A New Copper Alloy, CAC5, with Excellent Stress Relaxation Resistance for Automotive Electrical Connectors

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Many studies have been made of the Cu-Ni-Sn-P alloy system to develop a copper alloy for automotive electrical connectors because the scraps of the alloys are recyclable in the automotive electronics market. One remaining issue is that of controlling stress relaxation resistance in this alloy system. We have studied the effect of each alloying element on the stress relaxation resistance. The Cu-Ni-P alloy exhibits a higher resistance than either the Cu-Ni alloy or Cu-P alloy. This is probably because pairs that are formed between P and Ni atoms cause a drag force on moving dislocations. Annealing the P containing Cu based alloy for stabilization has improved the stress relaxation resistance. The result indicates that P, segregated at dislocations, decreases the density of mobile dislocations. A suitable combination of these effects enables the copper alloy, CAC5, to be used for automotive connectors even after long exposure to a high temperature environment.

Introduction

The packaging densities of electrical and electronic devices have been continuing to increase as the devices become smaller and their performance is multi-functionalized and upgraded. In line with this trend, connectors are required to be smaller. The greatest factor in downsizing the connectors is the performance of the conductive springs that form electrical contacts inside the connectors. When copper alloy springs are used in automotive environments, they are exposed to temperatures higher than the ambient temperature, which promotes stress relaxation and decreases the holding force of the springs. As a result, year by year there has been an increasing need for copper alloys with high resistance against stress relaxation for use in electrical terminals.

We have developed a copper alloy, CAC5, having stress relaxation resistance that satisfies the current requirements for automotive mounting. The newly developed alloy contains elements such as Ni, Sn, and P, which have conventionally been added to copper alloys, and it achieves said feature by the combination of an optimum composition and heat treatment. This paper reports on the mechanism at work as these additional elements increase the stress relaxation resistance.

1. The stress relaxation phenomena of electrical terminals

Fig. 1 schematically shows the cross-sectional front view and side view of a typical female box terminal. A connector consists of an array of such terminals in a housing. In the case of the example shown in the figure, a copper sheet is press punched and bent into a box shape. The surface of the copper sheet may be coated with a metal such as tin or gold, depending on the use environment and purpose.

The most important function when putting together terminals to be used as a connector is to maintain the contact force of the spring contact for an extended period of time for stability in keeping as low as possible the contact electrical resistance between the spring contacts and male terminal tabs.

The contact force, however, may decrease as time elapses, even when the displacement of the spring contact (d-t in Fig. 1) remains constant, as in the case where a male tab is inserted into the spring beam of the female (Fig. 1). This is due to the decreasing stress inside the spring exerting the contact force. The major factors accelerating this decrease in stress are the temperature and the amount of stress in the initial state. In the example shown in Fig. 1, the pre-use clearance, d, increases with the passage of time and approaches the thickness, t, of the male tab. This phenomenon, called "stress relaxation", requires special attention when using parts such as automotive connectors in high temperature environments.

The resistance against this stress relaxation must be increased for stability in keeping the contact electrical resistance as low as possible. The electrical contact resistance, R_c, is roughly expressed as $R_c \approx \rho\sqrt{\frac{H}{F_N}}$, wherein ρ is the electrical conductivity of

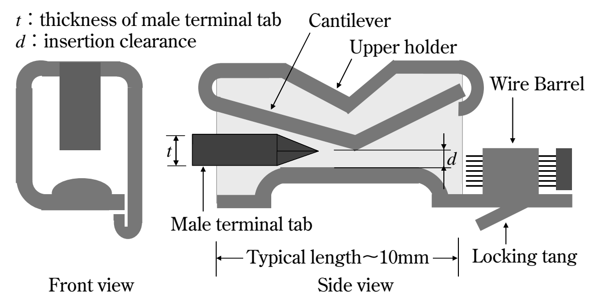

Fig. 1 Cross section shape of female terminal

the material constituting the surface, F_N is the vertical reaction force (contact force) pressing the contact against the surface, and H is the hardness of the surface. In the example shown in Fig. 1, F_N is approximated as $F_N=-k(d-t)$, in which t is the thickness of the male terminal tab, d is the insert clearance of the female terminal and k is the spring constant.

