heat treatment at 1273 K for 30 minutes. After that, they were hot-rolled, subjected to milling and cold-rolled. Finally, they were subjected to solution heat treatment in a salt bath at 1148 to 1248 K for 30 seconds and promptly cooled by water.

The solution heat treatment was conducted at the temperatures shown in Table 2 with reference to the solubility curve temperature for each alloy stated in REFERENCES 7. Then, these alloys were subjected to an aging heat treatment in an argon atmosphere at 798 K for two hours, then cold-rolled (processing rate: Red.≧20) to be provided in the thin plate material with 0.16 mm of the plate thickness. In addition, they were subjected to low temperature annealing in an argon atmosphere at 673 K for 30 minutes. Table 2 shows the experimental methods.

First, the grain structures of the thin plate material were observed with an optical microscope. After that, these plates were thinned by electropolishing and the microstructures were observed with a transmission electron microscope (TEM). The tensile strengths of the thin plate material were measured using tensile tests (specimens of JIS Z 2241-13B, rolling direction, crosshead speed 10 mm/m), and the electrical conductivities were measured (room temperature) with a four-terminal method (length of the measured terminal 100 mm). In addition, strip samples of 10 mm in width and 70 mm in length and also rolled in a longitudinal direction were processed so that burrs on the end face do not appear, and they were provided as specimens. The stress relaxation tests were based on the cantilever block method of the Japan Copper and Brass Association Technical Standard (JCBA) T309 (2004). The initial deflection displacements h_0 shown in Figure 1 were calculated according to the formula (1) so that the load stress was 80% of the yield stress which is the 0.2% of the yield strength, and the load was applied until *time* = maximum 1000 hours at the holding temperature *Temp.* = 393 K. The permanent deflection displacements h_1 at each time were measured and the stress relaxation rates were obtained from the equation (2).

$$h_0 = (\sigma \times L)/(1.5 \times E \times t) \qquad (1)$$

$$\text{Stress relaxation rate} = h_1/h_0 \times 100 \qquad (2)$$

(σ: load stress, E:Young's modulus, t: plate thickness, L: span length)

Table 1 Chemical compositions of the samples.

alloy	Elements						
	Co	Si	Sn		Mg		Cu
	mass%	mass%	mass%	at%	mass%	at%	
1	0.95	0.24	—	—	—	—	Bal.
2	0.95	0.24	0.15	0.08	—	—	Bal.
3	0.95	0.24	0.45	0.24	—	—	Bal.
4	0.95	0.24	—	—	0.10	0.26	Bal.
5	0.95	0.24	—	—	0.20	0.52	Bal.
6	0.95	0.24	0.15	0.08	0.10	0.26	Bal.
7	1.10	0.27	—	—	—	—	Bal.
8	1.10	0.27	0.15	0.08	0.10	0.26	Bal.
9	1.40	0.35	—	—	—	—	Bal.
10	1.40	0.35	0.15	0.08	0.10	0.26	Bal.

Table 2 Experimental method.

Process	Alloy									
	1	2	3	4	5	6	7	8	9	10
Melting and casting	—									
Homogenization heat treatment	1273 K × 30 min (In the atmosphere)									
Hot rolling	—									
Milling	—									
Cold rolling	*Red.*≧90%									
Solution heat treatment	1148 K × 30 s						1198 K × 30 s		1248 K × 30 s	
Aging heat treatment	798 K × 2 hr (In an argon atmosphere)									
Cold rolling	*Red.*≧20%									
Low temperature annealing	673 K × 30 min (In an argon atmosphere)									

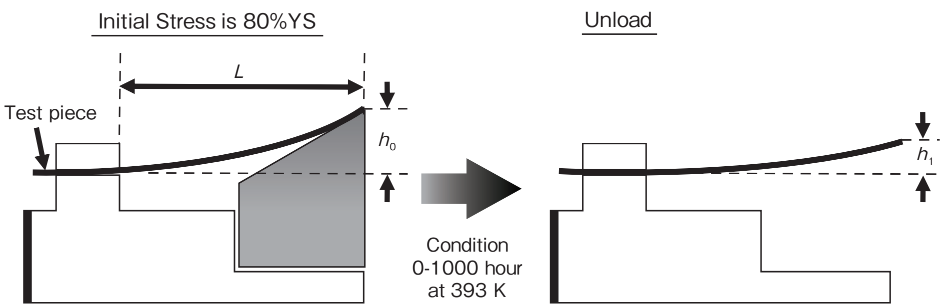

Figure 1 Schematic illustration of the stress relaxation test.

