Journal of Ceramic Processing Research. Vol. 8, No. 5, pp. 324~330 (2007)

J O U R N A L O F
Ceramic Processing Research

Improvement of properties of self-flowing low-cement castables based on brown-fused alumina

Cem Göğtaş[a], Akın Odabaşı[a], Levent Sezer[a], Filiz Çınar[b], Şule Güner[c], Niyazi Eruslu[a] and Necip Ünlü[a]*

[a] *Istanbul Technical University, Metallurgical and Materials Science Engineering Department, 34469 Maslak, Istanbul, Turkey*
[b] *Istanbul Technical University, Prof. Dr. Adnan Tekin High Technological Ceramics and Composites Research Center, 34469, Maslak, Istanbul, Turkey*
[c] *Refsan Refrakter ve Insaat Ltd. Sirketi, Sultan Selim Cad. Ucar Sok. No:10/A, 34330, 4. Levent, Istanbul, Turkey*

A new self flowing brown-fused alumina based castable with 5 wt.% cement has been developed. An Andreason mathematical model (q=0.25) was used to adjust the granulometric particle size distribution. To achieve optimum self-leveling flowability, 5.6% water was used. The main physical and mechanical properties of the present castable were studied. Phase analysis using X-ray diffraction (XRD), scanning electron microscopy (SEM) and apparent porosity (AP), bulk density (BD), water absorption (WA), cold crushing strength (CCS), hardness, and self-leveling flowability were investigated as a function of the firing temperature. The castable exhibited low AP and WA, and high CCS values with an increase in the firing temperature as a result of the corresponding phases.

Key words: Workability, Cement, Refractory castable, Mechanical properties, Characterization.

Introduction

A great interest in developing new refractory compositions has continued since Sainte-Claire Deville, who was the first producer of refractory concrete high temperature crucibles sometime before 1856 [1, 2]. Throughout the last 36 years, a number of research and development (R&D) studies have been performed by castable refractory manufacturers to produce castables with lower production and application costs, versatility, and performance at high temperatures [3]. As a result of those R&D investigations through decreasing the cement content, low cement castables (LCCs) and ultra-low cement castables (ULLCs) [4-6] which have superior physical properties (i.e., high density, low porosity, high cold and hot strengths and high abrasion and corrosion resistance) than those of the conventional ones, have been inserted into the severe applications of high performance castables. In the mid 1980s, self-flowing castables (SFCs), which are LCCs or ULLCs with a consistency after mixing that allows them to flow and degas without application of vibration, has joined into the family of refractory concretes [1, 7-9]. However, despite these characteristics and a wide variety of compositions of the self-flow technology, ranging from fused silica and bauxite-based ones to high alumina and silicon carbide-based castables, have been studied since 1980s [6, 10, 11], the development of SFCs with improved flow characteristics and their physical properties is underway. This study focuses on developing the quality of self-flowing refractory castables through the preparation of a brown-fused alumina (BFA)-based castable with a low cement content.

*Corresponding author:
Tel : +90 212 285 3382
Fax: +90 212 285 2925
E-mail: unlu@itu.edu.tr

Methodology

Brown-fused alumina from Qing dao Asian Minerals Co. Ltd. China (Al_2O_3-96.25, Fe_2O_3-0.14, TiO_2-2.64, SiO_2-0.90 wt.%), calcined alumina from Eczacibasi Doga Madencilik San. Ve Tic. A.S. Turkey (Al_2O_3-99.50, Fe_2O_3-0.02, TiO_2-0.006, SiO_2-0.018, Na_2O-0.030 wt.% surface area-0.8 m^2/gr, density-3.9 g/cm^3), rotary bauxite from Qing dao Asian Minerals Co. Ltd. China (Al_2O_3-88.30, Fe_2O_3-1.48 wt.%, density 3.32 g/cm^3), microsilica 920D from Elkem Refractories, Norway (SiO_2-92.4, H_2O-0.4, L.O.I.-0.98 wt.%), cement Secar71 from Lafarge, France (Al_2O_3-72.7, Fe_2O_3-<0.3, TiO_2-<0.8, Na_2O+K_2O-<0.6, MgO-<0.3,CaO-29.2 wt.%, density-3.0 g/cm^3) and dispersant Darvan7S (D7S) from R.T. Vanderbilt Company, Inc., USA were used as starting materials. Table 1 shows the chemical composition of the investigated self-flowing low cement castable. According to Andreasen's packing model [12], the particle size distribution (q=0.25) of this composition was adjusted to a theoretical curve. Experiments have shown that 5.6 wt.% water is satisfactory to obtain a self-flowing well-dispersed castable system. The components of the castable were dry mixed for 4 minutes, then the castable suspension was prepared by

