Journal of the European Ceramic Society 22 (2002) 2603–2607

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Mechanical behaviour of yttria tetragonal zirconia polycrystalline nanoceramics: dependence on the glassy phase content

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Received 10 November 2001; received in revised form 7 March 2002; accepted 20 March 2002

Abstract

Nanocrystalline yttria tetragonal zirconia polycrystals (YTZP) with different amounts of an amorphous phase have been deformed at moderate temperature (1150 °C) and at constant strain rates. The aim of this work was the study of the influence of that glassy phase on the mechanical response of these nanocrystals. Transmission electron microscopy (TEM) analysis and atomic force microscopy (AFM) pictures of the deformed and as-received samples have been carried out in order to determine the grain size distribution and clarify the possible deformation mechanisms. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Glassy-phase; Plastic deformation; YTZP nanocrystals

1. Introduction

Nanoceramic materials have received considerable interest for the last decades.[1] Recently, yttria tetragonal zirconia polycrystals (YTZP) in the nanometer range have become a particular keystone among them. This fact is due to the intrinsic mechanical properties, particularly the superplasticity, exhibited by submicron-sized YTZP materials.[2,3] This is a very important property, not only from a basic point of view, but also when applications are considered: ceramic forming and joining[4–6] can take advantage of superplasticity. In theory, these two processes should be improved if grain sizes decrease. That is the reason why YTZP nanoceramics[7] have become a very attractive and challenging research goal.

Plasticity of YTZP nanocrystals has deserved a systematic research effort only quite recently.[8–10] Previous works on this topic were limited by the fact that no fully-dense materials were available. Gutiérrez-Mora et al. has reported a first work on the main features of high temperature plastic deformation[11,12] on fully dense materials. Although grain boundary sliding seems to be the deformation mechanisms, the accomodation mechanism associated with the deformation is still unclear. In addition to that, the macroscopic law for plasticity is different from that found in submicron-scaled specimens of the same material.

Another open question is the effect of glassy-phases on plastic deformation. Some works are already published[13,14] for submicron YTZP samples, but it is still the object of controversy how the deformation mechanisms alter when glassy phases are present in a significative amount.

This work presents some preliminary results on the high temperature mechanical behaviour of YTZP nanoceramics, with special attention to the influence of glassy phases on the mechanical response.

2. Experimental procedure

Samples of YTZP ceramics with different amounts of a glassy phase, from 5 to 15 wt.%, were supplied. Samples were sintered at 1300 °C for 1 h, after preheating at 800 °C for 3 h. The chemical analysis of the as-received samples revealed that the glassy-phase was composed of 80 wt.% SiO_2, 15 wt.% Na_2O, and 5 wt.% SrO. The

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PII: S0955-2219(02)00122-X

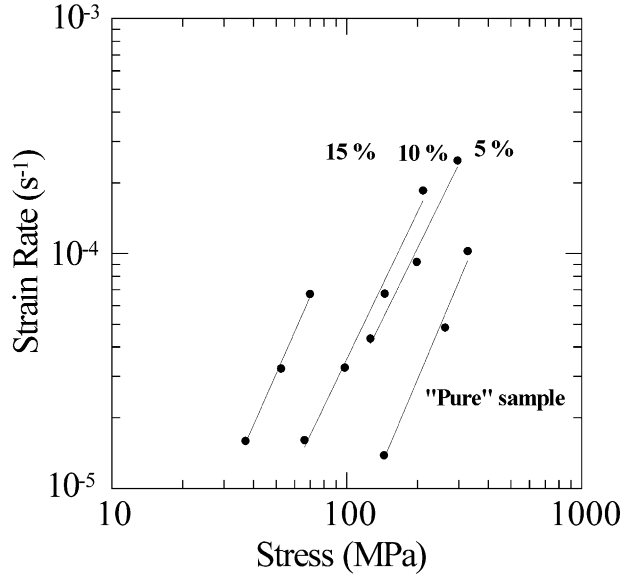

Fig. 1. Strain rate versus the stress for the set of samples under study. All tests were made at the same temperature; i.e. 1150 °C.

experimental densities are all higher than 97% the theoretical value as measured on pure specimens (6.1 g cm^{-3}). Samples with no glassy-phase, which will be called "pure" from now on, were also available.

