Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 29 (2009) 53–58

www.elsevier.com/locate/jeurceramsoc

Hot bending strength and creep behaviour at 1000–1400 °C of high alumina refractory castables with spinel, periclase and dolomite additions

L.A. Díaz*, R. Torrecillas

Centro de Investigación en Nanomateriales y Nanotecnología (CINN), Consejo Superior de Investigaciones Científicas (CSIC), C/Francisco Pintado Fe 26, 33011 Oviedo, Spain

Received 20 February 2008; received in revised form 12 May 2008; accepted 24 May 2008
Available online 21 July 2008

Abstract

The modulus of rupture and creep behaviour of refractory castables at high temperature (1000–1400 °C) with additions of spinel, periclase and dolomite has been studied. Three processing routes for obtaining refractory concretes within the alumina-rich zone of the Al_2O_3–MgO–CaO ternary system were employed. To achieve high temperature mechanical properties special attention was paid to the processing route (synthetic spinel, periclase and dolomite additions), and the composition (effect of synthetic or self-forming spinel and CaO contents).

The results demonstrate that these refractory castables show a highly viscoplasticity behaviour at temperatures >1100 °C and a hot bending strength depending on the loading rate. Refractory castables made with synthetic spinel have lower high temperature bending strength values than castables made with periclase additions owing to their less viscoplastic behaviour. In this work neither the amount of spinel nor processing route chosen were found to have any significant influence on the hot bending tests between 1100 and 1400 °C. The creep tests show that in the temperature range of 1100–1300 °C the main reaction governing deformation is the interaction between the alumina and the calcium aluminate cement phases. Above 1300 °C, castables made first with dolomite, then with periclase and finally with synthetic spinel are more prone to deformation in that order.

Keywords: Refractory castables; Hot modulus of rupture; Creep behaviour; Spinel; Periclase; Dolomite

1. Introduction

Refractory castables are widely used as structural materials in many high temperature and high-pressure applications, such as coal-gasification pressure vessels, reactors in petrochemical processes, industrial incinerators, etc., and especially in the iron and steel industry.[1] In the high-alumina region of the Al_2O_3–MgO–CaO ternary diagram system refractory castables possess a high refractoriness and spinel possesses a wide primary field of crystallization containing within its structure a large quantity of metallic cations (Fe^{2+}, Fe^{3+}, Mn^{2+}, etc.).[2–4] Knowledge of the thermomechanical properties and behaviour of such materials is very important when selecting a structural refractory at high temperatures. Several authors have investigated the mechanical behaviour of alumina-spinel refractory castables.[5–12] The mechanical strength of the refractory castables at room temperature is related to the quality of the packaging of the particles and the presence of hydrates.[3] In the temperature range of 300–900 °C, the decrease in mechanical properties is due to the destruction of the hydrate network of the cement and an increase in the porosity of the paste.[5,6] However, Díaz[3] and Simonin et al.[11] have demonstrated that a decrease in these properties at low firing temperatures is due to the thermal expansion mismatch between the coarse grains and the matrix. However, modifications to the cement content and aggregate-size distribution can also produce significant changes in the mechanical strength of refractory castables at room temperature.[5]

The hot modulus of rupture of alumina-spinel castables containing 20 wt% spinel and 1.36–2.04 wt% CaO generally increases as the CaO content and temperature increase from 1300 to 1500 °C.[13] An increase in the spinel content also improves

* Corresponding author.
E-mail addresses: ladiaz@incar.csic.es (L.A. Díaz), rtorre@incar.csic.es (R. Torrecillas).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2008.05.044