3. RESULT AND STUDY

3.1 Effect of the Alloy Composition on the Strength and the Electrical Conductivity

The thin plate material of the Alloys, having the compositions shown in Table 1, were manufactured through the processes from melting and casting to low temperature annealing shown in the experimental method stated in Table2. The low temperature annealed material tensile strengths and the electrical conductivities of the manufactured Alloy-1, -6, -7, -8, -9 and -10 were measured. The measured data were plotted against the Co concentrations, respectively, and shown in Figure 2.

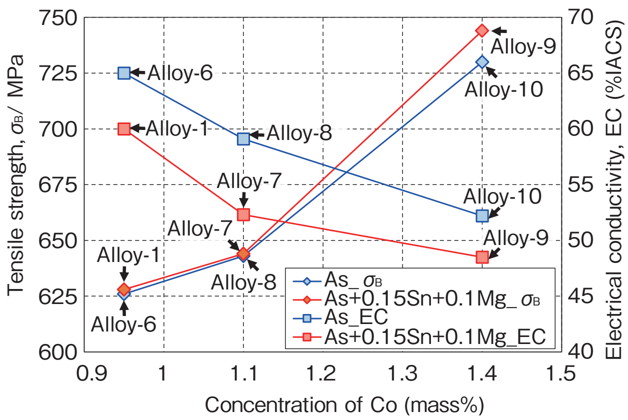

Figure 2 Changes in the tensile strengths and the electrical conductivities of the Alloy-1, -6, -7, -8, -9 and -10 after annealing at 673 K vs the Co concentration.

As the Figure 2 shows, the higher the Co concentration, the higher the tensile strength of the low-temperature annealed material. This is assumed to be because Co and Si added by the solution heat treatment are all dissolved in the matrix, and the added Co and Si are all in the ideal states which can contribute to strengthening the precipitation. Then, the increase in strength is caused due to the fact that the larger the amount of Co and Si dissolved by the solution heat treatment, the larger the amount of the fine precipitates contributing to the strength are generated at the aging heat treatment. In addition, the strength slightly increased due to the solid solution strengthening of Sn and Mg.

In contrast, the electrical conductivity of the low temperature annealed material decreased as the amount of the added Co and Si increased. The assumed reason is that the amount of Co and Si remaining in the matrix increased after the aging heat treatment, in addition the electrical conductivity decreased by adding Sn and Mg.

3.2 Effect of the Alloy Composition on the Microstructure

Figure 3 shows the optical microscope images of the low temperature annealed materials. The average grain size of the samples created was about 10 to 20 µm. Here, Alloy-3, -8 and -10 with Sn and Mg added also had almost the same grain size. It is reported that the difference of the stress relaxation rates is about two to four percent within the range of the grain size in a Cu-Ni-Si based alloy, which is a precipitation type similar to a Cu-Co-Si base alloy[5]. Although it was assumed that the influence of the grain diameter difference appeared in the stress relaxation property of the specimen used in this experiment, the influence of the particle diameter was not taken into consideration based on the assumption that the influence was small.

