Microstructure and Hardness of Copper Powders Consolidated by Plasma Pressure Compaction

T.S. Srivatsan, B.G. Ravi, A.S. Naruka, L. Riester, S. Yoo, and T.S. Sudarshan

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Bulk fine-grained copper samples were prepared by consolidating copper powders using the technique of plasma pressure compaction (P^2C). The specimens were obtained by consolidating the powder particles under conditions of electrical pulse and no-electrical pulse and at two different temperatures. Results reveal that pulsing of the powders prior to consolidation led to higher microhardness values than the samples that were obtained by consolidating the powder particles under no-pulse. Both nanohardness and microhardness increased with an increase in the temperature of consolidation. Samples consolidated at the higher temperature revealed evidence of grain coarsening. The influence of processing variables on microstructure development and hardness is presented and discussed.

Keywords copper powders, hot isostatic pressing, plasma pressure compaction

1. Introduction

One of the viable methods of powder processing necessitates the application of stress on the compact during the stage of sintering cycle. Achievement of high density and resultant improvement in mechanical properties can be accomplished with pressure-assisted consolidation. This results in either a reduction or a complete elimination of porosity. Pressure-assisted consolidation techniques, such as (a) uniaxial hot press, (b) hot isostatic pressing (HIP), (c) forging, and (d) extrusion, are being increasingly used to consolidate metal powders with the objective of achieving superior physical and mechanical properties. Although application of an external pressure tends to accelerate consolidation, key factors that limit final density of the product are (1) pore structure, (2) the presence of oxides and/or other secondary phases on the surface of the powders, and (3) the presence of gas porosity.[1] Closure of the pores, during pressure-assisted sintering, is dependent upon the relative size of a pore with respect to size of the grain. Generally, grain growth occurs at the high temperatures associated with densification due to the conjoint and mutually interactive influences of exposure time and an acceleration of mechanisms such as grain boundary diffusion.[2] Accordingly, the actual time of pressure application should be minimized so as to avoid excessive growth of the grains. However, if the grains are small with respect to the final pore size, as a direct result of initial packing or presence of large inclusions, then closure of the pore is not favored.[3]

Metal powders can be successfully densified by plastic flow that occurs at pressures above the yield strength. The strength of the material decreases at the high temperatures associated with sintering. In many systems, pressure-assisted consolidation is an attractive, viable, and preferred choice because the material has low strength at high temperatures and application of pressure during the sintering cycle promotes densification by plastic flow. However, pressure-assisted sintering suffers from a contamination of powder particle surface. For example, in HIP, surfaces of the compact are contaminated by the container. This necessitates the need for removal of the contamination either by chemical dissolution or by machining. Formation and presence of surface films is a problem commonly associated with fine metal powder.[4,5] Enrichment of the powder particle surfaces, with an impurity, can hinder full densification resulting in an essentially weak consolidated product. A rapid densification process developed by Materials Modification Inc. (MMI, Fairfax, VA) is based on plasma pressure consolidation. The technique of plasma pressure compaction (P^2C) is a short time, high-temperature, low-pressure process, which has been successfully used to compact coarse (>20 m), fine (between 1 and 20 m), and ultrafine (nanometer) metallic and intermetallic powders to full density and near-net shapes.[6,7] The purpose of this research paper is to examine the influence of process conditions on the microstructure, density, and microhardness of bulk copper specimens made by consolidating powder particles.

T.S. Srivatsan, B.G. Ravi, and **A.S. Naruka,** Department of Mechanical Engineering, The University of Akron, Akron, OH 44325-3903; **L. Riester,** Mechanical Characterization and Analysis Group, High Temperature Materials Laboratory, Oak Ridge National Laboratory, Oak Ridge, TN 37831; and **S. Yoo** and **T.S. Sudarshan,** Materials Modification Inc., Fairfax, VA 22031. Contact e-mail: tsrivatsan@uakron.edu.

