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13. ABSTRACT (Maximum 200 words) <p>This work focused on the specifics of densification of nanocrystalline powders using an externally applied pulsed electrical current. Studies were performed to characterize the surface structure of select metal nanopowders (Ni, Al and Ta) and understand differences due to handling and storage conditions. For the oxygen sensitive Ta, methods were designed to clean previously coated nanoparticle surfaces. Grain growth behavior of nanocrystalline materials was characterized by in-situ TEM with and without an externally applied electrical current. An integrated heating/electrical biasing holder was designed and built for in-situ TEM coarsening studies.</p> <p>For field sintering of nanomaterials, a more detailed characterization of the commercial SPS machine was required, and temperature evolution and distribution, and heating rate effects were evaluated. Based on the experience in SPS sintering of conventional parts (19 mm in diameter and 5 mm thick) from Ni nanoparticles, large specimens (thickness up to 19 mm) were sintered for mechanical testing. Ta nanopowders (40 nm) were sintered to a final density of 12.9 g/cm³ at 1200°C. The grain/crystallite size very small (2.5 nm). This was also attributed to a phase transformation from tetragonal to cubic in Ta. Mechanical property characterization is being performed on large Ni specimens and sintered Ta at ARL, Aberdeen Proving Ground, Maryland.</p>				
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(1) Foreword

This grant enabled an extensive study of a novel sintering technique (field activated sintering) to process metal nanoparticles into fully dense bodies, which preserve an ultrafine grain size. The challenges of sintering nanometric particles were addressed (e. g., contamination and grain growth) by means specific to electric field application. Large parts for more conventional mechanical testing have been consolidated.

The experience gained during this work was also helpful to improve the field sintering technique, build new instruments, and process difficult-to-sinter Army relevant materials.

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(3) List of Appendices, Illustrations and Tables – included in text

(4) Statement of problem studied

The aim of this work was to develop a basic understanding of the processing of nanocrystalline powders into final dense parts with ultrafine grain size, which imparts enhanced mechanical properties. First, the characterization of air exposed metal nanoparticles was sought to detect differences from conventional powders in surface structure and contamination effects. Next, the coarsening behavior of metal nanoparticles was characterized by in-situ TEM with and without electrical current application. For these studies, a new in-situ TEM holder was designed and built.

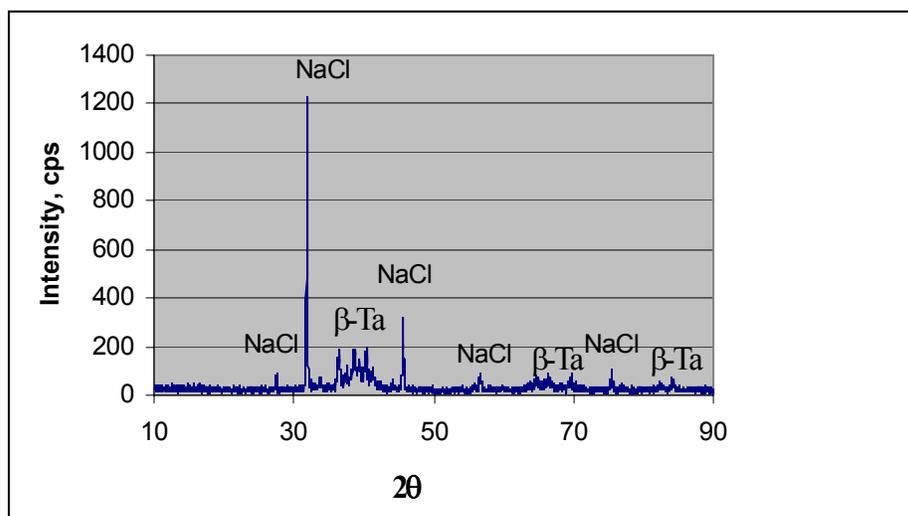
To overcome the challenges of nanopowder densification, an electrical field activated sintering technique (FAST) was used due to its ability to clean up the initial powder particle surfaces and achieve high density values. Two main features of FAST processing required further attention when sintering nanoparticles: heating rate effects and

temperature evolution and distribution. The effect of heating rate was studied to provide insight into densification mechanisms, and its effect on retaining a fine grain size. Temperature evolution and distribution were evaluated in FAST sintering to be used for processing large parts. The goal of the FAST research was to gain a basic understanding of the field activation and interactions between densification and coarsening, and apply this understanding to process nanocrystalline Ta parts for microstructure and property characterization.

