

Young's modulus evolution at high temperature of SiC refractory castables

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Received: 11 December 2009 / Accepted: 11 March 2010 / Published online: 27 March 2010
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Abstract The evolution of Young's modulus versus temperature has been evaluated in SiC-based hydraulically bonded refractories used in waste-to-energy (WTE) plants. Two types of low cement castables (LCC) with 60 and 85 wt% of SiC aggregates have been considered. The study was conducted by the way of a high temperature ultrasonic pulse-echo technique which allowed in situ measurement of Young's modulus during heat treatment starting from the as-cured state up to 1400 °C in air or in neutral atmosphere (Ar) and during thermal cycles at intermediate temperatures (1000 and 1200 °C). For comparison in order to facilitate interpretation, thermal expansion has also been followed by dilatometry performed in the same conditions. Results are discussed in correlation with phase transformations occurring in the oxide matrix (dehydration at low temperature, crystallization of phases in the CaO–Al₂O₃–SiO₂ system) above 800 °C and damage occurring when cooling. The influence of oxidation of SiC aggregates on elastic properties is also discussed.

Introduction

Silicon carbide based refractories are widely used in the linings of boilers of energy production units because of their good mechanical properties at high temperature and high thermal conductivity, which is an advantage for thermal exchange applications [1]. Among this type of materials, hydraulically bonded castables are interesting because they can be cast into structures of complex shapes.

Although the knowledge of the mechanical behaviour at high temperature of oxide-based castables [2–4] and studies of thermomechanical properties of SiC reinforced structural ceramics or composites [5] are both well documented in literature, very little work has been done in the same field for SiC-based castables [6]. This paper reports results obtained within the framework of the French national research program “DRuIDe” (Durability of Refractories used for Waste Incineration) supported by the French National Research Agency (ANR). It concerns the evolutions of Young's modulus of two hydraulically bonded silicon carbide refractory castables used in waste-to-energy (WTE) plants, determined by the way of an ultrasonic high temperature pulse-echo technique during cycling at various temperatures up to 1400 °C. Jointly, thermal expansion experiments have also been performed under the same environmental conditions. The results are interpreted in correlation with phase transformations and microstructural changes which occur during temperature cycles and the effect of atmosphere (oxidizing or not) is discussed.

Experimental details

Materials

The materials under examination are two low cement castables (LCC), manufactured by CALDERYS (92446 Issy les Moulineaux Cedex, France), referred as SF60 and CV85, with 60 and 85 wt% of SiC aggregates, respectively, with particle grain size up to 3 mm. They were supplied as shaped bricks of dimensions 40 × 40 × 160 mm³, cured by heating 48 h at 110 °C, which was found to achieve the formation of stable hydrates [3] and then stored at a constant room temperature in sealed bags. Samples for

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Table 1 Main characteristics of the castables

| | SF60 | CV85 |
|---|----------|----------|
| <i>Formulation</i> | | |
| SiC (wt%) | 60 (1) | 85 (1) |
| CaO (wt%) | 1.4 (1) | 2.1 (1) |
| Calcium-alumina cementitious phase (wt%) | ~5 (2) | ~7 (2) |
| Silica-alumina phases (wt%) | ~35 (2) | ~8 (2) |
| Water requirement (%) | 6.9 (1) | 6.5 (1) |
| <i>Characteristics at 20 °C in the as-cured state</i> | | |
| Apparent density (g cm ⁻³) | 2.58 (2) | 2.44 (2) |
| Opened porosity (%) | 15.6 (2) | 15.9 (2) |
| Young's modulus E_0 (GPa) | 62.2 (2) | 83.5 (2) |

(1) CALDERYS data, (2) Laboratory evaluation

experimentations are cut from these bricks and heated again at 110 °C after machining to get out residual water.

Table 1 summarizes the main characteristics of the two materials in the cured state. Roughly, the materials can be considered as composites with SiC aggregates embedded in a matrix composed of a calcium-alumina cementitious phase and of other silico-alumina phases. The weight proportions of these constituents have been evaluated from data communicated by CALDERYS.

It is important to notice for further interpretation of the evolutions of properties found during heating that, besides their difference in SiC content, the two materials are somewhat different in their matrix composition: more cementitious phase in CV85 and more silica-alumina phases in SF60.

Apparent density and opened porosity measurements were carried out by an Archimedes method in water. Young's modulus was measured at room temperature by a classical ultrasonic pulse-echo technique using longitudinal and shear waves [7]. The two materials exhibit similar porosity and density, but the elastic modulus of CV85 is superior to that of SF60 because of the greater amount of SiC which is a stiffer material [8]. Anyway, the Young's moduli of the two materials are very low compared to that of pure SiC ceramics (~400 GPa). This is a consequence of porosity and cracks in the cementitious matrix and of weak cohesion between matrix and aggregates.

