Development of Superior Heat Resistant Cu-Si Alloys Dispersed with Fine Mo5Si3 Particles

Development of Superior Heat Resistant Cu-Si Alloys Dispersed with Fine Mo_5Si_3 Particles

Shimpei Hasegawa[1,*1], Kazuyoshi Nakao[1], Akio Nishimoto[1] and Katsuya Akamatsu[1]

[1]*Department of Chemistry and Materials Engineering, Kansai University, Osaka 564-8680, Japan*

A demand exists for Cu alloys with high strength and superior heat resistance. Mo_5Si_3, the most stable intermetallic compound in the Mo-Si system, has been added to Cu in order to improve the resistance to heat, corrosion, and oxidation of Cu alloys. However, it is difficult to disperse Mo homogeneously in the Cu matrix with ingot metallurgy, because Mo does not dissolve in Cu and each density is widely different. In this study, a mechanical alloying (MA) process and a pulsed electric-current sintering (PECS) process were applied. In the MA process, Mo and Si powder was firstly milled for 648 ks to produce a Mo-Si system intermetallic compound. Then the pre-alloyed Mo-Si powder was added to Cu powder, and was milled for 648 ks. Powder mixtures oxidized during the MA process were reduced by a reaction with hydrogen gas. After reduction, the powder mixtures of Cu-Mo-Si (CMS) alloys (Cu-0-30 mass% Mo-Si) were sintered using a PECS apparatus. XRD analysis revealed that Mo_5Si_3 was detected in the pre-alloyed Mo-Si powder after milling and in the sintered specimen of CMS alloy. In addition, no Cu oxide was detected by XRD analysis while Si oxide was detected. Microstructure observation of sintered specimens revealed that the mixing phase of Cu, Mo, and Si was formed homogeneously and Mo_5Si_3 was dispersed homogeneously in the Cu matrix. Density measurement and hardness test revealed that the density decreased and the hardness increased by increasing Mo-Si content.

Keywords: *copper alloy, molybdenum silicide, mechanical alloying, pulsed electric-current sintering*

1. Introduction

Strength and heat resistance of Cu alloys used as electrical and electronic materials have posed design problems in the development of electrical machine parts. A consequent demand has arisen for the development of Cu alloys of higher strength and superior heat resistance while maintaining high electrical conductivity. Currently, heat resistant Cu alloys generally used are Cu materials containing a small addition of Ag. They are used as coil materials in electrical apparatus, electric wire, and trolley wire. Cu alloys with small additions of Sn, Fe or Zr to increase heat resistance are also used as lead frame materials[1)].

This study investigates Cu-Mo-Si alloys to develop a new Cu alloy with higher heat resistance. Mo_5Si_3, which is the most stable intermetallic compound in the Mo-Si system, was added to Cu in order to improve resistance to heat, corrosion, and oxidation of the Cu alloys.

Ingot metallurgy was considered as the preparation process for the Cu-Mo-Si alloy. However, it is difficult to disperse Mo homogeneously in the Cu matrix with ingot metallurgy because Mo does not dissolve in Cu and the each density is widely different, making it difficult to prepare a Cu-Mo-Si system alloy. Therefore, a mechanical alloying process was used to prepare a Cu-Mo-Si alloy powder in this study.

Mechanical alloying uses collision and friction from the motion of churning balls. The alloyed powder is prepared by placing the powder from pure metals in a churning pod together with the balls, producing repeated micro-scale collisions in which the powder fractures or joins. While this process is not energy efficient, it is able to produce meta-stable, nano-scaled, and amorphous alloys which cannot be produced by ingot metallurgy[2)].

Powder prepared by the mechanical alloying process is fine-grained, so that sintered material using this powder can form a supersaturated solid solution whose fine-grained structure provides improved mechanical properties. However, the heat during sintering results in a coarse crystal grain if the sintering time is too long. A pulsed electric-current sintering process, requiring a relatively low temperature and short sintering time, was therefore used[3)].

In this study, we investigated the preparation of Cu-Mo-Si alloy powder by a mechanical alloying process, and sintering of the alloyed powder by a pulsed electric-current sintering process. And then the properties of the Cu-Mo-Si alloy were evaluated.