2. Experimental Procedures

2.1 Material and Sample Preparation

High-purity copper powders, with an average particle size of 13 (μm, were consolidated by the technique of P^2C. In this technique, the copper powders are poured into a graphite die without any additive or binder. A constant uniaxial pressure was applied to the powders, through the graphite plungers and the compaction process were initiated by applying a pulsed DC voltage (3 V maximum and 2000 A average current) to the powder compact. The consolidated samples measured 25 mm in diameter and 15 mm in thickness. The consolidation conditions and relative density of the samples are summarized in

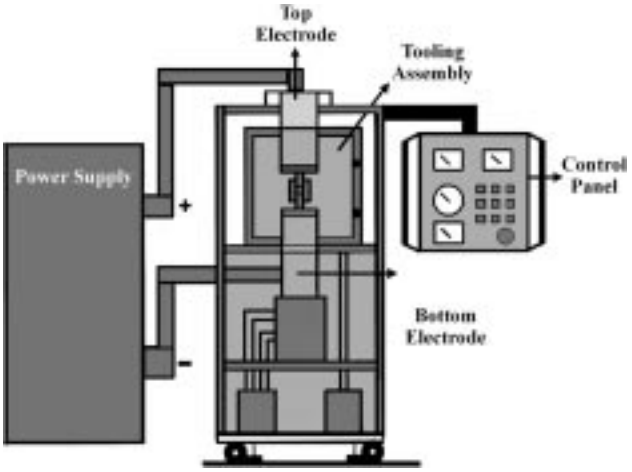


Fig. 1 A schematic of the plasma pressure consolidation (P^2C) setup

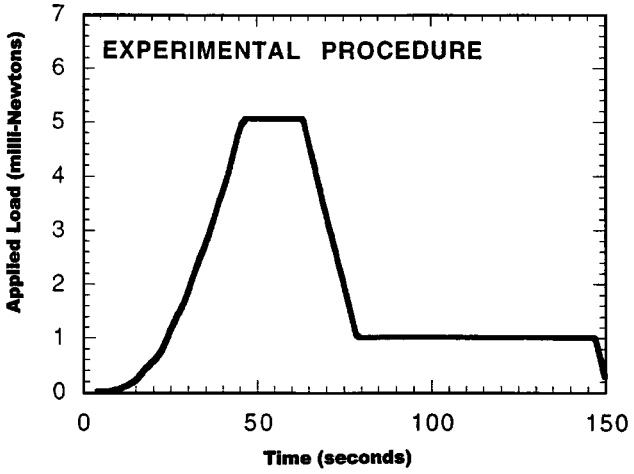


Fig. 2 A typical load-time sequence of the Nanoindenter II test machine

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

Sample	Particle size (micron)	Pulse	Temperature	Time (min)	Pressure (MPa)	Density (%)
1	13	Yes	880	3	40	98
2	13	No	900	5	40	95
3	13	Yes	900	3	40	98

Table 1. In an attempt to establish the influence of a DC pulse on consolidation, the samples were made under conditions of electrical pulse and no-electrical pulse. The consolidated samples measured 25 mm in diameter and 15 mm in thickness. The consolidation conditions and relative density of the samples are summarized in Table 1. A schematic of the plasma pressure consolidation equipment is shown in Fig. 1.

2.2 Microstructural Examination

The as-consolidated samples were prepared for examination in the optical and scanning electron microscopes. The defect features in the consolidated sample include irregular surface cracks, stringlike and angular features, and small cavities such as microscopic pores and voids. Sample preparation involved an initial wet grind and coarse polish on progressively finer grades of silicon carbide impregnated emery paper using copious amounts of water both as a coolant and lubricant. The samples were then fine polished using 5 and 1 μm alumina suspended in distilled water. Finish polishing to a perfect mirror finish was achieved using 1 μm diamond paste with water as the lubricant. The as-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. Precise density measurements of the consolidated bulk copper samples were made using the Archimedes' principle according to ASTM Standard B328-94.