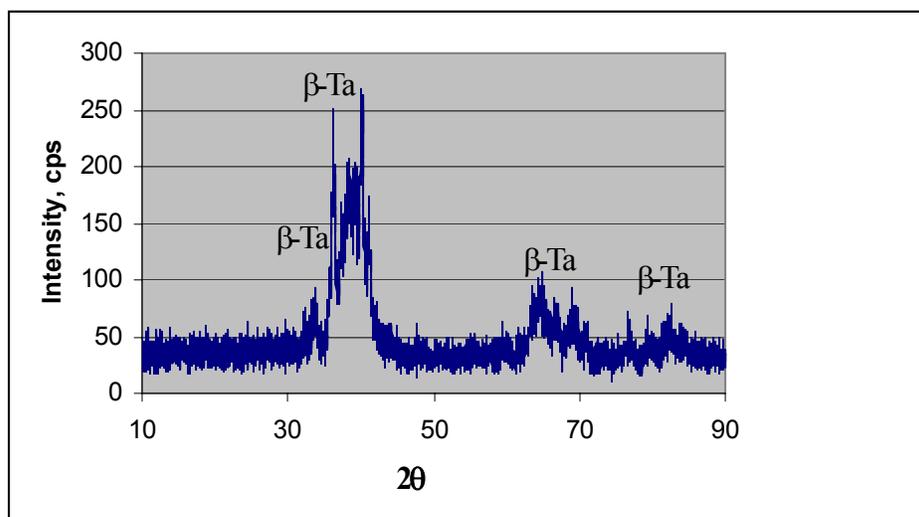
(5) Summary of the most important results

a) Nanoparticle characterization

Transmission Electron Microscopy (TEM) was used to characterize the particle size and distribution, and particle surfaces of nanoparticles handled under real conditions. Ni, Cu and Al were exposed to air, while Ta surface was coated by the manufacturer. High resolution TEM studies indicated differences in the chemistry and structure of surface oxides on Ni, Cu and Al nanopowders, as expected from their different oxygen affinity. While Al nanoparticles were covered by a 3 nm thick amorphous and compact surface oxide layer, Ni nanoparticles were surrounded by a non-uniform, crystalline surface oxide layer. Elemental analysis indicated that the Al nanoparticles contained O and Si and that the oxygen is associated with the particle surface layer, while no oxygen confinement in the surface layer was found in Ni nanoparticles. XPS confirmed the NiO presence in the surface layer of Ni particles. The oxygen sensitive Ta nanopowders are covered by a thick NaCl layer. Two methods to clean the NaCl coating were designed and used. The chemical method involved the dissolution of NaCl in anhydrous glycerol. The physical cleaning involved NaCl evaporation during a carefully designed annealing cycle (20°C heating rate, dwell at 900°C for 5 min, increase temperature to 950°C and dwell for 45 min, cooling to room temperature). The cleaning of tantalum powders was checked by XRD (Fig. 1) and TEM prior to sintering.



a)



b)

Figure 1. XRD patterns of : a) initial Ta powders, b) Ta powders after cleaning.

b) Coarsening Studies

For these studies, a custom designed integrated in-situ heating/electrical biasing transmission electron microscopy holder was built at National Center for Electron Microscopy in Berkeley. The holder was designed to apply a constant electrical current to a 2.1 mm square TEM specimen. The specimen holder assembly consists of the ceramic insulator in the bottom, the two biasing wires which run across the insulator, the specimen with the conducting film side facing down onto the wires, and a top insulating washer placed between the specimen and the hold-down screw ring (Fig.2). The holder will be used for other in-situ studies (e. g., electrical conductivity in functional materials).

