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Elastic properties and microstructure: study of two fused cast refractory materials

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Abstract

Young's modulus evolutions versus temperature have been studied for two fused cast materials containing 40 or 95 wt.% of zirconia. During the manufacturing process involving cooling from very high temperatures, internal stresses can bring on damage in the microstructure. Young's modulus has been measured by using a high temperature ultrasonic pulse-echo technique. Characteristic phenomena have thus been identified in accordance with chemical and mineralogical compositions, and physico-chemical transformations. Young's modulus is affected by the individual contributions of intrinsic properties of each phase, but also by damage due to thermal expansion mismatch between the phases. Thus, the glassy phase involves changes related to the viscosity evolution at high temperature. Furthermore, the allotropic martensitic transformation of zirconia produces effects on Young's modulus: either direct or induced by the volume change. A simple Hashin and Shtrikman analytical model has been used to bring out some explanations about these effects.

Keywords: Young's modulus; Al_2O_3; ZrO_2; SiO_2; Refractories

1. Introduction

Fused cast refractories are mostly used in glass tanks were they undergo corrosion. The manufacturing process of these refractory blocks is similar to the casting of metals and to melting and pouring of glass, but with much higher melting points. This process must be well controlled, that is, slow cooling after melting at very high temperature to allow crystallisation while avoiding stresses and further cracks. The first heating-up is also critical for the in service behaviour of these materials. In particular, thermal gradients should be minimized. Thus, it is of great interest to study their mechanical behaviour versus temperature, in order to provide comprehensive and new information about characteristic temperatures where microstructural changes take place. In the present paper, a high temperature ultrasonic technique (up to 1550 °C) is applied to determine the Young's modulus evolutions which are correlated with microstructural transformations. This work is a part of a global French research programme on industrial refractory materials (PROMETHEREF), which aims to produce comprehensive elements of their thermo-mechanical properties, and acquire predictive tools of their behaviour.[1,2]

2. Materials

Two fused cast refractories belonging to the alumina–zirconia–silica system have been specifically manufactured for this study by Saint-Gobain.[a] The first one (AZS) contains 43 wt.% of alumina and 40 wt.% of zirconia, the whole being surrounded by 17 wt.% of a silico-aluminate glassy phase. The second one is a high zirconia material (HZ) with 94 wt.% of zirconia crystals and only 6 wt.% of glassy phase. In both materials, zirconia is entirely monoclinic. A representation of the microstructure of these materials is reported in Fig. 1. The microstructure of AZS is the most complex one, with primary crystals of zirconia and domains of alumina–zirconia eutectic composition, within a silica rich glassy phase. The HZ material only presents more or less thin layer of glassy phase filling the intergranular space between zirconia grains. Therefore, it is expected that the two materials exhibit rather different mechanical behaviours.

