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A study of microstructure and hardness of bulk copper sample obtained by consolidating nanocrystalline powders using plasma pressure compaction

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Abstract

Bulk copper samples were prepared by consolidating ultrafine-grained copper powders using the technique of Plasma Pressure Compaction. The microstructure and hardness are compared with a sample made from consolidating micron-sized powders using identical processing conditions. Samples made by consolidating nanometer powders revealed evidence of grain coarsening and a higher density than the sample made from consolidating micron-sized powders. Both nanohardness and microhardness measurements revealed an increase in hardness of the bulk sample obtained by consolidating the smaller sized powders. Influence of powder particle size and processing variables on microstructure, to include the presence and distribution of artifacts, density, and microhardness are discussed.

Keywords: Microhardness; Microstructure; Ultrafine-grained materials

1. Introduction

Ultrafine grained materials have spurred considerable scientific attention and technological interest because the small grain size can result in notable improvements in mechanical, magnetic, optical and other physical properties. Several studies related to developing an understanding of the mechanical response of materials having smaller grain size has been limited by the difficulty associated in producing bulk samples. Resurgence of interest in understanding the mechanical behavior of ultrafine-grained metals and ceramics originates from the unique mechanical properties first observed for these materials prepared by the technique of inert gas condensation followed by in-situ consolidation [1–6]. Several other research studies, in the time period spanning the last two decades, have provided convincing evidence that the macroscopic features of ultrafine-grained (UFG) materials, having grain sizes in the range of nanometers [7–10], are substantially determined by the grain boundaries (GB). Materials having nanocrystalline structure maintain true polycrystallinity with crystal size of the order of few nanometers [8,10]. In such materials, the volume fraction of grain or interphase boundaries becomes comparable to volume fraction of the grain [11]. This research paper describes the results of a study on the microstructure and hardness of bulk samples of copper made by plasma pressure compaction of nanocrystalline copper powders. The results are related to intrinsic microstructural features that include porosity and other processing-related artifacts, and density. The mechanical properties are compared with a bulk sample obtained by consolidating 13 μm copper powders under identical processing conditions.

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2. Experimental procedures

2.1. Sample preparation

High purity copper nanopowders, with an average powder particle size of 100 nm, were procured from ULTRAM (Denver, CO, USA) and consolidated by the technique of Plasma Pressure Compaction (P^2C) [12,13]. In this processing technique, the copper nanopowders are poured into a graphite die without any additive or binder. Owing to the large surface area of the starting nanopowders only small amounts (by weight) of the powder could be accommodated in the die. The fine powders were compressed using graphite plungers. More powders were added in order to obtain a green body. A pressure of 40 MPa was applied to the powder compact through the graphite plungers. Direct application of DC voltage and an external pressure, for a time duration of 3 min, aids in accelerating densification of the material by inducing resistance heating and promoting plastic deformation at the inter-particle contact surfaces. The resistance heating causes the heat to be concentrated at the interparticle points of contact. This raises the local temperature and thus facilitates diffusion. Since powder consolidation occurs at a high current density (approximately 1440 A/cm^2), the resultant I^2RT product (known as 'Joule Heat') is large. This results in locally high temperatures causing the heating rates to reach as high as 500°C/min. Normally, the current does not flow through the green compact immediately upon application of the DC voltage. This is because an effective current path has still not been established. On the other hand the current is expected to flow through the powder particle contact zones, which are the paths of least resistance. The consolidated samples measured 25 mm in diameter and 13 mm in thickness. Using identical principle, bulk samples were made by consolidating 13 μm size copper powders acquired from Atlantic Equipment Engineers (Bergenfield, NJ, USA). A schematic of the plasma pressure consolidation equipment is shown in Fig. 1. The process variables are summarized in Table 1. Precise density measurement, based on Archimedes' principle according to ASTM standard B328-94, was made on the consolidated bulk copper sample [14].

2.2. Microstructural characterization and indentation testing

The as-consolidated samples were prepared for examination, in the optical and scanning electron microscopes, to identify possible microscopic defects that influence mechanical behavior. The samples were prepared in accordance with standard procedures for metallographic examination. The polished samples were chemically etched using a solution mixture of potassium dichromate, sulfuric acid and distilled water. The etched samples were observed in an optical microscope and photographed using standard bright-field illumination. The polished and etched samples were also examined in a scanning electron microscope (SEM) to determine the morphology of surface cracks, size and morphology of grains, and distribution of processing-related artifacts.