Table 1. Composition (in wt %) and self-flowability of the self-flowing low-cement castable

Brown-fused alumina	
3-5 mm	16
1-3mm	22
0-1mm	31
Calcined alumina HTM 30	10
Rotary bauxite	
0-0.063 mm	8
Microsilica 920D	8
Cement Secar71	5
Dispersant D7S	0.05
Water	5.6
Self-flowability (%)	150

mixing 5.6 wt.% water in a Hobart Model mixer for another 4 minutes. Flow value measurements were performed by pouring the castable suspension into the truncated flow cone as described in ASTM standard C230. The working time of the self-flowing brown-fused alumina castable was measured according to ASTM C1446-99. For the physical tests such as apparent porosity (AP), bulk density (BD), water absorption (WA) and cold crushing strength (CCS), the samples were cast by a simple tapping technique with cube-type moulds (50 mm), then cured for 24 h at room temperature (25 °C). After demoulding, these samples were dried at 110 °C for 24 h then fired at different temperatures (1000, 1200 and 1500 °C) for 2 h (Fig. 1) and furnace-cooled. DIN 51056 was used to determine the apparent porosity (AP), bulk density (BD) and water absorption (WA) of the samples. The cold crushing strength (CCS) was measured by a Naber Model press according to DIN 51067. Five samples were tested for each different temperature and their standard deviations calculated. After the tests of CCS, to determine the phase formation of the samples fired at 110 °C for 24 h and 1000, 1200 and 1500 °C for 2 h, the fractured samples were crushed and sieved to –90 μm size for X-ray diffraction (XRD) analysis. A Rigaku model diffractometer with Ni filtered Co K_α radiation operating at 40 kV and 30 mA and a scanning interval 2θ between 10° and 80° was used. A microstructural evaluation of the fired castable samples was made with a JEOL JSM-T330 scanning electron microscope operated at 15 kV and linked with an energy dispersive spectrometry (EDS) attachment. The surfaces of the mounted samples were mechanically polished with 60-, 120-, 180-, 240-, 320-, 600-, 800-, and 1200-grit silicon carbide abrasive papers and then polished with water-based diamond solutions of 6, 3 and 1 μm in size. Final polishing was completed using a 0.05 μm alumina suspension. For each polishing step, 20 minutes was applied due to the matrix containing ceramic particles of high hardness. The samples were coated with a thin layer of gold and examined in backscattered and secondary electron imaging modes. Hardness tests were conducted on a Schimadzu Model microhardness tester. In order to obtain reliable statistical data, at least 50 measurements were made on each sample.

Results and Discussion

Phase analysis of the castables at different firing temperatures

Figure 2 shows a series of X-ray diffractometry (XRD) patterns taken from the investigated castables fired to the temperatures ranging from 110 to 1500 °C. Figure 2a is the XRD pattern of the castable sample fired at 110 °C for 24 h showing strong diffraction peaks belonging to the corundum phase with the chemical formula Al_2O_3 which has a rhombohedral structure

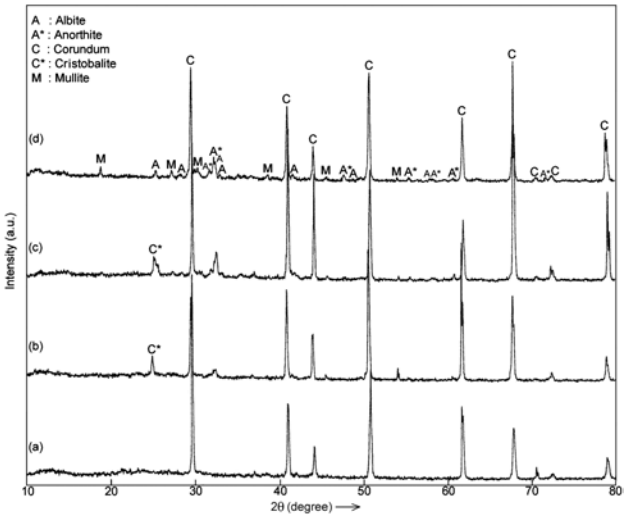

Fig. 2. XRD patterns of the castables fired at (a) 110 °C for 24 h, (b) 1000 °C for 2 h, (c) 1200 °C for 2 h and (d) 1500 °C for 2 h.

