

Effect of Chromium Behavior on Mechanical and Electrical Properties of P/M Copper-Chromium Alloy Dispersed with VGCF

Hisashi Imai, Kuan-Yu Chen, Katsuyoshi Kondoh, Hung-Yin Tsai, Junko Umeda

Abstract—Microstructural and electrical properties of Cu-chromium alloy (Cu-Cr) dispersed with vapor-grown carbon fiber (VGCF) prepared by powder metallurgy (P/M) process have been investigated. Cu-0.7 mass% Cr pre-alloyed powder (Cu-Cr) made by water atomization process was used as raw materials, which contained solid solute Cr elements in Cu matrix. The alloy powder coated with un-bundled VGCF by using oil coating process was consolidated at 1223 K in vacuum by spark plasma sintering, and then extruded at 1073 K. The extruded Cu-Cr alloy (monolithic alloy) had 209.3 MPa YS and 80.4 IACS% conductivity. The extruded Cu-Cr with 0.1 mass% VGCF composites revealed a small decrease of YS compared to the monolithic Cu-Cr alloy. On the other hand, the composite had a higher electrical conductivity than that of the monolithic alloy. For example, Cu-Cr with 0.1 mass% VGCF composite sintered for 5 h showed 182.7 MPa YS and 89.7 IACS% conductivity. In the case of Cu-Cr with VGCFs composites, the Cr concentration was observed around VGCF by SEM-EDS analysis, where Cr_{23}C_6 compounds were detected by TEM observation. The amount of Cr solid solution in the matrix of the Cu-Cr composites alloy was about 50% compared to the monolithic Cu-Cr sintered alloy, and resulted in the remarkable increment of the electrical conductivity.

Keywords—Powder metallurgy Cu-Cr alloy powder, vapor-grown carbon fiber, electrical conductivity.

I. INTRODUCTION

IN recent years, Cu and Cu alloys with high strength and high electrical conductivity have been widely used in industry as important functional materials. In general, Cu alloys, such as brass and bronze, have potentials for mechanical property improvement by solid solution strengthening and precipitation strengthening. However, the electron can transfer in the matrix easily under a small amount of alloying elements [1]. Therefore, it is difficult to produce Cu alloys with both high strength and electrical conductivity by the conventional metallurgical method.

Carbon nanotubes (CNTs) exhibit excellent properties, such as a high Young's modulus and electrical conductivity [2], [3]. They are expected to improve both mechanical and electrical properties by the dispersion of CNTs in the materials. In the previous report, Mg alloy with CNTs and Ti with CNTs

composites had high strengths because of the dispersion strengthening of the CNTs and in-situ formed carbides during sintering in the metal matrix [4]-[6].

There were previous research studies related to the mechanical property and electrical conductivity of Cu alloys [7]-[9]. The Cu alloys had high strength by precipitation strengthening; however, the electrical conductivity was decreased by increasing the amount of alloy elements [10], [11]. The conductivity of the Cu alloy could be improved by using heat treatment (aging) [12], [13] and carbon addition [14]. Author's previous study showed that Cu-Ti with CNTs had both high strength and high electrical conductivity [15]. The reaction between Ti and CNTs was caused dispersion strengthened and electrical pass in the matrix.

In this study, vapor-grown carbon fibers (VGCFs), which are multi-walled carbon nanotubes, were added to produce a Cu-Cr alloy with both high strength and high electrical conductivity. A small amount of chromium as alloying element had been added in order to increase wettability between the Cu matrix and VGCFs. A rapidly solidified Cu alloy powder was used in this study, and the effects of the reactions between VGCFs and chromium as alloying element during the sintering on the tensile strength and electrical conductivity of the consolidated materials was investigated.