2. Experimental procedure

2.1 Preparation process of powder mixture

The starting powder used was Cu powder (99.9 % purity and 150 μm average particle size), Mo powder (99.9 % purity and 0.8–1.7 μm average particle size), and Si powder (99.99 % purity and 10 μm average particle size), all produced by Rare Metallic Co., Ltd.. The intermetallic compounds generated in the Mo-Si system are Mo_3Si, Mo_5Si_3, and $MoSi_2$. In this study, Mo_5Si_3 which is the most stable intermetallic compound having a low standard free energy of formation, was added as reinforcing material. In preparing Mo_5Si_3, Mo and Si were weighed to given an 85 mass% Mo-15 mass% Si stoichiometric composition. They were prepared by a mechanical alloying (MA) process in order to produce the pre-alloyed powder of Mo_5Si_3.

The powder was weighed to give the composition of Table 1 in a glove box of nitrogen atmosphere. The weighed powder was placed in a pod of the same atmosphere, with pod and balls both made of Fe-Cr system stainless steel (produced by Fritsch Japan Co., Ltd.). The content of the pod was 250 ml. Ten balls of 20 mm in diameter and ten balls of 10 mm in diameter were selected from our preliminary study. Furthermore, about 3–5 ml methanol was added to increase the recovery rate of the mixed powder. The pod and the balls were coated with Cu to reduce contamination of the mixed powder from Fe and Cr components of the pod and balls during mixing. Similarly, the pod and the balls were coated with Mo

*1 Graduate Student, Kansai University

Table 1 Nominal composition of CMS alloys (mass%).

	Nominal composition		
	Cu	Mo	Si
CMS1	Bal.	0.85	0.15
CMS5	Bal.	4.25	0.75
CMS10	Bal.	8.50	1.50

Table 2 Conditions of MA.

	Rotation / rpm	Milling time / ks
Mo coating	460	648
Cu coating	270	648
Mo-15 mass%Si	460	648
Cu-1 mass%Si	270	648
CMS alloy	270	648

powder for preparing Mo_5Si_3. The method used was to place a weighed amount of Cu or Mo powder with composition as in Table 1 in the pod with the balls, hermetically seal the pod after adding 3–5 ml methanol, and mix the powder in a planetary ball mill (produced by Fritsch Japan Co., Ltd.). The MA conditions are shown in Table 2.

The mixed powder oxidizes because in the MA process it is difficult to control an atmosphere, the milling time is long (648 ks), and the temperature is elevated. A hydrogen reduction process was therefore applied to the Cu-Si powder and CMS alloy before sintering. In this hydrogen reduction process a hollow quartz tube containing the mixed powder was inserted into a reaction tube of 27 mm inner diameter and 1000 mm length. nitrogen gas was then allowed to flow at a rate of 15–20 ml/min for 648 ks to reduce oxygen in the reaction tube. The hydrogen reduction was then conducted for 648 ks, with the temperature of the furnace increased to 1003 K by thermo regulator, while hydrogen gas flowed at a rate of 15–20 ml/min. After hydrogen reduction, the furnace was cooled to room temperature by the passage of nitrogen and hydrogen gas mixture.

2.2 Preparation process of sintered specimen

The mixed powder at the completion of hydrogen reduction was sintered by a pulsed electric-current sintering (PECS) apparatus (produced by Sumitomo Coal Mining Co., Ltd.). The mixed powder was filled to a thickness of about 5 mm in a graphite die with a 70 mm outer diameter and 19 mm inner diameter. Mold lubricant containing boron nitride was then sprayed over the area in which the die and punch came into contact with the specimen. After decreasing the chamber pressure to 9.8×10^{-5} Pa, the specimen was sintered at a pressure of 54.9 MPa and a temperature of 1073 K. The heating rate was 20 K/min. After sintering, the specimen was cooled to room temperature in a vacuum.

A sintered CMS alloy was heat treated for 3.6 ks at 873 K, 973 K, and 1073 K to investigate how a property of the CMS alloy changes with heat treatment. The CMS alloy was encapsulated in a quartz tube with argon atmosphere to prevent oxidation while undergoing heat-treatment and then it was water-quenched.

