International Journal of ISSI, Vol. 14 (2017), No. 2, pp. 43-48

The Role of Nano SiC Whiskers on the Strength and Density of Aluminum Silicate-SiC-C Compounds as a Reinforced Steelmaking Refractory

E. Karamian [1], R. Emadi *[2], A. Monshi [3], H. Emadi [4]

[1] *Advanced Materials Research Center, Department of Materials Engineering, Najafabad Branch, Najafabad, Iran*
[2, 3] *Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran*
[4] *School of Mechanical Engineering, College of Engineering, University of Tehran, Tehran, Iran*

Abstract

This study describes the role of in situ nano SiC whiskers on the strength and density of alumina silicate–SiC-carbon refractory compounds. The prepared specimens were composed of 65 wt. % chamotte as alumina silicate compound, 15 wt. % SiC-containing material regenerates and 10 wt. % fine coke and 10 wt. % liquid resole as binder. Different values of additives (such as silicon and ferrosilicon metal) were added to a batch of 100 g of mixture. Cold crushing strength (CCS) and bulk density(BD) were measured after tempering at 200 ºC for 2h and firing at 1100 ºC and 1400 ºC for 2h. At low temperature of 200 ºC, the resit structure was formed in resole and by in-creasing the cross linking, the CCS values were approximately achieved 65 MPa. But at high temperature of 1400 ºC, in situ β-SiC whiskers of nano sized diameter were formed, and the CCS values improved by almost four times in the samples containing 6 wt. % ferrosilicon metal. The cross linking was destroyed at 1100 ºC and in situ β-SiC whisker was not fully formed.

Keywords: Alumina silicate; Chamotte, SiC; Carbon, Silicon; Resole.

---

1. Introduction

Chamotte-SiC-carbon refractory compounds not only show superior slag corrosion and erosion (wear) resistance, but also excellent thermal shock and mechanical properties. These refractories consist mainly of aluminum-silicate and carbon, which are bonded by carbon bonds formed by carbonization of phenol-resin (resole) during firing of the refractories. The development of alumi-na silicate-SiC-C resin bonded ramming monolithic refractory for iron making application (such as iron and slag runner in blast furnaces, and electric-furnace spouts) is an important recent refractory development which can be evolved from the high performance chamotte-carbon and bauxite-carbon refractory compounds [1, 2)].

Carbon does not wet molten metal and does not melt, that is an excellent advantage to using refractories. The major drawback is its oxidation at 1650 ˚K (1377 ˚C), which results in lower den-sity, high porosity and reduced strength [1, 3)]. In order to improve the oxidation resistance of car-bon-containing refractory compounds, the so-called antioxidants have been often added. Among the antioxidants Al and Si are the most widely used. However, by examining the behavior of Al in the refractory compounds, the following problems have been observed:
(1) Al particles low melting point, due to decreasing refractoriness (2) The reaction of Al and water, therefore Al cannot be used in carbon-containing refractory compounds, in which the water-containing binders are used. Based on the above consideration, it is necessary to develop new antioxidants with excellent hydration resistance and high melting point such as Si-containing antiox-idants [4)]. Mostly metallic silicon and aluminum are added to the material as the sintering agent to improve the mechanical strength and abrasion resistance under oxidation. The effect of metallic silicon size on properties of alumina-carbon brick was 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

---

**Corresponding author*
Tell: +98 31 33912750, Fax: +98 31 33912752
E-mail: remadi@cc.iut.ac.ir
Address: Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran
1. Assistant Professor
2. Professor
3. Professor
4. PhD Student

under oxidation. The influence of β-SiC bond to the mechanical strength has not been clarified 5).

Generally, modulus of rapture vs. firing temperature increases and at given temperatures (1100, 1200, 1300, 1500 ºC) by increasing grain size of silicon up to more than 100 microns, the modulus of elasticity decreases. The amount of formed SiC decreases and remained Si increases for coarse particles. The current study 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 grain size to enhance Si reaction. The results of other works show that SiC addition in the 4 to 16 % range is beneficial to improve the mechanical properties as well as thermal shock resistance 6).

Large influence of the role of SiC materials on oxidation prevention have been shown by thermodynamic investigations and observations on the results after using.

SiC behavior in Al_2O_3-SiC-C bricks is illustrated as the following reactions 7):

$$SiC(s) + CO(g) = SiO(g) + 2C \qquad \text{Eq. (1)}$$

$$SiO(g) + CO(g) = SiO_2(s) + C(s) \qquad \text{Eq. (2)}$$

The most successful and commonly used ramming mixes were based on phenol-formaldehyde resins. The cured strength of these products was high because of polymerization of the resin that is called resit structure, at about 200 º C (Fig. 1). However, at elevated temperatures, due to oxidation in the carbonaceous bond phase, the products became weak in which created high porosity, lower density and reduced strength 1).