II. EXPERIMENTAL PROCEDURE

Cu-Cr pre-alloy powders (Cu 99.3 mass% and chromium 0.7 mass% with mean particle size 159.3 μm) were prepared by the water atomization process. VGCF with 20-50 nm in diameter and 500-1000 nm length was used in this research. The SEM observation results of these materials are shown in Fig. 1, Fig. 2 shows the schematic of fabrication process of the elemental mixture of Cu-Cr with VGCF composite powder. First, Cu-Cr pre-alloy powder with 0.02 mass% oil (Clesafe oil: JX Nippon Oil & Energy) was mixed by ball milling (AV-2: ASAHI RIKKA Co.) for 3.6 ks at 120 rpm. Then the Cu-Cr alloy powder with 0.1 mass% VGCF mixtures were prepared by rocking milling (RM-05: SEIWA GIKEN Co.) for 3.6 ks at 700 rpm. The temperature to remove Clesafe oil was investigated by thermo gravimetric analysis (DTG-60: SHIMADZU Co.) under the heating rate of 0.17 K/s in Ar gas atmosphere [16]. From the TG analysis profile, the oil could be successfully removed under 673 K.

Hisashi Imai, Katsuyoshi Kondoh, and Junko Umeda are with Joining and Welding Research Institute Osaka University, Japan, 11-1 Mihogaoka, Ibaraki city Osaka prefecture Japan (e-mail: imai@jwri.osaka-u.ac.jp, kondoh@jwri.osaka-u.ac.jp, umedaj@jwri.osaka-u.ac.jp).

Kuan-Yu Chen and Hung-Yin Tsai are with Department of Power Mechanical Engineering, National Tsing-Hua University, Taiwan (e-mail: s9933577@m99.nthu.edu.tw, hysai@pme.nthu.edu.tw).

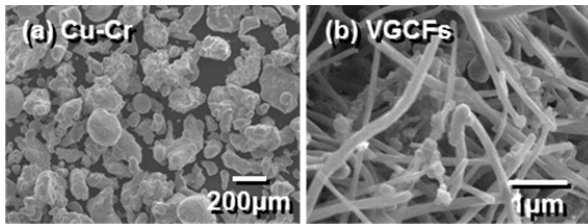


Fig. 1 SEM observation on Cu-0.7 mass% Cr pre-alloy powder (Cu-Cr) (a) and VGCFs (b)

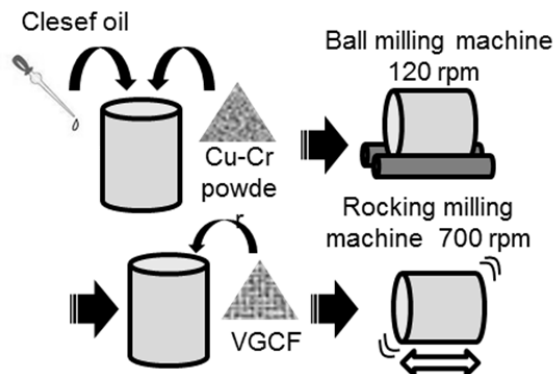


Fig. 2 Process of making Cu-Cr with VGCFs

Cu-Cr with VGCFs composite powder and monolithic Cu-Cr powder were sintered by using Spark Plasma Sintering (SPS, SPS-1030: SPS SYNTEX INC) process at 1223 K for 1.8 and 18 ks under 30 MPa pressure in vacuum (6 Pa). Cu-Cr with VGCFs compacts were preheated at 1073 K for 800 s with a heating rate of 2 K/s in Ar atmosphere by the infrared ray gold image furnace (TPC-1000:ULVAC Co.). After preheating, the compact was immediately extruded by using hydraulic press (2000 kN SHP-200-450: SHIBAYAMAKIKAI Co.) under an extrusion ratio of 12.8. Electrical conductivity was measured by electrical conductivity meter (AutoSigma 3000: GE Inspection Technologies). Mechanical properties of extruded composite were evaluated by tensile testing equipment (AUTOGRAPH AG-X: SHIMADZU) with a strain rate of $5 \times 10^{-4} \text{ s}^{-1}$. The microstructural observation by scanning electron microscope (SEM, JSM-6500F: JEOL) was carried out on raw powder and consolidated specimens. As-received raw VGCFs and VGCFs dispersed in the wrought Cu alloy were analyzed using Raman spectroscopy (HORIBA, LabRam ARAMIS SC-O). 532 nm laser was selected with the acquisition time of 10 s. X-ray energy dispersive spectroscopy (EDS EX-64175JMU: JEOL) on SEM and Transmission Electron Microscopes (TEM, JEM-2100F: JEOL) were used for composition analysis. The TEM observation samples were prepared by the focused ion beam apparatus (FIB, FB-2000S: Hitachi).

