Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 3447–3452
www.elsevier.com/locate/jeurceramsoc

Conversion from nano- to micron-sized structures: experimental observations

Zhijian Shen*, Hong Peng, Jing Liu, Mats Nygren

Department of Inorganic Chemistiy, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden

Abstract

When consolidating nano-sized powders of various oxides and non-oxides susceptible or not susceptible to liquid-phase sintering by SPS technique, we observed a common feature of rapid conversion from nano- to micron-sized structures. The conversion is strongly temperature-dependent and above a critical temperature (T_g) grain growth occurs very rapidly. Below T_g there is a narrow temperature window where nano-sized powders can be fully densified without or with very limited grain growth. Above T_g rapid grain growth takes place in fully densified bodies owing to the high driving force provided by the large surface energy of nano-sized grains. This in turn favours the preparation of ceramics with tailored microstructures, e.g. in situ reinforced ceramics. In this presentation, examples will be given to demonstrate the possibility to utilize the benefit gained from nano-structure to produce complex shaped ceramic components by superplastic forming and then converting the ductile nano-sized structure into a rigid in situ reinforced microstructure by post annealing above T_g.

Keywords: Al_2O_3; $BaTiO_3$; Grain growth; Kinetics; Microstructures; Nano-ceramics; Si_3N_4; Sintering; SPS

1. Introduction

When sintering nano-sized precursor powders densification is very often accompanied with an accelerated grain growth, because the capillary driving forces for densification via surface diffusion and grain growth relying on bulk diffusion become comparable in magnitude when the particle/grain size reduces to nano-level.[1] In order to suppress grain growth during densification it is therefore necessary to enhance the densification kinetics and/or to depress grain growth kinetics, i.e., to widen up the processing temperature window that yields nano-structured ceramics.

Over recent years we have applied a comparatively new sintering technique namely Spark Plasma Sintering (SPS) to consolidate nano-sized powders of various oxides and non-oxides. The SPS technique is similar to the conventional hot pressing process, i.e., the precursor powders are loaded in a die and an uni-axial pressure is applied during the sintering. However, instead of using an external heating source, a pulsed direct current is allowed to pass the electrically conducting die, in applicable cases also, through the sample. This implies that the die also acts as a heating source. Because of the efficient thermal transfer, the pressure applied, and, as discussed below, the presence of an electrical field that most possibly enhances diffusion/grain growth processes, very fast densification processes can be achieved. In fact utilizing the SPS technique the compaction process progress very rapidly and efficiently, i.e., is accomplished within a few minutes while the grain growth process is activated above the densification onset temperature, T_d. This implies that the SPS process provides us with unique possibilities to prepare nano-structured ceramics and allows us to follow the grain growth in fully densified bodies. It goes without saying that the grain growth process in nano-structured ceramics is thermal activated. Thus according to our experience a drastical increase of the grain growth rate occurs slightly above the critical grain growth onset temperature, T_g. The potential to separate grain growth process from the densification one bears implications for producing polycrystalline ceramic materials with nano-structures and novel properties.

In this article, we are giving a brief overview of observations gathered in connection with densification of aluminium oxide and barium/strontium based titanium oxides and liquid-phase sintering of silicon nitride-based ceramics. The grain growth kinetics is difficult to

* Corresponding author. Tel.: +46-8-162388; fax: +46-8-152187.
E-mail address: shen@inorg.su.se (Z. Shen).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2003.10.033

explore in the latter systems as it is frequently masked by the phase transformations and reactions leading to the formation of various sialon solid solution phases that occurs simultaneously.

2. Experimental

The SPS process was carried out in vacuum in a spark-plasma sintering apparatus, Dr. Sinter 2050 (Sumitomo Coal Mining Co. Ltd., Japan). The precursor powders were loaded in a cylindrical carbon die with an inner diameter of 12 or 20 mm. The temperature was automatically monitored and regulated either by a thermocouple inserted in the graphite die or by an optical pyrometer focused on the surface of the die. In most cases the heating rate was set to 100 °C/min in the temperature range of interest, and a pressure of 50 MPa was applied from the start to the end of the sintering cycle. The set-up allows a cooling rate of >350 °C/min^{-1} in the temperature range of 1800–1000 °C.

