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# Effect of SiC–graphite–Al-metal addition on low- and ultra-low cement bauxite castables

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## Abstract

Eight batches of low- and ultra-low cement castables were prepared from calcined Chinese bauxite and high alumina cement (HAC). The effect of alumina-cement replacement by SiC, graphite and aluminum metal on the sinterability and properties of these castables was investigated. Physical properties such as bulk density and apparent porosity of hydrated and sintered castables were studied. The sintered castables were also characterized for their solid phase compositions and microstructure using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. In the castables containing SiC, new phases such as mullite ($3Al_2O_3 \cdot 2SiO_2$), SiC, and quartz ($SiO_2$) were formed at the expense of calcium aluminate phases (i.e. CA and $CA_2$; the main cement phases). Generally, the bulk density of the control castable sample was the highest among all prepared samples, while the batches containing graphite showed the lowest bulk density. The presence of Al-metal reduced the oxidation of SiC and consequently increased the densification of the castables compared with castables containing graphite only. Cold crushing strength (CCS) of the hydrated specimens i.e. green castables, decreased as the additives contents increased at the expense of HAC which is responsible for the bonding at room temperature. The highest CCS value of the sintered castable was obtained for the sample containing 6 wt.% SiC, 3 wt.% CA and 0.5 wt.% Al-metal.

*Keywords:* D. SiC; Castables; Ultra-low cement; Bauxite

## 1. Introduction

Recently, there was a great deal of interest in improving the quality of refractory castables through decreasing the aluminous cement content; i.e. 4–8% cement for low cement castables (LCC), 1–3% cement for ultra low cement castables (ULCC), or <1% cement for zero cement castables (ZCC) [1–4]. Advanced refractory castables (LCC and ULCC) are complex mixtures of calcium aluminate cement, ultra fine materials, aggregates and admixtures. These castables develop very high performance during and after heating. They are used when thermal shock resistance or resistance against abrasion and corrosion by slag or melted metals are required. These castables require good control installation, i.e. rheology and hardening kinetics, which are influenced not only by the intrinsic reactivity of the calcium aluminate cement, but also by the interactions between fillers and calcium aluminate cement [5–9].

The attraction of low cement and ultra low cement castables for refractory applications is due to their high strength, thermal shock resistance, corrosion resistance, and their economic effect derived from the use of natural bauxite resources. They have already been successfully employed in molten iron torpedo cars, blast furnace troughs and incinerator linings and may yet acquire wider applications in high temperature industries. Recently, a group of additives was appeared in the refractory industry that triggered a new prospect for castable producers. The additives comprise ultra fine particles, for example silica, alumina, mullite, spinel and SiC.

In previous investigations [10–16], lower amount of cement, in conjunction with fine grain-sized materials having high surface area and dispersing aids, were used. Those materials were silica fume, $Al_2O_3$, $Cr_2O_3$, $ZrO_2$, $TiO_2$, SiC, clay mineral and carbon. It was concluded that the presence of such

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materials promote refractory properties such as volume stability and well balanced physical and hot mechanical properties. The presence of zircon with fine alumina as a filler tends to form mullite/$ZrO_2$ composite after firing. The formation of mullite and zirconia is of vital importance as these bonding phases exhibit high refractoriness, low creep rate, low thermal expansion, good chemical and thermal stability, and good toughness and strength [17,18].

Nowadays, low and ultra low cement castables containing SiC have gained wide acceptance as materials for hot metal and slag runners. Silicon carbide is being introduced to enhance the thermomechanical properties of the composite under operating conditions. Some authors studied high temperature strength and thermal shock of ultra low cement castables in relation to their microstructure feature. These castables have been composed of SiC-containing bauxite. They found that castable specimens had significantly improved in hot modulus of rupture at 1400 °C [17–19]. However the problem of SiC oxidation limits its presence in refractory castables. The aim of the present work is to investigate the effect of SiC, graphite and Al-metal on the sintering and properties of bauxite castables.