Ultra low load indentations were performed on the samples using the Nanoindentation technique [15,16]. The Nano Indenter II at the High Temperature Materials Laboratory (HTML) at Oak Ridge National Laboratory (ORNL) (Nano Indenter is a registered trademark of Nano Instruments, Inc at Oak Ridge, TN, USA) has a displacement resolution of 0.16 nm and a load resolution of 0.3 μN. Indentations were made using a three-sided diamond pyramid Berkovich indenter [17]. The indenter has nearly the same area-to-depth ratio as the four-sided Vickers, which allows these hardness values to be directly compared [16]. The indentation experiments were performed using a load–time sequence as shown in Fig. 2. Indentation positions were individually located, using an optical microscope with a 1500× magnification, on the polished sample surface. The sample table with the highly accurate optical encoders enabled the indentations to be positioned well within the grain interior and away from grain boundaries and processing-related artifacts. The depth and rates of loading and unloading were programmed. Indentations were made at ten different locations on the sample surface to provide a good statistical sampling. On account of the softness of the material (copper) each indentation sequence was composed of an approach segment (Segment 1) to locate the surface. The sample was then loaded to a specified target depth during Segment 2 and held at that stage. The holding period was referred as Segment 3. Segment 4 was the unloading segment. In these sets of experiments, the

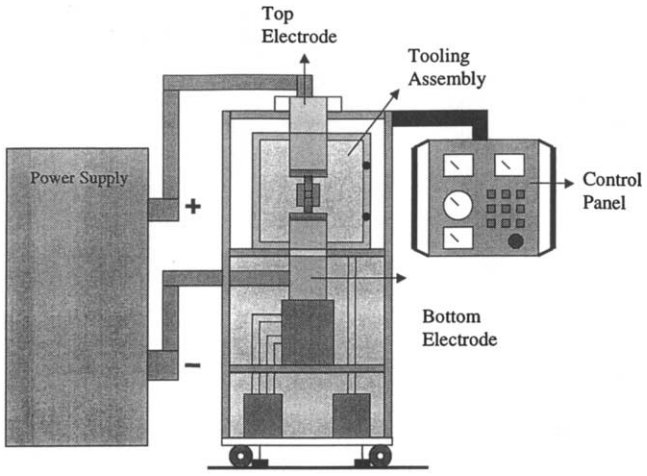

Fig. 1. A schematic of the plasma pressure consolidation (P^2C) set up.

Table 1
Summary of process conditions used and density of the bulk samples

Sample	Particle size	Process conditions			Density (%)
		Temperature (°C)	Time (min)	Pressure (MPa)	
#A	100 nm	880	3	40	99
#B	13 μm	900	5	40	95

indentation depth was fixed allowing the load to vary as a direct function of hardness rather than penetration depth as is the case of standard microhardness techniques. This procedure has the advantage of producing indents of constant size and depth and the indentation system has the ability to measure contact stiffness during indentation.

Using a Buehler Micromet II microhardness tester, Vickers microhardness (H_v) measurements on polished surfaces of the as-compacted sample(s) were made using a load of 50 g and a dwell time of 15 s at room temperature. Each hardness value represents the average of five such measurements and is reported as pressure in GPa.

3. Results and discussion

3.1. Initial microstructure

The microstructure of the consolidated samples in both the as-polished and polished plus etched conditions was imaged using (a) bright field illumination in an optical microscope at low magnifications, and (b) a scanning electron microscope at higher magnifications. Representative optical and scanning electron micrographs of the bulk samples made from 100 nm copper powders (referred to as SAMPLE A) and 13 μm copper powders (referred to as SAMPLE B) powder are shown in Figs. 3 and 4.

Scanning electron microscopy observations of the polished and etched surfaces of the as-compacted copper Sample #A revealed: (a) grain size ranging from 1 to 3 μm, with an average grain size of 2 μm (Fig. 3a), and (b) a near-uniform distribution of microporosity through the width of the sample (Fig. 3b). Since the pores were of irregular morphology, it is highly possible that a large proportion of the porosity originates from the rejection of entrapped gases, since gas porosity generally exhibits a near-spherical morphology. Bright field optical micrograph of Sample #B revealed a population of fine grains, of varying size and shape, having well defined grain boundaries (Fig. 4a). Scanning electron microscopy observations revealed the presence of fine irregular pores, of varying size, primarily at and along the grain boundaries and few near-spherical shaped pores related to gas porosity located well within the grain interior (Fig. 4b).

