INFLUENCE OF OXIDATION ON THE HIGH-TEMPERATURE MECHANICAL PROPERTIES OF ZIRCONIA/NICKEL CERMETS

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ABSTRACT

The influence of an oxidizing atmosphere on the high-temperature plasticity of zirconia/nickel cermets has been studied by conducting creep tests in air. The resulting microstructure has been characterized by scanning, conventional and high-resolution electron microscopy. Despite the large microstructural changes, the composites do not exhibit mechanical degradation.

Keywords: cermet, zirconia, nickel, oxidation, plasticity.

1. INTRODUCTION

Nowadays ceramic-metal composites (cermets) based on zirconia and nickel are intensively studied due to their high-value added and multifunctional applications as sensors, thermal barriers and particularly anodes for solid oxide fuel cells (SOFCs) [1-

3]. These cells operate at high temperatures in a reducing environment. Accidental oxidation of the metal phase in the anode can occur for different reasons (system shutdown, seal leakage, fuel supply interruption) and lead to microstructural and mechanical changes that may have significant effects on the integrity and performance of anode-supported SOFC.

The mechanical properties of oxidized zirconia/nickel cermets have already been investigated at room temperature by 4-point bending tests [4]. These authors found an increase in the bending strength of samples oxidized at temperatures below 650 ºC and crack development at higher temperatures. This different behavior was explained in terms of reduction of porosity resulting from the volume expansion during oxidation of the metallic Ni to NiO and the stresses generated in the zirconia matrix. However, no mechanical data at the fuel cell operating temperatures are available. The aim of the present paper is thus to investigate the high-temperature mechanical properties of zirconia/nickel cermets deformed in oxidizing atmosphere and the resulting microstructure. The results are compared with previous studies on the same materials carried out in argon atmosphere which prevents the oxidation of the nickel phase [5,6].

2. EXPERIMENTAL PROCEDURE

The cermets used in this study were fabricated by ICMM (Instituto de Ciencia de Materiales-CSIC, Madrid, Spain); details of the processing route can be found elsewhere [7]. Two sets of high-purity 3 mol% Y_2O_3-stabilized tetragonal zirconia/Ni cermets with relative nickel contents of 20 and 40 vol% (hereafter referred to as Ni20 and Ni40, respectively) were produced in reducing atmosphere at a final sintering temperature of 1430ºC. X-ray analysis confirmed that the as-received composites consist only of metallic Ni and tetragonal ZrO_2. The density of both batches was about 85% of the theoretical values determined by the rule of mixtures.

Prismatic specimens with dimensions 4x3x3 mm^3 were cut from the as-received cermets for mechanical tests. Compressive experiments were carried out under constant load at temperatures T between 1000 and 1250 ºC and nominal stresses σ between 15 and 100 MPa; air was supplied as oxidant from the beginning of the experiments. Identical tests but in argon atmosphere for preserving metallic Ni are discussed elsewhere [5]. Experimental data, length of the specimens vs time, were plotted as log $\dot{\varepsilon}$ - ε curves (creep curves), with $\dot{\varepsilon}$ and ε the strain rate and true strain, respectively. Data were analyzed using the standard high-temperature power law for steady state deformation [8]:

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

where A is a constant, n the stress exponent, Q the activation energy for flow and R the gas constant. The values of n and Q, which are related to the deformation mechanism, were deduced from sudden σ or T changes during a creep test.

Microstructure characterization of as-received and deformed samples was carried using a Philips XL-20 SEM and a Philips CM-200 TEM (Microscopy Service, Universidad de Sevilla, Spain). TZP/TZP grain boundaries and TZP/Ni interfaces were characterized at atomic level by using a JEOL JEM-ARM 1250 HRTEM with a point to point resolution of 0.12 nm; the chemical composition of these boundaries was analyzed in a VG HB

501 UX STEM with a thin windows (NORAN) energy-dispersive x-ray spectrometer (Max-Planck Institute for Metal Research, Stuttgart) [9].