Advantages of resole binder consist of, environmentally friendly, easy mixing, and high residual carbon. The disadvantage of resole binder is pyrolization of resist structure, that is called polymer carbon and at temperature range of 350-550 ºC, the products gets weak (Fig. 1). The usage of additives such as silicon and ferrosilicon is to reinforce the resit structure by increasing the cross linking. Cross-linking reactions in general are those which lead to the formation of insoluble and infusible polymers in which chains are joined together to form these dimensional network structures. A sample cross linking reaction is exemplified by polymer chains with several func-tional groups designated A that are capable of reacting among themselves to form chemical bonds A-A (Fig. 2) 8). Cross-linking changes and generally improves physical and mechanical properties such as bulk density and cold crushing strength. 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 8).

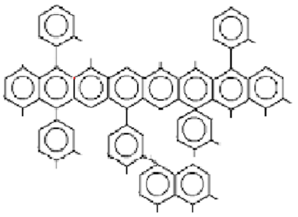

Fig. 1. Polymer carbon 8).

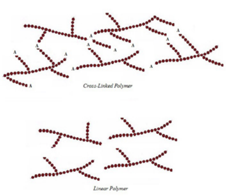

Fig. 2. Linear polymer and cross-linked polymer 8).

2. Materials and Methods

2. 1. Sample preparation

Specimens were prepared by mixing 90 wt. % aggregate, 10 wt. % resole as a binder with different amounts of additives. Silicon and ferrosilicon additives are used in this study. The composition consists of chamotte (0–3 mm, 65 wt. %), crushed sagger which is a SiC-containing material regenerates (15 wt. %) and fine coke (10 wt. %) as aggregates with different amounts of ad-di-tives of silicon and ferrosilicon metal.

The chemical compositions and phase contents of the raw materials are given in Tables 1 and 2 respectively. The raw materials were dry mixed for 5 min by a twin blade mixer, then the resole liquid was added gradually and mixing continued for another 5 min. The mixture was packed into metal molds with dimension of 50×50×50 mm^3 and then formed by hydraulic press under the pressure of 4 MPa. Pressed samples were tempered at 200 ºC for 2h. Finally, the samples were fired at 1100 ºC and 1400 ºC for 2h in a coke environment to avoid oxidizing atmosphere (under CO gas atmosphere). The specimens cured and fired were characterized according to ASTM standards (C0020-00R05 for CCS test and C0133-97R03 for A.P and B.D tests). The tests were carried out as follows: bulk density, apparent porosity (AP), cold crushing strength, also X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used in some cases. Cold crush-ing strength was measured by hydraulic testing machine type Amsler model D3010/2E. BD and AP were determined using Eq. (3) and Eq. (4).

$$BD\ (g/cm^3) = W_1 / (W_2 - W_3) \qquad \text{Eq. (3)}$$

$$AP\ (\%) = [(W_2 - W_1) / (W_2 - W_3)] \times 100 \qquad \text{Eq. (4)}$$

Base on Archimedes law, W_1, W_2, and W_3 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, respectively.

2. 2. Characterization

An X-ray diffraction (XRD) instrument (Philips Xpert-MPD System) with Cu $K_{\alpha 1}$(λ_1=1.5405 Å) and Cu $K_{\alpha 2}$(λ_2=1.5443 Å) and Ni filter was used for phase analysis and the voltage of 30 KV and current of 25 mA were employed. In order to study the phase fluctuations, the XRD experiment was studied with a rate of 0.04 degrees/sec between 5-80 degrees.

Scanning electron microscopy (SEM, Philips XL30) was used for microstructure investiga-tions. X-ray florescence (XRF) was also used for elemental analysis and oxides content calcula-tions (Table 1).

3. Results and Discussion

3. 1. Cold crushing strength and bulk density results

Figs. 3-5 show the influence of additives on cold crushing strength of chamotte-SiC-C resole bond refractory. Figs. 6-8 illustrate the effect of additives on bulk density of chamotte- SiC-C resole bond refractory.

