J Mater Sci (2006) 41:5190–5193
DOI 10.1007/s10853-006-0434-8

The role of metal–ceramic interfaces on the high temperature mechanical response of nanostructured nickel–yttria tetragonal zirconia polycrystals (Ni–YTZP)

Ana Morales-Rodríguez · Diego Gómez-García ·
Carmen García-Gañán · Eugenio Zapata-Solvas ·
Arturo Domínguez-Rodríguez

Received: 8 September 2005 / Accepted: 15 February 2006 / Published online: 29 July 2006

Abstract High temperature creep of a metal–ceramic composite consisted of yttria tetragonal zirconia polycrystals (YTZP) with a certain amount of nickel grains (Ni–YTZP, 2.5% vol.) has been studied. The average grain size of YTZP grains was 0.20 μm, whereas that of the Ni grains was 50–70 nm. This work reports the mechanical response under creep of such composite materials. It is found that the activation energy for creep is significantly higher than that reported in similar systems with much larger nickel grains. This fact has been explained in terms of the chemical nature of the metal–ceramic interfaces.

Introduction

Ni–YTZP is a metal–ceramic system under intense study due to its intrinsic potential capabilities: YTZP is a landmark in the field of superplastic ceramics and Ni is added in order to improve electrical properties without altering mechanical response. Ni has been chosen as a metallic partner in Ni–YTZP due to several reasons, which are commented extensively elsewhere [1], the main one is the reasonably close match in both elastic modulus and thermal expansion coefficients [2].

This metal–ceramic system is a very interesting one, being the goal of a very intense research. In what follows we will refer to the terms ‘‘microNi–YTZP’’ and ‘‘nanoNi–YTZP’’. The first one means a composite with YTZP ceramic grains several hundreds of nanometers size and Ni grains a few microns size. The term ‘‘nanoNi–YTZP’’ refers to a composite material similar in nature to the previous one, but Ni grains being several tenths of nanometers size. The key difference is that the Ni particles are at least one order of magnitude smaller for ‘‘nanoNi–YTZP’’ specimens. This paper concentrates on nanoNi–YTZP plasticity only.

Concerning microNi–YTZP, a careful study of the high temperature mechanical response has been recently reported by Morales-Rodríguez [3]. The main features of high temperature plasticity in this one can be summarised as follows:

(i) Grain boundary sliding accommodated by zirconium cation diffusion is the deformation mechanism: no microstructural changes are detected after deformation by SEM and TEM observations [4]. In addition to that, the activation energy for creep is similar to that of the zirconium cation diffusion in YTZP.
(ii) No nickel particles-induced hardening is reported: mechanical response is essentially controlled by the ceramic phase only. No influence of the amount of Ni particles is measured, at least up to a maximum amount of 40% vol. [5].

Regarding nanoNi–YTZP composites, the fracture toughness at room temperature of these composite materials can be quite different from that of the parent ceramic system as reported and modelled by Pecharromán et al. [6]. No data on their high

---

A. Morales-Rodríguez · D. Gómez-García ·
C. García-Gañán · E. Zapata-Solvas ·
A. Domínguez-Rodríguez (✉)
Departamento de Física de la Materia Condensada,
Universidad de Sevilla, apartado 1065, Av. Reina Mercedes,
s/n, Sevilla 41012, Spain
e-mail: adorod@us.es

temperature plasticity response are still available in literature. The purpose of this work is to cover this gap, at least partially.

Experimental procedure and results

NanoNi–YTZP samples, prepared according to a sintering route described elsewhere [6], have been cut into parallelepipeds for uniaxial compression tests. The microstructure was studied prior to deformation through scanning electron microscopy (SEM) consisting of nanometric Ni particles (50–70 nm) uniformly embedded in the YTZP ceramic grain structure with an average grain size equal to 200 nm. The whole amount of Ni particles was 2.5% vol. A maximum amount of 10% vol. of Ni particles is compatible with a fully homogeneous microstructure in nanoNi–YTZP specimens. If the Ni amount increases beyond this value, Ni particles coalescence occurs. In that case, their size is no longer nanometric [5, 6].

Creep tests have been performed through the standard procedure reported in [3] using a prototype machine at temperatures between 1,200 °C and 1,250 °C, high enough for grain boundary sliding activation, but still low enough to avoid grain growth. Figure 1 displays one of the creep tests.

Steady-state strain rates have been fitted to the conventional high temperature creep equation [7] written as follows:

$$\dot{\varepsilon} = A\sigma^n D_0^{\mathrm{eff}} \exp\left(\frac{-Q}{kT}\right) \qquad (1)$$

where $\dot{\varepsilon}$ is the steady-state strain rate, A is a constant including the grain size dependence, σ is the applied stress, n accounts for the $\dot{\varepsilon}$ dependence with stress and D_0^{eff} is the effective diffusion coefficient preexponential term of the species accommodating grain boundary sliding (a certain combination of grain boundary diffusion and lattice diffusion coefficients). Finally, the Arrhenius term includes the activation energy of the rate-controlling process, Q. The other symbols have their usual meaning.

