

Development of a Cu-Ni-Si Copper Alloy Strip for Narrow Pitch Connectors

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ABSTRACT Connectors for boards and modules are becoming narrower in pitch due to multipolarization and smaller because electronic devices are becoming compact and multifunctional. A copper alloy strip used for electric contact materials in these small-sized connectors requires high strength and good performance to bending. Furukawa Electric improved these two conflicting features under the control of the metal structures: we have developed a new Cu-Ni-Si alloy (Colson alloy) EFTEC-820 (C64775: Cu-2.3Ni-0.65Si-0.5Zn-0.15Sn-0.1Mg-0.15Cr). This paper reports the improved features of this alloy and our grain-refining technology that contributes to achieving these features.

1. INTRODUCTION

1.1 Development Background

Connectors for electric devices (mobile phones and notebook PCs) are becoming lower in height and narrower in pitch. The materials used for these connectors require a high strength, a good performance to bending and a good plating performance.

The terminals of the connectors for automobile wire harnesses are becoming smaller due to multipolarization. It is because the numbers of electric devices such as electronic control units (ECUs) and because the amounts of wiring are increasing. Moreover, the temperature at which these connectors are used is becoming higher (such as in engine compartments). The materials used for in-vehicle terminals require improvements in high strength together with better performance to bending, and connecting reliability at high temperatures.

We have developed a high-performance copper alloy strip EFTEC-820 that meets these requirements.

1.2 Features of EFTEC-820

Table 1 shows the chemical composition of EFTEC-820. It is a Cu-Ni-Si alloy where Ni and Si are the major components. It contains sub additional elements: Zn, Sn, Mg and Cr.

Table 1 Chemical composition of EFTEC-820 (mass%) (Representative value).

Ni	Si	Zn	Sn	Mg	Cr	Cu
2.3	0.65	0.5	0.15	0.1	0.15	Bal.

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Figure 1 shows the relation between the electrical conductivity and the tensile strength of various copper alloys. Table 2 shows the representative values of EFTEC-820's mechanical features. EFTEC-820 is of two types: temper H and temper EH. EFTEC-820 shows a high strength and a good performance to bending. Table 3 shows the representative values of EFTEC-820's physical characteristics. EFTEC-820 shows a 38%IACS electrical conductivity, therefore EFTEC-820 is suitable not only for signal connectors but also for certain kinds of power connectors.

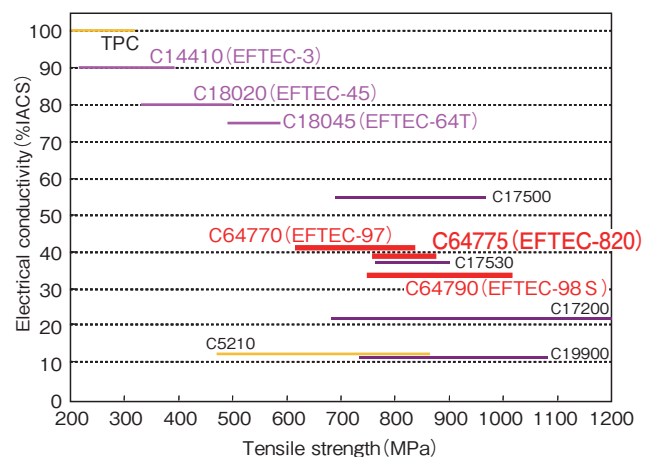


Figure 1 The electrical conductivity versus the tensile strength of EFTEC-820 and other copper alloys.

Table 2 The mechanical features of EFTEC-820 (Representative value).

	H	EH
Tensile strength (MPa)	790	840
0.2% proof stress (MPa)	745	815
Elongation (%)	10	7
Vickers hardness	245	255
Young's modulus (GPa)	130	
Poisson's ratio	0.33	
Minimum bendable radius		
(Bad way, 90°- W bend, w=1 mm)	0R	0.7 tR

Table 3 The physical features of EFTEC-820 (Representative value).

	%ACS	
Electrical conductivity		38
Thermal conductivity	W/mK	157
Coeff. of thermal expansion	$\times 10^{-6}/^{\circ}\text{C}$	17.8 (20~300°C)
Density	g/cm^3	8.8

1.3 The Design of the Alloy of EFTEC-820

Table 4 shows the design overview of EFTEC-820. To make copper alloys high in strength, hardening by plastic working processes such as rolling is a general method. Performance to bending workability deteriorates when such a method is applied, and therefore could not meet the severe demands of recent years. We succeeded in improving strength and performance to bending by applying a proactive control of two kinds of metal structures: precipitate structures and grain size.

