Electric Conductivity and Mechanical Properties of Carbide Dispersion-Strengthened Copper Prepared by Compocasting

Kiyoshi Ichikawa* and Masakazu Achikita**

*Mechanical Engineering Laboratory, Agency of Industrial Science and Technology, Tsukuba, Ibaraki 305, Japan

**Central Research Laboratory, Sumitomo Metal Mining Co., Ltd., Ichikawa, Chiba 272, Japan

The electrical conductivity and the mechanical properties of dispersion-strengthened (DS) coppers produced by compocasting at a rotation speed of 25 s^{-1} with the addition of fine carbide particles in the range of 0.5 to 30 mass% WC, TaC, TiC, VC and NbC were analyzed experimentally. Homogeneous dispersion of carbide particles was observed in the microstructures of all the DS coppers containing more than 5 mass% carbide. If any carbide particle had the same size of 1 to $2\text{ }\mu\text{m}$ in the DS coppers, the Vickers hardness, H_v , was given by the following equation: $H_v = 53.4 + 3.5 V_p^{0.9}$, where V_p was the volume percentage of carbide particles. The ultimate tensile strength of carbide particles could be evaluated using the measured ultimate tensile strength value of copper, the fractions of area occupied by copper and carbide particles, and the measured ultimate tensile strength value of DS copper. The calculated ultimate tensile strength values of WC, TaC, TiC, VC and NbC particles were 961 MPa, 539 MPa, 568 MPa, 641 MPa and 755 MPa, respectively. Similarly, the electrical conductivity of carbide particles could be also evaluated. Their calculated electrical conductivity values were in the range of the published values of electrical conductivity of the carbides.

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I. Introduction

Commercial metal-nonmetallic particulate composites are generally produced using such powder metallurgy techniques as mechanical mixing, sintering, infiltration, and mechanical alloying. If the composites could be made by a casting process, there would be a great reduction in the manufacturing costs. When nonmetallic particles are added to fully molten metal, however, many of them are rejected and cast out onto the surface of the melt because they cannot be wetted by the metal. Five methods have been offered to overcome this difficulty⁽¹⁾⁻⁽¹⁰⁾. The first method is to improve the wettability between metal and nonmetal by a metallic coating of the nonmetallic particles before casting⁽¹⁾⁻⁽⁴⁾. The second is to add an element promoting wettability to the melt before the addition of nonmetallic particles⁽⁵⁾⁽⁶⁾. The third is to force spray dispersion of ceramic powders in the molten steel as it is poured into a metallic mold using a compressed inert gas⁽⁷⁾. The fourth is to improve the wettability by a metallic coating on the graphite particles and addition of a titanium element, and to prevent the floating of graphite from the melt by squeeze casting⁽⁸⁾. The fifth is to add non-wetted ceramic particles into the molten metal and solidify them by rotational stirring⁽⁹⁾⁽¹⁰⁾.

Representative of the fifth method is the "compocast process", which involves making a homogeneous metal matrix composite using rotating stirrer during the solidification of an alloy and adding nonmetallic particles, whiskers and fibers⁽⁹⁾⁽¹⁰⁾. However, the compocast

process, proposed by Mehrabian and Flemings⁽¹⁰⁾, has heretofore been primarily applied to an alloy with a freezing range between the beginning and the end of solidification. As the conventional compocasting experiment has been carried out under the condition of air or reducing atmosphere, excellent mechanical properties in the compocast alloy could not be obtained because of the entrapment of air or inert gas into the partially solidified alloy⁽¹¹⁾.

On the other hand, such oxide particles as Al_2O_3 , ThO_2 , ZrO_2 and SiO_2 have been used for strengthening of the copper matrix in the conventional dispersion-strengthened copper made by internal oxidation⁽¹²⁾⁻⁽¹⁴⁾, coprecipitation⁽¹⁵⁾⁽¹⁶⁾, and mechanical mixing⁽¹⁷⁾. However, commercial dispersion-strengthened (DS) copper does not include much oxide because of a steep decrease in electrical conductivity when oxides are added, even though the tensile strength is improved with increased oxide content⁽¹⁸⁾.

