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The preparation of dendrite- and needle-shaped alloy particles coated on copper powders by polyvinylpyrrolidone in displacement reaction and thermal conductivity on composites' characterization

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ABSTRACT

This study focused on the preparation of dendrite- and needle-shaped alloy particles coated on the surface of copper powders by different molecular weights of polyvinylpyrrolidone (PVP)—namely, 3500, 8000, 10,000, 55,000 and 360,000—in displacement reaction and the thermal conductivity on composites' characterization. The structure, size, and morphology of the particles were investigated using scanning electron microscopy (SEM). The EDX demonstrated that the alloy particles simultaneously have different ratios of copper (Cu) and silver (Ag) elements for dendrite-shaped and needle-shaped alloy particles. The 15% of PVP with a molecular weight of 8000 g/mol formed the largest dendritic-shaped Ag–Cu alloy particle, with an average width of 3 ± 1 μm, in which 60% of Ag–Cu alloy particles included resin to enhance composites with the largest thermal conductivity at 0.5956 W/(m K).

1. Introduction

Dendritic-shaped silver particles have been widely applied in amperometric sensing of nitrite [1] and hydrogen peroxide [2], biosensors [3], and superhydrophobic films [4] as well as for surface-enhanced Raman scattering (SERS) substrate for sensing analytes [5]. Several methods have been used in recent years for the preparation of dendritic silver structures, such as displacement reaction [6], galvanic displacement reaction [7,8], microwave irradiation [9], ultraviolet irradiation [10,11], electrodeposition [12], polyol process [13], tetrathiafulvalene-assisted formation [14], electrochemical [15], photocatalytic reduction [5], and biomineralization [3]. A displacement reaction is a simple, cost-effective, fast, and versatile strategy for synthesizing silver particle, which uses metal materials such as copper foils [6], copper powder [16], magnesium powder [17], iron plates [18], Zn particles [19], and zinc plates [20]. As the standard reduction potential of these metal materials (M) were lower than silver (Ag), these metals oxidize more easily than silver. The electron transfer reaction from a lower reduction potential of metal materials to silver is a simple reduction–oxidation reaction of $M + 2Ag^{+} \rightarrow M^{2+} + 2Ag$.

In this study, the dendritic-shaped and needle-shaped Ag–Cu alloy particles coated on the surface of copper powders simultaneously with or without the addition of polyvinylpyrrolidone (PVP) generated different results that Zhao et al.'s [16] copper powders coated by irregular-shaped columnar nanostructured silver films due to the displacement of the reaction in an aqueous system with PVP and citric acid at room temperature. In addition, the PVP is usually used as a protecting agent in silver nitrate and ethylene glycol solution as the N and O in the polar groups have a strong affinity for silver ions and silver nanoparticles using the polyol method to control the morphologies and sizes of silver nanostructures [21]. We found only few studies that investigates PVP use for displacement reaction. Only Khanna et al. [22] studied the PVP-coated silver nanopowder via displacement reaction, and Nishino and Kanno [23] studied the dendrite-shaped silver obtained by ionic exchange from fine copper particles on acrylic plastic plate in the 0.1 μM of PVP's molecular weight (MW) 40,000 and 0.1 M of $AgNO_3$ aqueous solutions on displacement reaction at 25 °C for 24 h, which only formed a few silver dendrites. To date, this study has focused on how different MW of PVP influence the formation of the dendrite-shaped and needle-shaped alloy particles coated on copper particles in the displacement reaction. This study investigates which MW and PVP content can prepare larger dendrite-shaped or needle-shaped particles in order to apply such content to increase the thermal conductivity of composites, which is a different approach from many previous studies as most research has used PVP to prepare metal nanoparticles. In addition, this study used displacement reactions to form and shape

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the components of particles coated on copper particles, which also differs from the results of previous research. No study has yet investigated the different MW of PVP influences on the formation of particles in the displacement reaction. Thus, the current study used commercial Cu powders as the sacrificial metal to react with a silver nitrate ($AgNO_3$) solution and different MW of PVP as capping agents. The different MW and concentration of PVP in the morphological control of dendrite-shaped alloy particle structures coated on copper powders and thermal conductivity of composites are discussed in detail.

2. Experimentation

2.1. Materials

The 99% copper powder (Cu) provided by Alfa Aesar, USA, was an average size at 45 μm (325 mesh). The silver nitrate ($AgNO_3$) was supplied by Hwang Long Co., Ltd., Tainan, in Taiwan. The MW 3500 and 8000 of polyvinylpyrrolidone (PVP) were purchased from Acros Organics, and the 10,000, 55,000, and 360,000 MW were purchased from Sigma–Aldrich.