3. RESULTS AND DISCUSSION

Figure 1 is a SEM micrograph illustrating the microstructure of the as-received Ni20 composite. The nickel inclusions (bright phase) are rounded, isolated from each other and rather uniformly distributed throughout a porous zirconia matrix (gray phase), with an average particle size of about 1 μm. Zirconia grains have also an equiaxed shape but a much finer microstructure with an average grain size of 0.13 μm. Ni40 exhibits identical features except for some contact between nickel particles due to the fact that its metal content is above the percolation limit (found to be close to 34 vol% from electrical measurements [7]).

After deformation in air, the samples exhibit a green color distinct of nickel oxide, in contrast to as-received and argon-deformed samples which were black. SEM observations on cross-sections revealed a degree of oxidation close to 100% over the entire volume of the samples. This result is consistent with thermogravimetric investigations in air on massive zirconia/nickel cermets performed by Stathis et al. [4], which have shown that the nickel oxidation was completed at about 700ºC. No evidence of macroscopic failure of the samples was observed even for the larger strains attained ($\varepsilon = 60$ %).

Figure 2 shows the microstructure of air-deformed Ni20 cermet (now NiO particles appear grey and the zirconia matrix is bright in SEM). NiO particles have an equiaxed shape, developing intragranular pores occasionally in contrast with dense Ni inclusions in the samples deformed in argon [5] that exhibited an elongated shape with the largest diameter oriented perpendicular to the loading axis in agreement with their low creep resistance. The final density of the samples after deformation remained roughly constant due to a balance between reduction of the original porosity by creep and formation of intragranular porosity inside the oxidized particles. The zirconia matrix grains do not experience any significant change in shape and size in both air and argon creep conditions, as could be expected from the superior ductility (i.e., grain boundary sliding [10]) and the insensitivity of creep strength on testing atmosphere [11] exhibited by tetragonal zirconia.

It must be pointed out that no crack development by cavity or microcrack coalescence was observed in the oxidized specimens, despite the large nominal volume expansion accompanying the Ni oxidation. Waldbillig et al. [12] have recently shown that 8 mol% Y_2O_3-stabilized zirconia/nickel cermets with a coarse microstructure experienced negligible volume changes upon reduction and reoxidation. These results suggest that the existing pores helped to accommodate the volume expansion, avoiding the formation of cracks and failure of the specimens. The improved fracture toughness and strength of the tetragonal zirconia matrix is likely to contribute also to relax the stresses caused by the Ni oxidation.

TEM observations showed the absence of dislocations inside both the zirconia and the NiO grains, as found in as-received and Ar-deformed cermets [6]. However, HRTEM observations (Fig. 3) revealed a striking feature: the development of a glassy film of about 1 nm thick along TZP-TZP grain boundaries and TZP-NiO interfaces. This amorphous layer has also been observed at multiple grain junctions. Such a film is not present at all in as-received and Ar-deformed samples [6], in which lattice fringes of two neighboring zirconia grains are contacted directly each other at the boundary without any secondary grain boundary phase in HRTEM. There are no results about formation of ternary compounds in the TZP/NiO system, even at extreme conditions of high pressures and temperatures [13]. Jun et al. [14] have recently shown that NiO wets zirconia after heat treatment at temperatures up to 1000ºC. This adherence, non-existent in the TZP/Ni system [13,15], could be responsible for the formation of the vitreous interphase detected along zirconia/NiO interfaces. The presence of this phase at zirconia/zirconia grain boundaries could be due to the grain neighbor switching that occurs during deformation by grain boundary sliding [8]. A glassy film may have detrimental effects on the ionic conductivity of these materials [16]. EDXS microanalysis performed along zirconia grain boundaries and in adjacent grains evidenced a significant yttrium segregation towards the boundaries, with an enrichment factor close to 2 with respect to the overall yttria content. This value is similar to those reported in as-received and Ar-deformed cermets [6] and monolithic yttria-stabilized zirconia [10,17]. It is concluded therefore that cation segregation is not affected by the oxidation process.

Regarding the creep strength of the composites, figure 4 shows the creep curves for Ni40 deformed in air and argon at similar levels of stress and temperature. It can be seen that the former specimen is much more creep resistant than the latter by a factor close to 100; the difference in strength decreases about a factor of 20 for Ni20 cermets. The presence of well defined steady states (Fig. 4a) indicates again that the samples retained their structural integrity after the nickel oxidation.