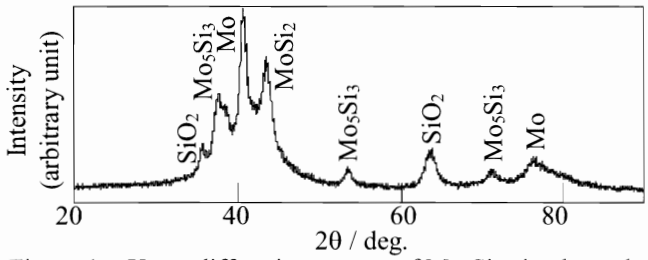

Figure 1 X-ray diffraction pattern of Mo-Si mixed powder.

Table 3 Chemical composition of CMS alloys (mass%).

	Chemical composition				
	Cu	Mo	Si	Fe	Cr
CMS1	Bal.	0.22	1.56	4.72	0.63
CMS5	Bal.	0.88	1.57	7.71	1.06
CMS10	Bal.	2.20	1.46	9.82	1.33

Each CMS alloy was subjected to X-ray fluorescence analysis to determine the quantity of each elemental component, XRD analysis to identify chemical compounds, microstructure observation using SEM and EDX, density measurement by the method of Archimedes, hardness measurement using a Vickers micro-hardness tester, and an electrical conductivity measurement using a Sigma-tester. Specimens were polished with #1200 emery paper to conduct X-ray fluorescence analysis, XRD analysis, density measurement, hardness measurement, and electrical conductivity measurement. Specimens were further polished using a range of abrasives from #160 emery paper to 0.05 μm alumina powder to observe micro-structure using SEM and EDX.

3. Results and discussion

In this study, CMS specimens are labeled according to the following schema. A CMS specimen with 99 mass% Cu added to 1 mass% Mo_5Si_3 is named CMS1, with specimens named CMS5 and CMS10 having respectively 5 and 10 mass% of Mo-Si.

Results of XRD analysis of Mo-Si mixed powder are shown in Figure 1. XRD analysis revealed that Mo_5Si_3 was present in the pre-alloyed Mo-Si powder after milling. Therefore, it is conceivable that Mo_5Si_3 was produced by MA.

Specimens prepared by the PECS process were subjected to X-ray fluorescence analysis. The results of the analysis are shown in Table 3. Fe and Cr existed in all specimens, as a result of using a pod and balls made of Fe-Cr system stainless steel. It is difficult to control such impurities, although using a mill with super hard balls can decrease impure components significantly. Additionally, the CMS alloys show lower amounts of Mo than the target composition, probably because more Mo adhered to the pod and balls than Cu and Si in the mixing stage. Results of

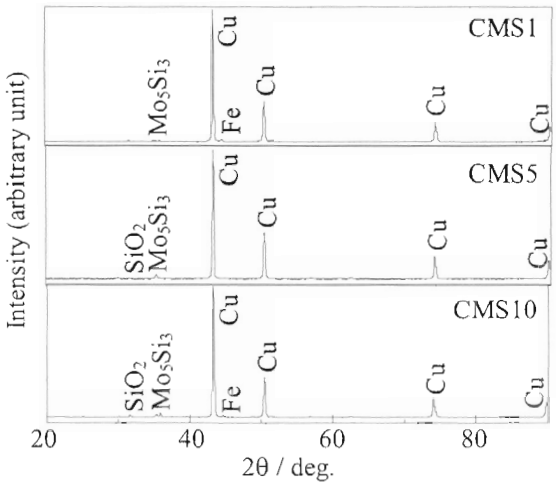

Figure 2 XRD pattern of sintered CMS alloys.

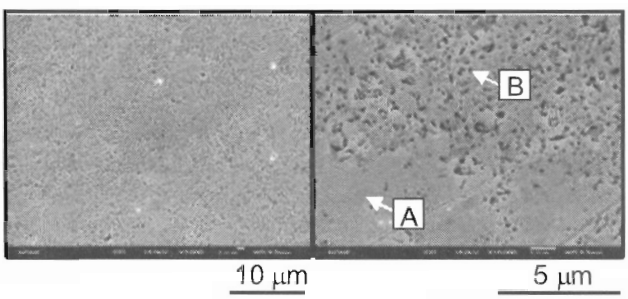

Figure 3 SEM micrograph of CMS1 alloy.