It is commonly observed that in the SPS apparatus the sample is exposed to a higher temperature than the one recorded by the thermocouple or optical pyrometer, respectively. The difference strongly depends on various conditions, e.g. the geometrical configuration and electrical property of the die, the heating rate and pressure applied, the thermal insulation of the die, the chamber volume, and atmosphere inside the camber etc.[2] Our previous studies have verified that under the experimental conditions applied in this study, this temperature difference is about 75 °C.[3] The temperatures referred to below are the recorded ones.

The bulk densities of the sintered specimens were measured according to Archimedes' principle. The crystalline phase assemblies present in the sintered samples were determined from their Guinier–Hagg X-ray powder diffraction patterns. Monochromatic CuK_{α_1} radiation was used with Si as internal standard. Both polished and fracture surfaces of the prepared samples were examined in a scanning electron microscope (SEM; Jeol JSM 880) equipped with an energy-dispersive spectrometer (EDS, LiNK *ISIS*). The grain growth is examined by estimating the width and length of the largest grains formed. The average size of the 10 largest grains that could be clearly distinguished in SEM micrographs of the fractured surfaces was measured. Five randomly selected, equally magnified areas of each sample were recorded and used for these measurements. The sizes of the selected grains were determined without any correction by an image analysis program (Image tool, UTHSCSA).

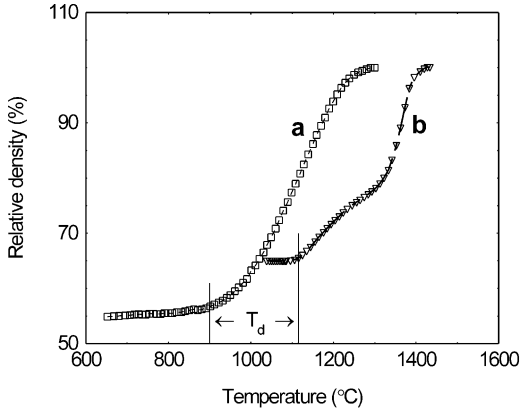

Fig. 1. The relative densities plotted versus the temperature for; (a) a nano-sized α-Al_2O_3 powder with an average particle size ~200 nm; (b) a lithium-doped dual phase α–β sialon ceramic, $LiSi_{8.5}Al_{3.5}O_{3.9}N_{12.6}$ using nano-sized α-Si_3N_4 powder (~100 nm) as starting powder.

3. Results and discussions

The variation of the relative density during the consolidation of two representative samples, one aluminium oxide nano-powder (Taimicron DAR) and a lithium-doped dual phase α–β sialon ceramic with α-Si_3N_4 (Ube, E-10) as one of the main precursors, are presented in Fig. 1. The samples are heated at a rate of 100 °C/min and pressure of 50 MPa was applied. No holding time at the final sintering temperatures was used. The densification starts at ~900 °C (T_d) and stops at ~1250 °C for aluminium oxide and starts at ~1100 °C (T_d) and stops at ~1400 °C for the sialon sample. In both cases the main part of the densification occurs within a period of 3 min, showing that the densification kinetics in the SPS process is radically faster than in conventional sintering processes. In general, it has been verified that fully dense compacts can be obtained at temperatures 200–300 °C higher than the onset temperature, T_d, of the densification.[3–7]

3.1. Aluminium oxide

The grain growth process starts at a slightly higher temperature than T_d as shown in Fig. 2. Once activated, the grain growth process progresses very rapidly. However, it is possible to determine a temperature "window", labelled regime II in Fig. 2, within which fully dense compacts can be obtained without or with very limited grain growth.[6] The critical temperature, T_g, above which the grain growth rate becomes appreciable is determined not only by the properties of the precursor powders, e.g. their particle size, reactivity, degree of agglomeration, etc., but also by the applied heating rate and pressure. The use of well de-agglomerated nano-sized precursor powders appears to be crucial in order to suppress grain growth and to obtain homogeneous microstructures.