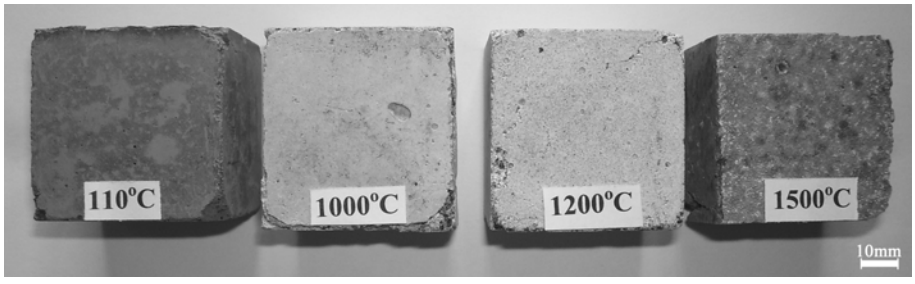

Fig. 1. Self-flowing low cement castable samples applied to the CCS tests.

with lattice parameters [13] a = b = 0.4758 nm, c = 1.2991 nm. This result is expected due to the excess of alumina in the present castable composition. In addition, the phases of anorthite and albite having triclinic structures with the chemical formulae as $CaAl_2Si_2O_8$ and $Na(Si_3Al)O_8$, and lattice parameters a = 0.81756 nm, b = 1.2872 nm, c = 1.41827 [14], and a = 0.8165 nm, b = 1.2872 nm, c = 0.7111 [15], respectively, are present. As seen in Fig. 2b, the XRD pattern of the castable sample fired at 1000°C for 2 h presents diffraction peaks indexed as arising from the reflection planes of phases of the corundum, anorthite, albite with the same lattice parameters mentioned earlier, and one SiO_2 phase which has a tetragonal structure with lattice parameters a = b = 0.49732 nm, c = 0.69236 nm [16] indicating a minor content of cristobalite. This crystalline form of SiO_2 reveals the devitrification process of microsilica particles starting about 1075°C, as mentioned by Chakravorty and Ghosh [17]. The castable sample fired at 1200°C for 2 h (Fig. 2c) consisted of the main phases of the rhombohedral corundum, tetragonal cristobalite, triclinic anorthite and albite as those observed in Fig. 2b. In addition to the diffraction peaks observed at 1200°C (Fig. 2c), the measured main peak positions, namely 2θ=18.9°, 27.3°, 30.1°, 30.4°, 38.6°, 47.6° and 53.9° for the XRD scan in Fig. 2d matched the card values of the mullite phase ($Al_6Si_2O_{13}$), which has an orthorhombic structure with lattice parameters a = 0.75456 nm, b = 0.76898 nm, c = 0.28842 nm [18]. The cristobalite peak (2θ=25.1°) disappears after firing at 1500°C as seen in Fig. 2d. It is considered that this minor content of crystobalite has reactioned with alumina from the matrix and formed mullite at high temperature (≥1400°C). This is similar profile to the XRD results observed for the refractory castable containing 6 wt% of microsilica (MS6) prepared by Gerotto et al. [19, 20].

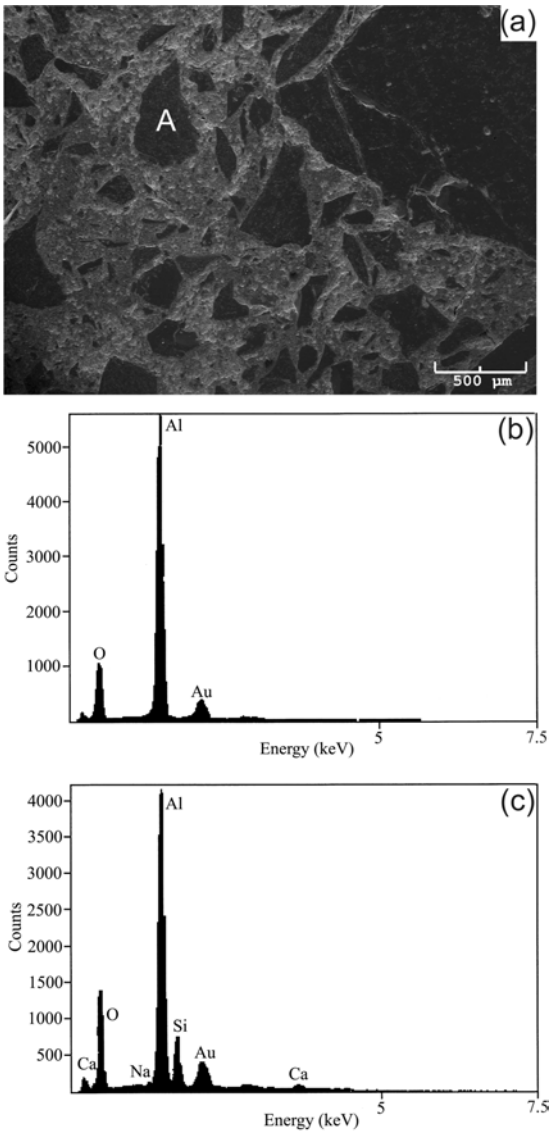

Fig. 3. (a) SEM micrograph of the castable fired at 110°C for 24 h, (b) EDS pattern at a specific point A and (c) EDS pattern of the average composition of the whole matrix.

