Journal of the European Ceramic Society 22 (2002) 2615–2620
www.elsevier.com/locate/jeurceramsoc

Plasticity of nanocrystalline yttria-stabilized tetragonal zirconia polycrystals

Felipe Gutiérrez-Mora*,[1], Arturo Domínguez-Rodríguez, Manuel Jiménez-Melendo

Departamento de Física Materia Condensada, Universidad de Sevilla, 41080 Seville, Spain

Received 19 December 2001; received in revised form 15 March 2002; accepted 11 April 2002

Abstract

The high-temperature behavior of nanocrystalline yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) with an initial grain size of 120 nm has been studied in uniaxial compression as a function of stress (5–200 MPa) and temperature (1150–1250 °C). The creep parameters, $n=2$ and $Q=630$ kJ/mol, were obtained for all experimental conditions. Evaluation of the strain rates showed that the material was more creep resistant than expected for very fine-grained materials. An interface-controlled mechanism is proposed to account for the experimental results. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Plasticity; Creep; Grain boundary

1. Introduction

Nanocrystalline materials have been widely studied in the last decade with the prospect of possessing better properties compared to their conventional counterparts. First studies dealt with the processing techniques to obtain fully dense bulk materials in order to test the novel properties.[1] From a mechanical point of view, sinterability or ductility are expected to improve with grain refinement. Also superplastic behavior may be obtained at lower temperatures and strain rates may be enhanced at a fixed temperature in these materials, allowing commercialization of net shaping applications such as superplastic forming[2,3] or superplastic joining.[4,5]

The high-temperature mechanical data are scarce (for a review see Ref. 6) due to the difficulty of fabricating large fully dense bulk samples retaining a nanocrystalline nature for testing. Most of these studies were carried out using porous materials, so that strains resulting from densification would mask the deformation results. High-temperature deformation data in ceramics is specially limited and only preliminary studies have been performed in systems such as TiO_2,[7,8] and yttria-stabilized zirconia (YSZ).[9–15]

The high-temperature mechanical behavior of conventional YSZ has been reported by many authors [for a review see Ref. 16] and it is commonly accepted that the primary deformation mechanism is grain-boundary sliding (GBS). The steady state strain rate $\dot{\varepsilon}$ at high temperatures is usually expressed by the constitutive creep law:

$$\dot{\varepsilon} = A\frac{Gb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{\sigma}{G}\right)^{n}D \tag{1}$$

where A is a dimensionless constant, G the shear modulus, b the magnitude of the Burgers vector, k the Boltzmann constant, T the absolute temperature, d the grain size, p the inverse grain size exponent, σ is the stress, n is the stress exponent and D the appropriate diffusion coefficient given by

$$D = D_0\exp(-Q/RT) \tag{2}$$

with D_0 the pre-exponential factor which contains a frequency factor and Q the activation energy of the mechanism controlling creep; R is the gas constant.

For identical materials tested in similar experimental conditions there is a considerable scatter in the mechanical parameters characterizing the creep behavior (n, p and Q). This fact has led to different interpretations for the strain rate controlling mechanism.[17–19]

---

* Corresponding author. Tel.: +1-630-252-5025; fax: +1-630-252-4798.

E-mail address: gutierrez@anl.gov (F. Gutiérrez-Mora).

[1] Now at Energy Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4838, USA.

PII: S0955-2219(02)00124-3

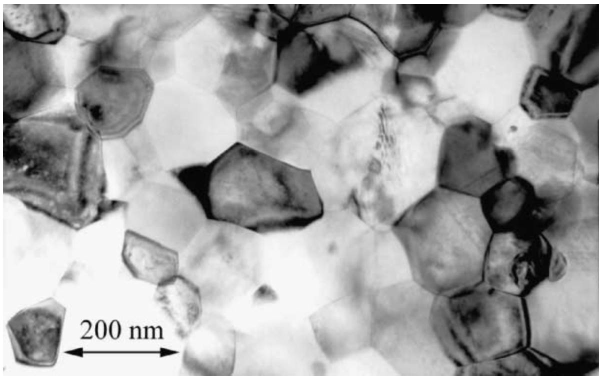

Fig. 1. Typical microstructure of the as-received materials before deformation. The mean grain size is equal to 0.12 μm.