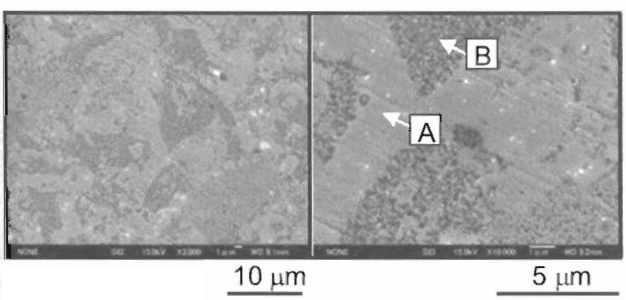

Figure 4 SEM micrograph of CMS5 alloy.

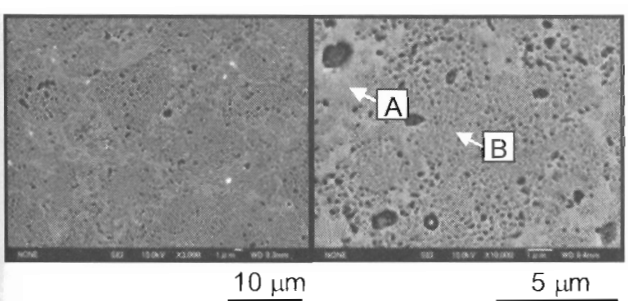

Figure 5 SEM micrograph of CMS10 alloy.

XRD analysis of sintered CMS alloy specimens are shown in Figure 2. XRD analysis revealed that Mo_5Si_3 (2θ = 38.3, 39.7, 42.8, 56.9, and 70.0 degrees) was detected in the sintered specimen of CMS alloy. In addition, no Cu oxide was detected by XRD analysis while Si oxide was detected. This result suggests that hydrogen reduction was effective. Reduction of Si was difficult in this study.

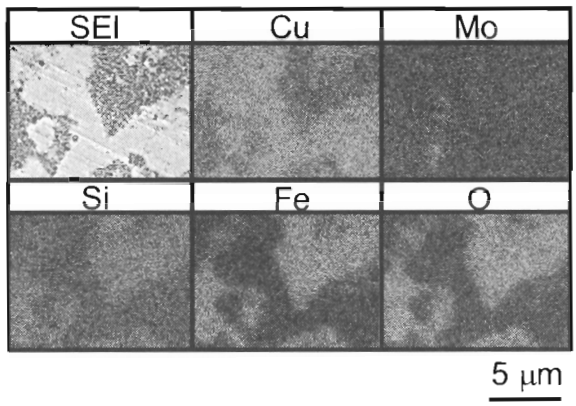

Figure 6 SEI and EDX analysis of CMS5 alloy.

Results of microstructure observation by SEM and EDX element analysis are shown in Figures 3–6. Results of microstructure observation by SEM of CMS1, CMS5, and CMS10 are shown in Figures 3–5, respectively. The result of EDX analysis of CMS5 is shown in Figure 6. CMS1 and CMS10 qualitatively resembled these results.

Qualitative analysis of CMS1 in Figure 3 using EDX showed that area A is a Cu matrix and area B is a mixing phase dispersed Cu, Mo, and Si homogeneously. Furthermore, Fe, Cr, and O were dispersed homogeneously in the mixing phase. For this reason, Cu and Mo-Si formed the mixing phase and Mo-Si dispersed nearly homogeneously. Grain boundary of the Cu matrix and mixing phase was not distinct. Similar results were obtained for the specimens of CMS5 and CMS10 as for CMS1, as shown in Figures 4 and 5. Unlike the CMS1 specimen, grain boundary between the Cu matrix and mixing phase was distinct in the CMS5 and CMS10 specimens. Moreover, mixing phases were more often observed in the CMS10 specimen.

Results of density measurement are shown in Figure 7. These results revealed that the density decreased with increasing Mo-Si content. It is conceivable that because density of Fe (7.87 g/cm^3) is lower than density of Cu (8.93 g/cm^3), density tended to decrease with increasing heat treatment temperature.

Results of hardness measurement using a Vickers microhardness tester are shown in Figure 8. Hardness tended to increase with increasing Mo-Si content. This may occur because Mo_5Si_3 is harder than Cu. Moreover, hardness tended to decrease with increasing heat treatment temperature. This is probably the result of coarsening of grains following heat treatment.

Results of electrical conductivity measurement using a Sigma-tester are shown in Figure 9. Electrical conductivity tended to decrease with increasing Mo-Si content, probably because the amount of Cu decreased with increasing Mo-Si additives. In addition, electrical conductivity tended to decrease with increasing heat treatment temperature. This is probably caused by the heat treatment increasing the formation of oxides and levels of Si dissolved in Cu.