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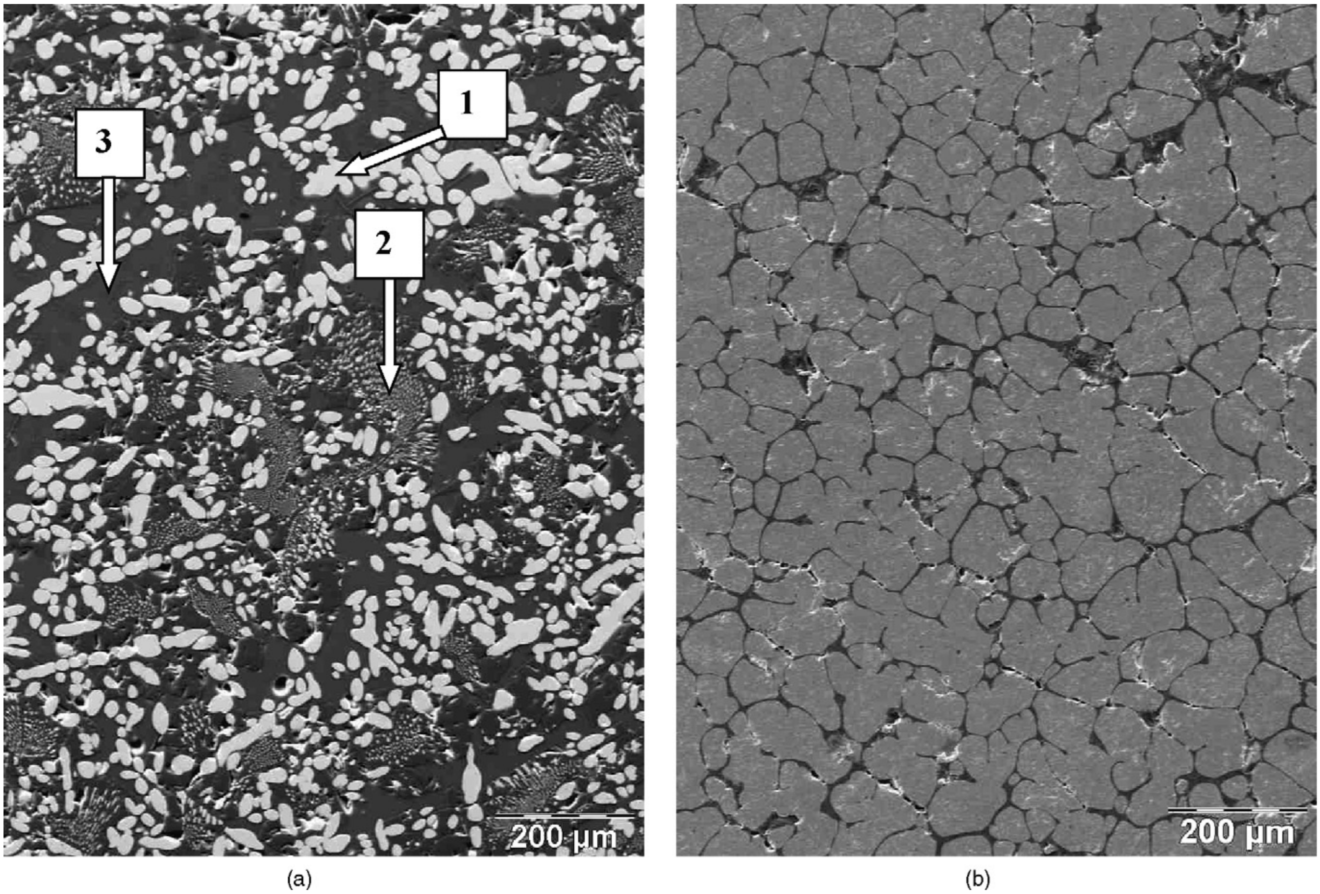

Fig. 1. Microstructure of the materials: (a) AZS with primary ZrO_2 (1), Al_2O_3–ZrO_2 eutectics (2) and glassy phase (3); (b) HZ with the glassy phase filling the ZrO_2 grain boundaries.

3. Experimental procedure

The variations of Young's modulus have been monitored versus temperature by the way of a pulse-echo technique based on the measurement of the propagating velocity of ultrasonic waves.[3] A wideband pulse of ultrasonic compressional wave, produced by a magnetostrictive transducer is guided through the sample via an alumina buffer rod bonded to the sample with a refractory cement. The central frequency of the waves is around 140 KHz. Multiple reflections produce a series of echoes corresponding to successive round trips within a parallelepipedic sample. The determination of the time delay τ between two successive echoes allows the calculation of Young's modulus by the following equation[3]:

$$E = \rho\left(\frac{2L}{\tau}\right)^2,$$

where L and ρ are length and density of the sample, respectively. The dimensions of the tested specimens were 7 mm × 7 mm × 100 mm, the lateral dimension being required to be low enough compared to the wavelength for long bar mode propagation. Tests are carried out during thermal cycles at 5 °C/min between 20 and 1550 °C.

