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High temperature stress relaxation in Ti- and Cu-doped reaction bonded Al_2O_3

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Abstract

The high temperature plastic behavior of reaction-bonded alumina doped with copper and titanium oxide has been studied by means of stress relaxation tests in air providing the strain rate vs. stress curves at fixed temperature in a very straightforward way. The experimental data have been correlated with the microstructural observations and X-ray diffraction to deduce the deformation mechanism. The material shows plastic behavior at temperatures above 950 °C. Around 1000 °C, a linear plastic deformation law has been observed and both below and above this temperature the stress exponent takes higher values.

Keywords: Plasticity; Reaction-bonding; Stress relaxation

1. Introduction

Several studies have demonstrated the sensitivity of the plastic behavior of aluminum oxide to the presence of small amounts of dopants, if we focus our interest in the reduction of the sintering temperature and the improvement of the plastic behavior, the doping with equimolar amounts of CuO and TiO_2 has been demonstrated to achieve that goal.[1] The solubility of Cu and Ti in the Al_2O_3 lattice is drastically increased when these two species enter in equimolar amounts. The reason for this is the compensation in the valences which allows the substitution of Al without creating vacancies in the oxygen sublattice. The result is the formation of charged lattice points, Cu^{+2} cations surrounded by an excess of oxygen (and therefore a negative charged region) and Ti^{+4} with a deficiency of surrounding anions (positively charged). It is possible that these two different types of charged substitutional defects will attract each other and will associate inside the lattice forming more complex defects. This compensating effect is thought to be the reason for the high solubility observed in this system. Also, the presence of these species seems to alter drastically the diffusion processes inside the lattice producing an increase in the densification and plastic deformation rates at high temperature. This increase in the rate of the diffusional processes can be used to reduce the sintering temperatures and to promote plastic deformation at temperatures well below what is needed for deforming undoped alumina.

The material studied in this work was produced by means of a reaction bonding technique in which the starting powder is a mixture of metal and oxides, this procedure will be described in detail below and will be referred to with the initials RBAO (reaction bonded aluminum oxide). Reaction forming of ceramics exhibits various advantages when compared with conventional manufacturing. Low raw materials costs, near-net-shape tailorability and glassy-phase-free grain boundaries are the most attractive attributes for numerous technical and high performance applications.[2,3]

The mechanical characterization of the samples was carried out by means of stress relaxation tests. The main advantage of this experimental method is the possibility of obtaining the strain rate-stress curves for a fixed temperature, covering up to five orders of magnitude in the strain rate, in a single test lasting less than one day. This is judged to be a nearly constant- microstructure measurement, due to the short period of time needed to complete the tests.[4–6] The complete mechanical data of

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a material in a defined range of temperatures can be obtained with a small number of tests, the details of how these tests were conducted will be given below.

2. Experimental procedure

2.1. Material fabrication and characterization

The material used in this study was fabricated in TUHH (Technical University of Hamburg-Harburg, Germany) by a reaction bonding process, as a starting material a mixture of aluminum metal and oxides was used. The composition of this powder was (in wt.%): Al 29.6%, Al_2O_3 33.8%, 2Y-TZP 29.7%, CuO 3.5% and TiO_2 3.5%. The mixture was ball milled after suspension in acetone for 7 h. After cold drying the powder in air for 24 h, bars were isostatically pressed at 325 MPa and subjected to a process of oxidation-free sintering with the following schedule: the temperature was increased from room temperature to 400 °C in 6 h, and held constant for another 6 h, in a second step the temperature was increased to 450 °C in 3 h and held at this second temperature for another 6 h, finally the temperature was increased to 1000 °C in 9 h to finish the oxidation of the aluminum and sinter the material at this temperature for 1 h. Finally the samples were sinter-forged at 1150 °C under a uniaxial stress of 20 MPa during 20 min. Final samples have a relative density in excess of 95% and an average grain size of about 0.5 μm.