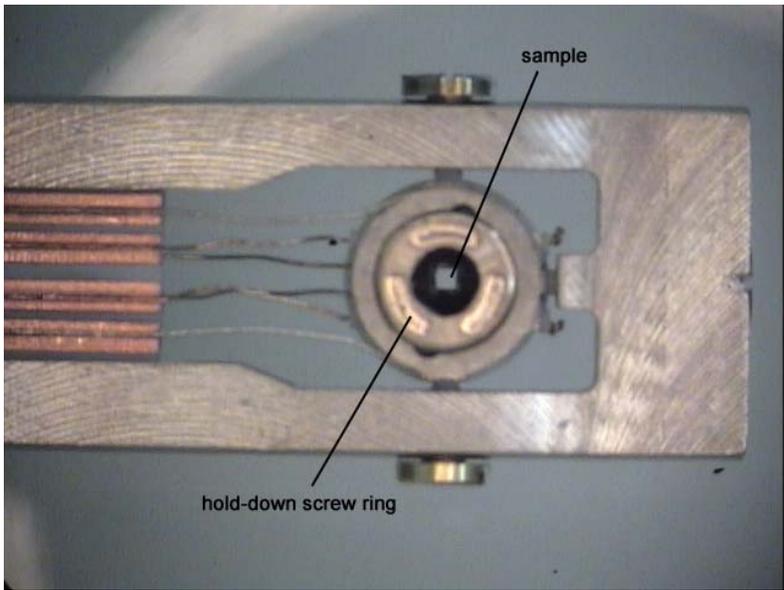


Figure 2. The top view of the holder with the sample inserted.

The grain coarsening rate in nanocrystals was found to be described by an equation similar to that of conventional materials:

$$\text{Eq. (1)} \quad G^n - G_0^n = kt$$

where G is the average grain diameter, G_0 is the initial grain diameter, n is the grain growth exponent, k is an Arrhenius type constant and t is time. A value of 3 was found for n .

When an electrical field was applied, grain growth was accelerated (Fig. 3) and the k values were larger.

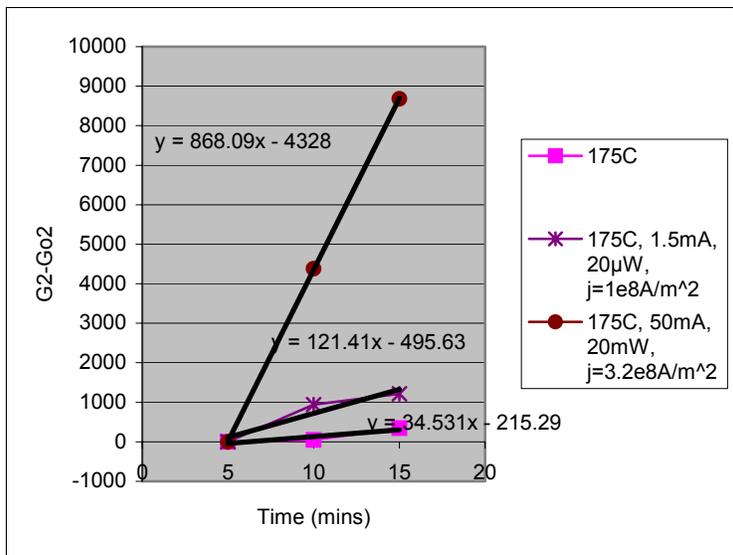


Figure 3. Grain growth kinetics under applied current (1.5 mA and 50 mA) as compared to conventional grain growth at the same temperature (175 °C).

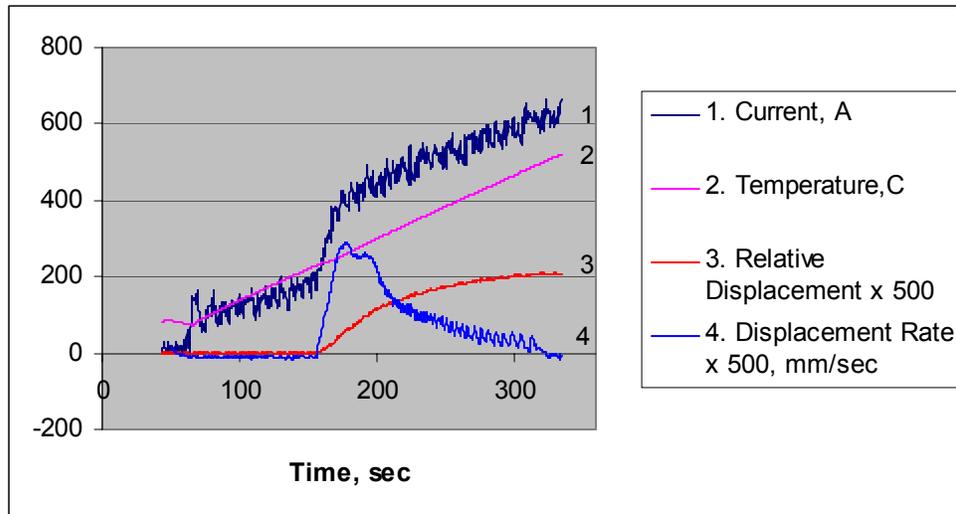
The results indicated that the augmentation of the k values with current density could not be explained by Joule heating alone. This unexpected result was attributed to either experimental factors (non-standard specimens, various resistances, lack of temperature measurement directly on the sample) or changes in the activation energy or pre-exponential constants with applied current.

