Cold Isostatic Pressing of Alumina–Graphite Castables, a New Technology to Manufacture Special Refractories

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The refractory materials of the special refractories like ladle shroud (LS) and submerged entry nozzle (SEN) should have adequate chemical and mechanical properties such as high temperature mechanical strength and thermal shock resistance. Currently, alumina, graphite and additives are mixed with a phenolic resin or coal tar pitch, packed into a molding frame by a jig, formed by cold isostatic pressing (CIP), dried and finally fired in a reducing atmosphere, usually under coke, at more than 1 000°C. The purpose of this research is to introduce a novel technique to provide LS and SEN from alumina-graphite castable refractories by using CIP without a need to firing under reducing atmosphere. Compositions in relation to physical-mechanical properties are investigated and mixtures like 55 % alumina, 20 % refractory cement, 15 % graphite, 5% micro silica and 6–8 % water have shown to be promising and giving suitable results.

KEY WORDS: alumina–graphite; castable refractory materials; cold isostatic pressing; submerged entry nozzle; ladle shroud.

1. Introduction

At Present, continuous casting is the most efficient and economical method to manufacture steel in the world. For the production of high quality steel, the process involves the use of nozzles for controlling the flow of melt from the ladle to the mould. The most critical components of the flow control system are LS and SEN. LS is used between the ladle and the tundish and the function of SEN is to protect the molten steel stream whilst teeming the tundish into the mould. The required properties for LS and SEN are extensive, they include excellent resistance to thermal shock,1–3) mechanical strength to withstand the molten steel stream and high temperature, 4) vibration and handling, 5) high corrosion and erosion resistance to molten steel, mould flux and slag,6,7) clogging resistance,8–11) particularly for aluminum killed steel and suitable cost of production.12)

For the time being, alumina–graphite materials have been of wide use to cope with these requirements and satisfy these demands. Materials of conventional continuous casting nozzles of molten steel comprise alumina, graphite, silica and silicon carbide. These materials when mixed together have many useful properties for steel making applications, including low thermal expansion (<4×10−6 K−1), high thermal conductivity (>10 W·m−1·K−1), good thermal shock resistance and low wet ability by slag or molten metal.13) Nowadays, alumina, graphite and other materials are mixed with a phenolic resin or coal tar pitch, and then the resulting mixture is packed into a molding frame. A forming jig is used to adjust the thickness of inner wall portion. After packing, the jig is removed and the mixture is formed by CIP, then drying and finally the nozzles are fired in reducing atmosphere, usually under coke, at a temperature of more than 1 000°C for some time to produce a ceramic matrix composite with ceramic bonds in the form of a LS or SEN.14)

The purpose of the present research is to provide a suitable refractory material for continuous casting LS and SEN that can be produced from castable refractories by using CIP without the need to soak in reducing atmosphere with high cost of firing. Application of castable refractories has recently been accelerated in the refractory technology for the purpose of labor saving and cost reduction, to be replaced by pre-formed refractories especially for ladles.15) In the refractories for continuous casting, monolithic refractories are applied to the lining of ladles and tundishes, but not for LS or SEN. In fact, in the case of these monolithic refractory materials, it is not necessary to generate the high temperature ceramic bond and sintering is performed during using and we use hydraulic bonds instead of ceramic bonds in the produced product. Accordingly, only drying is required and elimination of firing is a great economical advantage. If LS and SEN could be made by castable refractories, considering that they must be fired at more than 1 000°C and also in reducing atmosphere, the cost reduction is really encouraging. High alumina cements have played an important role as hydraulic binders for castable refractories, because they have good performance and properties. The main mineral phases are CA, CA₂ and traces of C₁₂A₇ and α-Al₂O₃ while C and A stand for CaO and Al₂O₃.
respectively. Calcium aluminate (CA) is the most important hydraulically setting cement phase. Hydration starts by forming the hexagonal crystals of CAH₁₀ and C₂AH₈ (H stand for H₂O) which depending on time and temperature of hydration convert to the cubic crystals of C₃AH₆ and AH₃. During firing these hydrates break down, leaving very reactive products, which in turn recrystallize to anhydrous calcium aluminates. This recrystallization produces a framework of sintered material at a temperature lower than that, which would have been required to sinter the anhydrous aluminates cement powder.