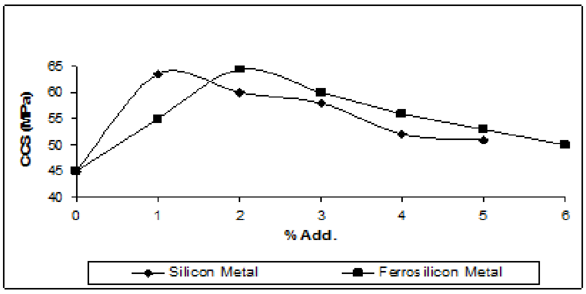

Fig. 3. Effect of silicon additives on CCS of chamotte-SiC-C compounds (200 ºC, 2h).

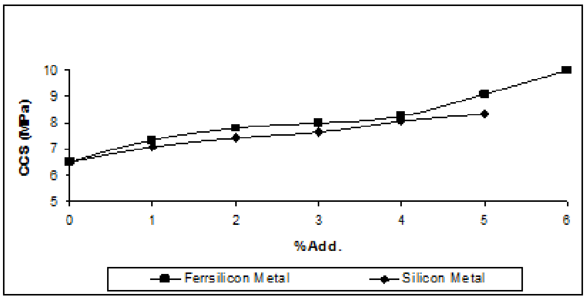

Fig. 4. Effect of silicon additives on CCS of chamotte-SiC-C compounds (1100 ºC, 2h).

Table 1. The chemical composition of raw materials (XRF results).

Material	Al_2O_3	SiO_2	CaO	SiC	C	Si	Fe	Particles size (mm)
Iranian chamotte	40	54	3.0	----	----	----	2.0	0-3.0
Crushed sagger	45	15	1.0	38	----	----	----	0-3.0
Fine coke	10	6	1.0	----	81	----	----	0-3.0
Ferrosilicon metal	----	----	----	----	2	72	24	0-0.05
Silicon metal	----	----	----	----	1.0	97	1.0	0-0.05
Resoled tempered at 800 °C	----	----	----	----	40	----	----	----

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

Material	Major phase	Medium and Minor phase(s)
Iranian chamotte	Mullite($3Al_2O_3.2\ SiO_2$)	Cristobalite (SiO_2)
Sagger crushed	SiC-α	Mullite($3Al_2O_3.2\ SiO_2$) , α-Al_2O_3
Coke	Graphite	Al_2O_3, SiO_2
Ferrosilicon metal	$FeSi_2$	Si
Silicon metal	Si	-------

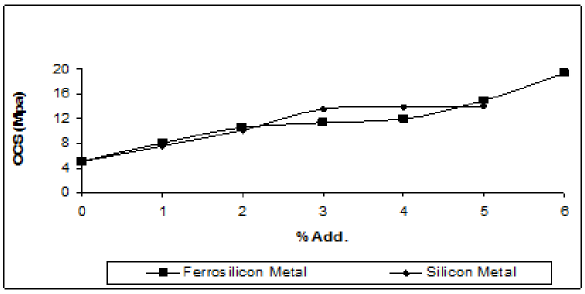

Fig. 5. Effect of silicon additives on CCS of chamotte-SiC-C compounds (1400 ºC, 2h).

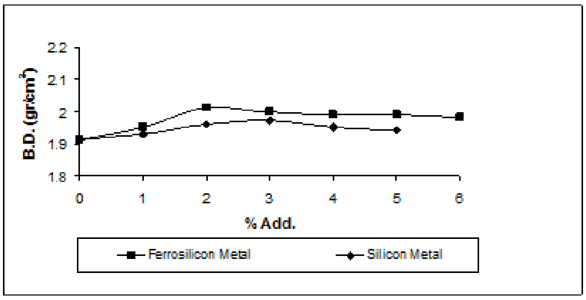

Fig. 6. Effect of silicon additives on B.D. of chamotte-SiC-C compounds (200 ºC, 2h).

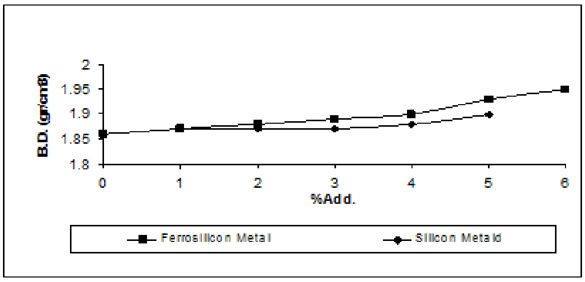

Fig. 7. Effect of silicon additives on B.D. of chamotte-SiC-C compounds (1100 ºC, 2h).