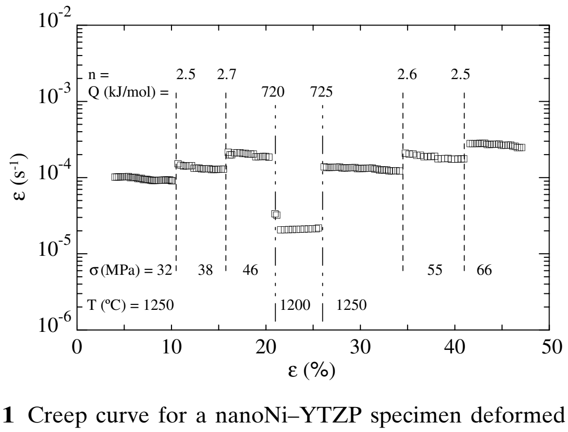

Fig. 1 Creep curve for a nanoNi–YTZP specimen deformed at the experimental conditions displayed in the plot. The activation energies are close to 720 kJ/mol

Data analysis from all the creep tests shows that the activation energy for nanoNi–YTZP specimens is 700 ± 50 kJ/mol. This value is much higher than that reported for the activation energy in pure YTZP and microNi–YTZP's, where the usual value is 475 ± 25 kJ/mol, being this one the activation energy for lattice diffusion of cations in YTZP specimens [8]. Concerning the stress exponent n, a value of 2.5 ± 0.3 has been measured. This value is in good agreement (within the experimental uncertainty) with the reported one in high-purity YTZP polycrystals of the same average grain size and also in microNi–YTZP cermets with YTZP grains of the same size [3, 5]. This value is the result of a grain boundary sliding mechanism accommodated by cation diffusion with a threshold stress [3, 5].

Modelling and discussion

Nature of the metal–ceramic interface

The stability and the high adhesion of nickel on to the YTZP ceramic can be explained through a charge transfer schematised in Fig. 2: nickel atoms adjacent to the ceramic lattice planes oxidises to a +2 valence state. This implies a formal transfer of electrons and an excess of negative charge on the metal particle. The

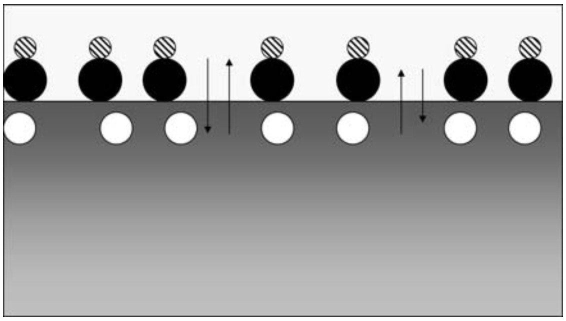

Fig. 2 Schematic showing the charge transfer mechanism at the origin of the nature of the Ni–YTZP interface. Ni atoms (dashed circles) are oxidised to Ni^{2+} and bind to oxygen anions (black circles). This effect induces the creation of oxygen vacancies (white circles) at the ceramic interface, which minimises the electrostatic energy stored at the ceramic interface. This mechanism is active as long as the metal interface is thin enough, since the Debye screening length in metals is very small

electrical neutrality is established through an increment of the number of oxygen vacancies at the ceramic interface [9]. Nickel cations strongly bind to the oxygen atoms. Hence, a monolayer of nickel oxide is generated.

The existence of such thin nickel oxide layer accounts for the stability of this metal–ceramic interface, since the Ni–O bonding is very strong and the lattice parameter of NiO is close to that of YTZP. This last point explains the excellent matching of the Ni metal and YTZP interface as observed in [10]. Recent results achieved through computer simulation [11] and XPS and XANES [12] studies agree with these statements. Moreover, it is in consistent agreement with the reported results of the mechanical response at room temperature [1, 13].

Influence on the mechanical response

YTZP is a model-system in which cation segregation at the interfaces has revealed to be crucial concerning its mechanical features. Segregation proceeds as a consequence of the size factor induced by the substitutional yttrium cations into the cation lattice of zirconium. This fact gives rise to an excess of elastic energy to be released through displacement of the bigger cations to the grain boundaries. A large number of papers have been devoted to the study of such segregation on the mechanical response of YTZP. Segregation is the keystone of the main features of YTZP mechanical response. The segregation has been used to explain the superplastic flow stress in terms of the ionic sizes of the segregate cations [14, 15]; also, its presence is at the origin of the threshold stress in YTZP [16]. Besides, it modifies the cation diffusion, affecting the accommodation mechanism while grain boundary sliding proceeds. That second effect can be particularly detectable when going down to the nanoscale [17].