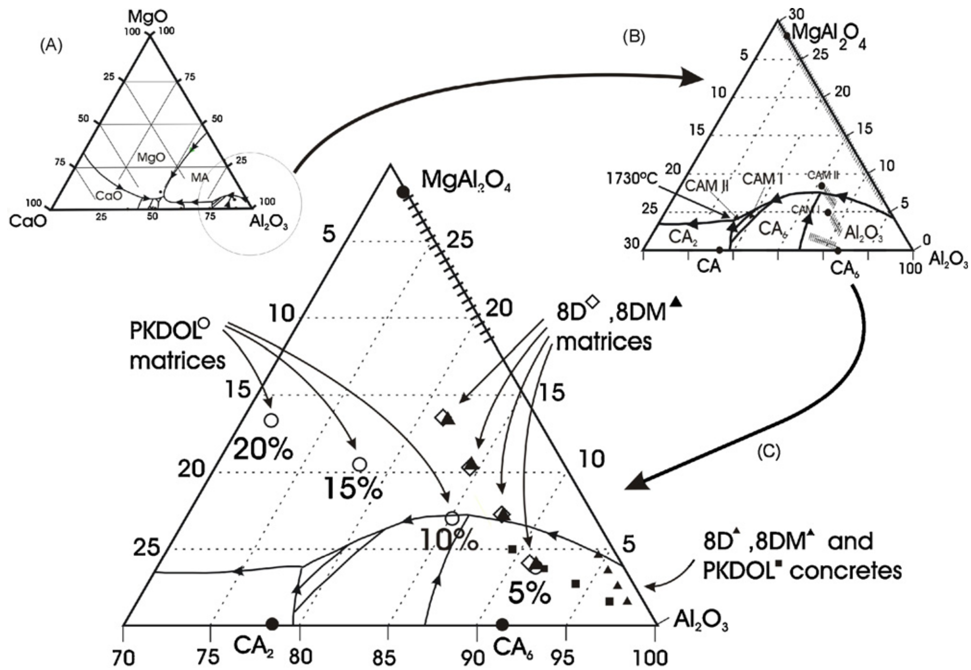

Fig. 1. (A) Al_2O_3–MgO–CaO ternary phase equilibrium diagram, (B) Al_2O_3-rich zone, and (C) location of all the compositions designed in the Al_2O_3-rich zone.

the hot strength of alumina-spinel refractory castables in the temperature range of 1000–1500 °C.[14] However, at temperatures >1000 °C, these refractory castables show significant viscoelastic–plastic behaviour[15–17] and the bending strength is dependent on the loading rate. In view of this, only creep and creep rupture properties should be considered when evaluating the usefulness of a refractory castable. Until now there have been few studies on the creep properties of such materials owing to their chemical and mineralogical complexity.[17–24]

The purpose of this work has been to investigate the hot bending strength of high-Al_2O_3 refractory castables in the temperature range of 1000–1400 °C and their high temperature deformation (creep) employing different processing routes and bearing in mind the following variables:

- Processing route (additions of synthetic spinel, periclase and dolomite to the matrix of refractory castables).
- Composition (effect of synthetic or self-forming spinel and CaO contents) with a view to explaining the factors responsible for mechanical behaviour at high temperature.

2. Experimental procedure

2.1. Castables

In the Al_2O_3–MgO–CaO diagram ternary system, three kinds of refractory castables were elaborated.[26] The coarse and intermediate aggregates were formed by tabular alumina and white corundum, while the fine and ultrafine fractions were made up of the following raw materials:

(1) Calcined alumina, synthetic spinel and calcium aluminate cement.
(2) Calcined alumina, magnesia and calcium aluminate cement.
(3) Calcined alumina, dolomite and calcium aluminate cement.

The refractory castables were elaborated with 5, 10, 15 and 20 wt% contents of synthetic spinel (labelled 8D). In the case of magnesia, calculations were made to ensure that once equilibrium had been reached at high temperature (1650 °C), the spinel contents were 5, 10, 15 and 20 wt% (the so-called 8DM). In the case of dolomite (labelled PKDOL) only the 5% composition coincided with 8D 5% and 8DM 5%, the other PKDOL compositions retaining similar magnesia contents. The calcium aluminate cement (CAC) content was kept constant for all compositions (8 wt%), except for those prepared with dolomite, where 2 wt% was used for PKDOL 5 and 10% and 1.5 wt% for the PKDOL 15 and 20% compositions, respectively. Fig. 1 shows the position of all the elaborated compositions.

The processing of these castables has been described in a previous work.[25] Bars of 25 mm × 25 mm × 150 mm were cast in metal molds and were cured at room temperature in air-tight containers for 24 h and then dried at 110 °C for another 24 h before firing.[3] The specimens subjected to the hot modulus of rupture measurements were tested in a three-point bend configuration with a span of 127.5 mm. In accordance with the ASTM C583-80 norm, they were tested at an imposed load rate of $13\,N\,s^{-1}$ in a high temperature testing machine (Instron, model 8562). In addition, some compositions were also tested at a constant imposed displacement rate of $0.002\,mm\,s^{-1}$. Three specimens were evaluated and the average value was taken.