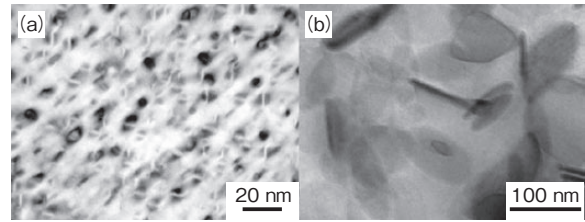
Table 4 Three features of EFTEC-820 and the techniques to achieve them.

Features	Techniques
1. High strength	Increase in precipitates density
2. Good bendability	Refinement of grains with Zener-pinning
3. Good reliability	Improvement in heat resistance and plating performance

Following chapters show the details of the alloy design under control of the metal structures and the good characteristics of EFTEC-820.

2. HIGH STRENGTH

EFTEC-820 is a Cu-Ni-Si copper alloy. Hardening occurs when Ni-Si compounds finely precipitate. EFTEC-820 densely and finely controls precipitates by applying an appropriate heat-treating process and improves strength. Figure 2 shows the states of Ni-Si compounds observed by transmission electron microscopy (TEM). (a) (EFTEC-820) shows a dense Ashby-Brown contrast that represents a coherency strain¹⁾. The high strength is achieved when the strain is in lattice. (b) shows the state of a precipitate structure when the tensile strength is about 100 MPa lower with the same composition. It shows larger precipitates and no dense strain contrast like in (a).

**Figure 2** TEM images of Ni-Si precipitates. ((a) EFTEC-820, (b) Other Cu-Ni-Si alloy that has large precipitates.).

3. IMPROVEMENT IN BENDING PERFORMANCE

This chapter shows a phenomenon where the crystal grains are refined by adding Cr into a Cu-Ni-Si alloy. Effects of bending performance improvement caused by the phenomenon are also shown.

3.1 Measuring Method

First, alloys in four levels of Cr amounts (Table 5) were produced in strip forms by hot and cold rolling. Second, recrystallized structures were obtained by a heat treatment solution at a temperature of 1073 K. Using specimens after the heat treatment solution, the average grain sizes were measured with an optic microscope, and the average sizes and volume fractions with a TEM. The components elements of the precipitates were analyzed with an Energy Dispersive X-ray Spectroscopy (EDX). After that, the precipitates went through an age-hardening heat treatment and a cold rolling, then they were adjusted to about TS=790 MPa which corresponded to temper-H and to about TS=840 MPa which corresponded to temper-EH.

Table 5 Chemical compositions of specimens (mass%).

alloy name	Ni	Si	Zn	Sn	Mg	Cr	Cu
alloy-1	2.30	0.55	0.50	0.15	0.08	-	Bal.
alloy-2	2.32	0.68	0.50	0.15	0.09	0.05	Bal.
alloy-3	2.32	0.68	0.50	0.15	0.08	0.10	Bal.
alloy-4	2.32	0.69	0.50	0.15	0.09	0.20	Bal.

The performance to bending was evaluated by a 90° W-type bend and a 180° closely-attached U-type bend based on Japan Copper and Brass Association technical standard (JCBA-T307 (2007)). The evaluation methods are shown in Figure 3. In the 90° W-type bend test, the bending was applied at various inner bending radii. After that, the Minimum Bendable Radius (M.B.R: the minimum radius which does not cause a crack on the top of the bending part) was divided by the thickness of the specimens, then the result was standardized and used as an indicator of the performance to bending. Also, assuming various connector designs, the widths of the specimens were changed in the range 0.25–10 mm, and, their dependency was studied. At the 180° closely-attached U-type bend test, the bending was applied without an inner radius, and, the result was evaluated with the exist-

ence or the nonexistence of a crack on the top of the bending part.

For information purposes, our company's conventional Cu-Ni-Si materials (C64770 (EFTEC-97), C52100(8 mass%Sn-Cu)) were compared. Table 6 shows chemical compositions of the evaluated materials.