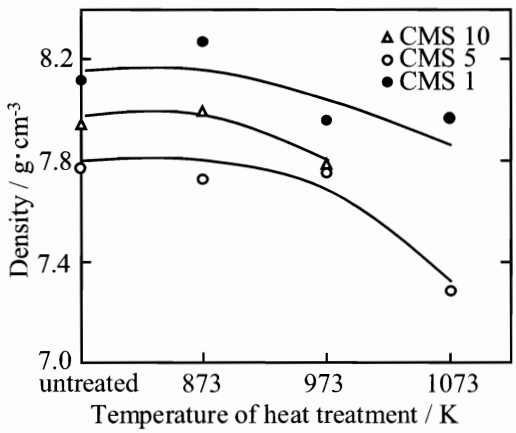

Figure 7 Relation between Mo-Si content, temperature of heat treatment, and density of CMS alloys.

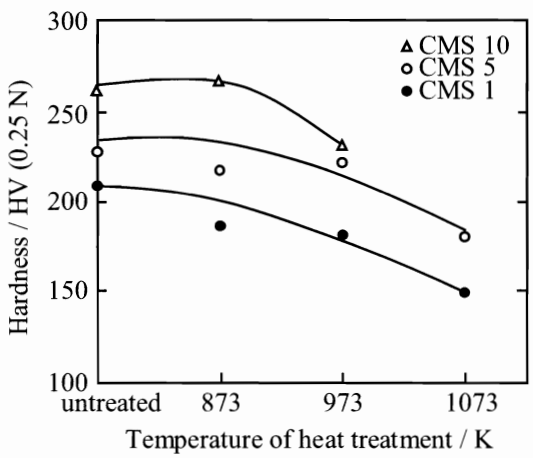

Figure 8 Relation between Mo-Si content, temperature of heat treatment, and hardness of CMS alloys.

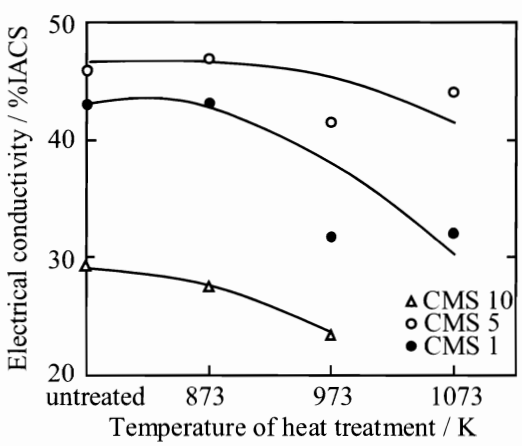

Figure 9 Relation between Mo-Si content, temperature of heat treatment, and electrical conductivity of CMS alloys.

4. Conclusions

Cu-Mo-Si (CMS) alloys were produced by mixing Cu powder and Mo-Si powder using a mechanical alloying (MA) and pulsed electric-current sintering processes. The microstructure, density, hardness, and electrical conductivity of CMS alloys were then examined. The results obtained from this study are as follows:

1) X-ray fluorescence analysis revealed that contamination with Fe and Cr occurred from the pod and balls used in MA.
2) XRD analysis revealed that Cu oxide and Mo_5Si_3 were not detected.
3) CMS alloys were identified by microstructure observation. Cu matrix and mixing phase dispersed Cu, Mo, and Si were formed homogeneously. Furthermore, Fe, Cr, and O were dispersed homogeneously at the mixing phase.
4) Density measurement revealed that the density decreased with increasing Mo-Si content. In addition, density tended to decrease with increasing temperature of heat treatment.
5) Hardness tended to increase with increasing Mo-Si content. Additionally, hardness tended to decrease with increasing temperature of heat treatment.
6) Electrical conductivity tended to decrease with increasing Mo-Si content. In addition, electrical conductivity tended to decrease with increasing heat treatment temperature.

References

1) Y. Murakami: *Copper and Copper Alloy Fundamentals and Industrial Technology*, Japan Brass Makers Association (1988) 419, 426.
2) H. Miura and K. Takagi: *Powder Metallurgy Science* (German, Randall M.), Uchida Rokakuho (1995) 88-89.
3) M. Tokita: J. Soc. Powder Technol. Jpn. **30** (1993) 790-793.