Materials Letters 144 (2015) 168–172

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Featured Letter

Smaller crystallites in sintered materials? A discussion of the possible mechanisms of crystallite size refinement during pulsed electric current-assisted sintering

Dina V. Dudina [a,b,*], Alexander G. Anisimov [c], Vyacheslav I. Mali [c], Natalia V. Bulina [a], Boris B. Bokhonov [a,b]

[a] Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of Russian Academy of Sciences, Kutateladze street 18, Novosibirsk 630128, Russia
[b] Novosibirsk State University, Pirogova street 2, Novosibirsk 630090, Russia
[c] Lavrentiev Institute of Hydrodynamics, Siberian Branch of Russian Academy of Sciences, Lavrentiev Avenue 15, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 13 November 2014
Accepted 13 January 2015
Available online 21 January 2015

Keywords:
Pulsed electric current-assisted sintering
Crystallite size refinement
Melting
Solidification
Phase transition
Chemical reaction
Reduction
Oxides

ABSTRACT

One of the most well-known and technologically attractive advantages of pulsed electric current-assisted sintering is its capability of fast and efficient consolidation of nanostructured powders into nanostructured or submicron-grained compacts. But can the application of pulsed electric current produce crystallites in the sintered material smaller than those that were present in the powder? Microscopic observations of this effect have been reported for inter-particle contacts formed during Spark Plasma Sintering and high-voltage consolidation. Our results obtained on Spark Plasma Sintered porous compacts consolidated from electrolytic copper powder suggest that finer crystallites in the sintered material than those in the raw powder can form in areas other than necks between the particles. Based on the electron microscopy and X-ray diffraction evidence as well as results obtained by other authors, we consider two possible mechanisms of crystallite size refinement during pulsed electric current-assisted sintering: rapid solidification of locally formed melt and reduction of oxide films present on the surface of powder particles in a reducing environment of the sintering die/chamber causing the in situ formation of metal particles. The possibilities of crystallite size refinement are further examined in a broader context as related to phase transitions and chemical reactions in the sintered materials.

1. Introduction

The mechanisms of fast and efficient consolidation of fine-grained materials by pulsed electric current-assisted sintering have been widely discussed in the past two decades [1,2]. A great majority of research publications deal with low-voltage consolidation, also known as Spark Plasma Sintering (SPS). The possibility of nanostructure preservation during high-voltage consolidation of powders has also been demonstrated [3]. But can the application of pulsed electric current produce crystallites in the sintered material smaller than those that were present in the powder? Microscopic evidence of this effect has been reported for the material located in the inter-particle contact areas for Spark Plasma Sintering [4–8] and high-voltage electric discharge consolidation [9]. During high-voltage consolidation of a molybdenum powder under pressure, finer grains in the inter-particle regions formed due to enhanced plasticity of the material, and at higher energies of electric pulses – due to solidification of the melt [9]. Possibilities of local melting at inter-particle contacts have been predicted theoretically for materials processed by Spark Plasma Sintering [4] and high-voltage consolidation [9].

In most experimental investigations, the presence of refined zones locally formed in the sintered samples was confirmed using direct observations by electron microscopy, and no estimation of an average crystallite size from X-ray diffraction (XRD) line broadening had been made for the sintered samples. Worth particular attention is the work of Shearwood and Ng [10], who did carry out the XRD analysis of Spark Plasma Sintered tungsten and suggested that small precipitates of metallic tungsten formed as a result of reduction of tungsten oxides during sintering were the reason of the size of the coherently scattering domains of the sintered material changing little with sintering temperature. In our work, we utilize the XRD as a method allowing for a quantitative characterization of the volume of the material containing refined

* Corresponding author. Tel.: +7 383 233 24 10; fax: +7 383 332 28 47.
E-mail address: dina1807@gmail.com (D.V. Dudina).

http://dx.doi.org/10.1016/j.matlet.2015.01.042
0167-577X/

zones and combine it with electron microscopy to study the refinement effect in compacts Spark Plasma Sintered from electrolytic copper powder. Possible mechanisms of the crystallite size refinement are discussed.

2. Material and methods

Electrolytic copper powder (PMS-1, 99.5 wt%, Russian Federation) was used in this study. The content of oxygen in this powder is 0.8 at% (GOST 4960-2009, State Standard of the Russian Federation). Spark Plasma Sintering of the powder was carried out using a SPS Labox 1575 apparatus (SINTER LAND Inc.). Graphite dies of 20 mm internal diameter and graphite punches were used. The wall of the die was lined with carbon foil. Circles of carbon foil were placed between the sample and the punches. The temperature during the SPS was controlled by a pyrometer focused on the die wall. The sample was heated up to the maximum temperature, then the current was switched off and the sample was cooled down to room temperature. In pressure-assisted experiments, a uniaxial pressure of 12 or 40 MPa was applied at the beginning of the sintering cycle and kept constant through the cycle. The die/punch assemblies used for pressure-assisted and pressure-less experiments are shown in Fig. 1. Dense and porous cylindrical compacts 2–3 mm thick were obtained. After sintering, the circles of carbon foil could be easily removed from the compacts. Polishing operations were not applied to the compacts in order not to introduce plastic deformation into their surface and subsurface layers. For comparison, a cold-pressed compact was annealed in a flow of argon for 2 min at 750 °C. XRD patterns of the powder and sintered compacts were recorded using an X-ray diffractometer (D8 ADVANCE, Bruker) with Cu Kα radiation. XRD patterns of the compacts were taken from their flat ends. The crystallite size and strain were calculated by the Double-Voigt method [11] realized in TOPAS 4.2 software (Bruker AXS). The instrumental function was calculated using the fundamental parameters approach [12]. The microstructure of the coatings was studied by Scanning Electron Microscopy (SEM) using a Hitachi-3400S and Merlin Carl Zeiss Scanning Electron Microscopes. Secondary electron (SE) and back-scattered electron (BSE) imaging modes were used. Energy-dispersive spectra (EDS) of selected regions of the cross-sections of the samples were recorded.