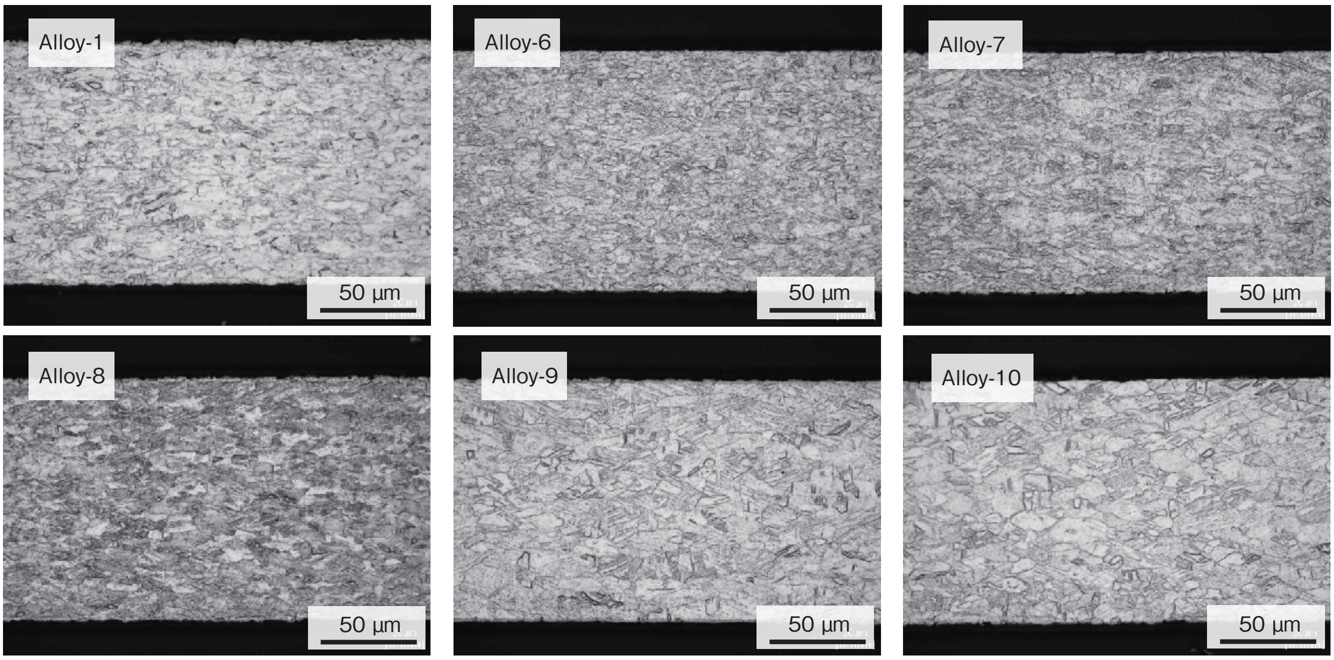

Figure 3 Optical microscope images of the specimens.

Figure 4 shows the TEM bright field images of the low temperature annealed Alloy-7 and -9. As a precipitation concentration at aging heat treatment increases along with the increase in the amount of Co and Si solid solution, a large amount of the precipitation of the Co-Si compounds of about 10 nm[2] were observed.

3.3 Effect of the Concentrations of Co and Si on the Stress Relaxation Property

Figure 5 shows the results of the stress relaxation tests for the low temperature annealed materials of the Alloy-1, -7 and -9. The stress relaxation rates increased with the time duration in every case. Figure 6 is the graph plotting the stress relaxation rates after testing for 25, 100 and 200 hours on the Co concentrations of the Alloy-1, -7 and -9. The stress relaxation rates decreased as the Co and Si concentrations increased. This is a kind of a creep phenomenon caused by a stress relaxation phenomenon generated by a movement of the dislocations[6]. And it is assumed, as shown in Figure 4, Alloy-9 which had a higher Co concentration than Alloy-7 had higher density of the precipitates in the Cu matrix. Then, as shown schematically in Figure 7, the stress relaxation property was improved because the precipitates inhibited the movement of the dislocation movements.

