Fabrication of W/Cu FGM By Aqueous Tape Casting

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Abstract. Tungsten Copper-based metals (W/Cu) were extensively used as electrical contact materials in switching systems for the electric power industry. In this paper, a novel investigation to prepare Tungsten Copper-based metal composite materials according to functionally graded material (FGM) concept and the method of tape casting was reported. Cu-coated W powders with different Cu weight fraction were synthesized via electricless plain in methanol-water solvent. The green tapes with different composition and thickness were laminated and then sintered to prepare W-Cu functionally graded materials. XRD, EDS, SEM and metallographic analyses were used to characterize the material microstructure and combination between different layers. The results showed that the Cu-coated W powders had grate compressibility leading to wettability of powders. The parallelism and flatness of intermediate layer were good and the combination was tight.

1. Introduction

Electrical contact material in a variety of electrical applications was very important. Because of high strength and high conductivity coupled with low thermal expansion coefficient, W-Cu alloys had been widely used in the field of power engineering and plasma technology, such as contact materials for medium and high voltage interrupters as well as welding electrode [1, 2]. However, the fabrication of W-Cu composites proved to be difficult due to their mutual insolubility of W and Cu, in addition the high melting temperature of W (3410 °C) compared to that of Cu (1083 °C) [3, 4]. Traditional powder metallurgy (PM) technology often resulted in drawbacks such as low densification, microstructure inhomogeneity and limited composition variation. In recent years, many investigations had been published to develop processing of W-Cu composites. It had been found that electrical properties of contact materials were strongly influenced by high purity, high relative sintered density and a fine homogeneous microstructure [5-13]. Actually, temperature and current distributions form the contact surface to bulk were non-uniform during a switch action, which implied that the electrical contact material should be inhomogeneous to match with such non-uniform property distributions [14]. Obviously, a contact material with ideal operating parameters was very difficult to fabricate by conventional manufacturing technique [15]. Functionally graded material (FGM) concept was suitable to prepare a good electrical contact material [16].

In this paper, A potential and possible method for W-Cu electric contact materials that were prepared by electricless plain technology, tape casting technology and vacuum heating-press sintering technology was reported, and some characteristics were investigated simply.
2. Experimental
In the tape casting process, powders, binders and plasticizers were dispersed in a solvent to form slurry. The slurry was layered onto a moving belt and passed beneath the blade edge that shaped the slurry into a green tape of steady thickness. When the solvents evaporated, the particles coalesce into a relatively dense, flexible dried tape. The dried tape was then cut to size for next process. After layers had been stacked, the multilayer was sintered.

However, the tape casting of metal matrix composites was in its early stages. Cu-coated W powders were synthesized via electricless plain. SEM (Fig.1a) examination revealed an irregular and polyhedral shape of the metal crystal with a clean and smooth surface of grains. The particles had a size distribution in the range of 6-20 μm approximately. The copper plating solution was composed of copper sulfate solution (0.08M CuSO₄ · 5H₂O, 0.24M C₆H₄O₆KNa · 4H₂O) and formaldehyde solution (20M HCHO, 30 wt.% NaOH). Plating was carried out at 40 °C in a container with magnetic stirring. During the reaction process, the pH value of the system was kept as a constant (11) by adding NaOH solution. After plating, the powder was washed with distilled water to remove chemical solutions. And then dried and weighed to ensure that the nominal value of Cu was deposited on W.

The binder conferred its mechanical strength to the tape by forming organic bridges into the tape during solvent evaporation. Polyvinyl alcohol (PVA1788) and a low boiling point were used as binder in the slurry preparation. The dispersant agent used was acrylic ammonium salt polymer enables to wet Cu-coated W powders and leaded to a good dispersion of the powders in the slurry by developing repulsive forces between particles. Glycerin was used as the plasticizer enabled to make the tape more flexible by decreasing the glass transition temperature of the PVA skeleton.

After formulation, the slurry was mixed 12 hours at 20 rpm using planetary milling. Once been homogenized, the mixture was degassed 5 minutes and then directly layered onto a Mylar silicon film using two motorized doctor blade at the desired thickness. After solvent evaporated at room temperature, the as-cast green tape could be cut to any desired shape. The Cu-coated W composite tape layer was then to be stacked and the sample was sintered by vacuum heating-press sintering at 930°C, 60 MPa. The powders, the tapes and the sintered samples were characterized by SEM, XRD, EDS.

3. Results and discussion
Tungsten powders were coated with copper by electroless plating method using formaldehyde solution as a reducing agent. The Cu layer covering a W particle was controlled by the content of CuSO₄·5H₂O. The Cu-precipitation is proceeding according to the following reaction:

\[
\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \rightarrow \text{Cu}^{0} + \text{H}_2 + 2\text{H}_2\text{O} + 2\text{HCO}_2^-. 
\]
The surface and cross-section (SEM) micrographs of the investigated powders of Cu-coated W powder are shown in Fig.1b and d, respectively. It is evident that the surface of the W particle is coated with a layer of tiny copper. The deposited Cu-coating layers consisted of particles with dome clusters or egg-shaped tops [17]. The Cu-coated W particles of Cu-loading are analyzed using EDS. Spectra of both W and Cu were in evidence, as illustrated in Fig.1b and c.

Fig.2 shows SEM images of the surface of green tapes. It can be seen that the particle distribution in slurry is very uniform, but there are many small uniform holes, which are mainly caused by evaporation of the solvent.

Because of a high dihedral angle in the W-Cu system, the W-W network was retained, even after Cu melt formation and the resulting tungsten skeletal rigidity restricts capillary force induced densification [17-18]. On the other hand, the micrograph of coated composites shows in Fig.3, reveal that the Cu coating separated the tungsten particles, thereby greatly reducing the degree of contact between the tungsten particles, even though the Cu content is low. In case of coated composites, due to the existence of Cu-Cu contacts, their sintering before the onset of Cu liquid formation behave like homogeneous sintering system in which densification is obtained by volume and grain boundary diffusion mechanisms. Thus, a highly contiguous microstructure is expected. Tungsten coated with copper composites might have a reduced level of solid state sintering between W-W contacts, but more densification would occur by rearrangement. The microstructures of coated W-Cu composites
reveal homogeneous structure. The XRD result of W-Cu composites, only peaks related to copper and tungsten are seen and no compound between these two elements has been formed in Fig. 4.

**Figure 5.** Metallic phase microstructure analysis of W-Cu density graded materials with 40-100wt.%Cu.

**Figure 6.** Variation of the relative density of W-Cu composites with varying Cu-coated W weight fraction.

Fig. 5 shows a representative microstructure of a graded W/Cu composite. A one dimensional gradient ranging from Cu (left) to W (right) is clearly visible within a distance of about 1.4mm. The gradient is continuous and accompanied by an increase in the size of W dark areas. The parallelism and flatness of intermediate layer are good and the combination is tight. The interface diffusion of different layers is obvious. The relative densities of the final W-Cu samples could achieve to 96.2%-99.3% as Cu weight fraction varying from 40 wt. % to 100 wt. % as shown in Fig. 6.

4. Conclusions

(1) W-Cu composition powder with core-shell structure was successfully prepared by electricless plain. Only two spectra of both W and Cu were fond by using EDS. Cu was highly dispersed throughout the whole W.

(2) The green tapes of W-Cu composition had a smooth surface and homogenous structure.

(3) The individual compositions were fabricated into monolithic tapes for characterization by laminating multiple layers together, hot-pressing to nearly-full density. The excellent planarity and parallelism between the layers were separated from each other by clearly defined interfaces, indicating that the initial design could be kept stable.

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