Measurement of Young's modulus at high temperature

Measurements of the Young's modulus E of the specimens have been made via a high temperature ultrasonic technique working in a long bar mode (lateral dimension of the propagation medium inferior to the wavelength), whose principle has been detailed elsewhere [9] and which has been successfully used to investigate the microstructural evolutions of various ceramics at high temperature [10, 11]. This pulse-echo method uses ultrasonic compressional

waves generated by a magnetostrictive transducer working at low frequencies (inferior to 300 kHz). The ultrasonic pulse is sent into a parallelepipedic sample through a refractory alumina wave guide. Figure 1 represents the principle of the device.

An electronic equipment (signal acquisition by a digital oscilloscope and a specific software package) automatically measures and records the time delay τ corresponding to one round-trip of the wave through the sample. Then, the Young's modulus E of the material is given by the following equation:

$$E = \rho \cdot \left(\frac{2L}{\tau}\right)^2 \tag{1}$$

where L and ρ are sample length and density, respectively.

The characteristics of the different parts of the ultrasonic line have been adapted to highly heterogeneous refractory concretes with large grains and high porosity: this involves a low ultrasonic velocity and a high ultrasonic attenuation. For this work, the dimensions of samples, machined from the bricks supplied by CALDERYS, and the wave frequency are $140 \times 11 \times 11 \text{ mm}^3$ and 60 kHz, respectively.

Experiments have been performed during thermal treatments consisting in heating/cooling rates of 5 °C/min from room temperature to T_{max} , with a dwell at T_{max} , into an Argon flux or in free air to study the impact of oxidation. Because phase transformations, including oxidation of SiC, induce dimensional and mass variations, it can be necessary to make corrections in Eq. 1 for density variations and thermal expansion to obtain the true value of Young's modulus at temperature T :

$$E(T) = E_0 \left(\frac{\tau_0}{\tau(T)}\right)^2 \cdot \left(1 - \frac{\Delta l(T)}{l_0}\right) \cdot \left(1 + \frac{\Delta m(T)}{m_0}\right) \tag{2}$$

where the suffix 0 is related to the values measured at room temperature, $\frac{\Delta m}{m_0}$ and $\frac{\Delta l}{l_0}$ are the variations of sample mass and length, respectively. These corrections can be obtained from thermogravimetric analysis (TGA) and thermal expansion measurements performed in the same conditions than the ultrasonic tests. Anyway, it has been shown elsewhere [12] that, for the two tested refractories, the variations induced by these phenomena are negligible. Therefore, the $E = f(T)$ curves are obtained from the simplified equation:

$$E(T) = \rho_0 \cdot \left(\frac{2L_0}{\tau(T)}\right)^2 \tag{3}$$

Thermal expansion and characterization of microstructure

Thermal expansion or contraction effects have been measured during thermal cycles similar to those used for

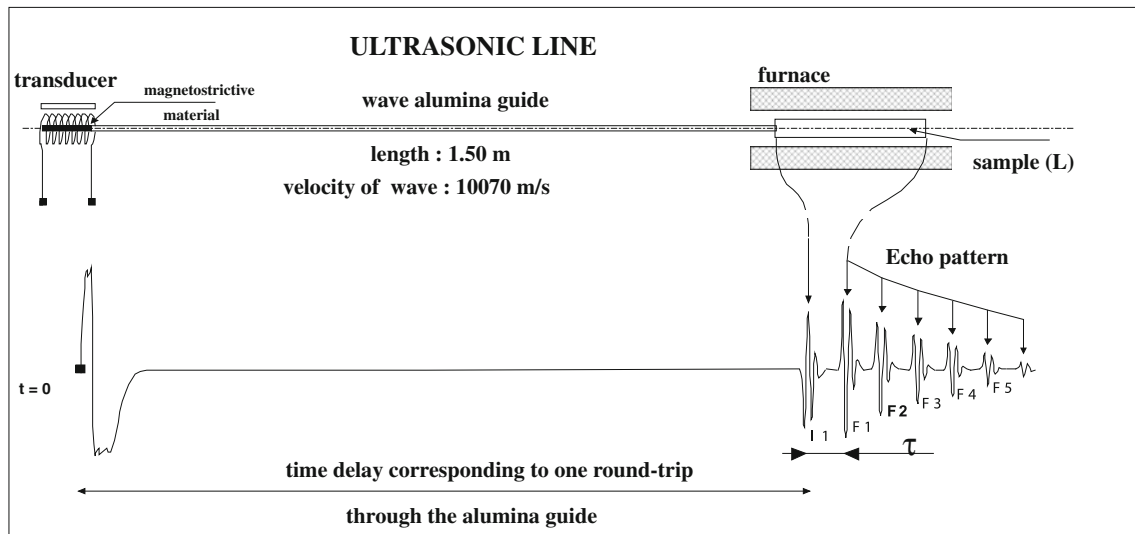


Fig. 1 Principle of ultrasonic Young's modulus measurements at high temperature

ultrasonic experiments, with a commercial dilatometer (DI 24, Adamel Lhomargy), using samples of $9 \times 9 \times 15 \text{ mm}^3$ machined in the bricks supplied by CALDERYS.