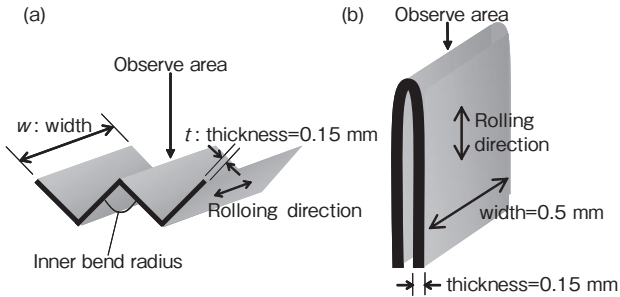


Figure 3 The test method of bendability education. ((a) A 90° W-type bend test, (b) A 180° closely-attached U-type bend test.).

Table 6 Chemical compositions of bend test specimens (mass%) (Representative value).

	Ni	Si	Zn	Sn	Mg	Cr	P	Cu
C64775 (EFTEC-820)		0.65				0.15		
Former Cu-Ni-Si alloy C64770 (EFTEC-97)	2.30	0.55	0.5	0.15	0.1	-	-	Bal.
C52100	-	-	-	8.0	-	-	0.1	

3.2 Effect of Grain Refinement by the Addition of Cr

Figure 4 shows the relation between the average crystal grain sizes of heat treated solution materials and the amount of Cr. When Cr was not added, the size of the grain was about 20 μm. When Cr was added, the size of the grains was about 5 μm. That was because the grains were refined by the addition of Cr. The effect saturated at around 0.1 mass% of the Cr addition.

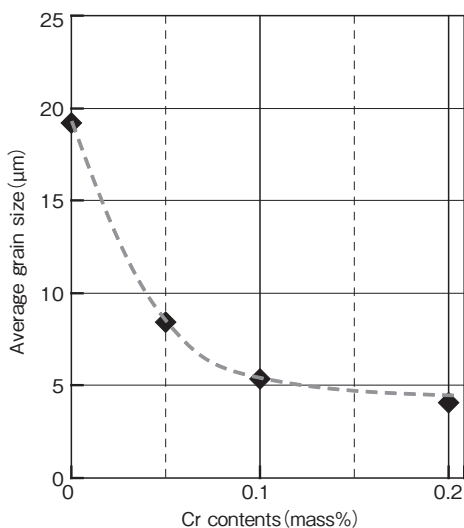


Figure 4 Relation between the average grain sizes and the Cr content in treated solution specimens.

Figure 5 shows the precipitate states of the alloy-1–4 after heat treatment solution is observed with a TEM. In all four alloys, 20–100 nm of the spherical precipitates were dispersed. The more Cr was added, the more was the ratio of the volume the precipitates. Figure 5 (a) shows some Ni-Si compounds that did not dissolve when Cr was not added, but the number of compounds was dominantly small compared to the case when Cr was added. Figure 6 shows the result of a componential analysis of a precipitate in the grain boundary. The precipitate was a Ni-Si-Cr ternary compound.

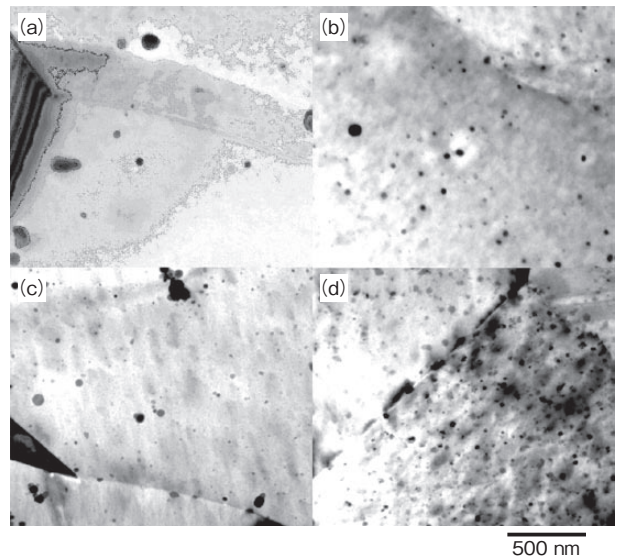


Figure 5 TEM images of the specimens solution treated. ((a), (b), (c), (d) indicate alloy-1, -2, -3, -4 respectively.).