2.2. Synthesis of particles

For purification, the Cu powders were dispersed in 1 M of acetic acid (SHOWA) and vibrated by the ultrasonic oscillator for 30 min at room temperature. The copper powders were subsequently filtered and washed with distilled water to remove the acetic acid with a pH of 6–7 solution after which it was dried at 120 °C for 10 h. The 100 mL of 0.06 M $AgNO_3$ solution was mixed with 5 g of purification Cu powders and 15% of different MW of PVP or PVP of 8000 for various content using a magnetic stirrer for 30 min at room temperature, respectively, then dried in a vacuum oven at 100 °C for 6 h to remove the water from the particles.

2.3. Preparation of composites

The composites based on epoxy resin were prepared by mixing the 60 wt% of particles with the resin (bisphenol-A, GY 260, Araldite, Taipei, Taiwan) and hardener (HY 956, Araldite, Taipei, Taiwan) at a ratio of 10:1 by weight. After being mixed, the composites were placed in a 70 mm diameter pan and cured for 2 h at 120 °C.

2.4. Characteristics of alloy particles

The X-ray diffraction (XRD) pattern of Cu powder and particles prepared were obtained using a Rigaku TTRAX III rotating anode diffractometer with a Ni-filtered Cu Kα radiation source (Tokyo, Japan). The phases were identified using files acquired from the Joint Committee on Powder Diffraction Standards (ICCD). Analyses of the surface morphologies of the particles were conducted using scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX) with electron dispersion spectroscopy characterization using a JEOL JED 2300 instrument (Tokyo, Japan).

3. Results and discussion

3.1. Characteristics of particles by displacement reaction

Fig. 1(a and b) and (c and d) show SEM images of particles coated on copper powders subjected to displacement reaction for

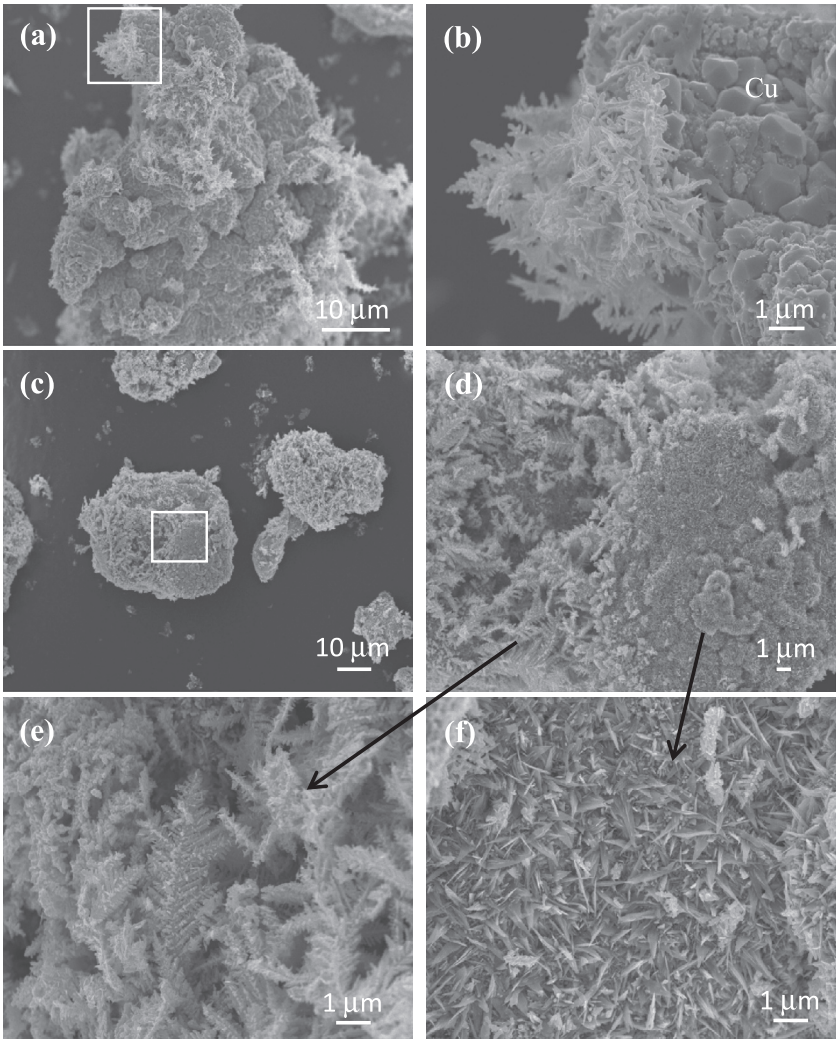

Fig. 1. SEM images of particles prepared for different reaction times: (a and b) 10 min, (c and d) 30 min, (e) dendritic-shaped particles, and (f) needle-shaped particles.