Microstructural and Electrical Properties of Copper–Titanium Alloy Dispersed with Carbon Nanotubes via Powder Metallurgy Process*1

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Microstructural and electrical properties of powder metallurgy (P/M) copper alloy with carbon nanotubes (CNTs) were investigated. The Cu–0.5 mass% Ti pre-alloyed powder (Cu–0.5Ti) was made by water atomization process. The powders coated with un-bundled CNTs by using the zwitterionic surfactant water solution containing CNTs were consolidated at 1223 K in vacuum by spark plasma sintering, and then extruded at 1073 K. The P/M Cu–0.5Ti alloy without CNTs (monolithic alloy) had 202 MPa yield stress (YS) and 42.5 International-Annealed-Copper-Standard % (IACS%) conductivity. The extruded Cu–0.5Ti composite alloy containing CNTs revealed small decrease of YS compared to the monolithic Cu–0.5Ti alloy. On the other hand, the composites indicated a higher electrical conductivity than that of the monolithic alloy. For example, Cu–0.5Ti with 0.19 mass% CNTs showed 175.8 MPa YS and 83.5 IACS% conductivity. In the case of the Cu–0.5Ti composite with CNTs, the intermetallic compounds such as Cu2Ti and TiC were observed around CNTs by TEM-EDS analysis. The amount of the solid solute Ti in the above Cu–0.5Ti composite alloy matrix was 10% of the monolithic Cu–0.5Ti alloy, and resulted in the remarkable increment of its electrical conductivity due to the decrease of solid solute Ti content. [doi:10.2320/matertrans.Y-M2013846]

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Keywords: Cu–0.5Ti alloy, carbon nanotubes, electrical conductivity, solid solute titanium

1. Introduction

Improving the utilization efficiency of the heat and electrical energy is an important issue from a viewpoint of using resources. In particular, reduction of vehicle weight by using light materials or high strength materials has been promoted for the energy conservation. On the other hand, electrical components increase with increasing high-performance products. Therefore, a percentage of the wire and electrical components in the products is increasing. If the copper alloys, which are often used in wire and electrical components, have high strength and high electrical conductivity, light-weight effect of the device is improved and directly related to energy conservation. In general, copper alloys such as brass and bronze have the high strength with the addition of other elements for the solid solution hardening and precipitation strengthening effects.1,2) On the other hand, copper alloys with a few elements have a suitable thermal and electrical conductivity since there are few barriers for electron transfer in the matrix.3) Therefore, it is difficult to produce copper alloys with both high strength and electrical conductivity by the conventional metallurgy method.

The study of the metal composite with high strength and high electrical conductivity by dispersed carbon materials has been investigated. Carbon nanotubes (CNTs) exhibit excellent properties such as high Young’s modulus and electrical conductivity.4,5) They are expected to improve both mechanical and electrical properties by their dispersion in the materials. However, it is difficult to uniformly distribute CNTs in the metal matrix because CNTs are easily bundled by van der Waals interaction force between carbon atoms of their outermost walls. Powder metallurgy (P/M) process is used for preparation of CNTs reinforced metal matrix composites6–8) with higher specific gravity compared to polymers such as rubber and plastic etc.9,10) In our previous reports, the wet process using a few kinds of surfactants (surface active agent), consisting of both hydrophobic and hydrophilic groups, was also performed for making metal/CNTs composite. Mg/CNTs and Ti/CNTs composites have been prepared by using the wet process, and they had a higher strength compared to each monolithic pure metal11,12)

The purpose of this study was to develop P/M Cu–Ti alloy with high strength and high electrical conductivity by dispersing CNTs via wet process. In general, a copper hardly forms stable compounds with graphite including CNTs. Therefore, oxides or voids existed between carbon and copper matrix when preparing CNTs reinforced copper alloy composites by P/M process. As a result, copper composites with CNTs did not have high strength or high electrical conductivity.13) In this study, the reaction and diffusion of titanium, contained as an alloying element in Cu alloy powder, were used in order to improve the CNTs and copper matrix bonding. Cu–Ti binary alloys had high ultimate tensile strength (UTS) of about twice as that of pure copper by precipitation strengthen, and 30 International-Annealed-Copper-Standard % (IACS%) electrical conductivity.14) High electrical conductivity of Cu–Ti alloy was significantly reduced due to supersaturated Ti alloying elements. The rapidly solidified Cu–0.5 mass% Ti alloy (Cu–0.5Ti) powder was used in this study. The effect of the reaction between CNTs and Ti elements on tensile strength and electrical conductivity of consolidated materials was investigated.