3.2. Barium/strontium titanites

Almost fully dense compacts of $BaTiO_3$ and $SrTiO_3$ were obtained at 900 and 925 °C, respectively, using nano-sized precursor powders and a heating rate of 100 °C/min, a pressure of 50 MPa and no holding time, as seen in Fig. 3. $SrTiO_3$ can be densified at 900 °C, but in that case a prolonged heating time and a higher pressure (100 MPa) must be applied. In both cases the grain growth starts at $T > 925$ °C, and initially a distinct bimodal grain structure is formed containing very coarse grains (10–20 μm in size) and nano-sized grains, see Fig. 4. It is remarkable that a minor increase of the sintering temperature (25 °C) results in an increase of the grain size by almost two orders of magnitude, indicating the difficulty of preparing nano-structured ceramics of this type of compounds.[7]

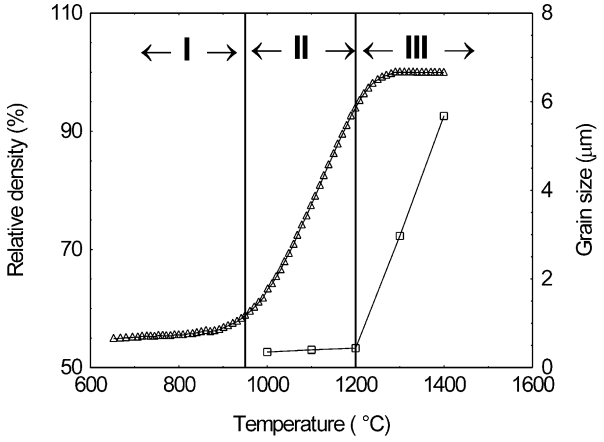

Fig. 2. Relative density and average grain size of aluminium oxide in compacts quenched from sintering temperatures ranging from 1000 to 1400 °C when a heating rate of 100 °C/min and a pressure of 50 MPa are applied. Within temperature regime I there is no densification or grain growth, whereas in regime II densification occurs, accompanied by very limited grain growth, and within regime III fast grain growth occurs in a fully dense body.

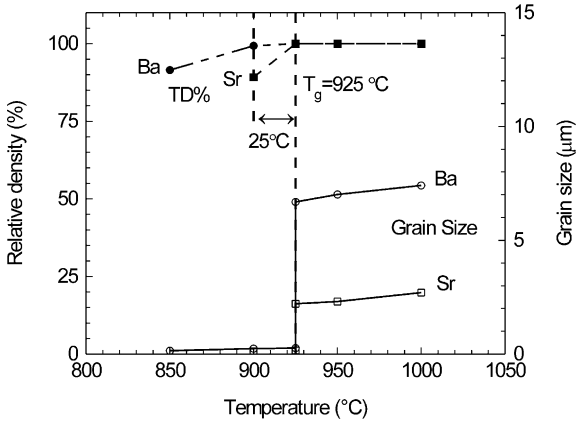

Fig. 3. Relative densities and average grain size obtained by SPS processing of $BaTiO_3$ and $SrTiO_3$ nano-powders plotted versus the temperature. Fully dense nano-sized ceramics can be obtained within a very narrow temperature window (25 °C).

These experimental observations clearly reveal that the densification and grain growth processes are thermal-activated and strongly temperature-dependent. The feasibility of densification without grain growth relies on the promotion of grain-boundary diffusion and simultaneously suppresses the grain-boundary migration. It seems that the latter has high activation energy than the former, thus requiring higher temperatures to be activated. During SPS processing the samples are effectively heated and it has been argued that a discharge process that originates from the electric field set up by pulsed direct current enhances the densification rate. Anyhow, in order to obtain nano-sized ceramics the use of high heating rates and pressures is not enough but the final sintering temperature has to be below T_g.