2.2. Matrices

Considering that the matrix of the castables constituted by the finer grain sizes is the factor mainly responsible for the high temperature deformation of the castables, in this work the fraction with a grain size smaller than 125 μm was considered to be the matrix. Dry castable raw material mixtures were sieved under 125 μm and mixed with water (1.75–2.13 water/cement ratio). The samples were then cast using the same procedure as that described in a previous work.[25] Creep tests were performed with cylindrical specimens of height 40 mm, external diameter 30 mm and an internal hole of diameter 10 mm. A differential technique was employed to measure the deformation. The specimens were heated at a constant rate of 10 °C/min below 1000 °C and 5 °C/min up to the final temperature test. A soaking time of 30 min was maintained before testing and then a fixed load of 2 MPa was applied. Deformation under load versus temperature was recorded from room temperature up to 1100, 1200, 1300 and 1400 °C for all the matrices designed. The phase evolution with temperature was previously studied by X-ray diffraction (XRD).[25]

3. Results and discussion

3.1. Effect of spinel content on the hot modulus of rupture of the refractory castables

The hot modulus of rupture results (maximum load) for the Al_2O_3–spinel refractory castables (8D compositions 5, 20 wt% with synthetic spinel) are shown in Fig. 2. Fig. 2 shows that the results coincide almost totally. In general, there is an increase in the hot modulus of rupture with increasing temperature from 1000 to 1200 °C. Thereafter it decreases until 1400 °C. These results are not in agreement with those presented in the literature,[13,14] specially if one takes into account that the testing conditions, calcium aluminate cement content, etc., are not identical. It is not possible therefore to compare the results. Moreover, some of our hot bending tests were carried out under two different sets of conditions: some specimens were tested for both the imposed load rate and the constant displacement rate. The results (Fig. 3) show that these refractory castables exhibit high viscoplasticity at temperatures >1100 °C, their hot bending strength depending on the loading rate.[11] In fact the mechanical behaviour is not improved even with the addition of spinel. The effect of adding spinel is explained below, taking into account the factor of temperature and deformation.

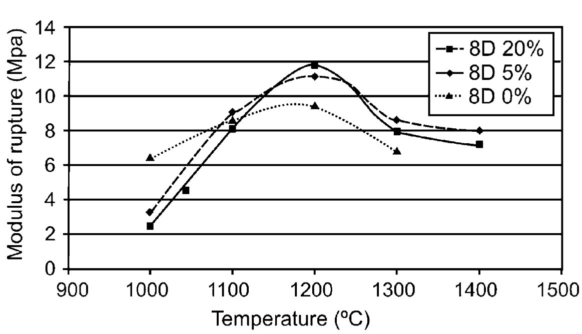

Fig. 2. Hot modulus of rupture results from the refractory castables made with synthetic spinel (5, 20 wt%) and without synthetic spinel.

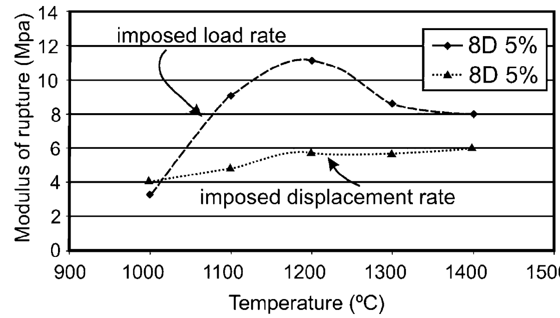

Fig. 3. Hot modulus of rupture results (8D 5% refractory castable composition) under two different conditions: constant imposed load rate ($13\,N\,s^{-1}$) and constant imposed displacement rate ($0.002\,mm\,s^{-1}$).

3.2. Effect of the processing route on the hot modulus of rupture of the refractory castables

The results do not show any significant differences (Fig. 4). There are two coincident values at 1000 and 1400 °C. However, between both temperatures, owing to the different vitreous phase contents of the refractory castables, the results are completely different. It is significant that the bending strength values of the 8DM materials are higher than those of the 8D compositions. This is because the 8DM castables exhibit greater viscoplasticity than the 8D refractory castables and because the imposed load rate yields higher values. The processing route influences the mechanical behaviour at high temperature between 1000 and 1400 °C. The refractory castables made with synthetic spinel are less viscoplastic than the 8DM and PKDOL materials in these temperature ranges.