III. RESULTS AND DISCUSSION

Fig. 3 shows the SEM observation on Cu-Cr powder coated with 0.1 mass% VGCFs. In the mixing method used in this experiment, VGCFs were uniformly dispersed on the Cu alloy powder surface without the damage. The some aggregation of

VGCFs as size of about 10 micron meter existed at unevenness on powder surface.

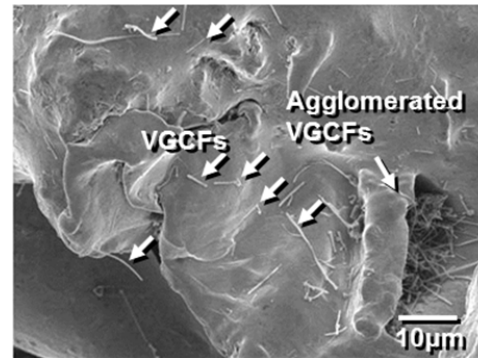


Fig. 3 SEM observation on powder surface of Cu-Cr pre-alloy with VGCFs

The tensile properties of hot extruded Cu-Cr with VGCFs composite on s contents were shown in Fig. 4. Cu-Cr without VGCFs had 274 MPa UTS, 209 MPa YS and 24.3% elongation. YS and UTS of extruded Cu-Cr with VGCFs slightly decreased compared to the monolithic Cu-Cr alloy. Mechanical properties of extruded materials of Cu-Cr with VGCFs sintered for 0.5h and Cu-Cr with VGCFs sintered for 5h had same levels. The elongations of them were almost same as the monolithic Cu-Cr alloy.

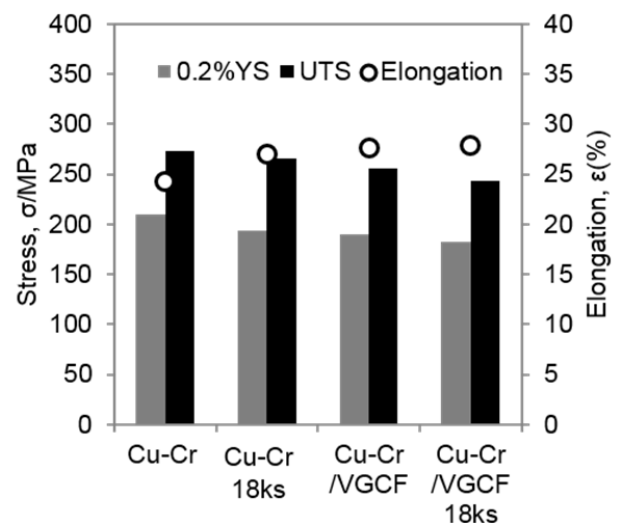


Fig. 4 Tensile properties of extruded materials of Cu-Cr and Cu-Cr with VGCFs composite sintered for 1.8 ks and 18 ks.

The electrical conductivities of the monolithic Cu-Cr and Cu-Cr with VGCFs composites were shown in Fig. 5. The electrical conductivities of composite materials increased compared to the monolithic alloy. The electrical conductivities of Cu-Cr with VGCFs sintered for 1.8 ks and that sintered for 5h were 86.4 IACS% and 89.7 IACS%, respectively. In general, an electrical conductivity of Cu with CNTs composite is not improved because of the low wettability between matrix and CNTs. However, in this research, these materials used Cu-Cr with VGCFs powder had high strength and improved

electrical conductivity. In addition, long time sintered material of Cu-Cr with VGCFs composite had higher electrical conductivity compared to composite material for short sintered time.

