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High temperature deformation of spinel–zirconia composites
Effect of zirconia content

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Abstract

Creep experiments have been performed on a spinel matrix and two composites, containing 20 and 30 wt.% of zirconia particles, respectively, in stress and temperature ranges 8–200 MPa and 1350–1410 °C. The creep rates may be described as the result of two sequential processes that occur at low and high stress, respectively. In addition, a threshold stress was observed that strongly complicated the determination of the stress and grain size exponents and of the activation energy at low stress.

The plastic flow of composites may be deduced from that of the spinel matrix by an inclusion model that considers the zirconia grains as soft inclusions. This description reinforces the role of spinel–spinel boundaries in the deformation of the composites, in agreement with measurements of grain boundary sliding capacity for the two kinds of boundaries present in the composites.

A model developed by Artz et al. [E. Artz, M.F. Ashby, R.A. Verrall, Interface controlled diffusional creep, Acta Metall. 31 (1983) 1977–1989] may account for the creep rates of the matrix at low stress with a good accuracy. This model supposes that the boundary dislocation density is the factor that limits the creep rates in this low stress range. The grain boundary sliding is probably accommodated by grain boundary diffusion in the whole stress range.

Keywords: Composite; Plasticity; Spinel; ZrO_2

1. Introduction

In a previous paper [1], the plastic behaviour of a 5 wt.% ZrO_2–$MgAl_2O_4$ composite has been investigated by creep tests performed between 1350 and 1410 °C in the stress range 8–200 MPa. These experiments showed that the creep rate sensitivity to stress, the so-called stress exponent n in the usually high temperature creep equation:

$$\dot{\varepsilon} = K\frac{\sigma^n}{d^p}\exp\left(-\frac{Q}{RT}\right), \qquad (1)$$

continuously increases when the stress level σ decreases. In this relation $\dot{\varepsilon}$ is the stationary creep rate, K a constant, d the grain size, p the grain size exponent, Q the activation energy for creep, and R and T having their usual meaning. Such an increase in the stress exponent n at low stress has been already reported in the case of fine-grained zirconias [2,3] in temperature and stress ranges analogous to those used in [1]. Similarly to Berbon and Langdon [4] and Charit and Chokshi [5], the $\dot{\varepsilon}$–σ curve shape [1] has been analysed by considering that grain boundary dislocations behave as discrete sources and sinks for vacancies [6,7]. Their density was assumed to increase with stress, which leads to a stress exponent in the range 2–3 when low stresses are applied. When the stress increases, the dislocation density becomes higher and higher and the continuum model of sources and sinks may be applied. For this reason the creep rate is then controlled by the vacancy flux rate between sources and sinks; it may be described by an expression similar to the expressions proposed by Nabarro–Herring [8,9] or Coble [10] in which the creep rate is proportional to stress. The transition from the low stress range to the high stress one is very progressive, which corresponds to a stress exponent continuously changing with stress. Similarly two sequential processes may account for this observation: the creation of sources or sinks and the migration of point defects. In addition to the stress exponent evolution with stress, the presence of a threshold stress, depending upon

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Table 1
Main characteristics of the various materials

Material	SZ0	SZ5 [1]	SZ20	SZ30
Grain size (μm) (S/**Z**)	1.2/–	0.85/**0.37**	0.67/**0.41**	0.67/**0.57**
Zirconia grains (vol%)	0	3.2	13.7	21.3
Large grains (vol%)	3.5	3	0	0
Relative density (%)	95.2	99.4	99.3	98.5

Grain sizes in bold characters refer to the ZrO_2 phase.

