Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 31 (2011) 2763–2774
www.elsevier.com/locate/jeurceramsoc

Refractory concretes uniaxial compression behaviour under high temperature testing conditions

Evariste Ouedraogo[a,b,c,*], Mohsen Roosefid[a,b,c], Nicolas Prompt[d], Cyrille Deteuf[d]

[a] Grenoble-INP, Laboratoire 3SR, 3SR, BP53, 38041 Grenoble cedex 9, France
[b] UJF, Laboratoire 3SR, 3SR, BP53, 38041 Grenoble cedex 9, France
[c] CNRS UMR 5521, 3SR, BP53, 38041 Grenoble cedex 9, France
[d] TRB, 7, Rue de la Neuville, 62152 Nesles, France

Received 10 March 2011; received in revised form 4 July 2011; accepted 13 July 2011
Available online 4 August 2011

Abstract

Two refractory concretes with the same matrix composition, one based on andalusite aggregate and the other on bauxite aggregate, have been studied at temperatures ranging from room temperature to 1200 °C maximal temperature. Samples dried at 110 °C during 24 h to create dried standard specimens and others, fired at different temperatures, were subjected to several uniaxial compression test conditions conducted at various temperatures. The evolution of the materials' global behaviour from quasi-brittle to viscous was evidenced and correlated to their microstructure evolution. Loading/unloading, creep, and strain rate jump tests helped define the damageable and viscoplastic nature of the behaviour. The influence of the firing temperature and duration on the materials' behaviour is also reported and discussed. In conclusion, potential constitutive equations that are able to fit the material recorded behaviour are suggested.

Keywords: Creep; Mechanical properties; Strength; Refractories; High temperature

1. Introduction

Refractory concretes are monolithic castables composed of refractory cement, high temperature-bearing aggregates, and minimum water content. Some other constituents, such as silica fume, are included in small amounts in order to improve the flow ability or other chemical or physical properties. High temperature working domains, such as for metal making, are used to build high temperature bearing layers with refractory fired bricks made of magnesia or other ceramic materials. Although these materials are convenient, the construction of a large and complex geometry is time consuming and costly. Moreover, in many cases the need for joints between the bricks creates disorder with long use. Similar to ordinary concrete, refractory concrete has the ability to conform to geometrically complex shapes, which reduces building time and hence the building cost. This advantage is effective in the initial construction and also in eventual repairs. These advantages are so great that refractory materials suppliers try to use concrete in place of refractory bricks whenever possible. But at very high temperatures (over 1700 °C), refractory bricks remain strongly competitive. Furthermore, the use of castables requires a drying phase to be added to the building schedule, which may reduce the time saved compared with the use of bricks.

Refractory concrete materials are employed in various huge industrial applications, for structures that almost always undergo cyclic thermal loadings. For instance, they are used as the wearing lining or security lining in blast furnaces,[1] as the security lining in steel making ladles, [2–5] and in plans for electricity producing reactors.[6]

In all of these applications, the refractory concrete life can be divided into three or four periods characterized by heating, cyclic service conditions, cooling, and eventually, reparations. During the heating period, the temperature of the refractory concrete increases for the first time and the material undergoes thermal shock.[7] This phase may result in damage to the material and

* Corresponding author at: Grenoble-INP, Laboratoire 3SR, 3SR, BP53, 38041 Grenoble cedex 9, France. Tel.: +33 476 82 52 97; fax: +33 476 82 70 43.
E-mail address: Evariste.Ouedraogo@hmg.inpg.fr (E. Ouedraogo).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2011.07.017

should be modelled with care. In the second phase, corresponding to cyclic service conditions, damage generally develops during the first thermal cycles, followed by a slow increase in potential damage until stabilization. During the third period, the cooling phase, the material is also prone to damage since the temperature gradient is inversed and the external layers are subjected to a notably damageable tension state of stress. An investigation into the fired material would help in understanding the mechanisms that act during this critical material life stage.[8,9,1,10] After cooling is complete, the structure is inspected, and according to the level of degradation observed, it is decided whether to withdraw the entire bearing (first) or the safety (second) linings made from refractory concrete, and to rebuild them. In the case where no substantial degradation is observed in the bearing and/or the safety linings, the structure can be reused. However, since the linings materials have been fired, this raises the question as to whether their behaviour has significantly changed or not. The answer to that question requires an investigation into the fired material behaviour. Finally, it should be noticed that in some applications, the refractory concrete is heated and cooled before the first service use, so a numerical simulation of the structure requires knowledge of the fired material behaviour. In the present study, special attention is paid to the influence of the firing conditions on materials behaviour.

Depending on the conditions of use, a number of factors influence the weakness or cracking of refractory concretes: oxidation due to high temperature and air interaction, erosion when movement of hot molten fluids is present, microstructure differential expansion, and macroscopic thermo-mechanical stress induced by the thermal gradient that necessarily acts on the working temperature linings. Among these factors, the influence of the thermo-mechanical stress on the behaviour of these materials is the primary subject of the present work.

As with ordinary concrete, the behaviour of refractory concrete in tension and compression is dissymmetric, in that the tensile strength is disproportionately lower than the compressive strength. The fracture and failure of such materials are dominated by extension strain; these damaging extension strains can be induced by the presence of tensile stresses or by a compression state of stress in the plane perpendicular to the compression direction. Tensile tests are of the utmost importance as a way to determine material failure resistance, but these tests are somewhat difficult to conduct,[11–14] particularly at elevated temperatures.[15] Their main problem is the localisation of the deformation that is induced mainly by the material's heterogeneous composition. This often prevents access to tensile post-peak behaviour. However, compression tests are easier to operate at high temperature and are often used to characterize the high temperature behaviour of refractory or brittle materials.[16–18].

Many studies on refractory concrete investigate the material at room temperature after it has been fired at various temperatures. The studies measure the material residual properties after heat treatment through tensile,[12,13] bending,[19,20,8] or compression tests.[15,21] Few studies investigate the material behaviour when subjected to high temperature.[22,23,10] Such studies are very useful for modelling industrial structures made of these materials. The material behaviour should be modelled, and necessary tests performed that determine the evolution of the model parameters with temperature. This is one of the aims of the present study.

Table 1
Data relative to the composition of the two refractory concretes (Marzagui et al.[15]).

Castable type	Bau-ULCC	And-LCC
Aggregate type	Bauxite	Andalusite
Al_2O_3 (wt%)	85	58
SiO_2 (wt%)	10	37.5
CaO (wt%)	1.1	2.3
Fe_2O_3 (wt%)	1	0.9
Maximum aggregate size (mm)	5	5
Water requirement (wt%)	4.2–5.2	4.5–5.5
Open porosity (vol.%)	10	6
Apparent density (kg/m^3)	2970	2600

The present paper reports original work on the experimental characterization of two refractory concretes subjected to high temperature (20–1200 °C). Uniaxial compression tests were conducted on a wide range of strain rates (10^{-9}–10^{-5} s^{-1}). The paper is divided into sections. The first section describes the materials' chemical composition and initial thermal conditioning, the specimen size and geometry, and the various testing conditions. Section two reports on the results of all the tests performed on standard and fired materials. These results are then discussed in the last section with reference to microstructure evolution.

2. Experimental procedure

2.1. Characteristics of materials and specimens

Two commercial refractory castables, used in the same industrial application as security linings, have been provided by TRB Company in accordance with all partners participating in a national research program on refractory materials.[23] The first material is an ultra-low cement content and bauxite-based castable (Bau-ULCC), made of bauxite aggregates, fumed silica, α-alumina, and calcium–alumina cement. The second material is a low cement content and andalusite-based castable (And-LCC), made of andalusite aggregates, fumed silica, α-alumina, and calcium–alumina cement.[15] The same fumed silica content characterizes both materials. In the bauxite-based castable (Bau-ULCC), the α-alumina content is double what it is in the andalusite-based material (And-LCC). The chemical compositions of the refractory castables supplied by TRB Company are listed in Table 1, and micrographs are presented in Fig. 1. The high mismatch between the silica contents of the two materials is mainly due to the high silica content in andalusite aggregates compared with bauxite aggregates. For both materials, the maximum aggregate size is close to 5 mm.

