

# Microstructural and mechanical consequences of thermal cycles on a high zirconia fuse-cast refractory

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## Abstract

A qualitative and quantitative study of microstructural evolution and mechanical damage was carried out on a high zirconia fuse-cast refractory containing some intergranular glassy phase during high temperature thermal cycles. Microscopy, X-ray diffraction, resonance frequency and acoustic emission were investigated to relate the microstructural evolution to the damage as function of temperature. A detailed description of the mechanisms responsible for the evolution was achieved and three parameters were clearly identified as contributing to the overall behaviour. The glassy phase above  $T_g$  accommodates strains and stresses of the structure and heals some cavities or cracks. The zirconia phase transformation induces both cracking and healing, or closure. The thermal expansion mismatch between zirconia and glass, responsible for stress generation during cooling at low temperature, induces cracking and crack closure during heating. Another surprising observation was the delayed cracking after few days at room temperature resulting in stress relaxation, even on very small specimens. The overall behaviour is in the end not reversible, and this was clearly shown by in situ observation of cracking.

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## 1. Introduction

Fuse-cast refractories are used in the glass industry for furnace lining owing to their superior corrosion/erosion resistance.<sup>1</sup> Compared to conventional sintered refractories, their specificity is related to the fabrication by melting that leads to very specific microstructures.<sup>2,3</sup> They are acknowledged to contain a continuous glassy phase distributed between several crystallised phases of complicated and convoluted shapes. This specific microstructure is the result of a slow and controlled cooling from the fusion at high temperature, called annealing. Moreover, due to the large dimensions of the cooled industrial blocks, chemical, microstructural and mechanical heterogeneities exist between different areas of the massive blocks, generating some differences in thermomechanical behaviour. In addition, the important thermal gradients generated during the cooling stage, lead to an initially damaged material at room temperature.

Among the existing range of fuse-cast refractories containing zirconia,<sup>4</sup> the very high zirconia (HZ) material presents a two-phase microstructure, composed of zirconia grains in an intergranular glassy phase. It has been shown to be sensitive to high temperatures, developing a specific damage mode,<sup>5</sup> caused by the reversible zirconia phase transformation,<sup>6,7</sup> glassy-phase viscosity evolution, and thermal expansion mismatch between the two phases. Zirconia exhibits three well-defined polymorphs,<sup>8,9</sup> the monoclinic, tetragonal, and cubic phases. The monoclinic phase is stable up to about 1170 °C where it transforms to the tetragonal phase, which is stable up to 2370 °C. From this temperature, the cubic phase exists up to the melting point of 2680 °C. Of greatest significance is the martensitic monoclinic to tetragonal transformation, associated with a large volume change (3–5%). This is sufficient to exceed elastic and fracture limits even in relatively small grains of  $ZrO_2$  and can only be accommodated by cracking.<sup>10</sup> The glassy phase also plays a major role at high temperature in mechanical properties of such materials because of its migration within all the structure, promoting creep, controlling cracking and simultaneously healing or blunting cracks or cavities.<sup>11–13</sup>

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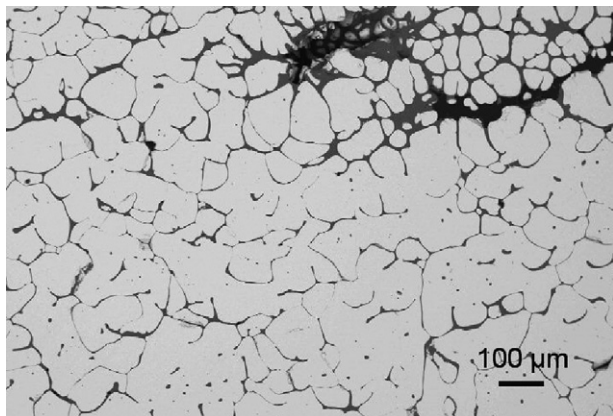


Fig. 1. Microstructure of a high zirconia fuse-cast refractory showing zirconia grains (around 100  $\mu\text{m}$ ) and the intergranular glassy phase (between 1  $\mu\text{m}$  and 20  $\mu\text{m}$ ).

The purpose of this paper is to investigate the different mechanisms of damage and healing during thermal cycling, without any other mechanical loading. The damage has been quantified by measurement of the elastic modulus and by microstructure analyses, before, during and after one or two successive thermal cycles. The evolution of the Young's modulus is highly sensitive to the microstructure evolution, including phase transformation and/or redistribution and cracking. The latter has also been revealed at room temperature by acoustic emission.

## 2. Materials and techniques

### 2.1. Materials

A very high zirconia fuse-cast refractory (94 wt.%) manufactured by SEPR (Société Européenne de Production de réfractaires, Le Pontet) was selected for this study. The material contains 94 wt.% zirconia and 6 wt.% of glassy phase. Scanning electron microscopy (Fig. 1) reveals zirconia grains surrounded by an apparently continuous glassy phase. The intergranular thickness (1–20  $\mu\text{m}$ ) is large compared to conventional sintered materials and was shown to play a significant role in the high temperature mechanical behaviour. According to the dilatometry measurements of the supplier, the intergranular glassy phase presents a transition at about 780  $^{\circ}\text{C}$ . It also revealed that the monoclinic to tetragonal transition begins at around 1130  $^{\circ}\text{C}$  when heating and that the reverse phase transformation occurs at about 1000  $^{\circ}\text{C}$  when cooling. A volume contraction (respectively expansion) of 4%, closed to the theoretical value is associated to this martensitic transformation.