4. Results

4.1. Behaviour of the alumina–zirconia–silica material (AZS)

The variations of Young's modulus versus temperature during a heating–cooling cycle up to 1550 °C for this material are plotted on Fig. 2. It should first be noticed that, if compared with intrinsic Young's modulus of dense alumina and pure monoclinic zirconia, about 380 GPa[3] and 240 GPa[4], respectively, the initial value of modulus is somewhat low. Moreover, the curve globally describes a hysteresis loop which is characteristic of a closure-opening mechanism of microcracks, on heating and cooling coarse grained materials.[5] In the present case, the creation of cracks occurs during the manufacturing of the products because of internal stresses developed when cooling. These cracks are then healed at the first heating-up. Several other points can be emphasized on the curve presented on Fig. 2. Five temperature domains (three on heating and two on cooling) have been distinguished:

- During step 1, a gradual decrease of the modulus, followed by a slight inflection around 800 °C, is observed.
- The increase in step 2 is abruptly interrupted by a sudden drop at about 1150 °C, which approximately corre-

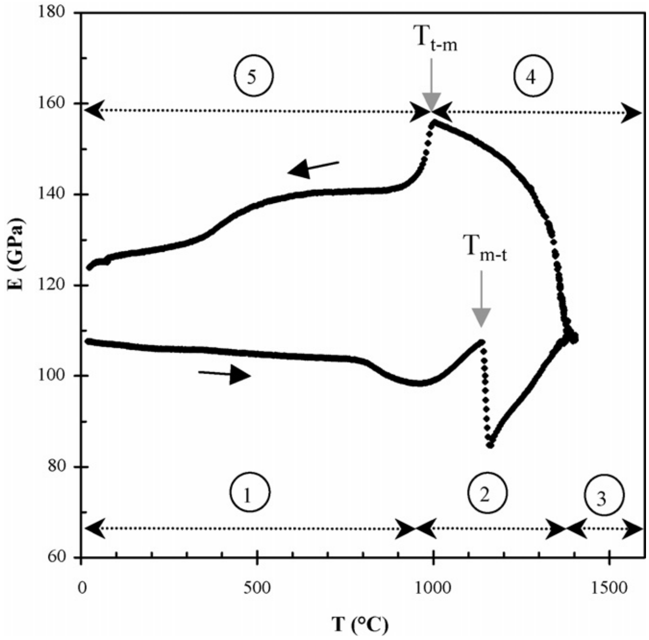

Fig. 2. Young's modulus variations during a thermal cycle up to 1550 °C for the AZS material.

sponds to the monoclinic to tetragonal transition of zirconia ($T_{m–t}$).[6]

- After that, in step 3, a decrease of E begins, but it is accompanied by an important attenuation of the waves which made the signal not exploitable above 1400 °C.
- The fourth step, presenting the cooling part of the curve from 1550 to about 1000 °C, then shows a considerable increase, and at the end, the modulus is around 58% greater than the value reported at the same temperature on heating.
- The last part of cooling (step 5) begins with a sharp drop of Young's modulus around 1000 °C, temperature where the tetragonal to monoclinic transformation is expected ($T_{t–m}$).[6] Then, after a plateau, a gradual decrease is observed below 450 °C. The final value of the modulus remains 15% higher than the initial one.

The drops in Young's modulus at $T_{m–t}$ and $T_{t–m}$ attributed to the reversible allotropic transformation of zirconia are accompanied by the well-known dilatometric effects associated to this transformation, that is, shrinkage on heating, and expansion on cooling.[7] These effects, as measured by thermal expansion experiments[2] are reported in Fig. 3.

4.2. Behaviour of the high zirconia material (HZ)

For the HZ sample, variations of Young's modulus versus temperature in the same conditions as AZS are illustrated in Fig. 4. Similar to this latter, the curve also describes here a hysteresis loop. Despite the high content in zirconia (94 wt.%), the initial value of the modulus (~130 GPa) is lower than that of pure monoclinic zirconia (~240 GPa). Five steps can also be noticed on the curve:

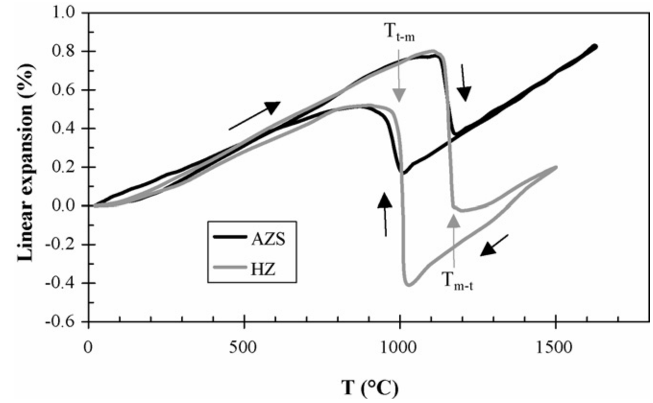

Fig. 3. Thermal expansion curves for the AZS and HZ materials during thermal cycles up to 1600 °C.