The testing methods for the stress relaxation characteristic are standardized in ASTM E328, EMAS3003 and in Japan Copper and Brass Association Technical Standard (hereinafter JCBA-T309)[7]. Methods for directly measuring the change in contact force are available; however, in most cases, the ratio of the permanent deflection displacement against the initial deflection displacement of a spring contact is used to calculate the stress relaxation rate. **Fig. 2** depicts the most common cantilever method for testing the stress relaxation characteristic. A copper alloy specimen has a thickness, t, Young's modulus, E, determined from the cantilever deflection, and 0.2% proof strength, $\sigma_{0.2}$. The specimen deflects d in the span of l, deflected, for example, by a spacer, and is heated. Typically, the test is conducted at 150℃ for 1,000 hours. An acceleration test, used, for example, for alloy development, may be conducted at 180℃ for 24 hours. When the specimen is mounted, l and d are adjusted such that the maximum stress of the outermost surface becomes approximately 80% of the proof strength[7]. The specimen is dismounted after a predetermined heating time. The permanent deflection displacement, δ, remaining in the specimen at this time, is the change caused by the stress relaxation, and the stress relaxation rate, SRR(%), is defined by $SRR=\frac{\delta}{d}\times 100$: the smaller the stress relaxation rate, the higher the stress relaxation resistance and the better the performance of the spring.

In the initial state, the deflection displacement of the beam does not contain the permanent deflection displacement, δ. Therefore, the deflected beam returns elastically to the original state as soon as the male tab is pulled out. Once the stress relaxation occurs, however, the deflected beam does not return to the original state even when the male tab is pulled out, leaving a permanent deflection displacement. This indicates deterioration in the elastic performance of the spring that is expected to exert a force proportional to the deflection displacement of the beam. The amount of the stress relaxation is determined by converting this permanent deflection displacement to the stress.

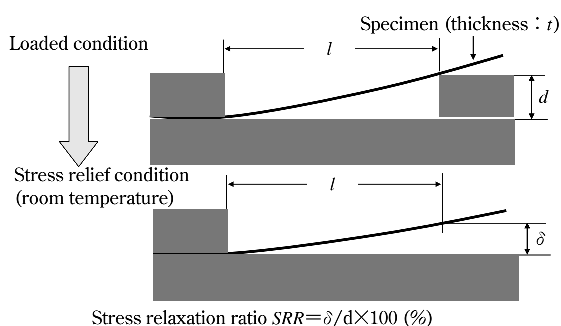

Fig. 2 Schematic illustration of cantilever stress relaxation test

2. The background of the development of the CAC5 alloy

Age-hardenable copper alloys, such as beryllium copper alloy, have an excellent stress relaxation resistance[1), 2)]. However, copper alloys used for automotive applications are required to be recyclable and easy to manufacture on a mass scale. The conventional copper alloys, such as brass, which has been widely used in this field, and phosphor bronze, which has been used mainly in European vehicles, have become unable to respond to the recent need for the stress relaxation characteristic[3)-5)].

It was with this background that Kobe Steel started to develop technologies for increasing the stress relaxation resistance of copper alloys that contain Ni, P and Sn as major alloying elements. Such an alloying composition allows melting and reusing, as-is, of the recycled scraps of tin plated sheets, especially the highly heat-resistant tin plated sheets with Ni underplating, and helps to conserve resources. CAC5 is an alloy in which the major alloying elements described above are optimized for balancing stress relaxation resistance, mechanical properties and electrical conductivity. The alloy has the typical composition of Cu-0.8wt% Ni-1.2wt% Sn-0.07wt% P.

3. How elements contained in CAC5 affect the stress relaxation phenomenon

3.1 The effect on the stress relaxation resistance

The addition of Sn to the copper alloys increases the stress relaxation resistance, but not to the extent of satisfying the requirement for automotive mounting[6)]. This effect is considered to be caused by the Cu and Sn atoms, which have a large atomic radius ratio and form the Cottrell atmosphere that pins dislocations[5)]. As for the addition of Ni, attempts were made to improve the stress relaxation resistance, and it has turned out that the ratio between the additive amounts of Ni and P is important in realizing that characteristic. When the stress relaxation rate is

small, as in the case of CAC5, yield points were found to appear at both the ambient temperature and a temperature (200℃) that is close to the automotive mounting environment. In this case, serrated flow is also found to appear. **Fig. 3** shows the stress-strain relationships at these two temperatures for various Ni and P composition ratios. It should be noted that these stress-strain curves were measured on specimens that had been fully recrystallized such that the yield points and the serrated flow appeared clearly. The stress relaxation rates in the figure are values obtained by measuring the final products. The stress relaxation resistance improves in certain ranges of Ni and P addition and their ratio for a given amount of Sn. On the basis of the discovery described above, a study was conducted on the effect of the addition of Sn, Ni and/or P on the stress relaxation characteristic.