Previous studies devoted to investigating the high-temperature mechanical behavior of TZP/Ni cermets in argon atmosphere [5] showed that the deformation process was mainly governed by the ceramic matrix due to the very low creep resistance of the metallic phase at those temperatures. A quantitative analysis of the creep behavior of oxidized cermets requires the knowledge of the mechanical properties of monolithic zirconia and NiO. While tetragonal zirconia has been extensively studied in the past few years [10], available data for NiO are very scarce [18] and prevents a detailed analysis. An extrapolation of the creep data of NiO at the present testing conditions (with $n = 1$ and $Q = 390$ kJ/mol [18]) shows that zirconia and nickel oxide exhibit similar creep resistances when corrected with their respective volume fractions; thus both phases would contribute to the overall creep behavior of the composites, which is consistent with the hardening exhibited by the oxidized materials compared to the original TZP/Ni cermets (Fig. 4).

4. CONCLUSIONS

3 mol% Y_2O_3-stabilized tetragonal zirconia/Ni cermets with 20 and 40 vol% of metal content have been deformed in compression at high temperatures in air to investigate the effect of nickel oxidation. The composites retain their structural integrity even at the largest strains studied (60%). It is believed that the large volume expansion associated to the oxidation of nickel is accommodated by the preexisting pores and the superior toughness of the zirconia matrix. HRTEM observations revealed the presence of a glassy film along grain boundaries and interfaces, which is absent in the as-received and

the argon-deformed cermets. The creep rates of oxidized composites are drastically reduced respect to their values under argon atmosphere.

AKNOWLEDGEMENTS

This work has been possible thanks to the financial support of the Ministerio de Ciencia y Tecnología through the projects MAT2000-1117 and MAT2003-04199-C02-02 (Spain) and the Max-Planck-Gesellschaft through the research program PMT-CT-2000-00051 (Germany). The authors are also grateful to S. López-Esteban for material processing and to J. Thomas and M. Kelsch for technical assistance.

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FIGURE CAPTIONS

Fig. 1. SEM micrograph of as-received Ni20 cermet. Nickel inclusions (bright phase) are homogeneously dispersed into a porous (black) zirconia matrix (grey).

Fig. 2. SEM micrographs of deformed Ni20 cermets at 1250 ºC under air. NiO particles appear grey. The stress axis is vertical.

Fig. 3. High-resolution electron micrographs of: (a) TZP/Ni interface; and (b) TZP/TZP grain boundary of air-deformed Ni20 cermet, showing the presence of a 1nm-thick glassy phase along the boundaries. The reticular planes observed are indicated.

Fig. 4. Creep curves of Ni40 composite deformed in (a) air and (b) argon. The creep strength is much higher in (a).