3.3. Creep behaviour of the matrices

The study of creep behaviour in the matrices of the high alumina refractory castables was carried out bearing in mind the following variables:

(a) Processing route and temperature.
(b) Composition.

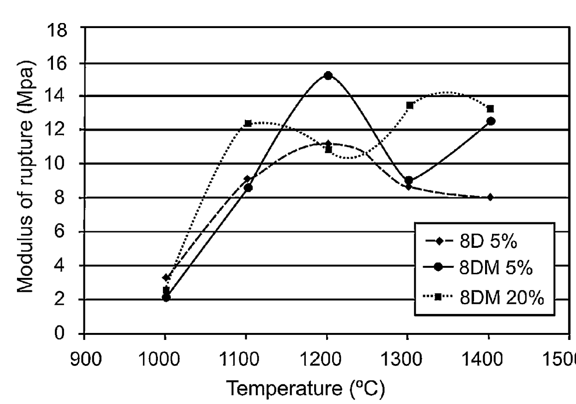

Fig. 4. Hot modulus of rupture results from the refractory castables made with periclase (8DM 5%, and 8DM 20 wt%).

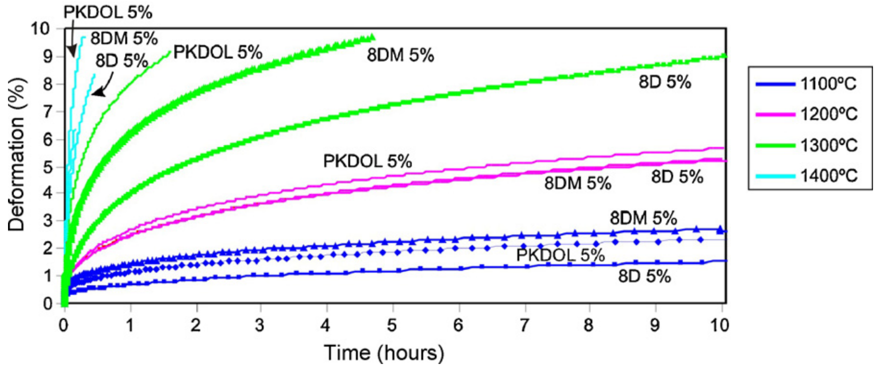

Fig. 5. Creep curves of the matrices of the 8D, 8DM and PKDOL refractory castables at different temperatures.

3.3.1. *Effect of the processing route and temperature on creep behaviour*

Fig. 5 shows the deformation of the matrices of the elaborated 8D, 8DM and PKDOL (5 wt% spinel content) refractory castables at different temperatures. These compositions were formulated at the same point in the Al_2O_3–MgO–CaO diagram ternary system and therefore they possess the same average chemical composition. The results (Fig. 6) present a similar behaviour up to 1200 °C but at 1300 °C the differences in the deformation rates are more apparent, principally in the first region of primary creep. The 8D 5% matrix composition reaches 9% deformation after 10 h, and 8DM 5% and PKDOL 5% after 3.5 and 1.5 h, respectively. However, tests carried out for longer periods of time show that once the stationary state is reached the deformation rate is similar in the three cases. This can be explained as follows:

(1) The load-relaxation tests conducted under compression at low initial stress (2 MPa) showed a marked relaxation with an increase in temperature, principally in the temperature range of 1200–1300 °C. This may be related to an increase in the amorphous phase content.[11]
(2) The lower invariant point in the Al_2O_3–MgO–CaO ternary diagram occurs at 1321 °C[26] and the impurities present in the periclase and dolomite raw materials possibly favour the appearance of the vitreous phase at a lower temperature than 1300 °C.