2. Experimental Procedure and Materials

Raw materials include Tabular Alumina T64 (48 mesh) produced by Alcoa, Secar 80 and Plenium cement from Lafarge Company, flake graphite powder of very fine particle size made in China, silicon carbide with two sizes of 200 mesh and 0–1 mm made in Germany and Iranian micro silica in the form of silica fume were used. Some alumina-graphite compositions were prepared in accordance with the composition analysis listed in Tables 1–5. They were used for determination of the best composition for alumina-graphite, cement content, the effect of water content, micro silica content and influence of micro silica and water together. The following process produced all the samples of this study. The raw materials were dry mixed and then the water was added gradually. After kneading, the resulting mixture (plastic body) was packed into a rubber mould, and then formed by CIP under a pressure of 400 bars and removed from the mould into air. Then after 24 h, the green bodies were dried at 130°C for 2 h without any other firing. The specimens of 100×25×25 mm were cut for the measurement of cold modulus of rupture (CMOR), bulk density (BD) and apparent porosity (AP). CMOR was measured by three point bending Universal Test type compressing testing machine. Cold crushing strength (CCS) was measured with cylindrical specimens of 50 mm diameter and 50 mm height. Tensile strength (TS) was determined by using the same size cylindrical sample (φ50×50 mm), according to the Brazil method using axial compression. Tensile strength S was determined by the following Equation:

\[ S = 2P/pDL \]

Where P is the load, D is the sample diameter and L is the sample length. In order to determine the properties, samples were tested according to ASTM standards. An immersion test was used for measuring the resistance of the samples in molten steel. Two samples with composition of MW4 (see Table 5) were immersed in molten steel at 1600°C for 20 min. Both samples were made by castable refractories and firing at 600°C and 1400°C for 3 h respectively. For studying the effect of some additives on CCS of Al₂O₃–C samples, one of the best formulations MW4 (Table 5) was selected. The additives included silicon carbide and Plenium cement. Plenium cement was used instead of Secar 80 cement. Also with increasing of silicon carbide, the same weight percent of tabular alumina was decreased.

3. Results and Discussion

3.1. Effect of Graphite Content on Properties

Graphite has a function of improving wetting resistance against molten steel and increasing thermal conductivity. In this record, Figs. 1 through 3 shows the effect of flake graphite content on the CMOR, TS and CCS respectively of samples containing 20 wt% cement and 6 wt% water (see also Table 1). The results showed that by increasing graphite content, the strength of samples decreased. This could be related to discontinuation of hydraulic bonds around aggregates in the matrix by graphite, or lubrication effect of graphite with respect to bonded particles.

| Table 1. Composition of alumina–graphite samples, 20 g cement and 6 g water added to 100 g batches. |
| Sample | A1 | A2 | A3 | A4 | A5 | A6 | A7 |
| Alumina(wt%) | 100 | 95 | 90 | 85 | 80 | 75 | 70 |
| Graphite(wt%) | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| Cement(g) | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Water(g) | 6 | 6 | 6 | 6 | 6 | 6 | 6 |

| Table 2. Composition of samples for determination of the best cement content. |
| Sample | B1 | B2 | B3 | B4 | B5 |
| Alumina(wt%) | 70 | 65 | 60 | 55 | 50 |
| Graphite(wt%) | 15 | 15 | 15 | 15 | 15 |
| Water/Cast % | 6 | 8 | 10 | 12 | 14 |

| Table 3. Composition of samples for Determining the effect of water content. |
| Sample | BW1 | BW2 | BW3 |
| Alumina(wt%) | 55 | 55 | 55 |
| Graphite(wt%) | 15 | 15 | 15 |
| Cement(wt%) | 30 | 30 | 30 |
| Water/Cast% | 8 | 10 | 12 |

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4 and 5 show bulk density and apparent porosity of samples with increasing graphite content, it seems that by addition of graphite, AP and BD both will decrease because the density of graphite is less than alumina and voids of matrix are filled by smaller particles of graphite. It seems that 15 wt% graphite is the best content because over this content, the strength will reduce and less than this content, clogging process will appear.

3.2. Cement Content

Figure 6 shows the effect of cement content addition on CCS (W in plot stands for water content that is added to the samples). The cement/water ratio of the samples is constant (2.5), the plot indicates that CCS will decrease by increasing cement content. Because after CIP of samples, extra physical water goes out from matrix and some cracks are produced, these cracks cause the decreasing of strength of samples.

3.3. Water Content

Figure 7 illustrates that CCS is decreased by the addition of water content, because increasing the water could produce open porosities and cracks after firing and consequently BD is decreased (Fig. 8) and AP is increased (Fig. 9). Conventional castables have a cement content of 15 to 30%, which provide sufficient strength, and they also have a water demand exceeding 7 to 10% and the extra water
goes into pores and remains, it might even be useful for completion of the hydraulic bonds, but by using CIP we need only 6–8% water. The physical properties including the strength are critically affected by the amount of water needed for the mixing of the castable. Increasing the water addition by 1% above 8% results in an increase of about 2–3% in the open porosity in dried castable, in other words using CIP that means a similar behavior to low cement castables reduces the water demand of the castables.