The aim of this paper is twofold. First, to study if nanocrystalline YSZ can be deformed superplastically at lower temperatures and faster strain rates than the conventional YSZ. Second, to determine if the deformation mechanisms for conventional materials can be extrapolated to the nanocrystalline range.

2. Experimental procedure

Fully dense nanocrystalline ZrO_2–1.7 mol% Y_2O_3 was fabricated using powders prepared by chemical precipitation from mixed nitrate solutions. These powders were cold pressed at 300 MPa into cylinders and presintered in air at 1100 °C for 2 h. Finally, hot-isostatic pressing was performed for 4 h at 1350 °C in argon pressure of 150 MPa. A detailed description of the fabrication method was given somewhere else.[20]

Samples of 4×2×2 mm were cut and polished for high-temperature compressive tests performed in air at constant load. Temperatures between 1150 and 1250 °C and stresses between 5 and 200 MPa were used.

Microstructures of as-produced and subsequent to deformation were characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Grain size *d* (defined as the equivalent planar diameter) was measured from TEM pictures using a semiautomatic image analyzer (Zeiss Kontron Videoplan) averaging over more than 200 grains on each sample.

3. Results

Fig. 1 is a TEM image of the as-fabricated material. Well-faceted equiaxed grains, typical of the tetragonal phase, can be clearly observed. A mean grain size d of 120 nm was obtained from direct measurements of several thin foils.

Stress exponents and activation energies were calculated directly in compressive creep experiments at con-

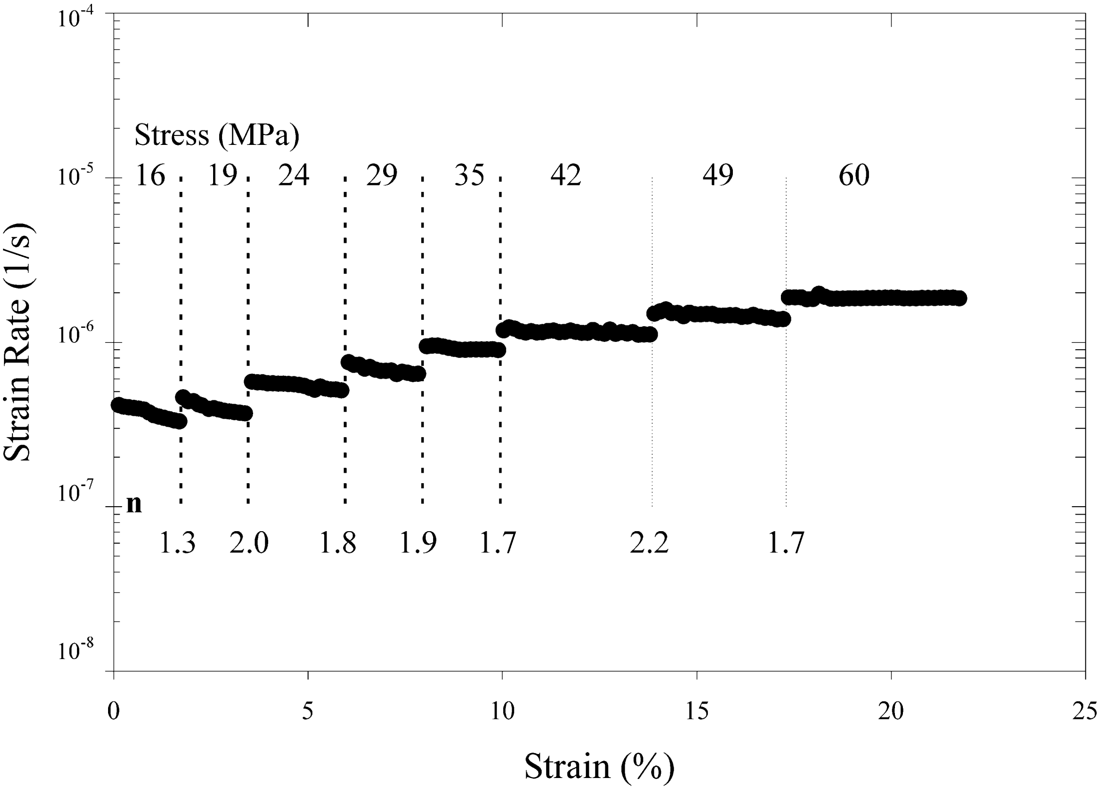

Fig. 2. Creep test to determine the stress exponent at 1150 °C in the as-received samples.