### 2.2. Modulus measurement

The dynamic Young's modulus has been determined both at room and at elevated temperatures by the impulse excitation technique (IET). This technique is especially adapted to investigate the evolution of damage since it can be conducted on large specimens and induces small strains that do not damage

further the sample. Rectangular bar-shaped samples of nominal dimensions 150 mm  $\times$  25 mm  $\times$  15 mm were machined from a large cast block. The samples were placed on two lightweight fibrous refractory supports located in the nodes of the first bending mode. The sample is automatically excited by the impact of a small ceramic projectile. The resulting vibration acoustic signal is captured by a microphone and analysed using the Resonance Frequency and Damping Analyser (RFDA, IMCE, Diepenbeek, Belgium). The Young's modulus values have been calculated from the determined bending vibration frequency according to the provision of the European standard EN 843-2. For high temperature measurements, the test set-up is placed in a dedicated furnace (RFDA-HT1750, IMCE, Diepenbeek, Belgium). During the thermal treatment, the sample is periodically excited by the impact of the ceramic projectile. The vibration signal is as previously captured by a microphone located outside the furnace, a ceramic tube above the sample being used as acoustic waveguide. Tests have been run at temperatures ranging from 800  $^{\circ}\text{C}$  to 1500  $^{\circ}\text{C}$ . In order to circumvent the intrinsic dispersion of modulus values from specimens to specimens, the evolution was represented as a ratio of final to initial value:  $E/E_0$ .

### 2.3. Acoustic emission (AE)

During the final stage of specimen cooling (room temperature included), the AE technique was used to record microcracking. The recorder is a commercial Mistras 2001, supplied by EPA (Euro Physical Acoustics), and connected to two 40-dB preamplifiers. At room temperature two R15 resonant transducers were placed directly in contact with the bar at both ends. A silicon grease is applied at the sample-sensors interface to optimize the coupling. The use of two linear transducers allows a linear location of the AE sources, i.e. of microcracking. The recorded parameters were the cumulative AE event counts, amplitudes, duration, frequencies and energies.

### 2.4. High temperature environmental scanning electron microscope (ESEM)

The microstructure has been analysed in an ESEM. For in situ measurements a small furnace, that can reach 1450  $^{\circ}\text{C}$ , is introduced in the microscope. This technique has been chosen to follow the microstructure evolution during heat treatments up to about 1400  $^{\circ}\text{C}$ . Heating of the specimen is achieved by means of the resistive platinum sample-holder. Postheat-treatment observations were conducted in high vacuum mode (standard) on gold-coated specimens.

### 2.5. High temperature cycles

The specimens used for modulus and acoustic activity measurements have been submitted to the same thermal cycle, i.e. heating at 5  $^{\circ}\text{C}/\text{min}$  and cooling at 1.7  $^{\circ}\text{C}/\text{min}$ . Only the specimens imaged by ESEM were, for practical reasons, submitted to a different cycle, i.e. heating and cooling at 20  $^{\circ}\text{C}/\text{min}$ .

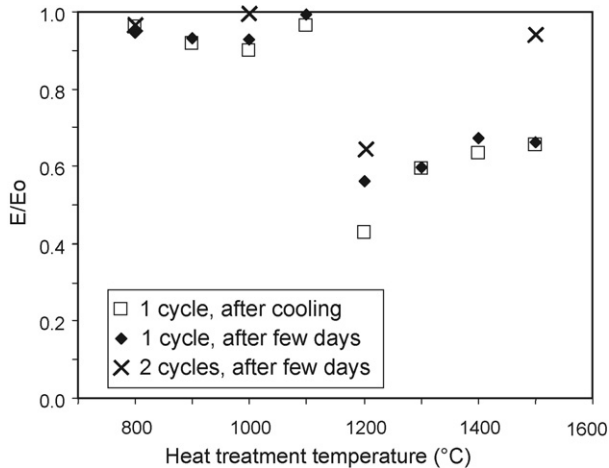


Fig. 2. Influence of the heat treatment temperature on the elastic modulus. The mechanical damage is illustrated by the decrease of the ratio of the elastic modulus on the initial modulus. The open squares represent the ratio just at the end of the first heat treatment, the black diamonds the ratio a few days after the first cycle and the cross the ratio a few days after a second thermal treatment.

### 3. Results and discussion

Several heat treatments have been conducted and modulus and microstructures were analysed both in situ at high temperature and after treatment, at room temperature.