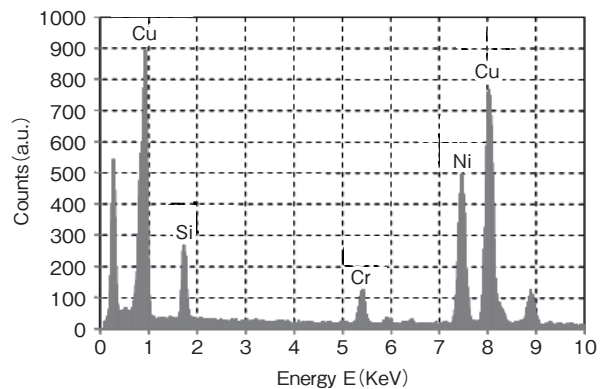


Figure 6 EDX spectrum of a compound on the crystal grain boundary.

Various test results have been reported and several models have been proposed about Zener-pinning. Zener-pinning is an effect that disperses particles pin grain boundaries. It has been formulated in formula (1), using the grain size $[R]$, the average size of a dispersed particle $[r]$ and the volume fraction of a dispersed particle $[f]$ ²⁾.

$$R = \beta \cdot r / f \quad (\beta: 4/3 \sim 4/9) \quad (1)$$

Figure 7 analyzes the relation between the ratio of the average particle size [r] to the volume fraction [f] and the grain size [R] in alloy-1–4.

A proportional connection existed between r/f and R . Its proportionality coefficient was about 0.5. Zener-pinning applied on these Cu-Ni-Si alloys were confirmed. The reason behind the restrictive effect of crystal grain growth is increased by the addition of Cr is because the Cr compounds that disperse as second phase particles increases even with heat treatment solution that Ni and Si dissolve, thus a high pinning force is obtained.

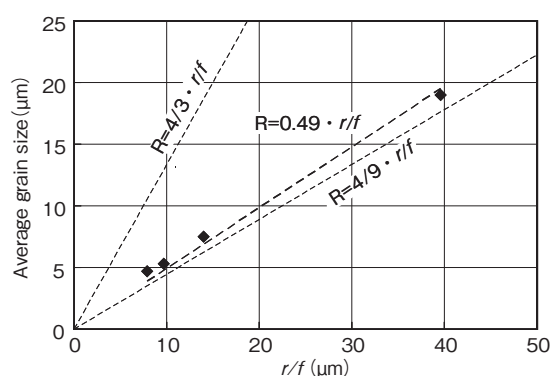


Figure 7 Relation between the average grain size and the r/f (r : size of a particle, f : volume fraction.)

3.3 Relation Between the Grain Size and the Performance to Bending

Figure 8 shows the observation of the cross section of the W-bend part in alloy-1 and -4. These alloys were pretreated by a heat treatment solution and an age-hardening-heat treatment. Alloy-1, whose grain size was about $20 \mu\text{m}$, had big increases on the surface and small cracks. On the other hand, alloy-4, whose grain size was controlled to $5 \mu\text{m}$, had no crack. Extended lines of arrows indicated the regions where the changes in the metal structures were larger than other regions. The regions between the arrows remained the same after the deformation. The regions that arrows indicate absorbed the most part of the entire deformation. These deformed regions had zonal shapes of about $5 \mu\text{m}$ width in about 40° direction from the bent surface. They developed through grain boundaries and several grains. Therefore, they were confirmed as shear bands⁴⁾. Minor cracks in the bent surface of alloy-1 formed along these shear bands. That is, the process of bend cracking in Cu-Ni-Si alloys progresses in this order: the generation of shear bands, the concentration of the deformation into the shear bands, the destruction caused by the deformation along the shear bands. On the other hand, alloy-4, whose crystal grains were

finely controlled with the addition of Cr, had more shear bands than in alloy-1. As a result, the effect that deformation volume in each shear band was reduced and restrained the generation of the cracks.