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2. Experimental Procedure

Cu–0.5Ti powder, used as raw material, was prepared by the water atomization using pure copper ingot with titanium additions. It had a mean particle size of 150 μm. Titanium content of copper alloy was 0.544 mass%. Multi-Walled carbon nanotubes with diameter Φ 20–50 nm and length 0.5–1.0 μm were used in this study. These raw materials were shown in Fig. 1.

Cu–0.5Ti with CNTs (Cu–0.5Ti/CNTs) composite powders were prepared by dipping raw Cu–0.5Ti powder into the zwitterionic surfactant water solution (3-(N,N-dimethylstearlammonio) propanesulfonate solution) with CNTs. The amount of CNTs coated to Cu–0.5Ti powder had been adjusted using the concentration of the solution. The un-bundled CNTs and the zwitterionic surfactant films covered powder surface. From the thermo-gravimetric analysis results in the previous research, surfactant films were completely decomposed and removed over 673 K. Therefore, Cu–0.5Ti/CNTs composite powders were heated to 873 K in H2 gas (2.2 L/min) and Ar gas 0.8 L/min atmosphere. The total carbon content of Cu–0.5Ti/CNTs composite powder was assumed to be the amount of CNTs coated on Cu alloy powder. The carbon content was measured by infrared absorption method using carbon analyzer (EMIA-221V: HORIBA). In this study, the composite powders with various amounts of CNTs were prepared using the solutions with different concentrations of carbon nanotubes.

Cu–0.5Ti/CNTs composite powders were sintered by using spark plasma sintering (SPS, SPS-1030: SPS SYNTEX INC) process at 1223 K for 1.8 ks under 30 MPa pressure in vacuum (6 Pa). Cu–0.5Ti/CNTs compacts were preheated at 1073 K for 800 s with a heating rate of 1 K/s in Ar gas atmosphere by the infrared ray gold image furnace (TPC-1000: ULVAC Co.). After preheating the compact, it was immediately extruded by using hydraulic press machine (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 composites were evaluated by tensile testing equipment (AUTOGRAPH AG-X: SHIMADZU) with a strain rate of 5 × 10−4 s−1. The microstructural observation by scanning electron microscope (SEM, JSM-6500F: JEOL) was carried out on raw powder and consolidated specimens. X-ray energy dispersive spectroscopy (EDS, EX-64175MU: JEOL) on SEM and Transmission Electron Microscope (TEM, JEM-2100F: JEOL), and wavelength dispersive X-ray spectrometer (WDS, Inca wave: Oxford instruments) were used for analysis of solid solute titanium elements in the matrix. TEM observation samples were prepared by the focused ion beam apparatus (FIB, FB-2000S: Hitachi).

3. Results and Discussions

Figure 2 showed SEM observation results of the surface of Cu–0.5Ti/CNTs composite powder after heat treatment at 873 K using Ar–H2 gas. Un-bundled CNTs existed on the powder surface of raw powder used in this experiment. The previous work showed that the surface layer of CNTs remained after heat treatment in hydrogen gas atmosphere, and Raman spectra also showed no change after heat treatment in hydrogen atmosphere. Therefore, it could be confirmed that CNTs subjected no thermal damage after heat treatment in this study.