3.3. Silicon nitride

During the liquid-phase sintering of silicon nitride-based ceramics densification, phase transformation/reactions and grain growth often take place simultaneously making it difficult to study the kinetics. In the SPS process, however, the densification is promoted by the rapid formation and homogenisation of the formed liquid-phase, as the diffusion is enhanced by the high heating rate used and by the electric field set up that in turn enhance the motion of charged species. Fully dense compacts are thus typically obtained in the temperature range 1450–1550 °C using only a few minutes of holding. These compacts consist of nano-sized grains and have crystalline phase assemblies that are far from their thermodynamic equilibriums. It provides us with a unique opportunity to follow the phase transformation/reactions and grain growth processes that take place during subsequent heating and annealing at higher temperatures.

The phase evolution and grain growth in fully dense bodies of an Yb-stablized α-sialon ($Yb_{0.35}Si_{9.75}Al_{2.25}O_{1.2}N_{1.48}$) and a silicon nitride (with 7.5% Y_2O_3 and 2.5% Al_2O_3 additions) ceramic as function of sintering temperature and annealing time at 1500 °C are given in Fig. 5. In the case of the α-sialon ceramic the phase transformation is not accompanied with any obvious grain growth up to 1650 °C, while in the case of the silicon nitride ceramic the phase transformation and grain growth occur concurrently even at a temperature as low as 1500 °C. However, at 1400 °C fully densified compacts of the latter compound could be obtained and in that case almost no phase transformation and grain growth could be found, implying that the grain size and β-phase content of this compact resembled that of the silicon nitride precursor powder, e.g. ~220 nm and less than 10%, respectively. In both cases the grain growth process is strongly temperature-dependent and progresses very rapidly when it is activated as seen in Fig. 5a and b. When one approaches a sufficiently high

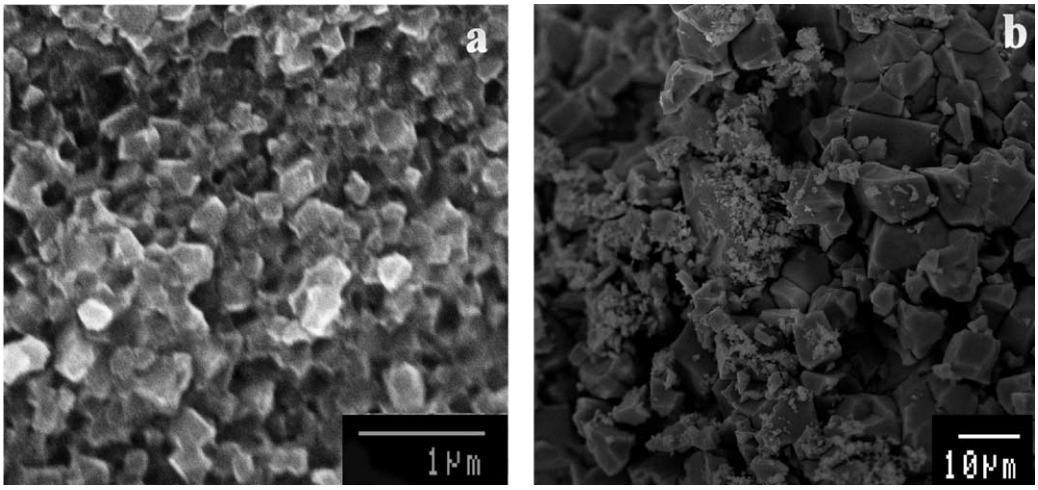

Fig. 4. Microstructures of $BaTiO_3$ sintered at 900 °C (a) and at 925 °C (b). Identical sintering conditions have been used besides the sintering temperature. Note the different grain sizes.