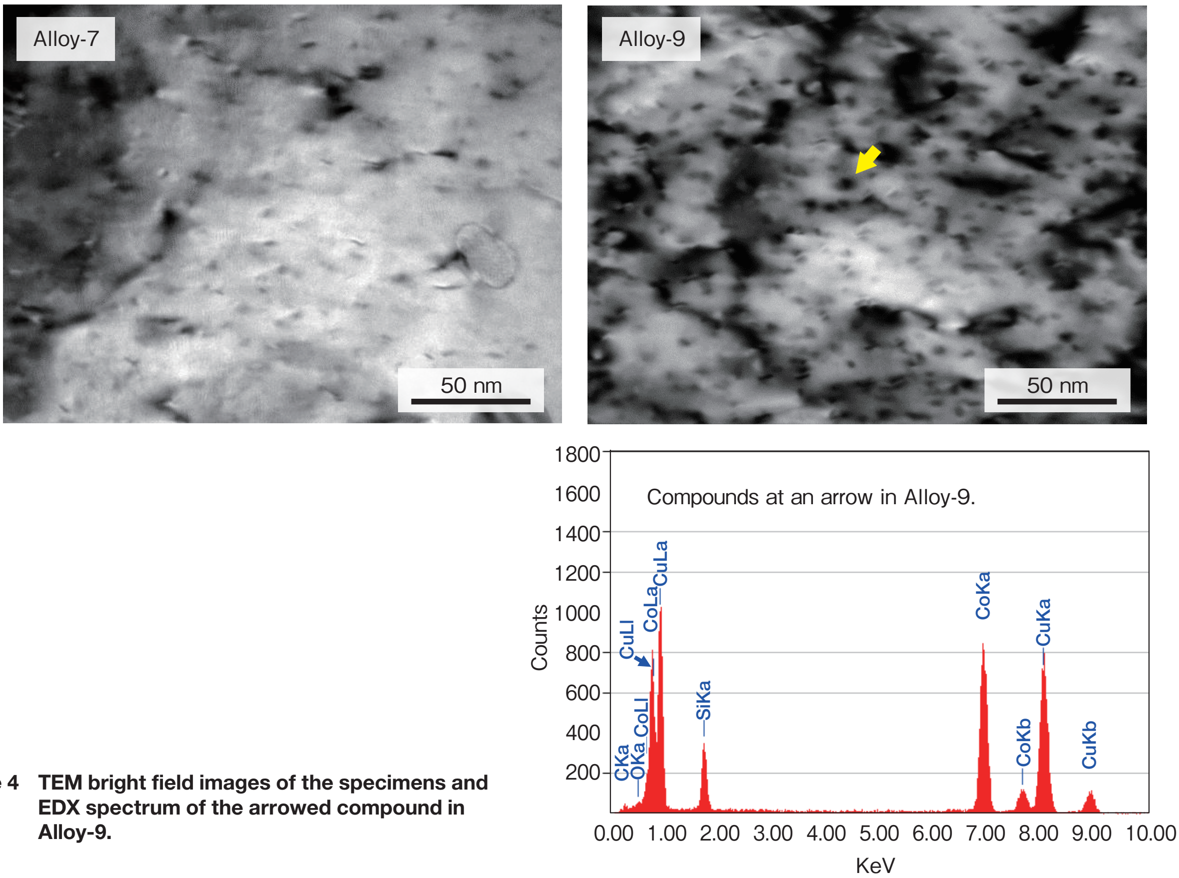

Figure 4 TEM bright field images of the specimens and EDX spectrum of the arrowed compound in Alloy-9.

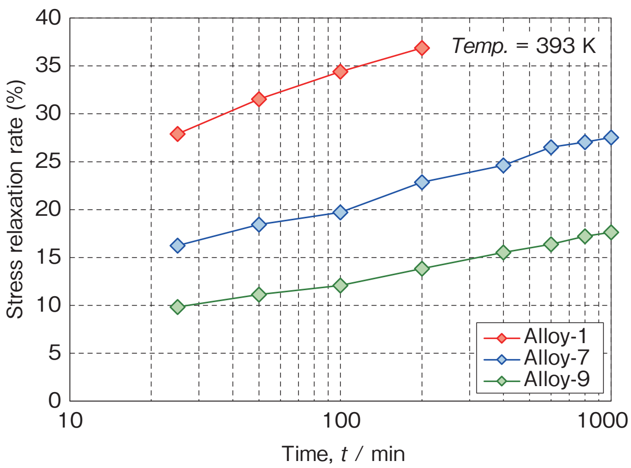

Figure 5 Changes in the stress relaxation rates of the Cu-Co-Si alloys vs the testing time.

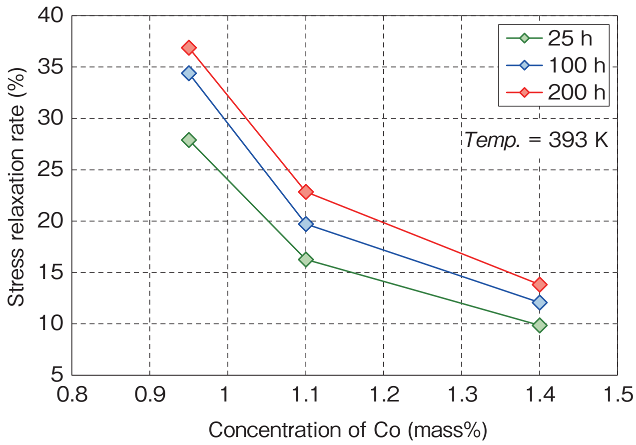

Figure 6 Changes in the stress relaxation rates after testing vs the concentration of Co.