The microstructural investigation

The scanning electron microscopy (SEM) technique was used to evaluate the resultant microstructures of the present castable. Figure 3(a) is a SEM micrograph of the castable sample fired at 110°C for 24 h showing a microstructure with a high quantity of the corundum phase as confirmed by the EDS pattern of the indicated point, A [Fig. 3(b)]. The corundum grains were homogeneously embedded in the matrix. The EDS pattern in Fig. 3(c) shows the average composition of the whole matrix. Further, there are no visible cracks in the matrix. The Au peak seen in the EDS patterns originate from the gold-coated surface of the samples. Figure 4(a)-(c) shows the microstructure of the castable samples fired at 1000, 1200, and 1500°C for 2 h, respectively. It is clear from Fig. 4(a), (b) and (c) that increasing the temperature from 1000°C through 1500°C reveals the formation of a dense and compact microstructure of the castable sample. As seen from Fig. (4c), it is difficult to distinguish the particles from the matrix due to both having close weighted average atomic numbers, so the atomic number consistently may be similar. Therefore, a detailed SEM study at a higher magnification in the backscattered electron mode in Fig. 4(d) shows the particles and matrix structure much more clearly. The EDS patterns of the point indicated in Fig. 4(d) are given in Fig. 4(e) and (f), and reveal the corundum phase and the average composition of the matrix.

Physico-mechnical properties of the castable at different firing temperatures

– Self-flowability and working time

The self-flowability is the most important characteristic for which a flowable adhesive composite flows with no application of external energy (vibration) [8, 21]. As given in Table 1, the self-flowability of the