## 2. Materials and experimental procedures

### 2.1. Materials

In this investigation, graded calcined Chinese bauxite (65 wt.% coarse; 2.36–0.6 mm, 10 wt.% medium; 0.60–0.25 mm, and 25 wt.% fine; <0.25 mm) was used as starting aggregate. A constant weight i.e. 90 wt.% of the graded aggregate together with 10 wt.% of high alumina cement (Lafarge, C-80) was used to prepare the control castable batch. Another different castables batches were prepared with substituting the aluminous cement by some additives such as SiC, graphite and aluminum metal. The batch compositions of the starting materials are given in Table 1. The prepared castable samples are designed as No., 0, 1, 2, 3, 4, 5, 6, 7, and 8.

### 2.2. Preparation and characterization

The dry mixes were hand mixed for 3 min at 25 °C with an adequate amount of water, which was determined for each batch according to the standard ‘‘good ball in hand’’ test. The mixed batches were then casted into cubes of 25 mm side length in steel molds using a vibrating table at a frequency of 50 Hz and 4 min vibrating time. The castable samples were left in their molds for 24 h in a 100% relative humidity cabinet. The hydrated samples were then de-molded and further cured for 48 h under water in the same cabinet. The samples were fired at 1500 °C for 2 h. The hydrated and fired samples were subsequently tested for their bulk density (BD) and apparent porosity (AP) by Archimedes method according to ASTM standard C133-91 and Egyptian standard 1859 (1990). The fired castables were also characterized for their solid phase compositions using a Philips 1730 X-ray diffractometer with Ni filtered Cu $K_\alpha$ radiation at a scan speed of $1°2\theta\ \mathrm{min}^{-1}$. A Joel JSM- T 330 scanning electron microscopy (SEM) was used to examine the microstructure of the fired samples. Cold crushing strength (CCS) of the hydrated and fired castbles was carried out using a hydraulic machine of SEIDNER, Riedlinger, Germany, having a maximum loading capacity of 600KN. For determining the physical properties (BD & AP) and CCS of hydrated and fired castables, five samples were tested and the average reading values were recorded.

Table 1
Batch composition of the prepared castables.

| Batch No. | Batch composition | | | | |
|---|---|---|---|---|---|
| | SiC | CA | Graphite | Al-metal | Aggregate |
| 0 | – | 10 | – | – | 90 |
| 1 | 8 | 5 | 2 | 0.5 | 84.5 |
| 2 | 6 | 5 | 2 | 0.5 | 86.5 |
| 3 | 8 | 3 | 2 | 0.5 | 86.5 |
| 4 | 6 | 3 | 2 | 0.5 | 84.5 |
| 5 | 8 | 5 | – | 0.5 | 86.5 |
| 6 | 6 | 5 | – | 0.5 | 88.5 |
| 7 | 8 | 3 | – | 0.5 | 88.5 |
| 8 | 6 | 3 | – | 0.5 | 90.5 |

## 3. Results and discussion

### 3.1. Phase composition

Figs. 1 and 2 show XRD of the investigated castable samples fired at 1550 °C. It appears that the control castable sample [free from additives (batch No. zero)] composed mainly of α-alumina (corundum), with minor CA and $CA_2$ minerals resulting from the polymorphous conversion of the calcium aluminate hydrated products into their original phases. Fig. 1 exhibits XRD of the batches No. 1, 2, and 3, while Fig. 2 shows XRD of the batches 5, 7 and 8 compared with the control batch (batch No. zero). In both castable series, as we proceed from low to high batch number, the peak intensities of CA or $CA_2$ phases have decreased. In the same time, a new line characterizing mullite ($3Al_2O_3\cdot 2SiO_2$), SiC, and quartz ($SiO_2$) phases are detected. This means that after firing at 1550 °C, a part of SiC is oxidized into silica and some of the librated silica has been reacted with fine alumina from the matrix resulting in mullite formation, while the other part of SiC could persist against oxidation. This could be explained as follows; on firing up to 1550 °C, some of SiC were oxidized librating $SiO_2$. The librated $SiO_2$ formed a layer around the remaining SiC grains, and providing a protection against further oxidation. The amount of SiC was more pronounced in the batches No. 2 and 3.