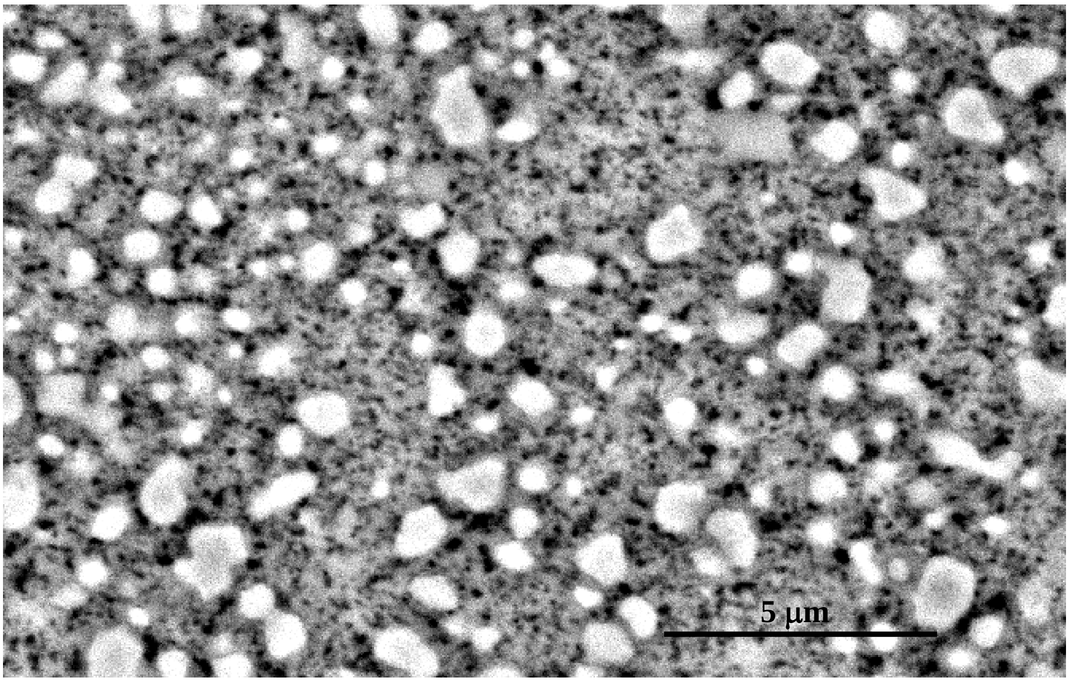

FIGURE 1

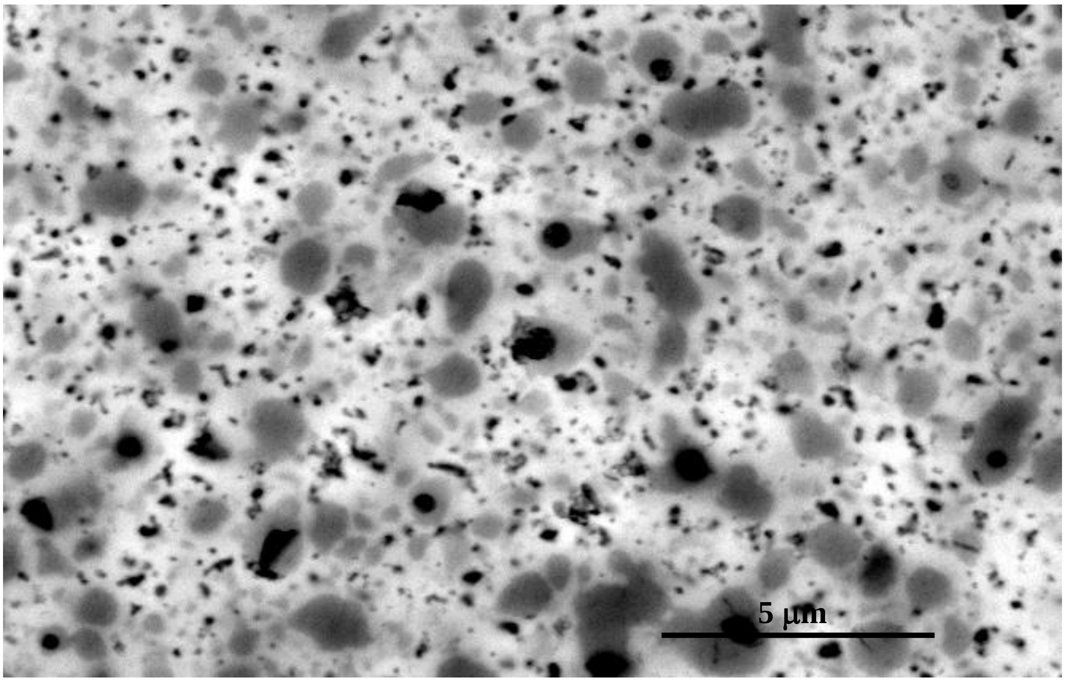

FIGURE 2

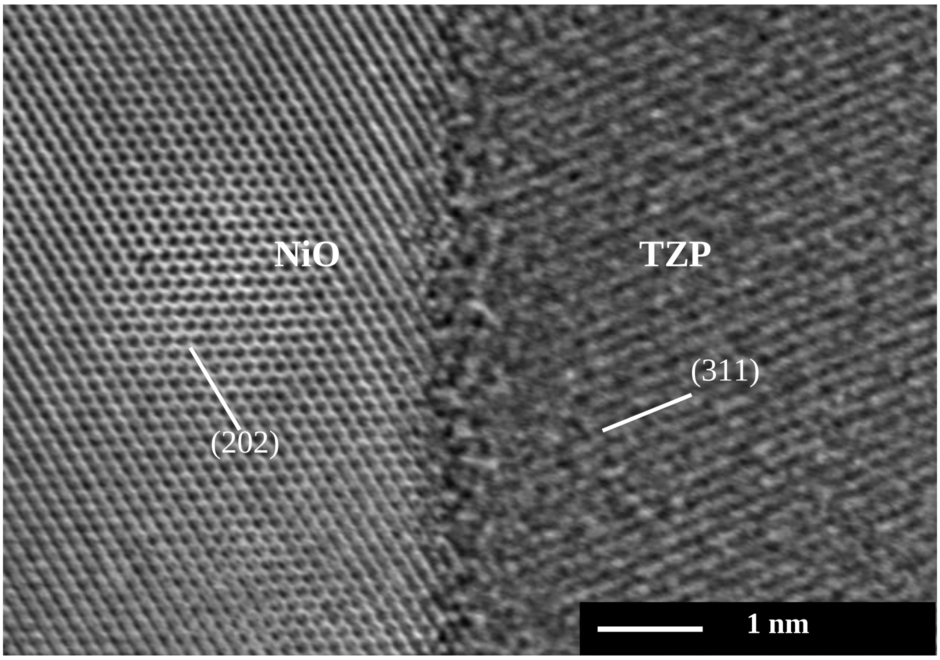

FIGURE 3a

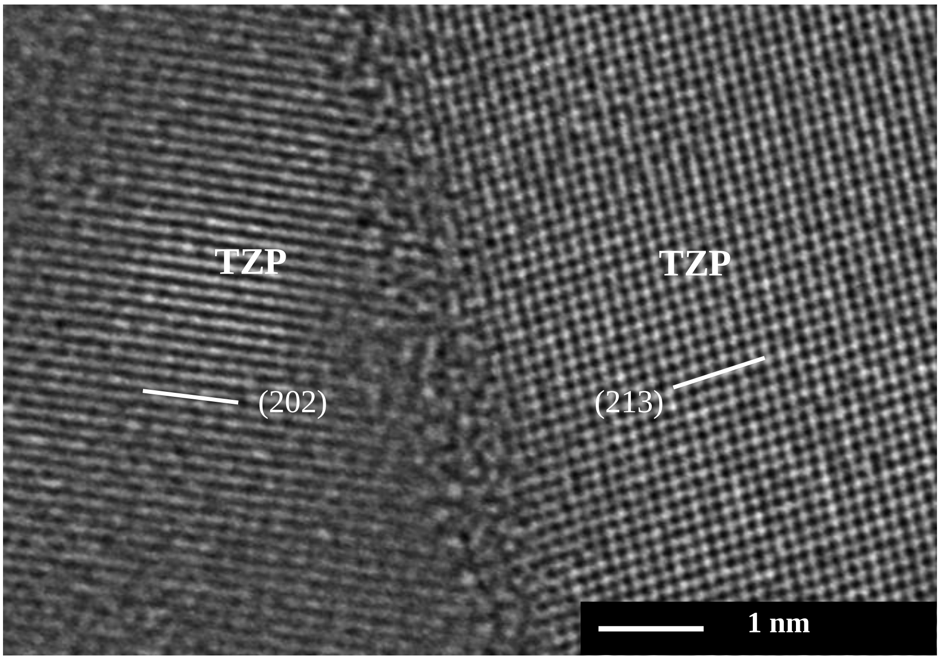

FIGURE 3b