3.4. Effect of Micro Silica

Figure 10 shows the effect of micro silica addition on CCS of samples, CCS is increased with adding up to 5 wt% of micro silica due to filling of porosity by micro silica. By adding more than 5% of micro silica CCS is reduced due to increasing in pores as primary crack sources and decreasing in density (see also Figs. 11 and 12). It is probable that very high surface area of fume silica particles, about 200,000 cm²/g, can cause a reduction of hydraulic bond between cement particles that have a surface area of less than 10,000 cm²/g. Therefore, up to 5 wt% silica fume which fills the pores, generally increase the bonds and strength goes up. But, more than that develops separation between hydraulically bonded particles, and strength goes down. Owing to its spherical, small sized particles, micro silica fills the pores between larger grains of cement and gives a better particle size distribution and more packing, leading to a decrease in water demand of the castables. However, the high specific surface area of the micro silica particles tends to increase the water demand, giving a net effect of increased water demand compared to a conventional castable. Also, the increase in water demand is almost directly proportional to the amount of micro silica used in castable. It seems that superplasticizers or water reducing agents can be used to provide advantage in micro silica castables in reducing the water demand.

There are several physical mechanisms by which micro silica contributes to the enhancement of properties of castables. These include the increased strength of the bond between the pastes and aggregate and increasing the cohesiveness of the mixtures. But, as experiments indicate, there is a limit to this enhancement and reduction in strength occurs after the optimum. Micro silica also increases the density of cast by the filler packing effect, and by providing a more re-
fined pore structure. For the above mechanisms to take place, it is essential that micro silica particles be well dispersed in a mixture.

3.5. Influence of Cement and Micro Silica Together

Figure 13 illustrates the effect of addition of cement on CCS of samples containing different amounts of micro silica. It seems that by addition of up to 15–20% cement and 5% micro silica, pore filling occurs. By using higher amount of cement, mechanical strength had a reduction, due to lack of hydraulic bonds, on the other hand for the formation of hydraulic bond we need enough water and in our samples water content is constant (6 g water to 100 g batch). Also at sample with 15–20% cement, voids successively filled by smaller particles and reducing or increasing of cement has an effective role on changing porosities (see Figs. 14 and 15). It seems that by increasing micro silica and reducing cement content, we can get the same content of CCS, producing low cement castables.

3.6. Influence of Micro Silica and Water Together

Figure 16 shows the effect of micro silica addition on CCS for two groups of samples containing 6 wt% water and 8 wt% water. The samples with 8 wt% water had considerable strength, because porosities were completely filled by micro silica and the required water for hydraulic bonds is available, but in the samples with 6 wt% water, the hydraulic bonds are reduced.

3.7. Influence of Additives on Al₂O₃–C Samples

Effect of SiC with two sizes (200 mesh and 0–1 mm) on CCS of Al₂O₃–C samples is shown in Fig. 17. There is a significant difference in CCS of samples with 5 wt% and 10 wt% fine and coarse silicon carbide addition, and with no addition. It seems that silicon carbide could strongly keep matrix components. Therefore by using of silicon carbide, mechanical strength will be improved. Also large size silicon carbide (0–1 mm) has a more effective role in increasing of CCS than fine (200 mesh) SiC. We might be able to present this hypothesis that since SiC has a structure of covalence bonds between Si and C, the surface Si and C atoms in each particle have not satisfied covalent bonds with the neighbor atoms and are probably forced to have unstable double bonds between each other on the surface layer of the particles. When hydraulic bonds of cement content start to develop in contact to SiC particles, especially larger particle sizes, contribute to these not satisfied unstable covalent bonds and probably form some covalent bonds in the structure. The result is marked increase of strength at
the presence of SiC for these not fired samples.

Sugino, Hayamizu, Kawashima and Ohtsuka\(^{18}\) have performed a nice study on the behavior of Si-based materials in alumina–graphite nozzles, in both industrial and laboratory scale samples. Nozzle A containing 42.0% Al\(_2\)O\(_3\), 24.5% C, 18% SiO\(_2\), 3.3% Si, 3.5% SiC, after actual industrial use for 174 min, has shown outstanding reduction in apparent porosity (from 15.6% before use to 12% after use) and remarkable increase in modulus of rupture, MOR (from 57 to 154 kgf/cm\(^2\)). On the contrary, nozzle B without Si or SiC, has shown increase of apparent porosity (from 17.1 to 18.6%) and reduction in MOR (from 74 to 62 kgf/cm\(^2\)). Mixture of nozzle A was prepared in the laboratory and heat treated to 1000–1500°C with intervals of 100°C. X-ray diffraction peak of Si decreased at 1200°C and disappeared at 1300°C, while the peak of SiC increased from 1200 to 1500°C. The peak of cristobalite was discerned at the threshold of 1300°C. It was concluded that such changes in Si-based materials due to heat treatment history exert significant influence on changes in the quality and properties of nozzles in industrial applications.