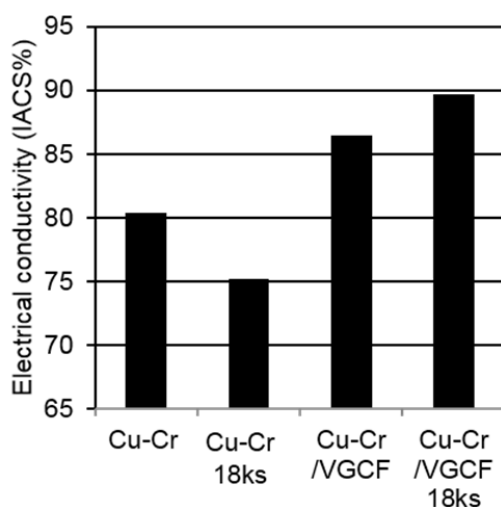


Fig. 5 Electrical conductivities extruded materials of Cu-Cr and Cu-Cr with VGCFs composite for several sintering time

Fig. 6 showed the fractured surfaces of tensile test specimens; Cu-Cr with VGCFs (a) and P/M Pure Cu with 0.1 mass% VGCFs (b). In the case of Cu-Cr with VGCFs composite alloy, VGCFs were dispersed on the fracture surface, and bonded well with Cu-Cr alloy matrix. On the other hand, VGCFs was not existed on fracture surface of P/M Pure Cu with 0.1 mass% VGCFs. Mechanical properties of this material was low compared with pure Cu [15]. It was considered that these VGCFs reinforced Cu-Cr matrix by the suitable bonding.

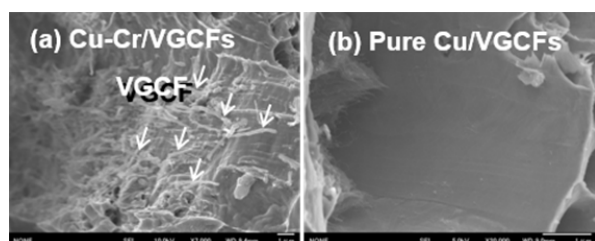


Fig. 6 SEM observation on fractured surfaces of tensile test specimens of Cu-Cr/VGCFs (a) and pure Cu/VGCFs (b)

SEM-EDS analysis on Cu-Cr composite with VGCFs was shown in Fig. 7. In the case of monolithic Cu-Cr (a), there was little chromium segregation around primary particle boundaries. Solid solution of chromium in monolithic Cu-Cr alloy was detected as 0.6-0.5 mass% by EDS point analysis. On the other hand, chromium was concentrated at primary particle boundaries in Cu-Cr with VGCFs as shown in (b) and (c). There was also carbon in same area. The carbon was considered to be derived from VGCFs. The concentrated area of Cu-Cr with VGCFs sintered for 5 h was wider than that of sintered for 0.5 h. There were 0.1-0.3 mass% and 0.05-0.2 mass% solid

solution of chromium in 0.5h sintering material and 5h sintering material, respectively. The amount of chromium solid solution in Cu-Cr alloy matrix with VGCFs was about half of the amount of that without VGCFs.

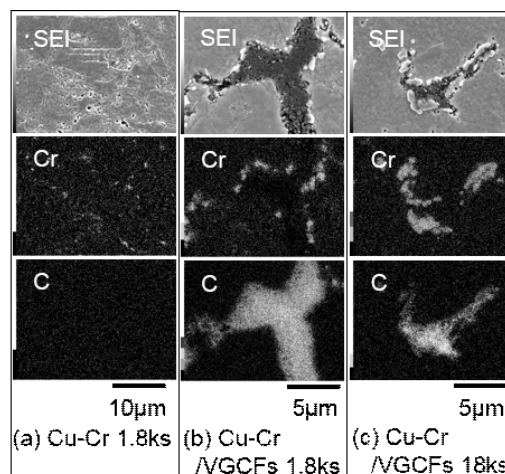


Fig. 7 SEM-EDS analysis of extruded material of Cu-Cr (a), Cu-Cr with VGCFs composite sintered for 1.8 ks (b), and Cu-Cr with VGCFs composite sintered for 18 ks (c)