In the present study, carbide particle-strengthened coppers with good electrical conductivity and excellent mechanical properties were produced by compocasting with the addition of highly conductive carbide particles up to 33 vol% instead of lowly conductive oxide particles, and their electrical conductivity, Vickers hardness and ultimate tensile strength were analyzed experimentally.

II. Experimental Procedure

The specimens used in the present work were five kinds

1: Tungsten mesh heater, 2: reflector, 3: thermocouple for temperature control, 4: automatic shutter, 5: water-cooled outer tube, 6: hopper, 7: cooling water, 8: video camera, 9: sight port, 10: rotor axis, 11: stirrer, 12: electrode, 13,14: graphite crucible, 15: thermocouple for temperature measurement, 16: chamber and 17: crucible support.

Fig. 1 Experimental apparatus for vacuum compocasting.

of metal-ceramic particulate mixtures composed of 99.99 mass% purity copper blocks and carbide particles with 0.5 to 30 mass% of mixture content: WC, TaC, TiC, VC and NbC. The size of the carbides was 1 to 2 μm except WC which was 0.68 μm . Figure 1 shows a schematic illustration of the experimental apparatus used to disperse carbide particles uniformly and to destroy dendritic copper crystals⁽¹⁹⁾ formed during the solidification of vacuum-melted copper by the rotation of a stirring bar at a speed of above 20 s^{-1} (1200 rpm).

A chamber provided in the panel of the door permitting insertion of a crucible into the chamber and inspection of the chamber interior constitutes a vacuum container. The chamber is partitioned into upper cooling and lower heating rooms by a tungsten shutter operated by an air cylinder. In the lower heating room, there is a tungsten mesh heater where two concentric crucibles are set on a support bar for moving automatically. The upper cooling room holds a water-cooling outer tube and a stirrer is suspended downward into this tube. The stirrer can be rotated at a superhigh speed of up to 84 s^{-1} by a motor positioned at its upper end. The motor is on a rotary shaft with a detecting unit connected with a digital unit for simultaneous display and record of the torque of the stirrer and the rotational speed. The temperature measurement is made by a Pt94%Rh6%–Pt70%Rh30%

thermocouple 0.5 mm in diameter connected with a recorder, of which the tip is set at the center of the bottom surface of the crucible as shown in Fig. 1.

Two methods were preliminarily examined for the addition of carbide particles: one was the conventional compocasting process of adding the carbides from a hopper on the chamber into the copper solidifying by rotational stirring, and the other was a new process of heating both copper blocks and carbide particles in the crucible until the copper melted. It was recognized that the tensile properties of the DS copper ingot made using the new process are superior to those made by the compocasting process.

The experimental procedure was as follows. First of all, pure copper blocks together with one of the carbide particles were placed in the crucible. Then the chamber was evacuated with a vacuum pump and the shutter above the heating furnace was closed to increase heating efficiency. When the degree of vacuum in the chamber reached 1×10^{-3} Pa, the raw materials in the crucible were heated to produce a mixture of molten copper and solid carbide particles on the melt. After the mixture in the crucible had been thoroughly melted and maintained for 1.8 ks at 100 K above its equilibrium melting point, the shutter above the furnace was opened and the support bar was raised by an elevating mechanism until the crucible was inside the water-cooling outer tube. Then the stirring rotor was gradually inserted into the mixture in the crucible until the leading end of the rotor was 10 mm from the bottom floor of the crucible. Then, a flow of cold water through the water-cooling outer tube was begun to cool the mixture at a rate of 0.5 K/s, while rotation of the stirrer was continued at a low speed of 18 s^{-1} .

This rotational rate was raised within 10 s to a high speed in two stages of 20 and 25 s^{-1} after the copper had substantially reached the temperature where it would begin solidification. The rotational speed was then increased at an even rate so as to prevent the semi-solid mixture from being scattered by a sharp increase in rotation speed. The rotational stirring was continued for a period of 20 s after the solidification was confirmed by reading the cooling curve of the recorder and the torque value on the digital display device. Then the support bar was lowered until the leading end of the stirring rotor was 0.2 m from the bottom floor of the crucible in order to prevent the rotor adhering to the compocast ingot.