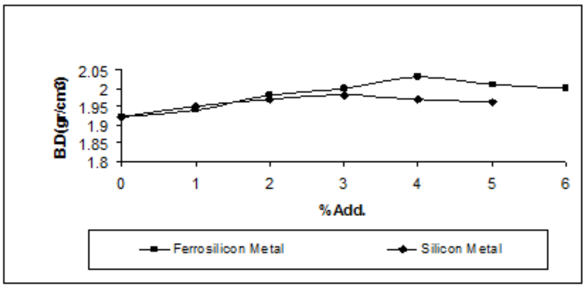

Fig. 8. Effect of silicon additives on B.D. of chamotte-SiC-C compounds (1400 ºC, 2h).

Fig. 9 shows microstructures of chamotte-SiC-Carbon refractory resole bond containing 6 wt. % ferrosilicon as the additive and fired at 1100 °C for 2h. Figs. 10 and 11 show microstructures of chamotte- SiC-C refractory resole bond, fired at 1400 °C for 2h, containing 6 wt. % ferrosilicon metal and 5 wt. % silicon metal as the additives, showing SiC whiskers of about 75-200 nm in diameter in the microstructure. SiC whiskers were developed from ferrosilicon and silicon metal particles in the microstructure.

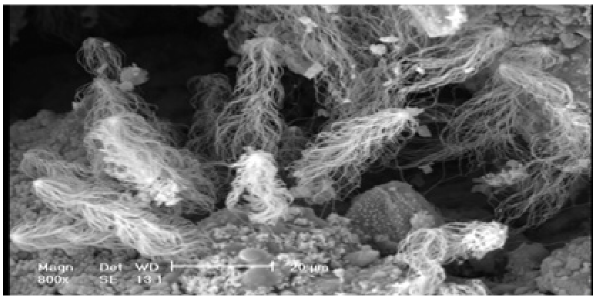

Fig. 9. Micrograph of chamotte-SiC-C compounds containing 6 wt. % ferrosilicon as the addi-tive, fired at 1100 °C for 2h, small quantities of SiC whisker are observed.

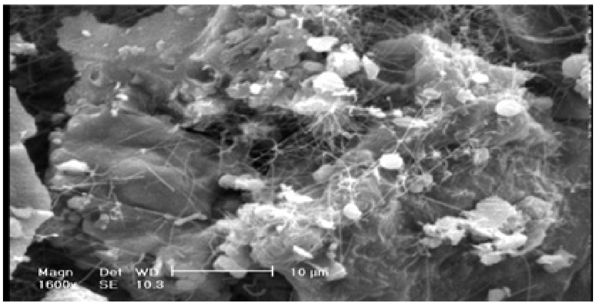

Fig. 10. Micrograph of chamotte-SiC-C compounds containing 6 wt. % ferrosilicon metal, fired at 1400 °C, showing SiC whiskers of about 80 nanometers in diameter in the microstructure.

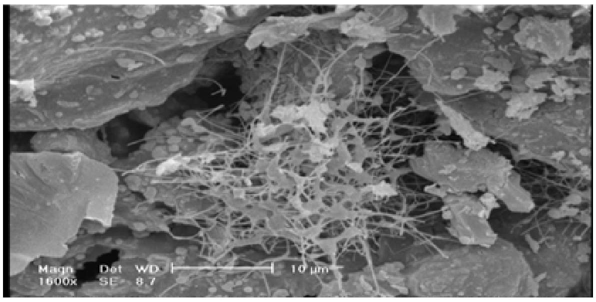

Fig. 11. Micrograph of chamotte-SiC-C compounds containing 5 wt. % silicon metal, fired at 1400 °C, SiC whiskers are developed from silicon metal particles in the microstructure.

3. 3. Phase Compositions

Phase compositions by XRD results are shown in Fig.12 (fired at 1100 ºC for 2h) and Fig. 13 (fired at 1400 ºC for 2h), containing 6 wt. % ferrosilicon metal as the additive.

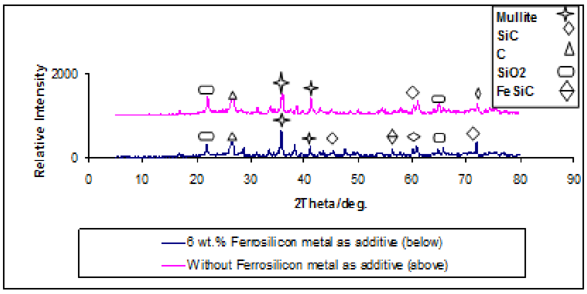

Fig.12. XRD results of fired chamotte-SiC-C compounds (1100 °C, 2h).