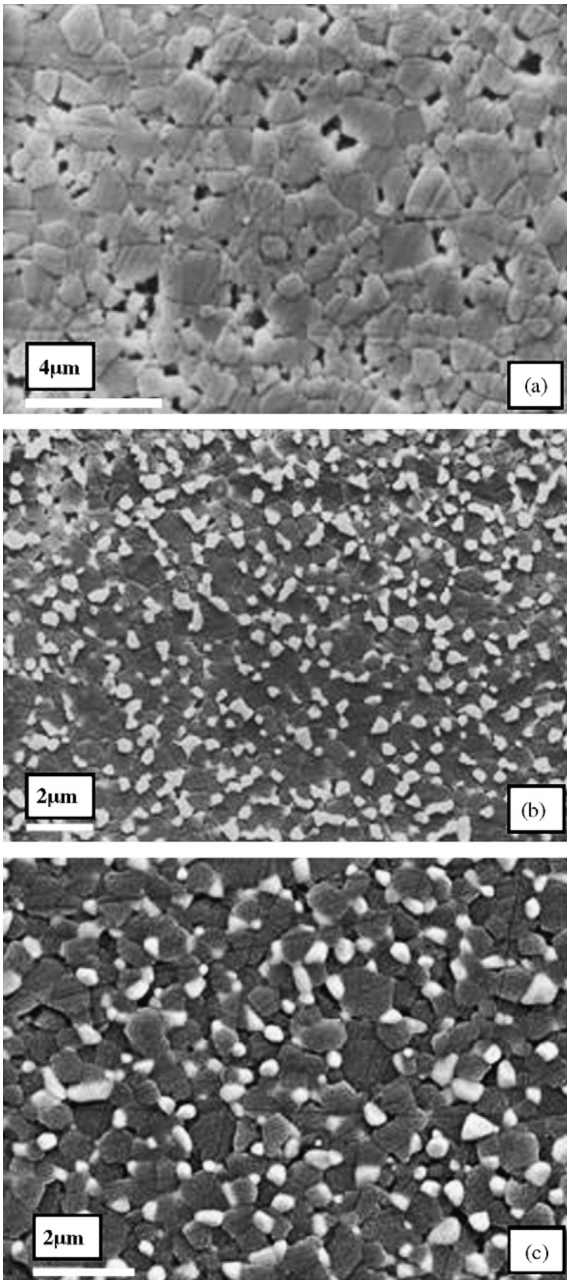

Fig. 1. SEM micrograph of SZ0 (a); SZ20 (b); and SZ30 (c) specimens. Zirconia grains are the white ones. Note that the zirconia grains are homogeneously distributed.

grain size, was proved [1]. This threshold strongly affected the determination of the parameters n, p and Q at low stresses.

In the present paper, we attempt to account for the effect of the zirconia particle content on the plasticity of these materials by studying the creep behaviour of a spinel matrix and of two composites containing 20 and 30 wt.% of zirconia particles, respectively. The various objectives of this work concern (i) the role of the two types of grain boundaries mainly implied in the deformation mechanisms of these materials; (ii) the low stress plastic flow, the finer grain sizes obtained by increasing the zirconia content favouring the probability of a threshold stress; and (iii) the matter diffusion process in the composites and in the matrix. If the effect of the zirconia particle content upon the composite plasticity may be estimated, then it will be possible to appreciate the plastic behaviour of a homogeneous fine-grained spinel matrix.

2. Experimental procedure

A spinel matrix and two composites, containing 20 and 30 wt.% of ZrO_2 particles, respectively, were elaborated. Afterwards they were named SZ0, SZ20 and SZ30 according to their ZrO_2 weight content, SZ5 being the material investigated in [1]. The matrix was obtained from a commercial $MgAl_2O_4$ spinel powder (Baikowski S30CR, Annecy, France) and the composites were fabricated by coating the particles of the spinel powder with a zirconia sol–gel [11]. The powder mixtures were then dried, fired and pressed as disks. The three materials were sintered at 1550 °C for 1 h. Their main structural features are given in Table 1. Fig. 1 shows the typical microstructures of the three materials.

Compression creep tests were carried out in air in the stress range 8–200 MPa at three temperatures: 1350, 1380 and 1410 °C. Specimens had dimensions of 3 mm × 3 mm × 7 mm. Some specimens were also annealed in order to study the effect of a grain size change on the creep rate. From creep curves, the stationary creep rates $\dot{\varepsilon}$ were measured and at first analysed according to relation (1).

To evaluate changes in grain sizes, grain shapes and phase distributions prior to and after creep experiments, scanning electron microscopy (SEM) was used.

3. Results

The creep curves of SZ0, SZ20 and SZ30 materials are characterized by a very short transient creep followed by a steady state that lasted until the test conclusion (ultimate strain higher than 60% sometimes). Fig. 2 illustrates the effect of stress on the stationary creep rate at 1380 °C. The SZ5 creep rates are equally reminded to facilitate the discussion. The four curves are similar and do not exhibit a very noticeable influence of the material composition. When stresses are higher than 20–30 MPa, creep rates augment with the increase in zirconia content. Nevertheless, in the analysis of these curves, the effects of grain size and density must not be neglected since these parameters depend on material. At low stress, the relative behaviour is more intricate and must be carefully analysed. The changes in stress exponent n (the slope of the $\dot{\varepsilon}$–σ curves) with stress are presented in Fig. 3. A strong increase in n may be noted at low stress, n values as high as 5 being observed.