The characterization of the microstructure of materials at room temperature before and after heat treatments, have been made by the way of classical methods:

- opened porosity and bulk density measurements by an Archimede's method in water added with a wetting agent;
- observation of polished sections by scanning electron microscopy (SEM);
- X ray diffraction analysis (XRD) of powders obtained by grinding of bulk materials. In order to avoid the saturation of XRD diagrams by the intense SiC peaks and to be able to detect the crystallization of oxide phases in the matrix, most of analyses have been performed on simplified materials assumed to be equivalent to the matrix. They were concretes manufactured from a mix of the finest particles (cement, silica-alumina phases, SiC small particles) obtained by sieving of the powder used for the fabrication of castables, conventionally with diameters lower than $200 \mu\text{m}$ [12].

Results and discussion

Thermal cycles at high temperature

The temperatures of these first experiments were deliberately selected to be higher than the maximum temperature (about $1200 \text{ }^\circ\text{C}$) reached in the combustion chambers of a WTE. The aim was to identify the different steps of microstructural transformations or damage, which occur

within a wide range of temperature, in order to determine the limit of potential use of SiC-based refractory castables.

Measurements in non-oxidizing atmosphere

Experiments were first performed in Argon. Figures 2 and 3 report the Young's modulus evolution and thermal expansion obtained during thermal cycles at a rate of $5 \text{ }^\circ\text{C}/\text{min}$ (dwell 0.1 h) up to $1400 \text{ }^\circ\text{C}$ under Argon for the two as-cured materials.

One can notice that the curves are plotted from the continuous measurement of E during the temperature cycling of one sample. When cooling, a fracture of the coupling cement between the waveguide and the sample sometimes occurs because of a thermal contraction mismatch at the interface [9]. In such a case, a value of E at room temperature after cooling is obtained by a new coupling and an indicative dotted straight line replaces the missing part of the curve.

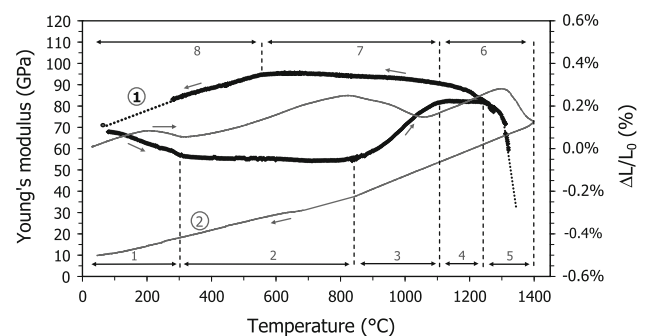


Fig. 2 Young's modulus variations (curve ①) and thermal expansion (curve ②) during a thermal cycle up to $1400 \text{ }^\circ\text{C}$ under argon for as-cured SF60

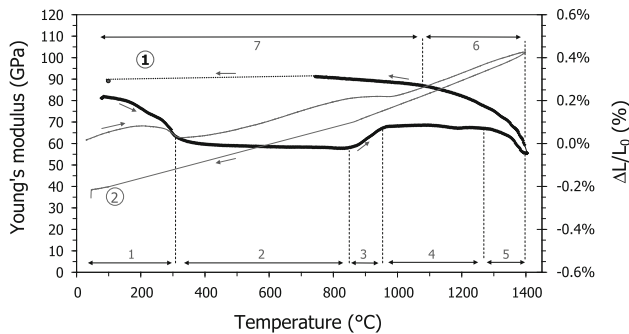


Fig. 3 Young's modulus variations (curve ①) and thermal expansion (curve ②) during a thermal cycle up to 1400 °C under argon for as-cured CV85

Compared to thermally stable materials which exhibit regular and reversible variations of E versus temperature (in general a decrease for sintered ceramics) [10], the $E = f(T)$ curves of Figs. 2 and 3 are irreversible and show characteristic effects in particular temperature domains, similar for the two compositions, which are hereafter described.

SiC aggregates being stable up to very high temperature in non oxidizing environment, microstructural changes and phase transformations which occur when heating SiC-based refractory concretes are only expected in the oxide part of the matrix (cement and silico-alumina phases) as for previously studied oxide-based concretes [3, 4].

Domain (1): from 20 to 300 °C for both materials (Figs. 2 and 3).

A continuous decrease of E is to be noted from 20 to 200 °C. Then an important decrease of Young's modulus is associated to shrinkage above 200 °C. This effect has been well documented for cementitious oxide castables [3]. It is irreversible and corresponds to dehydration of the cementitious matrix which is accompanied by shrinkage and a decrease of mechanical properties (strength and elastic moduli).