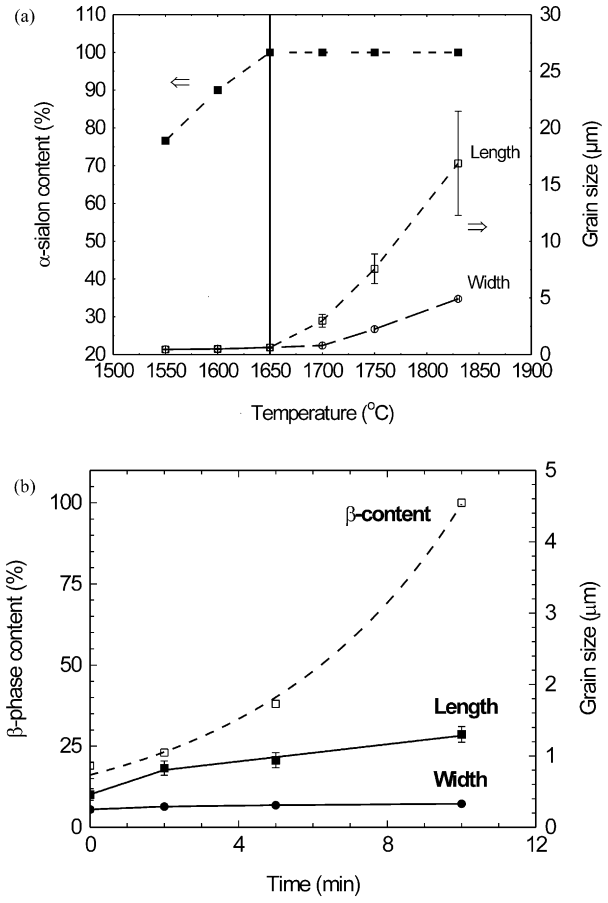

Fig. 5. Phase content and average size of the largest grains for: (i) an Yb-stablized α-silaon, $Yb_{0.35}Si_{9.75}Al_{2.25}O_{1.2}N_{14.8}$ heated to various temperatures at a rate of 200 °C/min using a pressure of 50 MPa and no holding time (a); (ii) a silicon nitride ceramic doped with 7.5% Y_2O_3 and 2.5% Al_2O_3 heated to 1500 °C using a heating rate of 200 °C/min and pressure of 50 MPa (b).

temperature the nano-sized equi-axed grains are convert into well-faceted elongated grains up to 5–10 μm in length within a few minutes, as seen in Fig. 6. Applying higher heating rates favours the growth of elongated grains via a dynamic ripening mechanism, i.e., by bringing compacts consisting of a nano-sized microstructure and a liquid-phase that grossly deviates from thermodynamic equilibrium to higher temperatures, a strong chemical driving force for grain growth is created.[3]

Up to now it has been commonly accepted that the α- to β-Si_3N_4 phase transformation and reactions leading to the formation of various sialon phases are beneficial to grain growth (ref. 8 and the references therein). Our observations seem, however, to indicate that there is no obvious correlation between phase transformation/reactions and grain growth, i.e. phase transformation/reactions and grain growth are two individual temperature-dependent processes that in most sialon systems can be studied separately as the onset temperature for the phase transformation/reactions (T_t) and grain growth (T_g) are sufficiently different while for silicon nitride T_g and T_t are very similar. This thus implies that it is difficult to avoid grain growth in connection with the α- to β-Si_3N_4 phase transformation in the latter case.