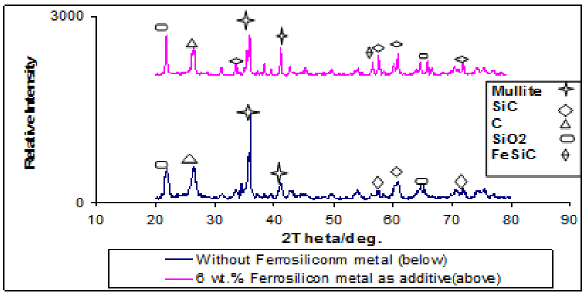

Fig.13. XRD results of fired chamotte-SiC-C compounds (1400 ˚C, 2h).

3. 4. Discussion

The effect of additives on the samples containing Iranian chamotte as the main aggregate (65 wt.%) are in a way that silicon and ferrosilicon metal generally increase cold crushing strength at all heat treatments of 200 ºC,1100 ºC and 1400 ºC, also increase the bulk density. The reason of strength increase at low temperature of 200 ºC is related to the cross linking formation in phenol formaldehyde resole structure or resit. The Si has a strong effect in small amount of 1 wt. %, due to a large amount of covalent bonds related to pure silicon. The effect is reduced for 2 wt. % and above, probably by an interfering effect of Si atoms. It seems that ferrosilicon is less effective than silicon and shows a maximum CCS for 2 wt. % and reduces the strength for 3 wt. % and above. SEM photomicrographs have proved that SiC whiskers of nano sized diameter has developed in samples at 1100 ºC .The reason for increasing the strength in the samples which was not clarified in some cases 5), is now evident to be related to the development of nano sized whiskers of SiC. Needles of mullite in glassy phase of matrix might be good for nucleation positions for starting and growth of SiC whiskers at temperature of 1100 ºC. At 1400 ºC, the driving force is high enough for the production of SiC whisker in the samples (Figs. 10 and 11).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. Formation of SiC by Ferrosilicon Alloys and Silicon have been studied by J. Pedro et al. 9). The formation of SiC has been done by the following Eq. (5):

$$Si(s) + C(s) \rightarrow SiC(s) \qquad \text{Eq. (5)}$$

At 1100 ºC, the Gibbs free energy for SiC is negative (-10420 Cal), so the formation of this product is thermodynamically feasible at such a temperature.

4. Conclusion

- At low temperature of 200 ºC, the resit structure was formed 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 refractory compound. There is a limit of 3 wt. % ferrosilicon for cross-linking at 250 ºC.
- At temperature of 1100 ºC the cross linking was destroyed, since the formation of SiC whiskers was only started due to the presence of $FeSi_2$ and not developed. Therefore, CCS values have not fully improved. ß-SiC whiskers were synthesized by the VLS process using Fe catalyst especially at1100 ºC.
- At high temperature of 1400ºC, the driving force is high enough for the production of SiC whiskers. Since in situ β-SiC whiskers of nano sized diameter were created, due to the presence of both Si and $FeSi_2$. Therefore, CCS values have improved in the samples con-taining 6 wt. % ferrosilicon metals by almost four times, approximately 20 MPa, which is remarkable for carbon containing refractory compounds.
- A hypothesis is given that probably high glassy content of the matrix of chamotte has caused high surface tension and high amounts of needles of mullite in chamotte, have caused more nucleation of in situ SiC whiskers at high temperature of 1400 ºC.
- At high temperatures above 800 ºC (such as 1100 ºC and 1400 ºC), resit structure was destroyed and graphite as a crystalline carbon state was formed.

References

[1] S.B. Bosall, D.K. Henry: J. Am. Ceramic Soc., 13(1985), 331.
[2] F. Chan, B. B. Aregent, William E.lee: J. Am. Ceram. Soc., 81(1998), 3177.
[3] J. R. Parsons, P. Forest, H. L. Rechter, United States Patent Number: 3810768, (1974), 1.
[4] K. Yamaguchi, S. Zhang, J. YU. Hashmato: J. Ce-

ramic Soc. Japan., (1991), 341.
[5] K. Akamine, T. Suruga, J. Yoshitomi, K. Asona: Internationals feuerfest- colloquium, Achen, (2006), 1.
[6] Fangbao, Ye, M. Rigaud, X. Liu, X. Zhong: Ceramics Int., 30(2004), 801.
[7] H. Nishio and A. Matsuo: Taikabutsu Overseas., 15(1995), 15.
[8] J. I. Kroschwitz: Concise Encyclopedia of Polymer Science and Engineering, Wiley & Sons, New York, (1990), 213.
[9] J. Y, R. Pedro, H. Long, N. Saha-chaudhury, B. Russell and S. Veena: ISIJ Int., 46(2006), 1570.