The temperature changes experimented during tests at 10 and 100 MPa were used to estimate the effect of temperature on

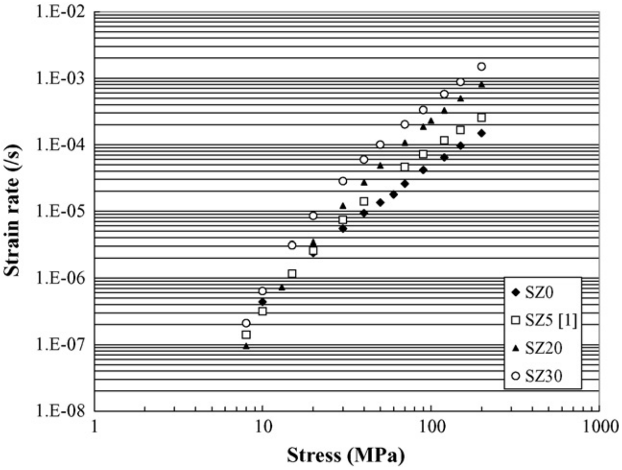

Fig. 2. Plot at 1380 °C of the creep rates vs. stress for the three materials experimented in this work and the material SZ5 [1].

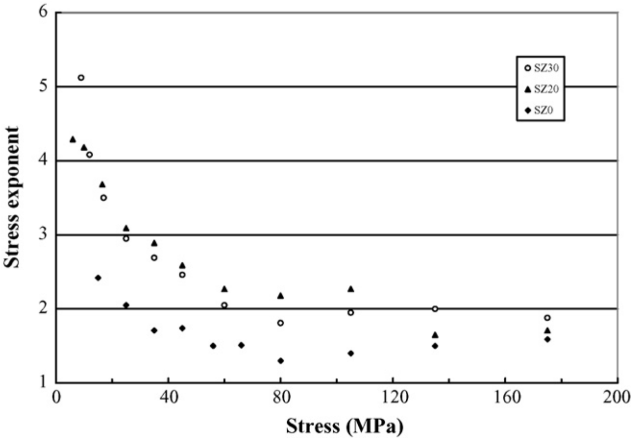

Fig. 3. Evolution at 1380 °C of the experimental stress exponent *n* vs. stress for the SZ0, SZ20 and SZ30 materials.

the stationary creep rate. The activation energies Q are about 600 kJ mol^{-1} at 100 MPa and range from 800 to 1100 kJ mol^{-1} at 10 MPa (Table 2). The values measured at 10 MPa are surprisingly high; these are only experimental values of the activation energy that do not directly account for the rate controlling mechanism.

The effect of grain size on the creep rate is more complicated to evaluate owing to the difficulty in separating the influence of the two phases. It has been determined only for the SZ20 material at 1380 °C according to relation (1) by using an average grain size. Note that the relative change of the average grain size does not strongly differ from that of spinel grain size since the zirconia volume content is low. Practically, after a strain of 10% in the steady state, the specimen was unloaded and annealed 48 h at 1450 °C. Then the stress was again applied and the test carried on up to a strain of 20%. The stationary rates at 10 and 20% were compared, the final grain sizes being measured by SEM. At 13 and 90 MPa the experimental grain size exponents p_{exp} were 0.06 and 1.6, respectively (for an ultimate average grain size of 1 μm). At the same stresses these values were 0.56 and 1.9, respectively, for SZ5.

Table 2
Activation energies Q at low (10 MPa) and high (100 MPa) stress, threshold stress and values of coefficients A and B in relations (2) and (3) for the various materials

Material	SZ0	SZ5 [1]	SZ20	SZ30
Q (kJ mol^{-1}) (10 MPa)	800	1100	1053	1030
Q (kJ mol^{-1}) (100 MPa)	590	620	650	565
Threshold stress (MPa)	2–3.5	4–5	5–7	5–7
A (10^{-8} s^{-1} MPa^{-2})	1	1.1	2.4	5.3
B (10^{-6} s^{-1} MPa^{-1})	1.2	3.1	17	20

4. Discussion

The present results are very similar to those reported for SZ5 [1], which suggests that identical deformation mechanisms probably operate for all the materials.