When attention is focused on the Ni–YTZP system, the presence of Ni particles does not seem to alter essentially the main picture on the deformation mechanism: grain boundary sliding accommodated by cation diffusion along the lattice or along the grain boundary. What is the leading difference is the path of the cation diffusion governing the accommodation mechanism. Indeed, two types of YTZP grains can be identified in the composite under study: those which are not in contact with pure Ni grains (type I grains), and those having at least an interface in common with a Ni particle (type II grains). Let f_α be the fraction of type I grains. These ones slide each other during creep, lattice cation diffusion (D_{latt}) being the accommodation mechanism. However, this is not the case for type II grains. For these ones, cations diffuse along the ceramic–metal interface, because the Ni–O bonding is very strong, being that one the effective path for the accommodation process. The associated cation diffusion is D_{gb}. This diffusion coefficient is most likely to be very different from the lattice diffusion one in the following sense:

Zirconium atoms at the ceramic–metal interface must migrate along such interface, which is particularly rich in O–Ni bonding. Consequently, migration is disfavoured by the strong bonding energy between Ni–O, which must be overcome for Zr diffusion along the grain boundaries.

In consequence, it is reasonable to admit that D_{gb} can be written as:

$$D_{\mathrm{gb}} = D^0_{\mathrm{gb}} \exp\left(-\frac{\varepsilon}{kT}\right) \tag{2}$$

where ε is the activation energy of Zr along the grain boundary in the presence of Ni–O bonding and D^0_{gb} is a preexponential factor. The effective diffusion coefficient for creep, admitted that the relative weight of them is equal to the relative ratio of the two sets of grains, under the commonly accepted hypothesis of minimal entropy production [18], can be written as:

$$\frac{1}{D_{\mathrm{eff}}} = \frac{f_\alpha}{D_{\mathrm{latt}}} + \frac{1-f_\alpha}{D_{\mathrm{gb}}} \tag{3}$$

If Zr diffusion along grain boundaries in type II grains is the slowest path, then Eq. 2 can be written:

$$D_{\mathrm{eff}} = \frac{D^0_{\mathrm{gb}}}{1-f_\alpha} \exp\left(-\frac{\varepsilon}{kT}\right) \tag{4}$$

Hence, the effective activation energy $Q_{\mathrm{eff}} = \varepsilon$. This effective diffusion coefficient can justify the high value of $Q = 700 \pm 50$ kJ/mol of the activation energy for creep as determined experimentally. This value is much higher than that of the Zr diffusing along the bulk. Future trends in research on this composite would demand the assessment of this determination by means of other techniques, particularly diffusion measurements.

Conclusions

Charge transfer from the nickel to the YTZP interfaces on nanoNi–YTZP composites accounts for the stability of YTZP–Ni interfaces.

The strong interface matching can give rise to the high values of the activation energies for creep in this composite.

Acknowledgements The authors would like to acknowledge the financial support awarded by the Spanish ‘‘Ministerio de Educación y Ciencia’’ through the project MAT2003–04199–CO2-02.

References

1. Quin CD, Derby B (1992) J Mater Res 7:1480
2. Li M, Shen P (2005) Mat Sci Eng A 398:309
3. Morales-Rodríguez A (2004) PhD. dissertation, Universidad de Sevilla
4. Morales-Rodríguez A, Bravo-León A, Domínguez-Rodríguez A, Jiménez-Melendo M (2004) Mater Sci Forum 447–448: 347
5. Morales-Rodríguez A, Bravo-León A, Domínguez-Rodríguez A, Jiménez-Melendo M. submitted to J Am Ceram Soc
6. Pecharromán C, Esteban-Betegón F, Bartolomé JF, Richter G, Moya JF (2004) Nano lett 4:747
7. Poirier J (1985) Creep of crystals, Cambridge University Press, Great Britain, UK
8. Jiménez-Melendo M, Domínguez-Rodríguez A, Bravo-León A (1998) J Am Ceram Soc 81:2761
9. Perusin S, Viguier B, Monceau D, Ressier L, Andrieu E (2004) Acta Mater 52:5375
10. López-Esteban S (2002) PhD. Dissertation. Universidad Complutense de Madrid
11. Beltrán JI, Gallego S, Cerda J, Muñoz MC (2005) Adhesion at Ni–ZrO_2 interfaces. Presented at the international workshop on interfaces: interfaces by design, Santiago de Compostela, June 26–30
12. Sotiropoulou D, Ladas S (1998) Surf Sci 408:182
13. López-Esteban S, Bartolomé JF, Moya JS, Tanimoto T (2002) J Mater Res 17:1592
14. Mimurada J, Nakano M, Sasaki K, Ikuhara Y, Sakuma T (2001) J Am Ceram Soc 84:1817
15. Nakatani K, Nagayama H, Yoshida H, Yamamoto T, Sakuma T (2003) Scripta mater 49:791
16. Gómez-García D, Lorenzo-Martín C, Muñoz-Bernabé A, Domínguez-Rodríguez A (2003) Phil Mag 83:93
17. Domínguez-Rodríguez A, Gómez-García D, Lorenzo-Martín C, Muñoz-Bernabé A (2003) J Eur Ceram Soc 23:2969
18. Philibert J (1984) Sol St Ionics 12:321