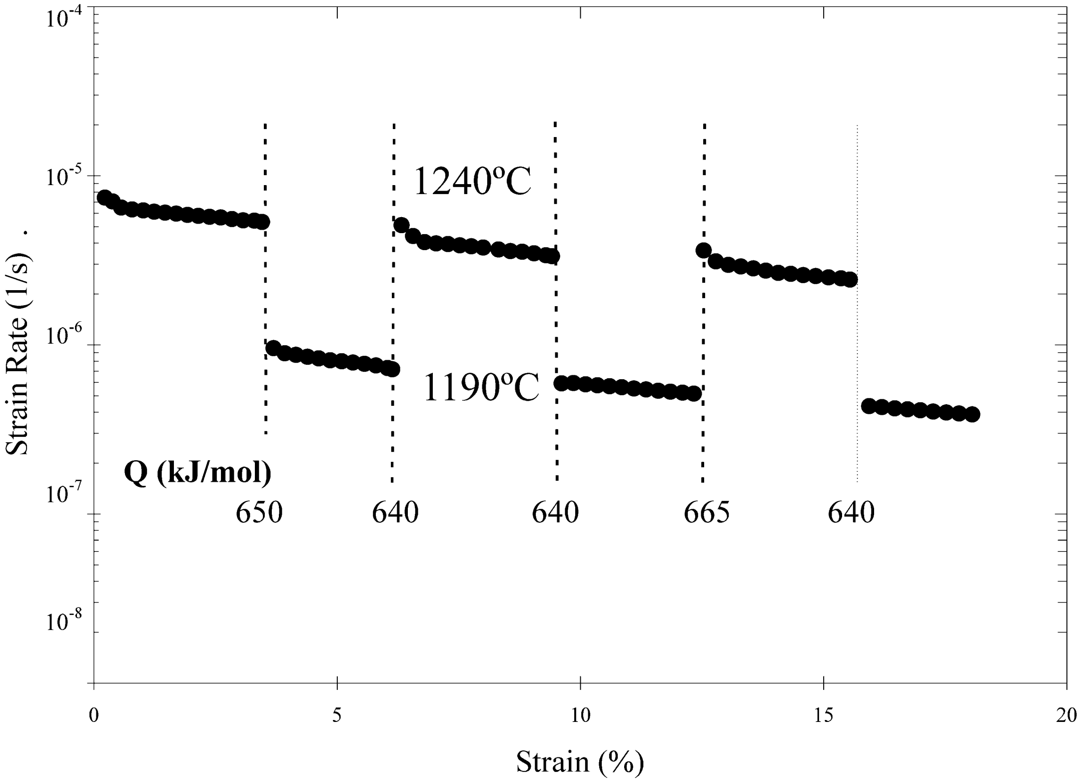

Fig. 3. Creep test to determine the activation energy between 1190 and 1240 °C using $\sigma = 13$ MPa.

stant load by changing the load and the temperature respectively. Typical tests are shown in Figs. 2 and 3 in a strain rate vs. strain plot. The results for the stress exponent and activation energy in the different experimental conditions are given in Tables 1 and 2, respectively. As shown in Table 1, the stress exponent is approximately 2 at all stresses and temperatures used.

The values of the stress exponent for conventional Y-TZP (0.3 μm $< d <$ 1 μm) follows two well-separated trends according to the purity of the material.[16] For highly pure samples (impurity content below 0.10 wt.%), the stress exponent is 2 for high stresses, while values of n as high as 5 have been reported for low stresses. The transition stress from the low-stress regime to high-stress regime is both grain size and temperature dependent. On the other hand, less pure materials (impurity content >0.10 wt.%) exhibit $n = 2$ throughout the whole range of stresses and temperatures.