Fig. 8 showed Raman spectra collected from as-received raw VGCFs, heat treated VGCFs, and VGCFs dispersed in the sintered Cu-Cr composite. D-band and G-band were observed in Raman spectra of semiconducting and metallic VGCFs. D-band involves a defect which breaks the basic symmetry of graphene sheet [17]. D-band and G-band peak ratio (I_G/I_D) of raw VGCFs was 3.3. After heat treated, this tendency was not changed. On the other hand, I_G/I_D of VGCFs dispersed in the Cu-Cr with VGCFs composite was around 1.3, that is, the peak intensity of D-band became stronger in the composite. It was suggested that there was a reaction of VGCFs in the sintered Cu-Cr with VGCFs material.

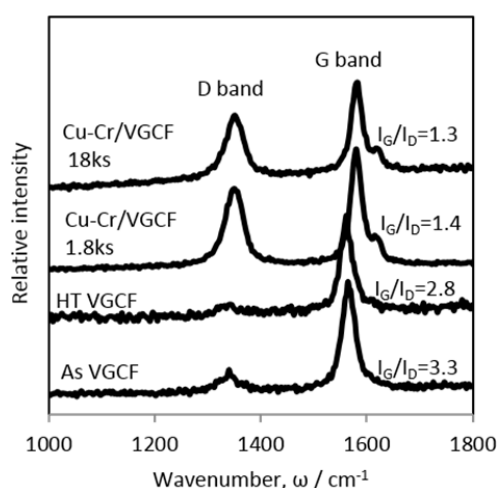


Fig. 8 Raman spectra collected from as-received raw and heat treated VGCFs, and those dispersed in sintered Cu-Cr with VGCFs material

Fig. 9 shows the TEM-EDS analysis results of the Cu-Cr

with VGCFs composite material. Chromium was concentrated around VGCF from EDS result, while Cr_{23}C_6 was detected by a diffraction pattern. In the case of Cu-Cr with VGCFs, the chromium amount of solid solution to Cu is about 0.3 mass% at 1173 K, and chromium carbide is stable at 1173 K (Gibbs free energy; $\Delta G_{\text{Cr}_{23}\text{C}_6}$: -83.5 kJ/mol [Cr]) [18]. Thus, the chromium atoms contained in the Cu matrix reacted with VGCFs, and resulted in strong bonding between the matrix and VGCFs through the formation of carbide. At the same time, the electrical pass of the Cu matrix was increased due to decreasing the amount of the solid solution of the titanium and chromium atoms in the matrix.

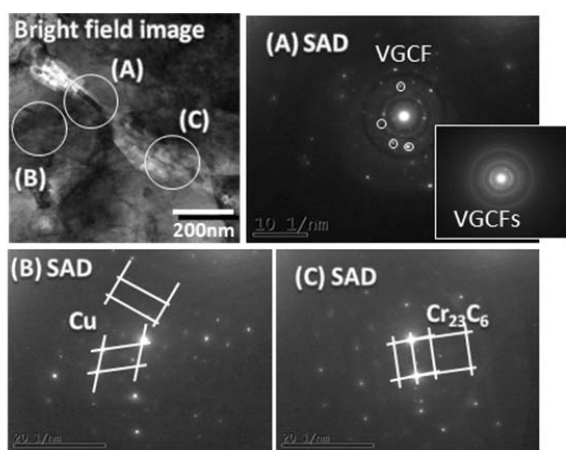


Fig. 9 TEM-EDS observation and chromium mapping results of extruded Cu-Cr with 0.1 mass% VGCFs

IV. CONCLUSION

In this paper, the effects of the reactions between the chromium as alloying element and VGCFs in the Cu alloy on the mechanical and electrical properties were investigated. The results of this study are summarized as follows:

Extruded material of Cu-Cr with VGCFs sintered for 5h had 244 MPa UTS, 183 MPa YS and 27.8% elongation. The tensile strength of composite material of Cu-Cr with VGCFs decreased significantly compared to the monolithic Cu-Cr alloy. This result caused to decreasing the solid soluted chromium in the Cu matrix. However, there were VGCFs on fracture surface of tensile test specimen by SEM observation.