3.2 Experimental method

The following compositions were prepared: 99.99% Cu, Cu-1.5% Ni alloy, Cu-1.5% Sn alloy, Cu-0.75% Ni-0.75% Sn alloy and the same alloys with a 0.14% addition of P. The alloys not containing P are hereinafter referred to as "alloys without P", and the alloys containing P, as "alloys with P". All percent (%) designations represent the atomic percent. The cast metals were homogenized, cold rolled by 50% and annealed at 650℃ for 5 min. After the annealing, all the alloys exhibited recrystallization structures with a grain size of approximately 10μm. The annealed samples were cold rolled further by 40%, and some of the samples were subjected to a low temperature annealing at 300℃ for 30s.

Transmission electron microscope (TEM) specimens were prepared from the samples annealed at 650℃ for 5 min, and the TEM observation was conducted at an accelerating voltage of 200kV. The conductivity represents the average of ten values measured by a conductivity meter using an eddy current method.

Plate-type tensile specimens, each having shoulders and a parallel portion with a dimension of $20^{l} \times 6^{w} \times 0.25^{t}$ mm, were prepared from the samples such that the longitudinal direction of the parallel portion became parallel to the rolling direction. These specimens were tensile tested in a temperature range from 20℃ to 250℃ at an initial strain rate of 3×10^{-3} s^{-1}. Also prepared was another set of specimens, each having a span length of 30mm and a longitudinal direction parallel to the rolling direction. These specimens were subjected to the stress relaxation test in accordance with the cantilever method of JCBA-T309[7]. Each of these specimens was initially deflected such that its surface stress became equivalent to 80% of the 0.2% proof strength at the ambient temperature. These specimens were held in a nitrogen atmosphere at 180℃ for 24h, and the stress relaxation rate was determined by measuring the permanent deflection displacement.

3.3 Experimental results

3.3.1 Strength and conductivity

Table 1 shows the mechanical properties and

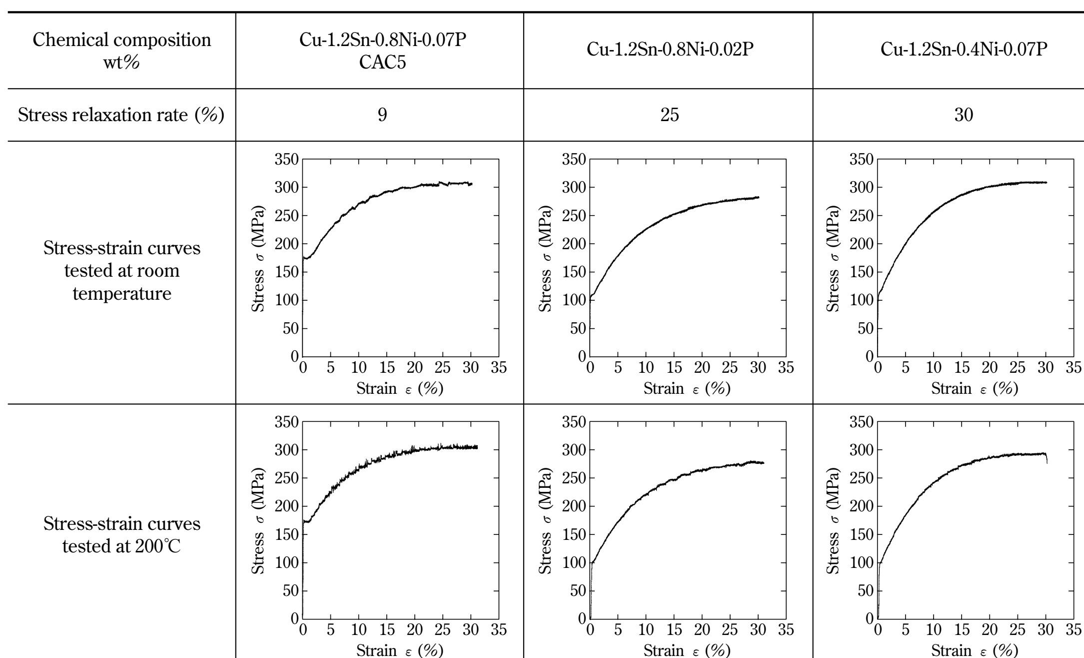

Fig. 3 Relationships between stress relaxation rates and stress-strain curves for annealed CAC5 and similar composition alloys, tested at room temperature and 200℃