Fig. 1 shows an X-ray diffraction pattern of the material, two crystalline phases can be clearly identified, monoclinic zirconia and α-alumina, some traces of tetragonal zirconia can also be observed. This pattern is consistent with a total dissolution of the dopants in the alumina matrix, thus the material is a two phase material with compositions: $Al_{1.908}Cu_{0.046}Ti_{0.046}O_3$ and $Y_{0.039}Zr_{0.961}O_{1.980}$ (2 mol% Y_2O_3 doped ZrO_2). Here it has been assumed that none of the yttrium has been incorporated into the alumina lattice, the reason for the destabilization of the zirconia grains can be either due to the ball milling process or to the grain growth produced during sintering. The evidence of the total dissolution of the copper and titanium into the alumina supports that these species are present in the material as Cu^{2+} and Ti^{4+}, been incorporated into the alumina in the ratio $CuTiO_3$ and thus not introducing vacancies into the oxygen sublattice.[1]

The characterization of the microstructure of the materials was carried out by means of transmission electron microscopy on thin films, the use of scanning electron microscopy was also tried but some difficulties in producing a good etching of the polished surfaces prevented us obtaining decent observations. Until this problem is solved (maybe by the use of an appropriate chemical etching) TEM has been the only way of

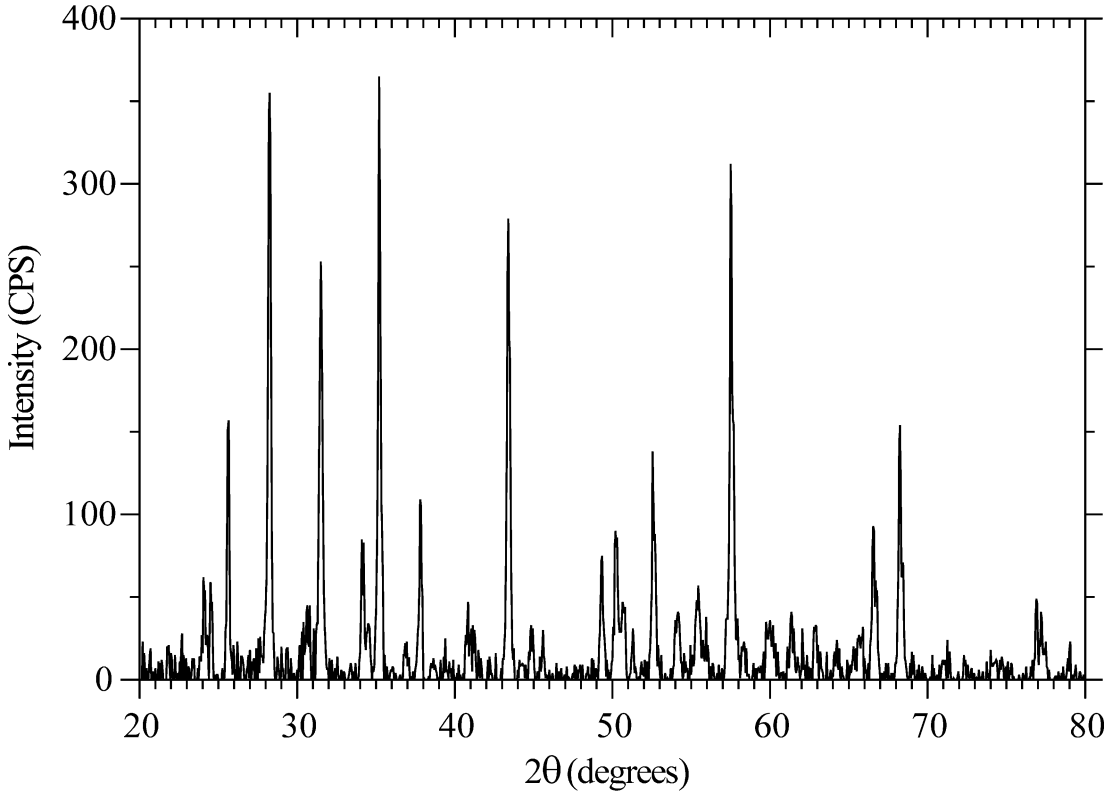

Fig. 1. X-ray diffraction pattern of a sintered sample, only peaks corresponding to α-Al_2O_3 and monoclinic ZrO_2 are evident.

