Development of Machinable High-Strength Copper-Based Alloys by Sulfide Dispersion^{*1}

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Studies on the properties of Cu-S-Ti and Cu-S-Zr alloys containing 0.8-1.6 at% S, and 0.4-2.7 at% Ti or Zr were carried out. Titanium and zirconium formed (Ti, Cu)S and (Cu, Zr)₂S, respectively, which were uniformly dispersed. Age-hardening phenomena were observed in the alloys having the composition ratio of Ti/S > 1 or Zr/S > 1, which indicates that the soluble titanium and zirconium in the Cu-matrix after formation of sulfide result in age-hardening. (Ti, Cu)S and (Cu, Zr)₂S were found to be the effective inclusions for improving the machinability. The Cu-S-Ti and Cu-S-Zr alloys developed by sulfide dispersion are very promising as a new type of copper-based alloys having high strength, high electrical conductivity and good machinability.

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1. Introduction

The recent progress of electronic devices requires the miniaturization of components, such as switches, connectors and springs. Therefore, copper alloys as comprising materials of those electronic components must have not only high strength and high electrical conductivity but also high workability, such as bending strength, punching-ability and machinability.

It is well known that the microstructural control of fine inclusions improves punching-ability and machinability. In particular, a small amount of lead has long been used as an additive in steels, aluminum and brass, because lead is the most effective element for improving the machinability of these materials by minimizing the damage to other properties. However, it has become necessary to replace lead with nontoxic materials, because the potential of lead leaching into water from industrial scrap is known to be a health hazard. Sulfide inclusion is expected to be a promising candidate for improving the machinability of alloys. In the case of the steels, MnS inclusion is aggressively utilized for improving the machinability. In copper-based alloys, the free-cutting copper alloy adding sulfur to pure copper is known.¹⁾ However, there have generally been very few attempts to utilize sulfides for microstructure control of copper-based alloys because Cu₂S formed in the alloys causes hot shortness²⁾ and discoloration.³⁾

The present work is one of a series of systematic studies⁴⁻¹¹⁾ on the phase equilibria and morphology of various sulfides in metals focusing on the formation of sulfide in Cu-Ti^{12,13)} and Cu-Zr^{14,15)} high strength copper alloys showing an age-hardening effect. Ti sulfide and Zr sulfide in copper alloy are expected to be chemically and thermodynamically stable.^{16,17)} The microstructure, mechanical properties, electrical conductivity and machinability of copper-based alloys with varying Ti, Zr and S contents were investigated to develop new machinable high strength Cu-S-

Ti and Cu-S-Zr alloys using both precipitation hardening and the Ti and Zr sulfide inclusions.

2. Experimental

2.1 Sample preparations

Alloy ingots weighing about 250 g each were prepared from oxygen-free copper, sponge titanium, sponge zirconium and Cu₂S powder by induction melting in magnesia crucibles under an argon atmosphere. The copper was melted first, and then alloying elements were added to the molten copper in order of titanium or zirconium and Cu₂S. After the addition of Cu₂S, the bath was kept in the molten state for 5 minutes and then poured into a permanent mold with a diameter of 20 mm.

The ingots were hot-rolled to a thickness of 5 mm at 1073 K. Small specimens were cut from the sheet and sealed in quartz capsules with argon. The Cu-S-Ti and Cu-S-Zr specimens were annealed at 1273 K and 1173 K for 20 minutes, respectively, and then quenched in ice water. They were then cold-rolled to a thickness of 1 mm and sealed in evacuated quartz capsules. The specimens were aged at 573-873 K for 1 hour and then quenched in ice water.

Two different sulfur content series of alloys were prepared. Sulfur compositions of sulfur-lean and sulfur-rich alloys are 0.8 at% and 1.6 at%, respectively. Ti and Zr contents were designed as the atomic ratio of Ti/S or Zr/S to be about 0.5, 1, 1.7 and 2.6. Nominal composition of specimens are Cu-0.8 at% S-(0.4, 0.8, 1.4, 2.1) at% Ti, Cu-1.6 at% S-(1.6, 2.7) at% Ti, Cu-0.8 at% S-(0.8, 1.4) at% Zr and Cu-1.6 at% S-(0.8, 1.6, 2.7) at% Zr. The chemical analysis of alloy composition has not been conducted. However, the results of average chemical composition of alloys measured by an area analysis of a scanning electron microscope equipped with an energy dispersive X-ray micro-analyzer (SEM-EDX) well agreed with the nominal composition.