Dependence of the tensile properties of hot extruded Cu–0.5Ti/CNTs composite on CNTs contents was shown in Fig. 3, where the result of P/M extruded pure copper was also shown. Cu–0.5Ti without CNTs had 308.3 MPa UTS, 202.1 MPa yield stress (YS) and 38.9% elongation. YS and UTS of extruded Cu–0.5Ti/CNTs decreased with increasing CNT contents compared to the monolithic Cu–0.5Ti alloy. In case of the conventional high strength copper alloys, the elongation was decreased with increasing the tensile strength by aging precipitation behavior of alloying elements. On the other hand, the elongation of Cu–0.5Ti/CNTs composites was over 30%. It was almost same as that of the monolithic Cu–0.5Ti alloy. Cu–0.5Ti with 0.19 mass% CNTs had 308.3 MPa UTS, 202.1 MPa YS and 38.9% elongation. Y of Cu–0.5Ti/0.19CNTs composite was 2 times as that of pure copper. The electrical conductivities of the monolithic Cu–0.5Ti and Cu–0.5Ti/CNTs composites were shown in Fig. 4. Monolithic Cu–0.5Ti had 42.5 IACS% almost same as Cu–0.5Ti materials by ingot metallurgy (I/M) (39.8 IACS%). This result showed that powder bonding of monolithic Cu–0.5Ti sintered material was strong and the effect of oxide films of primary particle boundaries on electrical conductivity...
was small. The electrical conductivities of Cu–0.5Ti/CNTs composites increased compared to the monolithic alloy. The electrical conductivity of Cu–0.5Ti with 0.19 mass% CNTs was 83.5 IACS%. It showed the highest electrical conductivity of all samples in this study. In general, an electrical conductivity of Cu/CNTs composite was not improved because of a low wettability between the matrix and CNTs. However, in this research, these materials used Cu–0.5Ti/CNTs powder had high strength and improved electrical conductivity.

Microstructural observation and analysis on the compositions of extruded Cu–0.5Ti/CNTs composite materials were carried out for investigation of their mechanical and electrical properties. Figure 5 showed the fractured surfaces of tensile test specimens. In the case of Cu–0.5Ti/CNTs composite alloy, CNTs were dispersed on the fracture surface, and bonded well with Cu–0.5Ti alloy matrix. It was considered that these CNTs reinforced Cu–0.5Ti matrix by the suitable bonding. On the other hand, the aggregation of CNTs existed in the matrix of Cu–0.5Ti with 0.34 mass% CNTs as shown in Fig. 5(b). It was considered that this aggregation of CNTs, which existed in the primary particle boundaries, reduced the powder bonding and included the air. As a result, the mechanical property and electrical conductivity decreased. SEM-EDS analysis on the monolithic Cu–0.5Ti and Cu–0.5Ti composite with CNTs were shown in Fig. 6. Table 1 showed titanium solid solution in the monolithic Cu–Ti and Cu–Ti with 0.19 mass% CNTs by WDS analysis. In case of the monolithic Cu–0.5Ti alloy Fig. 6(a), there was no titanium elements concentration around the primary particle boundaries. Solid solution of titanium in the monolithic Cu–0.5Ti alloy was detected as 0.224 mass% by WDS analysis. On the other hand, titanium was concentrated at primary particle boundaries in Cu–0.5Ti alloys with 0.19 mass% CNTs as shown in Fig. 6(b). The carbon elements were also detected in same area. The carbon was considered to be derived from CNTs. There was 0.026 mass% solid solution of titanium in the composite. The amount of solid solute Ti in Cu–0.5Ti alloy matrix with CNTs was about 10% of the amount of that without CNTs. Therefore, titanium elements were precipitated during the sintering, and then, they were diffused at the primary particle boundaries near CNTs. The defused titanium was remained at the primary particle boundaries during the cooling. It was considered that this concentrated titanium was affected for CNTs dispersed on fracture surface of tensile test specimen of Cu–0.5Ti/CNTs extruded material as shown Fig. 5.
Figure 7 showed TEM-EDS observation and point analysis results of extruded Cu-0.5Ti alloy with 0.19 mass% CNTs. Titanium was detected at the interface between copper alloy matrix and CNT. There were TiC and Cu$_4$Ti at the interface of CNT with Cu-0.5Ti matrix from TEM-EDS point analysis results. It means solid soluted titanium elements in Aggregation of CNTs.