The amorphous phase content of some castables was also evaluated as a function of temperature by measuring the dissolution kinetics in a hydrofluoric acid (HF) solution.[27] Fig. 7 shows an overlapping of the phase evolution with temperature and the presence of an amorphous phase, corresponding to the 8D 10% matrix composition. Between 1200 and 1300 °C the process is different: $C_{12}A_7$ disappears completely, and before the formation of CA_6, CA dissolves and enters the vitreous phase. In addition, the sharpness of the X-ray diffraction Al_2O_3 peaks diminishes owing to the high amorphous grade of the material. Taking into account the above-mentioned changes two factors may explain the behaviour in the 1100–1400 °C temperature range:

(a) *Calcium aluminates*: CA_2 formation occurs due to a dissolution-precipitation process through a transitory liquid phase. At 1300 °C, there is no crystalline phase in the refractory castable (except for CA_2), that is able to keep the large grains together. Consequently, the matrix of the refractory is able to plastically absorb the marked expansion (13.6% relative volume increase) when CA_2 crystallizes. All the compositions, independently of the processing route, can be expected to be affected by the microstructural evolution of the calcium aluminate and by the appearance of a transitory liquid phase.
(b) *Presence of free MgO*: the transitory liquid phases formed from the synthetic spinel materials obtained are not of a ternary nature. At these temperatures, the kinetics of dissolution of the spinel is low. However, refractory castables with self-forming spinel, obtained by the addition of periclase and dolomite that react with alumina at high temperature, possess eutectic liquid phases with a low viscosity leading to an improvement in the viscoplastic process.

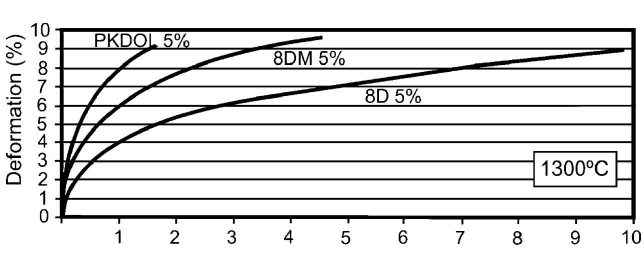

Fig. 6. Creep curves of the matrices results under a constant load (2 MPa) for the 8D, 8DM and PKDOL 5% matrices at 1300 °C.

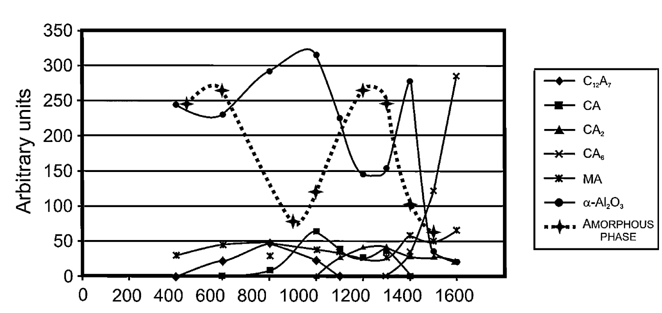

Fig. 7. Phase evolution with temperature and the amorphous phase content of the 8D 10% matrix composition.

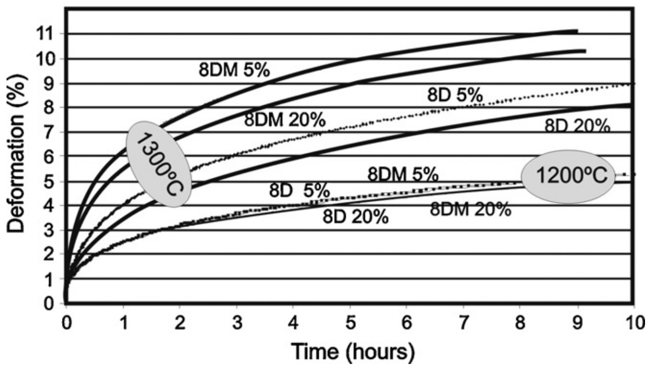

Fig. 8. Graph results for the deformation of the 8D 5, 8D 20, 8DM 5 and 8DM 20% matrices at 1200 and 1300 °C under compression.

3.3.2. *Effect of the composition (spinel content) on creep behaviour*

Fig. 8 shows the deformation curves of the 8D and 8DM matrices with extreme spinel compositions (5 and 20 wt%) at the temperatures of 1200 and 1300 °C. At 1200 °C the processing route and spinel content do not influence the deformation curves. However, at 1300 °C materials obtained with periclase show more deformation in the first part of primary creep. In both the 8D and 8DM concretes the spinel content seems to decrease slightly in this first region of deformation. However, at the second deformation stage of creep the rate is practically the same independently of the processing route or the spinel content. The PKDOL matrix compositions are situated in different compatibility triangles to the 8D and 8DM matrix compositions except for PKDOL 5%. At 1100 and 1200 °C the behaviour is similar for these materials (Fig. 5). At 1300 °C significant differences can be observed. Matrices with additions of dolomite present considerable deformation in the first region of primary creep compared to the 8DM and 8D matrix compositions. It seems that free MgO and CaO oxides have a significant influence on the viscosity of the vitreous phase at these temperatures.

