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Short communication

Influence of additives on nano-SiC whisker formation in alumina silicate–SiC–C monolithic refractories

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Abstract

This study describes the effect of additives on increasing cold crushing strength (CCS) and bulk density (BD) of alumina silicate–SiC–C monolithic refractories. Two series of carbon-containing monolithics were prepared from Iranian chamotte (sample A) and Chinese bauxite (sample B), as 65 wt.% in each case together with, 15 wt.% SiC-containing material regenerates (crushed sagger) and 10 wt.% fine coke (a total of 90% aggregate) and 10 wt.% resole (phenol formaldehyde resin) as binder. Different values of additives (such as silicon and ferrosilicon metal) are added to the mixture and BD, apparent porosity and CCS are measured after tempering at 200 °C for 2 h and firing at 1100 °C and 1400 °C for 2 h. At low temperature of 200 °C, Si and ferrosilicon contribute to the formation of stronger cross-linking in the resit structure and provide CCS values of as high as about 65 MPa. At 1400 °C, SiC whiskers of nano-sized diameter are formed due to the presence of Si and $FeSi_2$ and improve CCS values of as high as about 3–4 times in sample containing 6 wt.% ferrosilicon metal as additive.

Keywords: B. Whiskers; C. Strength; D. Al_2O_3; E. Refractories

1. Introduction

The development of alumina silicate–SiC–C resole bonded ramming monolithic refractory for iron making application (such as iron and slag runner in blast furnaces, furnace bottom and electric-furnace spouts) [1] is a very important recent refractory development which can be considered as evolved from the high performance chamotte–carbon and bauxite–carbon refractories. This class of refractories not only shows superior slag corrosion and erosion (wear) resistance, but also excellent thermal shock and mechanical properties. Monolithic refractories containing bauxite aggregate has shown higher densification and mechanical properties due to the presence of some impurities such as iron which help liquid phase sintering, and consequently, improved mechanical properties [2]. These refractories consist mainly of aluminosilicate and carbon, which are bonded by carbon bonds formed by carbonization of phenol formaldehyde resin (resole) during firing of the refractories [1,3].

Carbon does not been wet by molten metal and will not melt, that is an advantage excellent for refractory use. Its great weakness is that it will oxidize at low temperatures above 600 °C, which creates high porosity, lower density and reduced strength [1,4]. In order to improve the oxidation resistance of carbon-containing refractories, the so-called antioxidants (such as aluminum and silicon metal) have been often added [5]. However, by examining the behavior of Al in the refractories, low melting point Al particles, decrease refractoriness and the reaction of Al and water, limits its use with water-containing binders. Based on the above consideration, it is necessary to develop new antioxidants with excellent hydration resistance and high melting point such as Si-containing antioxidants. Effect of metallic silicon size on properties of alumina–carbon brick is studied, and reported that the added metallic silicon reacts under the reducing atmosphere with carbon in the brick and produces so-called β-SiC bond which contributes to improvements of the mechanical strength and the abrasion resistance under oxidation. The influence of β-SiC bond to the mechanical strength has not been clarified [6].

Generally, modulus of rapture vs. firing temperature is increased and at a given temperature (1100, 1200, 1300, 1500 °C) by increasing particle size of silicon up to more than

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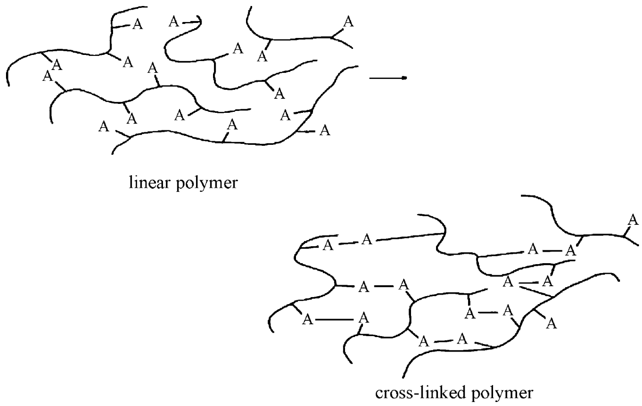

Fig. 1. Linear polymer and cross-linked polymer.