- Step 1, with a quasi-constant value of the modulus from room temperature to 500 °C, followed by an increase up to 800 °C.
- In step 2, after a regular decrease from 800 °C, a sharp drop occurs around 1150 °C ($T_{m–t}$), during the monoclinic to tetragonal transformation of zirconia. Then, a slight increase is observed.
- As for the AZS, during the third step above 1300 °C, Young's modulus begins to drop, but, no measurement could be made above 1400 °C because of the increase of the attenuation of ultrasonic waves.
- Step 4 is characterized by an increase of modulus at the beginning of cooling. Nevertheless, this effect is lower than that observed in the AZS in the same temperature range.
- In step 5, on the contrary of AZS, a sharp increase occurs at 1000 °C ($T_{t–m}$), corresponding to the reverse transformation of zirconia. This is followed by a regular increase of the mod-

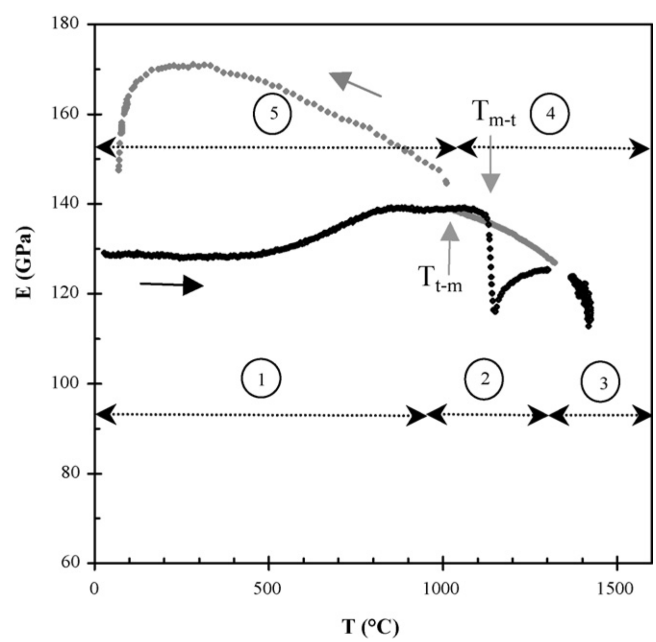

Fig. 4. Young's modulus variations during a thermal cycle up to 1550 °C for the HZ material.

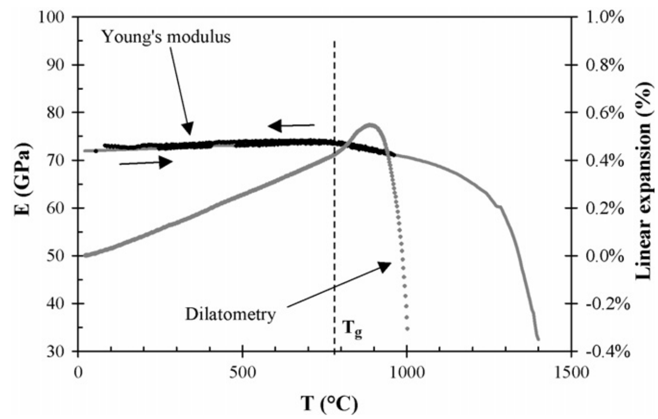

Fig. 5. Thermal expansion and Young's modulus variations (extrapolated up to 1400 °C) for the glassy phase vs. temperature.

ulus down to 200 °C. Below this temperature, the modulus drops significantly.

5. Discussion

The variations of E versus temperature are in close relationship with microstructural transformations. Understanding the intrinsic properties of each constituent could be of a good help for the interpretation of the phenomena observed in the whole material in the temperature range 20–1550 °C.