The specimens were prepared by mixing the raw materials with a controlled water addition, then casting them in moulds under controlled vibrations and immediately wrapping them in

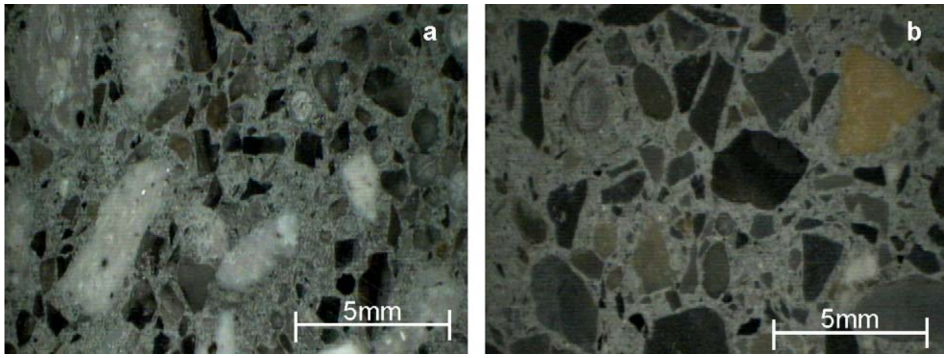

Fig. 1. Micrographs of the two studied materials (a) And-LCC, and (b) Bau-ULCC refractory concretes (Marzagui et al.[15]).

plastic. They were cured at room temperature over 24 h and then extracted from the mould prior to a 110 °C-24 h drying step.

The specimens used for the mechanical tests were "grinded", and then cured over 24 h at 110 °C; this created the so-called standard dried material. After machining, some specimens were previously fired at 700, 900, and 1200 °C for either 5 or 150 h. These temperature levels are consistent with targeted industrial applications. The firing thermal cycles were characterized by 1 °C/min heating and cooling rates and by a 5 h isothermal dwell at the maximum firing temperature. The fired specimens are labelled according to fired temperature and duration, for example, 900/5 h. This study used cubic specimens with a 40 mm side length. Grinding on two of the cube's opposite faces was performed last in order to insure parallelism, with a maximum tolerance of 30 μm in accordance with ISRM standards.

2.2. Mechanical tests conditions

Mechanical tests were performed on an original high temperature high capacity experimental set-up. The set-up consisted of a ZWICK electromechanical 400 kN capacity testing machine equipped with a PYROX 1600 °C maximum use temperature furnace. The furnace heat is due to molybdenum electrical resistances. A special device, made of aluminium rings, alumina rods, and two LVDT sensors, measures the differential displacement of the upper face of the specimen toward its lower face, i.e., the variation in specimen height; the sensors indications are then independent of the machine compliance (Fig. 2). The specimen height variation is the mean value of the two LVDT sensor indications. This high temperature extensometer has been developed and validated.[24] Mechanical tests were conducted at room temperature and at high temperature, at 20, 250, 500, 700, 900, and 1200 °C. The choice of suitable temperatures was based on microstructure observations through dilatometer tests and elastic modulus measurements using an ultrasonic technique.[15,25] These tests showed that the above temperatures were representative of the materials' behaviour. The mechanical experimental set-up was configured to perform uniaxial compression tests on cubic specimens with 40 mm side lengths. Some of the tests were performed at ambient temperature on specimens equipped with strain gauges placed on two opposite faces. The strains were then measured locally without any influence of the set-up test environment. This procedure allowed for the detection of eventual parallelism defects in the specimen, which would induce bending stress.

In order to ensure the validity and robustness of the tests at high temperatures, a special test protocol was applied. In particular, a thermal cycle was defined as follows. First the specimen was heated at a constant heating rate of 200 °C/h until the target temperature was reached. Next was the dwell stage of temperature, which lasted for 5 h plus the time necessary to perform the mechanical loading. Finally, after the completion of the mechanical test, there was a cooling phase characterized by a 150 °C/h rate.

Some of the compression tests were carried out by applying monotonic loading, whereas other tests used loading and unloading sequences applied at various stress levels up to the peak stress or beyond it. The monotonic loading tests were performed at a constant displacement rate of 0.1 mm/min standard value. However, with the strain rate jump tests, upgrading displacement rates were successively applied. Creep tests were conducted at 900 °C on various types of specimens, in which a constant load was applied to the specimen and its response in displacement recorded. An overview of the various tests carried out in the present study is presented in Table 2.

3. Results

3.1. Standard dried materials

A typical uniaxial stress–strain curve of And-LCC refractory concrete at room temperature is shown in Fig. 3. It is characterized by an approximately linear stress increase up to a maximum value (peak stress), followed by a sharp stress decrease in the so-called post-peak domain. The peak stress is about 96 MPa, and the corresponding strain (at peak stress) is 0.3–0.4%. A monotonic loading test curves, shown as test curves having loading–unloading cycles, are well superposed. The unrecoverable strains evidenced after the unloading cycles are at low value before the peak stress ($\leq$0.1%) and become noticeable in the post-peak domain ($\geq$0.3%). The peak stress appears as a limit value after which macrocracks form and failure mechanisms act with great consequences.

A similar evolution has been globally observed for Bau-ULCC refractory concrete. In Fig. 4, the plots of three different tests exhibit very good superposition, indicating very good

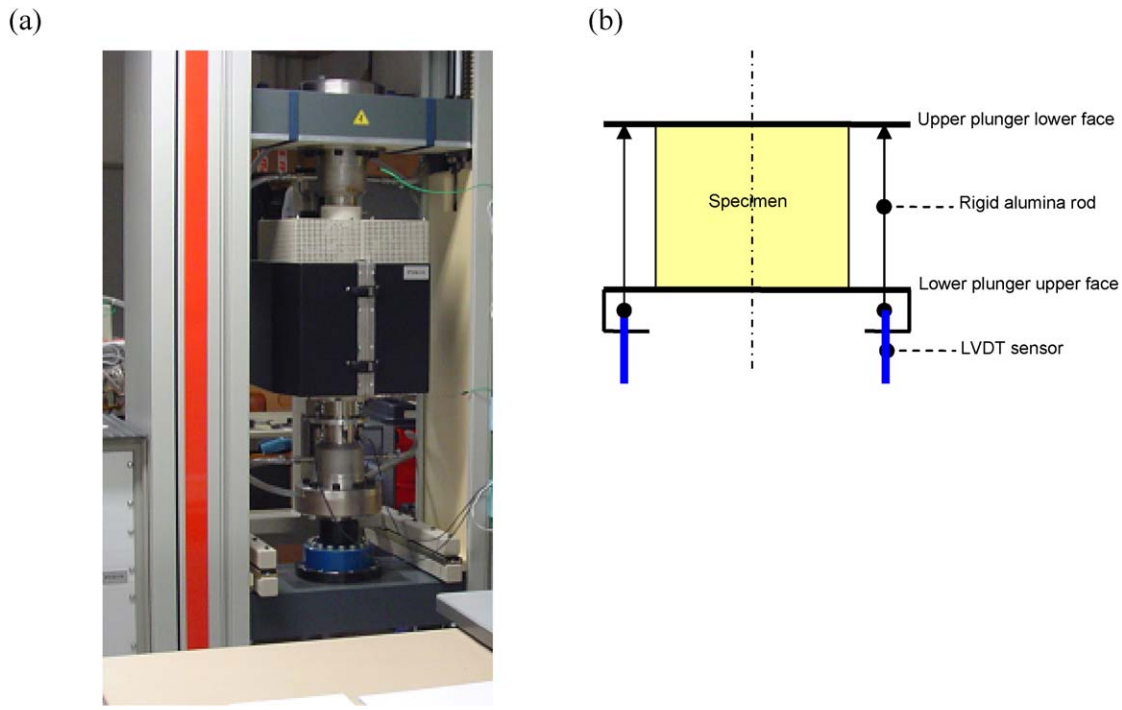

Fig. 2. (a) Schematic of the high temperature experimental set-up, and (b) principle of differential measurement of the specimen height variation.