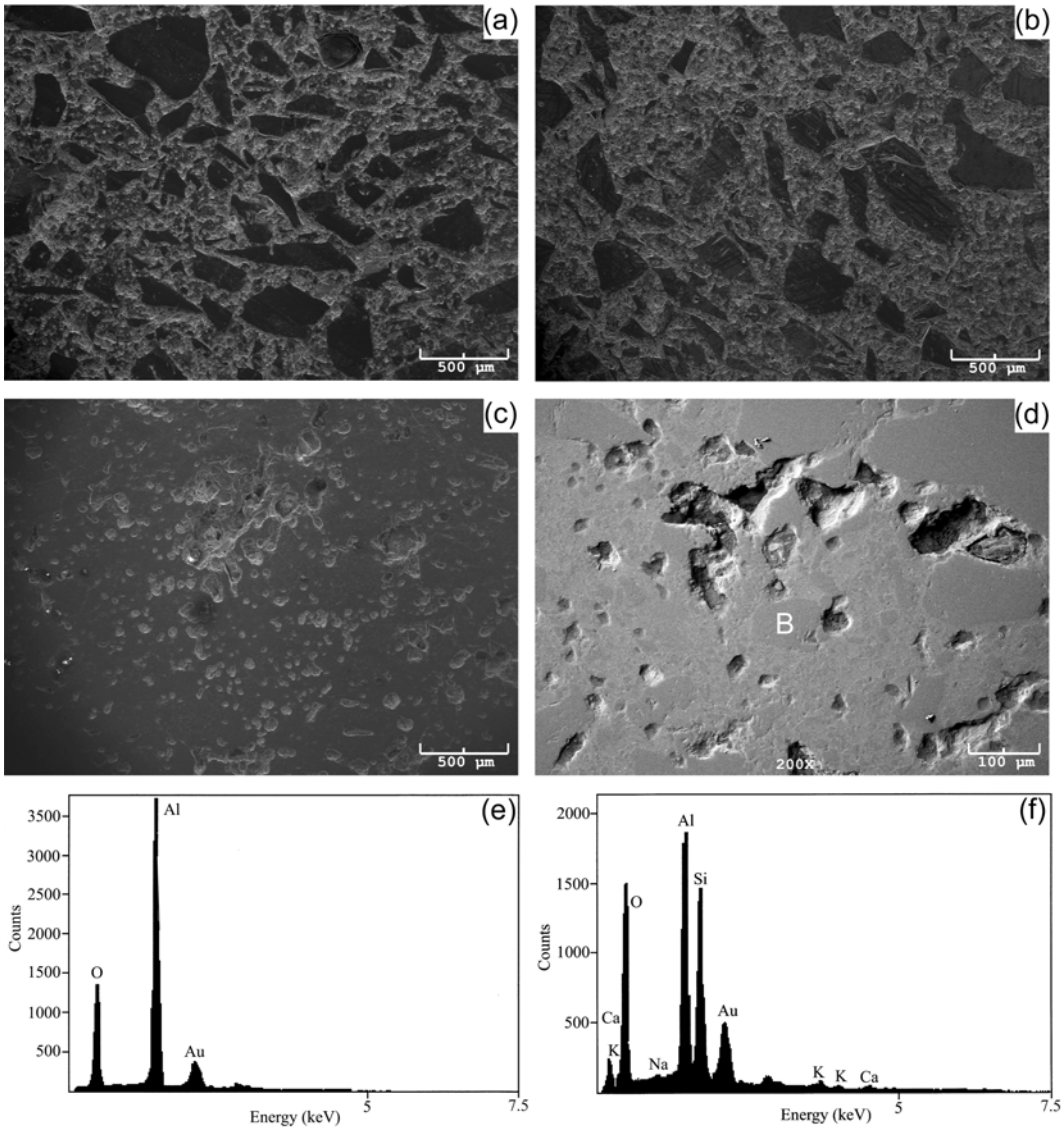

Fig. 4. SEM micrographs of the castables fired for 2 h at (a) 1000°C, (b) 1200°C and (c) 1500°C, (d) 1500°C in backscattered electron mode, (e) EDS pattern at a specific point B in Fig. 4(d) and (f) the average composition of the whole matrix in Fig. 4(d).

present castable is 150 where 5.6% water content is the optimum addition for obtaining an acceptable self-flowability property. The working time of the self-flowing castable refractories indicates the elapsed time from the first addition of liquid during mixing, until the mix only achieves 25% self-flow, as described in ASTM C 1446-99. The working time was determined as 134 minutes at room temperature (25°C). Controlling the rheology (flow and workability) of a low-cement SFC mix which clearly affects the final properties, i.e. density, porosity and strength, depends on the chemical properties, particle size and shape, purity of the raw materials and composition of the refractory mix. Widening of the overall particle-size range of a castable refractory, thus, the granulometry of the SFC, and having a rounded morphology of the raw materials, considerably improve the SFC's flow and workability [22]. Further, the type of the additive system in refractory castables has a significant affect on the rheology of the castables [23-25]. For instance, even though the primary function of the addition of microsilica in refractory castables is to act as a filler, the presence of a significant amount of microsilica has been found to be effective to improve the flow behavior [8].

Bulk density and apparent porosity

The BD and the AP of the present self-flowing brown-fused alumina castable as a function of the firing temperatures (110, 1000, 1200 and 1500°C) are shown in Fig. 5. As can be seen, the BD decreases slightly from 3.17±0.014 gcm^{-3} at 110°C to 3.07±0.01 gcm^{-3} at 1000°C, but increases to 3.17±0.007 gcm^{-3} at 1500 °C. Evaporation of water from the cast shapes creates porosity, which results in decreased BD and increased AP (14.91±0.08%) at 1000°C. Chakraborty [26] mentioned the AP at 110°C and 800°C for properly design-

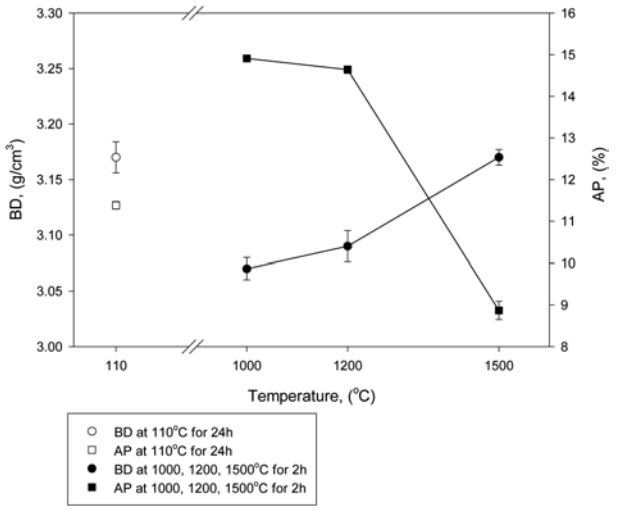

Fig. 5. The BD and AP of the castable at different firing temperatures.

