O U R N A L O F

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Characterization of the physical properties of a self-flowing low-cement castable based on white-fused alumina

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

^aIstanbul Technical University, Metallurgical and Materials Science Engineering Department 34469 Maslak, Istanbul, Turkey ^bIstanbul Technical University, Prof. Dr. Adnan Tekin High Technological Ceramics and Composites Research Center 34469, Maslak, Istanbul, Turkey

^cRefsan Refrakter ve Insaat Ltd. Sirketi, Sultan Selim Cad. Ucar Sok. No:10/A, 34330, 4. Levent, Istanbul, Turkey

A white-fused low cement refractory castable was prepared from pure refractories that consisted of 77 wt.% white fused alumina, 10 wt.% calcined alumina, 8 wt.% microsilica, 5 wt.% cement and 0.05 wt.% dispersant. Optimum self-leveling flowability was achieved by using 5.6 wt.% water. To determine the effect of the firing temperature on the white-fused low cement refractory castable, studies of apparent porosity (AP), bulk density (BD), water absorption (WA), cold crushing strength (CCS), hardness, X-ray diffraction (XRD) and microstructural-based evaluation using electron probe microanalyser (EPMA) were performed. The present castable heat treated at 1500 °C for 2 h exhibited the following properties: the AP -14%, the BD -3.12 gcm⁻³, the WA -2.5%, the CCS -2000 kgcm⁻² and the hardness -3185 kgmm². The new white-fused alumina castable presents unique properties that would make it desirable to use in industrial refractory applications.

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

Introduction

Since the discovery of the first refractory concrete by Sainte-Claire Deville, in France [1-5], the continuous advances in the refractory ceramics have resulted in increasing the number of refractory castable systems [6-12] even though the castables have complex refractory formulations, requiring high quality, precision-sized aggregates, fillers, binders and additives [1, 13-14]. In the 1969s, the refractory castables with a low cement content i.e. 4-8% were recognised as having excellent cold and hot strengths by Prost and Pauillac [1, 15]. Trends for decreasing the CaO content in these castables were the origin of the low (LCC) and ultra-low cement castables (ULCC) [6, 16]. Although their significantly improved physical and thermomechanical properties such as high density, low porosity, high cold and hot strengths, creep resistance, hot modulus of rupture, and corrosion resistance, selecting the low and ultra-low cement castables as the lining materials showed the deficiencies and difficulties *i.e.* inefficient mixing, excess water additions, difficult placement, and inexperienced personnel on the quality of installation and the performance of the lining [1]. Investigations to solve these disadvantages caused the arising of a new type of high performance refractories, known as self-flowing castables (SFCs) which are characterized by a consistency

after mixing that allows the material to flow and degas without the application of external energy (vibration) [1, 16-18]. Due to the cohesive consistency of the selfflow castables, installation can be achieved without separation of the fine material or the fluid phase from the aggregate. Further, these castables easily fill the complex forms and shapes by self-flowing under their own weight in the range of 4.5 to 8.0 % of water addition [1]. Application ability of the self-flow technology to a wide variety of compositions and their limitations such as controlling of the setting time, placement and demoulding time, and dilatant flow behaviour, the investigations on research and development of the self-flow technology are still underway. This work focuses on developing the quality of self-flowing refractory castables through the preparation of a white-fused alumina (WFA) based castable with a low cement content.