2.3 Indentation Procedure and Mechanical Properties Computation

Ultralow load indentations were performed on the samples using the nanoindentation technique.[8,9] The Nano Indenter II at the High-Temperature Materials Laboratory, Oak Ridge National Laboratory (ORNL) (Nano Indenter is a registered trademark of Nano Instruments, Inc., Oak Ridge, TN) 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.[10] The indenter has nearly the same area-to-depth ratio as the four-sided Vickers, which allows these hardness values to be directly compared.[9] The nanoindenter is equipped with a numerically controlled loading unit and a high-resolution measurement system for measuring the indentation depth. Smoothness of the sample was the most important criterion for valid indentation data. Indentation positions were individually located on the sample surface using an optical microscope with a 1500× magnification. The sample table encoded the positions with reasonable accuracy, enabling 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 and a pattern for a set of ten indents was established. Because of the softness of the material (copper), each indentation sequence consisted of four segments. During segment 1, the indenter approached the sample surface. The sample was then loaded to a specified target depth during segment 2 and held there. The holding period was referred to as segment 3. Segment 4 was an unloading segment. A typical load-time sequence used for testing is shown in Fig. 2. Since in this test sequence a fixed penetration depth was selected the load varied 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. The indentation system also has the ability to continuously measure contact stiffness during indentation. The hardness and Young's Modulus computations were carried out based on the technique developed by Oliver and Pharr.[9]

Using a Buehler (Lake Bluff, IL) Micromet II microhardness

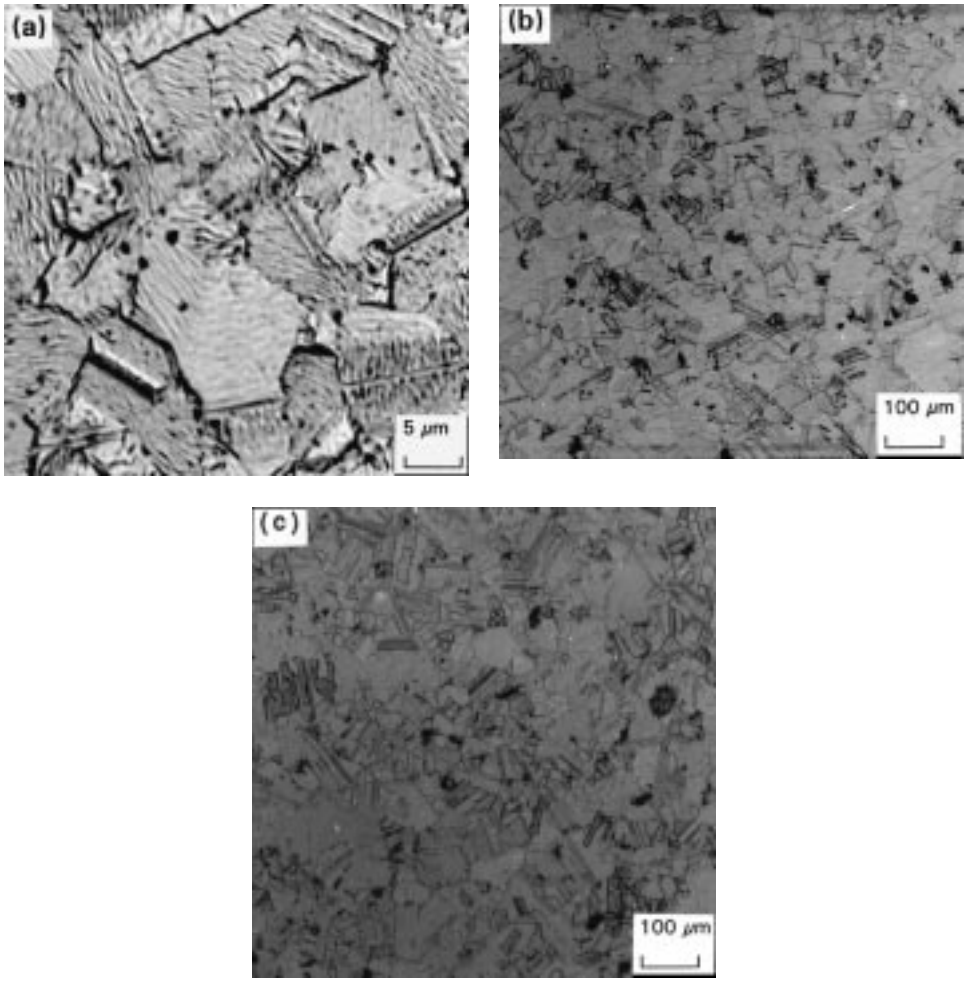


Fig. 3 Bright-field optical micrographs of the polished and etched copper samples showing the morphology and size of grains and the distribution of porosity: (**a**) sample 1 (consolidated at 40 MPa for 3 min at 880 °C under pulse); (**b**) sample 2 (consolidated at 40 MPa for 5 min at 900 °C under no-pulse); and (**c**) sample 3 (consolidated at 40 MPa for 3 min at 900 °C under pulse)