VGCFs were reacted with chromium, and then a carbide compound appeared around VGCFs in Cu-Cr with VGCFs composites. The extruded Cu-Cr with VGCFs had high strengths because of the bonding between the Cu matrix and VGCFs through the formation of carbide by the reaction between the solid solute elements and VGCFs during sintering. At the same time, the electrical pass of Cu-Cr matrix was increased because of the decreasing amount of the elemental solid solution in the matrix.

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REFERENCES

- [1] A. Lee, N. Grant. Properties of Two High Strength, High Temperature, High Conductivity Cu Base Alloys. *Materials Science and Engineering*, 60, 213-223 (1983).
- [2] N. Khandoker et al. "Tensile Strength of Spinnable Multiwall Carbon Nanotubes", *Procedia Engineering*, 10, 2572-2578 (2011).
- [3] S. Xie et al., "Mechanical and Physical Properties on Carbon Nanotube", *Journal of Physics and Chemistry of Solids*, 61, 1153-1158 (2000).
- [4] K. Kondoh et al., "Microstructural and Mechanical Analysis of Carbon Nanotube Reinforced Magnesium Alloy Powder Composites", *Materials Science & Engineering A*, 527, 4103-4108 (2010).
- [5] S. Li et al., "Powder Metallurgy Ti-TiC Metal Matrix Composites Prepared by In-situ Reactive Processing of Ti-VGCFs System", *Carbon*, 61, 216-228 (2013).
- [6] Y. Shimizu et al., "Multi-Walled Carbon Nanotube-Reinforced Magnesium Alloy Composites", *Scripta Materialia*, 58, 267-270 (2008).
- [7] D. Laughlin, J. Cahn, "Spinodal Decomposition in Age Hardening Cu-Titanium Alloys", *Acta Materialia*, 23, 329-339 (1975).
- [8] A. Potter, A. Thompson, "On the Mechanism of Precipitation Strengthening in Cu-Ti Alloys", *Scripta Materialia*, 18, 1185-1188 (1984).
- [9] K. Maki et al., "Solid-solution Cu alloys with high strength and high electrical conductivity", *Scripta Materialia*, 68 (2013), 777-780.
- [10] S. Nagarjuna et al., "Effect of Prior Cold Work on Mechanical Properties, Electrical Conductivity and Microstructure of Aged Cu-Ti Alloys", *Journal of Materials Science*, 34, 2929-2942 (1999).
- [11] S. Nagarjuna et al., "On the Variation of Mechanical Properties with Solute Content in Cu-Ti Alloys", *Materials Science and Engineering A*, 259, 34-42 (1999).
- [12] S. Semboshi et al., "Microstructural Evolution of Cu-1 at % Ti Alloy aged in a Hydrogen Atmosphere and Its Relation with the Electrical Conductivity", *Ultramicroscopy*, 109, 593-598 (2009).
- [13] S. Suzuki et al., "Electrical and Thermal Conductivities in Quenched and Aged High-Purity Cu-Ti Alloys", *Scripta Materialia*, 48, 431-435 (2003).
- [14] T. Oku et al., "Effects of Titanium Addition on the Microstructure of Carbon/Cu Composite Materials", *Solid State Communications*, 141, 132-135 (2007).
- [15] H. Imai et al., "Microstructural and Electrical Properties of Cu-titanium Alloy Dispersed with Carbon Nanotubes via Powder Metallurgy Process", *Materials Transactions*, 55, 3, 522-527, (2014).
- [16] H. Imai et al., "Effect of Chromium Precipitation on Machinability of Sintered Brass Alloys Dispersed with Graphite Particles", *Materials Transactions*, 52, 7, 1426-1430, (2011).
- [17] M.S. Dresselhaus et al., "Raman Spectroscopy of Carbon Nanotubes," *Physics Reports*, 409, 47-99, (2005).
- [18] M. Small et al. "Calculation and evaluation of the Gibbs energies of formation of Cr_3C_2 , Cr_7C_3 , and Cr_{23}C_6 ", *Metallurgical and Materials Transaction A*, 12, 1389-1396, (1981).