#### 3.1. Modulus evolution

The impact of a thermal treatment on the integrity of the material has been assessed by the measurement of Young's modulus at room temperature before and after two successive identical thermal cycles. Test temperatures in the range 800–1500 °C have been investigated. The results of this first series of experiments, expressed as ratio between final and initial  $E$  values, are summarized in Fig. 2.

A first observation is the presence, irrespective of the case considered, of a clear transition in behaviour between 1100 °C and 1200 °C. Up to 1100 °C, one observes a limited decrease (maximum 10% of the initial value) of the elastic property of the sample; from 1200 °C, the loss of property is significant: 40% of the initial value on average. This transition clearly relates to the monoclinic-to-tetragonal phase transformation undergone by the zirconia main phase at about 1130 °C.

Two other features also deserve attention. On the one hand, the loss of property caused by this phase transformation can apparently be partly recovered by raising the maximum test temperature. The modulus tends indeed to increase with increasing temperature above 1200 °C. This is clearly visible if we compare the  $E/E_0$  ratio measured immediately at the end of the first thermal cycle, after a treatment at 1200 °C and 1500 °C, respectively. On the other hand, and more surprisingly, the Young's modulus decreases during a prolonged stay at room temperature after heat treatment. As can be seen in Fig. 2, the ratio between the Young's modulus measured after about 3 days at room temperature (in fact the initial values of the specimens before the second thermal cycle) and  $E_0$  is always lower than

the ratio between the Young's modulus measured on the same specimen immediately at the end of the first run and  $E_0$ . This additional decrease is particularly significant in the case of the 1500 °C-treated sample.

Finally, carrying out a second heat treatment leads to a further but limited damaging of the material.

In order to get insights in this apparently complex behaviour, the evolution of elastic modulus has been continuously monitored as a function of temperature during similar thermal treatments. Depending on the location of the sample within the cooled block, the microstructure is slightly different, which induces slight variations in room temperature modulus value and in the evolution of the modulus during the first part of the heating. However the results that follow are representative of all observations and encompass the main common features.

The evolution of Young's modulus with heat treatment up to 1500 °C is presented in Fig. 3. As expected, the stiffness decreases with increasing temperature up to around 600 °C. This decrease is followed either by a plateau or a weak maximum in the range 600–900 °C. Above 900 °C, the loss of stiffness accelerates and above 1100 °C, a steep and localised decrease of the modulus is recorded. As said before, this drastic change of properties coincides with the occurrence of the monoclinic-to-tetragonal phase transformation of the zirconia phase. It is thereby amplified by the loss of properties of the intergranular phase well above its glass transition temperature. Although the very high damping makes difficult to record a reliable signal above say 1350 °C, a slight increase of property is observed up to 1500 °C. It can probably be attributed to the redistribution of the low viscosity glassy phase in the structure that may heal some decohesions, cracks or porosities.

The cooling part of the cycle shows distinctive features. Between 1500 °C and 1000 °C, the modulus continues to slightly increase. Between 1000 °C and 900 °C the reverse phase transformation induces a localised increase in the modulus. Unlike the monoclinic-to-tetragonal transformation, the reverse transition does not induce any damage. Most probably the associated positive volume variation may close remnant cracks or deco-

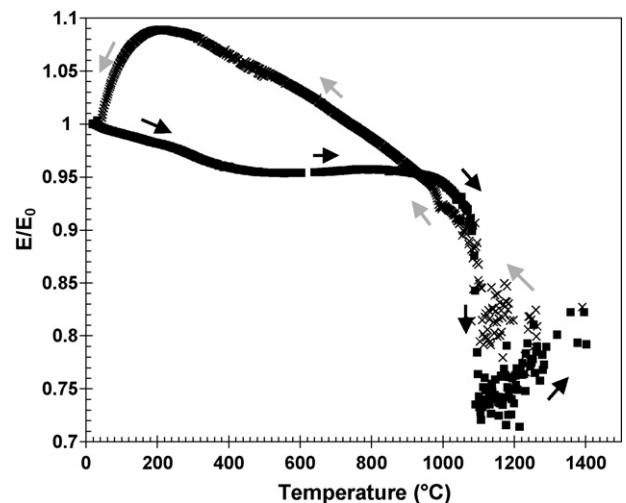


Fig. 3. Evolution of the elastic modulus during a thermal cycle at 1500 °C.

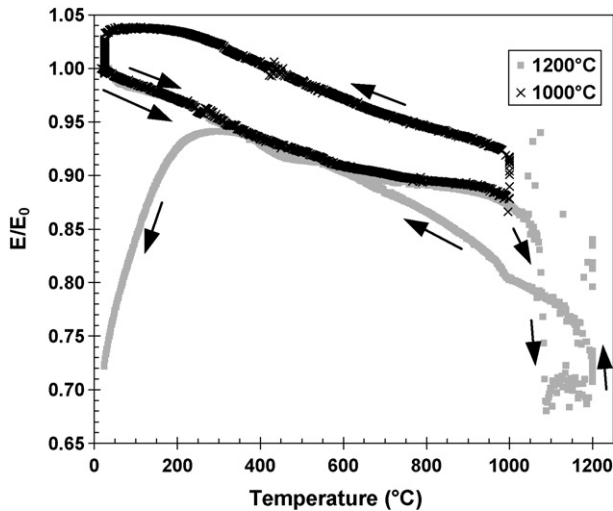


Fig. 4. Evolutions of the elastic modulus during 1000 °C and 1200 °C thermal cycles, in order to show the effect of the zirconia phase transformation.

hesions. After that, a more or less monotonic increase of the modulus takes place with decreasing temperature down to about 200–300 °C. Below, say 200 °C, the Young's modulus levels off rapidly. The final value reached at room temperature is in this case but slightly lower than the starting value.