For stresses lower than 40–50 MPa, when the square root of the creep rate is plotted versus stress, Fig. 4 shows that linear relations may be obtained if a threshold stress, increasing with the zirconia content, is taken into account. This means that the low stress rates may be related to stress by a relationship as:

$$\dot{\varepsilon}_{\mathrm{ls}} = A(\sigma - \sigma_0)^2 \qquad (2)$$

In this relation, σ_0 is the threshold stress and A a parameter related to grain size and temperature but independent of stress. The threshold stress values are presented in Table 2. The relation (2) is similar to that obtained for the low stress range in SZ5 material [1]. Owing to the decrease in stress exponent towards 1 when stress increases, the relation (2) cannot account for the high stress range, which necessarily requires that a second mechanism operates at high stress.

Concerning the threshold stress, its variation with the ZrO_2 content most probably originates from the connected spinel grain size changes than directly from the ZrO_2 content. This is a consequence of the higher ductility of the zirconia phase relative to the spinel one, which implies that the zirconia phase has only a minor influence in the deformation process [12].

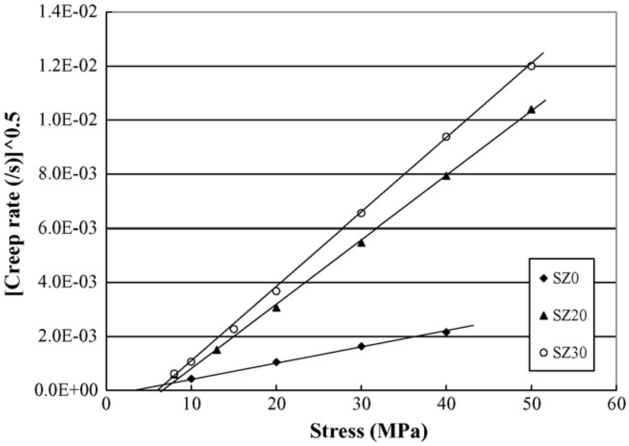

Fig. 4. Plot of the square root of the creep rates vs. stress in the low stress range and estimate of the threshold stress for the SZ0, SZ20 and SZ30 materials.

Several theoretical or experimental works [6,7,13,14] predict a threshold stress proportional to the grain size inverse, i.e. $\sigma_0 = \Phi/d$, relation in agreement with our previous results for SZ5 [1]. In this work, the presence of a threshold stress and its $1/d$ dependence are supported by the low value of p determined at 13 MPa for SZ20 ($p_{\text{exp}} = 0.06$) as explained hereafter.

From relations (1) and (2) (through the parameter A), an enlargement of the grain size must entail a decrease in the creep rate. Nevertheless from relation (2) (through σ–σ_0) the same grain size enlargement, by reducing the threshold stress value, must augment the effective stress σ–σ_0. These two opposed effects may balance each other which may lead, for certain grain size conditions, to a very weak influence of the grain size on the creep rate. This is probably the reason of the so small grain size exponent determined at 13 MPa.

In the high stress range, a decrease in the stress exponent, like the one reported for the SZ5 composite, was noted (Fig. 3). This observation supports the assumption that a same rate-controlling mechanism, with a stress sensitivity of one, operates in this stress domain for SZ5 and the three other materials. Thus the high stress rates may be expressed as:

$$\dot{\varepsilon}_{\text{hs}} = B\sigma \tag{3}$$

B is a parameter that only depends upon grain size and temperature. Considering the $\dot{\varepsilon}$–σ curve shape, the two mechanisms described by relations (2) and (3) are sequential ones [1], i.e. the resultant creep rate $\dot{\varepsilon}$ is controlled by the slowest one and is related to low and high stress rates by:

$$\dot{\varepsilon} = \frac{(\dot{\varepsilon}_{\text{ls}} \times \dot{\varepsilon}_{\text{hs}})}{(\dot{\varepsilon}_{\text{ls}} + \dot{\varepsilon}_{\text{hs}})} \tag{4}$$

From relations (2)–(4), the coefficients A and B have been determined. Their values are presented in Table 2 for $T = 1380$ °C.

The determination of accommodation mechanisms requires the knowledge of the true grain size dependence of A and B in relations (2) and (3). We have assumed that A and B may be related to the average grain size d by:

$$A = \frac{A^*}{d^a} \tag{5a}$$

$$B = \frac{B^*}{d^b} \tag{5b}$$

So as to determinate the exponents a and b, the change in the experimental grain size exponent p_{exp} with stress has been explored from the initial and final grain sizes, for three arrangements of a and b exponents in relations (5a) and (5b) corresponding to various possibilities of controlling mechanisms: (i) $a = 1$ (interface reaction) and $b = 3$ (grain boundary diffusion); (ii) $a = 2$ (volume diffusion) and $b = 3$; and (iii) $a = 2$ and $b = 2$. Creep rates were then estimated for initial and final grain sizes using relations (4), (2) and (3) in which A and B were determined from relations (5a) and (5b), A^* and B^* being calculated from initial conditions, as Φ in $\sigma_0 = \Phi/d$ too. The grain size exponent was finally deduced. Fig. 5 shows the expected curves as well as the experimental values. The best agreement is obtained for values of a and b equal to 1 and 3, respectively. This analysis also shows that an experimental value of 3 will be only observed for very high stresses, well above those experimented in this work.