Table 2 Vickers microhardness measurements on the consolidated copper samples

		Microhardness (GPa)					
Sample	Process Conditions	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Average Hardness (GPa)
1	Pulse 880 °C 3 min 40 MPa	0.55	0.42	0.46	0.50	0.42	0.47
2	No-Pulse 900 °C 5 min 40 MPa	0.58	0.48	0.47	0.51	0.57	0.52
3	Pulse 900 °C 3 min 40 MPa	0.66	0.50	0.61	0.52	0.49	0.56

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 micrographs of the samples are shown in Fig. 3. Figure 4 provides representative scanning electron micrographs of the microstructure, at different locations on the sample surface, of sample 3.

The polished surface of the as-compacted copper sample 1 reveals appreciably more macroscopic porosity in comparison with samples 2 and 3. The pores were appreciably larger than the powder particle size. The higher amount of macroscopic porosity is responsible for the lower microhardness of sample

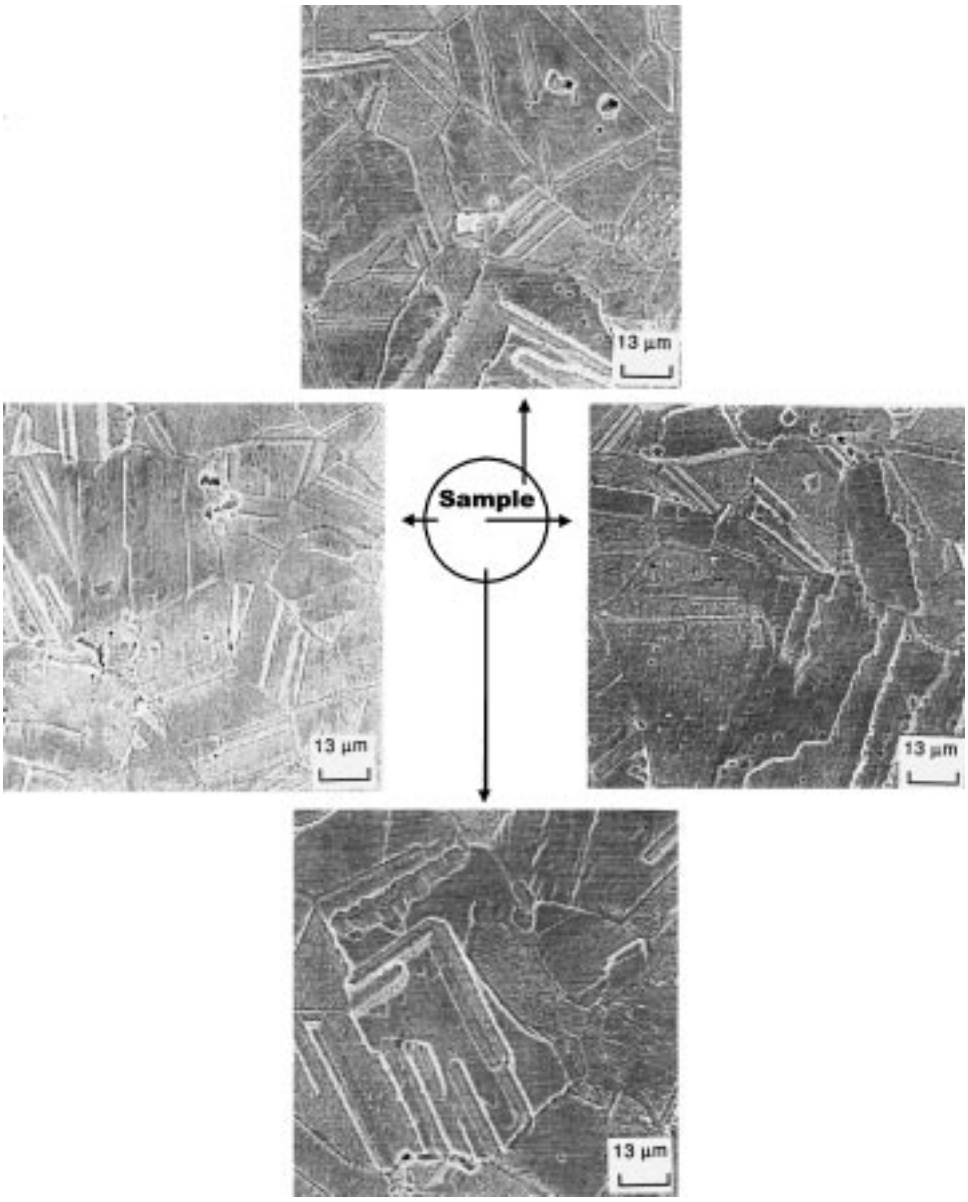


Fig. 4 Scanning electron micrographs of the polished and etched copper sample 3 (consolidated at 40 MPa for 3 min at 900 °C under pulse) showing size, morphology, and distribution of the microscopic pores at different locations

1 when compared to the other samples, which had been heat treated at a higher temperature. Besides, because of the lower temperature during consolidation (T = 880 °C), visual observations reveal the final grain size to be comparatively smaller for sample 1 than for sample 2 (T = 900 °C) and sample 3 (T = 900 °C). No measurement of grain size was made in this study. Occurrence of grain growth during consolidation by the P^2C technique has been reported in an independent study on iron powders.