Methodology

In the present study, the materials used are white-fused alumina from Minermet S.P.A. Italy (Al_2O_3 -99.57, Fe₂O₃-0.06, SiO₂-0.13, Na₂O-0.24 wt.%), calcined alumina from Eczacibasi Doga Madencilik San. Ve Tic. A.S. Turkey (Al_2O_3 -99.50, Fe₂O₃-0.02, TiO₂-0.006, SiO₂-0.018, Na₂O-0.030 wt.% surface area-0.8 m²/gr, density-3.9 g/cm³), microsilica 920D from Elkem Refractories, Norway (SiO₂-92.4, H₂O-0.4, L.O.I.-0.98 wt.%), cement Secar 71 from Lafarge, France (Al_2O_3 -72.7, Fe₂O₃-<0.3, TiO₂-<0.8, Na₂O + K₂O-<0.6, MgO-<0.3, CaO-29.2 wt.%, density -3.0 g/cm³) and dispersant Darvan7S (D7S) from R.T. Vanderbilt Company, Inc., USA. Table 1 shows the chemical

^{*}Corresponding author:

Tel : +90 212 285 3382

Fax: +90 212 285 2925 E-mail: unlu@itu.edu.tr

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

White-fused alumina	
3-5 mm	18
1-3 mm	22
0-1 mm	29
0-0.063 mm	8
Calcined alumina HTM 30	10
Microsilica 920D	8
Cement Secar 71	5
Dispersant D7S	0.05
Water	5.6
Self-flowability(%)	140

composition of the studied white-fused self-flowing low cement castable. According to Andreasen and Andersen's packing model [19], the particle size distribution (q = 0.25)of this composition was adjusted to a theoretical curve. Experiments have revealed 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 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 white-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 scanning interval 2θ between 10° and 80° was used. 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. Microstructural-based evaluation of the fired castable samples was made with an CAMECA SX 100 model electron probe microanalyser (EPMA) operated at 15 kV. A recently developed EPMA-based imagining or mapping method was used to determine the elemental distribution in the castable matrix. 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 solution 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 using Bal-tec/SCD005 sputter coater.

Results and Discussion

Phase analysis of the castables at different firing temperatures

Fig. 2 shows X-ray diffraction patterns (XRD) of the studied self-flowing low cement castables fired to the temperatures ranging from 110 °C to 1500 °C. As seen in Fig. 2(a), the X-ray scan of the castable sample fired to 110 °C for 24 h revealed strong diffraction peaks belonging to the corundum phase with the chemical formule Al_2O_3 which has a rhombohedral structure with lattice parameters [20] a = b = 0.4758 nm, c = 1.2992 nm. This observation is expected due to the excess of alumina in the present castable composition. In addition, the sodium aluminum oxide phase having an hexagonal structure with the chemical formula as NaAl₇O₁₁, and lattice parameters a = b = 0.5592 nm, c =2.2711 nm [21] is present. The formation of NaAl₇O₁₁ in the alumina castable is attributed to the main impurities present in white fused aluminas such as sodium and potasium [1,22]. Few weak peaks of the phases of anorthite [23] and albite [24] having a triclinic structure with the chemical formulae of $CaAl_2Si_2O_8$ and $Na(Si_3Al)O_8$, and a =



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



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.

0.8161 nm, b = 1.2858 nm, c = 0.7112 nm [24], respectively, are also observed, as seen in Fig. 2(a). Fig. 2(b) is the XRD pattern of the castable sample fired at 1000 °C for 2 h showing the diffraction peaks indexed as arising from the reflection planes of phases of the corundum, sodium aluminum oxide, anorthite, and albite phase with the same lattice parameters mentioned earlier. It is also clear that since both anorthite and albite phases have the same crystal structure with lattice parameters very close to each other, the respective X-ray peaks for both phases, are coincident with each other. The castable sample fired at 1200 °C for 2 h (Fig. 2(c)) consisted of the main phases of the rhombohedral corundum, triclinic anorthite and albite as observed in Fig. 2(b), and few SiO₂ phases which has a tetragonal structure with lattice parameters a = b = 0.49732 nm, c = 0.69236 nm [25] indicating a minor content of cristobalite. This crystalline form of SiO₂ reveals the devitrification process of microsilica particles starting about 1075 °C, as mentioned by Chakravorty and Ghosh [26]. As seen in Fig. 2(d), the castable sample fired at 1500 °C for 2 h showed similar phases of corundum, anorthite, albite and cristobalite as those observed in the castable sample fired at 1200 °C. No traces of the mullite phase were found. Further, the mullite formation in the present castable system requires higher temperatures. The formation of mullite in LCC and ULLCs have been investigated by several researchers [27-29], who reported that the nature of the alumina-rich component and the presence of other minor components have a significant affect on the formation of the mullite phase.