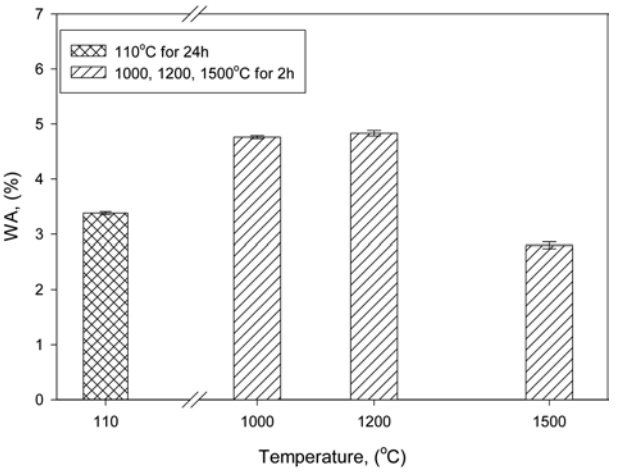

Fig. 6. The WA of the castable at different firing temperatures.

ed low cement castables (LCC) should be 10% and 14%, respectively. These values are close to those of the presently investigated castable sample. However, above 1000°C, because of densification of the composition, the AP decreases to 8.87±0.22% at 1500°C. This type of behavior of the porosity was similarly reported for low cement castables by Hundere and Myhre [27].

Water absorption

The WA data given in Fig. 6 confirms the nature of the densification characteristics and verifies both the AP and the BD in Fig. 5. The WA was reduced from 3.38±0.028% at 110°C to 2.8±0.06% at 1500°C. Further, the WA value (2.8±0.06%) of the present castable sample at 1500°C is higher than the WA value (≈2.0%) of the self-flow ultra low cement high alumina castable containing 5 wt.% of microsilica [28].

Cold crushing strength

Figure 7 shows the development of cold crushing strength (CCS) as a function of the firing temperature.

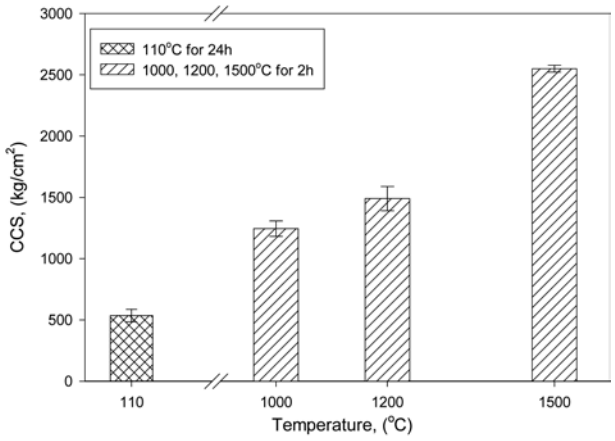

Fig. 7. The CCS of the castable at different firing temperatures.

The values of CCS increase gradually from 536±51 kgcm^{-2} for 110°C dried samples to 2550±28 kgcm^{-2} for the samples fired at 1500°C. Although our castable sample, fired at 110°C, is ≈0.5 times weaker than the self-leveling low cement tabular alumina castable with 4.7% water addition [29], after firing at 1000°C no strength degradation is observed in our castable sample, but the self-leveling low-cement tubular alumina castable [29] exhibited a significant decrease in the CCS. Furthermore, these CCS values are significantly higher than that of a lightweight low cement self-flowing castable [30], i.e. 536±51 kgcm^{-2} at 110°C and 1245±63 kgcm^{-2} at 1000°C vs. 296 kgcm^{-2} at 110°C and 887 kgcm^{-2} at 1000°C [30]. From 1000°C through 1200°C, the anorthite, albite and minor cristobalite phases crystallise (Fig. 2b and Fig. 2c) and a gradual increase observed in the CCS shows the ceramic bond formation. Because of the high reactivity of microsilica, a reduction in porosity and a significant amount of the increase in CCS explains the superior properties of microsilica-containing castables in the temperature range of 1000-1200°C [1]. The present castable exhibits the highest values of CCS at a firing temperature of 1500°C due to the formation of the mullite phase (Fig. 2d) that causes the growth of elongated needle-shaped mullite crystals which strengthens the structure at high heat treatment temperatures [4]. The CCS value at 1500°C is similar to that of the self-leveling low-cement tabular alumina castable [29].