Further insight has been gained by carrying out two additional treatments. The first one was conducted at a temperature of 1200 °C (Fig. 4). The evolution of the elastic modulus up to the test temperature is almost similar as in the 1500 °C treatment, except that the marked loss of elastic property caused by the  $m-t$  transformation is not compensated owing to the limited time at high temperature in this case. Accordingly, when cooling, the modulus of the specimen remains significantly lower than during the heating portion of the thermal cycle. The decrease of property below 300 °C is also larger. The treatment at 1200 °C appears thus more detrimental to the integrity of the specimen than the one at 1500 °C, this, in agreement with the previous observation (Fig. 2  $E_{1200^\circ\text{C}}/E_0$  of 40% vs.  $E_{1500^\circ\text{C}}/E_0$  of 10%). However, this difference in elastic properties tends to reduce with time owing to the subsequent room temperature degradation phenomenon already mentioned. The second treatment was conducted up to a maximum test temperature of 1000 °C, avoiding thereby the occurrence of the  $m-t$  phase transformation. For such thermal cycle the evolution of Young's modulus (Fig. 4) shows a hysteresis but is on the whole almost reversible. Nevertheless, the decrease of modulus when cooling below 300 °C is again obvious. This result confirms that the zirconia transformation is not the only cause of the damage at low temperature. Thermal expansion mismatch also plays a significant role. Complementary experiments suggest that higher is the duration of the dwell at 1000 °C, higher is this increase of the modulus at this temperature and then higher is the decrease of the modulus at low temperature during cooling.

As shown above cracking occurs both during heating and cooling, and more surprisingly, we have noticed that the material keeps on evolving at room temperature after heat treatment. To better understand this phenomenon, the modulus and the

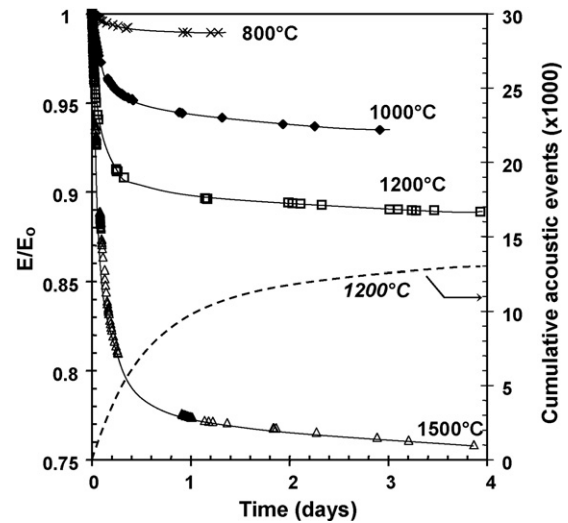


Fig. 5. Decrease of the Young's modulus vs. time at room temperature after a heat treatment at various temperatures. Comparison with the cumulative acoustic activity after a thermal cycle at 1200 °C, for revealing room temperature microcracking.

AE were recorded after heat treatment when the specimen is again at room temperature. As shown in Fig. 5, the decrease of modulus, that started below about 250 °C, continues at room temperature with time, even after few days, irrespective of the geometry or dimension of specimen. The evidence of acoustic emission also displayed in Fig. 5 after a 1200 °C thermal cycle as an example, suggests that this evolution can be associated to microcracking. This was also observed for other temperatures (1000 °C and 1500 °C). The AE is not localised but rather dispersed along the specimen (Fig. 6), suggesting a diffused cracking process, decreasing with time. Furthermore the AE amplitude decreases with time, as does the modulus. This is therefore a strong evidence of crack propagation with the specimen during the final cooling part of the thermal treatment. An important cause of the microcracking is obviously the reverse tetragonal to monoclinic transformation that exhibits a volume expansion of about 4%. Thereby, the thermal mismatch between the zirconia main phase and the glassy intergranular phase generates additional stresses when cooling to room temperature.

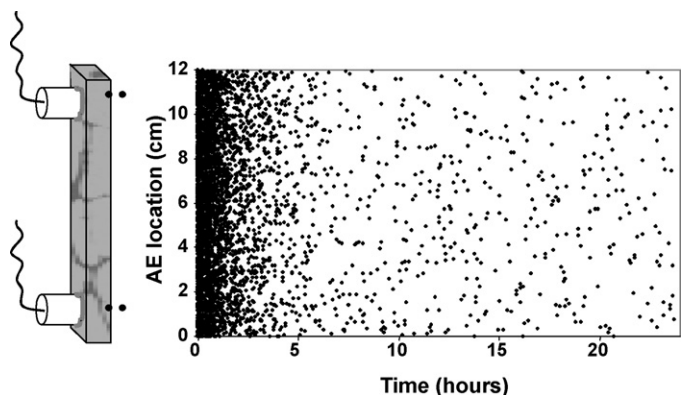


Fig. 6. Homogeneous distribution all along the sample and decrease with time of the acoustic events, at room temperature after a heat treatment at 1200 °C.