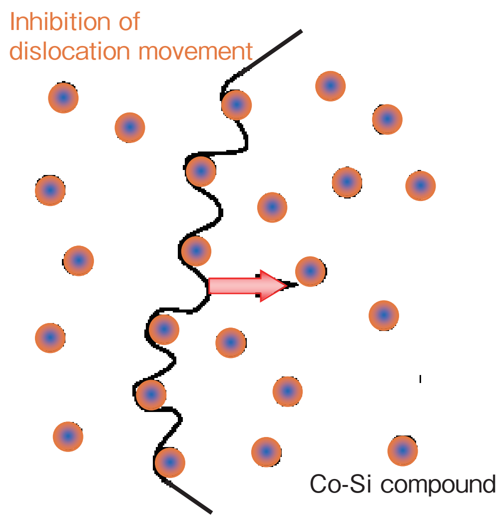

Figure 7 **Schematic illustration of the dislocation movement inhibited by the Co-Si compounds.**

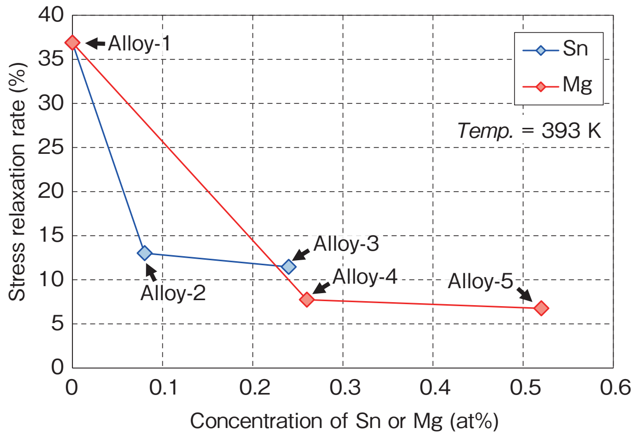

Figure 9 **Changes in the stress relaxation rates after testing for 200 hours vs the Sn or Mg concentrations.**

3.4 Effect of the Addition of Sn and Mg on the Stress Relaxation Property

Figure 8 shows the results of the stress relaxation tests for the low temperature annealed materials of the Alloy-2, -3, -4, -5 and -10.

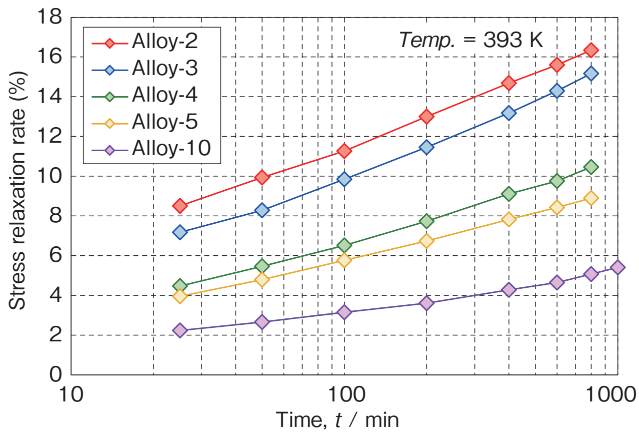

Figure 8 **Changes in the stress relaxation rates of the Cu-Co-Si-Sn-Mg alloys vs the testing time.**

Comparing the Alloy-1 in Figure 5 with the Alloy-2, -3, -4 and -5 in Figure 8, the addition of Sn or Mg onto the Cu-Co-Si alloys lowered the stress relaxation rates and improved the stress relaxation properties.

Figure 9 is a graph plotting the stress relaxation rates after 200 hours of the stress relaxation tests on the Sn or Mg concentrations.

The stress relaxation rate was remarkably lowered by adding 0.08at% (0.15mass%) in the case of Sn and 0.26at% (0.1mass%) in the case of Mg, but when the addition was further increased, the changes in the stress relaxation rates were little. In addition, when comparing at the same atomic concentration, Mg has a higher effect of improving the stress relaxation property than Sn. It is presumed that in the Cu-Co-Si matrix, Mg forms a Cottrell atmosphere, which will be described later, more than in case of Sn, but more detailed research is required. In addition, comparing the results of the Alloy-9 in Figure 5 and the Alloy-10 in Figure 8, simultaneous addition of Sn and Mg improved the stress relaxation property more than when they were separately added.