The graphite stirring rotor has a thickness of 30 mm at the upper end to 25 mm at the lower end, with the four corners cut as illustrated in Fig. 2. The graphite inner crucible is 78 mm in outer diameter, is tapered from a magnitude of 60 mm in inner diameter at the upper end to 55 mm at the lower end, and 130 mm in depth. The values of torque induced by the viscosity of solidifying mixtures were recorded on a digital printer and the standard value of torque during the rotation of the stirrer was based on an empty crucible under the same conditions as those when the mixture was compocast.

Microscopic observation was then made of the top, middle and bottom sections cut transversely from the compocast ingots. Tensile test pieces were also machined

Fig. 2 Transverse section of the mold and stirrer.

Fig. 3 Size and shape of test piece used in the present work.

from the compocast ingots as illustrated in Fig. 3. The tensile test was carried out in air at room temperature using a strain rate of $1.67 \times 10^{-2} \text{ s}^{-1}$.

III. Experimental Results

1. Scanning electron microscopy and X-ray microanalysis

The distribution of elements in the transverse sections in the top, middle and bottom parts of DS coppers compocast with the addition of carbide particles up to 33 vol% observed by scanning electron microscope. As an example, the X-ray images of three elements and the back-scattered electron image in the middle section of the DS copper compocast at a rotation speed of 25 s^{-1} with tungsten carbides added by 1.2 vol% WC is shown in Fig. 4. Figures 4(a), (b) and (c) show the X-ray images of carbon, tungsten and copper, respectively. Figure 4(d) shows the back-scattered electron image. The tungsten carbide particles were seen to have relatively uniform dispersion and local aggregate agglomeration. This ingot was recognized as a homogeneous DS copper, because the same dispersion of WC particles was noted on its top and bottom sections.

Fig. 4 X-ray images of (a) carbon, (b) tungsten and (c) copper element and (d) back-scattered electron image in the middle section of a dispersion-strengthened copper with addition of 2 mass% WC.

2. Electrical conductivity

The electrical conductivities measured of the DS coppers compocast at a rotation speed of 25 s^{-1} with addition of carbide particles up to 22 vol% are shown in Fig. 5. The electrical conductivity of the pure copper blocks used in the present work was 103.3%IACS. The electrical conductivity of the DS coppers decreased from 98.9 to 77.9%IACS with increasing addition of 0.6 to 12.5 vol% WC, decreased from 103.4 to 73.4%IACS with increasing addition of 0.6 to 13.4 vol% TaC, decreased from 95.4 to 50.4%IACS with increasing addition of 1.1 to 22.2 vol% NbC, decreased from 95.2 to 47.6%IACS with increasing addition of 1.8 to 31.2 vol% TiC and decreased from 89.0 to 56.9%IACS with increasing addition of 1.6 to 29.0 vol% VC.

When the minimum value of the electrical conductivity acceptable for commercial lead frame materials was assumed to be 60%IACS, the DS coppers compocast with addition of carbide particles of 42 to 46 vol%, i.e. up to 46 vol% WC, 44 vol% TaC, 43 vol% TiC, 43% NbC and 42 vol% VC, were available for them (see Section IV.1). In any case it was confirmed that the electrical conductivities would not decrease greatly with increased carbide content as compared with those of commercial oxide dispersion-strengthened coppers produced by powder metallurgy technique⁽¹⁸⁾ as also presented in Fig. 5.

3. Hardness

The values of Vickers hardness measured on the DS copper ingots compocast at a rotation speed of 25 s^{-1} with addition of carbide particles up to 33 vol% are shown in Fig. 6. The hardness of the pure copper used in this work was Hv 53.4. The Vickers hardness of the compocast DS coppers increased from Hv 70.8 to Hv 197 with increasing addition of 0.6 to 19.7 vol%WC, increased from Hv 59.2 to Hv 155 with increasing addition of 1.1 to 32.9 vol%NbC, and increased from Hv 57.3 to Hv 110 with increasing addition of 0.6 to 21.0 vol%TaC.

Fig. 5 Relation between content of carbide particles and electrical conductivity in dispersion-strengthened coppers.

Fig. 6 Relation between content of carbide particles and Vickers hardness in dispersion-strengthened coppers. The solid line was calculated from the equation of $Hv = 53.4 + 3.5V_p^{0.9}$.