(a-1) Cu-0.5Ti with 0.19 mass% CNTs (High magnification)  
(a-2) Cu-0.5Ti with 0.19 mass% CNTs (Low magnification)

(b) Cu-0.5Ti with 0.34 mass% CNTs

Fig. 5 Fractured surface of tensile test specimens Cu-0.5Ti/CNTs composites with (a) 0.19 mass% CNTs and (b) 0.34 mass% CNTs.

(a) Monolithic Cu-0.5Ti alloy  
(b) Cu-0.5Ti with 0.19 mass% CNTs

Fig. 6 SEM-EDS analysis on (a) monolithic Cu-0.5Ti and (b) Cu-0.5Ti/CNTs.

Table 1 Solid solute Ti in monolithic Cu-Ti and Cu-Ti with 0.19 mass% CNTs by WDS analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solid solute Ti in the matrix (mass%)</th>
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<tr>
<td>Cu-0.5Ti (monolithic alloy)</td>
<td>0.224</td>
</tr>
<tr>
<td>Cu-0.5Ti with 0.19 mass% CNTs</td>
<td>0.026</td>
</tr>
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</table>

Figure 7 showed TEM-EDS observation and point analysis results of extruded Cu-0.5Ti alloy with 0.19 mass% CNTs. Titanium was detected at the interface between copper alloy matrix and CNT. There were TiC and Cu$_4$Ti at the interface of CNT with Cu-0.5Ti matrix from TEM-EDS point analysis results. It means solid soluted titanium elements in
raw Cu–0.5Ti powder were precipitated as Cu–Ti compounds during the SPS sintering. The compounds were decomposed at 1223 K. 18) Gibbs free energy of Cu₄Ti at 1173 K is −11.3 kJ/mol [Ti],19) and that of TiC is −170.0 kJ/mol [Ti].20) Cu₄Ti was dissolved at 1158 K according to Cu–0.5Ti phase diagram. 18) It was considered that Cu–Ti compounds were decomposed during the sintering at 1223 K and TiC was produced via reaction between CNTs and Ti diffused forward the primary particle boundaries. CNTs and these compounds were dispersion strengthening factors of Cu–0.5Ti/CNTs composite materials because the interfacial bonding between CNTs and Cu–0.5Ti matrix was improved by formation of the above compounds. The electrical conductivity of copper matrix was increased because of decreasing the amount of solid solution of titanium in the matrix due to the formation of TiC.

Relationship between YS and electrical conductivity of Cu–X%Ti composite was shown in Fig. 8. The results of Cu–0.5Ti/0.19 mass% CNT was also shown in the same figure. In the case of Cu–X%Ti alloys, there was a trade-off balance between YS and electrical conductivity as same as the previous research. 3) The electrical conductivity decreased with increasing YS of Cu–X%Ti alloys. On the other hand, P/M Cu–0.5Ti/CNTs composite prepared in this study had higher strength and electrical conductivity compared with the Cu–X%Ti alloys.

4. Conclusions

The copper alloy composite with high strength and high electrical conductivity were developed by P/M process. The effect of titanium addition of the copper alloy composite with CNTs on characteristics was evaluated. The results were summarized as follows;

(1) Cu–0.5Ti/0.19 mass% CNTs composite alloy had 175.8 MPa YS. It was about 2 times as YS of pure copper. The electrical conductivity of Cu–0.5Ti/0.19 mass% CNTs composite alloy was 83.5 IACS%. The electrical conductivities of Cu–0.5Ti/CNTs composite alloys were increased compared to the monolithic Cu–0.5Ti alloy.

(2) In the case of Cu–0.5Ti/CNTs composite, CNTs were reacted with titanium alloying elements of the raw powder. The extruded Cu–0.5Ti/CNTs composite alloy had a high strength because of suitable bonding between copper matrix and CNTs by reaction of Ti with CNTs. The electrical conductivities of Cu–0.5Ti/CNTs alloy with CNTs increased with increasing CNTs contents. The electrical conductivity of copper matrix was increased because of decreasing the amount of solid solute titanium elements in the matrix by formation of TiC.

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<table>
<thead>
<tr>
<th>Point</th>
<th>C (at %)</th>
<th>Ti (at %)</th>
<th>Cu (at %)</th>
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