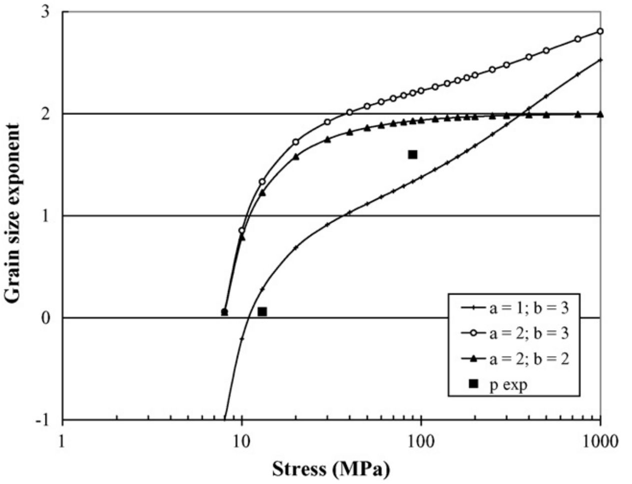

Fig. 5. Comparison of experimental values of the grain size exponent (full squares at 13 and 100 MPa) with those calculated from the relations (2) and (3) for various values of the grain size exponent in the low stress (a) and high stress (b) relations (5a) and (5b), respectively. The initial and final grain sizes are 0.59 and 1 μm, respectively. The best accordance is observed for $a = 1$ ($\dot{\varepsilon}$ is proportional to d^{-1}) at low stress and $b = 3$ ($\dot{\varepsilon}$ is proportional to d^{-3}) at high stress.

The influence of temperature in relations (2) and (3), through the creep activation energy, is difficult to precise, especially at low stress, since the temperature dependence of the threshold is not known. At high stress, the creep activation energies for the matrix and the composites are very similar. At low stress we have assumed that the results obtained for the SZ5 composite are still valid. They showed that the low stress activation energy is about 560 kJ mol^{-1} when the effect of temperature is taken into account in coefficients A and B of relations (2) and (3). Finally, the activation energies are of the same order than the energy reported by Béclin et al. [15] for a spinel material for which no threshold was observed.

4.1. *Effect of volume fraction of zirconia particles*

Description of composite plasticity from that of the matrix needs to know the interactions between the two phases, the matrix and the zirconia grains, during creep tests. Owing to differences in ductility and grain size between spinel and zirconia phases, a consequence of which is an enhanced plasticity when the zirconia content increases, it is probable that zirconia grains behave like soft inclusions in the composites. Consequently, we have attempted to describe the plastic flow of the composites by using a mixture rheological law previously proposed by Chen [16] and Yoon and Chen [17].

In that theory, the flow rate $\dot{\varepsilon}_{\text{comp}}$ of a composite containing a volume fraction V of hard or soft inclusions, is related to the flow rate of the matrix $\dot{\varepsilon}_{\text{mat}}$ through the expression:

$$\dot{\varepsilon}_{\text{comp}} = (1 - V)^q \dot{\varepsilon}_{\text{mat}} \tag{6}$$

where q is an exponent depending on the stress exponent n of the matrix flow rate and on the ductility of the inclusions: $q = -(53n + 7)/36$ for soft inclusions [16] and $q = (n + 4)/2$ for hard inclusions [16,17]. This theory does not imply the knowledge of the representative law of zirconia plastic flow and does not inform on it.

Description of the plastic flow over the entire stress range requires two sequential mechanisms with different stress exponents. Consequently the theory [16] has been applied to each mechanism, according to the following relations deduced from the Eqs. (2), (3) and (6), with the exponent q calculated for the case of soft inclusions. This leads to:

$$\dot{\varepsilon}_{\text{comp}} = (1 - V)^{-3,14}\dot{\varepsilon}_{\text{mat}} \quad \text{at low stress} \tag{7a}$$

$$\dot{\varepsilon}_{\text{comp}} = (1 - V)^{-1,67}\dot{\varepsilon}_{\text{mat}} \quad \text{at high stress} \tag{7b}$$