Table 1 Mechanical properties and electrical conductivity of specimens

Specimen	0.2% proof stress (MPa)	Elongation (%)	Electrical conductivity (%IACS)
Cu-(0.14P)	150 (290)	10 (8)	100 (65)
Cu-1.5Ni-(0.14P)	350 (380)	4 (4)	48 (41)
Cu-0.75Ni-0.75Sn-(0.14P)	370 (410)	6 (6)	36 (33)
Cu-1.5Sn-(0.14P)	410 (470)	8 (8)	28 (25)

conductivity of the alloys with and without P. Each value in parenthesis represents the measurement result for each alloy containing P. The addition of Sn to pure Cu results in a solid solution strengthening, and the amount of this strengthening is greater than that contributed by the Ni addition. The combined addition of Ni and Sn results in an intermediate value. The addition of P to the pure Cu and to the three alloys increases their proof strengths. The elongation is decreased by the addition of Ni and/or Sn, with Ni addition resulting in a greater decrease than Sn addition. The combined addition of Ni and Sn results in an intermediate decrease. The conductivity of the alloys without P decreases with the increasing amount of Sn and Ni additives. The contribution per unit concentration of Sn to the resistivity of Cu is $2.8\times10^{-8}\Omega$m, which is greater than that of Ni, $1.2\times10^{-8}\Omega$m[8]. The conductivity of the alloys without P, estimated from these values, substantially matches the experimental values shown in Table 1. The addition of P to these alloys decreases their conductivity.

In the metallographic structure observation using a TEM, spherical particles having a diameter of approximately 15nm were observed only in the alloy containing both Ni and P (**Fig. 4**). The analysis based on energy dispersive X ray spectroscopy and selected area diffraction patterns has clarified that these particles are an intermetallic compound of $Ni_{12}P_5$[9]. The volume fraction of the $Ni_{12}P_5$ phase is estimated to be approximately 0.002, from the conductivity measurement and the contributions of Ni and P to the resistivity of Cu. This indicates that approximately 1/3 of the 0.14% of added P is contained in the precipitated phase. On the basis of the fact that the volume fraction of the $Ni_{12}P_5$ particles is rather small and their sizes are relatively coarse, the contribution that the $Ni_{12}P_5$ particles make to the strength is considered to be small.

According to Fleischer and Friedel's theory concerning solid solution strengthening, the increment, τ_m, of the critical shear stress of a binary alloy exhibiting solid solution strengthening depends on the solute atom concentration, c, and the atomic radius ratio, ε, of the solute atom against the matrix atom, and is expressed by the following equation[10), 11)]:

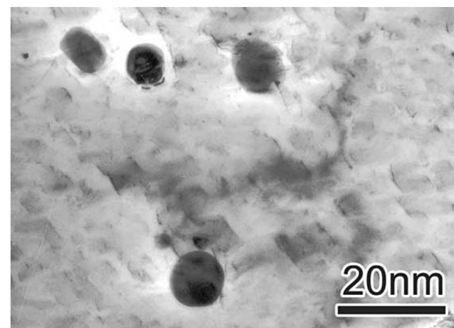

Fig. 4 TEM image of $Ni_{12}P_5$ particles in Cu-1.5Ni-0.14P alloy before cold rolling by 40% reduction

$$\tau_m \propto |\varepsilon| c^{1/2} \quad (1)$$

The atomic radius ratios of Sn and Ni against Cu are +13.8% and −2.3%, respectively[12], the atomic radius ratio of Sn being greater than that of Ni. This explains the results, shown in Table 1, that an increase in the additive amount of Sn increases the amount of solid solution strengthening. The atomic radius ratio of P against Cu is large, −14.8%[12], hence the strength improvement brought about by the addition of P is considered to be mainly attributable to the solid solution strengthening by P.