4. Conclusions

All the data presented above lead to the following conclusions:

(a) At temperatures above 1000 °C, the refractory castables elaborated exhibit considerable viscoelastic–plastic behaviour. The hot bending strength at these temperatures depends on the loading rate and the results (maximum tension) have no real meaning.
(b) At temperatures between 1100 and 1400 °C, neither the spinel content nor the processing route chosen to make the castables influence the hot bending tests.
(c) The main microstructural evolution of high alumina refractory castables with temperature occurs during the first part of primary creep. There is significant plastic deformation at lower temperatures than 1100 °C. The $CA + A \rightarrow CA_2$ is the fundamental reaction governing deformation in this region. This is produced through a dissolution–precipitation mechanism in the transitory liquid phase. Consequently, the material experiences more or less deformation depending on its progress at the time of the reaction.
(d) When the reaction terminates at approximately 1300 °C, depending on the location of the matrix composition castable in the Al_2O_3–MgO–CaO ternary diagram system, the materials possess mainly CA_2 and Al_2O_3 and exhibit the same rate of deformation, independently of the processing route. Both the synthetic and the self-forming spinels play a secondary role in the deformation mechanism.
(e) Between 1100 and 1200 °C, the deformation creep curves of all the refractory castables elaborated are similar. But at 1300 °C the castables begin to show further deformation: first those made with dolomite, then those elaborated with magnesia and finally those made with synthetic spinel. This is related to the appearance of a transitory liquid phase in the Al_2O_3–MgO–CaO ternary diagram system at this temperature (first eutectic point of the ternary system).

Acknowledgment

The authors wish to thank the European Union for its support under a Brite Euram Project, Contract No. BRPR-CT 97-0427.

References

1. Banerjee, S. and Abraham, T., Changing the face of the global refractories industry. *Am. Ceram. Soc. Bull.*, 1999 (May), 55–58.
2. De Aza, A.H., Diseño y desarrollo de materiales de alta alúmina con matrices de espinela y hexaluminato de calico. Unpublished Ph.D. Thesis, Universidad Autónoma de Madrid, Spain, 1997, p. 408.
3. Díaz, L.A., Materiales refractarios monolíticos de alta alúmina dentro del sistema Al_2O_3–MgO–CaO. Unpublished Ph.D. Thesis, Universidad Autónoma de Madrid, Spain, 2000, p. 238.
4. Díaz, L. A., Torrecillas, R., De Aza, A. H. and Pena, P., Effect of spinel content on slag attack resistance of high alumina refractory castables. *J. Eur. Ceram. Soc.*, 2007, **16**, 4623–4631.
5. Homeny, J. and Bradt, R. C., Aggregate distribution effects on the mechanical properties and thermal shock behavior of model monolithic refractory systems. In *Advances in Ceramics, New Developments in Monolithic Refractories, vol. 13*, ed. Robert E. Fisher. The American Ceramic Society, 1985, pp. 110–130.
6. Poon, C. S., Wassell, L. E. and Groves, G. W., High strength refractory aluminous cement. *Br. Ceram. Trans. J.*, 1987, **86**, 58–62.
7. Takahashi, N., Ishikawa, M. and Watanabe, K., The deformation behavior of low cement castables. Taikabutsu Overseas. In *Abstracts of the 10th Annual Colloquium of TARJ*, 1997, p. 96.
8. Mac Zura, G., Madono, M., Kriechbaum, G. W. and Sewell, B., Low moisture regular corundum/spinel castables with superior properties. In *Proceedings of Unified International Technical Conference on Refractories (UNITECR)'95*. Edited by The American Ceramic Society, Westerville, OH, 1995, pp. 179–186.
9. Dedenis, P., Le Doussal, H. and Meunier, P., Comportement Thermomécanique de Bétons Réfractaires Soumis à des Contraintes de Compression. *L'industrie Céramique et Verrière*, 1998, **935**, 178–182.
10. Nonnet, E., Lequeux, N. and Boch, P., Elastic properties of high alumina cement castables from room temperature to 1600 °C. *J. Eur. Ceram. Soc.*, 1999, **19**, 1575–1583.
11. Simonin, F., Olagnon, C., Maximilien, S., Fantozzi, G., Díaz, L. A. and Torrecillas, R., Thermomechanical behavior of high-alumina refractory castables with synthetic spinel additions. *J. Am. Ceram. Soc.*, 2000, **83**(10), 2481–2490.