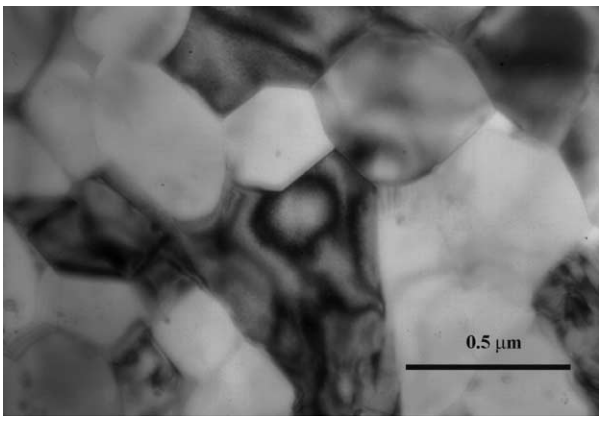

Fig. 2. Transmission electron micrograph of the sintered material, alumina grains as well as some space filling grains can be observed.

observing the microstructure. Figs. 2 and 3 show the prominent features observed, although the shape of the grains is very regular, some grains show an irregular, space-filling shape as can be observed in Fig. 2. In Fig. 3 the typical twinned structure of the monoclinic zirconia can be observed. From TEM observations it appears as if the structure consists of three different kind of grains in contrast with the results provided by the X-ray data. The reason for this discrepancy could be in the presence of two types of alumina grains. Due to the RBAO process it is expected that the material has alumina coming from two different sources, part comes from the original Al_2O_3 powder added to the mix and part was produced during the oxidation step of the RBAO process. It is plausible that these "new" grains incorporate most of the Cu and Ti and thus have a different chemical composition than the "old" ones. If the solubility of these species in the Al_2O_3 is high, the only expected effect in the X-ray diffraction pattern would be the shifting in the positions of the α-Al_2O_3 peaks. Under these conditions approximately 38% of the alumina would be "old" and 62% "new". The confirmation of this extreme would require the detailed study of the diffraction pattern and can be part of a further study.

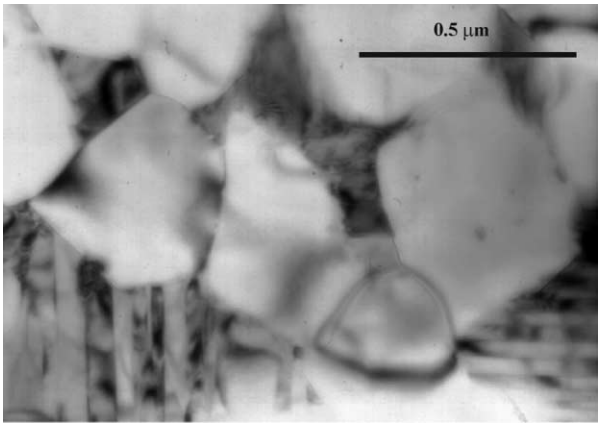

Fig. 3. Transmission electron micrograph of a sintered sample, both alumina and twinned zirconia grains (monoclinic) are visible.

2.2. Mechanical tests: stress relaxation

From the as-received materials, parallelepiped samples of approximate dimensions $3\times3\times6$ mm^3 were cut and ground for tests. For carrying out the tests an Instron 1165 universal testing machine was used. Prior to each test a calibration run without sample was carried out in order to determine the load-displacement curve for the experimental setting at those particular conditions. These curves were used to convert the load vs. time relaxation curves of the testing samples into instantaneous length vs. time curves. Numerical differentiation of these curves allows one to obtain the strain rate–stress curve for each temperature in just one test. Fig. 4 shows one of these calibration curves at 1000 °C. From the calibration run the displacement of the machine as a function of the applied load was obtained as:

$$\Delta = \Delta(P) \tag{1}$$

where Δ is the displacement and P the load.

For carrying out the stress relaxation tests, after stabilization of the sample and equipment at the temperature of the tests, the load was increased by means of the displacement of the cross-head until the desired stress level was achieved, then the machine was stopped and the curve load vs. time was recorded.

For sample loading, the cross-head was initially displaced an amount L_0 in order to reach the desired initial