Regarding the influence of Sn and Mg on the stress relaxation property as described above, a similar tendency has also been reported for a Cu-Ni-Si based Corson alloy[6]. This is assumed to be because Sn (atomic radius: 1.41 Å) or Mg (1.60 Å)having a relatively large difference in atomic radius from Cu (1.28 Å) as shown in Figure 10 has a large interaction with atomic vacancies and dislocations and inhibits dislocation movement by inhibiting vacancy diffusion and forming a Cottrell atmosphere, and also because Sn and Mg form clusters near the dislocation and their effect become larger[6]. It is presumed that the same mechanism works in the Cu-Co-Si based alloys.

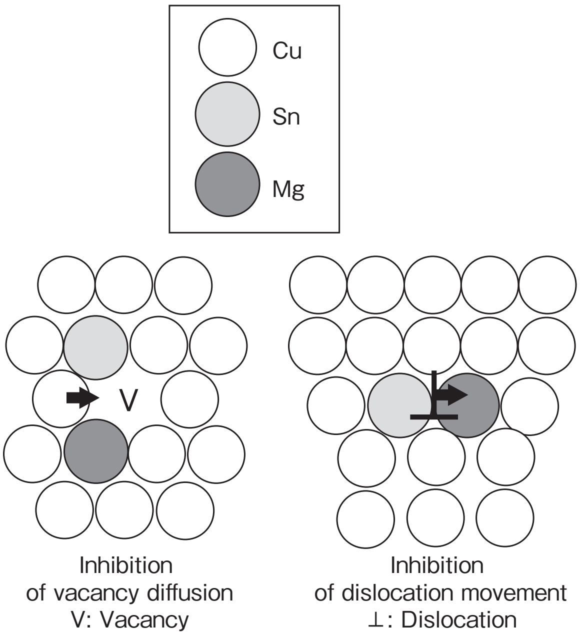

Figure 10 Schematic illustration of the inhibition of vacancy diffusion and dislocation movement.

Attempts were made to further improve the stress relaxation property by combining the effects of increasing the concentrations of Co and Si and adding Sn and Mg as described in 3.3. Comparing the Alloy-9 in Figure 5 in which the Co and Si concentrations were increased with the Alloy-10 in Figure 8 in which additional Sn and Mg were added, the stress relaxation rate of the Alloy-10 was lower. The amounts of Sn and Mg added in the Alloy-10 were determined as Sn=0.15mass% and Mg=0.1mass% in consideration of the results shown in Figure 9. With this component amount (Alloy-10), 740 MPa of tensile strength, 48%IACS of electrical conductivity and 5.7% of stress relaxation rate, as shown in Table 3, were obtained. Although the electrical conductivity of the specimen used in this experiment was less than 50%IACS, it was suggested that the tensile strength of 700 MPa or more, the electrical conductivity of 50%IACS or more and the stress relaxation rate of 10% or less were satisfied by optimizing the composition and the process.

Table 3 Properties of the new Alloy.

Cu-1.4mass%Co-0.35mass%Si-0.15mass%Sn-0.1mass%Mg		
Tensile strength	Electrical conductivity	Stress relaxation rate*
740 MPa	48%IACS	5.7%

*Test condition：120℃ × 1000 h

4. CONCLUSION

As a result of researching the influence of the Co and Si concentrations and the Sn and Mg addition amount on the strength, the electrical conductivity and the stress relaxation property in Cu-Co-Si based alloys, we have obtained the following findings and developed a Cu-Co-Si based alloy which has a strength equivalent to that of the existing Corson alloys, and also has an excellent electrical conductivity and an stress relaxation property.

1) When Sn or Mg are added to a Cu-Co-Si alloy, the electrical conductivity is lowered, but the rise in the tensile strength due to solution strengthening is little.
2) The stress relaxation property is improved by increasing the concentrations of Co and Si, appropriate solution heat treatment, aging heat treatment and low temperature annealing.
3) The stress relaxation property is improved by the addition of Sn and Mg, and it is further improved by the simultaneous addition of Sn and Mg as well as Corson alloys.
4) The Cu-1.4mass%Co-0.35mass%Si-0.15mass%Sn-0.1mass%Mg alloy made in this experiment, having 740 MPa of the tensile strength, 48%IACS of the electrical conductivity and 5.7 of the stress relaxation rate (120°C × 1000 hrs.), is the suitable material for high current connectors.

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