Presence of inter-particle regions in the green body compact is dependent on the conjoint and mutually interactive influences of powder particle size, powder particle shape and pressure experienced by the particles during consolidation. In the as-processed condition, the green compact consists of a random distribution of inter-particle contacts with a population of voids between the powder particles. The inter-particle contacts serve as potential sites for high local stress concentration. In pressure-assisted consolidation, even nominal low stresses are adequate enough to enhance the densification of copper powders due to the presence of local stress concentration. When the inter-particle contact is small, the effective stress at the contact is high and decreases as the contact grows in size. Flow of current through the green compact causes the inter-particle contact zone to be heated up faster than the interior of powder particle. Localized heating causes softening to occur at the inter-particle contacts. Concurrent application of an external pressure facilitates powder particle rearrangement and densification by promoting plastic deformation at all areas of inter-particle contact. Since the technique of P^2C relies on rapid consolidation (a fraction of total cycle time) and the isothermal holding time is only a few minutes, the energy (thermal plus mechanical) concentrated and available at the inter-particle regions may not be totally sufficient to facilitate complete particle contact. This results in the formation and presence of irregular shaped microscopic pores observed in Sample B. Rela-

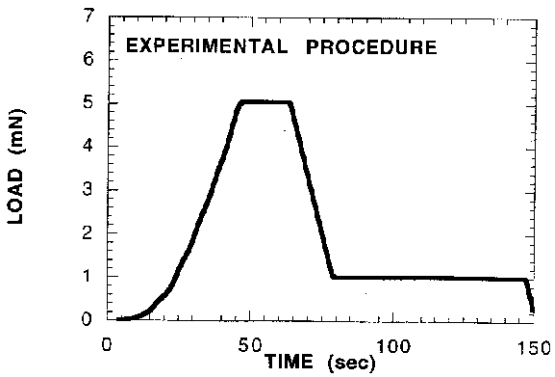

Fig. 2. A typical load–time sequence (peak load = 120 mN).