Concerning alumina, apart from its significant stiffness, there is no transformation which could influence the behaviour of the materials. Only a regular and reversible decrease of modulus versus temperature is observed.[3,8]

5.1. Young's modulus versus temperature in the glassy phase

To understand the effect of the glassy phase, studies have been made on samples of glass with a similar chemical composition as that of the silico-aluminate phase surrounding the grains in both refractories. Fig. 5 presents graphs obtained from Young's modulus and thermal expansion analyses. The glass transition temperature (T_g) is clearly identified from these curves at the first slope changes, about 780 °C. Young's modulus measurements could not be made above 1000 °C. Consequently, for temperatures above 1000 °C, the curve has been extrapolated, using results of reverse calculations from measurement on a simplified composition of fused cast material.[9]

5.2. Young's modulus versus temperature in zirconia

While the AZS systematically shows a drop of modulus during the transition of zirconia on heating and cooling, HZ presents a decrease on heating and an increase on cooling. Two types of effects can explain variations of modulus in materials containing a zirconia phase at the transition temperature:

- An intrinsic effect related to a difference of Young's modulus between the two phases.

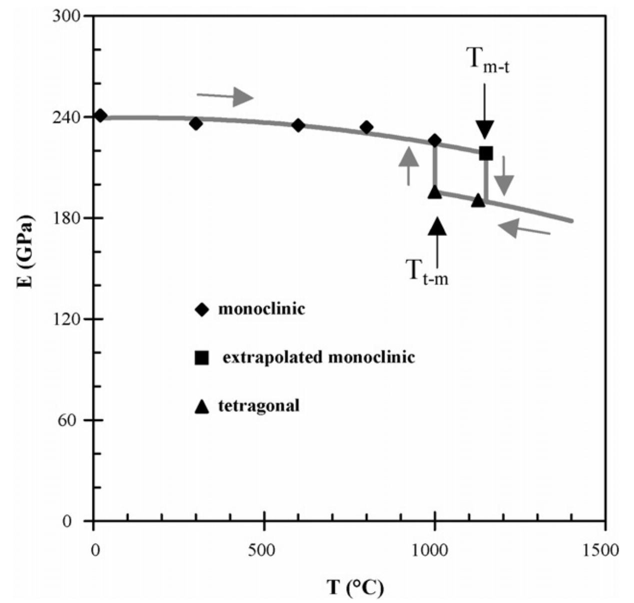

Fig. 6. Young's modulus variations of polycrystalline zirconia derived from measurements by Brillouin scattering on monoclinic single crystal and from lattice-dynamical calculations on pure tetragonal zirconia as reported in literature.[4,10,11]

- Extrinsic effects induced by the volume changes associated to this transition.

There are few works in literature about the elastic behaviour of pure zirconia. Reports about the elastic constants from 20 to 1000 °C of small pure monoclinic single crystals could however be found.[4] Brillouin scattering was used by authors to determine sound velocities in different directions of crystals in order to calculate elastic constants. They also deduced elastic moduli for a polycrystalline aggregate using Voigt, Reuss and Hill approximations. Other authors made an extrapolation of these monoclinic elastic constants values at the monoclinic to tetragonal transition temperature ($T_{m\text{–}t}$).[10] Concerning the tetragonal phase of pure zirconia, no experimental values were found. However, by using lattice-dynamical models, some authors[10,11] derived values of the elastic constants of a pure tetragonal zirconia in the vicinity of the tetragonal to monoclinic transition. Using these values, analytical equations[12] based on Voigt, Reuss and Hill approximations have been applied to calculate the elastic moduli of polycrystalline tetragonal zirconia at 1000 and 1127 °C (Fig. 6). To summarize, Young's modulus values for monoclinic phase were plotted and fitted from 20 to 1150 °C ($T_{m\text{–}t}$), and the values for pure tetragonal zirconia were added. Then, the curve was extrapolated up to 1600 °C, considering that the tetragonal phase follows the same trend versus temperature as the monoclinic one (Fig. 6). Despite its higher density, the tetragonal phase has a lower Young's modulus compared to monoclinic.