[7] Dependence of grain coarsening on consolidation temperature has also been observed during vacuum hot pressing.[11] The lower consolidation temperature for sample 1 accounts well for the smaller grain size in the final product. All three copper samples examined in this study revealed a population of fine grains, of varying size, having well-defined grain boundaries.

Scanning electron microscopy observations revealed the presence of fine microscopic pores, of varying size and shape: (a) irregular morphology at and along the grain boundaries and grain boundary triple junctions and interstitial porosity; and (b) near-spherical shape and within the grain interior. Sample 3 (T = 900 °C) revealed the least amount of residual porosity.

The presence of regions of space between the powder particles in the consolidated green body compact is largely dependent on the conjoint and mutually interactive influences of size, shape, and pressure experienced by the powder particles during consolidation. Prior to actual consolidation, the green compact consists of a random distribution of interparticle contacts with a population of voids between the powder particles. The interparticle contacts serve as potential sites for high local stress concentration. In pressure-assisted consolidation, even nominal

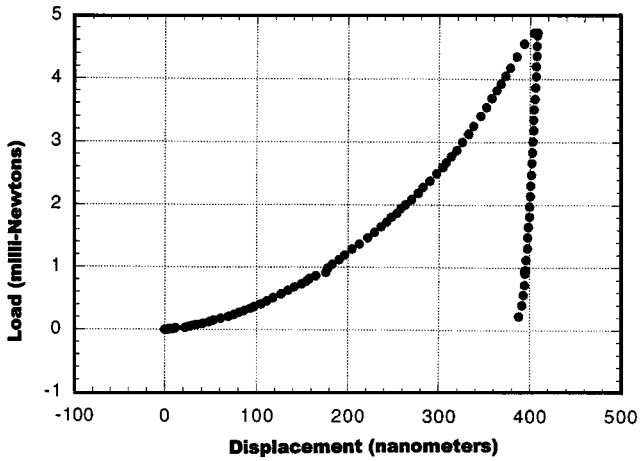


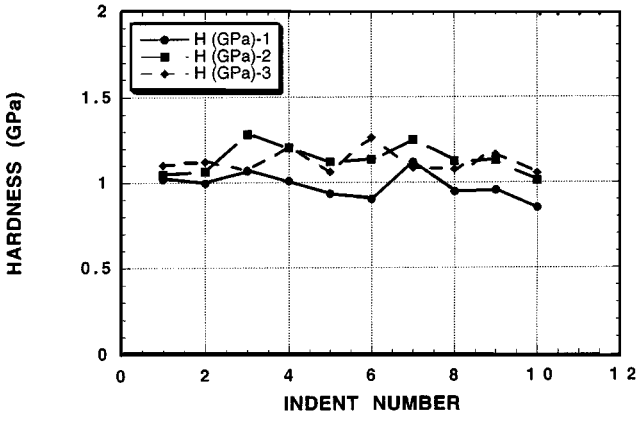
Fig. 5 A typical load vs indenter displacement record obtained for an experiment performed on mechanically polished copper sample