All samples were cut into parallelepipeds whose dimensions were approximately 2×2×4 mm. Tests were conducted in compression in an Instron 1185 machine at 1150 °C at different constant strain rates, in the range of 10^{-5} up to 5×10^{-4} s^{-1}. Compression was performed by means of alumina rams, at a crosshead speed ranged from 5 μm/min up to 50 μm/min. The test temperature is high enough to guarantee that diffusion can play a significant role; but it is low enough to avoid dynamical grain growth.[12] The testing set-up was equipped with alumina rams as compressing tools. SiC pads were inserted between the rams and the tested sample in order to avoid indentation in the rams.

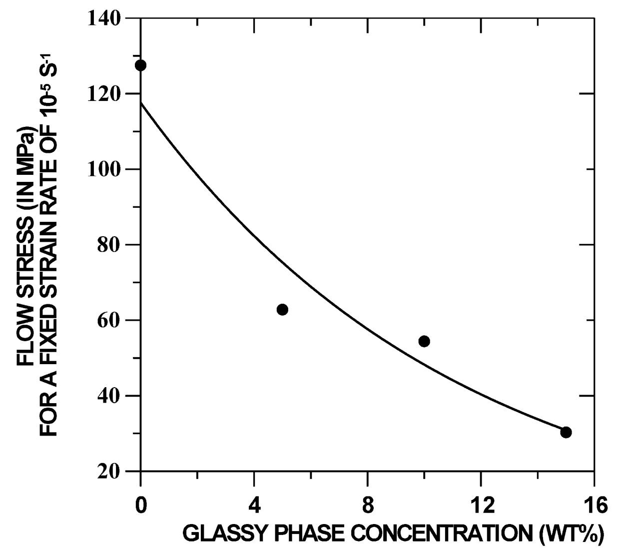

Fig. 2. Flow stress for constant strain rate test conducted at 10–5 s-1, as a function of the volume fraction of the glassy phase. The better empirical fit to the experimental data are superposed to them. That corresponds to the equation $\sigma = 118\ \exp(-0.09c)$, with a correlation factor of $r = 0.97$.

Subsequent to deformation test, thin slides were cut for TEM observation. TEM foils were prepared according to the conventional procedure described elsewhere,[15] and a Philips CM200 microscope was used for the observations.

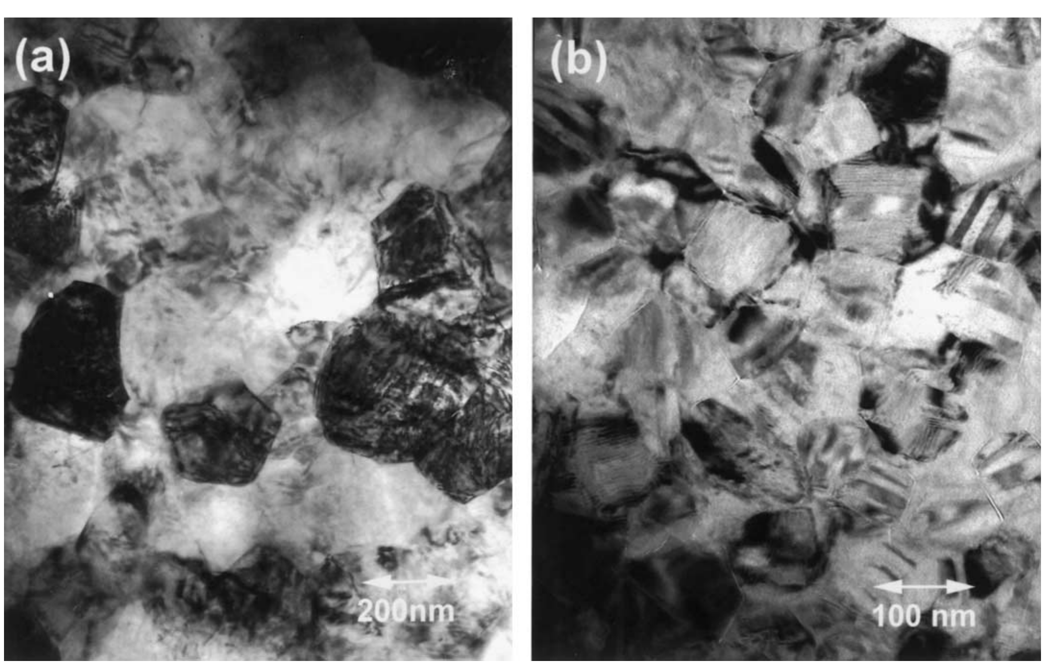

Fig. 3. TEM pictures of the microstructure after deformation for the pure (a) and the 15%-glassy phase-doped (b).