2.2 Sample tests

Micro Vickers hardness was measured on the surface of polished specimens under the condition of loading of 200 g for 15 seconds. The hardness was obtained as the average of

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10 measurement points. A tensile test was carried out under the condition of a cross-head speed of 0.5 mm/min. Electrical conductivity was measured by the eddy current method and was indicated by the international annealed copper standard unit, %IACS. Examination of microstructure was carried out using a SEM-EDX. The surfaces of mirror-polished sections to be examined by SEM-EDX were etched electrolytically in a 5 mass% sodium citrate-0.3 N sulfuric acid solution. Composition analysis of sulfide electrically extracted by a carbon replica method was carried out by a transmission electron microscope equipped with an energy dispersive X-ray micro-analyzer (TEM-EDX). Machinability was evaluated in the drilling test. The drilling tool used was of TiN-coated high-speed steel (HSS) which was 6 mm in diameter, 130 mm in length and 135° in point angle. The appearance of chips of the worked materials was observed.

3. Results and Discussion

3.1 Microstructure

Figure 1 shows the microstructure of the Cu-0.8%S-0.8%Ti and Cu-0.8%S-0.8%Zr alloys after hot-rolling. Fine precipitates smaller than 1 μm in diameter are uniformly dispersed in both specimens. A similar microstructure was observed in other alloys. The composition analysis of precipitates in the extracted carbon replica specimens by TEM-EDX revealed that (Ti, Cu)S containing a small amount of Cu is formed in the Cu-0.8%S-0.8%Ti alloy, as well as (Cu, Ti)₂S containing a small amount of Ti. (Ti, Cu)S is a major precipitate in the Cu-0.8%S-0.8%Ti alloy. On the other hand, (Cu, Zr)₂S containing a slight amount of Zr and Cu₉Zr₂ compound was observed in the Cu-0.8%S-0.8%Zr alloy. In

Fig. 1 Micrographs of (a) Cu-0.8%S-0.8%Ti and (b) Cu-0.8%S-0.8%Zr alloys.

Fig. 2 Variation of hardness (V. H.) and electrical conductivity (E. C.) of the Cu-0.8%S-Ti alloys with Ti content.

addition, a small amount of MgS was observed due to contamination from the crucible.

3.2 Effect of the addition of Ti and Zr

Figure 2 shows Vickers hardness and electrical conductivity of as-rolled Cu-0.8%S-Ti alloys as a function of Ti content. The hardness and electrical conductivity of the as-rolled samples increase and decrease with increasing Ti content, respectively. In the samples aged at 723 K for 1 hour, the electrical conductivity monotonously decreases with increasing Ti content, while the hardness shows the minimum at about 0.8%Ti, where the atomic ratio of Ti and S contents is equal. The electrical conductivity of the aged samples is higher than those of the as-rolled samples, while the hardness of aged samples is lower and higher than those of the as-rolled samples less than 1.5%Ti and above 2.0%Ti, respectively.

Vickers hardness and electrical conductivity as a function of Zr content in the Cu-0.8%S-Zr alloys are shown in Fig. 3. The hardness and electrical conductivity of both the as-rolled and aged specimens increase and decrease with increasing Zr content, respectively. The electrical conductivity tends to increase by aging at 673 K for 1 hour. On the other hand, the hardness of the aged specimens is lowered and raised when the atomic ratio of Zr and S contents, Zr/S, is below and above 1, respectively.

The increase in the hardness by aging in the high Ti or Zr containing alloys is considered to be the result of the precipitation-hardening observed in the Cu-Ti^{12,13)} and Cu-Zr^{14,15)} alloys. Namely, Ti and Zr atoms added to the Cu-0.8%S alloy form sulfides by reacting with S atom and do not contribute to age-hardening when the amount of Ti or Zr is small. With increasing Ti and Zr content, excess Ti and Zr atoms, which do not form sulfide, are considered to contribute to the precipitation hardening with aging.

3.3 Effect of aging temperature

Figure 4 shows the effect of the aging temperature on the Vickers hardness and electrical conductivity in the Cu-S-Ti

Fig. 3 Variation of hardness (V. H.) and electrical conductivity (E. C.) of the Cu-0.8%S-Zr alloys with Zr content.