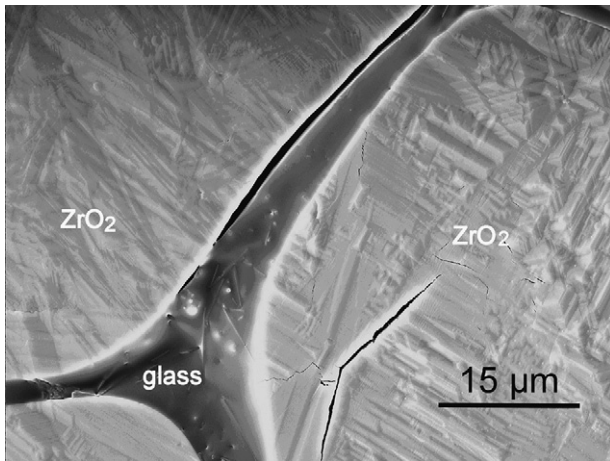


Fig. 7. SEM macrograph showing the emergence of some decohesion between zirconia grains and intergranular glassy phase after a heat treatment at 1200 °C. This phenomenon appears for thermal cycles conducted at a temperature higher than the zirconia phase transformation temperature.

Finally, it is worth stressing that the amplitude and the kinetics of the decrease depend on the maximum temperature of the heat treatment. The highest decrease is observed for the 1500 °C heat treatment. This could be explained by the fact that before the transformation, the material might be healed by the melted glassy phase between 1200 °C and 1500 °C. Therefore, the phase transformation induces a higher stress level.

### 3.2. Microstructural evolution

Scanning electron microscope (SEM) observations were carried out on specimens before and after (after more than 3 days) heat treatment, in order to visualise the corresponding microstructural modifications.

Two temperatures surrounding the zirconia transformation, 1000 °C and 1200 °C, were selected. Both thermal treatments have generated cracking both in zirconia grains and in the glassy intergranular phase. Indeed Young's modulus presents a decrease of 7% and 44% for the thermal treatment at 1000 °C and 1200 °C, respectively. Concerning zirconia, few cracks are observed either within the grains (Fig. 7) or from the grain edges (Fig. 8). The crack can cross several grains through the glassy phase that is either cracked or not. This suggests that cracking occurs either below the glass transition where the phase is brittle (Fig. 8) or above where the intergranular phase can accommodate strains (Fig. 9). Surprisingly for heat treatments at a temperature lower than 1200 °C, no decohesion is observed between grains and the glassy phase. Cracks rather propagated in one or in the other phase even when following grain edges (Fig. 8).

Cracking in zirconia grains shows specific features with convoluted shape on a very small scale, along the zirconia crystal planes. This is confirmed by the observation of the 1200 °C heat-treated sample where zirconia transformation induces surface relief and even more convoluted cracks. Indeed the grain surfaces are not flat any more, but many geometric shape crystals appear leading to surface relief. These are associated to

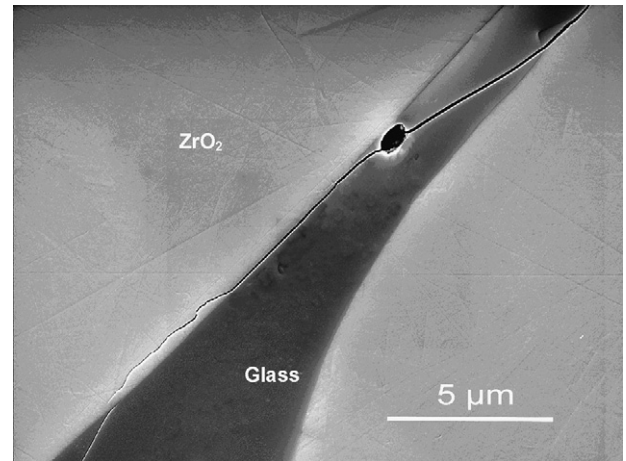


Fig. 8. SEM macrograph of a crack, crossing glassy phase and zirconia without creating decohesion, after a heat treatment at 1000 °C.

the tetragonal to monoclinic transformation that was shown to give several variants.<sup>12</sup> The transformation occurs with different variants and owing to both shear and volume change, they can induce a relief on the surface. Deville et al.<sup>14–16</sup> have shown a progressive growth of four different possible variants, leading to identified geometrical structures. A high temperature X-ray diffraction has revealed an evolution of the relative peak intensities relative to zirconia with temperature. This corresponds to the plane orientation change at the surface. In Fig. 10 we can see that microcracks follow the crystal edges and are slightly deviated by the intercrystal planes. They are the result of strain incompatibilities between the different variants. At 1000 °C the temperature is not high enough to make a tetragonal to monoclinic transformation cycle, but still the different variants exist and they deviate the crack. Moreover for a 1200 °C heat treatment the number of cracks either in the glassy phase or inside the grains is clearly much larger. Despite the short length of those cracks, their large opening suggests a significant deformation field.