Both phase transformation and grain growth take places via a similar mechanism of dissolution–diffusion–reprecipitation. The possibility to obtain sialon ceramics with very limited grain growth can in part be ascribed to that the liquid present in the sialon systems is formed at lower temperatures than the one formed in the silicon nitride case. In general, our observations reveal that $T_g \geqslant T_t \geqslant T_d$ in silicon nitride-based ceramics, as illustrated in Fig. 7. These critical temperatures are adjustable by composition and processing design. Any adjustment of the composition and/or processing parameters that results in a reduction of the kinetics of the densification and/or transformation, e.g. the curves a and b is replaced by the curves a′ and b′ in Fig. 7, may thus imply that the grain growth takes place during densification and/or phase transformation processes. With conventional sintering techniques, e.g. pressure-less

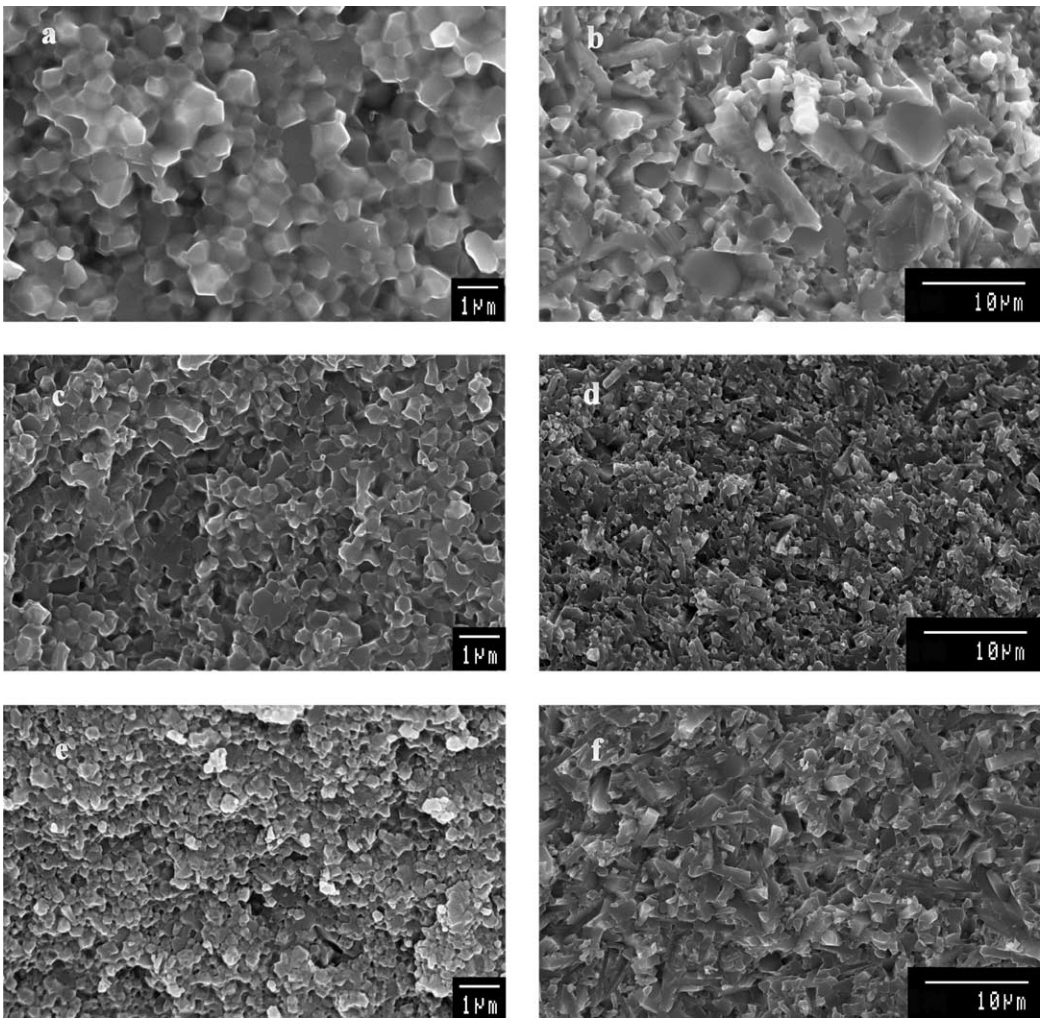

Fig. 6. SEM photos of the fractured surfaces of: (i) an α-sialon, $Yb_{0.35}Si_{9.75}Al_{2.25}O_{1.2}N_{14.8}$, heated to 1650 °C (a) and 1750 °C (b) using a pressure of 50 MPa and no holding time; (ii) a β-sialon, $Y_{0.01}Si_{1.91}Al_{0.215}O_{0.166}N_{2.66}$ heated to 1550 °C (c) and 1750 °C (d) using a pressure of 50 MPa and 4 and 5 mm holding times, respectively; (iii) a silicon nitride ceramic doped with 7.5% Y_2O_3 and 2.5% Al_2O_3 heated to 1450 °C (e) and 1830 °C (f) using a pressure of 50 MPa and 10 and 0 min holding times, respectively. Both nano- and tough interlocking microstructures are formed depending on the sintering conditions used. The α- and β-sialon samples are all monophasic; the nano-sized silicon nitride ceramic consists of only 10% β-phase (e) whereas the α- to β- transformation is completed in sample (f).

sintering, hot-pressing and gas pressure sintering, high temperatures are used to enhance densification kinetics, and the normally used sintering temperatures are well above the T_t and T_g ones observed in the SPS process.