Table 2
Overview of the different types of test performed and presented.

Material initial state	Treatment time	And-LCC	Bau-LCC
Standard dried at 110 °C	24 h	All types of test (except creep) at 20, 250, 500, 700, 900, 1200 °C	All types of test (except creep) at 20, 250, 500, 700, 900, 1200 °C
Fired at 900 °C	5 h	Ambient temperature tests + strain rate jumps tests at 900 °C	Ambient temperature tests
	150 h	Creep tests at 900 °C	Creep tests at 900 °C
Fired at 1200 °C	5 h	Ambient temperature tests + strain rate jumps tests at 1200 °C	Ambient temperature tests
	150 h	Creep tests at 1200 °C	Creep tests at 1200 °C

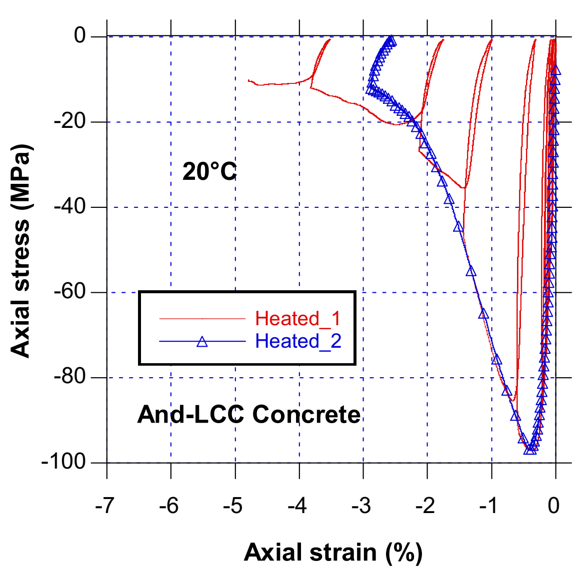

Fig. 3. Room temperature uniaxial compression responses of And-LCC refractory concrete are highly reproducible.

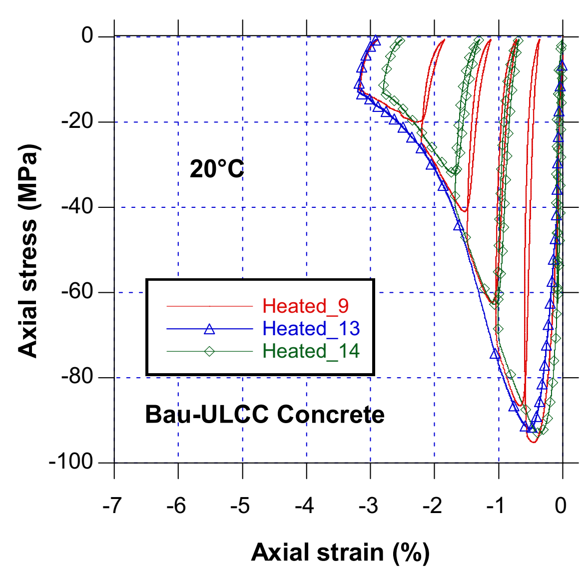

Fig. 4. Room temperature uniaxial compression responses of Bau-ULCC refractory concrete are highly reproducible.

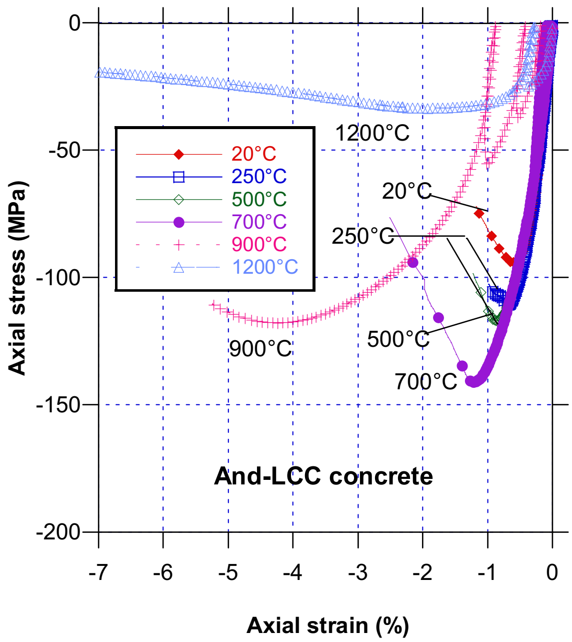

Fig. 5. Plot of uniaxial compression stress–strain curves of And-LCC refractory concrete tested at various temperatures, showing a change in the material behaviour between 700 and 900 °C.

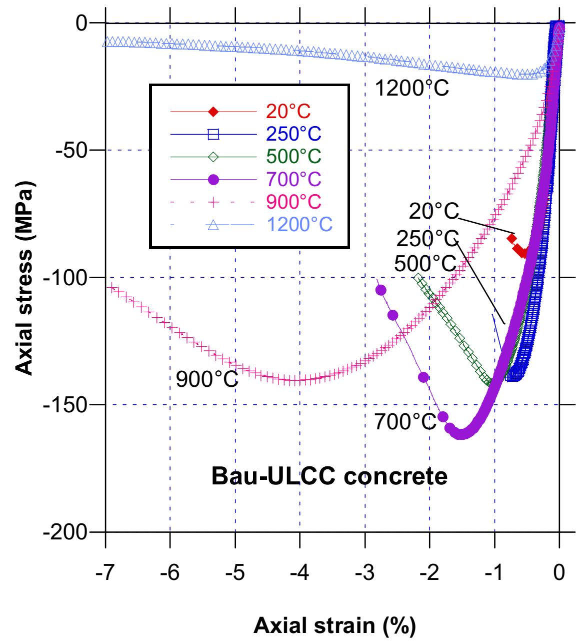

Fig. 6. Plot of uniaxial compression stress–strain curves of Bau-ULCC refractory concrete tested at various temperatures, showing a change in the material behaviour between 700 and 900 °C.

reproducibility of the performed tests. Once the peak load is reached, macrocracks appear and develop rapidly while the stress decreases sharply. The post-peak curve evolution is notably influenced by the machine compliance. A number of authors regard this phenomenon as interfering with the goal of understanding post-peak material behaviour.[11] They underline the necessity of testing on machines having very high stiffness, or a hydraulics machine press equipped with a stress control device.[26] Nevertheless, since the post-peak behaviour seems convenient, we assume that this measured behaviour is characteristic of the studied materials. To summarize, low unrecoverable strains are observed before the peak stress, and failure occurs for small values of strain that are typical of quasi-brittle materials. The decrease in the modulus of elasticity evidenced by up-grading loading/unloading cycles leads to the occurrence and development of damage in the material.

In order to investigate the evolution of the materials behaviour with increasing temperature, tests were conducted at 250, 500, 700, 900, and 1200 °C. The resulting stress–strain curves are displayed in Figs. 5 and 6, for And-LCC and Bau-ULCC refractory concretes, respectively. A general analysis of the evolution of these curves indicates the presence of two trends. First, tests performed at 250, 500, and 700 °C display similar behaviour with those at ambient temperature, as reported in Figs. 3 and 4. It should be noticed that both materials' strength increases with increasing temperature up to 700 °C. Second, by 900 °C, the stress–strain curves are well-rounded and the material ductility increases, while the material strength decreases with increasing temperature. An examination of the curves at 900 °C shows an important evolution in the material behaviour (Figs. 5 and 6). The strains developed by the material after the peak stress without brittle rupture are increased (3–4%, compared with 0.5–1.5% at lower temperatures), the strain at peak stress is about 4% (compared with 0.5–1.5% at lower temperatures), and the peak stress value is high: 118 and 136 MPa for And-LCC and Bau-ULCC concretes, respectively. At this temperature and above, a new ductility appears and its plastic or viscoplastic nature should be clarified. Loading and unloading test cycles exhibit important unrecoverable strains, in accordance with the four points bending tests on the same materials carried out by Marzagui.[27]

Results of the tests at 1200 °C clearly confirm the viscoplastic nature of the behaviour at 900 °C (Figs. 5 and 6). The maximum stress is reached rapidly and the stress level remains relatively constant over a large range of strain and then decreases slowly toward significant deformation. However, the obtained maximum stresses have significantly decreased to 20 MPa and to 30 MPa, for Bau-ULCC and And-LCC refractory concretes, respectively. These results illustrate an inversion in the compression behaviour of the two materials: And-LCC refractory concrete becomes more resistant than Bau-ULCC refractory concrete at 1200 °C. Moreover, the maximum strain supported by the material without significant loss of resistance is larger for And-LCC than Bau-ULCC refractory concrete. These general trends are valuable for both materials.