Fig. 4 Effect of aging temperature on (a) hardness and (b) electrical conductivity of the Cu-S-Ti alloys, where aging time is 1 hour.

alloys. The electrical conductivity increases slightly and the hardness is remarkably softened by aging above 673 K in the alloys containing Ti and S at an atomic ratio of $Ti/S=1$. The alloys containing Ti and S at a ratio of $Ti/S < 1$ show almost the same behavior. The hardness and electrical conductivity of the Cu-0.8%S-2.1%Ti ($Ti/S=2.7$) and Cu-1.6%S-2.7%Ti ($Ti/S=1.7$) alloys increase with increasing aging temperature, and show the maximum peaks at 723 K. Further elevation of aging temperature remarkably reduces both the hardness and electrical conductivity. On the other hand, in the Cu-0.8%S-1.4%Ti alloy ($Ti/S=1.7$), the electrical conductivity does not show remarkable change due to the aging temperature, and the hardness decreases above 723 K.

Fig. 5 Solubility limit of Ti and Zr on the Cu-fcc phase.^{11,18-20)}

Both the Cu-1.6%S-2.7%Ti and Cu-0.8%S-1.4%Ti alloys contain Ti and S at a ratio of $Ti/S = 1.7$. The former shows age-hardening but the latter does not. The age-hardening is caused by precipitation of solute Ti atoms in the Cu-fcc phase. Hence, the evaluation of the effective Ti content, C_{Ti}^{eff} , which does not form sulfide, is more useful in the discussion of age-hardening rather than Ti/S ratio. It is difficult to obtain the exact value of C_{Ti}^{eff} because sulfide is formed as $(Ti, Cu)S$. Here the formation of the ideal stoichiometry compound, TiS , is assumed, namely the value of C_{Ti}^{eff} is evaluated by the total Ti content minus the total sulfur content. The amount of C_{Ti}^{eff} in the Cu-0.8%S-1.4%Ti, Cu-0.8%S-2.1%Ti and Cu-1.6%S-2.7%Ti alloys is calculated as 0.6%, 1.3% and 1.1%, respectively. The solubility limit of Ti in the Cu-fcc phase is shown in Fig. 5.¹⁸⁻²⁰⁾ The solubility limit of Ti in the Cu-fcc phase is about 3.0 at%Ti at 1273 K, namely, the C_{Ti}^{eff} of the Cu-0.8%S-1.4%Ti, Cu-0.8%S-2.1%Ti and Cu-1.6%S-2.7%Ti alloys is able to completely dissolve in the matrix at 1273 K, while only 0.5%Ti can dissolve in the matrix at 723 K, which is the temperature showing the maximum of age-hardening in the Cu-0.8%S-2.1%Ti and Cu-1.6%S-2.7%Ti alloys. Therefore, the age-hardening is caused by the precipitation of the Cu_4Ti phase formed from solute Ti atoms of C_{Ti}^{eff} (about 1%) and their electrical conductivity increases with a decrease in the solute Ti in the matrix. The reason why the softening and reduction of electrical conductivity simultaneously occur above 773 K is the recrystallization and decrease of the precipitation of the Cu_4Ti phase resulting from the increase of the solubility limit of Ti with increasing aging temperature. The hardness and electrical conductivity in the Cu-0.8%S-2.1%Ti alloy after solution-treatment are 72.35 VHN and 14.5% IACS, respectively, which is similar to those of the specimen aged at 873 K. Furthermore, the solubility limit of Ti at 873 K is about 1%, as shown in Fig. 5. These facts suggest that Ti atoms of C_{Ti}^{eff} in the Cu-0.8%S-2.1%Ti and Cu-1.6%S-2.7%Ti alloys hardly precipitate as the Cu_4Ti phase by aging above 873 K. In the same way, the value of C_{Ti}^{eff} of the Cu-0.8%S-1.4%Ti alloy is comparable to the solubility limit of Ti in the matrix at 723 K. Hence, the Cu_4Ti phase is hardly precipitated by aging at 723 K and the age-hardening is not clearly shown.

Figure 6 shows the effect of the aging temperature on the

Fig. 6 Effect of aging temperature on (a) hardness and (b) electrical conductivity of the Cu-S-Zr alloys, where aging time is 1 hour.

