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Spark plasma sintering and hydrogen pre-annealing of copper nanopowder

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ABSTRACT

Copper nanopowders were sintered using Spark Plasma Sintering (SPS). Special attention was paid to the presence of natural surface oxide and reductive thermal treatments under H_2 atmosphere were carried out to remove it. The sintering mechanisms were investigated by the means of disrupted experiments at various temperatures to reach different shrinkage rates. Optimized experiments were also carried out to reach a maximum densification. The samples were characterized and compared using density measurement, X-ray diffraction, mechanical tests (tension and compression) and analysis of the fracture surfaces with scanning electron microscope. On the one hand, it results that during the SPS treatment, the raw powder undergoes a series of oxide transformations from CuO to Cu_2O. On the other hand, reductive treatment drastically decreases the sintering temperature, from 650 °C to 260 °C, to reach 90% density without grain growth. Higher mechanical strength, up to 750 MPa, also shows better consolidation.

1. Introduction

Copper alloys are competitive materials for electrical applications in electronics and electro-techniques domestics and industrials devices. However, nowadays these alloys meet the key issue of energy saving (that is reducing energy loss), in particular when high strength is necessary. So far, increasing strength is obtained either by solution or precipitation hardening, leading in both cases to a severe degradation of electrical conductivity. For example, solid solution of Sn or Zn produces yield strength in the range of 500 MPa. Precipitation of Be gives an extremely high yield strength of 1200 MPa, but in both cases, electrical conductivity is a mere 20% of the international annealed copper standard (IACS) [1,2]. Also, combination of grain refinement and very fine precipitation of chromium, produced by high pressure torsion, leads to high strength and conductivity [3]. An alternative to conventional alloying would be an appropriate copper grains refinement particularly well suited for small devices (active connections, micro coils etc.) [4].

Metals, alloys and composites with small grain size have been the subject of very intense studies for about three decades. In particular, they show high potential due to their tremendous mechanical properties [5–7]. Among widely used and popular techniques to obtain fine grains materials, one find the grain refinement of bulk specimens by severe plastic deformation [8,9] and the assembling of nanostructured particles or nanoparticles using various sintering techniques [10].

In this article we report on the sintering of copper nanopowders using the so-called Spark Plasma Sintering technique (SPS). The SPS tends to be intensively used for its short time processing [11] limiting grain growth for ceramic [12] and metallic [13,14] materials. For ceramic materials, the sintering mechanisms are quite well understood. This is not the case for metallic powders, since electric current that goes through the specimen, can cause specific effects such as electro and thermo migration [15,16]. Consequently, metallic materials prepared by SPS can show specific microstructures [17,18].

Our approach is based on the analysis of the microstructure evolutions at various stages of the SPS processing of a copper powder with initial particles size of about 50 nm. The natural sintering of this particular nanopowder was studied beforehand [19] and used as reference work for the present paper. We paid particular attention to the effect of the natural oxide layer on the behavior and propose a pre-annealing treatment under H_2 to improve the quality of the produced nanostructured copper material. Structural, morphological and mechanical (tension and compression) characterization have been used in this respect.

2. Experimental

Copper nanopowder was synthesized by a cryogenic melting technique [19]. An ingot of pure copper (about 50 g) is over-heated

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above the melting point (to about 1700 °C) and levitated by r.f. induction in a quartz tube filled with liquid nitrogen. The conditions lead to a high rate of copper vapor formation (1 g min^{-1}) rapidly quenched in the liquid N_2, eventually producing a continuous formation of the nanopowder. Thermal treatment was carried out on the loose powder under pure hydrogen flow to reduce the surface oxide. The heating rate of 1 °C min^{-1} was applied until 150 °C, which is the temperature just before the beginning of sintering [20].

SPS experiments were conducted under vacuum using a Dr. Sinter 515S Syntex machine. The copper powder (typical batch of 0.9 g) is inserted into a graphite die (8 mm in diameter) coated with Papyex (graphite paper). Preliminary experiments were performed at a heating rate of 50 °C min^{-1} up to 650 °C for both the raw and H_2 pre-annealed powders, allowing determining eventual events related to phase or/and structural change. 650 °C is about 2/3 of the melting point of copper (T_m=1085 °C) and corresponds to temperature range where sintering is controlled by volume diffusion for micron size powders ($>(T_m+273)/2$). Depending on these preliminary experiments, series of experiments were carried out to maximum temperatures from 120 °C to 650 °C for the raw powder and from 75 °C to 260 °C for H_2 annealed powder. These temperatures were set to obtain 25%, 50%, 75% and 100% of the maximum shrinkage.

After sintering, the density of the four pellets was determined by the Archimedean method. Structure and oxidation of the powders and pellets were examined by X-ray diffraction, using a Bruker D8 (Cu Kα radiation) in Bragg–Brentano configuration equipped with monochromator and fast detector. Pellets were then fractured for observations of the sintered microstructure using scanning electron microscopy (SEM FEG, LEO 1530), in particular for the evaluation of the grain size and the degree of sintering (the level of consolidation or particles welding). In addition, the sintering efficiency was assessed by mechanical investigation, also allowing first evaluation of the strength of the sintered parts. Experiments were carried out in compression with a MTS 20/M machine (maximum load 100 kN) and in quasistatic conditions, at a strain rate of 10^{-3} s^{-1}.