Relevant tests have been performed to evidence the materials viscous behaviour by examining their sensibility to strain rates changes. During this test the specimen was subjected to upgrading displacement rates, these are called strain rate jump tests. The tests performed on And-LCC specimens are reported in Fig. 7. Different displacement rates ranging from to 0.01 to 0.5 mm/min were applied to the specimen. Fig. 7 clearly shows that the resistance opposed by the material is dependent on the displacement rate applied according to the following well-known law: the larger the displacement rate the higher the stress

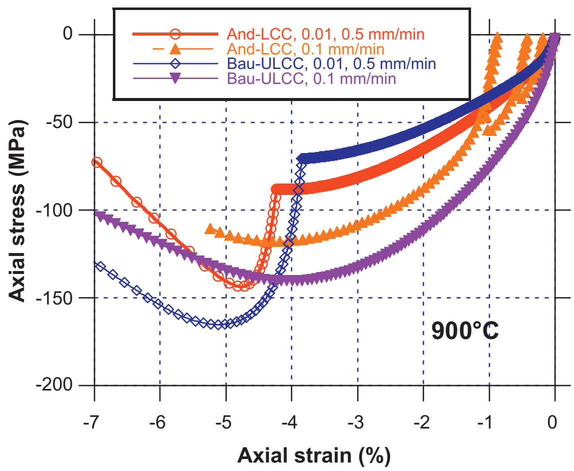

Fig. 7. Influence of applied strain rates or the strain rate changes (jump tests) on And-LCC and Bau-ULCC refractory concretes during tests performed at 900 °C.

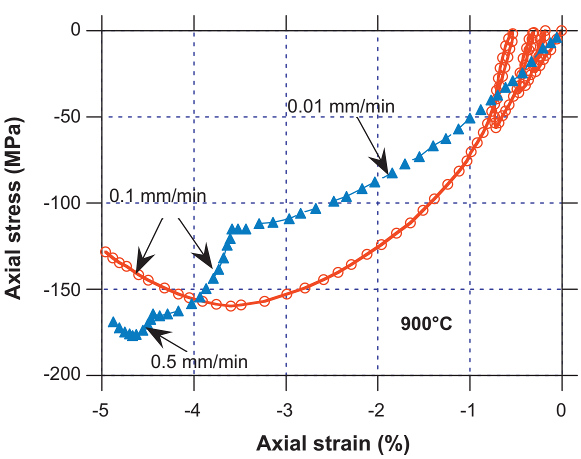

Fig. 8. Tests performed on the same material, preheated 900 °C/5 h And-LCC refractory concrete at various strain rates, show the sensibility to strain rate variation and an apparent slight influence of the material loading history (0.1 mm/min displacement rate).

reached; this is typical of viscous behaviour. Results recorded in Fig. 8 respond to the question, does the mechanical loading history have any influence on the material response for a given displacement rate? The answer appears to be yes; however, the effect is slight. The occurrence of viscoplasticity behaviour

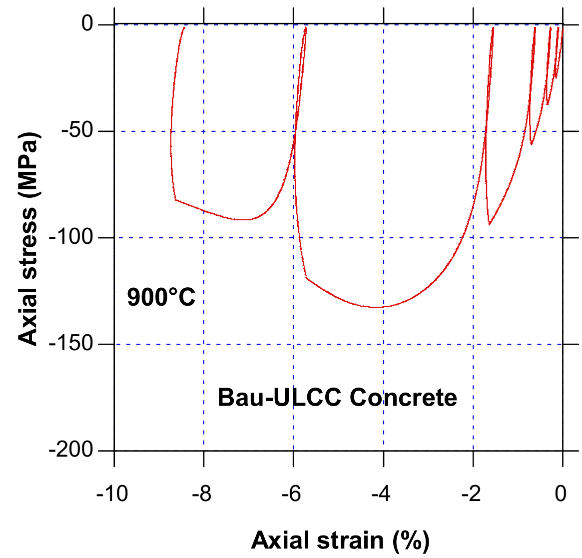

Fig. 9. Uniaxial compression test performed at 900 °C displaying the viscoplasticity behaviour evidenced by unrecoverable strain, and the rounding of the curve while reloading after a load–unload cycle (Bau-ULCC refractory concrete).

above 900 °C is evidenced by the load–unload tests illustrated in Fig. 9. It is characterized by the occurrence of irreversible time-dependent strains at any load level. Fig. 10 displays photos that illustrate the quasi-brittle behaviour of the materials at 700 °C. This behaviour is characterized by brutal failure, and the viscous behaviour over 900 °C is characterized by closed-ended macro-cracks. In either case, the material is damaged, and the difference in behaviour is clearly visible.

3.2. Fired materials

Fired materials have been studied at room temperature and at high temperatures. Fig. 11(A and B) shows the stress–strain curves of the compression tests performed on And-LCC refractory concrete fired at 900 °C and 1200 °C, respectively, at room temperature. The superposition of the monotonic loading and loading–unloading curves is good. The irreversible strain occurred before the stress peak was noticeable, compared with observations made on the standard dried material. It should be noted that the material strength increases when fired (120 MPa at 900 °C and 105 MPa at 1200 °C) compared with the standard

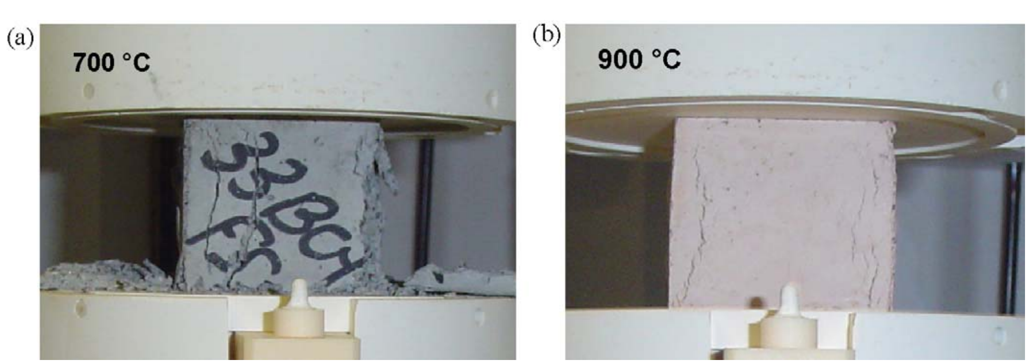

Fig. 10. Characteristic views of specimens of And-LCC refractory concrete in the final stage of uniaxial compression, where the material tested at 700 °C (a) present visible macro cracks whereas damage effects are attenuated by rise of viscosity at 900 °C (b).