Domain (2): from 300 to 850 °C for both materials (Figs. 2 and 3).

There is a slight decrease of E and an almost linear thermal expansion as for ceramics with a stable microstructure [10].

Domain (3): from 850 to 1100 °C for SF60 (Fig. 2) and from 850 to 970 °C for CV85 (Fig. 3).

The stiffness of the samples strongly increases and shrinkage is observed. These effects were found to be irreversible when cooling at intermediate temperatures (not plotted here). They are attributed to the crystallization of CA^1 [3, 4] and to the beginning of sintering of the oxides in the matrix. This effect is more important for SF60 because of the higher proportion of silica-alumina phases

¹ Cement notations: $CaO-Al_2O_3 = CA$; $CaO-2Al_2O_3 = CA_2$; $CaO-6Al_2O_3 = CA_6$; $CaO-Al_2O_3-SiO_2 = CAS$.

(cf. Table 1). This behaviour was found to be accompanied by a slight decrease of porosity [12].

Domain (4): from 1100 to 1240 °C for SF60 (Fig. 2) and from 970 to 1280 °C for CV85 (Fig. 3).

Densification of the matrix, resulting in shrinkage and increase of stiffness, is possible at a macroscopic scale as long as the SiC aggregates skeleton compaction allows. In domain (4), expansion takes place at the same time than the Young's modulus stabilizes, because of two phenomena:

- the partial accommodation of the shrinkage induced by sintering of the oxide matrix by an inter-aggregate redistribution of porosity;
- at 1100 °C, the phase CA_2 begins to form, which is a well known expansive process [3, 13].

In this domain, the average porosity remains quite constant for the two materials [12].

Domain (5): from 1240 to 1400 °C for SF60 (Fig. 2) and from 1280 to 1400 °C for CV85 (Fig. 3).

Several microstructural evolutions could have an influence on thermal expansion and elasticity in this temperature range:

- a decrease in the viscosity of amorphous phases in the system $CaO-Al_2O_3-SiO_2$ which leads to a shift from an elastic behaviour to a visco-plastic one, with a notable drop of Young's modulus. This is more important for SF60 because of the higher proportion of silica-alumina phases (Table 1); in this case, ultrasonic measurement was no longer possible above 1320 °C, because of the strong attenuation of the signal;
- the same phenomenon promotes sintering of the matrix with SiC grains, which can induce the shrinkage observed above 1300 °C in SF60;
- crystallization of new phases like CA_6 , CAS and mullite which involve volume and stiffness changes [13, 14]. Nevertheless, XRD analyses on samples did not clearly show these phases (except for mullite after treatment at 1500 °C in SF60), because of the high intensity of SiC peaks.

Domain (6): when cooling down to about 1100 °C for both materials (Figs. 2 and 3).

The two materials behave like sintered ceramics with a stiffness increase with increasing viscosity of intergranular phases and a quite linear thermal shrinkage with a coefficient of thermal expansion close to that of sintered SiC ($\sim 5 \times 10^{-6} K^{-1}$).

Domain (7): from 1100 °C down to 550 °C for SF60 (Fig. 2) and from 1100 °C down to 20 °C for CV85 (Fig. 3).

Young's modulus regularly increases like for a sintered ceramic. For CV85, it follows this trend down to room temperature.

Domain (8): only observed for SF60 (Fig. 2) when cooling below 550 °C.

In this range, an important drop of E is observed for SF60. It can be attributed to damage due to thermal expansion mismatch as frequently observed in refractory oxides [15]. In CV85 the high content of SiC, and the low content of oxide bonding phase minimizes this effect.

Measurements in air

The effects of atmosphere and of subsequent thermal cycling have been investigated by similar ultrasonic experimentations in air but limited at 1300 °C which appears to be a limit for the elastic behaviour of both materials. Figures 4 and 5 show the results of three similar successive thermal cycles. As a comparison, the curves obtained when heating under Argon have been plotted on the same figures.

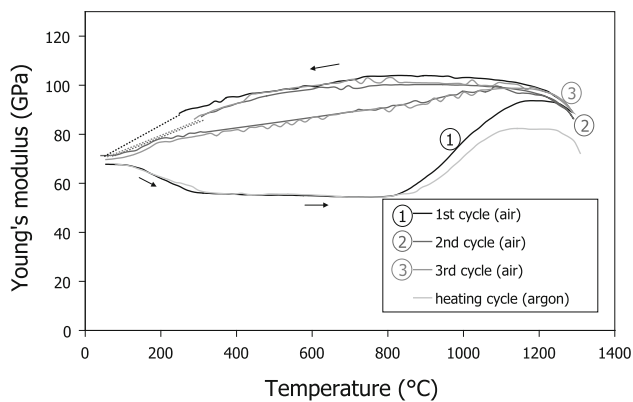


Fig. 4 Young's modulus variations in as-cured SF60 during three successive thermal cycles in air (curves ①, ②, ③). Comparison with heating in Ar

