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Microstructural and mechanical characteristics of Cu–Cu_2O composites compacted with pulsed electric current sintering and hot isostatic pressing

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ABSTRACT

This paper reports the influence of applied sintering process – pulsed electric current sintering (PECS) and hot isostatic pressing (HIP) – on the microstructure and mechanical properties of Cu–Cu_2O composites. In PECS fine-grained structure was obtained while in HIPing the grain growth was more noticeable, mostly due to the longer process time. The studies also showed that Cu_2O-phase distributed in Cu-matrix increased microhardness; at a fixed grains size Cu–Cu_2O structure had higher hardness than Cu so that 20% higher microhardness was obtained when Cu_2O was doubled from 19.1 to 37.2 vol%. At best, 99.1% density with 690 nm grain size and 1.35 GPa hardness were achieved by PECS whereas by HIP the same density with 1860 nm grain size gave 1.02 GPa hardness. The grain growth and the effect of second phase clustering on the grain growth were evaluated experimentally.

1. Introduction

Sintering is a thermal treatment for bonding particles into a predominantly solid structure via mass transport events. Most powder materials exhibit sintering at temperatures above one half of the melting point [1]. The driving force of sintering is the excess surface free energy available in the materials. There are several ways to enhance sintering either by altering the kinetics or driving force. The aim is nevertheless to reduce sintering time or sintering temperature without compromising the degree of densification [1]. The particle size of the powder and the process parameters have a considerable influence on the consolidation, densification and grain growth during the sintering process [2–4]. Most of the conventional methods of consolidation result in significant growth of the grain structure, and the desired benefits of fine-grained structure on material properties are not obtained [5]. To circumvent this, the non-conventional consolidation methods utilize high sintering speed, short sintering time and low temperature resulting in improvements in mechanical properties of the products due to the limited grain growth [5–9].

When small grain size is crucial, the precipitation hardening can be regarded as one of the possible limiting factors for the grain growth. Finely distributed particles can act as obstacles and barriers against moving dislocations inducing internal stresses that raise the hardness value [10–13]. Oxygen in copper has been suggested to contribute to these strengthening effects. Biro et al. [13] and Nieh et al. [14] have suggested oxygen to induce solid solution strengthening of copper. More recently Prasad and Rao [15,16] suggested that Cu_2O particles can pin down the grain boundaries and prevent dynamic recrystallization during hot compaction. Moreover, García et al. [10,17] observed increase of hardness as a result of the fine Cu_2O precipitates produced during hot compression of 99.9% pure copper. *In situ* formation of nano-scale Cu–Cu_2O composites was studied by Wu et al. [18]. They showed that the composite with 100–300 nm and some nano-scale Cu_2O significantly improved the hardness compared to pure copper; the hardness of Cu – 3 wt.% Cu_2O being 1.72 GPa (175 HV) whereas the corresponding value for copper was 1.04 GPa (106 HV).

In this paper two methods, namely hot isostatic pressing (HIP) and pulsed electric current sintering (PECS), are utilized. The conventional HIPing is a highly developed powder metallurgical (PM) method in which the main idea is to apply isostatic pressure to a heated component to induce plastic deformation and creep at particle–particle contact [2,3]. For the micrometer sized copper powders the process parameters of HIPing have been widely studied and modeled [2–4,19–21]. Song et al. [19] studied densification of the 15 μm copper powder and attained slightly better hardness than 0.78 GPa (80 HV) and densities of 99% and 98% of theoretical density (T.D.) with process parameters of 873 K – 50 MPa – 20 min and 773 K – 50 MPa – 60 min, correspondingly. Pavlov et al. [21] attained full density by HIPing electrolytic copper at 1123 K under 100 MPa for 30 min. Newman [2] and Meyer et al. [3] have simulated HIPing with 10 μm sized powder and showed that the

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expected grain size would be around 130–250 μm. Even though several authors have studied the suitable HIPing parameters for proper densification of copper [2,3,19–24], only few have evaluated the grain growth during processing [2,3] or hipping of Cu_2O containing copper [25,26]. The US Patent 6,909,185 [26] introduces a composite and its applications for a material containing copper and cuprous oxide (Cu_2O). HIPing was one of the processing methods specified with the process parameters of 3 h at 1073–1323 K.

Pulsed electric current sintering (PECS), also known as spark plasma sintering (SPS), utilizes pulsed high direct current (DC) and uniaxial pressure for compacting powders [27]. The pulsed current generates Joule heat in the die and powder allowing very high heating rates. It also provides a possibility to lower sintering temperatures to minimize grain growth [27,28]. PECS has been studied for compacting nano- and micronsized copper powders in [7–9,25,29,30]. In brief, Zhang et al. [7,8,30] obtained avg. 2200 nm grain size and density greater than 96% of T.D. using micronsized Cu powders, while using nanosized copper powder they obtained density >99% of T.D. [9]. In contrast to many reports about using PECS for compacting copper composites and alloys, the PECS of submicron sized copper powder is rare and only one study [31] on PECS compacting of Cu powder (60–100 nm) to prepare Cu–Cu_2O composites exists. The starting powder contained some Cu_2O and additional formation during process was related to absence of reducing atmosphere. Also, when processed at low temperature Cu_2O was submicron sized and evenly distributed, whereas at higher temperatures the grain size grew and distribution became more uneven. The hardness of the compacts was 1.69 GPa (723 K), 1.17 GPa (873 K) and 0.56 GPa (1173 K).