100 μm, the modulus of elasticity is decreased. For coarse particles of Si, the amount of formed SiC is decreased and this means that some Si unreacted. The paper [6] concludes that the strength and durability of the slide gate plates can be improved not by increasing the amount of silicon metal, but by decreasing the particle size to enhance Si reaction. The results of other workers show that SiC addition in the range from 4 to 16% is beneficial to improvement of mechanical properties as well as thermal shock resistance [7]. SiC behavior in Al_2O_3–SiC–C bricks is illustrated in reactions below [8].

$$SiC(s) + CO(g) = SiO(g) + 2C(s) \quad (1)$$

$$SiO(g) + CO(g) = SiO_2(s) + C(s) \quad (2)$$

Advantages of resole binder consist of, friendly environmental, easy mixing, high residual carbon. Disadvantage of resole binder is pyrolization of resit structure, that is called polymer carbon, at temperatures about 300–500 °C, and the products became weak [9].

If these polymer chains are exposed to conditions such that the functional groups do react, then all the chains in the reaction vessel will be tied to each other through A–A bonds (Fig. 1). Cross-linking improves physical properties. Phenol formaldehyde resins including resoles and novolacs are technologically useful cross-linking systems. Cross-linking agents must carry two or more functional groups per molecule [10].

2. Experimental procedure

Silicon and ferrosilicon additives are used in this study. Two series of compositions were prepared. The first composition (sample A) containing as aggregates a combination of chamotte (0–3 mm, 65 wt.%), crushed sagger which is a SiC-containing material regenerates (15 wt.%) and fine coke (10 wt.%) with different amounts of additives of silicon and ferrosilicon metal. The second one (sample B) containing as aggregates a combination of bauxite (20 wt.% coarse bauxite (1–3 mm), 45 wt.% fine bauxite (0–1 mm)), crushed sagger (15 wt.%) and fine coke (10 wt.%) with different amounts of additives of silicon and ferrosilicon metal. At low temperature of curing (200 °C), three other additives such as sulphur, carbon black and silica fume are also used. Since silica fume and carbon black were not so effective in increasing of CCS values, they were eliminated at higher temperature tests (1100 °C and 1400 °C). Chamotte, bauxite and sagger are used to increase the strength of refractory. Coke is used to lower the wettability with iron or steel melt. Both series consisted of 10 wt.% resole (phenol formaldehyde resin) as the binding agent. The chemical compositions and phase contents of the raw materials are given in Tables 1 and 2, respectively.

Specimens were prepared by mixing 90 wt.% aggregate and 10 wt.% resole as a binder with different amounts of additives on top of 100 wt.%. A twin blade mixer was used for dry mixing and kneading. The raw materials were dry mixed for 5 min and then the resole liquid was added gradually. Mixing continued for another 5 min. The mixture was packed into metal moulds with a dimension of 50 mm × 50 mm × 50 mm and then formed by hydraulic press under a low pressure of 4 MPa to act similar to ramming. Pressed samples were cured at 200 °C for 2 h. Finally, some of the samples were fired for 2 h at 1100 °C or 1400 °C in a coke environment to avoid oxidizing atmosphere. The specimens cured or fired were characterized according to ASTM standards. Mechanical test of Cold Crushing Strength (CCS) according to ASTM C-133-97 and physical tests of apparent porosity (AP) and bulk density (BD) according to ASTM C-20-92 were evaluated. Also X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed in some cases. Cold crushing strength (CCS) was measured by Hydraulic Testing Machine type Amsler model D3010/2E. BD and AP were determined by using the following equations:

$$BD = \frac{W}{W_f} \quad (3)$$

$$AP = \frac{(W_s - W)}{W_f} \quad (4)$$

Table 1
Chemical composition of raw materials.