Decoherions (Fig. 7) can be observed between zirconia and glassy phase when the maximum test temperature is higher than

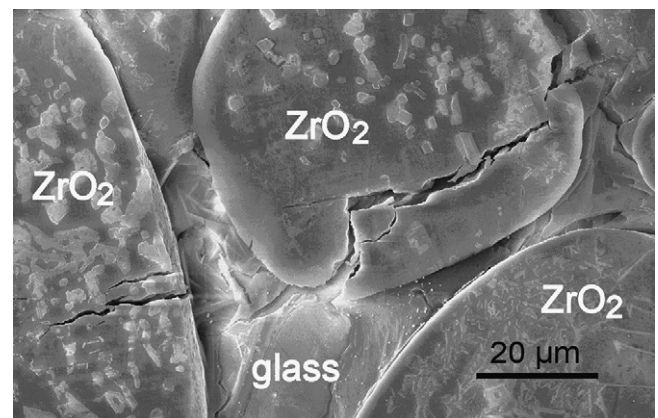


Fig. 9. SEM macrograph of significant damage of two zirconia grains, without cracking of the intergranular glassy phase. This illustrates the phenomenon of cracking before the cooling glass transition temperature.

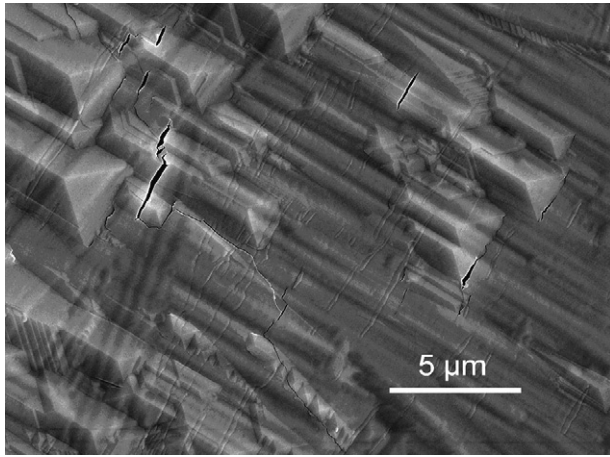


Fig. 10. Disclosure on polished surface of the zirconia intercrystalline planes due to the zirconia phase transformation during a heat treatment at 1200 °C. The cracks follow the created edges.

1100 °C. The extent of the zirconia phase transformation induces large stresses between the two phases, particularly during cooling when the reverse zirconia phase transformation takes place at a temperature near the glass transition. All these observations explain the strong modulus decrease observed after heat treatment, especially its significant decrease when the zirconia transformation has occurred. Microscopy allows only surface observations where despite the fraction of the strain accommodated by the volume increase, microcracks are present. This suggests that inside the grain the strain accommodation can only occur by crack formation. Another illustration of damage is the apparition of round-shaped cavities at the surface for thermal treatments at a minimum temperature of 1200 °C. These cavities are probably the result of the migration of the glassy phase from the joint boundary at  $T > T_g$ . Such cavities are not observed at lower temperature treatments because the viscosity is not low enough.

An increase of test temperature and/or of the dwell at temperature induces similar phenomena but more pronounced, especially in the zirconia grains, i.e. more cracks and higher surface relief. For instance at 1300 °C the transformation is more completed and a prolonged stay at high temperature allows the glassy phase to accommodate or heal the damage. Therefore during cooling the strain accommodation by cracking is more striking (Fig. 11).

Those results clearly show that thermal treatment induces complex and irreversible modifications of the microstructure. Since the mechanisms causing the damage evolution are multiple and operate at different temperatures, we have conducted in situ high temperature observations in order to identify the critical temperatures.

High temperature ESEM on zirconia being rather delicate, several thermal cycles up to 1357 °C have been required. At this temperature the material has definitely finished its transformation and can accordingly present all the behaviours suspected from the recorded elastic modulus evolution with temperature.

A first aspect that is clearly observed is the evolution of the glassy-phase viscosity (Fig. 12), which induces the displace-

ment of the glassy phase at the surface grain boundaries. During heating above  $T_g$  some grain boundaries get depleted of glassy phase and this effect is promoted by the phase transformation. During cooling the phenomenon reverses as observed by the reappearance of the glassy phase, especially at the reverse zirconia transformation temperature. But the situation is not fully reversible because at the end the local amount of glassy phase is lower at the grain boundary (at least on the surface).