Moreover, instead of calculating the creep rates of the composites from those of the matrix, we have preferred to estimate the creep rate of a dense matrix with a homogeneous grain size of 1.2 μm from experimental rates of the composites and of the matrix. In this last case pores were compared to soft inclusions. The validity of the theory is thus easier to establish. Accordingly, the relations (7a) and (7b) have been inverted:

$$\dot{\varepsilon}_{\text{mat}} = (1 - V)^{3.14}\dot{\varepsilon}_{\text{comp}} \quad \text{at low stress} \tag{8a}$$

$$\dot{\varepsilon}_{\text{mat}} = (1 - V)^{1,67}\dot{\varepsilon}_{\text{comp}} \quad \text{at high stress} \tag{8b}$$

The resultant creep rates were then finally deduced by using relation (4). Results are presented in Fig. 6. The four curves show a reasonable agreement, rates being reproducible within a factor two, which supports the hypotheses used to describe the plasticity of composites from the one of the matrix.

4.2. Implications for matrix behaviour

Experimental results and previous analysis agree to describe the matrix deformation from two sequential mechanisms. In addition, a threshold stress dependent upon the grain size is also present. This interpretation is similar to the one expressed in the case of SZ5 composite [1]. Consequently, plastic flows of the matrix and of the SZ5 composite likely originate from the same processes: the grain boundary sliding and a diffusion accommodation mechanism.

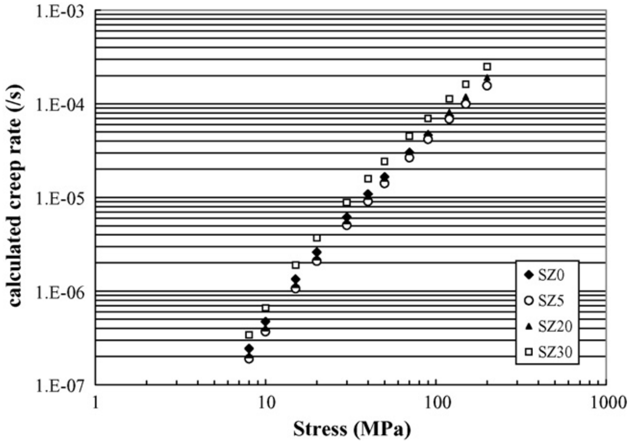

Fig. 6. Comparison, for a homogeneous matrix with a grain size of 1.2 μm, of the creep rates calculated from the experimental rates of the four tested materials using the relations (6) and (7).

At high stress, a stress exponent of 1 suggests an accommodation mechanism like volume or grain boundary diffusion [6,8–10]. Firstly the possibility of a volume diffusion accommodation has been considered. To this end, we have compared the experimental high stress creep rates to those calculated from the expression proposed by Ashby and Verrall [6] in the case of a volume diffusion accommodation. The intercalation model described by Ashby and Verrall, in which grain migration and grain switching are the processes by which deformation proceeds, is operative in fine-grained ceramics as recent works [18,19] have shown in zirconia and alumina–zirconia ceramics. For this reason this model has been preferred to the Nabarro–Herring creep model [8,9]. Note also that this model predicts rates about 100 times faster than those issued from the Nabarro–Herring model. For this calculation, a volume diffusion coefficient of the oxygen species of 4×10^{-20} m^2 s^{-1} (an average at $T = 1380$ °C between those measured by Reddy and Cooper [20] and Ando and Oishi [21]) and a grain size $d = 1.2$ μm were used. The bold line in Fig. 7 represents these rates; they are about 200 times slower than the experimental rates (the full line) in the high stress range and 10 times lower at least than those observed in the low stress range. Under these conditions, it seems difficult to attribute to volume diffusion a preponderant influence in plasticity of materials whatever the stress.

Consequently, the possibility of a grain boundary diffusion controlled creep has been considered. From ref. [6] and from experimental rates at high stress, the product δD_{gb} of the controlling species has been estimated to 3×10^{-24} m^3 s^{-1} at $T = 1380$ °C. This value is similar to the one for oxygen in alumina at 1380 °C [22].