The microstructural analysis

The electron probe microanalyser (EPMA)-based imaging/ mapping method was used to evaluate the resultant microstructures of the present castables. Fig 3(a-e) is



Fig. 3. EPMA image with a series of elemental maps showing the distribution of key elements in the castable sample fried at $110 \,^{\circ}$ C for 24 h. The scale bar at the right exhibits relative concentration. Map condition: 15 kV, 20 nA.

an EPMA image with a series of elemental maps 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 distribution of key elements. The corundum grains are homogeneously embedded in the matrix. The distribution of the Na and Ca elements in the castable fired at 110 °C for 24 h (Fig 3(d-e)), conforms with the XRD data shown in Fig 2(a). Based on the EPMA images of the castable samples fired at 110 °C for 24 h, and 1000, 1200 and 1500 °C for 2 h, given in Fig 4(a-d), no visible cracks were observed in the matrix. This justifies the lower level porosity and the high mechanical strength of the castable with a dense and compact microstructure. Fig. 5(a-f) shows the EPMA mapping of the castable sample fired at 1500 °C for 2 h. The elemental distribution of Al and O describes approximately the locations of the corundum particles, as marked "C" in Fig. 5(b). The mapping of the other key elements, i.e., Ca, Na, and Si, verifies the presence of the phases albite, anorthite and cristobalite, as determined by XRD given in Fig 2(d).

Physico-mechnical properties of the castable at



Fig. 4. EPMA images of the castable samples 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. 5. EPMA image with a series of elemental maps showing the distribution of key elements in the castable sample fried at 1500 °C for 24 h. The scale bar at the right exhibits relative concentration.

different firing temperatures Self-flowability and working time

The refractory castable is termed self-flowing when it shows the ability to spread out evenly on its own without application of external energy (vibration) [17, 30, 31]. As seen in Table 1, the self-flowability measurements showed that the studied castable presented self-flowing ability as 140 where the water content was 5.6%. The working time of the self-flowing castable refractories is described in ASTM C 1446-99 as the elapsed time from the first addition of liquid during mixing, until the mix only achieves 25% self-flow. The working time was determined as 122 minutes at room temperature (25 °C). The flowability and workability of a low-cement SFC mix have a significant effect on the final properties such as density, porosity and strength, based on chemical properties, particle size and shape, purity of the raw materials and composition of the refrectory mix. Widening of the overall particle-size range of a castable refractory, therefore, the granulometry of the SFC, and having a rounded morphology of the raw materials, considerably improve the flow and workability of the SFC [32]. Further, the type of the additive system in refractory castables has a significant affect on the rheology of the castables [33-35]. 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 [17]. As an example, the SFC mix containing brown-fused alumina with the same amount of both water and microsilica additions as used in the present study exhibited the selfflowability and working time of 150 and 134 minutes, respectively [36].

Bulk density and apparent porosity

Fig. 6 shows that as a function of the firing temperatures the BD and AP of the present self-flowing white-fused castable are measured between 3.04 and 3.12 gcm⁻³, and 7.8 and 14%, respectively. The BD decreases from 3.12 ± 0.03 gcm⁻³ at 110 °C to 3.04 ± 0.01 gcm⁻³ at 1000 °C, but increases to 3.12 ± 0.01 gcm⁻³ at 1500 °C. Removal of water from the castable creates porosity, which indicates a decreased BD and increased AP (14.00 ± 0.08%) at 1000 °C.



Fig. 6. The BD and AP of the castable at different firing temperatures.