Material	Al_2O_3	SiO_2	CaO	SiC	C	Si	Fe	S	Particle size (mm)
Chinese bauxite	85	6.9	0.15	–	–	–	0.5	–	0–1,1–3
Iranian chamotte	42	53	1.5	–	–	–	2.5	–	0–3
Crushed sagger	45	15	–	38	–	–	–	–	0–3
Fine coke	10	5	–	–	80	–	–	–	0–0.3
Ferrosilicon metal	–	–	–	–	2	72	23	–	0–0.15
Silicon metal	–	–	–	–	1.0	97	1.0	–	0–0.15
Silica fume	–	92	–	–	–	–	–	–	0–0.1
Carbon black	–	–	–	–	98	–	–	–	0–0.1
Sulphur powder	–	–	–	–	–	–	–	97	0–0.3

Table 2
Phase analysis of raw materials (XRD results).

Material	Major phase	Medium phase	Minor phase (s)
Chinese bauxite	$-Al_2O_3\alpha$	Mullite ($3Al_2O_3{\cdot}2SiO_2$)	TiO_2, SiO_2
Iranian chamotte	Mullite ($3Al_2O_3{\cdot}2\ SiO_2$)	–	Cristobalite (SiO_2)
Crushed sagger	$SiC\alpha-$	Mullite ($3Al_2O_3{\cdot}2SiO_2$)	$-Al_2O_3\alpha$
Fine coke	Graphite	–	Al_2O_3, SiO_2
Ferrosilicon metal	$FeSi_2$	Si	–
Silicon metal	Si	–	–

where W, W_s and W_f, respectively, are the weight of dried sample, saturated weight with water and weight of the sample in water suspended by a thin thread without contacting the vessel walls, but fully inside the water and reading by a digital balance under the vessel. In fact W_f is the weight reduction of saturated sample in the water which is equivalent to its volume.

An X-ray diffraction (XRD) instrument (Philips Xpert-MPD System) with Cu $K_{\alpha 1}$ ($\lambda_1 = 1.5405$ Å) and Cu $K_{\alpha 2}$ ($\lambda_2 = 1.5443$ Å) and Ni filter was used for phase analysis. In order to study precisely the phases, the XRD experiments were carried out with a rate of 0.04°/s between 5° and 80° (2θ). Scanning electron microscopy (SEM, Philips XL30) was used for microstructure investigations. X-ray florescence (XRF) was also used for elemental analysis and oxides content calculations (Table 1).

3. Results and discussion

Figs. 2–5 show the influence of additives on cold crushing strength, resole bond, alumina silicate–SiC–C refractory. Figs. 6–8 illustrate BD variations. Figs. 9 and 10 show fired microstructures at 1100 °C for 2 h. Figs. 11 and 12 show fired microstructures at 1400 °C for 2 h. Phase compositions by XRD results are given in Figs. 13–16.

The effect of additives on sample A containing Iranian chamotte as the main aggregate (65 wt.%) is such that silicon metal and ferrosilicon metal generally increase cold crushing

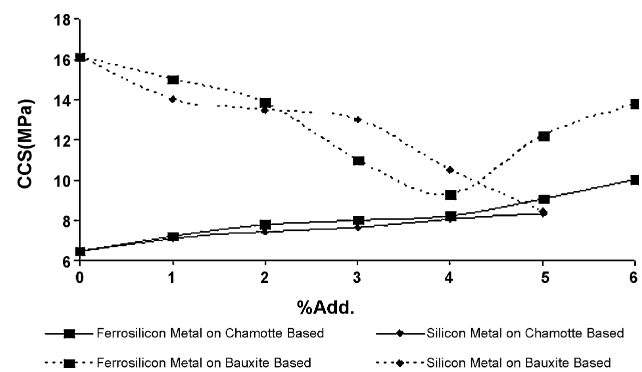

Fig. 4. Effect of additives on CCS of bauxite and chamotte based fired at 1100 °C for 2 h.

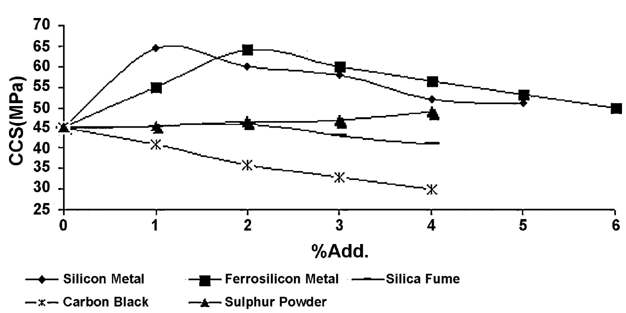

Fig. 2. Effect of additives on CCS of chamotte based cured at 200 °C for 2 h (sample A).