Table 1
Stress exponent from direct determinations for all experimental conditions

Temperature (°C)	Stress range (MPa)	Stress exponent n
1150	15–60	1.9±0.3
	30–100	1.8±0.3
1200	20–60	2.0±0.3

Particle induced X-Ray Emission (PIXE) (Centro Nacional de Aceleradores, Sevilla, Spain) was used to determine the main impurities present in the material. The analysis revealed an appreciable concentration of titanium ([Ti] = 0.12 wt.%).[21] This, along with the stress exponent trend, show that the behavior of the stress exponent in nanocrystalline YSZ is similar to that of the impure conventional materials.

The values for the activation energy for different experimental conditions are given in Table 2, where an average value of $Q \sim 630$ kJ/mol is obtained. The activation energy for creep in the superplastic regime has been commonly associated with that of bulk cation diffusion [$Q \approx 500$ kJ/mol] and it has been reported that the addition of impurity would reduce this value.[22,23] However, the activation energy obtained in this study is

Table 2
Activation energy from direct determinations for all experimental conditions

Temperature range (°C)	Stress (MPa)	Activation energy (kJ/mol)
1150–1200	41	635[a]
	50	600[a]
	85	600±30
1190–1240	13	650±20
	69	605±20

[a] Only one measurement of the activation energy.

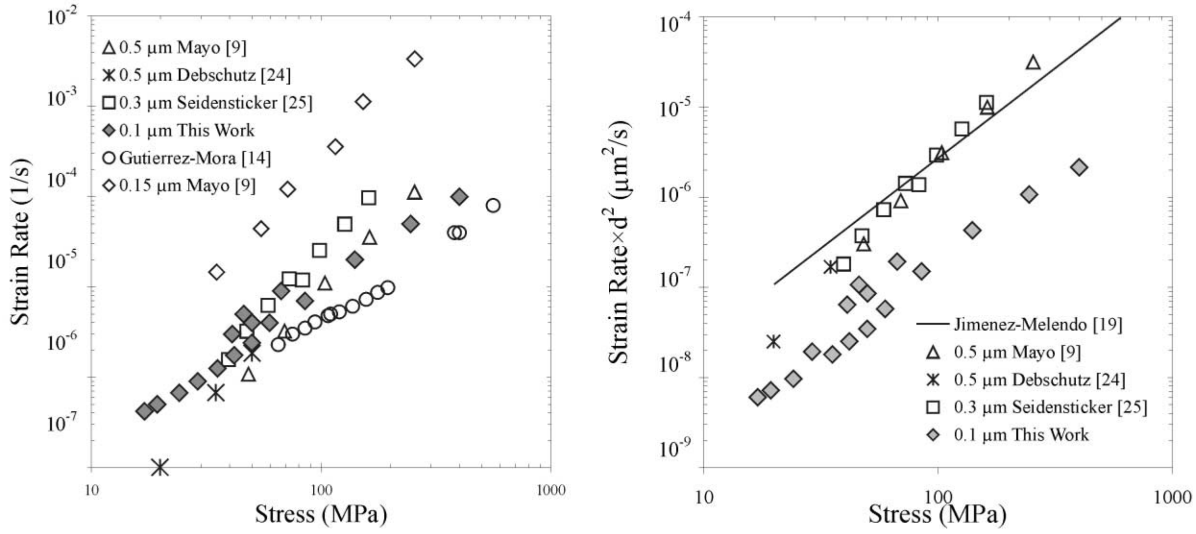

Fig. 4. (a) Comparison of the experimental results obtained at 1150 °C with data from literature in a strain rate versus stress plot. (b) Grain size normalized strain rate vs stress plot of experimental results at 1150 °C compared to literature data and a phenomenological equation [19].

higher than most of the values reported in literature for the creep of polycrystalline Y-TZP.

Another aspect of the high-temperature behavior, apart from the creep parameters, is the steady-state strain rate, since it is a measure of the creep resistance of the material. Supposing that nanocrystalline and conventional YSZ would deform by the same mechanisms, the same high-temperature creep law could be applied for both grain sizes. Taking into account that $\dot{\varepsilon}$ is inversely proportional to d^p [Eq. (1)], the strain rate increases as the grain size is reduced. Thus, depending on the value of p, a reduction from $d=0.5$ μm to $d=0.1$ μm results in an increase of the strain rate from 5 to 125 times for $p=1$ and $p=3$, respectively.