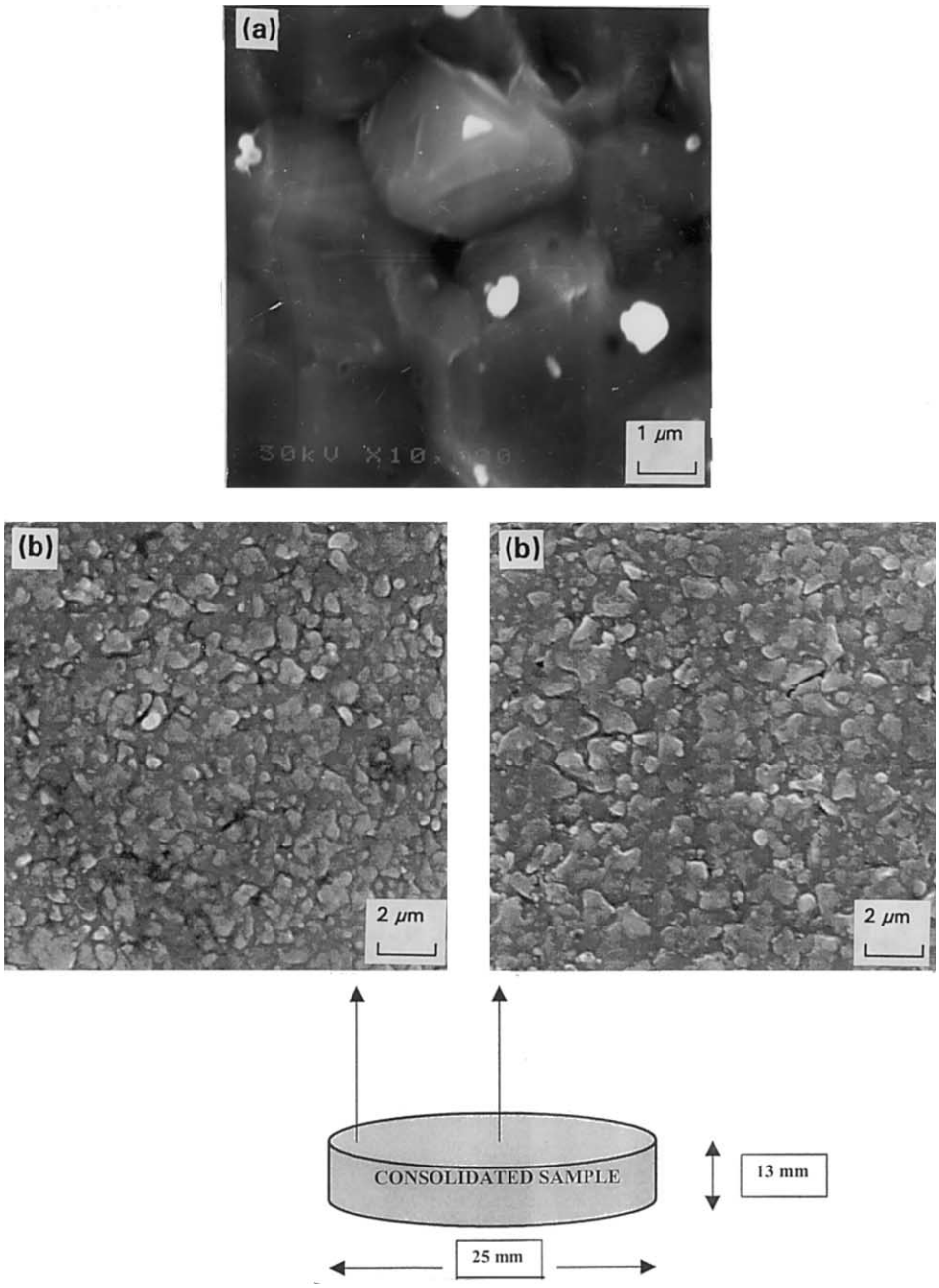

Fig. 3. (a) Scanning electron micrograph of polished and etched copper sample A showing the individual ultra-fine grains. (b) Scanning electron micrograph of the polished surface of Sample A (Consolidated at 40 MPa for 3 min at 880°C) showing uniform grain structure and near-uniform distribution of microporosity at both the center and edge of the sample.

tive densities of Sample A and Sample B are provided in Table 1.

3.2. Hardness

The indentation sites on these samples were chosen to be within the grain interior and away from grain boundaries and microscopic pores. There was minimum scatter in the hardness measurements. The overall hardness of Sample # A is 2.42 GPa, while that of Sample # B is 1.26 GPa. Results reveal a near two-fold increase in nanohardness with a decrease in powder size and are shown in the bar graph in Fig. 5a.

Microhardness measurements are summarized in Table 2. Since the samples were metallographically polished to perfect mirror finish to ensure smoothness the spatial variability was less pronounced in the as-compacted copper samples and the measured microhardness was observed to be near uniform throughout each as-compacted sample, indicating uniform density. The smooth surface facilitates in reducing the spread in measured hardness values.

The observed minimal variation in hardness measurement is a direct result of any one or combination of the following: (a) changes in load, (b) crystallographic orientation, (c) porosity, and (d) depth of penetration [18,19]. Microhardness measurements provide the net effect of strengthening from nanocrystalline grain size and the weakening effect resulting from the presence of processing-related artifacts. It is difficult to assess the exact magnitude of strengthening contributions from small grain size independent of the weakening effects. The fine microscopic pores, microscopic cracks and shallow voids, when intercepted by the pyramidal indenter, will result in a net decrease in the measured hardness below the hardness of the grain boundaries. Sample B, obtained by consolidating the 13-μm powders, has a density of 95% and a microhardness of 0.52 GPa. Sample A, obtained from consolidating 100 nm powders, has a density of 99% and microhardness of 1.88 GPa. The Sample A exhibited a near four-fold increase in microhardness when compared to Sample B (Fig. 5b). The increased microhardness of the nanocrystalline copper sample can be ascribed to a restriction of dislocation generation and mobility imposed by the ultrafine grain size. The presence of a minimal number of dislocations in each grain results in strengthening interactions and is exacerbated by the grain boundaries since their relative volume is large.