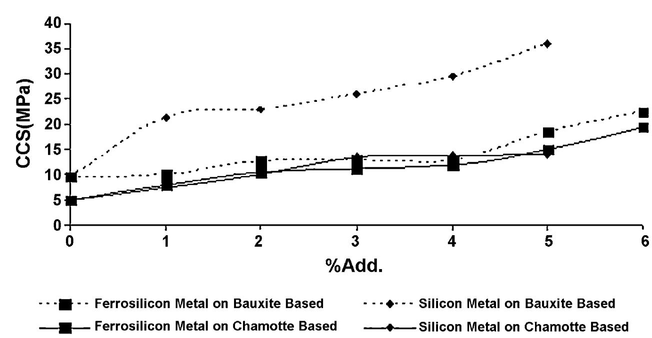

Fig. 5. Effect of additives on CCS of bauxite and chamotte based fired at 1400 °C for 2 h.

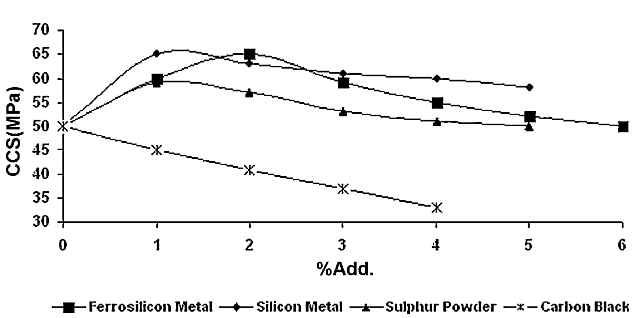

Fig. 3. Effect of additives on CCS of bauxite based cured at 200 °C for 2 h (sample B).

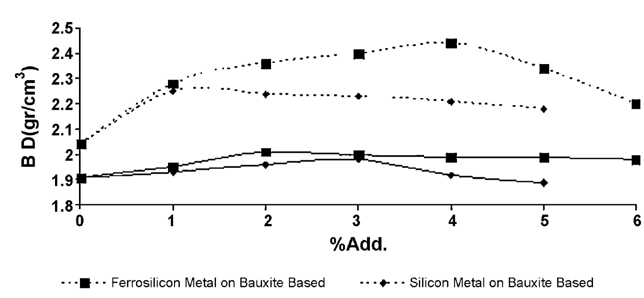

Fig. 6. Effect of additives on BD of chamotte and bauxite based cured at 200 °C for 2 h.

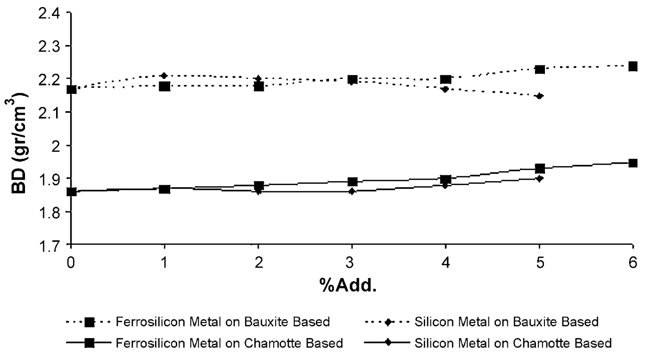

Fig. 7. Effect of additives on BD of chamotte and bauxite based fired at 1100 °C for 2 h.

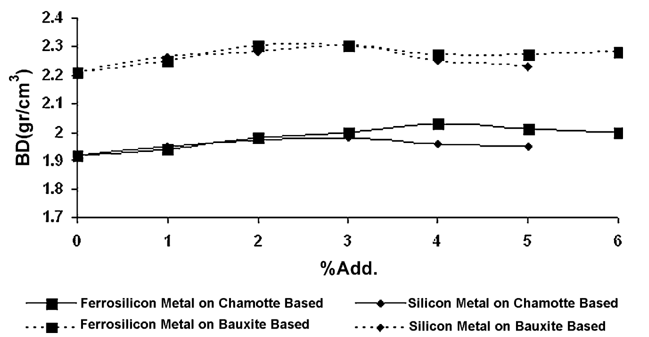

Fig. 8. Effect of additives on BD of chamotte and bauxite based fired at 1400 °C for 2 h.