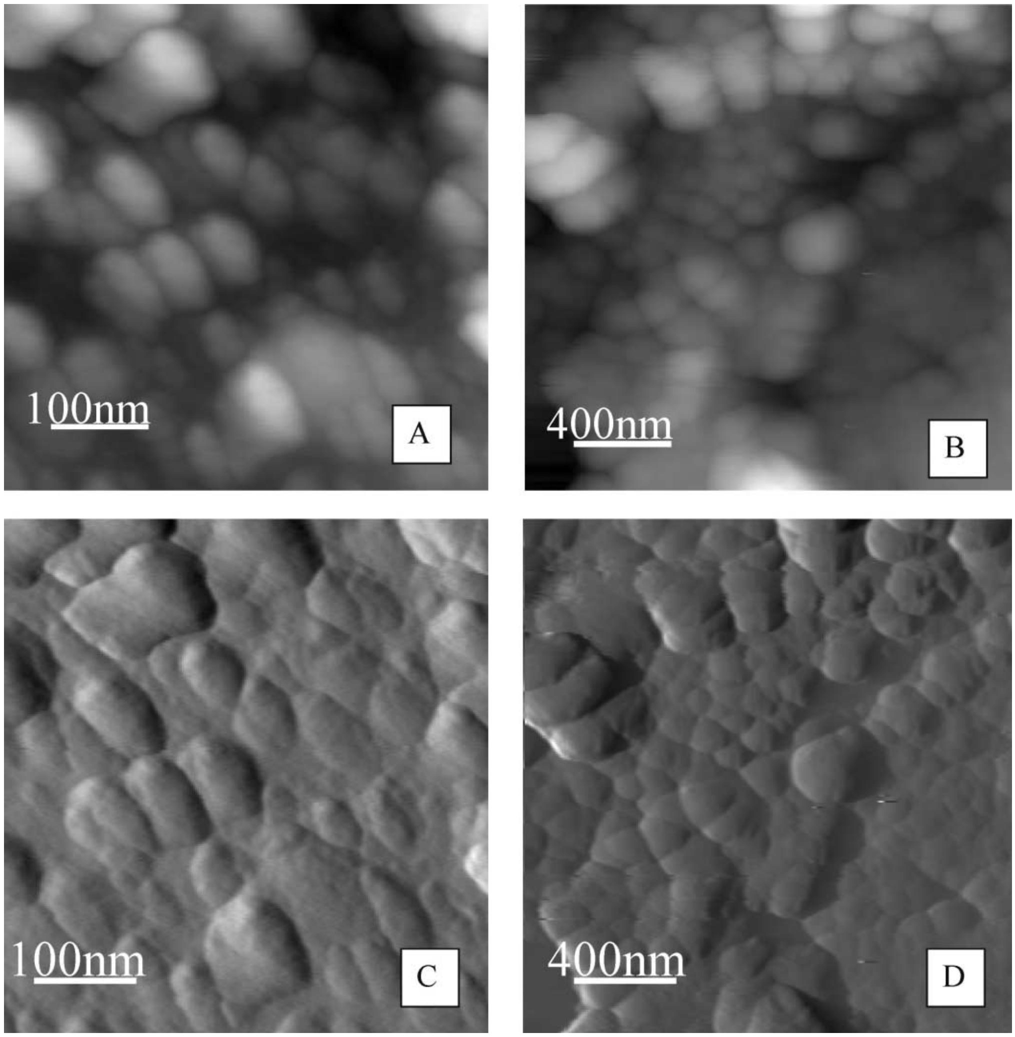

Fig. 4. AFM pictures of the microstructure after deformation for the pure (a) and the 15%-glassy phase-doped (b). (A) and (B) correspond to the real image in tapping mode, whereas (C) and (D) are the corresponding derivatives of (A) and (B), respectively. Notice that the grain boundaries are very-well revealed in the second set of pictures.