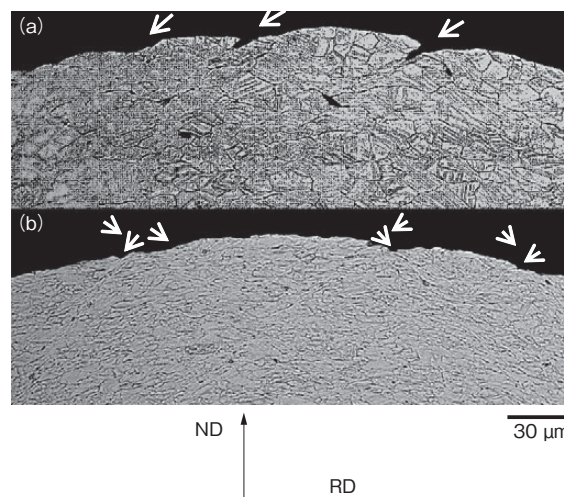
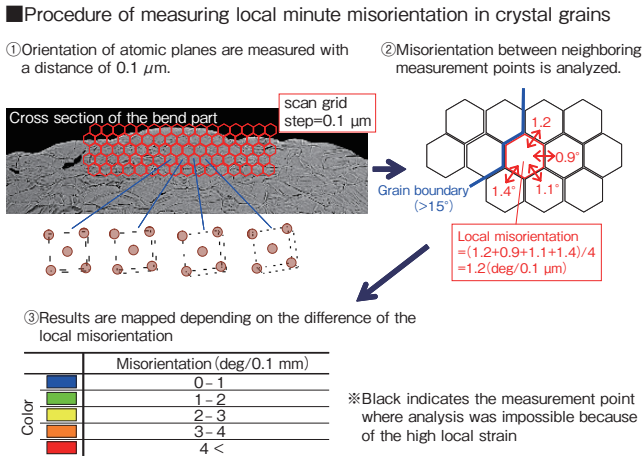
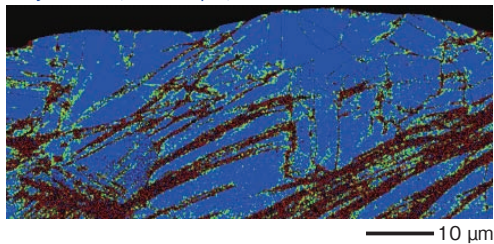


Figure 8 Cross section microstructures in bend specimens. (a) indicates alloy-1 and (b) indicates alloy-4. Extended lines of arrows indicate shear bands.)

The electron back-scattering diffraction (EBSD) method was used to preliminary quantify the local deformations above. Figure 9 shows the analysis of the local strains. The EBSD method measures crystal orientation by diffraction patterns that are obtained when a specimen is irradiated by electron. Continuous information of orientation distribution can be obtained by scanning electron. For that reason, the method has been proposed as a way to analyze microscopic deformation state in a material^{5), 6)}. It is difficult to obtain reliable orientation information in all measurement points because a clear diffraction image cannot be obtained in principle in the area where a material has a high strain. Although, qualitative discussion is possible, local minute misorientation was used to present the degree of a local strain. The analysis of a minute misorientation between measurement points with a distance of $0.1 \mu\text{m}$ is shown in Figure 9 with a color map. When misorientation was equal to or exceeded 15° , it was decided to be a grain boundary. Black lines are indicating it. In alloy-1 whose grain size was about $20 \mu\text{m}$, about 70% of its area was a low-strain area (indicated by blue). High-strain area (indicated by red) grew through crystal grain boundaries in a zonal shape in about 40° direction from the surface. On the other hand, in alloy-4 whose grain size was controlled to about $5 \mu\text{m}$, the deformation area was also in a zonal shape in about 40° direction from the surface. However, the area fraction indicated by red decreased and the area that had middle-strain (indicated by green) increased. Thus semiquantitative analysis using the EBSD method confirmed that the grain refinement had an effect of dispersing the shear bands that were generated when the bending deformation occurred.



Measurement results of the local misorientation
 alloy-1 (0 Cr), GS=19 μm, TS=735 MPa



alloy-4 (0.20 Cr), GS=4.4 μm, TS=747 MPa

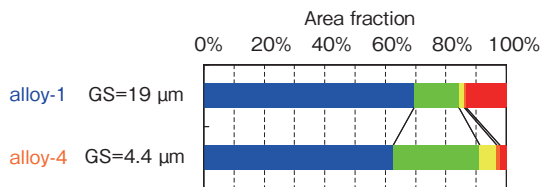
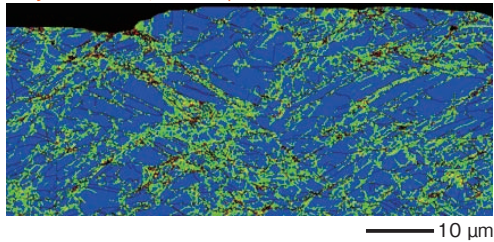


Figure 9 Analysis of cross section microstructures on bend specimens by kernel average misorientation (KAM).