c) Field Activated Sintering of Nanocrystalline Powders

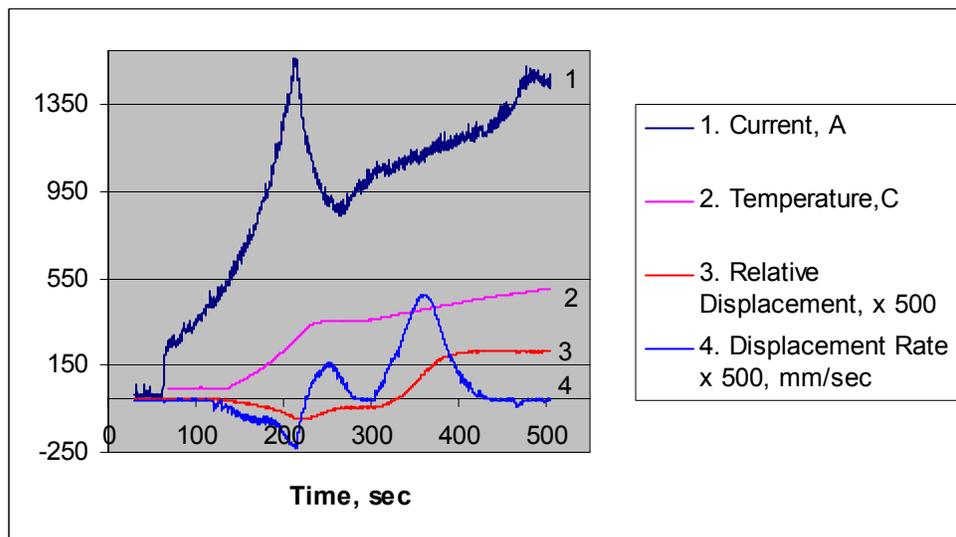
Heating Rate Effects

A basic study performed on conductive versus non-conductive powders indicated distinct effects of heating rate on densification and grain coarsening. The final grain size scales inversely with the heating rate in coarsening sensitive materials (i. e., with activation energies for densification greater than for grain growth). For the other materials, no grain growth dependence on heating rate was observed.

The heating rate plays an important role in the first densification stages, as well. At reasonable heating rates, the interparticle bonding in metals is weak and the particles may easily be rearranged by current activation and pressure application. At high heating rates (i. e., intensive current application), high density discharges lead to welding of the particles, thus preventing their sliding/rearrangement. This may account for a lower degree of densification in early sintering stages. Intensive densification is then shifted toward higher temperature (350°C) where the diffusion governed mechanisms are active (Fig. 4).



a)



b)

Figure 4. Current (1), temperature (2), shrinkage (3) and shrinkage rate (4) during FAST sintering of Ni nanopowders: a) heating rate 90°C/min b) step heating rate variation 210 °C/min (temperature range 145-350°C), then 50°C/min (temperature range 350-520°C).

Temperature Evolution During Field Activated Sintering

The temperature evolution during field activated sintering was examined both by experimental studies and finite element modeling. Calibrated thermocouples at different positions compared temperatures of different sintering specimens (graphite, pure silicon, and lithium silicate) up to 1100 °C. For higher temperatures a single-color pyrometer was

used. The positions of the thermocouple and the pyrometer eye point are shown in the inset in Figure 5. Joule heating, current densities and heat flux were simultaneously calculated by an ABAQUS finite element analysis of the experimental graphite-silicon die set assuming constant heating rates. Heat transfer by conduction and radiation was considered. Figure 5 shows the difference in measured temperatures at different locations.