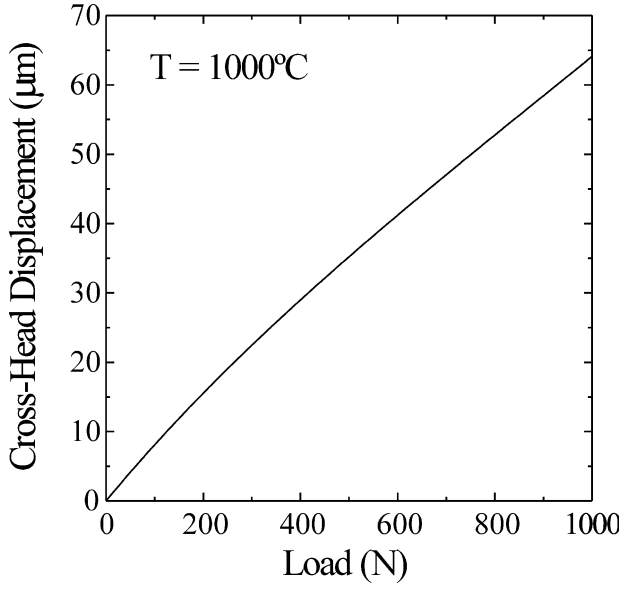

Fig. 4. Compliance calibration curve for the experimental setup at 1000 °C, one of these calibration curves was obtained for each experimental condition.

load P_0. Knowing the load, the corresponding change in length of the machine can be calculated from (1) as

$$\Delta_0 = \Delta(P_0) \tag{2}$$

from the calibration run. So from the total displacement of the cross-head L_0, Δ_0 corresponds to the machine and $L_0-\Delta_0$ to the sample. Thus, the length of the sample at the beginning of the relaxation test is

$$l_i = l_0 - L_0 + \Delta_0 \tag{3}$$

This calculation can be carried out at all times, providing the instantaneous length of the sample as:

$$l = l_0 - L_0 + \Delta(P) \tag{4}$$

From the instantaneous length, l, it is straight forward to calculate the instantaneous strain rate by using the expression:

$$\dot{\varepsilon} = -\frac{1}{l}\frac{\mathrm{d}l}{\mathrm{d}t} \tag{5}$$

by numerical differentiation.

On the other hand, the instantaneous stress can also be easily calculated. Assuming that plastic deformation takes place at constant volume and that the sample retains its shape, this means that

$$V = S_0 \cdot l_0 = S \cdot l \tag{6}$$

where S_0 and l_0 are the initial area and length of the sample respectively and S and l are the instantaneous values. The instantaneous stress is given by

$$\sigma = \frac{P}{S} \tag{7}$$

where P is the instantaneous load and S the instantaneous section of the sample. Combining Eqs. (6) and (7), the condition for constant volume gives

$$\sigma = \frac{P}{S_0}\frac{l}{l_0} \tag{8}$$

which allows us to calculate the instantaneous stress from the known values of the initial section and height and the instantaneous load and length. Together, expressions (5) and (8) produce the strain rate vs. stress curve from the relaxation curve. These curves are expected to agree with the ones obtained from stationary tests if primary creep is absent, which has to be verified in each case prior to carry on the tests.

3. Experimental results

Stress relaxation tests were carried out at temperatures between 950 and 1100 °C. Fig. 5 shows a typical relaxation curve load vs. time for a sample tested at 1000 °C. The results of the analysis in the form of strain rate vs. stress curves can be observed in Fig. 6, for the range of temperatures studied.

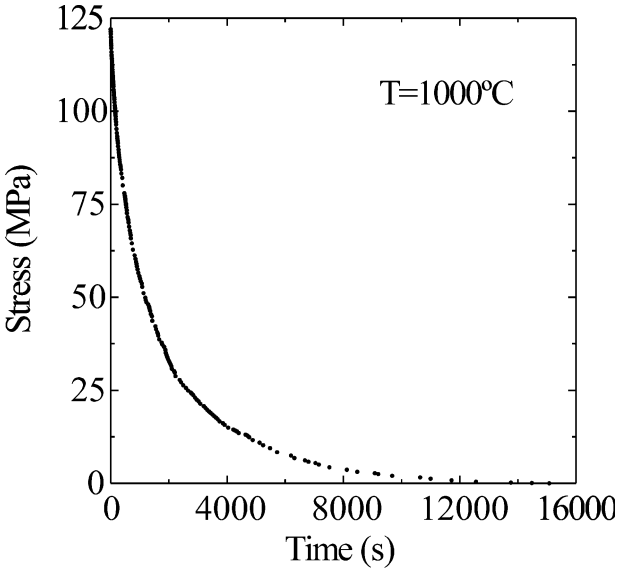

Fig. 5. Stress relaxation curve of a sample loaded at 1000 °C up to an initial stress of 125 MPa. The stress relaxes to zero in approximately 12,000 s (3 h).