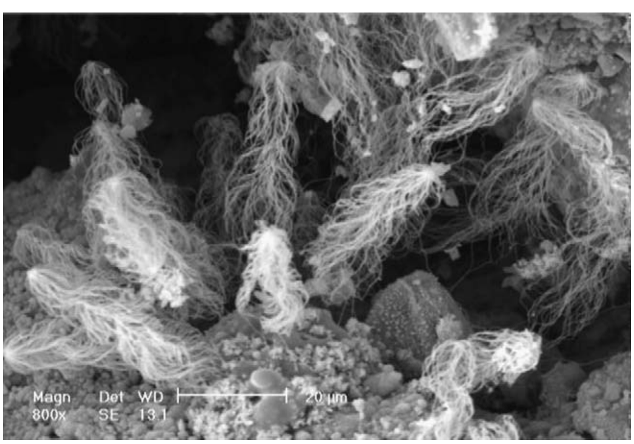

Fig. 9. Micrograph of chamotte–carbon refractory resole bond containing 6 wt.% ferrosilicon metal as additive, fired at 1100 °C, small quantities of SiC whisker are observed.

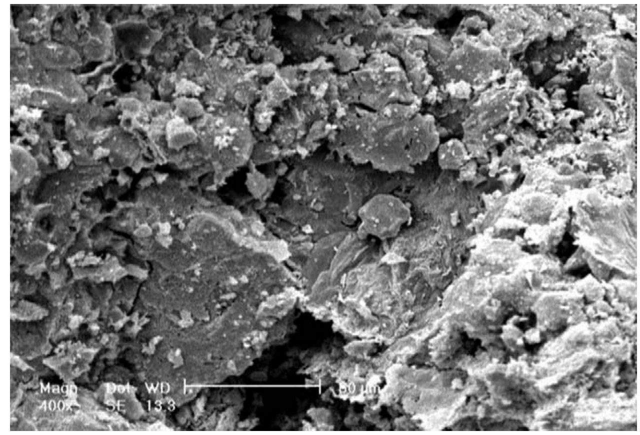

Fig. 10. Micrograph of bauxite–carbon refractory resole bond containing 5 wt.% silicon metal as additive, fired at 1100 °C, shows that no SiC whisker is formed.

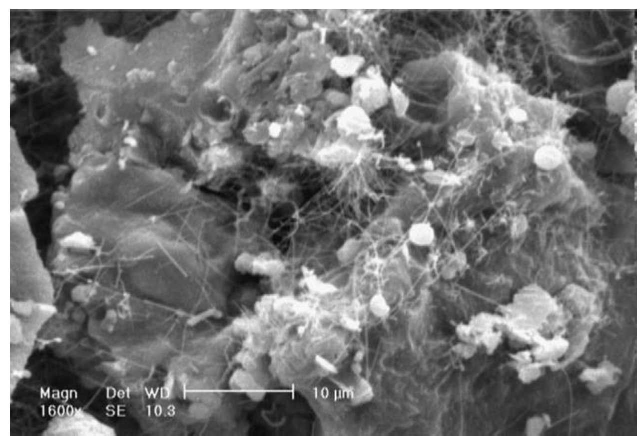

Fig. 11. Micrograph of chamotte–carbon refractory resole bond containing 6 wt.% ferrosilicon metal as additive, fired at 1400 °C, showing SiC whiskers of about 75 nm in diameter in the microstructure.

Fig. 12. Micrograph of bauxite–carbon refractory resole bond containing 6 wt.% ferrosilicon metal as additive, fired at 1400 °C, SiC whiskers are developed from ferrosilicon metal particles in the microstructure.

strength at all heat treatments of 200 °C, 1100 °C and 1400 °C, also increase bulk density. Sample B based on Chinese bauxite also shows CCS increase at 200 °C and 1400 °C, but CCS is reduced at 1100 °C. SEM photomicrographs have proved that SiC whiskers of nano-sized diameter has developed in sample A, but not in sample B at 1100 °C. The reason for increase of strength in sample A, which was not clarified in some cases [5], is now evident to be related to the development of nano-sized whiskers of SiC.