Hardness

Figure 8 shows the Vickers hardness values with standard deviations as a function of the firing temperature for the present castable. The castable sample fired at 110°C for 24h has a maximum hardness value of 2520±116 kg/mm^2. This value decreases to 1705±370 kg/mm^2 when the castable was fired at 1500°C for 2h. It is clear that the hardness decreases with an increase of the firing temperature. The reason for this significant variation in the hardness values can be attributed to the formation of both secondary crystalline phases, such as

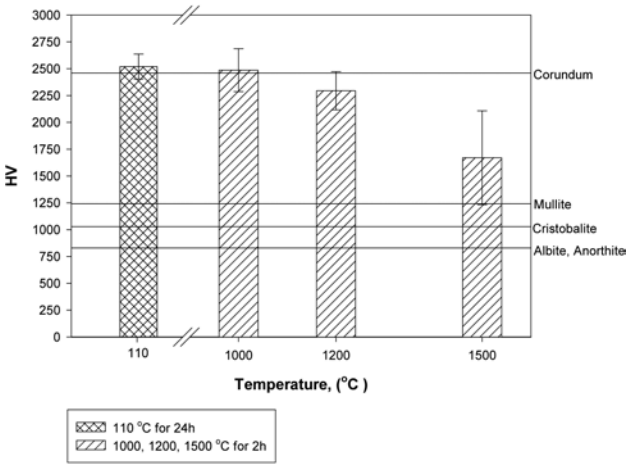

Fig. 8. Vickers hardness values with standard deviations as a function of the firing temperature for the present castable compared to corundum, anorthite, albite, cristobalite and mullite.

anorthite, albite, cristobalite and mullite, and a glassy composition. The mechanical characteristics of ceramic systems containing high-alumina contents are related to the phase composition (i.e. amount of corundum, a glassy phase composition, etc.) and microstructure (crystal size and shape, a glassy phase and secondary crystalline phase distribution, porosity, etc.) [31, 32]. In Fig. 8, the Vickers hardness values of the phases of corundum, anorthite, albite, cristobalite and mullite are obtained using the relationship [33]:

$$Hv=6.5\ H_M^{2.7} \quad (1)$$

where Hv is the Vickers hardness and H_M is the Mohs hardness, based on a best fit to the data provided by Szymanski and Szymanski [33]. For this analysis, the Mohs hardness values are also taken from by the literature of mineral science [34, 35]. As Fig. 8 shows, the Vickers hardness of the castable sample fired at 110°C for 24h is close to the calculated hardness value of corundum using the relationship mentioned above [33]. The calculated Vickers hardness values of the anorthite, albite and cristobalite are lower than that of the present castable sample fired at 1500°C for 2h. Further, the hardness range between 1300-2100 of the castable fired at 1500°C for 2 h is close to the calculated hardness value of the mullite.

Summary

A self-flowing brown-fused alumina based refractory castable with 5 wt.% cement has been prepared successfully. The present castable composition designed according to Andreasen's distribution coefficient q= 0.25 requires 5.6% water addition to achieve full self-flowing performance. The castable sample self-flowed under its own weight and easily filled intricate shaped molds without any vibration. The formation of the corresponding refractory phases such as corundum, anorthite, albite cristobalite and mullite was observed to have significant effects on the physico-mechanical properties in the temperature range of 1000-1500°C. The sharp decrease observed from 1200°C to 1500°C in AP due to the densification of the castable. The highest values of the CCS were obtained at a firing temperature of 1500°C. The hardness values were observed to decrease with increasing the firing temperature.

Acknowledgements

This research project is supported by Istanbul Technical University, Turkey, Research Fund (Project No: 30329). The authors wish to thank Ms. Çiğdem Çakir for her help and contributions during the SEM investigations of this study. In addition, Prof. Hüseyin Çimenoğlu from Istanbul Technical University for his help in hardness investigations is gratefully acknowledged.