The ultra-fine grained (UFG) copper is an interesting material due to its exceptional mechanical properties such as high strength, ductility, toughness, and hardness [5,7,32–34]. On the other hand, Cu_2O has semiconductive [18,26,35] and optical properties [35], high hardness [26] and low thermal expansion [26,31,36]. Thus, Cu–Cu_2O composites having a combination of both the constituents make good candidates for applications in the area of electrical and electronic industries [18], semiconductor [26] and optoelectronic devices [35] as well as in applications where good conductivity together with low thermal expansion is needed [26,31]. One of the main questions in processing are how to preserve the fine structure of the powder in the final product and what are the properties of the obtained bulk material. In HIPing of copper process times required for full density are in the order of hours [2,3,20,22,26], whereas the process times in PECS technique are on the order of minutes [7,9,25–29].

In the present study the two compaction methods, PECS and HIP, are compared for processing Cu–Cu_2O composites. In particular, the focus is on the grain growth during processing, grain size control by the distributed Cu_2O second-phase, the influence of Cu_2O clustering both experimentally and theoretically [37,38] and the resulting mechanical properties. Thermal stability of the composites is dealt in more details in [39].

2. Experimental procedures

The copper powder used was a commercial −625 mesh powder (99%) from MKnano (a division of M.K. Impex Canada) having a nominal average particle size between 0.50 and 1.5 μm. According to the image analysis on a set of SEM micrographs the average particle size was measured to be approximately 410 nm, most of the particles being smaller than 800 nm [25]. Since the powder was not stored or handled in a shielding atmosphere, oxidation was expected [31] and the actual starting powder was a Cu–Cu_2O composite powder. This was confirmed with the θ–2θ XRD (Philips PW3830) measurements by verifying the peaks of Cu_2O [25]. In the first set of experiments Cu powder with 2 wt.% Cu_2O (2.9 vol%) was used (PECS 1, 2, 4 and HIP 2), whereas for HIP 1 the amount of Cu_2O in starting powder was 16 wt.% (21.8 vol%) and for HIP 3 and PECS 3 it was 28 wt.% (36.2 vol%).

2.1. Pulsed electric current sintering

PECS compaction was carried out with the FCT HP D 25-2-type equipment in 7 Pa vacuum. The specimen size was Φ 20 mm × 4 mm obtained by inserting about 12 g of powder into the 20 mm diameter graphite mold. When mounting the mold construction, graphite foils were placed between the powder and the mold in order to shield the mold from the powder. After loading the powder to the mold the mold was placed to the processing chamber, which was then closed and vacuumed. The pressure was applied at the beginning of the processing cycle, except in the "100 ramp" cycle, where the pressure was increased to 100 MPa during the heating step. Heating was performed at a rate of 75 K/min. During the sintering, the process temperature was measured with a pyrometer through a borehole in the punch. Sintering experiments were carried out at three temperatures i.e. at 873, 973, and 1073 K, holding times being 6, 3, and 1 min, respectively. Then a cooling stage of 4 min took place and the chamber was opened after flooding it with inert gas.

2.2. Hot isostatic pressing

For comparison, three compacts were made by hot isostatic pressing (HIP) using a laboratory size HIP unit (ABB Autoclave systems Inc MiniHIP). The starting powder was sealed to seamless stainless steel tubes for vacuuming and processing. In the beginning of HIPing, the tubes were heated at a rate of 13 K/min. Isostatic pressure of 100 MPa with the argon gas atmosphere was applied and kept constant during the process. HIPing was performed at 948 K for 30 min (Sample HIP 1) and at 1073 K for 30 min (Sample HIP 2) or for 120 min (Sample HIP 3). A summary of the samples and PECS and HIP parameters are shown in Table 1.

2.3. Sample preparation and characterization

After compaction the PECS mold construction was opened and the graphite foils were removed from the sample surface with sand blasting. The HIP samples were cut out from the steel container with a diamond saw. Then the samples were wet ground with silicon carbide papers to 1200 mesh. The relative bulk density measurements were performed using the Archimedes method (Sartorius CPA224S, 0.1 mg). The samples were then further polished by using 1 μm diamond paste with ethanol as the lubricant. After polishing, the Vickers hardness was measured with Zwick & Co. KG "Z323" hardness tester at the load of 9.81 N as the average of five HV1 values, which was then converted to GPa. The oxygen content of the samples was measured with TC-436 DR oxygen analyzer. The value obtained was used to calculate the exact amount of Cu_2O in each sample. Theoretical densities (T.D.) of the samples were calculated by taking into account the presence of Cu_2O and using densities of 8.96 g/cm^3 for copper [10] and 6.14 g/cm^3 for cuprite [40]. The mechanically polished samples were further electrically polished and etched for 30 s in 65% nitric acid – ethanol to reveal the grain boundaries. The overall grain size of each compacted Cu–Cu_2O sample was evaluated from ten SEM micrographs (Hitachi FE-SEM S-4700). Micrographs were analysed carefully using the line analysis method as well as the ImageJ image-analysis to reveal grain size of Cu and to clarify the distribution, amount and size of Cu_2O. Evaluation of the chemical and phase composition was carried out with the SEM-EDS microanalysis and XRD, correspondingly.