3.4 Performance to Bending of EFTEC-820

3.4.1 W-type 90° Bend Test

Figure 10 shows the relation between the performance to bending and the tensile strength. The tensile strength of EFTEC-820 was 50 MPa higher than that of the C64770 (an existent Cu-Ni-Si alloy) and that of C52100 (a phosphorus bronze system alloy) when compared under the same bendability level.

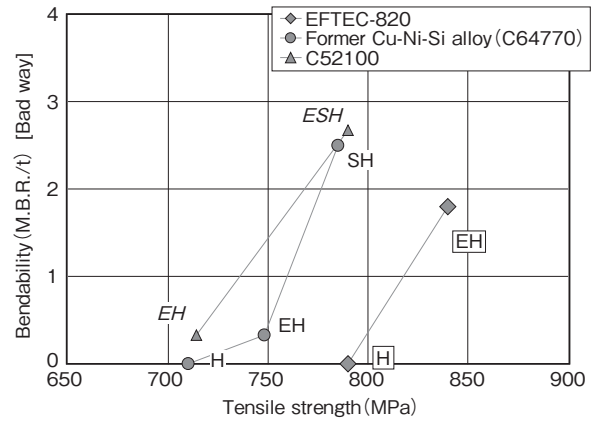


Figure 10 Relation between the bendability and the tensile strength.

Figure 11 shows the marginal bend radius when widths of specimens were changed in the W-type bend test. EFTEC-820(H) showed extremely good performance to bending without a crack when the widths of the specimens were in the range of 0.25–10 mm. In EFTEC-820 (EH), the narrower widths of specimens had the smaller marginal bend radii. When specimens were equal to or less than 1 mm in width, the bending with no crack was possible with 1t in inner radius. On the other hand, C52100's marginal bend radius was 2 t even with 1 mm in width. Thus, EFTEC-820 had a high strength and also could be bent without any crack under a severe bend radius equal to or less than 1t. It showed superior characteristics to the phosphorus bronze alloy which is universally used for contact materials.

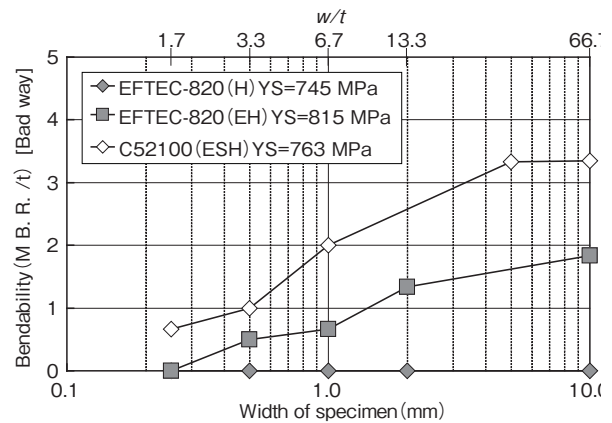


Figure 11 The relation between the widths of the specimens and the standardized marginal bend radius in a bend test.

3.4.2 The U-type 180° bend test

Figure 12 shows the observation results of the cross section of the top of the bending part after the U-type tightly-attached 180° bend test. (a) indicates that EFTEC-820 generated no crack at the bend part. On the other hand, a conventional Cu-Ni-Si alloy could not resist severe stress, therefore a crack of a few dozens of micrometer in depth was generated as indicated by the arrow in (b).

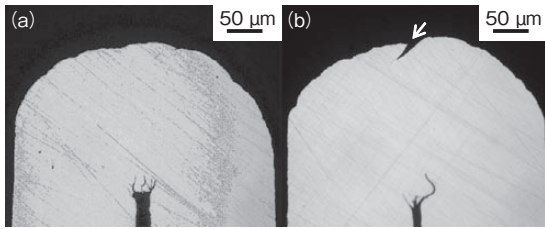


Figure 12 Cross section of the U-type bend specimens. ((a): EFTEC-820 (H), (b): Our company's conventional Cu-Ni-Si alloy (C64770). An arrow in (b) indicates a crack).