In addition to these experiments, H_2 pre-annealed samples were also SPS treated to reach maximum densification. These samples were sintered under compaction pressure of 100 MPa with heating rate of 50 °C min^{-1} up to 250 °C. 3 mm thick specimen was obtained in a Ø8 mm and 2 mm thick in Ø20 mm graphite die. From 8 mm die samples, specimens were cut off perpendicular to the sintering compression axis in parallelepiped shape with length of 7 mm and width of 2 mm and polished for compression tests. From 20 mm die samples, specimens were spark-eroded and shaped into dog-bone shape with length of 20 mm, a processing zone of length 10 mm and width 2 mm for tensile tests. Experiments were carried out with strain rate ($\dot{\varepsilon}$) comprised between 5×10^{-5} s^{-1} to 5×10^{-4} s^{-1}. Strain was measured from crosshead displacement and true strain was calculated with relevant correction of machine rigidity.

3. Results and discussion

3.1. Initial powder characterization

The copper nanopowder production process is characterized by an extremely high rate of nucleation and a low rate of particles coalescence. The particles have steady spherical shape and are partially aggregated. Their size-distribution follows a log-normal function with a maximum at 35 nm and standard deviation of about 15 nm [19,20]. After formation, the particles are passivated with formation of an initial cuprite Cu_2O layer [19,20], which eventually turns to tenorite CuO as presented in the XRD pattern of the initial powder (Fig. 1a). This initial pattern with copper and tenorite is analyzed following the Rietveld refinement method that

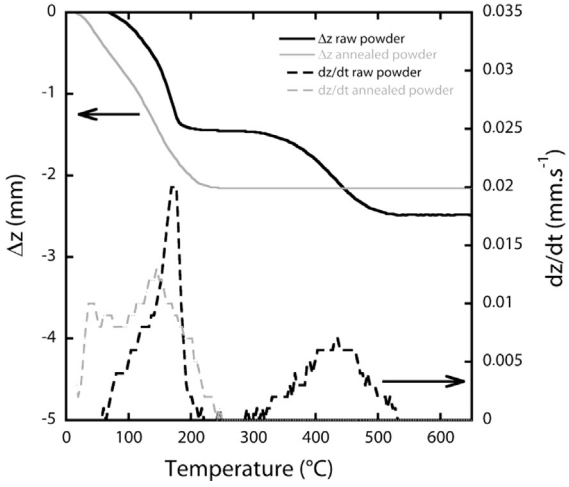

Fig. 2. Shrinkage Δz (bold curves) and its first derivative dz/dT (dotted curves) of the SPS experiment on the raw powder (in black) and on the H_2 annealed powder (in grey).

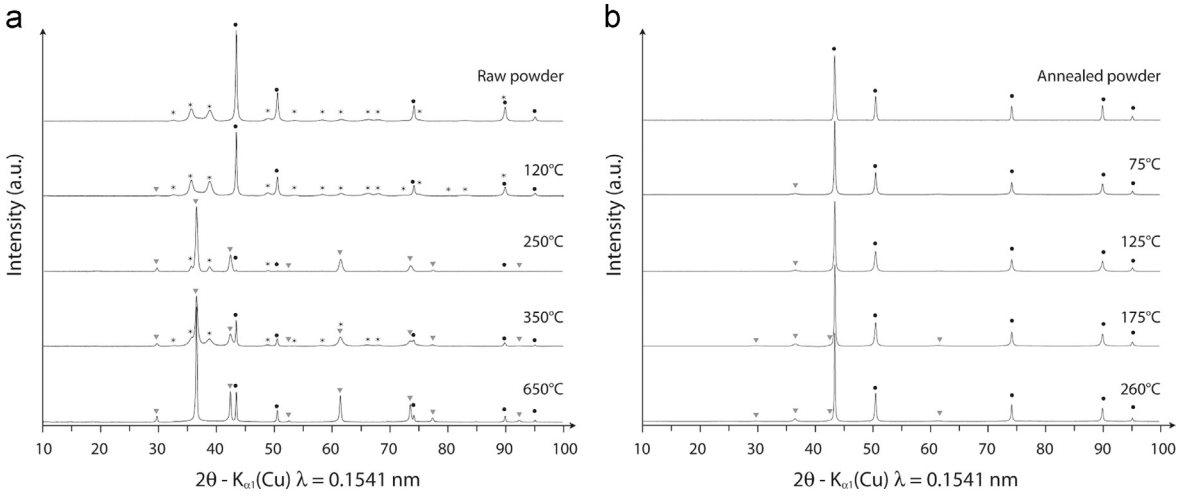

Fig. 1. XRD patterns of (a) raw powder and sintered pellets at 120, 250, 350 and 650 °C and (b) H_2 annealed powder and 75, 125, 175 and 260 °C. The copper phase (PDF no. 004-0836) is identified with •, the tenorite phase CuO (PDF n°048-1548) is identified with * and the cuprite phase Cu_2O (PDF n°005-0667) is identified with ▾.