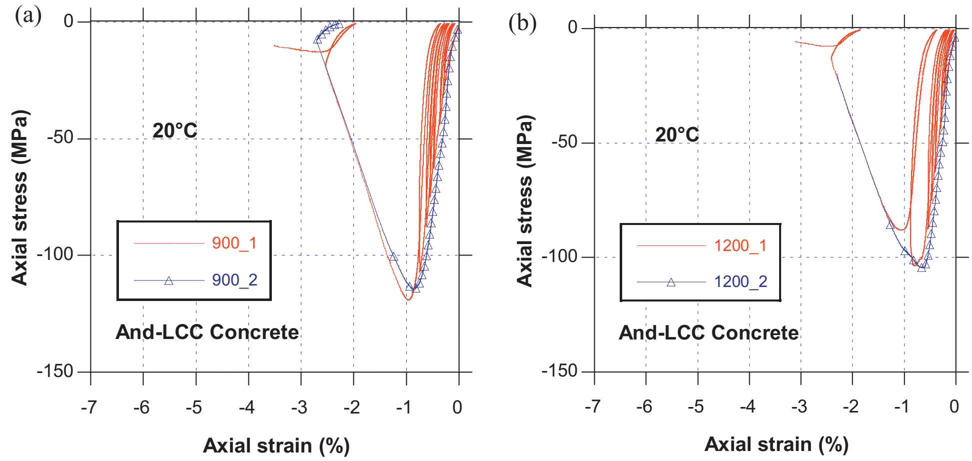

Fig. 11. Room temperature uniaxial compression behaviour of an And-LCC refractory concrete fired at 900 °C (a) and 1200 °C (b) over 5 h, showing increased presence of irreversible strains during the loading–unloading cycles in fired specimens.

dried materials (96 MPa). It is surprising to observe that firing the material at 900 °C over 5 h induces more resistance than firing it at 1200 °C over the same time. Possible explanations are that the phases present at 900 °C are different from those present at 1200 °C, and that the former phases induce less damage during the cooling process than the latter phases. Some of the tests showed that the strength reached at room temperature by And-LCC fired over 150 h was lower (MPa) than And-LCC fired at 900 over 5 h. These results indicate that the enhancement of the material strength is not proportional to the firing time. Moreover, various tests revealed that the fired specimens exhibited brutal brittleness beyond the peak stress. Lastly, there was observed a decrease in the modulus of elasticity, to 52 GPa (−24%) and 58 GPa (−15%), for 900 and 1200 °C fired materials, respectively. This is to compare with the 68 GPa value determined from the standard dried material. The result that the initial modulus of elasticity decreased is consistent with the damageable character of the cooling phase on such heterogeneous materials. It appears that heating followed by cooling operations on the refractory concrete strengthen it globally at ambient temperature, but induce more damageable behaviour prior to the peak of stress, and pronounced brittle behaviour beyond the peak of stress.

3.3. Creep tests

Creep tests have been performed on standard dried and fired specimens at 900 °C, to evaluate the effect of firing on the material behaviour. It is generally thought that firing the material stabilizes it from a chemical and physical point of view, as long as the operating temperatures are less than the firing temperature. Fig. 12 shows the results of 48 h duration creep tests under 10 MPa at 900 °C, performed on the two studied materials under various firing conditions. Standard dried And-LCC or Bau-ULCC materials exhibit a long primary creep (nonlinear part of the curve) lasting about 24 h, followed by a 24 h secondary creep. However, And-LCC or Bau-ULCC fired materials (900 °C-150 h) exhibit a short primary creep, about 2 h, followed by a long secondary creep period. The total creep strain reached after 48 h is about 1.1% for standard dried materials vs. 0.4% for fired materials; this is a nearly threefold decrease. The slopes of the linear part of the curves equal the secondary creep strain rate. The secondary creep rates are reduced in ratios of 3 and 2, for And-LCC and Bau-ULCC fired refractory concretes, respectively. Hence, firing has the effect of reducing the sensibility of the materials' primary and secondary creep behaviour. In summary, firing the material significantly reduces the material primary creep effects and secondary creep rates, but does not suppressed them even though the testing temperature was lower than the firing temperature. This conclusion can be extended to fashionable silica–alumina bricks, which are used in fired form.

3.4. Strain rate jump tests

In order to predict the viscous behaviour of the fired materials, this study has focussed only on And-LCC refractory concrete subjected to two firing temperatures, 900 and 1200 °C, over 5 h. Strain rate jump tests were performed at 900 °C on the material fired at 900 °C, and at 1200 °C on the material fired at 1200 °C.

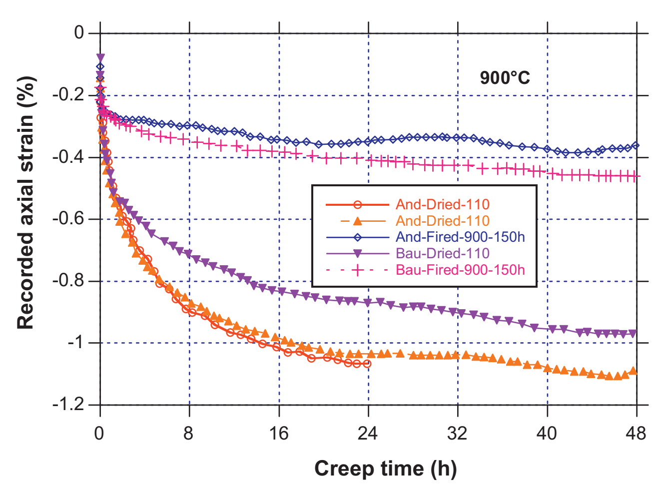

Fig. 12. Influence of the firing conditions during two-day time creep tests on various And-LCC and Bau-ULCC refractory concretes conducted at 900 °C under a 10 MPa applied compression stress.

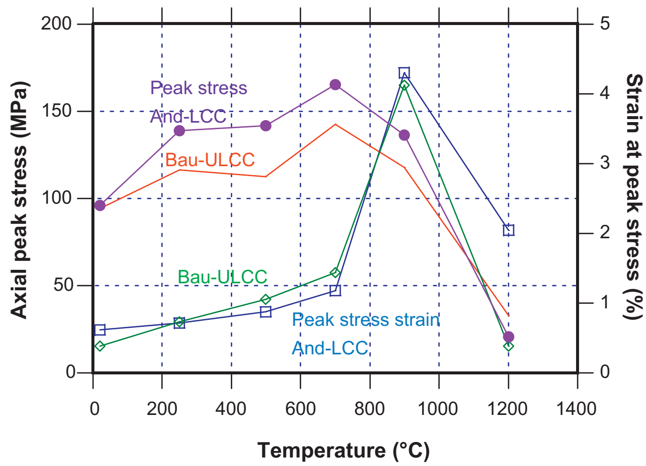

Fig. 13. Variation of the strength and the strain at peak stress of standard dried And-LCC and Bau-ULCC refractory concretes vs. temperature. Note that 900 °C appears to be a key transition temperature.

The examination of strain vs. time curves indicates a clear linear evolution at the different displacement rates. Hence, most of the occurring creep strain is of the secondary type. These results confirm those described above on the creep behaviour of fired material at 900 and 1200 °C over 150 h. After a 5 h firing period, the material primary creep properties reduce significantly. Moreover, the strain rate developed by the material is lower than that of standard dried materials. A test performed at 0.01, 0.1, and 0.5 mm/min displacement rates, at a temperature of 900 °C on 900 °C/5 h fired specimens (Fig. 8), shows the material strain rate sensibility despite the thermal treatment. The higher the strain rate applied, the greater the maximum stress reached. At the maximum displacement rate of 0.5 mm/min, the material develops some brittleness which is emphasized by the dotted lines ending the curve. This figure also shows the high stress level induced by the firing of the material (160 MPa at 0.1 mm/min, for instance). For the same type of test undertaken at 1200 °C on And-LCC fired at 1200 °C/5 h, it was observed that the sensibility to the strain rate variation exists and is even higher than at tests at 900 °C; it is caused by a greater variation in the maximum obtained stress at each jump for the same displacement rates. However, no tendency to brittleness was observed at 0.5 mm/min, as it was at 900 °C.