3.3.2 Stress relaxation characteristic

The stress relaxation rates of the alloys with and without P are shown in **Table 2**. The values in parentheses in the left column represent the amounts of P added to the test materials, while the ones in the middle and right columns represent the stress relaxation rates of the alloys with P. The middle column shows the stress relaxation rates of the as-cold-rolled materials, while the right column shows the stress relaxation rates of the material annealed at 300℃ for 30sec after the cold rolling. Comparing the values in the middle column, the single addition of Ni to pure Cu has almost no effect on the stress relaxation rate, while the addition of Sn, as well as the combined addition of Ni and Sn, decreases the stress relaxation rate. The addition of P to pure Cu, or to the alloy with Ni, significantly decreases the stress relaxation rate. The stress relaxation rate of the alloy with the single addition of Sn remains unchanged regardless of the addition of P. As far as the effect of the additive elements is concerned, these tendencies seen in the right and middle columns are almost the same. A comparison is made between the middle and right columns. After annealing, the stress relaxation rate decreases regardless of the composition; however, the rate for the alloys without P changes less, before and after the annealing. When P is added, the stress relaxation rate is smaller after annealing than it was before annealing.

Stress relaxation phenomena are considered to be creep phenomena caused by the movement of dislocations for relatively short distances[13], and are largely affected by the mobility of the dislocations. The mobility of dislocations generally decreases once the Cottrell atmosphere is formed by the solid solution atoms. This is known to often cause a serrated flow to appear on the stress-strain curves[14), 15]. The serrated flow, as shown in Fig. 3, is considered to be caused by the Cottrell atmosphere formed by the Sn, Ni and P atoms in the solid solution. Hence, the tested materials are also expected to exhibit a serrated flow in their stress-strain curves. With this in mind, the cold rolled material of the each alloy was tensile tested at 180℃. The results are shown in **Fig. 5** and **Fig. 6**. The alloy added with Ni alone does not show any serrated flow. While the alloys containing Sn show serrated flow and the increasing amount of Sn addition causes the stress amplitude of the serrated flow to increase. On the other hand, the addition of P to Cu causes no serrated flow to appear, and the addition of P to the Cu-Sn alloy has almost no effect on the stress amplitude of the serrated flow. However, Ni and P, coexisting in the alloy, cause the serrated flow to appear. Therefore, the improvement brought about in the stress relaxation resistance by the addition of Sn, as well as the combined addition of Ni and P, is considered to be caused by the formation of the Cottrell atmosphere, which increases the viscous resistance against the movement of dislocations.

Table 2 Stress relaxation rate of specimens before and after annealing at 300℃ for 30s, tested at 180℃ for 24h

Specimen	Stress relaxation rate (%)	
	Before annealing	After annealing
Cu-(0.14P)	50 (34)	45 (32)
Cu-1.5Ni-(0.14P)	45 (20)	42 (16)
Cu-0.75Ni-0.75Sn-(0.14P)	28 (23)	26 (15)
Cu-1.5Sn-(0.14P)	23 (23)	20 (18)