We also observe cracking in zirconia grains. Fig. 13 shows an example of cracks appearing around the zirconia phase transformation temperature (1091 °C) upon heating. When cooling (Fig. 13) we observe that the crack has grown below 728 °C, certainly due to the thermal expansion mismatch and remains till room temperature. During cooling the reverse phase transformation dilatation does not close such cracks as could be expected. It is important to note that although the material is already cracked because of the cooling stage inherent to its elaboration process, new cracks are created. It is all the more surprising as this material has already been submitted to a thermal cycle.

### 3.3. Discussion

In the earlier stage of the thermal cycle the modulus follows the natural decrease of elastic properties with increasing temperatures. Above 800 °C, either the slight increase or the stabilisation of the modulus is attributed to a change of characteristics of the secondary glassy phase above its glass transition temperature. The explanation is not clear yet but the increase of the thermal expansion of the glassy phase above its  $T_g$  could result in the closure of cavities or defects and therefore compensate the Young's modulus decrease. Above 1100 °C, the monoclinic to tetragonal phase transformation accompanied by a volume decrease causes a marked decrease of the modulus. It results from an extensive cracking of the zirconia phase despite the melted glassy phase that could accommodate these stresses. This is in agreement with the dilatometry measurement due to

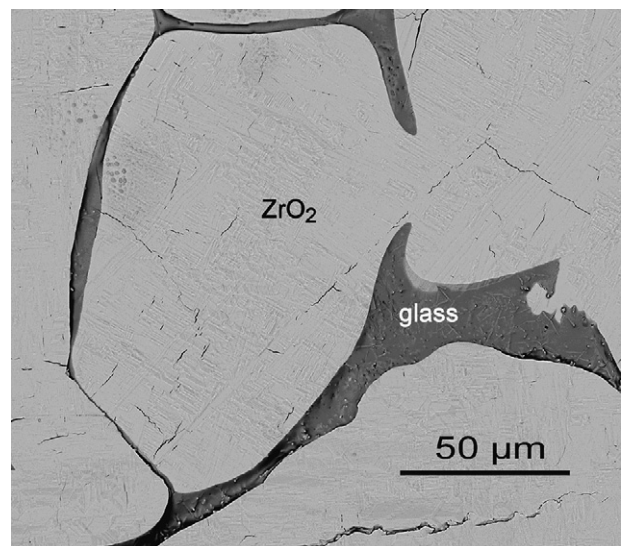


Fig. 11. SEM macrograph showing an distribution of cracks on the surface of a sample treated at 1300 °C.

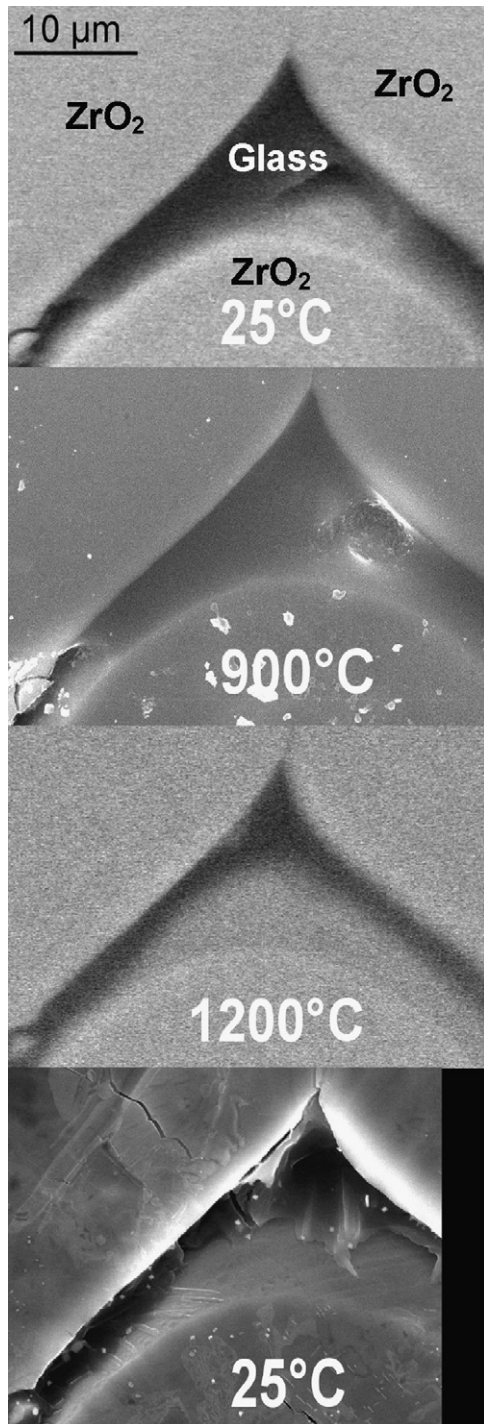


Fig. 12. In situ ESEM macrograph showing the evolution of the intergranular glassy-phase viscosity during a thermal cycle at 1357 °C. Note also the cracking of zirconia during cooling.

the zirconia phase transformation, closed to the theoretical value given for 4%.