As above, EFTEC-820 was confirmed to show good performance to bending even under severe bending like tightly-attached U-type 180° bend.

4. RELIABILITY

Copper alloys are subjected to multiple stresses of thermal stress and mechanical stress when they are used for electric contact materials in connectors. In that case, occasionally lowering the contact pressure occurs is caused by a creep phenomenon of the materials. The thermal stresses are sometimes causing a lowering of the plating adhesion in the plated materials. When Au or Ni plating is unsatisfactory by non-uniformity in base materials, occasionally chemical stress are causing partial corrosion in them. EFTEC-820's design considers the three causes of liability degradation that are described above. This chapter shows evaluations of these three causes.

4.1 Anti Stress Relaxation

4.1.1 Measuring Method

Figure 13 shows the measuring method of the stress relaxation rate. First, the specimens were loaded 80% of 0.2% yield strength with a cantilever beam method, and kept at 120–170° for 1000 hours (This method is based on Japan Copper and Brass Association technical standard (JCBA-T309 (2004))). Second, they were unloaded. Third, the stress relaxation rates were measured from residual plastic deformations.

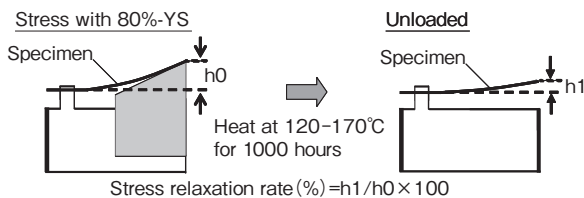


Figure 13 Measuring method of stress relaxation rate.

4.1.2 Result

Figure 14 shows the measurement results of the stress relaxation rate. They showed higher relaxation rates when the temperatures were higher. In particular, at 150 and 170°C, the stress relaxation rates were equal to or exceed 30 % in C52100. It caused significant lowering of the contact pressure from initial stress. On the other hand, EFTEC-820 had a low stress relaxation rate at these temperatures and showed a high reliability. A little amount of

Sn and Mg addition caused good stress relaxation resistance of EFTEC-820.

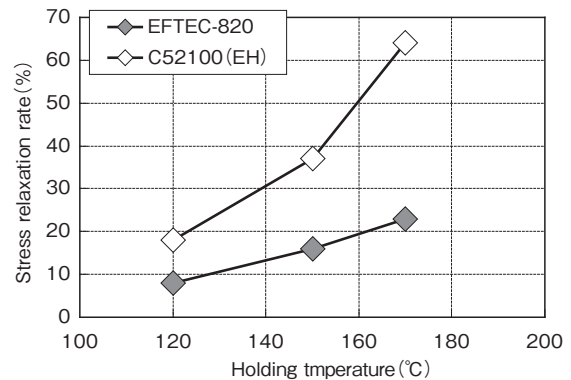


Figure 14 Relation between stress relaxation rate and holding temperature.

4.2 Characteristics of Sn Plated Materials

4.2.1 Measuring Method

Figure 15 shows the measuring method of the heat resistance of reflow-Sn plating. First, EFTEC-820 (H) initially plated with reflow-Sn was bent at 90°. Second, it was kept at 100–160°C for 120 hours. Third, it was bent back and had a peeling test with an adhesive tape. Observation of the adhesive tape that had been peeled and the overview of the specimen confirmed the existence or the nonexistence of the peeling of the Sn plating.

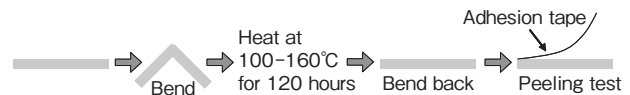


Figure 15 Measuring method of the heat resistance of the reflow-Sn plating.

4.2.2 Result

Table 7 and Figure 16 show the measuring results. EFTEC-820 showed good heat resistance because it had no peeling of the plating at all temperatures (100–160°C). On the other hand, other Cu-Ni-Si alloy that had low heat resistance of the Sn plating had peeling of the Sn plating beginning from the top of the bend part. Generation of Kirkendall voids is one of the reasons of the peeling of the Sn plating. Zn that is a sub addition element of the EFTEC-820 restrained it. In addition, it optimized the surface state of the base material and advanced the heat resistance of the Sn plating.