A direct comparison of strain rates for nanocrystalline and conventional YSZ at 1150 °C is given in Fig. 4. Very little data was found in the literature due to the relatively low temperature used, since most of the deformation of submicron YSZ has been carried out over 1250 °C. Fig. 4a is a plot of the absolute strain rate vs stress for different materials. It can be seen that the expected increase in $\dot{\varepsilon}$ does not occur; the nanocrystalline YSZ is as creep resistant as other materials with a larger grain sizes. Earlier results obtained in nanocrystalline YTZP that shows an increase in the strain rate[9] is also plotted. However, this material was 80% dense and the increase in $\dot{\varepsilon}$ can be attributed to densification processes taking place at the same time as deformation. More recent results in nanocrystalline 3Y-TZP[14] show considerable agreement with the present data. Although the grain size reported by Gutierrez-Mora et al.[14] was 40 nm as measured from XRD, later evidence suggested that the grain size was in fact larger and similar to the one of the as-received samples used in this work.

A comparison of different grain-sized materials can be more clearly made in Fig. 4b where the strain rate has been normalized with the square of the grain size[2]. Also the expression proposed for Jiménez-Melendo et al.[19] for impure YSZ obtained from an analysis of the data on conventional YSZ deformed between 1250 and 1450 °C is shown. The strain rate of the samples with a grain size of $d=0.1$ μm[3] are an order of magnitude slower than both the conventional material and the proposed expression.

Similar results have been found in other nanocrystalline materials. Deng et al.[26] found in nanocrystalline Ni-P that when decreasing the grain size from 0.3 μm to 30 nm the strain rate only increased in a factor of 2. Similarly, Sanders et al.[27] reported that the values of the strain rate for nanocrystalline Cu and Pd ($d\sim$10–50 nm) deformed two to four orders of magnitude slower than predicted from the conventional metals behavior.

Detailed microstructural characterization of the samples was performed after deformation. Grain growth only took place in the samples deformed under the more severe conditions (1250 °C) for a long period of time.

4. Discussion

The results obtained from the deformation tests do not agree with the interpretations of the mechanisms proposed to explain the experimental high-temperature mechanical data on conventional Y-TZP.[17–19] Although the value of the stress exponent is similar to those obtained for impure materials, the activation energy as

---

[2] d^2 Has been chosen to normalize the strain rate, because $p=2$ is the most accepted value proposed for the grain size exponent in the literature.

[3] To plot the strain rate, grain sizes have been multiplied for a factor 1.2 to compare with spatial grain size normally used in the literature.

well as the deformation strain rate disagree with those interpretations.

Experimental values of the strain rate along with microstructural observations indicate that the principal deformation mechanism is grain-boundary sliding. Pure difusional mechanisms such as Nabarro-Herring[28,29] and Coble[30] creep, can be ruled out since there is no appreciable elongation of the grains after the deformation.[21] A direct comparison[21] of the strain rates obtained in this work with typical grain-boundary sliding mechanisms[31,32] shows that the most approximate values to the experimental data are those grain-boundary sliding controlled by bulk cation diffusion. However, those mechanisms predict activation energy of the order of the cation bulk diffusion energy in disagreement with our results.

This disagreement can be explained at least qualitatively if the crystallographic structure and chemical composition of the grain boundaries is taken into account. Following the model proposed by Artz et al.,[33] the grain boundaries are not perfect sinks or sources for matter but discrete. Point defects are released and absorbed at the cores of grain-boundary dislocations when moving in a non-conservative motion in the grain-boundary planes. The presence of discrete sources and sinks modify the description of the deformation mechanism in two ways: first, by taking into account a finite number of dislocation in the grain boundary that depends on the grain size, and second, by considering a possible limitation of the mobility of the grain-boundary dislocations, e.g. presence of segregated impurities in the boundaries. This is called interface reaction controlled behavior.