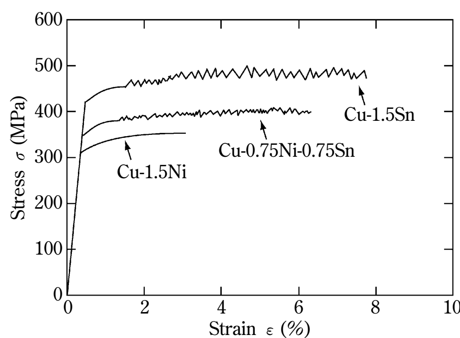

Fig. 5 Stress-strain curves of specimens tested at 180℃

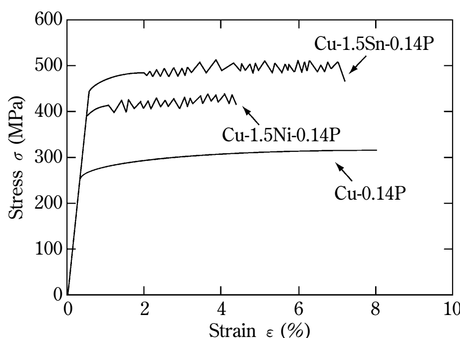

Fig. 6 Stress-strain curves of specimens tested at 180℃

3.4 Discussions

3.4.1 The effects of Ni and Sn

As described in Section 3.3.2, the addition of Ni to pure Cu has almost no effect on the stress relaxation rate, and the addition of Sn improves the stress relaxation characteristic. This is understood to be caused by the formation of the Cottrell atmosphere, contributing to an increase in the viscous resistance, on the basis of the fact that the Cu-Ni alloy does not show any serrated flow during the tensile test at 180℃, while the Cu-Sn alloy shows a serrated flow. The drag resistance, τ, exerted on the dislocations and caused by the Cottrell atmosphere, is given by the following equation[16]:

$$\tau=\frac{\alpha A^2 cv}{bDkT\Omega} \qquad (2)$$

wherein α is a constant, Ω is the volume per solute atom, b is the magnitude of Burgers vector, c is the concentration of the solute, D is the diffusion constant of the solute atom, v is the velocity of mobile dislocations, k is the Boltzmann's constant, T is the temperature, and A is given by the following:

$$A=\frac{4(1+\nu)}{3(1-\nu)}Gb\varepsilon R^3 \qquad (3)$$

wherein ν is the Poisson's ratio, R is the radius of the solute atom, G is the modulus of rigidity, and ε is plastic strain. According to Equations (2) and (3), τ depends on ν, c, ε and D.

The stress, $\Delta\sigma$, which is parallel to the longitudinal direction of the specimen and is relaxed during the stress relaxation test, is expressed as follows, using the Young's modulus, E, and the plastic strain, ε, caused by the plastic strain:

$$\Delta\sigma=E\varepsilon \qquad (4)$$

Now, the stress providing the initial deflection displacement and the stress required for providing the permanent deflection displacement are calculated to determine $\Delta\sigma$ from the difference between them. The Young's modulus, E, is determined to be 128GPa from the slope of the elastic region in the stress-strain curve of each alloy. These values were used to determine the average plastic strain rate, ε, and v was roughly estimated from the relationship, $\varepsilon=\rho bv$. Here, the initial dislocation density, ρ, was assumed to be

the same for all the alloys and to be $\rho=10^{15}m^{-2}$. The magnitude of the Burgers vector was assumed to be $b=2.6\times10^{-10}m$. The result indicates that the velocity, v, of the mobile dislocation is in the order of $10^{-16}ms^{-1}$ regardless of the types of the alloys.

A comparison is made between the drag viscous resistances of the Cu-Ni and Cu-Sn alloys. Values are placed in the above described v and Equations (2) and (3); i.e., $\nu=0.33$; $G=5.2\times10^{10}Pa$; and, for the atomic radii (R) of Sn and Ni, $1.41\times10^{-10}m$ and $1.25\times10^{-10}m$ are used, respectively[12]. Using the atomic radius ratio, ε, in Equation (1) gives $A=1.37\times10^{-30}Nm^2$ and $A=1.14\times10^{-29}Nm^2$ for Cu-Ni and Cu-Sn alloys, respectively. Using these values, as well as the diffusion constants in Cu at 180℃ of Sn and Ni, $D=2.31\times10^{-27}m^2s^{-1}$, $1.65\times10^{-31}m^2s^{-1}$ [4), 12)], $\alpha=4$, $c=0.015$, $k=1.38\times10^{-23}JK^{-1}$, and the aforementioned b, gives the drag viscous resistance at 180℃, $\tau=1.1\times10^{33}Pa$ for the Cu-Sn alloy and $\tau=3.4\times10^{36}Pa$ for the Cu-Ni alloy. As shown, the Cu-Ni alloy has a greater drag viscous resistance. On the other hand, the Cottrell atmosphere is formed only when the velocity, ν, of a mobile dislocation is greater than the critical velocity, v_0, as expressed by the following Equation 5[17].