### 3.2. Physico-mechanical properties

#### 3.2.1. Water of consistency

Fig. 3 shows water of consistency of the investigated castable samples prepared from bauxite. The water addition to castables has a significant and direct influence on the final properties and castable specifications. Excess water can reduce strength and increase shrinkage, while little water can produce

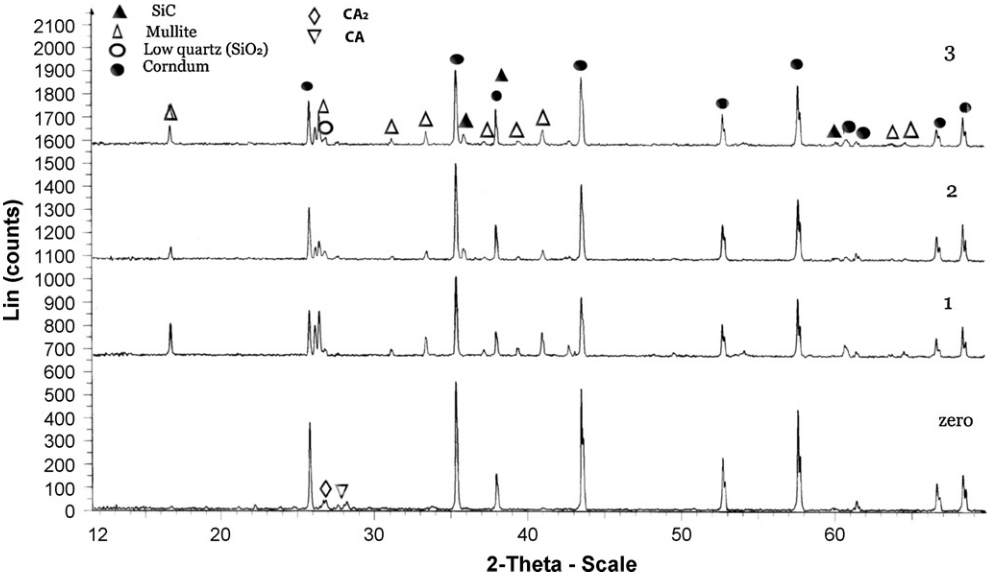

Fig. 1. XRD of sintered refractory castables at 1550 °C (batches no. 0, 1, 2, and 3).

voids in the castables, cause poor consolidation and produce a weak porous concrete. Fig. 3 exhibited a significant decrease in water consistency as the cement content in the matrix has decreased (which is the only cementing materials consuming water under going hydration) i.e. water consistency has decreased from batch No. 0 to 7.

### 3.2.2. *Bulk density and apparent porosity*

The densification parameters i.e. density and porosity of the hydrated castables were found to be in the range of 2.4–2.6 g/cm$^3$ and 20–30%, respectively, depending on the amounts of high alumina cement and the type of additives. Fig. 4 shows the densification parameters i.e. bulk density (BD) and apparent porosity (AP) of investigated castables series after firing at 1550 °C. Generally, the control sample exhibited the highest density and lowest porosity as compared with all prepared samples. Also, the batches No. 5, 6, 7 and 8 showed higher bulk density than the other series (No. 1, 2, 3, &4) and lower than the control sample. The higher value of BD for the sample No. 5, 6, 7 and 8 is due to the presence of Al-metal which lowers the oxidation of SiC. The apparent porosity proceeds oppositely to the bulk density. The lower bulk density of all samples compared with the control sample is due to the relatively oxidation of SiC and graphite. The oxidation of such SiC and graphite may form some carbon-containing gases; some of which could be trapped with the possibility of voids formation and consequently density inhibition. Each of them may improve the thermo-mechanical properties of the castables despite of their effect on lowering the density.