In the interface reaction controlled limit, the activation energy and the strain rate are modified from those of diffusion-controlled grain-boundary sliding. The activation energy increases because of the presence of an additional energetic term due to the annihilation and creation of point defects, which also decreases the strain rate, in agreement with the experimental results.

However, there are some problems related to the application of this model to our material. First, model starts from a mechanism with $n=1$ increasing to $n=2$ when considering the interface reaction, but most of the data for conventional superplastic Y-TZP in the regime where deformation is controlled by diffusion exhibit an stress exponent equal to 2. Second, there are no experimental data for a diffusion coefficient for the solute atoms in the grain boundaries, consequently no quantitative evaluation of this model can be made to compare with the experimental results. Third, no dislocations were observed in single crystals with the same composition deformed at temperature as high as 1400 °C. Studies are in progress to determine the residual stresses in Y-TZP in order to know if dislocations can create at grain boundaries.

5. Conclusions

The high-temperature deformation mechanism for nanocrystalline Y-TZP is grain-boundary sliding accommodated by grain-boundary dislocation motion controlled by cation bulk diffusion with an additional contribution of interface reactions. This contribution explains the high value of the activation energy and the reduced steady state strain rate. A reduction in grain size does not imply an increase in the strain rate for a constant stress compared to the conventional grain-sized materials or a reduction in the temperatures required for superplasticity.

Acknowledgements

This research was supported by CICYT under grant n° MAT97–1007-C02 (Ministerio de Educación y Ciencia-Spain), by the Fund for the Promotion of Research at the Technion (1998) and by the Israel Ministry of Science.

References

1. Gleiter, H., Nanocrystalline materials. *Prog. Mater. Sci.*, 1989, **33**, 223–315.
2. Nieh, T. G. and Wadsworth, J., Superplasticity and superplastic forming of ceramics. *Mater. Sci. Forum*, 1994, **170–172**, 359–368.
3. Kahandal, R and Yasui, K., Recent advancements in superplastic forming and diffusion bonding (SPF/DB) technology, 1997. *Mater. Sci. Forum*, 1997, **243–245**, 687–694.
4. Domínguez-Rodríguez, A., Guiberteau, F. and Jiménez-Melendo, M., Heterogeneus junction of yttria partially stabilized zirconia by superplastic flow. *J. Mater. Res.*, 1998, **39**, 1631–1636.
5. Gutiérrez-Mora, F., Domínguez-Rodríguez, A., Routbort, J. L., Chaim, R. and Guiberteau, F., Joining of yttria-tetragonal stabilized zirconia polycrystals using nanocrystals. *Scripta Mater.*, 1999, **41**, 455–460.
6. Mohamed, F. A. and Li, Y., Creep and superplasticity in nanocrystalline materials: current understanding and future prospects. *Mater. Sci. Eng.*, 2001, **A228**, 1–15.
7. Hahn, H. and Averback, R. S., Low-temperature creep of nanocrystalline titanium(IV) oxide. *J. Am. Ceram. Soc.*, 1991, **74**, 2918–2921.
8. Hahn, H. and Averback, R. S., High-temperature mechanical properties of nanostructured ceramics. *Nanostruct. Mater.*, 1992, **1**, 95–100.
9. Ciftcioglu, M. and Mayo, M. J., Processing of nanocrystalline ceramics. *Mater. Res. Soc. Symp. Proc.*, 1990, **196**, 77–86.
10. Prabhu, G. B. and Bourrel, D. L., The hot hardness testing for superplasticity in nanocrystalline yttria-stabilized tetragonal zirconia. *Scripta Metall. Mater.*, 1995, **33**, 761–766.
11. Betz, U., Scipione, G., Bonetti, E. and Hahn, H., Low temperature deformation behavior of nanocrystalline 5 mol% yttria-stabilized zirconia under tensile stresses. *Nanostruct. Mater.*, 1997, **8**, 845–853.
12. Chen, L., Rouxel, T., Chaim, R., Vesteghem, H. and Sherman, D., Superplasticity and creep in monoclinic Y-SPZ nano-grained zirconia. *Mater. Sci. Forum.*, 1997, **245–245**, 245–250.