low stresses are adequate enough to enhance the densification of powders due to the presence of local stress concentration.[1] When the interparticle 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 interparticle contact zone to be heated faster than the interior of the powder particle and the interparticle gap. The highly localized heating aids in softening the interparticle contact. Subsequent application of an external pressure and a DC voltage facilitates powder particle rearrangement and densification by inducing localized heating and promoting plastic deformation at all areas of interparticle contact. Since the present 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) available at the interparticle regions may not be totally sufficient to facilitate complete particle contact. This results in the formation and presence of interstitial porosity with an irregular shape at the particle boundaries.

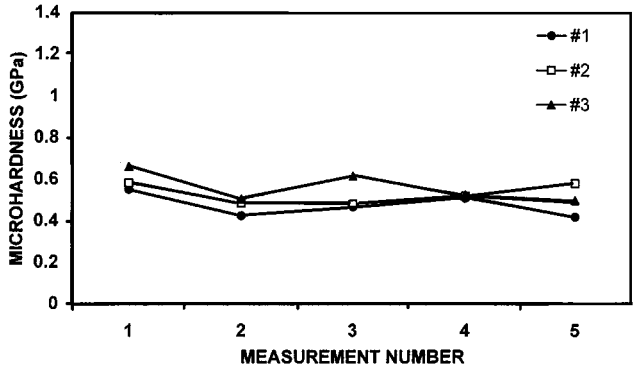
3.2 Hardness

Nanoindentation Results. A typical load-displacement curve of the nanoindenter for a copper sample (sample 1) is shown in Fig. 5. The experimental results on the three copper samples are summarized in Table 2 and plotted in Fig. 6(a). The indentation sites on these samples were chosen to be well within the grain interior and away from grain boundaries. There is minimum scatter in the hardness measurements. The overall hardness of sample 1 is 0.98 GPa, while that of sample 2 is 1.15 GPa. The hardness of sample 3 is higher than sample 1 and marginally inferior to sample 2. The hardness of the three samples is compared in the bar graph shown in Fig. 7.

The elastic modulus, as measured by the nanoindentation technique,[9] of the three samples is shown in the bar graph in Fig. 8. The elastic modulus of the pulsed copper sample (sample 3) (E = 134 GPa) is only marginally higher than that of the no-pulse counterpart (sample 2, E = 133 GPa). Also, a higher temperature of consolidation (sample 3) resulted in better elastic modulus than the sample (sample 1, E = 130 GPa) obtained by consolidating at the lower temperature. Overall, the elastic



(a)



(b)

Fig. 6 (**a**) Nanohardness data as a function of indent number on the three copper samples. (**b**) Microhardness traverse across the copper samples

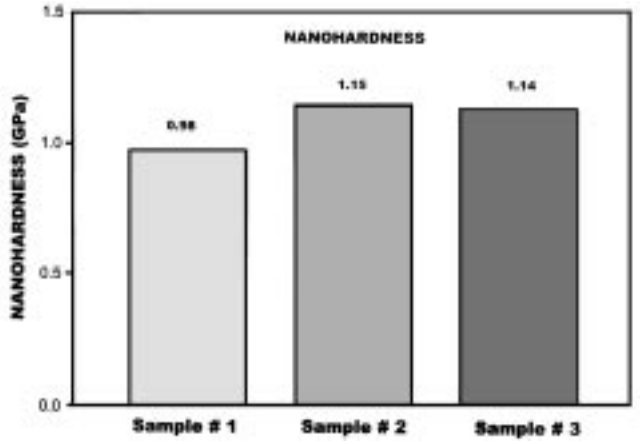


Fig. 7 Bar graph comparing the nanohardness of the three copper samples. The result used is the mean value of ten indents

modulus values accord well with the established values for annealed polycrystalline copper and copper alloys (E = 130 GPa). The stress state in the immediate vicinity of the indenter is complex and compressive directly under the tip. Microscopic cracks emanating from the pores would remain closed in pure