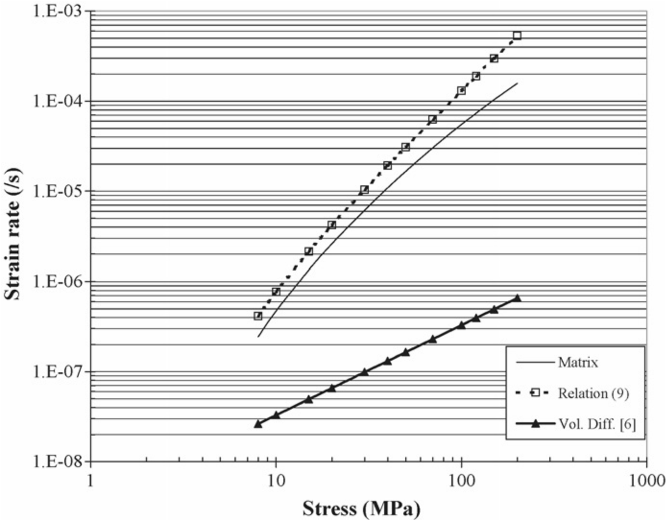

Fig. 7. Comparison at $T = 1380$ °C, for a SZ0 matrix with a grain size of 1.2 μm, of the rates calculated from a volume diffusion accommodation [6] (bold line with full triangles) or from an interface reaction mechanism (relation (9)) (dotted line with open squares) with experimental rates (full line without symbol).

Assuming the hypothesis that grain boundary diffusion is the accommodation process of grain boundary sliding in the whole experimental stress domain, the low stress behaviour has been analysed according to expression (13) in [1]. In this relation the stress σ has been replaced by an effective stress (σ–σ_0) to account for the experimental observation of a threshold stress σ_0, i.e.:

$$\dot{\varepsilon} = \frac{b b_{\mathrm{n}} D_{\mathrm{gb}} (\sigma - \sigma_0)^2}{2kT\mu d} \tag{9}$$

That relation supposes that (i) grain boundary dislocations are the sources and sinks for point defects; and (ii) their density is proportional to stress σ [7,13]. In this relation, b is the Burgers' vector of boundary dislocations ($\sim 1.5 \times 10^{-10}$ m), b_{n} the component of the Burgers' vector of grain boundary dislocations normal to grain boundary ($\sim 1 \times 10^{-10}$ m), $D_{\mathrm{gb}} = 5 \times 10^{-15}\ \mathrm{m^2 s^{-1}}$, μ the shear modulus of the material (1×10^{11} Pa) and $\sigma_0 = 2.5 \times 10^6$ Pa.

For a grain size of 1.2 μm, the rates calculated using relation (9) are represented by the dotted line in Fig. 7. In the low stress domain these rates are in good concordance with those obtained for the matrix.

In this analysis, the deformation rates at low stress are limited by the low density of grain boundary dislocations, at the origin of the grain boundary sliding. Such a behaviour, corresponding to an interface reaction, has already been reported in spinel materials whose Al_2O_3/MgO ratio varied from 1 to 1.8 [15,23–25]. The materials investigated in these studies had ultra-fine grain sizes ranging from 30 nm to 0.6 μm, these grain sizes favouring that observation.

The assumption of a low boundary dislocation density at low stress is supported by the decreasing grain boundary sliding ability of spinel–spinel boundaries in this stress range. Indeed, investigation by atomic force microscopy of grain boundary sliding in the SZ30 composite [12] showed that the sliding magnitude of spinel–spinel interfaces decreases at low stress with respect to that of spinel–zirconia boundaries, the relative ratio decreasing from 1.25 at 90 MPa to 0.75 at 12 MPa.

5. Conclusion

The creep experiments performed in this work have emphasized the importance of grain boundaries in deformation of fine-grained ceramics. Creep rates may be described by two sequential mechanisms, occurring at low and high stress, respectively. The presence of a threshold stress may explain the apparent values of stress exponent, grain size exponent and activation energy at low stress.

The plastic flow of composites may be described from that of the spinel matrix by an inclusion model [16,17] that considers the zirconia grains as soft inclusions. This description reinforces the role of spinel–spinel boundaries in composite deformation, in agreement with measurements of grain boundary sliding capacity for the two kinds of boundaries present in the composites [12].

When comparing the low stress behaviour of the matrix with that predicted by a model developed by Artz et al. [7], it results that grain boundary diffusion is likely the process that accommodates grain boundary sliding in the whole stress range. At low stress the boundary dislocation density is weak, which intrinsically limits the creep rates, while at high stress it is the diffusion process itself that is the limiting stage.

Acknowledgements

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References

[1] A. Addad, J. Crampon, R. Duclos, High temperature deformation of a 5 wt.% zirconia–spinel composite: influence of a threshold stress, J. Eur. Ceram. Soc. 22 (2002) 329–335.

[2] D.M. Owen, A.H. Chokshi, The high temperature mechanical characteristics of superplastic 3 mol% yttria stabilized zirconia, Acta Mater. 46 (1998) 667–679.