Deformed samples were also studied using non-contact atomic force microscopy. Olympus type cantilevers with a resonance frecuency of 80 kHz were employed. This technique is particularly useful to determine the grain size distribution and the surface roughness of the samples in nanoscaled specimens

3. Results

Fig. 1 shows the strain-rate versus flow stress plot for the whole set samples studied in this work. In the range of strain rates under consideration, data correlate to the following stress dependence:

$$\dot{\varepsilon} \propto \sigma^{2.2\pm0.2} \quad (1)$$

The plasticity of nanoceramics seems to be very sensitive to the presence of glassy phases, as can be seen in Figs. 1 and 2. In these samples, glassy phases have a remarkable softening effect. For example, if a plot of the flow stress versus the glassy phase concentration for a constant value of the strain rate is made (Fig. 2), it is posible to establish that a significant reduction of the flow stress can be detected between a pure and a 15%-doped specimen when compared. That is; a factor 4 exists between the corresponding flow stresses.

A rigorous interpretation of this phenomenom needs some information about the microstructural evolution. In order to proceed that way, TEM pictures for the whole set of specimens, either deformed and as-received, were obtained. Fig. 3a and b displays two micrographs for a pure and a 15%-doped deformed specimen, respectively. The main noticeable feature is the fact that the microstructure does not seem to be altered by deformation; that is, neither cavitation nor dislocation activity were detected. Even more, no significative differences can be measured between the doped and undoped specimens.

In addition to TEM, AFM pictures for the same types of specimens were taken, and they are shown in Fig. 4. The same results can be deduced from their analysis. The study of the grain size distribution from both the AFM and TEM micrographs permit us to calculate the grain size, close to 50±20 nm in all the cases.

Although not shown in this work, creep tests are under development to analyse the dependence with temperature. Our preliminary results point out a high activation energy (~6.4±0.3 eV/atom). This is slightly higher than the values measured in micron-sized samples (~5.5±0.5 eV/atom).[2,16]

4. Discussion

These results are consistent with a grain-boundary sliding deformation mechanism. This mechanism has been widely proposed in literature for submicron YTZP polycrystals.[16] Although it seems to correlate quite well with the no microstructural evolution in the nanoscaled specimens, the accommodation mechanisms for these nanocrystals is still under debate.[17,18]

A particularly important feature of the plastic deformation mechanism in these nanoceramics is the fact that no threshold stress existed in the range of stresses of our work. This is the most important difference with the case of the submicron materials. In fact, the predicted threshold stress for these nanoceramics at 1150 °C and with a grain size around 50 nm is as high as 160 MPa,[19] but no deviation from the stress dependence given in Eq. (1) is detected in any of the samples. The reason for the non-existence of a threshold stress is not known yet, and should be studied further.

The stress exponent is around 2 in all the samples. This fact is in very good agreement with those already found in submicron-sized specimens when glassy phases are present.[3,16] Concerning the influence of the glassy phase, the softening effect shown in Fig. 2 is in good agreement with previous work and more recent studies reported in literature for submicron-scaled specimens. In particular, Gust et al.[13] pointed out a reduction of the flow stress by a factor of 5 for YTZP doped with Barium Sulphure with a grain size of 400 nm at 1300 °C. The same order of magnitude was established by the authors for YTZP samples doped with Boron Sulphure, at the same conditions of work.[13] This result has been confirmed by Imamura et al.[14] by means of tensile experiments in the range of temperatures from 1300 up to 1500 °C, with the same kind of glassy phase used in Gust's work. This is quite similar to our results with YTZP specimens in the nanometer range.

Finally, the preliminary results on the temperature dependence of plasticity for YTZP nanocrystals are in good agreement with the few data reported in literature for samples with a mean grain size of 100 nm. There is a discrepancy with the values found in submicron specimens, as commented before. The reason for this discrepancy is not known, and it must be related to the accommodation mechanism playing the major role in these materials. A careful research project to explain the plastic deformation mechanisms in the nanometer range is in progress.

5. Conclusions

The high temperature mechanical response of YTZP nanocrystals doped with different amounts of an amorphous phases has been reported. Constant strain rate tests, as well as the microstructural characterization of the deformed and as-received by means of TEM and AFM have been carried out. The analysis of all the experimental ouputs have permitted to conclude that no threshold stress exist in these materials, and the softening effect of the glassy phase has been assessed. Grain boundary sliding seems clearly to be the deformation mechanism for all the cases studied. Future work must be devoted to the explanation of the high activation energy and the non-existence of a threshold stress in this system.