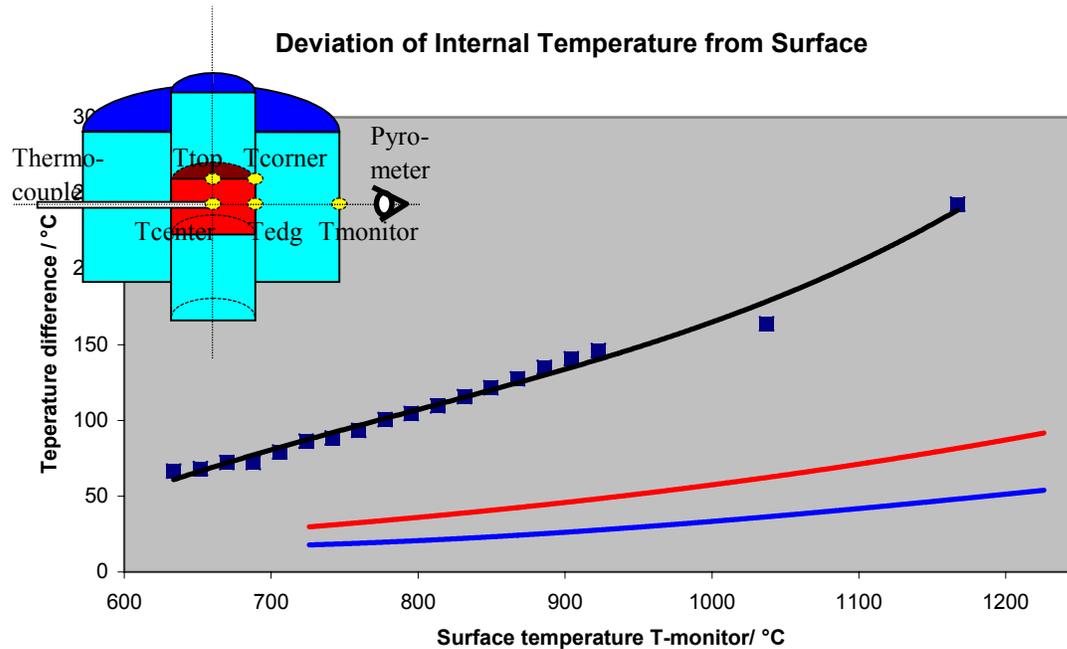


Figure 5. Experimental data (squares) show the temperature evolution of interior temperatures (T_{top} , T_{center} , T_{corner} ,) over the die surface temperature $T_{surface}$. The modeled data (blue - T_{top} and red- T_{edge}) show the calculated excess range over $T_{surface}$. The inset illustrates the location of different temperature measurements.

The FEM analysis is found to be in reasonably good agreement with experimental data (Fig. 5- blue and red lines). In both cases, an almost linear, or only weakly exponential correlation of inside-temperatures on surface temperatures is apparent. The modeling further confirms the experimental observation of punches acting as heat sources and the die as heat sink, thus T_{top} being the highest temperature the specimen experiences with lower temperatures for positions closer to the die (T_{edge}). Both model and experiment suggest an increase of this effect with higher temperatures.

FAST Sintering of Ni and Ta parts

The evolution of FAST densification of Ni nanopowders as a function of time and temperature is shown in Figure 4. Densification was found to start at relatively low temperature, i. e., around 230°C (at 90°C/ min) and proceeded with a high rate from the very beginning, consistent with the literature reports on field activated sintering. Based

on the understanding of the heating rates effects, a step heating rate variation was designed to achieve high density and retain a fine grain size (Fig. 4). The final densities of FAST sintered Ni nanopowders are 92-95%. The grain size of the samples sintered at 520°C is in the range 100-150 nm (Fig. 5). Higher sintering temperatures resulted in large grain sizes (e. g., 2 μm at 1000°C). The Ni sample sintered in a similar P²C machine at 700°C (at ARL) had a density of 96% and grain size of 250nm. The analysis of sintering mechanisms indicated little influence of applied pressure on densification of Ni, which is controlled primarily by surface-tension driven diffusion along interparticle boundaries, regardless of sintering temperature.