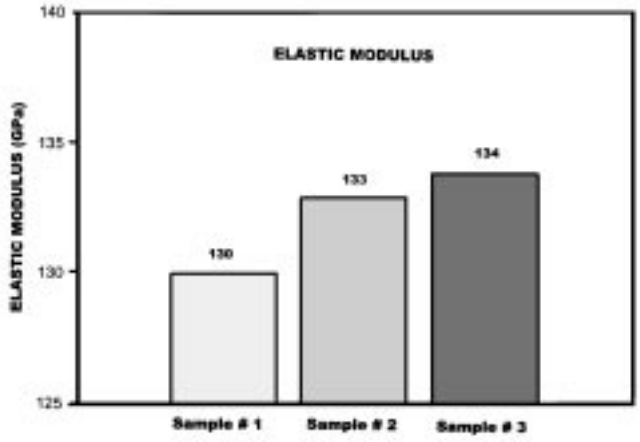


Fig. 8 Bar graph comparing the elastic modulus (GPa) of the three copper samples. The values used are the mean based on ten indents on each copper sample

Table 3 Nanohardness and elastic modulus of the consolidated copper samples

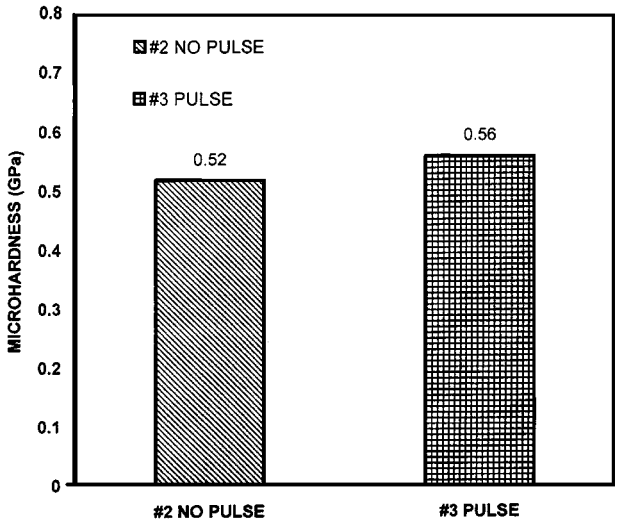
Sample	Process conditions	Nanohardness (GPa)	Elastic modulus (GPa)
1	Pulse, 880 °C, 3 min, 40 MPa	0.98	130
2	No-pulse, 900 °C 5 min, 40 MPa	1.15	133
3	Pulse, 900 °C 3 min, 40 MPa	1.14	134

compression and would not greatly affect the value of the elastic modulus measured by nanoindentation.

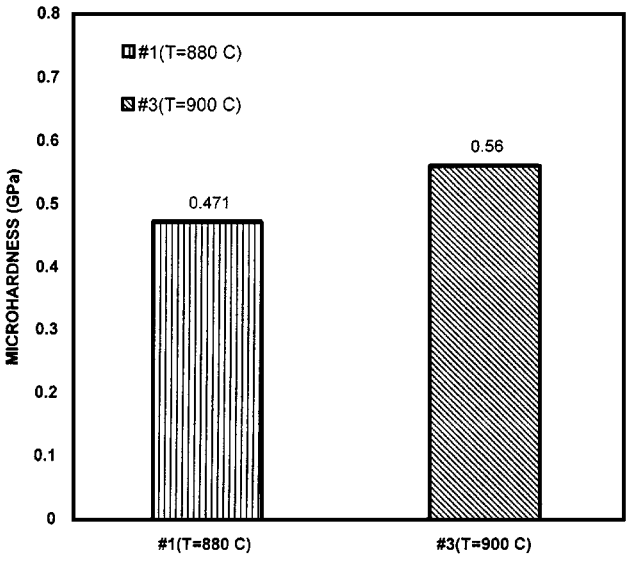
Microhardness. Vickers microhardness measurements, made well within the grain interior, are summarized in Table 3. The microhardness traverse across the three copper samples is illustrated in Fig. 6(b). The spatial variability was less pronounced in the as-compacted copper samples and the measured microhardness was observed to be nearly uniform throughout each as-compacted sample, indicating uniform densification. Polishing to a perfect mirror finish, ensuring smoothness of the sample, facilitates minimization of the spread in measured hardness values.