Acknowledgements

The authors would like to acknowledge the financial support awarded by the Spanish "Comisión Interministerial de Ciencia y Tecnología" through the project MAT2000–0622. Acknowledgements are extensive to Professor Chaim for specimens supply.

References

1. Gleiter, H., Nanostructured materials: basic concepts and microstructure. *Prog. Mater. Sci.*, 1989, **33**, 223–315.
2. Jiménez-Melendo, M. and Domínguez-Rodríguez, A., High temperature characteristics of superplastic yttria-stabilized zirconia. An examination of the flow process. *Acta Mater.*, 2000, **48**, 3201.
3. 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.
4. Domínguez-Rodríguez, A., Guiberteau, F. and Jiménez-Melendo, M., Heterogeneous junction of yttria partially stabilized zirconia by superplastic flow. *J. Mater. Res.*, 1998, **39**, 1631–1636.
5. Gutiérrez-Mora, F., Domígnuez-Rodríguez, A., Routbort, J., Chaim, R. and Guiberteau, F., Joining of yttria-tetragonal stabilized zirconia polycrystals using nanocrystals. *Scripta Mater.*, 1999, **41**, 455–460.
6. Domínguez-Rodríguez, A., Gutiérrez-Mora, F., Jiménez-Melendo, M., Routbort, J. and Chaim, R., Current understanding of superplastic deformation of YTZP and its application to joining. *Mater. Sci. Eng.*, 2001, **A302**, 154.

7. Mohamed, F. A. and Li, Y., Creep and superplasticity in nanocrystalline materials: current understanding and future prospects. *Mater. Sci. Eng.*, 2001, **A298**, 1–15.
8. Betz, U., Scipione, G., Bonetti, E. and Hann, H., Low temperature deformation behavior of nanocrystalline 5 mol% yttria-stabilized zirconia under tensile stress. *Nanostruct. Mater.*, 1997, **8**, 845–853.
9. Betz, U. and Hann, H., Ductility of nanocrystalline zirconia-based ceramics at low temperatures. *Nanostruct. Mater.*, 1999, **12**, 911–914.
10. Bhattacharya, S. S., Betz, U. and Hann, H., Some studies on the superplastic deformation behavior of nanocrystalline yttria-stabilized zirconia-based ceramics. *Scripta Mater.*, 2001, **44**, 1553–1556.
11. Gutiérrez-Mora, F., Domínguez-Rodríguez, A. and Jiménez-Melendo, M., Creep of nanocrystalline YSZP ceramics. *Nanostructuct. Mater.*, 1999, **11**, 531–537.
12. Gutiérrez-Mora, F., Jiménez-Melendo, M., Domínguez-Rodríguez, A. and Chaim, R., High temperature mechanical behavior of YSZ nanocrystals. *Key Eng. Mater*, 2000, **171–174**, 787.
13. Gust, M., Goo, G., Wolfenstine, J. and Mecartney, M., Influence of amorphous grain boundary phases on the superplastic behaviour of 3 mol%-yttria-stabilized tetragonal polycrystals (3Y-TZP). *J. Am. Ceram. Soc.*, 1993, **76**(7), 1681–1690.
14. Imamura, P. H., Evans, N. D., Sakuma, T. and Mecartney, M., High emperature tensile deformation of glass-doped 3Y-TZP. *J. Am. Ceram. Soc.*, 2000, **83**(12), 3095–3099.
15. Williams, D. B. and Carter, C. B., *Transmission Electron Microscopy*, I, Plenum Press, New York and London, 1996, pp. 155–172.
16. Jiménez-Melendo, M., Domínguez-Rodríguez, A. and Bravo-León, 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-stablized tetragonal zirconia. *Acta Mater.*, 1999, **47**, 2485–2495.
19. Domínguez-Rodríguez, A., Bravo-León, A., Ye, J. D. and Jiménez-Melendo, M., Grain size and temperature dependence of the threshold stress for superplastic deformation in yttria-stabilized zirconia polycrystals. *Mater. Sci. Eng.*, 1998, **A247**, 97–101.