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

These values conform with the values reported by Chakraborty [37] for properly designed low cement castables (LCC). Further, above 1000 °C, due to the densification of the castable, the AP decreases to $7.8 \pm 0.15\%$ at 1500 °C. A similar behaviour of the porosity was mentioned for low cement castables (LCCs) by Hundere and Myhre [38].

Water absorption

The WA data is given in Fig. 7 based on both the firing temperature and the results of AP. It is significantly clear that Fig. 7 confirms the nature of the densification characteristics and verifies both the AP and the BD in Fig. 6. First, the WA was increased from $3.22 \pm 0.34\%$ at 110 °C to $4.35 \pm 0.05\%$ at 1200 °C because of increase in the AP, then decreased to $2.5 \pm 0.06\%$ at 1500 °C, indicating a densification effect in the castable sample. The observed WA value at 1500 °C is closer to the WA value, $\approx 2.0\%$, of the self-flow ultra low cement high alumina castable containing 5 wt.% of microsilica [39].

Cold crushing strength and hardness

Fig. 8 shows the development of cold crushing strength (CCS) as a function of the firing temperature. The CCS of the castable gradually increase with the firing temperature, *i.e.*, 1300 ± 131 kgcm⁻² for 110 °C dried samples and 2000 \pm 113 kgcm⁻² for the samples fired at 1500 °C. When the firing temperature increases from 1000 °C through 1200 °C, the anorthite, albite, and minor cristobalite phases crystallise (Fig. 2(b), (c)) and a gradual increase is observed in CCS, indicating the ceramic bond formation. Due to the high reactivity of microsilica, a reduction in porosity and a significant increase in CCS exhibits superior properties of microsilica-containing castables in the temperature range of 1000-1200 °C [1]. At the firing temperature of 1500 °C, the CCS of the castable is about $2000 \pm 113 \text{ kgcm}^{-2}$ which is lower than the value obtained from self-flowing LC brownfused alumina castable having both similar water and microsilica additions [36]. This verifies the importance of the differences of the both corresponding phases and microstructure developed by the firing temperature.



Fig. 8. The CCS of the castable at different firing temperatures.



Fig. 9. Vickers hardness values with standard deviations as a function of the firing temperature for the castable.

Fig. 9 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 24 h has a hardness value of 2710 ± 245 kgmm². This value increases gradually to 3185 ± 275 kgmm² when the castable was fired at 1500 °C for 2 h. It is clear that the hardness increases with an increase of the firing temperature. The reason for this behavior in the hardness values can be attributed to the phase composition (*i.e.* the amount of corundum, a glassy phase composition, etc.) and microstructure (a crystal size and shape, a glassy phase and secondary crystalline phase distribution, porosity, etc.) as shown in the literature [34, 35] for the ceramic systems containing a high-alumina content.

Summary

A self-flowing white-fused alumina based refractory castable with 5 wt.% cement has been prepared successfully.

The XRD pattern of the castable sample fired to 110 °C for 24 h revealed corundum (Al₂O₃), sodium aluminum oxide (NaAl₇ O_{11}), anorthite and albite peaks. In addition to these peaks, few cristobalite (SiO_2) phases were also detected in the XRD patterns of the castable sample fired at 1200 °C for 2 h. The castable sample fired at 1500 °C for 2 h showed similar phases to those observed at 1200 °C. The EPMA mapping of the present castable fired at 1500 °C for 2 h verifies the presence of the phases of corundum, albite, anorthite and cristobalite, as determined by XRD. An increase in the firing temperature from 110 °C to 1000 °C causes a slight decrease in bulk density which then increases at 1500 °C. The WA of the castable exhibits a similar trend as AP does as a function of the firing temperature. The CCS and hardness increase with an increase of the firing temperature. The castable sample shows an especially high strength property compared to the conventional refractory castables. The self-flowing LC castable produced based on white-fused alumina has unique properties that would make it desirable to use in industrial refractory applications.

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