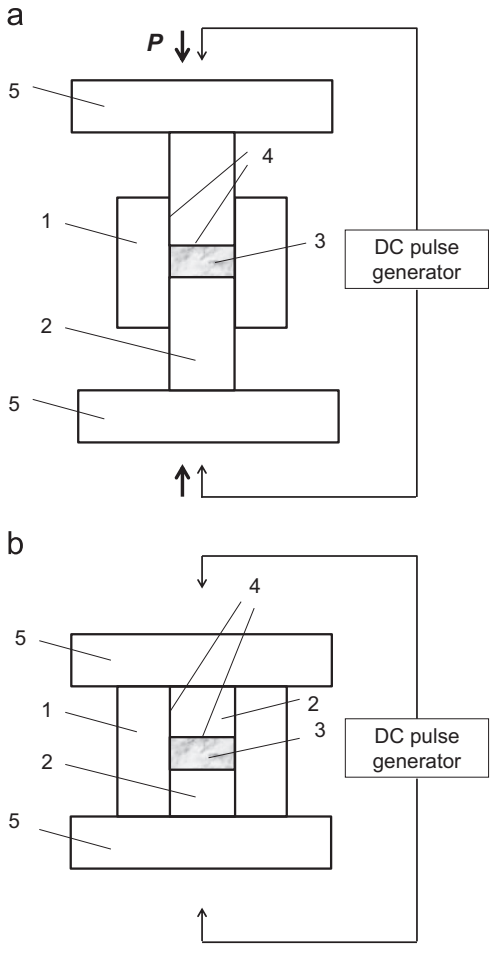

Fig. 1. Die/punch assemblies used for pressure-assisted (a) and pressure-less experiments (b): 1 – graphite die, 2 – graphite punches, 3 – sample, 4 – graphite foil, 5 – graphite spacers.

3. Results and discussion

We have investigated the structure of copper compacts varying in relative density. Unconventional processes between particles are more likely to occur at low pressures and high current densities [13], so a refined structure could be expected primarily in the porous samples. The XRD patterns of the electrolytic copper powder and consolidated samples are demonstrated in Fig. 2. As can be seen from Table 1, the size of crystallites in the Spark Plasma Sintered copper compacts has indeed decreased relative to that of the initial powder. The crystallites of the 96% dense material are larger than those of the porous compacts. The measured values of strain are lower than those observed in Spark Plasma Sintered Cu-based composites obtained from mechanically milled powders [14]. Figs. 3 and 4 show the morphology and surface of the grains of the electrolytic copper powder and fracture surface of the 73% dense Spark Plasma Sintered compact, respectively. A general view of the porous structure of the compact shown in Fig. 4(a) demonstrates terrace-step patterns on the surface of ligaments, which agrees with observations reported in Ref. [6]. While oxygen was detected in the central part of the compact by EDS, it was not found in the rim areas (the thickness of the rim area is about 2 mm) and regions adjacent to the flat ends of the sample. In those areas, fine precipitates on the surface of coarse grains were found (Fig. 4(b)–(d)). The precipitates have been confirmed not to be an oxide phase by comparing SE and BSE images of a selected region (Fig. 4(c) and (d)). In the presence of graphite as a material of the die/punches and foil lining the walls

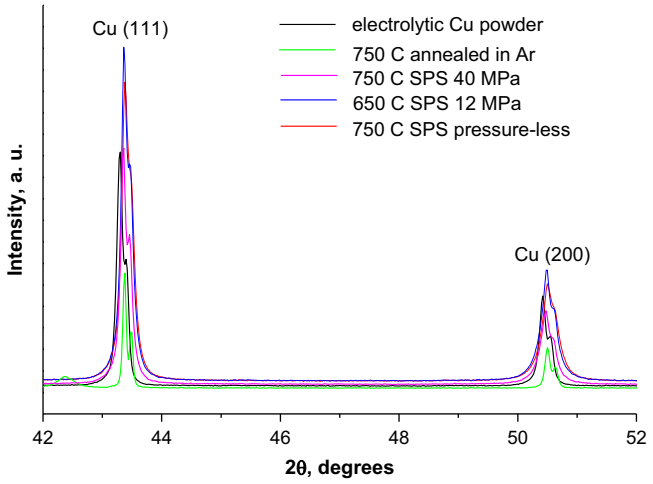

Fig. 2. XRD patterns of the electrolytic copper powder and consolidated samples – Spark Plasma Sintered an cold-pressed and conventionally annealed.