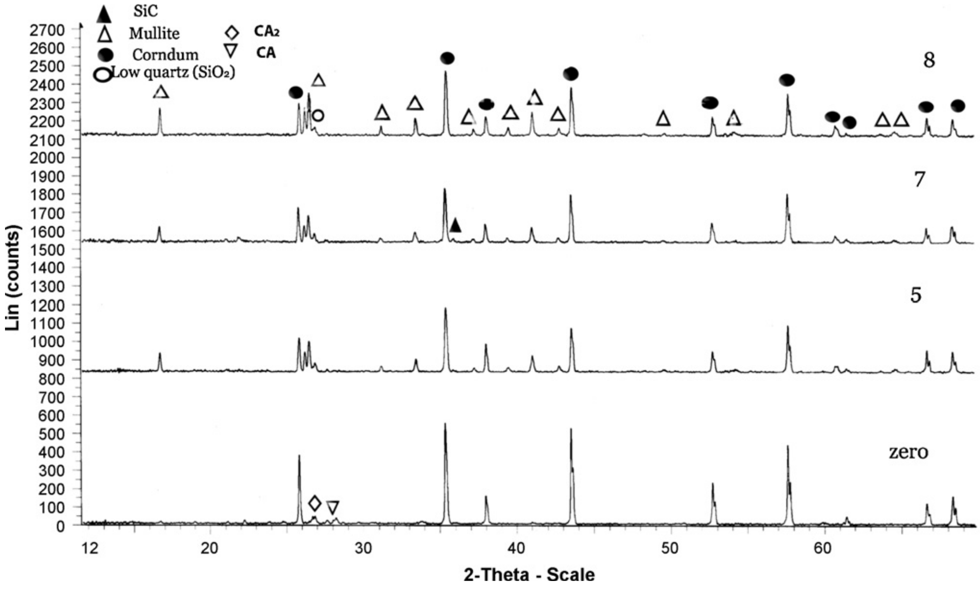

Fig. 2. XRD of sintered refractory castables at 1550 °C (batches no. 0, 3, 5, and 7).

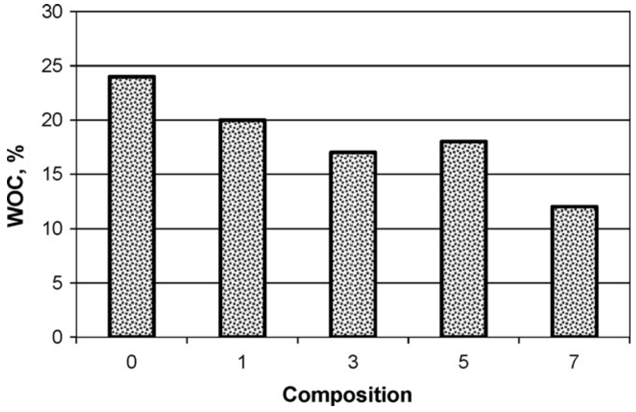

Fig. 3. Water consistency of the investigated castable samples.

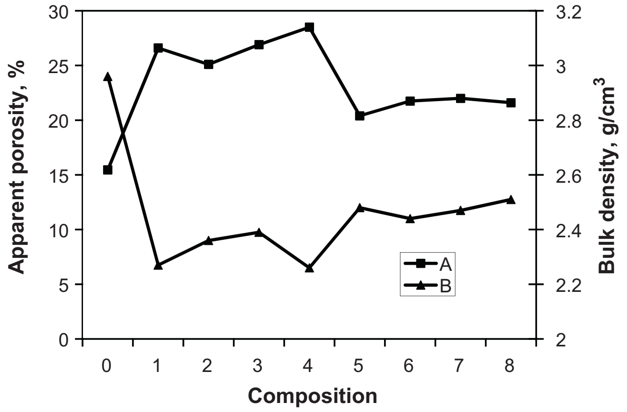

Fig. 4. Densification parameters of the prepared castables fired at 1550 °C.