In a parallel set of experiments, Sugino \textit{et al.}\(^{18}\) prepared samples 1 to 4 from 60% Al\(_2\)O\(_3\) and 30% graphite and 10% respectively of Si, SiC, SiO\(_2\) and mullite (3Al\(_2\)O\(_3\) · 2SiO\(_2\)). No significant changes were observed in samples 2 to 4 by the provided heat treatment. But in sample 1 containing metallic silicon, apparent porosity began to decrease at 1200°C and modulus of rupture was highest at 1300°C. X-ray diffraction peak of Si dropped at 1200°C and SiC was formed. It was concluded that the reaction \(\text{Si(s)} + \text{C(s)} \rightarrow \text{SiC(s)}\) was the main cause of changes. Optical observations of the microstructure showed that fibrous SiC was rapidly generated over 1200°C and then was observed at locations for pores and intergranular areas at the matrix. At 1300°C with highest MOR, the most densely generated fibrous silicon carbide was observed. The decrease of MOR at 1500°C was associated with coarse fibrous SiC. It was considered that this fibrous SiC changes its shape and amount under various conditions of temperature, atmosphere, added quantity of metallic silicon and grain size and in consequence is the main determining factor for the quality and properties of the nozzle. The fact of coarsening of fibrous SiC by the increase of temperature from 1300 to 1500°C, shown by Sugino \textit{et al.}\(^{18}\), might be an indication of unsatisfied covalent bonds on the outer layer surface atoms of fibrous SiC, willing to react and progress.

Georges \textit{et al.}\(^{19}\) has worked on six industrial Al\(_2\)O\(_3\)-graphite samples containing Si or Si or both and oxidized at 1400°C in oxygen, air, or CO–CO\(_2\) mixtures, corresponding to O pressures of 1–10.5 atm. They concluded that the first stage of the oxidation of SiC consisted of volatilization of SiO, leaving the SiC surface accessible to gas. The formation of SiO\(_2\) is from the oxidation of SiO and is first vitreous and then transforming into cristobalite. This might indicate that in the surface layers of SiC, if Si atoms disconnect the probable double covalent bonds with C atoms, develop triple covalent bonds with oxygen atoms in conversion of from SiC into SiO and not directly to SiO\(_2\), while SiC and SiO\(_2\) have both single covalent bonds. The same can be true for Si material that probably has double covalent bonds with other Si atoms in surface layers and single bonds in the bulk, and had shown similar behavior. This observation of first SiO and then SiO\(_2\) formation in oxidation of both Si and SiC is in agreement with the hypothesis. This matter, however, needs further attention and more literature survey and experimental data are required to support it and can not be claimed for more than a hypothesis in this paper.

Figure 18 shows the effect of using Plenium cement instead of Secar 80 cement. CCS of samples containing Plenium cement is higher. Specific surface area of Plenium cement is more, consequently Plenium cement make stronger bonds in comparing with Secar 80 cement.

| Properties                | Conventional Nozzles | Tested samples |
|---------------------------|----------------------|----------------|
| Composition (wt%)         | Al\(_2\)O\(_3\)       | 50-74          | 55-60          |
|                           | C                     | 20-30          | 15             |
|                           | SiO\(_2\)             | 0-25           | 5              |
|                           | SiC                   | 0-6            | 5-10           |
|                           | Cement                |                | 15-20          |
| Bulk density (gr/cm\(^3\))|                      | 2.2-2.5        | 2.2-2.5        |
| Apparent porosity (%)     |                      | 18-21          | 22-25          |
| Cold crushing strength (Kg/cm\(^2\)) | 180-220 | 180-250 |
| MOR (Kg/cm\(^2\))        |                      | 60-110         | 38-80          |

3.8. Comparison of Tested Samples with Conventional Nozzles

Table 6 shows the properties of alumina graphite samples have been experimentally produced through the above investigation in comparison with conventional alumina graphite nozzles. Tested samples have the same physical and mechanical properties in comparison with commercial nozzles. It seems that the best composition for alumina
graphite nozzles (LS and SEN) including, 55% wt alumina, 15 wt% flake graphite, 15–20 wt% high alumina cement, 5 wt% micro silica, 5 wt% silicon carbide and 6–8 wt% water.

3.9. Investigation of the Molten Steel Resistance of the Samples

Figure 19 shows the specimens after immersion test. Both samples that were fired at 600°C and 1400°C showed a good and similar behavior in molten steel. Also they showed less erosion tendency. This test illustrates that we can use alumina graphite nozzles with hydraulic bond without a need to firing at high temperatures.

4. Conclusion

It seems that LS and SEN can potentially be produced from alumina–graphite castable refractories by using CIP, without any expensive soaking at high temperatures. It has economical advantages in steel making industries.

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