Below T_g the obtained nano-structured ceramics are stable against grain growth, no matter if they consist of equilibrium or non-equilibrium phase constituents. This type of nano-structured ceramics is ideal for superplastic deformation. We have performed compression tests in SPS apparatus by loading cylindrical, fully compacted specimens with a diameter of 12 mm and a height of ~6 mm in a graphite die having an inner diameter of 20 mm, and heating this die with a constant rate of 40 °C/min under a uniaxial compressive load of 40 MPa applied via the punches of the graphite die. The load was applied at room temperature and was held constant during the entire deformation process, implying that the applied stress is decreased from 40 to 20 MPa at 50% strain, due to expansion of the surface area exposed to pressure. The compressive deformation strain, defined as $\Delta L/L_0$, where ΔL and L_0 represent the shrinkage of sample height and the original height of the sample before deformation, respectively, of two sialon ceramics is plotted versus the temperature in Fig. 8. Compressive strain rates in the order of 10^{-2} s^{-1} were obtained for $T \geqslant 1500$ °C. This is two to three orders of magnitude faster than previous findings. The formidable increase of the superplasticity is understood in terms of that the electric field set up by the pulsed direct current enhances the motion of the charged species in grain-boundary liquid phase thus promote the deformation process via enhanced grain-boundary sliding.[9,10] The nano-structures of the deformed pieces can be easily converted to tough self-reinforced microstructures consisting

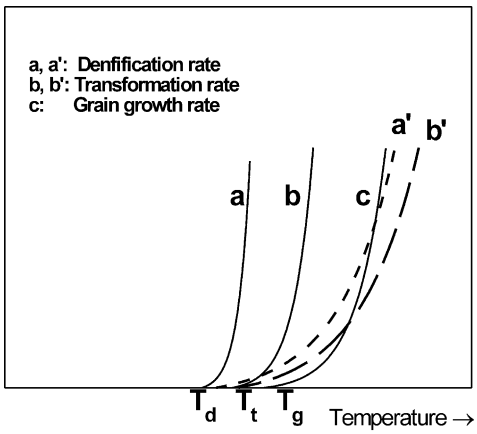

Fig. 7. A schematic drawing illustrating the kinetics of three temperature-dependent processes, densification, transformation and grain growth that often occur simultaneously in sintenng of silicon nitride-based ceramics. See also text.