12. Gajda, J. and MacGee, T. D., Elastic properties of calcium aluminate cement based concrete. *Am. Ceram. Soc. Bull.*, 1997, **76**(4), 81–85.
13. Chan, C. F. and Ko, Y. C., Effect of CaO content on the hot strength of alumina-spinel castables in the temperature range of 1000°–1500 °C. *J. Am. Ceram. Soc.*, 1998, **81**(11), 2957–2960.
14. Ko, Y. C. and Chan, C. F., Effect of spinel content on hot strength of alumina-spinel castables in the temperature range 1000–1500 °C. *J. Eur. Ceram. Soc.*, 1999, **19**, 2633–2639.
15. Simonin, F., Comportement thermomécanique de bétons réfractaires alumineux contenant du spinelle de magnesium. Unpublished Ph.D. Thesis, National Institute of Applied Sciences (INSA), Lyon, France, 2000, 166 p.
16. Simonin, F., Olagnon, C., Maximilien, S. and Fantozzi, G., Room temperature quasi-brittle behaviour of an aluminous refractory concrete after firing. *J. Eur. Ceram. Soc.*, 2002, **22**, 165–172.
17. Chan, C. F., Huang, F. J. and Ko, Y. C., Refractoriness under load of alumina-spinel castables. *Interceram*, 1997, **46**(2), 86–89.
18. Bray, D. J., Smyth, J. R. and McGee, T. D., Creep of 90+% Al_2O_3 refractory concrete. *Am. Ceram. Soc. Bull.*, 1980, **59**(7), 706–710.
19. Bray, D. J., Smyth, J. R. and McGee, T. D., Thermal/strain history on creep of refractory concrete. *J. Am. Ceram. Soc.*, 1982, **65**(6), 275–280.
20. Bray, D. J., Smyth, J. R., McGee, T. D. and Kim, G. D., Effect of cement content of refractory on the creep of a 90+% Al_2O_3 refractory concrete. *Am. Ceram. Soc. Bull.*, 1984, **63**(2), 287–289.
21. Liu, C. H., Mendoza, J. L. and Moore, R. E., Effect of dopants on the creep behavior of low and ultra-low cement refractory concretes. *Ceram. Eng. Sci. Proc.*, 1987, **8**(1–2), 1–8.
22. Lundeen, B. E. and McGee, T. D., Primary creep analysis of a commercial low cement refractory castable. In *Advances in Refractories Technology, Ceramic Transactions*, *vol. 4*, ed. R. E. Fisher. The American Ceramic Society, Westerville, OH, 1989, pp. 312–324.
23. Liu, C. H., Mendoza, J. L. and Moore, R. E., Effect of stress/strain history on the creep behavior of low cement refractory concretes. In *Advances in Refractories Technology, Ceramic Transactions*, *vol. 4*, ed. R. E. Fisher. The American Ceramic Society, Westerville, OH, 1989, pp. 325–340.
24. Rendtel, A., Hubner, H., Rodrigues, J. A. and Pandolfelli, V. C., Interpretation of the creep behavior of low-cement refractory castables based on the properties of the interaggregate glassy phase. In *Proceedings of Unified International Technical Conference on Refractories (UNITECR)'97*. Edited by The American Ceramic Society, Westerville, OH, 1997, pp. 71–80.
25. Díaz, L. A., Torrecillas, R., De Aza, A. H., Pena, P. and De Aza, S., Alumina-rich refractory concretes with added spinel, periclase and dolomite: a comparative study of their microstructural evolution with temperature. *J. Eur. Ceram. Soc.*, 2005, **25**, 1499–1506.
26. Majumdar, A. J., The quaternary phase in high-alumina cement. *Trans. Br. Ceram. Soc.*, 1964, **63**(7), 347–364.
27. Murat, M., Arnaud, Y., El Moussaouiti, M. and Comel, C., Determination des teneurs en alumino-silicates cristallises et amorphes dans les cendres volantes et mullites synthetiques. *Silic. Ind.*, 1984, **6**, 127–135.