### 3.3. Microstructure

The microstructural evolution of castables fired at 1550 °C was examined using scanning electron microscopy of representative regions of fractured specimens. Fig. 5 depicts SEM photomicrographs of castables after firing at 1550 °C for 2 h. SEM photomicrographs (Fig. 5a and b) of control castable exhibit densely packed microstructure with an abundant corundum grains of comparable sizes, euhedral and hexagonal, embedded in the matrix. The matrix is also included CA and some of liquid phases. Fig. 5c–f shows photomicrographs of castables No. 1, 3, 5, and 7, respectively. As we proceed from micrograph c to f, some needle-shaped mullite beside alumina grains appeared in the microstructure. The presence of such in

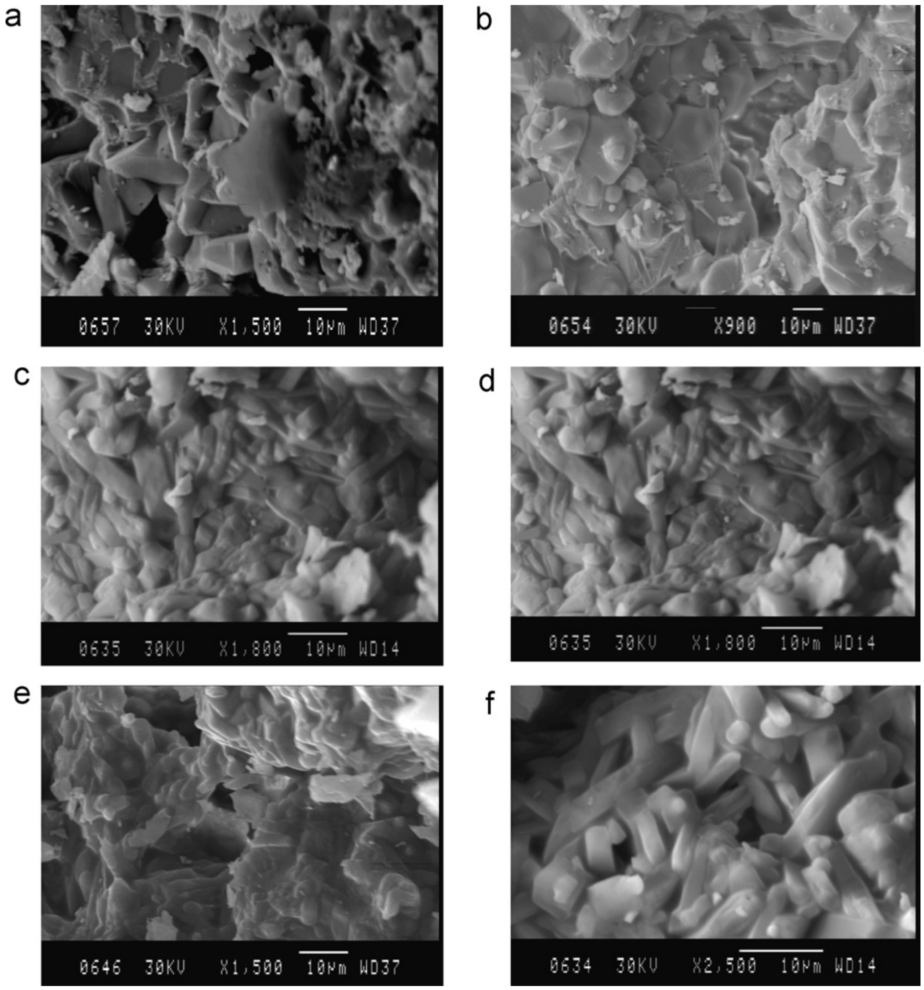

Fig. 5. Misconstrue of the prepared castables fired at 1500 °C [(a and b) batch no. 0, (c) no. 1, (d) no. 3, (e) no. 5 and (f) no. 7].