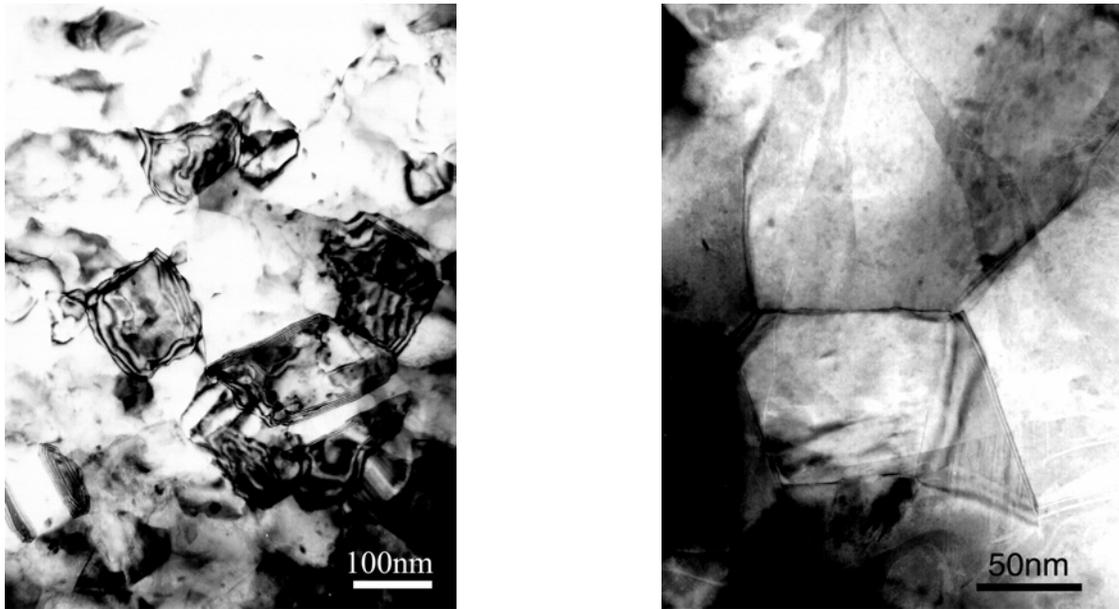


Figure 5. TEM micrograph of the FAST sintered Ni samples at temperature 520°C and heating rates of: a) 90°C/min; b) 210°C/min

For sintering large samples, long graphite dies (height 62 mm versus regular 40 mm) were designed and manufactured. Using these dies, dense samples with a diameter of 19 mm and height 19 mm were processed. Samples were sintered using a heating rate of 90 degree/min to the sintering temperature (600 °C) and dwelled at this temperature for 1 min. The applied pressure was 45 MPa. The density of the samples, measured using Archimede's method, was 95% of theoretical value. The large samples were prepared to perform mechanical testing at ARL.

The main problem in consolidation of Ta nanopowders (40 nm) was a significant grain growth tendency. Ta starts to coarsen at considerably lower temperature (1500 °C) as compared with other refractory metals such as tungsten and molybdenum (2200 °C) [1]. Field sintering of pure Ta was found to start at low temperatures (600°C). Sintering to 1700°C resulted in grain sizes of 10 μm . To avoid the excessive grain growth, FAST

sintering was carried out at 1200°C. The final density was 12.9 g/cm³, a value that can be explained due to some oxides still present, as shown in Figure 6. However, SEM analysis showed no pores.

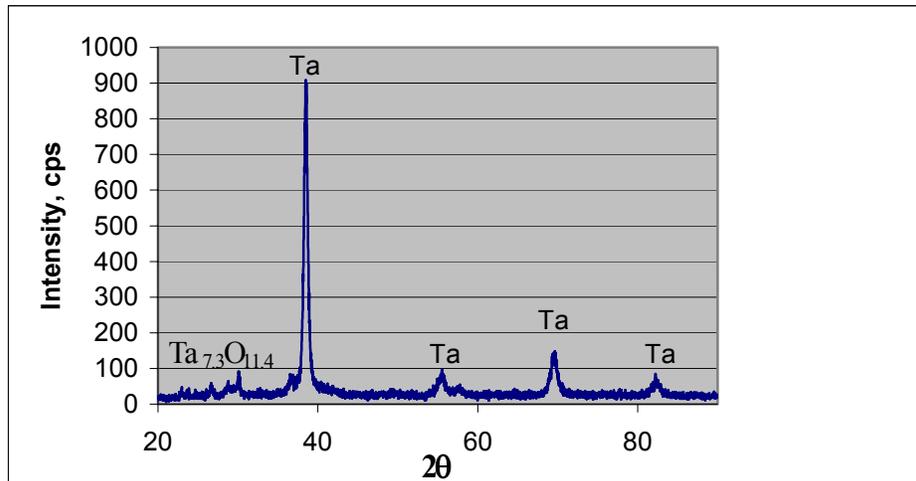


Fig. 6. XRD pattern of Ta consolidated at 1200°C for 1 min.