13. Betz, U. and Hahn, H., Ductility of nanocrystalline zirconia based ceramics at low temperatures. *Nanostruct. Mater.*, 1999, **12**, 911–914.
14. Gutierrez-Mora, F., Domínguez-Rodríguez, A. and Jiménez-Melendo, M., Creep of nanocrystalline Y-SZP ceramics. *Nanostruct. Mater.*, 1999, **11**, 531–537.
15. Bhattacharya, S. S., Betz, U. and Hahn, H., Some studies on the superplastic deformation behavior of nanocrystalline yttria-stabilized zirconia based ceramics. *Scripta Mater.*, 2001, **44**, 1553–1556.
16. Jiménez-Melendo, M., Domínguez-Rodríguez, A. and Bravo-Leon, A., Superplastic flow of fine-grained yttria-stabilized zirconia polycrystals: constitutive equation and deformation mechanisms. *J. Am. Ceram. Soc.*, 1998, **81**, 2761–2776.
17. Owen, D. M. and Chokshi, A. H., The high-temperature mechanical characteristics of superplastic 3 mol% yttria-stabilized zirconia. *Acta Mater.*, 1998, **46**, 667–679.
18. Berbon, M. Z. and Langdon, T. G., Examination of the flow process in superplastic yttria-stabilized tetragonal zirconia. *Acta Mater.*, 1999, **47**, 2485–2495.
19. Jiménez-Melendo, M. and Domínguez-Rodríguez, A., Like-metal superplasticity of fine-grained Y_2O_3-stabilized zirconia ceramics. *Philos. Mag. A*, 1999, **49**, 1591–1608.
20. Chaim, R. and Hefetz, M., Fabrication of dense nanocrystalline ZrO_2–3wt.%Y_2O_3 by hot-isostatic pressing. *J. Mater. Res.*, 1998, **13**, 1875–1880.
21. Gutierrez-Mora, F., PhD dissertation, University of Seville, Spain, 2001.
22. Gust, M., Goo, G., Wolfenstine, J. and Mecartney, M. L., Influence of amorphous grain-boundary phases on the superplastic behavior of 3-mol%-yttria-stabilized zirconia polycrystals (3Y-TZP). *J. Am. Ceram. Soc.*, 1993, **76**, 1680–1681.
23. Thavoriniti, P. and Sakuma, T., Influence of grain-boundary β-spodumene glass on the superplastic flow in tetragonal zirconia polycrystals (TZP). *Mater. Sci. Eng.*, 1995, **A202**, 249–255.
24. Debschütz, K. D., Caspers, B., Schneider, G. A. and Petzow, G., Critical evaluation of the compression test. *J. Am. Ceram. Soc.*, 1993, **76**, 2468–2474.
25. Seindensticker, J. R. and Mayo, M. J., Superplasticity in 3Y-TZP doped with small amounts of copper-oxide. *Scripta. Metall. Mater.*, 1994, **31**, 1749–1754.
26. Deng, J., Wang, D. L., Kong, Q. P. and Shui, J. P., Stress dependence of creep in nanocrystalline Ni-P alloy. *Scripta Metall. Mater.*, 1995, **32**, 349–352.
27. Sanders, P. G., Eastman, J. A. and Weertman, J. R., Elastic and tensile behavior of nanocrystalline copper and palladium. *Acta Mater.*, 1997, **45**, 4019–4025.
28. Nabarro, F. R. N., Deformation of crystals by the motion of single ions. In *Rep. Conf. on the Strength of Solids*, The Physical Society, London, 1948, p. 75.
29. Herring, C., Diffusional viscosity of a polycrystalline solid. *J. Appl. Phys.*, 1951, **21**, 437–445.
30. Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials. *J. Appl. Phys.*, 1964, **34**, 679–1682.
31. Ashby, M. F. and Verral, R. A., Diffusion-accommodated flow and superplasticity. *Acta Metall.*, 1973, **21**, 149–163.
32. Ruano, O. A. and Sherby, O. D., On the applicability of diffusional creep of polycrystalline materials at low stresses and intermediate temperatures. *Mater. Sci. Eng.*, 1984, **64**, 61–66.
33. Arzt, E, Ashby, M. F. and Verral, R. A., Interface-controlled diffusional creep. *Acta Metall.*, 1983, **31**, 1977–1989.