$$v\leq v_0\equiv\frac{3+2\sqrt{2}}{2}\frac{AD}{kTb^2} \quad\cdots\cdots(5)$$

From Equation (5), v_0, at 180℃ is estimated to be $1.8\times10^{-16}ms^{-1}$ for the Cu-Sn alloy and $1.6\times10^{-21}ms^{-1}$ for the Cu-Ni alloy. Comparing these values with $v\approx10^{-16}ms^{-1}$ obtained from Equation (4), the Cu-Sn alloy yields a similar value, while the Cu-Ni alloy yields a v_0, value that is significantly smaller. This indicates that, in the Cu-Sn alloy, the Cottrell atmosphere is formed by the Sn solute atoms, providing resistance to the movement of dislocations, while in the Cu-Ni alloy, no Cottrell atmosphere is formed. The reason for this significant difference is that the Sn atoms diffuse in the Cu matrix much more easily than do the Ni atoms. The Sn atoms move at a velocity in the same order of magnitude as the velocity of mobile dislocations, so that their chances for interaction are much greater than those of the Ni atoms that are essentially immobile.

From the above, it is understood that, at 180℃, the Ni solute atoms in the Cu-Ni alloy do not exert any drag resistance against the movement of dislocations and make little contribution to the improvement of stress relaxation resistance. It is concluded, on the other hand, that the Sn solute atoms in the Cu-Sn alloy cause the Cottrell atmosphere to be formed, decreasing the stress relaxation rate.

As shown in Fig. 5, an increasing additive amount of Sn increases the stress amplitude of the serrated flow. According to Russell[18], the stress amplitude of the serrated flow is proportional to the solute concentration. Also, Equation (2) shows that the drag resistance, caused by the Cottrell atmosphere and exerted on dislocations, is proportional to the solute concentration. Hence, it is understood that an increased additive amount of Sn increases the viscous resistance of dislocations and, as a result, improves the stress relaxation resistance.

3.4.2 The effect of P

The addition of P to Cu slightly improves the stress relaxation resistance; however, it does not cause the serrated flow to appear (Fig. 6). The v_0 value for the Cu-P alloy was estimated in a manner similar to that previously described. On the basis of $A=6.42\times10^{-30}Nm^2$, the diffusion constant at 180℃ of P in Cu, $D=6.33\times10^{-23}m^2s^{-1}$ [4)], and the above described values for b and k, the v_0 value at 180℃, $v_0=2.8\times10^{-12}ms^{-1}$, was obtained. This v_0 value is greater than the aforementioned $v\approx10^{-16}ms^{-1}$. Hence it is judged that, at 180℃, the Cottrell atmosphere is formed by the P atoms in the Cu-P alloy. However, the drag resistance, τ, of the Cu-P alloy is given as $\tau=2.7\times10^{28}Pa$, which is remarkably smaller than the $\tau=1.1\times10^{33}Pa$ of the Cu-Sn alloy. This implies that the drag resistance provided by the P atoms and exerted on dislocations is very small, making the P atoms move along with the dislocations. If this is true, a serrated flow is expected to appear on the stress-strain curve obtained from the tensile test conducted on the Cu-P alloy at a temperature lower than 180℃. With this in mind, the Cu-0.14% P alloy was tensile tested at 50 and 100℃; however, no serrated flow appeared on the stress-strain curve. Since this result was considered to be attributable to the small additive amount of P, an alloy with an increased additive amount of P, Cu-1.5% P alloy, was tensile tested at temperatures of 50, 100 and 180℃. The resultant stress-strain curve is shown in **Fig. 7**. The serrated flow appeared only at 100℃, with no serrated flow observed at 50℃ and 180℃. At 180℃,

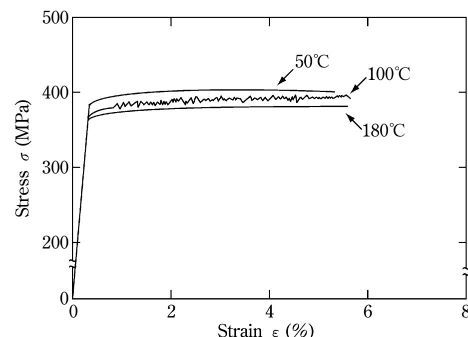

Fig. 7 Stress-strain curves for Cu-1.5P alloy, tested at 50, 100 and 180℃

the P atoms diffuse faster than mobile dislocations. As the temperature lowers, chances increase for the P atoms to interact with dislocations, causing the serrated flow to appear. When the temperature becomes even lower, the diffusion rate decreases, decreasing the opportunity for the atmosphere to form around the dislocations, making the serrated flow less likely to appear. Because of the small drag resistance, the addition of P is regarded as making a small contribution to the improvement of stress relaxation resistance.