The crystallite size determined by XRD technique using Halder – Wagner method [2] was 2.5 nm. A phase transformation from tetragonal to cubic modification was observed. XRD analysis shows the presence of only cubic phase in consolidated Ta. The small crystallite size is a result of transformation of tetragonal phase to cubic at the temperature higher than 800°C [3]. After crystallization of cubic phase during sintering, grain growth is very limited since the sintering time is very short (1 min) and temperature is low (1200°C). In addition, electrical field activation increases the nucleation rate, which favors a final small grain size.

(6) List of publications and technical reports:

“TEM Annealing Study of Normal Grain Growth in Silver Thin Films”, Dannenberg, R; Stach, E; Groza, JR; Dresser, BJ. Thin Solid Films, Dec. 8, 2000, V379(N1-2):133-138.

“Phenomenological Description of Grain Growth Stagnation for Nanocrystalline Films and Powders”, Dannenberg, R; Stach, E; Groza, JR., Journal of Materials Research, Apr., 2001, V16(N4):1090-1095.

“Effects of Heating Rate in Field Assisted Sintering”, L. A. Stanciu, V. Y. Kodash and J. R. Groza, Metallurgical and Materials Transactions, Oct. 2001, V32A: 2633-2638.

“Surface Characterization of Metal Nanoparticles” X. Phung, J. R. Groza, E. Stach, L. N. Williams, and S. Ritchey, Mat Sci Eng, 359, 2003, 261-268.

“Nanostructured Materials by Field Activated Sintering Technique, J. R. Groza and A. Zavaliangos, accepted in Reviews on Advanced Materials Science, 2003.

“Structural nanomaterials”, J. R. Groza and J. C. Gibeling, in ENCYCLOPEDIA OF NANOSCIENCE AND NANOTECHNOLOGY edited by Professor James A. Schwarz, Dr. Cristian Contescu, and Dr. Karol Putyera, January 2004 (American Scientific Publishers)

“Temperature Evolution During Field Activated Sintering”, M. Kraemer, J. R. Groza, A. Zavaliangos, submitted to Materials Science and Engineering A, 2003.

“Real Time Measurements of the Effect of Electric Fields on Grain Growth in Nanocrystalline Silver Thin Films”, E. Stach, X. Phung, J. R. Groza, K. Hukari and R. Dannenberg, to be submitted to J. Analysis and Microscopy.

“Field Effects in Sintering Metal Nanopowders”, V. Y. Kodash, K. Cho, R. L. Dowding, J. R. Groza, to be submitted to Mater. Sci. Eng., 2003.

(7) List of scientific participating personnel

Xuyen Phung (graduated MS in 2002), Vladimir Y. Kodash and Martin Kraemer (post-doctoral researchers), Lia A. Stanciu (PhD- graduation expected in December 2003) and Joanna R. Groza (professor).

(8) Report of Inventions

The experience gained while pursuing this work was applied to the sintering of additive-free SiC and B₄C materials with promising results. B₄C powders with a particle size of 200-300 nm and SiC powders of 50-100 nm were used for sintering without any additives. B₄C was sintered to 98% of theoretical density at relatively low temperature (1500°C) for 2 min and a pressure of 45 MPa. SiC was sintered to 95% of theoretical density at 1800°C for 2 min and a pressure of 45 MPa. The final grain size of B₄C was close to that of the initial powders. A minimal grain growth was observed for SiC (400-500 nm). The sintered parts are being evaluated by ARL and, if mechanical properties are superior to those by conventional sintering, a patent application will be filed.

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3. L. A. Clevenger, A. Mutscheller, J. M. E. Harper, C. Cabral, Jr., and K. Barmak ,
Journal of Applied Physics Vol 72(10), (1992), 4918-24.