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ScienceDirect

Scripta Materialia 101 (2015) 103–106

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

New approach of the evolution of densification mechanisms during Spark Plasma Sintering: Application to zirconium (oxy-)carbide ceramics

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Received 7 January 2015; accepted 30 January 2015
Available online 19 February 2015

The kinetics of spark plasma sintered $ZrC_{0.94}O_{0.05}$ ceramics have been investigated. A change of densification mechanism appears during the intermediate and final sintering stages. During this last stage, the deformation mechanism is similar to the one involved during creep of dense $ZrC_{0.94}O_{0.05}$ ceramics. The comparison of densification and creep strain rates seems to show that no specific effects strongly enhance strain rate during the final densification stage of Spark Plasma Sintering.

Keywords: Carbides; Spark Plasma Sintering; Densification; Mechanism; Creep

Spark Plasma Sintering (SPS), which is based on the simultaneous application of high temperatures, high heating rate (up to 1000 °C/min), high axial pressure, and high electric current intensity (low voltage), is an attractive consolidation technique, since it allows densification under shorter cycle times than other pressure-assisted sintering processes (*i.e.,* hot pressing or hot isostatic pressing) [1]. SPS provides accelerated densification and, due to its shorter cycle time, limited and/or controlled grain growth. However, divergent analyses of SPS mechanisms have been reported in a recent viewpoint set [2]. Because of the complex nature of various phenomena involved in SPS, some specific effects are suggested to explain SPS benefits, such as electromigration [3], electromagnetic effect [4] or thermal diffusion involved by possible high local temperature gradients [5].

In order to study and understand the densification mechanisms involved during SPS and to highlight potential specific effects, mechanisms have been studied by transposing constitutive equations developed for creep to densification [6–9]. In a previous paper [7], we have studied the densification mechanisms involved during SPS of zirconium oxycarbide powders following Bernard-Granger's model [6]. However, we have recently shown that, even if this approach is attractive by the limited experiments needed to study the sintering mechanism, the identified densification parameters (*i.e.,* stress exponent n, grain size exponent m and apparent activation energy Q) can be potentially biased due to the strong dependence of the determined parameters to precise evaluations of the effective stress acting on the powder bed and of the effective shear modulus, and to the negligence of the radial and tangential thermally-generated stresses [10]. Then, in a forthcoming paper [9], we propose and justify the generalisation of a more robust approach allowing the identification of reliable densification parameters during hot uniaxial pressing treatment. This approach based on classical creep investigation consists in comparing the normalised shrinkage rates in isothermal and isobar conditions at given density for several grain sizes.

In the present study, we have carried out the refined treatment of the kinetics data of spark plasma sintered zirconium oxycarbide ceramics, initially studied following Bernard-Granger's approach. More particular, in the present case, we have applied the new suggested robust approach. The objectives are:

(i) to highlight possible errors in the identified densification mechanisms introduced by Bernard-Granger's and Guizard's approach;
(ii) to study the evolution of the densification mechanisms during sintering, from the intermediate (*i.e.*, 75% < density < 90%) to the final (*i.e.,* density > 90%) stage of densification;
(iii) finally, to compare the identified densification mechanisms during the final sintering stage to the compressive creep mechanisms determined, in a companion study [11], for dense ceramics of the same controlled composition $ZrC_{0.94}O_{0.05}$. The objective is to bring out possible discrepancies in plastic deformation mechanisms that can be related to specific contributions induced during SPS.

As described in [7], zirconium oxycarbide powders with both the chemical composition $ZrC_{0.94}O_{0.05}$ (*i.e.,*

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http://dx.doi.org/10.1016/j.scriptamat.2015.01.028
1359-6462/

0.7 ± 0.1 wt.% O; 10.9 ± 0.1 wt.% C) and exhibiting a bimodal grain size distribution of 0.3 and 2 μm were synthesised using the carboreduction route. This route, often used in industrial processing, provides products with controlled chemical composition (*i.e.,* free carbon and oxygen contents) and morphologies which are then well suited to being sintered [12].

The SPS tests were conducted under vacuum using the apparatus (SPS-2080, SPS Syntex Inc., Kanagawa, Japan) located at the University of Toulouse, France (PNF^2 CNRS platform). The zirconium oxycarbide powders were placed in a 20.3 mm internal diameter graphite die which had been previously lined with 0.15 mm Papyex® (Mersen, France). The powder bed was pre-compacted at room temperature before being placed inside the SPS chamber.

The regulation temperature of the SPS furnace was measured by a digital IR pyrometer. The target temperature was measured by focusing the digital pyrometer on the outer surface of the graphite die. A previous work [13] has demonstrated and characterised the thermal gradient appearing between the sample and the graphite die surface during the SPS treatment of zirconium oxycarbide powders. Hence the actual temperature of the sample was corrected from the temperature measured by the IR pyrometer following the same method. The corrected soaking temperatures were 1944, 2006, 2187 °C.