The reason to develop only in sample A, might depend on higher amount of mullite and glassy phase in chamotte with respect to bauxite. Needles of mullite in glassy phase of matrix might be good for nucleation positions for starting and growth of SiC whiskers at low temperature of 1100 °C. At 1400 °C, the driving force is high enough for the production of SiC whiskers

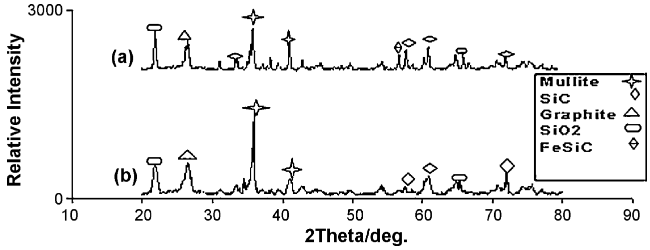

Fig. 13. XRD results of fired chamotte–carbon refractory resole bond fired at 1400 °C for 2 h (a) 6 wt.% ferrosilicon as additive; (b) without additive.

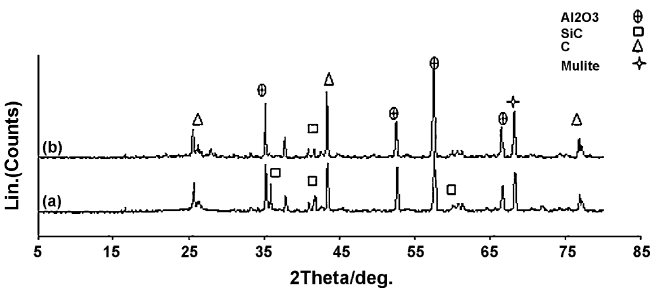

Fig. 14. XRD results of fired bauxite–carbon refractory resole bond fired at 1400 °C for 2 h (a) 5 wt.% silicon as additive; (b) without additive.

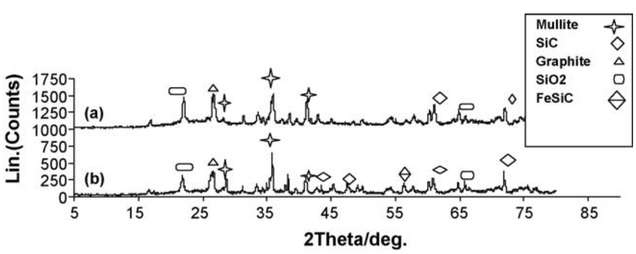

Fig. 15. XRD results of fired chamotte–carbon refractory resole bond fired at 1100 °C for 2 h (a) without additive; (b) 6 wt.% ferrosilicon.

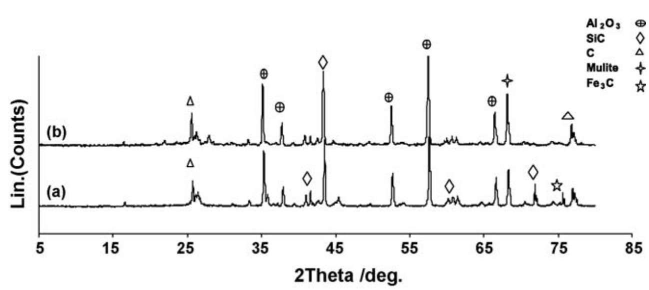

Fig. 16. XRD results of fired bauxite–carbon refractory resole bond fired at 1100 °C for 2 h (a) without additive; (b) 6 wt.% ferrosilicon.

in both samples A and B. But the concentration of whiskers at a comparable level of 6 wt.% ferrosilicon metal ($FeSi_2$) is more for chamotte matrix (Fig. 11) than bauxite matrix (Fig. 12). It seems that these whisker are formed on chamotte aggregates in Fig. 11, but are nucleated on $FeSi_2$ particles in Fig. 12 and outside of bauxite particles. The $FeSi_2$ spheres are observed in Fig. 12. These figures might support the hypothesis of SiC whisker formation due to surface tension of glassy matrix and nucleation effect of mullite needles on chamotte aggregates.