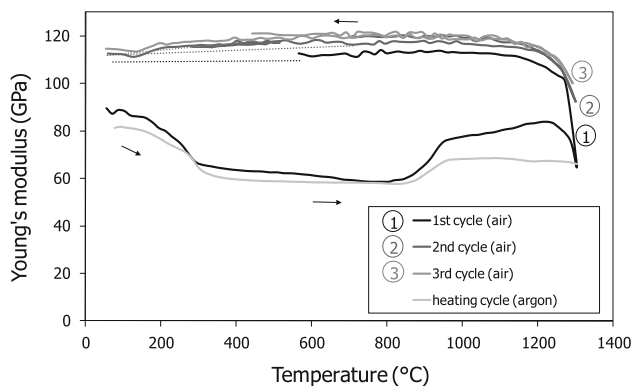


Fig. 5 Young's modulus variations in as-cured CV85 during three successive thermal cycles in air (curves ①, ②, ③). Comparison with heating in Ar

Four observations can be pointed out:

- an oxidizing atmosphere does not affect the elastic behaviour up to 850 °C, which is logical because the only phase transformation is dehydration and the oxidation rate of SiC is negligible in this temperature range;
- the increase of Young's modulus in domain (3) seems to be superior in air compared to the result in Ar (but it must be noted that the two curves are obtained with two different samples);
- when cooling, the obtained curves are rather the same than in Argon, but with a higher value at room temperature for CV85 (115 GPa after 1300 °C in air compared to 90 GPa after 1400 °C in Ar).

Moreover, two successive thermal cycles after the initial oxidation treatment, give reproducible curves, which shows that no additional oxidation occurs after the first cycle, for short time of heating in air.

Thermal cycles at intermediate temperatures

For WTE plants applications where the temperature reached at the hot face of the refractories is inferior to 1200 °C, it is important to study the behaviour of the materials subjected to thermal cycles at intermediate temperatures. As shown previously, after dehydration at low temperature (domain (1)), the two castables behave like ceramics with stable microstructure with a regular decrease of Young's modulus and a linear thermal expansion. Thermal cycling in this range (600, 800 °C) has confirmed the reproducibility of this phenomenon, independent on atmosphere, as well for Young's modulus as for thermal expansion [16]. At temperatures superior to 800 °C, specific effects (increase of Young's modulus, shrinkage) are observed which are attributed to phase transformations in the matrix and are dependent on atmosphere. Therefore, Young's modulus variations and thermal expansion have been investigated during thermal cycles performed in air or in Ar at 5 °C/min with dwells of 1 h at 1000 and 1200 °C, for the two as-cured materials. In order to focus on phenomena occurring above 800 °C, Figs. 6 and 7 represent results referred to the values reached when heating at 800 °C, written under the form: $\Delta E = E(T) - E_{800}$ and $\Delta L/L = (\Delta L/L_0)_T - (\Delta L/L_0)_{800}$, where E_{800} is Young's modulus at 800 °C, $(\Delta L/L_0)_{800}$ and $(\Delta L/L_0)_T$ are thermal expansion at 800 °C and temperature T , respectively. This representation avoids the problem of dispersion due to different samples in order to effectively compare results. The variations of elasticity and thermal expansion, measured during the temperature increase up to the dwells, follow the same rate of evolution than those observed when heating up to high temperature (Figs. 2, 3, 4 and 5).

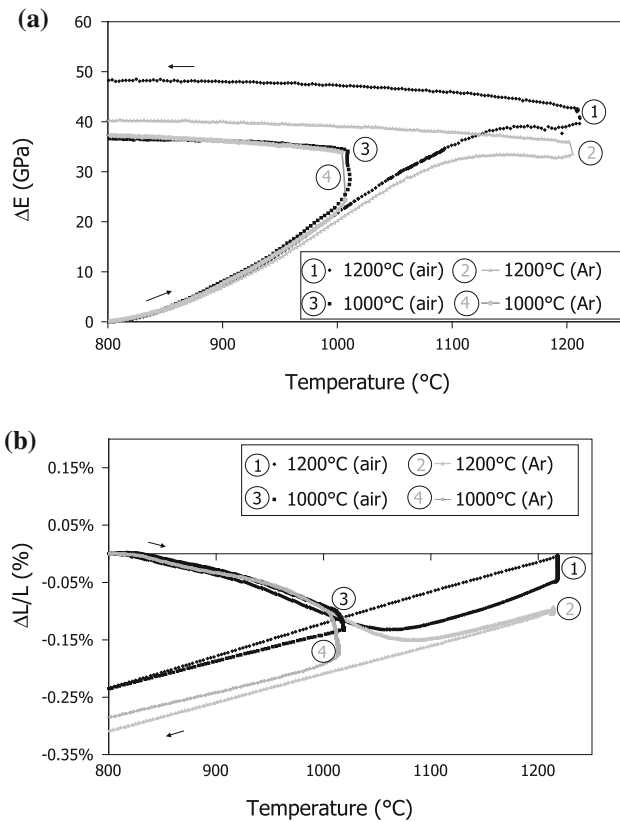


Fig. 6 Young's modulus variations (a) and thermal expansion (b) above 800 °C during two cycles at 1000 and 1200 °C in air and Ar for as-cured SF60