The heating rate was 100 °C min^{-1}, and the dwell times were ranged from 2 to 20 min. Tests were performed at different applied stresses of 25, 50 and 100 MPa.

During the SPS treatments, the displacement was recorded. For each experiment, a blank cycle was performed by submitting a fully dense pellet to a complete heating cycle, in order to remove the dilatation of the spacers, punches and powder from the recorded data. Finally, the evolution of the relative density on the isothermal dwell was calculated from the recorded axial displacement *via* the following expression:

$$\rho_i = \rho_f \cdot \frac{h_f}{h_i} \tag{1}$$

where ρ_i is the instantaneous relative density, ρ_f the final relative density (measured by Archimedes method and geometrically), h_f the final height of the sample and h_i the instantaneous height of the sample.

In addition to the identification of densification parameters, structural observations by transmission electron microscopy (TEM) were conducted to determine active deformation mechanisms. The study was performed using a JEOL 2010 microscope operating at 200 kV (JEOL, Tokyo, Japan). The thin foils for TEM were prepared by cutting thin slices with diamond wire (2×2 mm^2 section). These slices were then ground, dimpled and finally thinned down to perforation by Ar-milling with a 4 kV accelerating voltage with PIPS 691 apparatus (GATAN Inc., Pleasanton, USA).

As shown in [7], grain growth is negligible for relative density lower than 96% whatever the thermomechanical conditions, and the average grain size of pellets remains around 1 μm. Consequently, in the following, the normalised shrinkage rates under isothermal conditions will be studied for relative density lower than 96%.

To identify the densification parameters (*i.e.,* stress exponent and apparent activation energy values), the sintering kinetics evolution is studied in isothermal and isobar conditions, as shown in Figure 1a. Whatever the thermomechanical conditions, shrinkage rates exhibit a monotonous exponential decrease during the consolidation process.

During the isothermal dwell, the stress exponent values determined for given densities at several temperatures are determined from the slope of the curve representing $\ln\left(\frac{1}{\rho}\cdot\frac{d\rho}{dt}\right)$ as a function of $\ln(\sigma_{zz})$ (Fig. 1b). For relative densities ranging from 76% to 88% (*i.e.,* for the intermediate sintering stage), the stress exponent values remain low around 1–2 whatever the soaking temperatures and applied stresses. However, for density higher than 90% (*i.e.,* final sintering stage), the stress exponent increases to values around 3–4, as shown in Figure 2 that represents the evolution of the stress exponent values during the consolidation process. These new analyses lead to lightly different interpretations of the involved mechanisms. As a matter of fact, following the previous approach of Bernard-Granger and Guizard, the calculated values of stress exponent change with the macroscopic applied stress: at low macroscopic applied stress (25 MPa), a grain boundary sliding mechanism ($n \leqslant 2$) appears to govern the densification process, while a dislocation motion mechanism ($n \geqslant 3$) seems to operate at higher applied stress (100 MPa) [7]. At the opposite, based on the new approach, the predominant densification mechanism seems to be governed by the relative density evolution that impacts strongly the local effective stress evolution developed from the macroscopic applied stress. Besides the TEM structural observations agree with this interpretation: the specimen sintered at 2006 °C for 5 min under 25 MPa exhibits few dislocations for a relative density of 88% (Fig. 3a), whereas the specimen sintered at 2006 °C for 2 min under 100 MPa reveals the presence of a high density of dislocations for a relative density of 94% (Fig. 3b). Dislocations show a clear tendency to gather in a heterogeneous way along dislocation walls.

Determined apparent activation energies are similar to those estimated in [7] (Fig. 4). Activation energy is around 750–770 kJ mol^{-1} whatever the macroscopic applied stresses and for both considered sintering stages (*i.e.,* for relative densities of 82% and 90%). These values are close to the one found in the literature for zirconium lattice diffusion (*i.e.,* 720 kJ mol^{-1} [14]), and, conversely, is quite different from the value determined for carbon bulk self-diffusion (*i.e.,* 470 kJ mol^{-1} [15]) in ZrC_x.

Finally, during the final sintering stage (*i.e.,* for a relative density higher than 90%), the identified densification mechanism can be compared to the creep mechanism determined in a companion study [11]. Compressive creep experiments at 1600 °C were conducted on dense ceramics (relative density higher than 99%) of the same controlled composition $ZrC_{0.94}O_{0.05}$ with an average grain size of 4.7 μm. For an applied stress above 100 MPa, the determined creep parameters are: a stress exponent value of 3.3 ± 0.4, a grain size exponent value around 0, and an apparent activation energy (Q_{creep}) of 733 ± 12 kJ mol^{-1}. Therefore, it appears that the plastic deformation mechanism during the final sintering stage is similar to the one involved during creep, and is controlled by a power law creep regime.

If the involved mechanism is identical, the strain rates measured during SPS and creep experiments can be compared. The discrepancy of strain rates may be related to differences in the mechanical configuration (*i.e.,* uniaxial