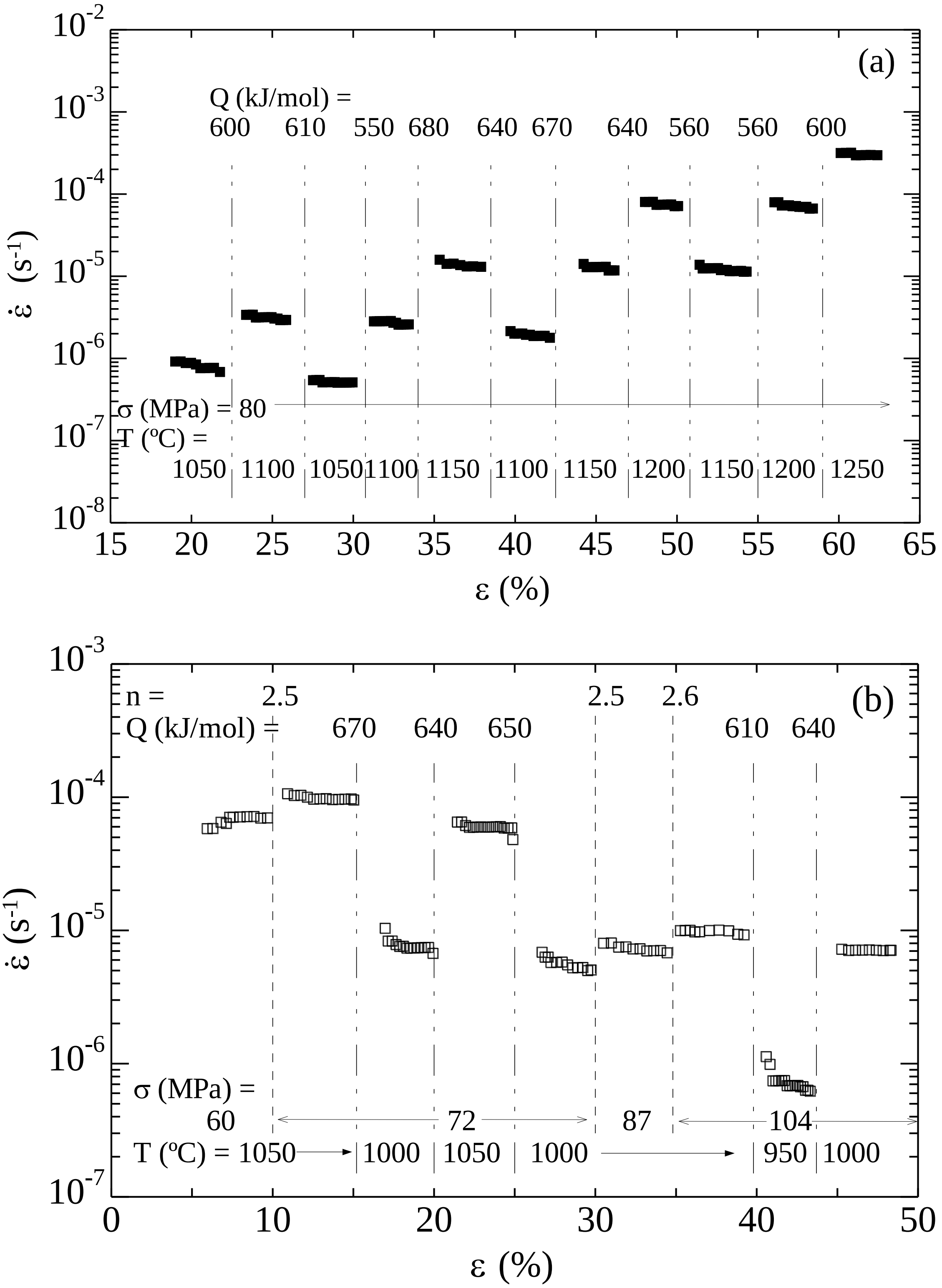
(a)
Q (kJ/mol) =
600 610 550 680 640 670 640 560 560 600
σ (MPa) = 80
T (ºC) =
1050 1100 1050 1100 1150 1100 1150 1200 1150 1200 1250
ε̇ (s-1)
10-2
10-3
10-4
10-5
10-6
10-7
10-8
15 20 25 30 35 40 45 50 55 60 65
ε (%)
(b)
n = 2.5 2.5 2.6
Q (kJ/mol) = 670 640 650 610 640
σ (MPa) =
60 72 87 104
T (ºC) = 1050 1000 1050 1000 950 1000
ε̇ (s-1)
10-3
10-4
10-5
10-6
10-7
0 10 20 30 40 50
ε (%)

FIGURE 4