Thermal cycling of SF60

Figure 6a shows that, whatever the atmosphere, the same increase of E is observed for the cycle at 1000 °C: the curves $\Delta E = f(T)$ are superimposed, as well as the value of ΔE during the dwell at 1000 °C (+10 GPa after 1 h). XRD, performed in powders with compositions assumed to be that of the matrices [12], mainly shows intense peaks corresponding to SiC and corundum in the as-cured state. After treatment at 1000 °C, the crystallization of new phases is detected, in particular CA, CAS_2 and traces of CA_2 and cristobalite, which can contribute to an increase of Young's modulus [14, 17], without any quantitative difference between the two atmospheres. Additionally, sintering begins to occur in the matrix, as shown by the shrinkage observed in Fig. 6b. It contributes also to the stiffening of material.

Nevertheless, the shrinkage observed during the dwell at 1000 °C is more important in Ar (−0.09%) than in air (−0.05%). This can be explained by the expansion due to oxidation in air, which is opposite to shrinkage due to sintering.

It must be noticed that all these effects are irreversible: when temperature decreases, the material behaves like a

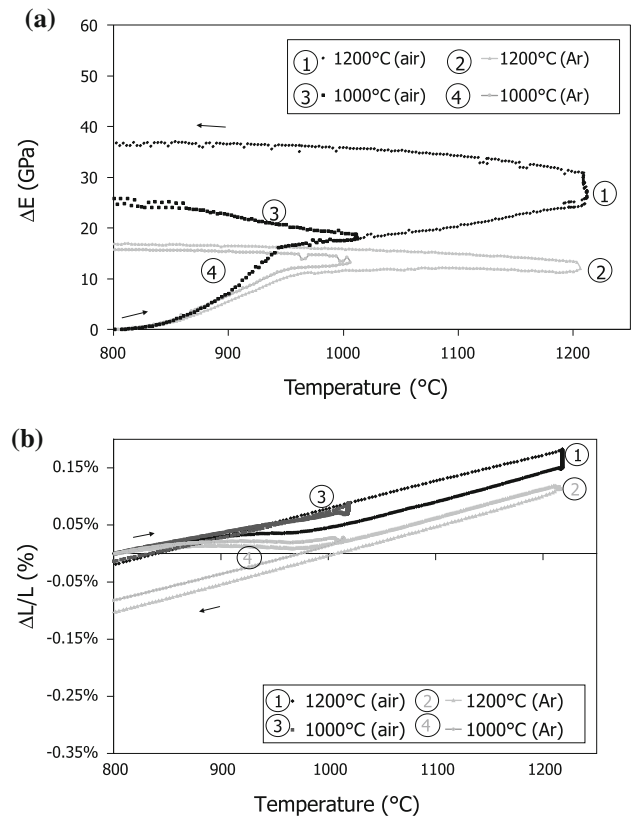


Fig. 7 Young's modulus variations (a) and thermal expansion (b) above 800 °C during two cycles at 1000 and 1200 °C in air and Ar for as-cured CV85

sintered ceramic, with Young's modulus slightly increasing and with a linear thermal contraction.

These phenomena are confirmed by the thermal cycles at 1200 °C. As for the 1000 °C cycle, there is little influence of atmosphere on the Young's modulus evolution, except above 1100 °C where E continues to increase in air to reach a higher value (about 8 GPa) after heating in air rather than in Ar (Fig. 6a). XRD, performed in powders with compositions assumed to be that of the matrices treated at 1200 °C, allowed to detect, additionally to the phases found at 1000 °C, an increase of the peak of cristobalite, but with no significant difference between treatment in air or in Ar. Therefore, it is probable that cristobalite is not the product of oxidation but comes from the crystallization of silica in the matrix. As at 1000 °C, sintering induces shrinkage (Fig. 6b), but with a difference according to atmosphere during heating: shrinkage is stopped after 1100 °C, but the rate of decrease in air is lower above 1020 °C. It is important to notice that the end of shrinkage does not mean that sintering is achieved in the matrix, but that the SiC aggregates skeleton, as mentioned before, blocks the contraction due to the densification of the matrix. During the dwell of 1 h at 1200 °C, as at 1000 °C, there is almost no dependence on atmosphere of

Young's modulus increase but a strong effect of oxygen on expansion (~ 0 in Ar and $+0.05\%$ in air).