Table 7 Result of the heat resistance adhesion test on the reflow-Sn plating.

	Holding temperature (°C)			
	100°C	120°C	140°C	160°C
EFTEC-820	○	○	○	○
Other Cu-Ni-Si alloy	○	×	×	×

○: The Peeling of Sn-plating did not occur ×: occurred

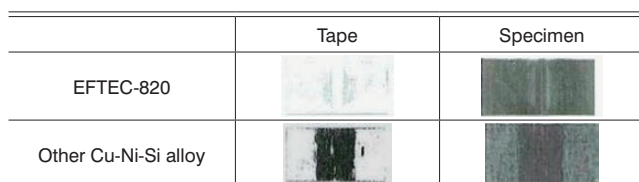


Figure 16 Result of the heat peeling test on the reflow-Sn plating at 140°C.

4.3 Au/Ni Plating

4.3.1 Measuring Method

First, specimens were pretreated with diluted sulfuric acid. Second, they were plated with Ni 1 μm thick, then plated with Au 0.1 μm thick. After that, the following environmental tests ((1)–(3)) were performed. The study of the effect of the corrosion was performed by measuring the contact resistance of the surfaces.

(1) Sulfidizing test

H₂S density: 3 ppm Holding temperature: 40°C
Holding time: 24 h Humidity: 70% RH

(2) Mixed gas test

H₂S density: 100 ppb NO₂ density: 200 ppb
Cl₂ density: 200 ppb
Holding temperature: 30°C Holding time: 24 h
Humidity: 70% RH

(3) Salt water spraying test (ISO9227)

NaCl density: 5% Holding temperature: 35°C
Holding time: 24 h, 96 h

4.3.2 Result

Figure 17 shows the contact resistance values after the environmental tests. EFTEC-820 showed no significant rise in the contact resistance. No corrosion in the base material by plating was observed. On the other hand, C19900, which was a comparative material, showed significant rise in the contact resistance after a mixed gas test and a salt water spraying test. Green corroded products of the copper were observed on them. That was because pinholes were generated by the inadequacy of the plating uniformity, thus the base material corroded.

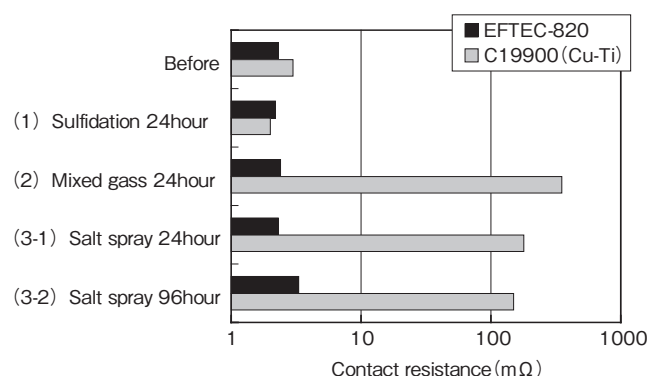


Figure 17 The contact resistance after the environmental tests.

5. CONCLUSION

- (1) When Cu-Ni-Si alloy was added in minute amount of Cr, Zener-pinning effect appeared caused by the disperse of the Cr compounds. It enabled the effective refinement of grains.
- (2) The performance to bending was improved by the grain refinement. The observation of the microstructures and the analysis by EBSD method showed shear bands that caused cracks when bending deformations occurred were dispersed.
- (3) The EFTEC-820's stress relaxation resistance, the heat resistance of the reflow-Sn plating and the Au/Ni plating performance were satisfactory.

The EFTEC-820 (a Cu-Ni-Si alloy (Colson Alloy)) that has both a high strength and a satisfactory performance to bending was developed by proactively controlling the precipitates and the grain sizes. It is optimal for B-to-B type and FPC type connectors that are becoming smaller because it has a high strength of about 800 MPa and a satisfactory performance to bending at the same time. The EFTEC-820 is also suitable for in-car small sized terminals because it has a good stress relaxation resistance and a heating resistance of the Sn plating. Moreover, EFTEC-820's high strength and good performance to bending contribute to the thinning of the copper alloy contact materials for connectors. Natural resource saving and cost-cutting can be possible by using EFTEC-820 instead of existing copper alloys.

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