4. Discussion

4.1. Materials behaviour

An analysis of the just-recorded test results shows that the standard dried materials exhibit quasi-brittle behaviour that is characterized by increasing strength up to 700 °C, and viscous behaviour over 900 °C that is characterized by decreasing strength with increasing temperature. The evolution of both materials' strength vs. temperature (Fig. 13) shows a maximal value at 700 °C. The strength increase at intermediate temperatures is moderate, whereas its decrease is strong at high temperatures. This behaviour is characteristic of heterogeneous refractory materials composed of constituents with glassy phases. The use of various microstructure investigation tools can help in understanding this behaviour; hence, dilatometry and environmental scanning electron microscopy investigations were performed on the matrices and the castables of the various studied materials by some of the research partners.[28] Dilatometry tests on the matrices of And-LCC and Bau-ULCC castables revealed an important shrinkage phenomenon in the 150–300, 800–950, 1050–1150, and 1200–1300 temperature ranges. This phenomenon is more pronounced for the Bau-ULCC matrix than the And-LCC matrix. However, the dilatometry tests on the castables showed continuous expansion with a slight attenuation at the matrix shrinkage temperature ranges. The average thermal expansion coefficient is about $5.6 \times 10^{-6}\,K^{-1}$ for the And-LCC castable, and $8.5 \times 10^{-6}\,K^{-1}$ for the Bau-ULCC castable. High Temperature ESEM observations of interfacial microcracks showed a continuous increase of their width with increasing temperature. At high temperatures (>1100 °C), vitreous phases appear accompanied with microcrack bridging phenomena.

The mechanical behaviour of the material can be correlated with these microstructure evolutions. At the start of heating (20–350 °C), the transformation of hydrates as a dehydration phenomena occurs in the material. The phenomena strengthened the binder links with the evacuation of water, while inducing shrinkage of the material accompanied with microcracking.[29] But the strengthening effect is preponderant since both refractory concretes show an increase in strength: from −96 MPa at 25 °C to −120 MPa at 250 °C for And-LCC, and from −92 MPa at 25 °C to −140 MPa at 250 °C for Bau-ULCC (Fig. 13). It should be noted that 250 °C is within the temperature range at which matrix shrinkage is important. Between 350 and 700 °C, the microstructure evolution is characterized by the presence of dehydration and the tightening of the binder links that contribute to the continuous increase in strength for both materials. The maximum stress is reached when the tested temperature is 700 °C, for material strength values equalling 140 and 164 MPa for And-LCC and Bau-ULCC concrete, respectively. The effect of dehydration is more pronounced for Bau-ULCC than for And-LCC, probably since the former has a higher open porosity (10%) for stocking free water than the latter (6%) (Table 1). It is likely that 700 °C is not the materials' optimal temperature; the optimum value is believed to occur between 700 and 800 °C. The second important matrix shrinkage temperature range is 800–900 °C. According to the mechanical tests results, this seems to be the beginning of the materials' viscous behaviour. The transition zone from quasi-brittle to viscous behaviour occurs in the range 800–900 °C.

Over 900 °C the materials' strength decreases as the strain before fracture increases. Strain rate jump tests performed as creep tests show that the materials display viscous behaviour above 900 °C. At high temperatures (>1100 °C), HT-ESEM micrographs show clearly that vitreous phases appear in the material, as characterized by densification induced by a sintering process and by the bridging of the macrocracks. The increase of the materials' sudden ductility at these temperature ranges is then the consequence of this microstructure evolution. The decrease in material strength is due to the appearance of viscous phases that migrate in the material and tend to fill the previous cracks. Hence, the microstructure evolution is consistent with the macroscopic mechanical behaviour observed at high temperature.

For temperatures ranging from 900 to 1100 °C, the materials' mechanical macroscopic behaviour cannot be explained by dilatometer test records nor by HT-ESEM observations. Indeed, from 800 to 1000 °C, HT-ESEM micrographs show that growth of microcracks appeared during the first dehydration state in the binder and the accentuation of aggregate/binder phase decohesions. This can explain the decrease in strength but not the viscous behaviour. In fact, no vitreous phases are visible in the HT-ESEM micrographs at temperatures lower than 1100 °C. An explanation is provided by other authors.[30] The presence of fume silica in the castables, which has the primary role of facilitating the formation of concrete and densifying the material, leads to the formation of glassy phases in the material at lower temperatures than predicted theoretically. Both studied materials contain the same content of silica fumed (10%), perhaps explaining why they develop viscous behaviour in similar temperature ranges. These results are comparable and consistent with those obtained on a carbon containing alumina refractory concrete used in a blast furnace main through.[10]

4.2. Comparative analysis of the two studied materials

Both studied materials have similar global behaviour: they are quasi-brittle from room temperature to 800 °C, and display viscous behaviour at temperatures above 900 °C. However, our investigation focuses on the several differences between the two materials. The strength of And-LCC is globally lower than that of Bau-ULCC for all temperatures, except at 1200 °C where an inversion occurs. The composition of the materials (Table 1) indicates that Bau-ULCC contains more alumina and less cement than And-LCC. The density of the former is also higher. These arguments support the greater resistance of the former. The matrix phase of the Bau-ULCC castable is very close to the aggregate material, emphasizing the trend of the binder phase as glue for the aggregate. Hence, at low temperature the resistance of the bauxite aggregates of Bau-ULLC is greater than that of the andalusite aggregates of And-LCC; the latter conduct to a higher strength than the former material. However, at high temperature the link between the aggregates and the binder phase is so strong, that microcracks initiated in the binder propagate through the aggregates in the case of Bau-ULCC concrete, yet they are stopped at the aggregate/binder phase interface for And-LCC. This phenomenon is clearly shown in some micrographs. At high temperatures, crack propagation becomes trans-granular in Bau-ULCC, but remains circum-granular in And-LCC. This observation can explain why the Bau-ULCC resistance becomes lower at high temperature than the And-LCC resistance, as shown by our results.

The Young's modulus for Bau-ULCC concrete is logically higher than for And-LCC concrete, essentially due to Bau-ULCC's higher alumina content (85% vs. 58% for And-LCC) at room temperature. But when temperature increases the presence of glassy phases, especially as induced by the fumed silica constituent trends, the differences reduce.

Hence for low and intermediate temperatures, Bau-ULCC concrete exhibits higher strength, but in high temperature domains (>1200 °C), And-LCC concrete fits better due to a higher resistance.

4.3. Influence of firing on the material behaviour

As both materials exhibit similar behaviour, the study of the influence of firing on the material behaviour focussed on the And-LCC material only. During the material cooling, the various phases that previously appeared recur with different physical properties. Particularly, the differences in the thermal expansion coefficient induce local residual tension stresses that are capable of creating cracks or microcracks through the material. Regardless of how the cooled material is microcracked, its strength at room temperature can be higher than the strength of the standard dried material. The results obtained on And-LCC and Bau-ULCC show that regardless of temperature, the resistance of the heated temperature is at least equal to that of the dried standard material: −120 MPa for 900 °C and −100 MPa for 1200 °C heating temperature, compared with −96 MPa for the standard material. However, the Young's modulus of the cooled material is lower than for the standard dried material: 54 GPa at 900 and 58 GPa at 1200 °C heating temperature compared with 68 GPa obtained for the standard dried material. The results of the tests performed are in agreement with general knowledge regarding these materials. At this point we examine the influence of the heating duration.

The viscous behaviour of standard vs. 900/5 h and standard vs. 1200 °C/5 h fired materials are reported in Fig. 14. The figure shows the maximal stress measured at a given displacement rate for the materials encountered. The variation of maximal stress depending on displacement rate is due to the presence of viscosity. In Fig. 14(b), except for the 0.1 mm/min strain rate, the response of the heated material is less than that of the standard dried material. Hence, it seems that firing the material at 1200 °C has lowered its viscous tendency. However, at 900 °C (Fig. 14(a)), the maximal stress recorded for the heated material is sensibly higher than the maximal stress for the dried material at all displacement rates. Moreover, the variation of the maximal stress from one displacement rate to another for the two materials is comparable. Thus, it seems that 5 h heating duration did not reduce the material viscous tendency; however, it generally increased the maximally obtained stress.