Thermal cycling of CV85

Figure 7 reports results obtained in the same conditions for CV85. Compared to the results obtained for SF60, there are important differences.

For the cycle at $1000\text{ }^{\circ}\text{C}$, this material behaves somewhat differently than SF60 for Young's modulus: the increase of E versus temperature is superior in air than in Ar above $900\text{ }^{\circ}\text{C}$. This could be due to an effect of oxidation because of the higher content of SiC in CV85 than in SF60 (cf. Table 1). The rate of increase of E versus temperature is smoothed in the two cases at $970\text{ }^{\circ}\text{C}$ that corresponds to the limit between domains (3) and (4) where the shrinkage induced by sintering of the oxide matrix is partially accommodated by an inter-aggregate redistribution of porosity, described above. This is a consequence of a more compact SiC skeleton in the case of CV85 than of SF60. Nevertheless, the interpretation is difficult because of the superposition of phase changes and sintering effects in the matrix, which is in lower proportion than SiC (cf. Table 1). This is consistent with the very low shrinkage observed on dilatometric curves. During the dwell at $1000\text{ }^{\circ}\text{C}$, there is no significant variation of modulus, whatever the atmosphere, and no length variation in Ar, though after 1 h in air there is a slight expansion of 0.006% .

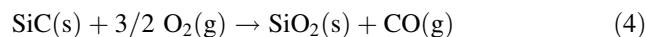
For the thermal cycles at $1200\text{ }^{\circ}\text{C}$, the variation of Young's modulus exactly follows the same curve up to $1000\text{ }^{\circ}\text{C}$ and, after, continue to slightly increase to reach a higher value (about 8 GPa) after heating in air rather than in Ar (Fig. 6a). During the dwell, E increases more in air ($+7$ GPa after 1 h) than in Ar ($+2$ GPa after 1 h). This denotes an effect of oxidation on Young's modulus more significant at $1200\text{ }^{\circ}\text{C}$ than at $1000\text{ }^{\circ}\text{C}$ and also more important than in SF60 for the same conditions. Anyway, the isothermal expansion at $1200\text{ }^{\circ}\text{C}$ (Fig. 7b) remains of the same order of magnitude than for SF60 (Fig. 6b).

XRD, performed with powders of the matrix composition [12], shows the same intense peaks corresponding to SiC as for SF60 in the as-cured state, but without the corundum peaks because of the lower proportion of silico-alumina phases (cf. Table 1). After treatments at 1000 and $1200\text{ }^{\circ}\text{C}$, the same CA and CAS_2 phases than in SF60 are detected, but because of the lower proportion of silica in the matrix, the peaks of cristobalite are lower and, once more, with no significant difference between treatment in air or in Ar.

Discussion on the effect of atmosphere

In the presence of oxygen, silicon carbide undergoes significant oxidation reactions at temperatures greater than

$900\text{ }^{\circ}\text{C}$ [18, 19]. Under high oxygen partial pressure that corresponds to the present conditions in dry air at 1000 and $1200\text{ }^{\circ}\text{C}$, passive oxidation occurs, classically according to the following equation:



In that case, an amorphous silica layer is formed on the surface of SiC, which controls the diffusion of oxygen. Crystallization of silica, which modifies the oxidation kinetics and is expected to occur after long reaction times at higher temperature [20], has not to be considered here. This is consistent with the fact that no significant difference in the cristobalite peaks was observed by XRD between treatments in air or in Ar.

In the case of SiC refractories, the material can be simply described as a composite with SiC grains into an oxide porous and microcracked matrix. Figure 8a is a schematic representation, assuming a spherical shape for grains. Considering the differences between the molar masses and between the densities of SiC and SiO_2 , it is easy to show that the balance between the consumption of SiC and the formation of SiO_2 , according to Eq. 4, leads to a mass gain and to an expansion of the grains. Figure 8b is