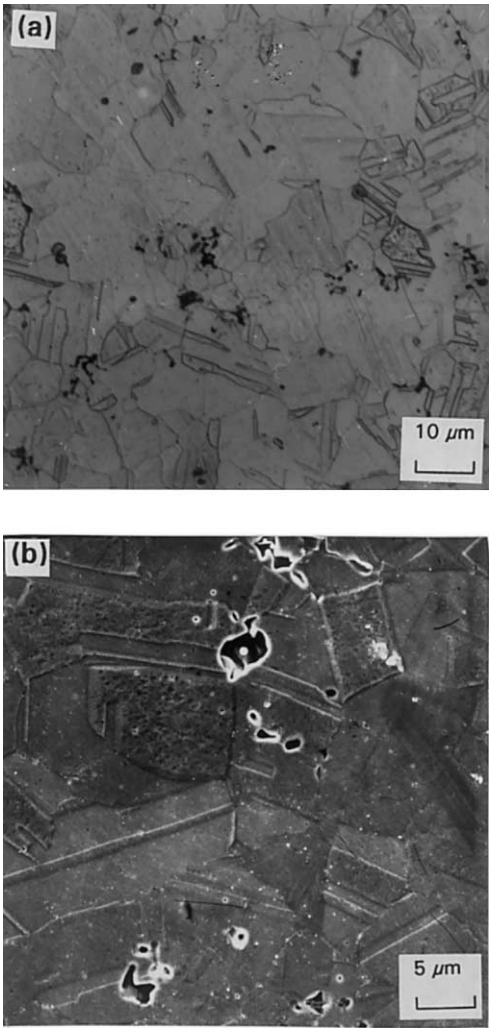

Fig. 4. (a) Optical micrograph of the polished and etched copper Sample B (Consolidated at 40 MPa for 5 min at 900°C) showing grain morphology and size, and distribution of porosity in the microstructure. (b) Scanning electron micrograph of the polished and etched copper Sample B showing size, morphology and distribution of microporosity in the microstructure.

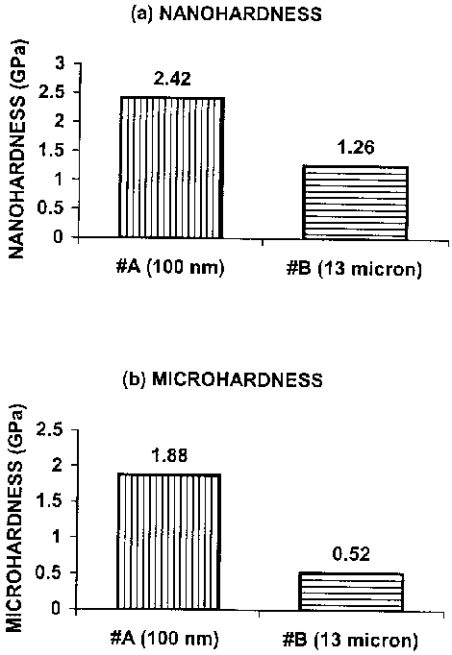

Fig. 5. Bar graph comparing the hardness of the two copper samples: (a) nanohardness, and (b) microhardness.

This recorded microhardness value accords reasonably well with reported microhardness values for copper [20–22]. Islamgaliev and co-workers [20] reported a microhardness value of 1.7 GPa for copper samples having an average grain size of 100 nm and made by severe plastic deformation. Alexandrov and co-workers [21] reported a microhardness of 1.85 GPa for bulk copper samples made from 150 nm starting powders by the technique of Severe Plastic Torsional Straining (SPTS) under a pressure of 1.5 GPa. These researchers also found the hardness to be non-uniform throughout the sample surface, being 10–12% less at the center than at the edges of the sample. Youngdahl and co-workers [22] found a hardness of 2.61 GPa for nanocrystalline copper with a grain size of 20 nm. In this research study, the bulk samples consolidated by the P^2C technique revealed near uniform microhardness values throughout the sample surface for both the 13-μm and 100 nm starting copper powders.

Table 2
Microhardness measurements on'the consolidated copper samples

Sample	Process conditions	Microhardness (GPa)					
		Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average
#A	880°C, 3 min, 40 MPa	1.84	1.83	1.96	1.92	1.86	1.88
#B	900°C, 5 min, 40 MPa	0.58	0.48	0.47	0.51	0.57	0.52

4. Conclusions

Based on the results obtained in a study on the influence of the technique of Plasma Pressure Compaction on microstructure and hardness of samples made from ultrafine copper particles, the following are the observations:

1. Copper nanopowders were consolidated by the technique of plasma pressure compaction to density of 99% at temperature 880°C and pressure of 40 MPa.
2. Microstructure of Sample B consolidated from 13-μm powders revealed well-defined grains with evidence of macroscopic porosity both at grain boundaries and within the grain interior. Microstructure of Sample A made from consolidating the 100 nm powders revealed a dense, near-uniform distribution of very fine microscopic pores through the width of the sample. Both samples revealed evidence of grain growth. Since the technique of plasma pressure compaction is a rapid consolidation process, the observed growth of grains is ascribed to be the end result of the high temperature process.
3. Microhardness of Sample A (100 nm powders) is four-times the hardness of Sample B. The nanohardness of Sample A is twice that of Sample B (13-μm powders). The lower microhardness of the consolidated bulk copper sample is attributed to higher residual porosity.

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