The hardness value of compocast DS coppers increased from Hv 69.2 to Hv 158 with increasing addition of 1.6 to 29.0 vol%VC, increased from Hv 58.9 to Hv 121 with increasing addition of 1.8 to 31.1 vol%TiC.

The hardness values of the commercial oxide dispersion-strengthened coppers fabricated by the powder metallurgy process⁽¹⁸⁾ are also represented in Fig. 6.

4. Ultimate tensile strength

The values of tensile strength measured at room temperature on the DS copper ingots compocast at a rotation speed of 25 s^{-1} with addition of carbide particles up to 33 vol% are shown in Fig. 7.

The ultimate tensile strength value of the pure copper blocks used in the present work was 142 MPa. The value of ultimate tensile strength of the DS coppers increased gradually from 163 to 304 MPa with increasing addition

Fig. 7 Relation between content of carbide particles and ultimate tensile strength in dispersion-strengthened coppers.

Fig. 8 Relation between content of carbide particles and elongation in dispersion-strengthened coppers.

of 0.6 to 19.7 vol%WC, and also increased gradually from 148 to 402 MPa with increased addition from 1.1 to 32.9 vol%NbC. Similarly, the tensile strength increased from 178 to 357 MPa with increasing addition of 1.8 to 31.2 vol%TiC. It increased from 153 to 269 MPa with increasing addition of 0.6 to 13.4 vol%TaC. It also increased from 163 to 323 MPa with increasing addition of 1.6 to 15.3 vol%VC.

The tensile strength values of commercial oxide dispersion-strengthened coppers made by powder metallurgy technique⁽¹⁸⁾ are also revealed in Fig. 7.

5. Ductility

The values of elongation measured at room temperature on the DS copper ingots compocast at a rotation speed of 25 s^{-1} with addition of carbide particles up to 33 vol% are shown in Fig. 8.

The elongation value of the pure copper blocks used in the present work was 46.3%. This value decreased from 50.0 to 3.0% with increasing addition of 0.6 to 19.7 vol%WC, and decreased from 58.4 to 5.0% with increasing addition of 1.1 to 32.9 vol%NbC. Similarly, the elongation value decreased from 44.0 to 12.9% with increased addition from 0.6 to 13.4 vol%TaC, and decreased from 32.8 to 8.9% with increased addition from 1.8 to 31.2 vol%TiC. It decreased from 43.7 to 21.8% with increasing addition of 1.6 to 15.3 vol%VC.

The elongation values of commercial oxide dispersion-strengthened coppers produced by the powder metallurgy process⁽¹⁸⁾ are also indicated in Fig. 8.

IV. Discussion

1. Experimental analysis on electrical conductivity

The electrical conductivity of a dispersion-strengthened metal, E_c , is assumed as follows:

Fig. 9 Comparison of the calculated electrical conductivities with the measured ones in dispersion-strengthened coppers.

$$E_c = E_c^M A_f^M + E_c^P A_f^P \quad (1)$$

where E_c^M is the electrical conductivity of metal matrix, A_f^M is the fraction of area occupied by the matrix, E_c^P is the electrical conductivity of nonmetallic particles, and A_f^P is the fraction of area occupied by the particles.

The electrical conductivity values of the carbide particles are determined by the method of least squares including substitution of two measured electrical conductivity values of pure copper and compocast DS coppers, and two calculated fractions of area occupied by the copper and the particles into eq. (1) (see Fig. 9). The value of $E_c^{\text{WC}} = 5.90 \times 10^7 / \Omega\text{-m}^{(20)}$ was used for the electrical conductivity of the copper matrix. As a result, the electrical conductivities of WC, TiC, VC and NbC particles are calculated to be 5.21×10^6 , 2.78×10^6 , 1.67×10^6 and $1.82 \times 10^6 / \Omega\text{-m}$, respectively.

The above-described values of carbide particles are in the range of the published electrical conductivity values of carbides (WC: $5.21 \times 10^6 / \Omega\text{-m}^{(21)}$, TaC: $2.44 \sim 3.33 \times 10^6 / \Omega\text{-m}^{(22)}$, TiC: $1.67 \times 10^6 / \Omega\text{-m}^{(22)}$, VC: $6.25 \sim 6.67 \times 10^6 / \Omega\text{-m}^{(23)}$, and NbC: $1.35 \sim 2.86 \times 10^6 / \Omega\text{-m}^{(22)}$).