The single addition of Ni or of P to Cu has little effect on the stress relaxation characteristic (Table 2). On the other hand, the coexistence of Ni and P in Cu significantly improves the stress relaxation characteristic, causing serrated flow to appear on the stress-strain curve (Fig. 5). It has been known that Ni and P form various compounds in Cu[19] and, as described in Section 3.3, $Ni_{12}P_5$ precipitates were confirmed to be formed in the present alloy. Hence, it is considered that, with P and Ni having strong affinity in Cu, the P atoms moving with dislocations and the Ni atoms in the solid solution provide resistance against the movement of dislocations through their chemical affinity[20]. Precipitates can be the source of resistance against dislocations that have just started to move. The stress relaxation, however, has already started to occur at this point in time; thus, the precipitates are considered to contribute almost nil to the improvement of the stress relaxation resistance of the present alloy.

3.4.3 The effect of the final heat treatment

In the case of the alloy without P, annealing at 300℃ for 30s after the 40% rolling does not cause any significant improvement in the stress relaxation resistance. On the other hand, the alloy with P shows a remarkable improvement (Table 2). As described previously, stress relaxation phenomena are regarded as creep phenomena caused by dislocations moving for short distances[13], and the stress relaxation characteristic depends significantly on the density of mobile dislocations. At 300℃, P has a greater D compared with Ni or Sn and also has a large atomic radius ratio, ε. Hence it is considered that dislocations are pinned by the P atoms during the annealing. It is reported that solid solution type Al-Mg alloys exhibit yield points on their stress-strain curves due to the pinning of dislocations by Mg[21]. With this in mind, the alloys with P were tensile tested at 180℃ before and after the annealing. **Fig. 8** shows, as an example, the stress-strain curves of the Cu-1.5% Ni-0.14% P alloy before and after the annealing. A yielding point is observed for the specimen after annealing, while no yielding point is observed for the specimen before annealing. Hence, it is understood that dislocations are pinned by the P atoms during the short-time annealing, decreasing the number of mobile dislocations, leading to the improvement of the stress relaxation resistance.

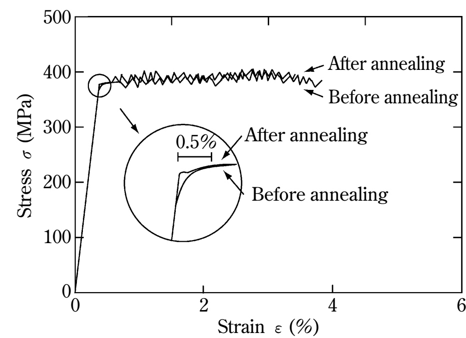

Fig. 8 Stress-strain curves for Cu-1.5Ni-0.14P alloy before and after annealing at 300℃ for 30s, tested at 180℃

3.4.4 Summary

(a) The improvement of stress relaxation resistance by the addition of Sn to Cu is attributable to the Cottrell atmosphere increasing the drag resistance of dislocations.
(b) The combined addition of Ni and P into Cu greatly improves the stress relaxation resistance. This is considered to be caused by P and Ni, the later having a strong affinity with P, pinning dislocations and producing a large drag resistance.
(c) For the Cu alloy with P addition, a low temperature annealing increases the stress relaxation resistance. This is considered to be caused by the pinning of dislocations by the P atoms during the annealing and the decreased mobile dislocation density.

Conclusions

In order to clarify the cause of the improved stress relaxation resistance of solid solution strengthening type Cu-Ni-Sn-P alloys, a study was made on the effect of each solid solution element on the dislocation drag resistance. The drag resistance was found to increase, particularly when Ni and P are added in combination. The stress relaxation rate is decreased by the final brief annealing at a low temperature. This is considered to be due to the P, in the solid solution, pinning the dislocations and decreasing the density of mobile dislocations. The above knowledge has been adapted for optimizing the actual production process, which has enabled the development of the CAC5 alloy. The alloy does not

require any heat treatment, such as the precipitation aging required by beryllium copper and Corson system copper alloys, but achieves the same level of stress relaxation resistance as the levels achieved by these alloys.

We will continue to strive to respond to the increasingly sophisticated needs by developing alloys exploiting the special characteristics of the materials.

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