Vickers hardness and electrical conductivity in the Cu-Zr-S alloys. The electrical conductivity of the Cu-0.8%S-0.4%Zr alloy ($Zr/S = 0.5$) slightly increases with increasing aging temperature and the hardness drastically decreases above 673 K. On the other hand, the alloys containing Zr and S at a ratio of $Zr/S > 1$ show slight age-hardening and tend to increase the electrical conductivity. Since the $(Cu, Zr)_2S$ and Cu_9Zr_2 phases are formed at solution treatment in the Zr-rich alloys, the effective Zr content, C_{Zr}^{eff} , which can be soluble in the Cu-matrix, is difficult to estimate. The solubility limit of Zr in the Cu-matrix as shown in Fig. 5^(12,21) is two orders of magnitude smaller than that of Ti. In addition, it is known that the Cu-Zr alloys show age-hardening by precipitation of the Cu_5Zr phase, even if a small amount of Zr, namely, about 0.01%, is added.⁽¹⁴⁾ Further investigations are necessary to permit detailed discussion of the relation between C_{Zr}^{eff} and age-hardening.

In the Cu-S-Zr alloys, the electrical conductivity increases by aging above 773 K, although the hardness drastically decreases. The electrical conductivity in the Cu-0.8%S-1.4%Zr alloy ($Zr/S = 1.7$) aged at 873 K for 1 hour is 71.7% IACS, which is higher than 56.3% IACS of the solution-treated specimen. Since the existence of solute Zr in the Cu-matrix drastically decrease the electrical conductivity,⁽¹⁵⁾ the precipitation of Cu_9Zr_2 and the solute Zr content in the Cu-matrix increase and decrease with increasing aging temperature, respectively. The softening at aging above 773 K is due to the coarsening of the precipitation by overaging. This tendency agrees with the previous results for Cu-Zr alloys.^(13,14)

Fig. 7 Mechanical properties of the tensile test of Cu-S-Ti alloys as a function of Ti content. (a) tensile strength, (b) 0.2% proof stress and (c) elongation.

3.4 Tensile test

Figure 7 shows the characteristic properties obtained by the tensile test for the Cu-S-Ti alloys as-rolled and aged at 723 K for 1 hour as a function of Ti content. The tensile strength and 0.2% proof stress of as-rolled samples increase with increasing Ti content while the elongation is evenly low. For the aged samples, the tensile strength and 0.2% proof stress tend to increase with increasing Ti content. The elongation of the low Ti content alloys is remarkably high, while that of the alloys containing Ti above 1% is almost constant. The tensile strength and 0.2% proof stress of the aged specimens decrease while the elongation increases compared with the as-rolled specimens containing Ti and S at a ratio of $Ti/S < 1$. For the specimens containing Ti and S at a ratio of $Ti/S > 1$ showing age-hardening, the tensile strength and 0.2% proof stress of the aged specimens hardly change, although the elongation increases.

The results of the tensile test for the Cu-S-Zr alloys as-rolled and aged at 723 K for 1 hour are as shown in Fig. 8. The tendency is almost same as that of the Cu-S-Ti alloys.

The relation between the electrical conductivity and tensile strength in the present Cu-S-Ti and Cu-S-Zr alloys is compared with that of some commercial copper-based alloys as shown in Fig. 9. It is known that there is a trade-off relation between strength and electrical conductivity. The alloys with

Fig. 8 Mechanical properties of the tensile test of Cu-S-Zr alloys as a function of Zr content. (a) tensile strength, (b) 0.2% proof stress and (c) elongation.

Fig. 9 Tensile strength versus electrical conductivity of Cu-S-Ti and Cu-S-Zr alloys aged at 673 K for 1 hour and corresponding values of some commercial copper-based alloys.

both $Ti/S > 1$ and $Zr/S > 1$ show high strength and, particularly, Cu-S-Zr alloys have higher electrical conductivity than Cu-S-Ti alloys with the same level of strength. For example, the tensile strength and electrical conductivity of the Cu-1.6%S-2.7%Zr alloy are 588 MPa and 58.1% IACS,

Fig. 10 Appearance of the chips of worked materials by drill testing of pure copper and Cu-2.7%Ti-1.6%S alloys.

respectively. Furthermore, the softening temperature is above 673 K as shown in Figs. 4 and 5, and those alloys have the same or better heat resistance than commercial copper-based alloys.

3.5 Machinability

Figure 10 shows the appearance of the chips of the worked pure copper and Cu-1.6%S-2.7%Ti alloy by the drilling test. The breakability of the chips of the Cu-1.6%S-2.7%Ti alloy is better than that of pure copper. All of the developed alloys have better breakability of chips than pure copper. It is considered that the sulfide inclusion acts as a nucleate for cracking chips by stress concentration. Further investigations involving detailed tests of the machinability of these alloys are necessary in the future.