However, creep tests performed under 10 MPa stress at 900 °C on dried standard and 900 °C/150 h specimens show a clear influence of the material firing duration (Fig. 12). The primary creep of the And-LCC and Bau-ULCC 150 h-fired-materials was reduced to 2 h, whereas it lasted 20–24 h for the dried standard materials. The creep strain of the fired materials was essentially due to secondary rather than primary creep for the dried standard materials. In this present case, 150 h was

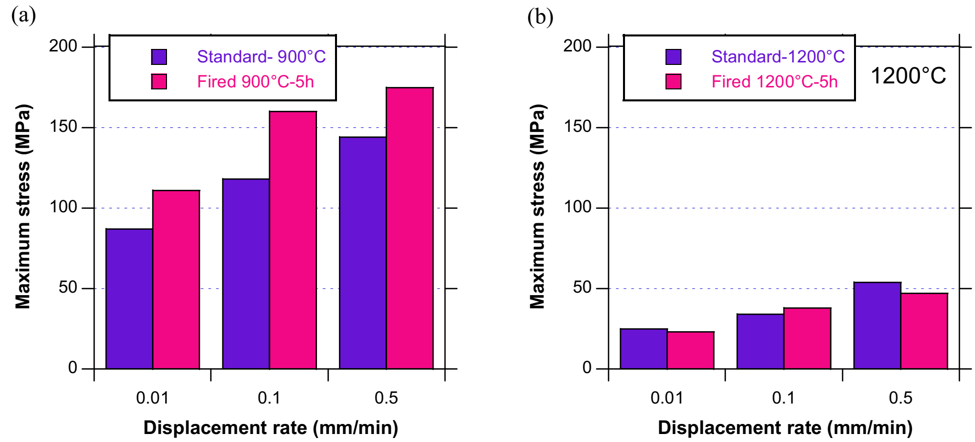

Fig. 14. Comparison of the maximum compression stress reached at various strain rates between And-LCC refractory concrete standard dried material, and (a) fired material at 900 °C/5 h tested at 900 °C, and (b) fired material at 1200 °C/5 h tested at 1200 °C.

Table 3
Characteristics of standard And-LCC refractory concrete viscous behaviour deduced from the strain rate jumps tests.

	Displacement rate (mm/min)			
	0.001	0.01	0.1	0.5
Strain rate (s^{-1}) at 900 °C	–	3×10^{-6}	3×10^{-5}	2×10^{-4}
Maximum stress at 900 °C (MPa)	–	87	118	144
Strain rate (s^{-1}) at 1200 °C	2×10^{-7}	3×10^{-6}	3×10^{-5}	2×10^{-4}
Maximum stress at 1200 °C (MPa)	6	25	34	54

Table 4
Characteristics of And-LCC refractory concrete viscous behaviour deduced from the strain rate jumps tests when fired at 900 °C/5 h.

	Displacement rate (mm/min)			
	0.001	0.01	0.1	0.5
Strain rate (s^{-1}) at 900 °C	–	2×10^{-6}	2×10^{-5}	1×10^{-4}
Maximum stress at 900 °C (MPa)	–	111	160	176
Strain rate (s^{-1}) at 1200 °C	–	3×10^{-6}	2×10^{-5}	2×10^{-4}
Maximum stress at 1200 °C (MPa)	–	23	38	47

Table 5
Characteristics of standard Bau-ULCC refractory concrete viscous behaviour deduced from the strain rate jumps tests.

	Displacement rate (mm/min)			
	0.001	0.01	0.1	0.5
Strain rate (s^{-1}) at 900 °C	–	3×10^{-6}	3×10^{-5}	1×10^{-4}
Maximum stress at 900 °C (MPa)	–	74	140	167
Strain rate (s^{-1}) at 1200 °C	3×10^{-7}	2×10^{-6}	3×10^{-5}	2×10^{-4}
Maximun stress at 1200 °C (MPa)	5	16.5	20	37

Table 6
Norton's law parameters deduced from isothermal high temperature strain rate jump tests with different initial conditions identified for And-LCC refractory concrete.

Testing temperature	Material initial state	A	n
900 °C	Standard dried	9.6×10^{-24}	9
	Fired 900/5 h	96×10^{-24}	8
1200 °C	Standard dried	12×10^{-14}	5.5
	Fired 1200/5 h	8×10^{-14}	5.3

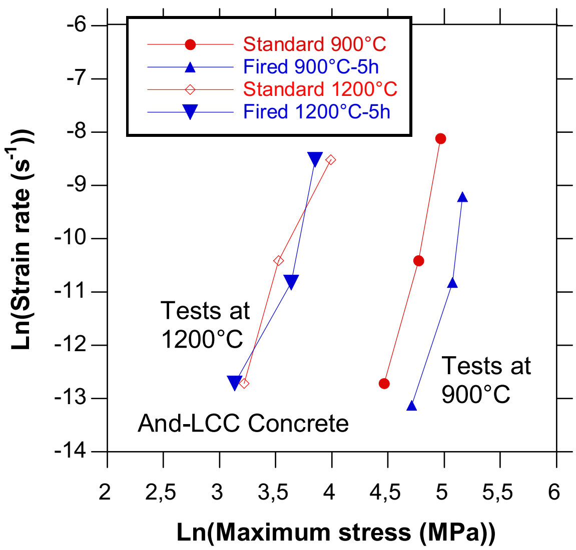

Fig. 15. Identification of a Norton power creep law on strain rate jump tests on And-LCC refractory concrete performed at 900 °C on standard dried and fired 900 °C/5 h material, and at 1200 °C on standard dried and fired 1200 °C/5 h material.

enough for a complete phase transformation leading to a radical change in the material behaviour.

In order to visualize the influence of the heat treatment on the material behaviour, the strain rate jump tests have been analysed using Norton's law. Tables 3 and 4 record the strain rate and the corresponding maximal stress reached at 900 °C and 1200 °C, for the standard dried and the 900 °C/5 h treated And-LCC refractory concrete, respectively. Table 5 provides similar results for the Bau-ULCC refractory concrete. The data from Tables 3 and 5 are plotted as log–log diagrams in Fig. 15. The Norton's law parameters calculated with the data for the And-LCC refractory concrete are reported in Table 6. The *n* parameter value is too high for such material: 5–9 instead of the more typical value of 2. The accounted strain rates are probably too high, so that Norton's law does not apply well. However, it seems that firing the material does not significantly change its behaviour at 1200 °C, since the *A* and *n* values are very similar for the dried and fired materials (Fig. 15– 1200 °C). However, at 900 °C the *n* values are a bit different ($n = 9$ for dried and $= 8$ for the fired material), thus the *A* values are very different, with a ratio of 10. Therefore, the differences visible in the evolution of the material resistance vs. the displacement rate at 900 °C (Fig. 14) are also illustrated significantly using a Norton's law (Fig. 15-900 °C) analysis.

The conclusion of this study is somewhat clear. However the two studied materials are used in the same application field (security lining at temperature ranging from 900 to 1200 °C) and their macroscopic behaviour similar in evolution, they remain very different as far as their microstructure behaviour is concerned. That is to say that the macroscopic thermo-mechanical behaviour, however important for stresses and strains calculations on industrial structures made of these materials, remains a part of the knowledge of such complex materials behaviour.

5. Conclusion

Two andalusite- and bauxite-based refractory concretes have been studied through various uniaxial compression mechanical tests, from room temperature up to 1200 °C. The material behaviour as well as the influence of the firing conditions has been analysed. The macroscopic evolution recorded has been correlated to microstructure observations by SEM. The major results are summarized below:

- The materials exhibited quasi-brittle behaviour with increasing strength from room temperature to 800 °C, and viscous behaviour with decreasing strength from 900 to 1200 °C. The 800–900 °C temperature range seems to be the material behaviour transition zone, and the maximal stress is recorded at 800 °C. The Bau-ULCC material has greater strength than And-LCC, except at 1200 °C.
- At intermediate temperatures (25–700 °C), the irreversible strains are low for the dried material but more pronounced for the fired materials prior to the peak stress. Beyond the peak stress, important irreversible strains occur accompanied by an important decrease of the modulus of elasticity. This indicates the onset of damage. At higher temperatures, viscoplastic irreversible strains are present all along.
- The development of viscous behaviour for both materials has to be correlated to microstructure observations and the material composition. In particular, the presence of silica fumed supposedly lowers the temperature at which the viscous phenomena are present, which is consistent with the macroscopic results.
- At room temperature, the thermal treatment generally increases the material's strength but decreases its modulus of elasticity. At high temperature, the long thermal treatment (150 h) greatly reduced the material sensibility to creep, especially primary creep. But in general, and particularly at 900 °C, the material never really stabilizes in spite of heat treatment.
- The two studied materials exhibited similar behaviour when the temperature increased, which emphasized the predominant role of the binder. However, Bau-ULCC concrete based on bauxite aggregates exhibited higher values of strength and modulus of elasticity than And-LCC concrete based on andalusite aggregates, except at 1200 °C where And-LCC strength was higher than Bau-ULCC strength.
- From a modelling point of view, this study has shown that elastic damageable constitutive equations could be used to model the material intermediate temperature behaviour, whereas a viscoplastic model or viscoplastic behaviour coupled with damage is required to ideally model the material behaviour at high temperature.