5.3. Influence of the elastic intrinsic properties of the constituents on the Young's modulus of the refractories

Considering the properties of alumina, glassy phase and zirconia, the variations of Young's modulus in the two fused

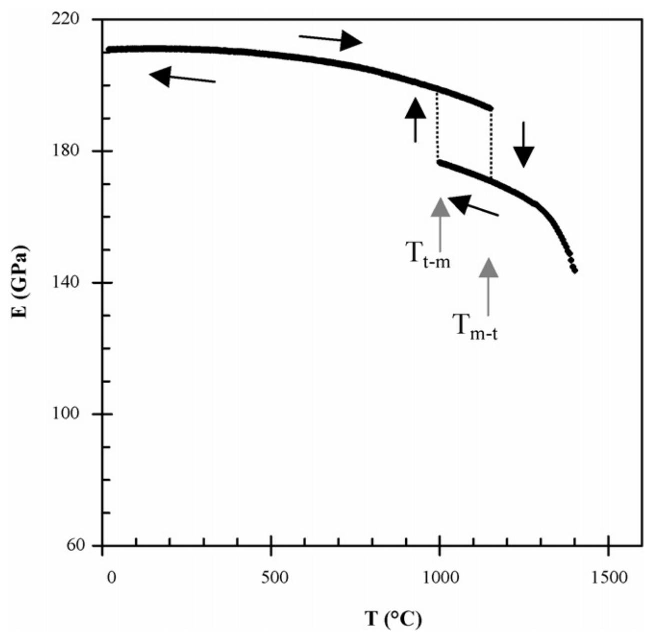

Fig. 7. Young's modulus variations in the HZ material derived from the Hashin and Shtrikman model.

cast refractories can, now, be related to intrinsic properties of each constituent. In this aim, an analytical model such as the Hashin and Shtrikman one for two-phase compounds has been applied.[13] This model allows the definition of two bounds, but only the lower one, which corresponds to stiff inclusions in a compliant matrix, was considered here. In fact, the bonding glassy phase, taken as the matrix, is the most compliant of the two constituents. Even if some difficulty appears for more than two-phase materials, the purpose here is only to predict trends for the behaviour of the refractory if intrinsic properties of the constituents are considered. In particular, it is important to keep in mind that this Hashin and Shtrikman model, does not take into account any damage in the materials. Moreover, since only Young's modulus variations versus temperature have been considered for these calculations, Poisson's ratios of all constituents were supposed to be constant in the whole temperature range.

5.3.1. The HZ refractory

Fig. 7 illustrates the result obtained from calculations in the case of the HZ material. This calculated curve shows reversible modulus effects at the transition temperatures of zirconia and follows the same trend as the experimental one on cooling down to 200 °C. Nevertheless, the experimental value of Young's modulus is much lower at room temperature (∼130 GPa, see Fig. 4) than the predicted value on Fig. 7 (∼210 GPa).

One reason is related to the approximations of the model:

- It corresponds to an ideal case excluding the presence of impurities or defects that may be found in the polycrystalline grains of the real material.
- The values of elastic properties of zirconia taken for calculations were derived from single crystals measurements.
- Damage is not taken into account.

A second reason comes from microcracking induced by internal stresses coming from thermal expansion mismatch between constituents when cooling, which involves the drop of Young's modulus below 200 °C.

When heating, the previously mentioned damage is partially healed by thermal expansion effects of grains embedded in a stiff glassy phase, inducing an increase of Young's modulus as it can be seen on the experimental curve above 500 °C.

The other point that must be highlighted, if experimental and calculated curves are compared, is the difference in the amplitudes of changes of Young's modulus during the transition of zirconia.

When heating, the experimental drop at the monoclinic to tetragonal transition (Fig. 4) is more important than the calculated one (Fig. 7). Then, in addition to the drastic drop of the modulus due to the change of elastic properties of zirconia at $T_{m\text{–}t}$ (direct effect), the thermal shrinkage associated to this transformation probably also induces debondings around zirconia particles, involving an intensification of the decrease of Young's modulus. So, there are both direct and indirect effects of the monoclinic to tetragonal transformation of zirconia.

Later to this, the glassy phase reorganizes itself in the intergranular space and fills the cracks, involving an increase of Young's modulus. Above 1300 °C, as predicted on the calculated curve, the viscosity of the glassy phase induces a strong decrease in Young's modulus.