At high temperature, between 1200 °C and 1500 °C the slight increase of the modulus is attributed to the glassy phase. Indeed at this stage the reduction of its viscosity (by a factor three between  $T_g$  and 1500 °C) promotes its migration and the healing of material discontinuities. This behaviour is amplified by a prolonged stay at these high temperatures. When Cooling from

1500 °C this healing process continues. Around 1000 °C the tetragonal to monoclinic transformation induces a slight increase of the modulus. Indeed the positive volume variation of the zirconia crystal leads to the closure of some cracks, cavities or decohesions. We would have rather expected a modulus decrease due to this volume expansion but the glassy phase again accommodates the strains. This intergranular accommodation allowing the free volume variation of the zirconia crystal is possible. However, it should be noted that the reverse phase transformation during cooling, as observed by dilatometry, presents a lower amplitude than during heating, probably because the higher glassy-phase viscosity in this temperature range partly limits the dilatation.

During cooling, between 900 °C and 500 °C, so below the glass transition, the thermal expansion mismatch induces a modulus decrease by cracking in opposition to the normal modulus increase. The stresses developed by the thermal expansion mismatch can be accommodated so that opened cracks exist. However below 500 °C the microstructure cracking becomes significant and from 300 °C leads to the observed decrease of modulus. This decrease continues at room temperature during a few days, even in the case of small specimens. This delayed

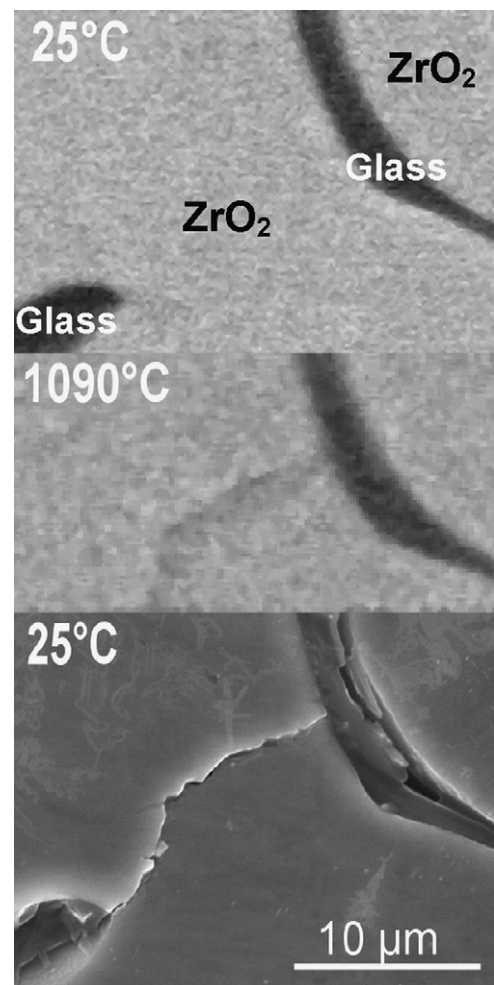


Fig. 13. In situ ESEM macrograph showing some zirconia grains cracking at heating during a thermal cycle at 1357 °C.

crack propagation is the response to the accumulated residual stresses during the thermal cycle and particularly during cooling under  $T_g$ . This is the evidence of a mechanism of slow crack growth, well known to be prominent in zirconia- and silica-based glasses. The AE clearly reveals cracking at room temperature. We can therefore deduce that all this cracking happens in the bulk of the material rather than in surface. Indeed the surface of the specimen accommodates the strains earlier in the cycle, hence cracks earlier. This widely cracked surface is then free and can relax stresses of the end of the cycle easily, unlike the heart of the structure that remains geometrically stressed. Finally as mechanical solicitations,<sup>13</sup> pure thermal cycles can induce residual stresses in materials.

Finally the observations of this study have confirmed that HZ material cracks during a thermal treatment, both upon heating and cooling, and even with higher intensity during cooling when  $T < T_g$ . The damaging and healing mechanisms operating at different temperatures, the maximum temperature of the thermal cycle finally dictates the final extent of damage. In particular, treatments above the zirconia phase transformation will be characterized by a larger level of damage. An important surprising observation is the irreversible nature of the phenomena: indeed some cracks healed during heating do not reopen during cooling although other cracks appear in the surrounding.

#### 4. Conclusion

The evolution of the elastic modulus of a high zirconia electrofused refractory material has been related to its microstructural evolution by scanning electron microscopy experiments both at room and high temperature. The evidence of damage was also shown by acoustic emission measurement at room temperature. A detailed description of the mechanisms responsible was achieved. Three parameters were clearly identified to contribute to the overall behaviour. The glassy phase above  $T_g$  accommodates strains and stresses of the structure and is capable of healing some cavities or cracks by migration. The zirconia phase transformation induces, depending on the case, cracking or healing and closure of microcracks and voids. The thermal expansion mismatch between zirconia and glass phases generates stresses that again lead to either cracking or crack closure. The overall behaviour is at the end not reversible, and this was clearly shown by in situ observation of cracking. Another surprising observation was the delayed cracking during a few days at room temperature due to stress relaxation, even on very small specimens, suggesting the evidence of significant residual stresses in the material.

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