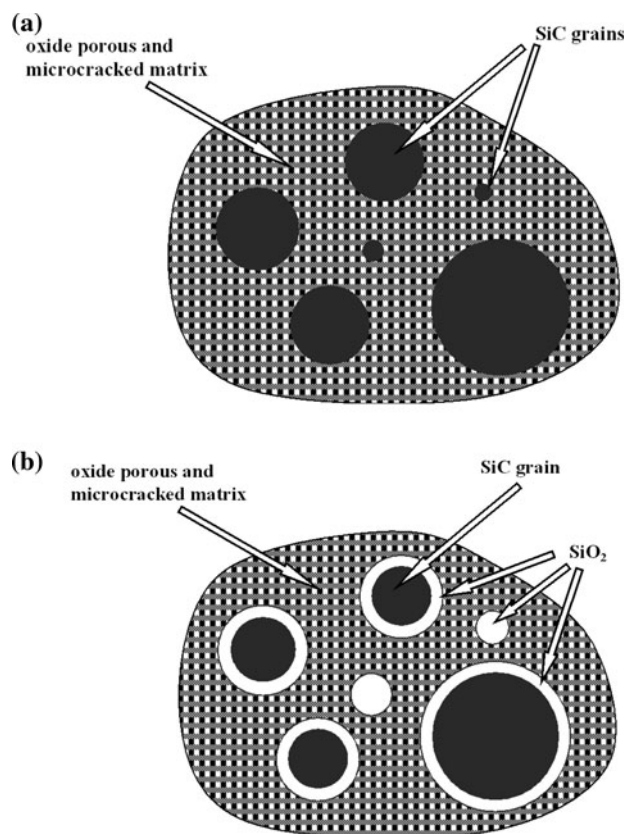


Fig. 8 Simplified model of two-phased refractory with spherical SiC aggregates into a microcracked porous oxide matrix: **a** initial state, **b** aggregates partially oxidized

a schematic representation of the material after a given oxidation state, assuming that all grains are in contact with air through cracks or porosities in the oxide matrix. For small grains, oxidation can result in a total transformation into silica; in such a case the diameter of the grain is multiplied by 2.3. Starting from experimental results of TGA analysis of the SiC powder alone in air at 1200 °C during 50 h, the rate of growth of the thickness of silica on a modelled SiC grain has been evaluated elsewhere [21]. Though the simplification included in the model (spherical shape and free contact of each grain with air), the result allows to explain the thermal expansion of SiC castables (with grain sizes ranging from 0.2 µm to 3 mm) when they are heated in air [21]. The order of magnitude found corresponds to the isothermal expansion (~0.05%) observed after 1200 °C in air in Figs. 6b and 7b.

One of the simplest approaches for the calculation of Young's modulus of a two-phased refractory, with aggregates stiffer than matrix, is the so-called Reuss equation [22]:

$$E = \frac{E_M E_A}{(1 - \nu) E_A + \nu E_M} \quad (5)$$

where E_M and E_A are Young's moduli of the matrix and aggregates, respectively, and ν the volume fraction of aggregates. In the case of the composite modelled in Fig. 8a, E_M is the modulus of the oxide microcracked and porous matrix, which is very low. The oxidation of SiC particles has two consequences: a consumption of SiC (stiff material, $E \sim 400$ GPa) and the formation of SiO₂ (soft material, $E \sim 70$ GPa). Then it should induce both a decrease of E_A and an increase of ν , because of the expansion associated to oxidation. Consequently this may involve a variation of the average Young's modulus of the materials. But a quantitative evaluation is hazardous, because the two phenomena act in an opposite way and the variations of the two parameters, E_A and ν , are probably very low for short times of oxidation in air: the study of the oxidation kinetic of the SiC powder showed that the thickness of silica formed after 1 h at 1200 °C in air is very low (~0.03 µm) [21]. Therefore, the variation of elastic properties of aggregates has probably a very poor effect on the global modulus of the refractory, because it only affects small aggregates, which represent a small fractional volume.

Moreover, SiC particles are not spherical but irregular and with numerous cracks [12]. Oxidation can heal these cracks and contribute to the creation of interparticle bonding by silica in the SiC skeleton. The consequence will be an increase of stiffness clearly observed in CV85 at 1200 °C in air (Fig. 7a). This phenomenon is not significant for SF60 (Fig. 6a), because of the lower content of SiC compared to that of CV85.

Conclusion

The use of the high temperature ultrasonic pulse-echo technique allowed to follow the evolution of elastic properties of SiC-based castables with hydraulic bonding during firing. As for oxide-based castables, dehydration induces an irreversible decrease of Young's modulus at low temperature during the first heating step and phase transformations in the oxide matrix induce strong irreversible modulus variations when heating above 800 °C. However, measurements performed in Ar and in air, pointed to some significant differences between refractories with SiC or oxide aggregates, linked to oxidation. Anyway the effect of oxidation on Young's modulus in the range 800–1200 °C, which is the domain of temperatures reached at the hot surfaces of refractories used in WTE plants, is rather limited. For the material with 60 wt% of SiC, it is negligible after 1 h at 1200 °C. But, for this material (SF60), the high content of oxide phases in the matrix leads to a strong viscous behaviour above 1240 °C. Increasing the SiC aggregates/oxide matrix ratio as for CV85 limits the viscous behaviour at high temperature but increases the dependence of Young's modulus on oxidation in the temperature range 1000–1200 °C. Of course the service conditions in a WTE plants are strongly different in time (several months at high temperature) and in atmosphere (presence of humidity and alkaline species for example) than the conditions of experiments discussed here. To understand their effect on elastic properties, further measurements should be made on post-mortem materials.

Acknowledgements The authors are thankful to the CALDERYS company for materials supplying and to the French National Research Agency (ANR) and the Limousin Region Council for their financial supports.

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