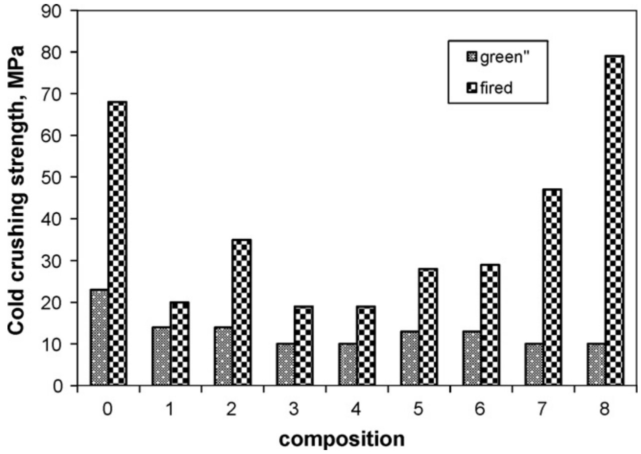

Fig. 6. Cold crushing strength of green and fired castables at 1550 °C.

situ formed phase (mullite) had given interlocking nature of such castables and reinforced the matrix confirming the high strength and refractory properties of castables. On the other hand, the impurities and aluminous cement presented in the castables (especially higher content-HAC batches), may form a low melting glassy phases which tend to decrease the refractory properties and their microstructure may appear as partially diffused structure in some regions. The influence of trace impurities presented during the processing of ceramics is well known and exploited in the control of densification, grain growth and morphology during sintering. The ability to control microstructure is important for achieving desired properties.

### 3.4. Mechanical properties

Mechanical property i.e. cold crushing strength (CCS) of hydrated (20 °C) and fired (1550 °C) investigated castables series is shown in Fig. 6. It can be seen that CCS of the hydrated specimens i.e. green castables, has decreased with increasing the additives contents at the expense of HAC which is responsible for the bonding on cold. Generally, for the fired castables, considerable value of strength was obtained for the intermediate batches after which a great improving in strength was obtained (batches 7 and 8). This is certainly due to the breakdown of weak hydraulic bonds and arising of new strong ceramic bonds on firing. A part of SiC was oxidized releasing $SiO_2$, some of this $SiO_2$ reacted with fine alumina from the matrix, resulting in mullite formation which is characterized by its high mechanical properties. This was reflected on the strength of the whole castable sample. The remaining part of $SiO_2$ has formed a thin layer around SiC to provide protection against oxidation. This layer is sintered only at temperatures >1250 °C so that the oxidation process is slowed down. The figure shows a great increase in the strength of the batches 2, 7 and 8. The increase in the content of non oxidized SiC, and formed mullite, explains the pronounced improvement in strength of the fired samples. The impurities in the bauxite aggregate increase the liquid phase sintering and decrease the porosity which consequently increases the mechanical properties. Also, the presence of higher content of mullite (as indicated from XRD Fig. 2) in the castables has improved the mechanical properties at that firing temperature.

One of the most important problems of carbon-bearing refractories is the oxidation of carbon at high temperature. The outstanding properties of materials disappear with the oxidation reaction, and the materials are destroyed. To prevent the oxidation and improve high temperature strength, the powder of antioxidant (20–150 μm) has to be added to the matrix region of materials, for example, Al, Mg, Si, their alloys carbides (SiC, $B_4C$ and $Al_4SiC_4$) and nitrides ($Si_3N_4$ and BN). So, in the present work, the addition of Al metal effectively inhibited the oxidation with possibility of $Al_4SiC_4$ formation as antioxidant.

The highest CCS value was obtained for the sample containing 6 wt.% SiC, 3 wt.% CA and 0.5 wt.% Al-metal. That composition is considered an optimum one compromising the bulk density and CCS.

## 4. Conclusion

It is concluded that the castables containing SiC, formed new phases such as mullite ($3Al_2O_3{\cdot}2SiO_2$), SiC, and quartz ($SiO_2$) at the expense of CA and $CA_2$, main cement phases. Generally, the densification parameters (bulk density and apparent porosity) of the control castable sample were the best among all prepared samples, while the batches-containing graphite showed the lowest bulk density. The presence of Al-metal lowered the oxidation of SiC and consequently increased the densification of these castables compared with castables containing graphite only. Cold crushing strength (CCS) of the hydrated specimens i.e. green castables, decreased as the additives contents increased at the expense of high alumina cement (HAC) which is responsible for the bonding on cold. The highest CCS value was obtained for the sample containing 6 wt.% SiC, 3 wt.% CA and 0.5 wt.% Al-metal. The presence of graphite had a negative effect on the properties of the prepared castables.