[3] M. Jimenez-Melendo, A. Dominguez-Rodriguez, High temperature mechanical characteristics of superplastic yttria-stabilized zirconia. An examination of the flow stress, Acta Mater. 48 (2000) 3201–3210.

[4] M.Z. Berbon, T.G. Langdon, An examination of the flow process in superplastic yttria-stabilized tetragonal zirconia, Acta Mater. 47 (1999) 2485–2495.

[5] I. Charit, A.H. Chokshi, Experimental evidence for diffusion creep in the superplastic 3 mol% yttria-stabilized tetragonal zirconia, Acta Mater. 49 (2001) 2239–2249.

[6] M.F. Ashby, R.A. Verrall, Diffusion-accommodated flow and superplasticity, Acta Metall. 21 (1973) 149–163.

[7] E. Artz, M.F. Ashby, R.A. Verrall, Interface controlled diffusional creep, Acta Metall. 31 (1983) 1977–1989.

[8] F.R.N. Nabarro, Deformation of crystals by the motion of single ions, Report of a conference on strength of solids, Bristol 1947, The Physical Society, London, 1948, pp. 75–90.

[9] C. Herring, Diffusional viscosity of a polycrystalline solid, J. Appl. Phys. 21 (1950) 437–445.

[10] R.L. Coble, A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys. 34 (1963) 1679–1682.

[11] R. Guinebretière, O. Masson, P. Ruin, G. Trolliard, A. Dauger, Sol gel coating of ceramic powders, Phil. Mag. Lett. 70 (1994) 389–396.

[12] A. Adda, J. Crampon, R. Guinebretière, A. Dauger, R. Duclos, Grain boundary sliding in a 30 wt% zirconia–spinel composite: influence of stress, J. Eur. Ceram. Soc. 20 (2000) 2063–2068.

[13] B. Burton, Interface reaction controlled diffusional creep: a consideration of grain boundary dislocation climb sources, Mater. Sci. Eng. 10 (1972) 9–14.

[14] A. Bravo-Leon, M. Jimenez-Melendo, A. Dominguez-Rodriguez, The role of a threshold stress in the superplastic deformation of fine-grained yttria-stabilized zirconia polycrystals, Scripta Mater. 34 (1996) 1155–1160.

[15] F. Béclin, R. Duclos, J. Crampon, F. Valin, Microstructural superplastic deformation in MgO·Al_2O_3 spinel, Acta Metall. Mater. 43 (1995) 2753–2760.

[16] I.W. Chen, Superplastic flow of two-phase alloys, in: B. Baudelet, M. Suery (Eds.), Superplasticity, Edition du CNRS, Paris, France, 1985, pp. 5.1–5.20.

[17] C.K. Yoon, I.W. Chen, Superplastic flow of two-phase ceramics containing rigid inclusions—zirconia/mullite composites, J. Am. Ceram. Soc. 73 (1990) 1555–1565.

[18] F. Béclin, J. Crampon, R. Duclos, Characterisation of grain rearrangement during superplastic creep of Al_2O_3–ZrO_2 composite, Br. Ceram. Trans. 102 (2003) 47–51.

[19] R. Duclos, Direct observation of grain rearrangement during superplastic creep of a fine-grained zirconia, J. Eur. Ceram. Soc. 24 (2004) 3103–3110.

[20] K.P.R. Reddy, A.R. Cooper, Oxygen diffusion in magnesium aluminate spinel, J. Am. Ceram. Soc. 64 (1981) 368–371.

[21] K. Ando, Y. Oishi, Effect of ratio of surface area to volume on oxygen self diffusion coefficients determined for crushed MgO-Al_2O_3 spinels, J. Am. Ceram. Soc. 66 (1983) C-131–C-132.

[22] R.M. Cannon, W.H. Rhodes, A.H. Heuer, Plastic deformation of fine-grained alumina (Al_2O_3): I. Interface-controlled diffusional creep, J. Am. Ceram. Soc. 63 (1980) 46–53.

[23] T. Sone, H. Akagi, Y. Takada, Abstract 94th meeting of the Am. Ceram. Soc., Minneapolis, 1992.

[24] R. Lappalainen, A. Pannikat, R. Raj, Superplastic flow in a non-stoichiometric ceramic: magnesium aluminate spinel, Acta Metall. Mater. 41 (1993) 1229–1235.

[25] J. Jamnik, R. Raj, Space-charge-controlled diffusional creep: volume diffusion case, J. Am. Ceram. Soc. 79 (1996) 193–198.