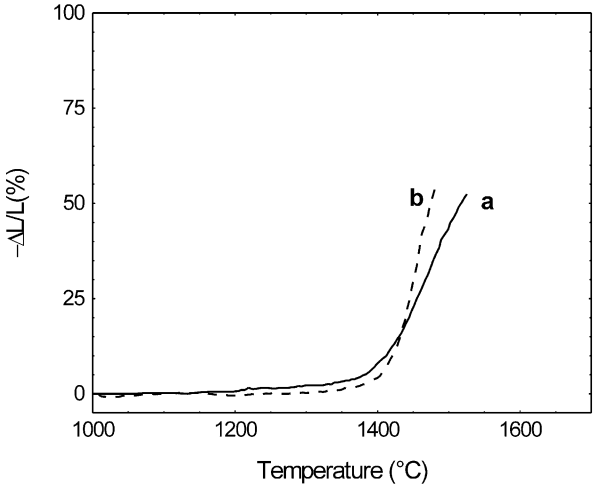

Fig. 8. Compressive strain curves recorded during superplastic deformation of two mono-phasic α-sialon samples with an overall composition of $Y_{0.175}Yb_{0.175}Si_{9.75}Al_{2.25}O_{1.64}N_{14.54}$ (a), and $LiSi_{8.5}Al_{3.5}O_{2.5}N_{13.5}$ (b).

of interlocking elongated grains by post annealing the deformed sample above T_g as discussed above.

4. Concluding remarks

The densification, phase transformation/reactions and grain growth are thermally activated processes that are strongly temperature-dependent. Fully dense nano-structured ceramics are prepared by enhancing the densification kinetics through spark plasma sintering. The nano-sized microstructures are converted to micro-ones very rapidly above the onset temperature of the grain growth. Below T_g the nano-grained structures are stable against grain growth no matter if they consist of equilibrium or non-equilibrium phase constituents, which opens up the possibility to perform superplastic forming. The enhanced kinetics of densification and deformation in the SPS process are ascribed to that the electric field set up by the pulsed direct current used to heat the sample enhances the motion of the charged species in grain-boundary liquid-phase.

Acknowledgements

This work is sponsored by the Swedish Research Council through grant 621-2002-4299.

References

1. Chen, I.-W. and Wang, X.-H., Sintering dense nanocrystalline ceramics without final-stage grain growth. *Nature*, 2000, **404**, 168–171.
2. Suganuma, M., Kitagawa, Y., Wada, S. and Murayama, N., Pulsed electric current sintering of silicon nitride. *J. Am. Ceram. Soc.*, 2003, **86**, 387–394.
3. Shen, Z., Zhao, Z., Peng, H. and Nygren, M., Formation of tough interlocking microstructures in silicon nitride ceramics by dynamic ripening. *Nature*, 2002, **417**, 266–269.
4. Gao, L., Shen, Z., Miyamoto, H. and Nygren, M., Superfast densification of oxide/oxide ceramic composites. *J. Am. Ceram. Soc.*, 1999, **8**, 1061–1063.
5. Shen, Z. and Nygren, M., Kinetic aspects of superfast consolidation of silicon nitride based ceramics by spark plasma sintering. *J. of Mater. Chem.*, 2001, **11**, 204–207.
6. Shen, Z., Johnsson, M., Zhao, Z. and Nygren, M., Spark plasma sintering of alumina. *J. Am. Ceram. Soc.*, 2002, **85**, 1921–1927.
7. Liu, J., Shen, Z. and Nygren, M. (in manuscript).
8. Petzow, G. and Herrmann, M., Silicon nitride ceramics. *Structure and Bonding (Berlin, Germany), (High Performance Non-Oxide Ceramics II)*, 2002, **102**, 47–167.
9. Shen, Z., Peng, H. and Nygren, M., Formidable increase in the superplasticity of ceramics in the presence of an electric field. *Adv. Mater.*, 2003, **15**, 1006–1009.
10. Shen, Z. Peng, H. and Nygren, M. Rapid densification and deformation of Li-doped sialon ceramics. *J. Am. Ceram. Soc.* (in press).