4. Conclusion

Microstructure, mechanical properties, electrical conductivity and machinability of sulfide-dispersed Cu-S-Ti and Cu-S-Zr alloys with 0.8-1.6 at% S and 0.4-2.7 at% Ti and Zr were investigated. The results obtained are as follows:

- (1) The alloys containing Ti, Zr and S at ratios of $Ti/S > 1$ and $Zr/S > 1$ show age-hardening when the effective Ti and Zr contents in the matrix corresponding to the solubility before aging, C_{Ti}^{eff} and C_{Zr}^{eff} , are high. Furthermore, the electrical conductivity increases by age-precipitation due to the decrease of solute Ti and Zr contents in the Cu-fcc matrix.
- (2) The tensile strength tends to increase with increasing C_{Ti}^{eff} and C_{Zr}^{eff} .

- (3) The property of breaking chips at drill-working is remarkably improved by dispersed sulfide inclusions in the Cu-Ti-S and Cu-Zr-S alloys.
- (4) Cu-S-Ti and Cu-S-Zr alloys with dispersed (Ti, Cu)₂S and (Cu,Zr)₂S are promising as a new type of copper-based alloys having high strength, high electrical conductivity and better heat resistance and machinability.

REFERENCES

- 1) *Metals Handbook, Nonferrous Alloys and Special-purpose Materials*, vol. 2, 10th ed., (ASM international OH, 1990) pp. 216.
- 2) M. Kanno and N. Shimohira: *J. JRICu*. **27** (1988) 35-44.
- 3) T. Koizumi, S. Huruya, T. Toshiaki and Y. Maeda: *J. JRICu* **16** (1977) 98-104.
- 4) K. Oikawa, N. Kawashita, H. Ohtani, K. Ishida and T. Nishizawa: *J. Jpn. Inst. Met.* **59** (1995) 1207-1214.
- 5) K. Oikawa, H. Ohtani, K. Ishida and T. Nishizawa: *ISIJ Int.* **35** (1995) 402-408.
- 6) K. Oikawa, K. Ishida and T. Nishizawa: *ISIJ Int.* **37** (1997) 332-338.
- 7) K. Oikawa, S.-I. Sumi and K. Ishida: *Z. Metallkd.* **90** (1999) 13-18.
- 8) Y. Ohuchi, K. Oikawa, I. Ohnuma and K. Ishida: *Mater. Sci. Forum.* **284-2** (1998) 509-516.
- 9) K. Oikawa, S.-I. Sumi and K. Ishida: *J. Phase Equilib.* **20** (1999) 215-221.
- 10) H. Ohtani, K. Oikawa and K. Ishida: *High Temp. Mater. Processing* **19** (2000) 197-210.
- 11) K. Oikawa, H. Mitsui, T. Ebata, T. Takiguchi, T. Shimizu, K. Ishikawa, T. Noda, M. Okabe and K. Ishida: *ISIJ Int.* **42** (2002) 806-807.
- 12) M. J. Saarivirta and H. S. Cannon: *Metals Prog.* **76** (1959) 81.
- 13) S. Nagarjuna, K. Balasubramanian and D. S. Sarma: *Mater. Trans., JIM* **36** (1995) 1058-1066.
- 14) M. J. Saarivirta: *Trans. AIME* **218** (1960) 43-4371.
- 15) D. Zhilli, A. Sekiya, W. Fujitani and S. Hori: *J. Jpn. Inst. Met.* **53** (1989) 672-677.
- 16) H. Kaneko, T. Nishizawa and K. Tamaki: *J. Jpn. Inst. Met.* **24** (1960) 837-841.
- 17) O. Knake, O. Kubashewski and H. Hesselman: *Thermochemical Properties of Inorganic Substances*, (Springer-Verlag, 1991) pp. 2100.
- 18) E. Raub, P. Walter and M. Engel: *Z. Metallkd.* **43** (1952) 112-118.
- 19) U. Zwicker: *Z. Metallkd.* **53** (1962) 709-714.
- 20) K. Nagata and S. Nishikawa: *Rep. Inst. Ind. Sci. Univ. Tokyo* **29** (1981) 99-138.
- 21) W. Showak: *Metall. Soc. AIME*. **224** (1962) 1297-1298.