References

1. W.E. Lee, W. Vieira, S. Zhang, K.G. Ahari, H. Sarpoolaky, and C. Parr, Int. Mater. Rev. 46[3] (2001) 145-167.
2. W.E. Lee and R.E. Moore, J. Am. Ceram. Soc. 81[6] (1998) 1385-1410.
3. A.R. Studart, W. Zhong, R.G. Pileggi, and V.C. Pandolfelli, The Am. Ceram. Soc. Bull. 77[12] (1998) 60-66.
4. M.F. Zawrah and N.M. Khalil, Ceram. Int. 27[6] (2001) 689-694.
5. H. Sarpoolaky, K.G. Ahari, and W.E. Lee, Ceram. Int. 28[5] (2002) 487-493.
6. S. Otroj, M.A. Bahrevar, F. Mostarzadeh, and M.R. Nilforoshan, Ceram. Int. 31[5] (2005) 647-653.
7. F.G. Brachet, R. Avis, and B. Clavaud, in Proceedings of the Unitecr'91, 1991, edited by German Refractories Association (GRA) p.186.
8. S.K. Das, R. Sarkar, P.K. Mandal, and S. Mukherjee, Am. Ceram. Soc. Bull. 82[2] (2003) 55-59.
9. P.C. Evangelista and C. Parr, Refrac. Appl. and News. 7[2] (2002) 14-18.
10. J.S. Masaryk, R.A. Steinke, and R.B. Videtto, in Proceedings of the Unitecr'93, 1993, edited by Asociación Latinoamericana de Fabricantes de Refractorios (Alafar) p. 527.
11. I.R. Oliveira, A.R. Studart, and V.C. Pandolfelli, Am. Ceram. Soc. Bull. 81[12] (2002) 27-34.
12. A.H.M. Andreasen and J. Andersen, Kolloid-Z. 50 (1930) 217-228.
13. Powder Diffraction File, Card no. 10-017, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA, (1992).
14. Powder Diffraction File, Card no.41-1486, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA, (1992).
15. Powder Diffraction File, Card no.10-0393, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA, (1992).
16. Powder Diffraction File, Card no.39-1425, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA, (1992).

17. A.K. Chakravorty and D.K. Ghosh, J. Am. Ceram. Soc. 74[6] (1991) 1401-1406.
18. Powder Diffraction File, Card no.15-0776, Joint Committee on Powder Diffraction Standards (JCPDS), Swathmore, PA, USA, (1992).
19. M.V. Gerotto, A.R. Studart, M.D.M. Innocentini, and V.C. Pandolfelli, Am. Ceram. Soc. Bull. 81[9] (2002) 40-47.
20. M.V. Gerotto, A.R. Studart, R.G. Pileggi, and V.C. Pandolfelli, Am. Ceram. Soc. Bull. 79[9] (2000) 75-83.
21. Y. Sen, Am. Ceram. Soc. Bull. 74[9] (1995) 117-118.
22. V. Jones, Ceram. Ind. 148[2] (1998) 49-53.
23. H. Fryda, K. Scrivener, T. Bier, and B. Espinosa, in Proceedings of the Unitecr 97, 1997, edited by M.A. Stett, (American Ceramic Society (ACerS)), p.1315.
24. C. Parr, B. Valdelièvre, and C. Wöhrmeyer, Refrac. Appl. and News. 7[3] (2002) 17-23.
25. I.R. De Oliveira, A.R. Studart, F.A.O. Valenzuela, and V.C. Pandolfelli, Cerâmica. 49[309] (2003) 11-16.
26. I.N. Chakraborty, Ceram. Int. 30[3] (2004) 487-490.
27. A.M. Hundere, and B. Myhre, in Proceedings of the Unitecr 97, 1997, edited by M.A. Stett, (American Ceramic Society (ACerS)), p.91.
28. M.D.M. Innocentini, A.R.F. Pardo, V.C. Pandolfelli, Permeability of high-alumina self flow refractory castable, in: German Refractory Association (GRA) (Ed.), Proc. of the Unitecr'99, Berlin, Germany, 1999, pp. 93-96.
29. G.W. Kriechbaum, V. Gnauck, J.O. Laurich, I. Stinnessen, G. Routschka, and J. van Heidjen, The matrix advantage system, a new approach to low moisture LC selfleveling alumina and alumina spinel castables, Proceedings of the XXXIX. Int. Feuerfest-Kolloquium Aachen, 1996, pp.211-218.
30. H. Feldborg, B. Myhre, Use of microsilica in a lightweight self-flowing refractory castable, in: German Refractory Association (GRA), (Ed.), Proc. of the Unitecr'99, Berlin, Germany, 1999, pp. 90-92.
31. E. Medvedovski, Wear. 249[9] (2001) 821-828.
32. T. Ebadzadeh and W.E. Lee, J. Eur. Ceram. Soc. 18[7] (1998) 837-848.
33. A. Szymanski, and J.M. Szymanski, in "Hardness Estimation of Minerals, Rocks And Ceramic Materials" (Elsevier, Science Publishers, Amsterdam, The Netherlands, 1989).
34. A. Szymanski, in "Technical Mineralogy And Petrography An Introduction To Materials Technology", (Elsevier, Science Publishers, Amsterdam, The Netherlands, 1989).
35. C. Klein, in "The 22nd Edition of the Manual of Mineral Science (after James D. Dana)", (John & Sons, Inc. USA, 2002).