2. Experimental analysis on hardness

It is recognized that the compocast DS coppers contain-

ing all the carbides except WC shows a regular increase in hardness with increasing carbide content. The reason is considered as follows. All the carbide particles 1 to 2 μm in size are uniformly dispersed and entrapped between the copper matrices in the compocast DS coppers. When the surface of the DS coppers is pressed locally by the Vickers hardness testing, the comparatively hard carbides existed in the very vicinity of the position can be forced easily in the soft copper matrices. Therefore, the hardness value is independent of the kind of carbides.

By computerizing the hardness values by means of the method of least square, the following empirical equation can be obtained as shown by the solid line in Fig. 6:

$$Hv = 53.4 + 3.5V_p^{0.9} \quad (2)$$

where V_p is the volume percentage of carbide particles.

The deviation in hardness of WC-dispersed coppers from eq. (2) must be owing to the WC particle size of 0.68 μm which is very smaller than the other carbide sizes of 1 to 2 μm .

3. Experimental analysis on ultimate tensile strength

The ultimate tensile strength, F_u , of a dispersion-strengthened metal is assumed as follows:

Fig. 10 Comparison of the calculated ultimate tensile strengths with the measured ones in dispersion-strengthened coppers.

$$F_u = F_u^M A_f^M + F_u^P A_f^P \quad (3)$$

where F_u^M is the ultimate tensile strength of metal matrix, A_f^M is the fraction of area occupied by the matrix, F_u^P is the ultimate tensile strength of nonmetallic particles, and A_f^P is the fraction of area occupied by the particles.

The ultimate tensile strength values of the carbide particles can be determined by the method of least square including insertion of two measured tensile strength values of pure copper and compocast DS coppers and two calculated fractions of area occupied by the copper and the particles into eq. (3) (see Fig. 10). The value of 142 MPa is used for the tensile strength of the copper. As a result, the ultimate tensile strength values of carbide particles of WC, TaC, TiC, VC and NbC can be calculated to be 961, 539, 568, 641 and 755 MPa, respectively.

V. Conclusions

The electrical conductivity and the mechanical properties of dispersion-strengthened (DS) coppers fabricated by compocasting at a stirrer speed of 25 s^{-1} with the addition of fine carbide particles in the range of 0.5 to 30 mass% WC, TaC, TiC, VC and NbC were analyzed experimentally.

The results are summarized as follows.

(1) The electrical conductivity values of the carbide particles can be evaluated using the measured electrical conductivity values of pure copper and compocast DS coppers, the calculated fractions of area occupied by the copper and the particles and the following equation:

$$Ec = Ec^M A_f^M + Ec^P A_f^P \quad (1)$$

where Ec , Ec^M and Ec^P are the electrical conductivities of DS coppers, copper matrix and the particles, respectively, and A_f^M and A_f^P are the fractions of area occupied by the copper and the particles, respectively. The calculated values of carbide particles are in the range of the published electrical conductivity values of carbides.

(2) The hardness of compocast DS coppers containing all the carbides 1 to 2 μm in size except WC has a consistently increasing tendency with increased carbide content. Therefore, the hardness value, Hv , of them can be expressed as follows:

$$Hv = 53.4 + 3.5V_p^{0.9} \quad (2)$$

where V_p is the volume percentage of carbide particles.

The hardness values of WC-dispersed coppers are deviated from eq. (2) because the WC particle size of 0.68 μm is very smaller than the other carbide sizes.

(3) The ultimate tensile strength values of carbide particles can be evaluated using the measured values of pure copper and compocast DS coppers, the calculated fractions of area occupied by the copper and the particles and the following equation:

$$F_u = F_u^M A_f^M + F_u^P A_f^P \quad (3)$$

where F_u , F_u^M and F_u^P are the ultimate tensile strengths

of DS coppers, copper and particles, respectively, and A_f^M and A_f^P are the fractions of area occupied by the copper and the particles, respectively. As a result, the ultimate tensile strength values of carbide particles of WC, TaC, TiC, VC and NbC can be calculated to be 961, 539, 568, 641 and 755 MPa, respectively.

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