Acknowledgments

The present study has been undertaken in the framework of a national research program PROMETHEREF on refractory materials held from June 2002 to December 2005. This program has been funded by the French Ministry of Industry and the three following companies TRB, Saint-Gobain (CREE), and EDF (Les Renardières). The following people have been involved in the refractory concrete team of this program, and we would like to acknowledge them: PhD students (Edwige Yeugo-Fogaing, Hicham Marzagui) under the supervision of senior researchers (Christian Gault, Marc Huger, Thierry Cutard). The authors also wish to thank the Ministry of Industry (Michel Mussino), TRB (Thierry Joly), EDF (Alain Guyonvarch, Patrick Billard, Yves Dutheillet) and the general coordinator of the program Michel Boussuge of ENSMP. The authors would lastly like to thank M. Antoine Miras of Laboratory 3S-R in Grenoble for technical support.

References

1. Prompt N, Ouedraogo E. High temperature mechanical characterisation of an alumina refractory concrete for blast furnace main through – Part I: General context. *Journal of the European Ceramic Society* 2008;**28**:2859–65.
2. Fredman TP, Saxen H. Model for temperature profile estimation in the refractory of a metallurgical ladle. *Metallurgical and Materials Transactions B* 1998;**29B**:651–9.
3. Huger M, Glandus JC, Gault C. Thermomechanical modelling of alumina–graphite ladle shrouds used in continuous casting. In: *Proceedings of the unified international technical conference on refractories*. 1999. p. 128–32.
4. Belt DA. First heat-up of ladle linings. In: *Proceedings of the unified international technical conference on refractories*. 1999. p. 292–4.
5. Egashira H, Aramaki K, Tomimatu H, Morimoto S, Yoshida T. Development of long-life slit plug material for steel ladle. In: *Proceedings of the unified international technical conference on refractories*. 1999. p. 308–11.
6. Andrieux CM. *Analyse et simulation des contraintes d'origine thermique sur des structures réfractaires de centrales LFC*. PhD thesis, University of Orleans, France; 1999. p. 172.
7. Singh JP, Thomas JR, Hasselman DPH. Analysis of effect of heat-transfer variables on thermal stress resistance of brittle ceramics measured by quenching experiments. *Journal of the American Ceramic Society* 1979;**63**(3–4):140–4.
8. Simonin F, Olagnon C, Maximilien S, Fantozzi G. Room temperature quasi-brittle behaviour of an aluminous refractory concrete after firing. *Journal of the European Ceramic Society* 2002;**22**:165–72.
9. Kolli M, Hamidouche M, Fantozzi G, Chevalier J. Elaboration and characterization of refractory based on Algerian kaolin. *Ceramics International* 2007;**33**:1435–43.
10. Ouedraogo E, Prompt N. High-temperature mechanical characterisation of an alumina refractory concrete for Blast Furnace main through – Part II: Material behaviour. *Journal of the European Ceramic Society* 2008;**28**:2867–75.
11. Van Mier JGM, Van Vliet MRA. Uniaxiale test for the determination of fracture parameters of concrete: state of the art. *Engineering and Fracture Mechanics* 2002;**69**:235–47.
12. Ghassemi Krakroudi M, Yeugo-Fogaing E, Gault C, Huger M, Chotard T. Effect of thermal treatment on damage mechanical behaviour of refractory castables: comparison between bauxite and andalusite aggregates. *Journal of the European Ceramic Society* 2008;**28**:2471–8.
13. Ghassemi Krakroudi M, Yeugo-Fogaing E, Gault C, Huger M, Chotard T. Anisotropic behaviour of andalusite particles used as aggregates on refractory castables. *Journal of the European Ceramic Society* 2009;**29**: 571–9.
14. Ghassemi Krakroudi M, Yeugo-Fogaing E, Gault C, Huger M, Chotard T. Damage evaluation of two alumina refractory castables. *Journal of the European Ceramic Society* 2009;**29**:2211–8.
15. Marzagui H, Roosefid M, Cutard T, Ouedraogo E, Prompt N, Deteuf C. Room temperature mechanical behaviour of two refractory castables. In: *Proceeding of the 4th international symposium on advances in refractories for the metallurgical industries*. August 2004. p. 645–59.
16. Sudhir B, Chokshi AH. Compression creep characteristics of 8 mol% Yttria-stabilized cubic-zirconia. *Journal of the American Ceramic Society* 2001;**84**(11):2625–32.
17. Das G, Masdiyasni KS, Lipsitt HA. Mechanical properties of polycrystalline TiC. *Journal of the American Ceramic Society* 1981;**65**(February (2)):104–10.
18. Vardoulakis I, Labuz JF, Papamichos E, Tronvoll J. Continuum fracture mechanics of uniaxiale compression on brittle materials. *International Journal of Solids and Structures* 1998;**35**(31–32):4313–35.
19. Koyama T, Hayashi S, Yasumori A, Okada K. Microstructure and mechanical properties of mullite/zirconia composites prepared from alumina and zircon under various firing conditions. *Journal of the European Ceramic Society* 1996;**16**:231–7.
20. Schmitt N, Berthaud Y, Poirier J. Tensile behaviour of magnesia carbon refractories. *Journal of the European Ceramic Society* 2000;**20**:2239–48.
21. Ewais EMM, Khalil NM. Refractory castables based on SiC slab waste. *Journal of the Ceramic Society of Japan* 2010;**118**(2):122–7.
22. Ohira H, Ismail MGMU, Yamamoto Y, Akiba T, Somiya S. Mechanical properties of high purity mullite at elevated temperatures. *Journal of the European Ceramic Society* 1996;**16**:225–9.
23. Boussuge M. Investigation of the thermomechanical properties of industrial refractories: the French programme PROMETHEREF. *Journal of Materials Sciences* 2008, doi:10.1007/s10853-008-2534-0.
24. Roosefid M. *Etude du Comportement Thermomécanique de deux Bétons Réfractaires silico-alumineux: Applications à une poche d'aciérie*. PhD thesis, National Polytechnic Institute of Grenoble, France; 2006. p. 272.
25. Yeugo-Fogaing E, Huger M, Gault C. Elastic properties and microstructure: study of two fused cast refractory materials. *Journal of the European Ceramic Society* 2007;**27**(2–3):1843–8.
26. Miyamoto M, Onoye T, Narita K. Deformation and failure behavior of refractories for the blast furnace at elevated temperatures. *Transactions of ISIJ* 1981;**21**:887–94.
27. Marzagui H. *Etude de deux bétons réfractaires silico–alumineux: microstructures et comportements thermomécaniques en traction et en flexion*. PhD thesis, Toulouse III – Paul Sabatier University; 2005. p. 229.
28. Marzagui H, Cutard T. Characterisation of microstructure evolutions in refractory castables by in situ high temperature ESEM. *Journal of Materials Processing Technology* 2004;**155–156**:1474–81.
29. Innocenti MDM, Cardoso FA, Akyioshi MM, Pandolfelli VC. Drying Stages during heating of high-alumina. Ultra-low-cement refractory castables. *Journal of the American Ceramic Society* 2003;**86**(7): 1146–8.
30. Nonnet E, Lequeux N, Bloch P. Elastic properties of high alumina cement castables from room temperature to 1600 °C. *Journal of the European Ceramic Society* 1999;**19**:1575–83.