But, as previously mentioned, further measurements could not be made above 1400 °C: the viscosity of the glassy phase is too low in this temperature range, then, an important attenuation of the ultrasonic waves is observed. Nevertheless, between 1300 and 1550 °C, the glassy phase is more readily redistributed between the particles, and microcracks are healed. This phenomenon will play a role during cooling.

At the beginning of cooling in the fourth part of the curve, the growth of the modulus is related to the increase of the viscosity of the glassy phase.

In the last step, as predicted by the calculated curve, the tetragonal to monoclinic transformation of zirconia also causes an increase of Young's modulus. However, this effect is less important than the calculated one. This could be linked to damage occurring in the material because of the expansion of zirconia at $T_{t\text{–}m}$ which has been observed elsewhere in similar materials.[14]

Below $T_{t\text{–}m}$, Young's modulus regularly increases as in the case of a stable sintered material, the zirconia grains being bonded by the stiff glassy phase below the glass transition temperature. Consequently, because of dilatometric mismatch, stresses are developed at grain boundaries and/or in highly anisotropic zirconia grains[6] and induce cracks at low temperature,[14] involving the deep Young's modulus decrease below 200 °C.

5.3.2. The AZS refractory

The microstructure of this material is complex. Two stiff phases are surrounded by a high amount of glassy phase (17 wt.%): monoclinic zirconia and particles of alumina–zirconia eutectic. In particular, the anisotropy of alumina–zirconia eutectic domains makes the prediction of Young's modulus and of the effect of monoclinic–tetragonal transformation, difficult to evaluate by a simple model. Therefore, the experimental curve (Fig. 2) will only be qualitatively discussed, taking into account the main features of the behaviour versus temperature of the single constituents (zirconia, glass, alumina).

- The first step of the curve, shows a slight decrease denoting a regular effect of temperature on Young's modulus.[8] But, since there is a greater amount of glassy phase in this case compared to HZ, the curve then shows an inflection at the glass transition temperature around 800 °C (see Fig. 5).
- During the second step, the viscosity drop of the glassy phase favours the closure of cracks and involves a large increase of modulus which continues after the monoclinic to tetragonal transformation of zirconia. Here also, direct and indirect effects of the transition of zirconia on heating may be mentioned to explain the great drop in modulus. Later to this transition, still because there is much more glassy phase in this case, the increase of modulus linked to the healing of cracks is more significant.
- After 1400 °C, the drastic drop of viscosity of the glassy phase did not allow any measurements because of a too much high ultrasonic attenuation.
- The growth of Young's modulus at the beginning of cooling (step 4) related to the increase of the viscosity of the glassy phase is also more important here, once more because of the great content in glassy phase in comparison with the other material.
- Though the tetragonal–monoclinic transition of zirconia induces an intrinsic increase of Young's modulus, the effect observed in AZS is a drop. This is probably due to the damage accompanying expansion of zirconia particles when cooling, in particular, into the alumina–zirconia eutectic particles, because of the stiffness of alumina which cannot accommodate the stresses provoked by this phenomenon. The influence of the intrinsic properties of zirconia is then masked. This damage continues at lower temperatures because of thermal expansion mismatch between the phases.

6. Conclusion

Young's modulus variations versus temperature in the two studied fused cast refractory present several similarities and differences. The hysteresis loop shape of the curves shows that the samples are initially damaged. The HZ material that only contains a third of the glassy phase content of the AZS is not greatly influenced by its glassy phase transition or its viscosity changes at high temperatures. In the AZS material however, the glassy phase then involves a significant increase of Young's modulus at the beginning of cooling after the healing of damage at high temperature. This reinforcement of the structure however induces a new damage in this AZS material during the transition of zirconia on cooling. In the HZ material the influence of this damage is lower than the intrinsic effect. On heating, the materials show a decrease of Young's modulus at the monoclinic to tetragonal transition of zirconia because of both intrinsic effect of zirconia and debondings created by the associated thermal shrinkage. At the end of cooling, another damage occurs because of thermal expansion mismatches. Anyway it is noteworthy that the fused cast process allows the fabrication of fully dense materials with more than 90 wt.% of monoclinic zirconia with good thermomechanical properties.

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