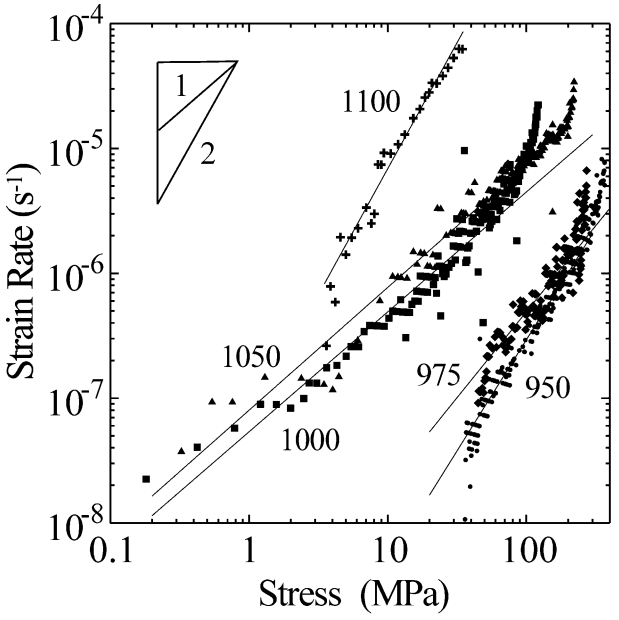

Fig. 6. Strain rate vs. stress curves deduced from stress relaxation tests at temperatures from 950 to 1100 °C. A region with a stress exponent of one can be observed at temperatures around 1000 °C.

It is assumed that the material deforms plastically according to the classical creep equation:

$$\dot{\varepsilon} = A \cdot \frac{\sigma^n}{d^p} \cdot \exp\left(-\frac{Q}{RT}\right) \quad (9)$$

where A is a constant, d is the grain size and T is the absolute temperature, n and p are the stress and grain size exponents which are characteristic of the deformation mechanism, Q is the activation energy of the process and R is the gas constant. The rest of the symbols have been defined previously.

The material shows significant plasticity at temperatures above 950 °C, but the behavior is very sensitive to the temperature. At temperatures around 1000 °C the material deforms with a stress exponent of 1 over a wide range of stresses, but both below and above this range an increase in the stress exponent to a value of about 2 can be observed. This plastic behavior is in contrast with that of pure alumina in which temperatures in the range of 1400 °C are needed for similar grain sizes in order to observe significant plastic deformation.

Preliminary results are consistent with the absence of primary creep unless for intermediate and low stresses, however the contribution of this type of creep can be important at high stresses/strain rates, which can explain the crossing of the curves in Fig. 6 at stresses around 100 MPa.

The use of materials with only one grain size prevented the determination of the grain size exponent and the change in mechanism observed in Fig. 6 made the possibility of obtaining an activation energy meaningless.

The microstructure of the samples after testing was very similar to the undeformed microstructure. For producing the curves observed in Fig. 6 it was only necessary to deform the samples for ~24 h to maximum strains of less than 1%. Thus it is not expected to observe a severe change in the microstructure after the tests. TEM observations did not provide any evidence for the activity of dislocations, and no change in the shape of the grains was observed.

These observations seem to indicate that in the conditions of the tests the main contribution to the plastic deformation is due to some kind of grain boundary sliding process. The narrow ranges in which defined mechanical behaviors were observed prevented the full determination of the parameters that characterize the deformation process, not allowing us to reach any conclusion about the possible accommodation processes or activation energies of the diffusion processes involved.

In any case, it has been demonstrated that the materials show significant plastic deformation at modest temperatures which can be put in correspondence with the increase in the diffusional processes observed in this system due to the co-doping with Cu and Ti by Ikuma et al.[7]

4. Conclusions

It has been demonstrated that stress relaxation tests are a powerful technique for the plastic characterization of this type of materials, allowing the determination of strain rate–stress curves in a single test for a fixed temperature.

In reference to the behavior of the material studied, the tests have shown a plastic behavior at temperatures above 950 °C, much lower than the temperatures for plastic deformation of undoped alumina. In a narrow range of temperatures (around 1000 °C) a linear plastic deformation law has been observed. Both below and above this temperature the stress exponent takes higher values indicating the presence of different deformation mechanisms. Microstructure observations are compatible with a grain boundary sliding mechanism although more work is needed in order to characterize completely the high temperature mechanical behavior in this system.

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