Sample 2, obtained by consolidating the 13 μm powders under conditions of no pulse, with a hold time of 5 min (at isothermal condition), has a density of 95% and a microhardness of 0.52 GPa. This value is less than the microhardness of sample 3 (0.56 GPa) obtained by consolidating the copper powders under conditions of an electrical pulse. The hardness (H_v) value, at constant temperature (T = 900 °C) of consolidation, reveals the pulse condition to be beneficial to hardness in the consolidation of the copper powders (Fig. 9a).

The effect of consolidation temperature on microhardness was also investigated. Samples 1 and 3 were consolidated under the same experimental conditions. However, sample 3 experienced a temperature of 900 °C, which is 20 °C more than the process temperature of sample 1. Although the density is around 98% for the two samples, an increase of 20% in the value of microhardness was observed for a nominal 20 °C increase in



(a)



(b)

Fig. 9 Bar graph showing the influence of (**a**) the pulse condition on the microhardness of copper. (**b**) Consolidation temperature on Vickers microhardness of copper. The microhardness values used are the mean based on ten indents

the consolidation temperature. Comparing the hardness values of sample 1 (pulse; T = 880 °C) with sample 3 (no-pulse; T = 900 °C) reveals an increase of 10% in the hardness value for a 20 °C increment in consolidation temperature (Fig. 9b). The higher microhardness of sample 3 than sample 1 is ascribed to the higher consolidation temperature. The results reveal that the microhardness of copper is sensitive to consolidation temperature, with a small increase in temperature resulting in a noticeable increase in microhardness. The most appealing rationale for the marginal decrease of density of the no-pulse sample is attributed to the presence of a large volume fraction of pores of varying size in the as-compacted sample.

4. Conclusions

Based on the results obtained in an experimental study aimed at understanding the influence of process conditions on microstructure and hardness samples made by consolidating fine copper powders, the following observations are made.

- Copper powders were successfully consolidated by the technique of plasma pressure compaction.
- Consolidation temperature and application of a DC pulse condition had a noticeable effect on hardness (nanoindentation and microhardness) and residual porosity of the as-compacted samples. Higher residual porosity resulted in lower hardness of the consolidated bulk copper sample. Process conditions were found to have little influence on elastic modulus of the bulk samples.
- Visual observations, at identical magnifications, revealed grain growth to be evident for the sample consolidated at the higher temperature.

Acknowledgments

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References

1. R.M. German: *Rev. Particulate Mater.,* 1994, vol. 2, p. 117.
2. J. Besson and M. Abouaf: *Acta Metall. Mater.,* 1991, vol. 39, p. 2225.
3. B.J. Kellett and F.F. Lange: *J. Am. Ceramic Soc.,* 1988, vol. 71, p. 7.
4. J.E. Smugeresky and R.M. German: *Metall. Trans. A,* 1978, vol. 9A, p. 253.
5. K. Hayashi and H. Kihara: in *Sintering 87,* I.S. Somiya, M. Shimada, M. Yashimura, and R. Watanabe, eds., Elsevier Applied Science Publishers, London, 1988, vol. 1, p. 255.
6. S.H. Yoo, T.S. Sudarshan, K. Sethuram, G. Subhash, and R.J. Dowding: *Powder Metall.,* 1999, vol. 42 (2), pp. 181-82.
7. R. Kalyanaraman, S. Yoo, M.S. Krupasankara, T.S. Sudarshan, and R.J. Dowding: *Nanostr. Mater.,* 1998, vol. 10, p. 1379.
8. M.F. Doerner and W.D. Nix: *J. Mater. Res.,* 1986, vol. 1, p. 601.
9. W.C. Oliver and G.M. Pharr: *J. Mater. Res.,* 1992, vol. 7, p. 1564.
10. M.M. Krushchov and E.S. Berkovich: *Indust. Diamond Rev.,* 1951, vol. 11, pp. 42-49.
11. G. Wang, Q. Meng, Z. Li, and E. Wang: *Nanostr. Mater.,* 1995, vol. 5, pp. 673-76.