## References

[1] M.F. Zawrah, N.M. Khalil, Effect of mullite formation on properties of refractory castables, Ceram. Int. 27 (2001) 689–694.

[2] B. Clavaud, J.P. Radal, A new generation of low-cement castables, in: R.E. Fisher (Ed.), Advances in Ceramics, vol. 13, New Development in Monolithic Refractories, Am. Ceram. Soc., Columbus, OH, 1985 , pp. 274–282.

[3] L. Prost, A. Pnillac Hydraulically setting refractory compositions, Fr. Pat. No. 6,934,405, 1969.

[4] B. Myhre, Strength developments of bauxite-based ultra low cement castables, Am. Ceram. Soc. Bull. 73 (5) (1994) 68–73.

[5] U. Schumaher, Untersuchungen an Zementarmen und Ultrafalishen Korundfeuerbetones PhD thesis, Rheinisch-Westfalishen Technishen Hohschule, Aachen, FRG, 1988.

[6] A. Mathieu, A. Campas, J. Bayoux, D. Richon, Calcium aluminate cement and reactive alumina, UNITECR'93 Congress, Sao Paulo, Brazil, pp. 672–682.

[7] B. Myhre, Hot strength and bond-phase reactions in low and ultra-low cement castables UNITECR'93 Congress, Sao Paulo, Brazil, pp. 583–594.

[8] M.F. Zawrah, N.M. Khalil, High alumina castables reinforced with SiC, Adv. Appl. Ceram. 104 (6) (2005).

[9] M.A. Serry, M.F. Zawrah, N.M. khalil, Bauxite-based low and ultralow cement castables, Br. Ceram. Trans. 101 (4) (2002) 165–168.

[10] L. Zaigeng, Z. Luning, Y. Guotian, Z. Ninheng, The effect of some ultra fine oxides on the properties of ultra low cement corundum based castables, in: 35th International Colloquium on Refractories, Aachen, 1992.

[11] G. Maczura, J. Kopanda, F. Rohr, Calcium aluminate cements for emerging castable technology, in: R.E. Fisher (Ed.), Advances in Ceramics, vol. 13, New Development in Monolithic Refractories, Am. Ceram. Soc., Columbus, OH, 1985, pp. 285–304.

[12] A. Hundere, B. Myhre, On the influence of superfine in high-alumina castables, in: 39th International Colloquium on Refractories, Aachen, 1996.

[13] A. Hundere, B. Myhre, Effect of different finest fractions ($SiO_2$ and/or $Al_2O_3$) in alumina based ultra low cement castables, in: Am. Ceram. Soc. 98th Annual Meeting Indianapolis, 14–17 April 1996, 1996.

[14] B. Sandberg, B. Myhre, J.L. Holm, Castables in the system $MgO–Al_2O_3–SiO_2$, UNTECR'95, Kyoto, Japan, November 19–23, 1993.

[15] B. Myhre, Microsilica in alumina based ultra low cement castables; the effect of microsilica addition on flow, in: 23rd ALAFAR Congress in Puerto Vallara Mexico, 6–10 November 1994, 1994.

[16] B. Myhre, Ultra low cement; casting and set properties of secar cements with additives, in: 20th ALAFAR Congress, Chile, 1990.

[17] B. Myhre, Cement free castables in the system $MgO–SiO_2$; the effect of bond phase modifier on strength, in: Am. Ceram, Soc., 93rd Annual Meeting in Cincinnati, Ohio, 15 May 1991, 1991.

[18] E. Yu, Piviniski, New refractory concrete and bonding systems, Refrac. Ind. Ceram. 39 (314) (1998) 91–99.

[19] W. Kronert, U. Schumacher, Use of low-cement and ultra low cement refractory castables in iron and steel industry furnace prospect Interceram, Aachen Proc. 1988 3 (8) (1989) 12–18.