The reason of strength increase at high temperatures is evident to be related to the formation of nano-SiC whisker, but the mechanism for CCS increase at heat treatment of 200 °C is related to the cross-linking formation in phenol formaldehyde resole structure or resit. For this temperature 5 different additions of silicon metal, ferrosilicon metal, sulphur, silica fume and carbon black were used. The first 2 are capable of increasing the cross-linking, but the next 3 were not so effective (Figs. 2 and 3). The Si has a strong effect in small amount of 1 wt.%. By considering Fig. 1, it is probable that formaldehyde (CH_2O) which act as cross-linking agent of A for the main monomer of phenol (C_6H_5OH) is interfered with a lot of Si atoms, each associated with covalent bonds, at the expense of decreasing the cross-links of phenol formaldehyde monomers. Formaldehyde is very reactive and readily polymerizes with ionic initiation [11]. Either anionic or cationic materials can initiate the polymerization reaction.

$$^{-}R + CH_2O \rightarrow RCH_2O^{-}(R{-}O^{-}{=}CH_2) \quad (5)$$

$$^{+}R + CH_2O \rightarrow RCH_2O^{+}(R{-}O^{+}{=}CH_2 \text{or} R{-}O{-}CH_2{}^{+}) \quad (6)$$

Ferrosilicon is less effective than silicon and shows a maximum CCS at 2% and reduces the strength for 3% and above. The type of effect is the same. Micro-silica or silica fume (small amorphous spherical particles of SiO_2) and carbon black, amorphous carbon, do not contribute to a stronger cross-linking, probably due to having an amorphous and non-crystalline nature and submicron size of the amorphous particles, but play the interfering effect to reduce CCS. Almost the similar effects are observed when the additives are used in bauxite based refractories of sample B (Fig. 3). Results in samples A and B confirm each other. The role of sulphur in increasing of CCS was good to some extent (Figs. 2 and 3), but not as effective as Si or ferrosilicon. At high temperature of above 800 °C, resit structure is destroyed and graphite phase as a crystalline carbon state is formed. XRD results show higher peaks of graphite phase at 1400 °C firing (Figs. 13 and 14) with respect to 1100 °C firing (Figs. 15 and 16).

4. Conclusions

1. The addition of silicon or ferrosilicon metal to aluminasilicate-carbon ramming monolithics with resole bond for iron making applications, improves mechanical properties and develop high strength and therefore wear resistance for applications such as blast furnace runners and troughs.
2. At low temperature of 200 °C these additions contribute to the formation of resit structure in resole and by increasing the cross-linking provides CCS values of as high as about 65 MPa, which is remarkable for a carbon-containing monolithic.
3. There is a limit of 1 wt.% for silicon and 2 wt.% for ferrosilicon to increase the cross-linking phenomena and raise the strength of the refractory, beyond which the interfering with formaldehyde is performed, effectiveness of cross-linking is reduced and the strength is lowered.
4. Three additives of silica fume, carbon black and sulphur were not so effective as compared with silicon and ferrosilicon metal.

5. SiC whiskers of nano-sized diameter are formed at 1400 °C in both samples containing chamotte and bauxite. At 1100 °C these whiskers are only observed in chamotte based refractory. A hypothesis is given that probably higher glassy content of the matrix of chamotte has caused higher surface tension and higher amounts of needles of mullite in chamotte rather than bauxite, has caused more nucleation of SiC whisker. The temperature of 1100 °C is a transient temperature that cross-linking is destroyed and SiC whisker formation is not fully formed yet.
6. Nano-SiC whiskers are shown in Figs. 9, 11 and 12. They act as reinforcing media to increase the strength of matrix. Fully developed whiskers at 1400 °C can act stronger in reinforcing glassy content matrix than just partially nucleated ones at 1100 °C.
7. In situ SiC whisker formation of both chamotte and bauxite based monolithic offer certain economical advantages with respect to separate production and use of such nano-whiskers.

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