

Chapter-1

(Introduction & Literature review)

1.1 Introduction

Refractories are materials (usually nonmetallic) that maintain sufficient physical and chemical stability identity to be used for structural purposes in high-temperature environments encountered in the process industries. ASTM C71 defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures, or as components of systems, that are exposed to environments above 1,000 °F (811 K; 538 °C). While refractories are always exposed to high temperatures, the effect of other environmental conditions play a significant role in the performance of refractories during service. These include mechanical stresses, thermal cycling and associated stresses, erosion and corrosion by hot gasses and such molten materials as metals, slags, or glasses. Today, refractories are essential to the industry. Without refractories, few manufacturing processes could be carried out. The production of metals, cement, glass, petroleum products, and much of our electrical energy depends on refractories. Few people know relatively what refractories are or realize their importance because these materials seldom come to the attention of the general public. Refractories are usually sent directly from their point of manufacture to another factory, where they are used to make consumer items that bear no trace of the refractories that were essential for their production. In addition to

the category of refractories characterized by large-scale utilized in the process industries, there are others that are used for more specific applications. For example, in the aerospace industry extremely high temperatures are encountered from propulsion systems and friction heating at high velocities in the atmosphere. There are also applications in the field of nuclear energy. Such applications that may require the extensive use of refractories are a vital factor in the success of a particular system.

Refractories are classified primarily by their chemical composition and the forms in which they are used. To a lesser extent, refractories may be identified by association with a particular function such as thermal insulation, or a special manufacturing process such as fusion casting. Although the types of refractories manufactured for the industrial use are vast, it should be recognized that only a few chemical elements form refractory compounds are available in sufficient quantities to be used economically. The advantage of all “heavy” refractories are manufactured from compounds that involve the elements: silicon, aluminum, magnesium, calcium, chromium, and zirconium. The oxides of these elements are individually used or in various combinations. Recently and with increasing frequency, these elements are used in conjunction with carbon. Carbon or graphite refractories are also used with carbon as the sole constituent in the form of blocks or bricks.

Iron and steel industries are the major consumers of refractories. The world steel association provided recent figures in 2013; the total crude steel production was 1607.2 million tons (MT). China is currently the biggest steel producing country, which accounted for 48.5% of the world steel production

in 2013. With the rapid rise in production, India has become a 4th largest producer of the crude steel and the maximal producer of sponge iron in the

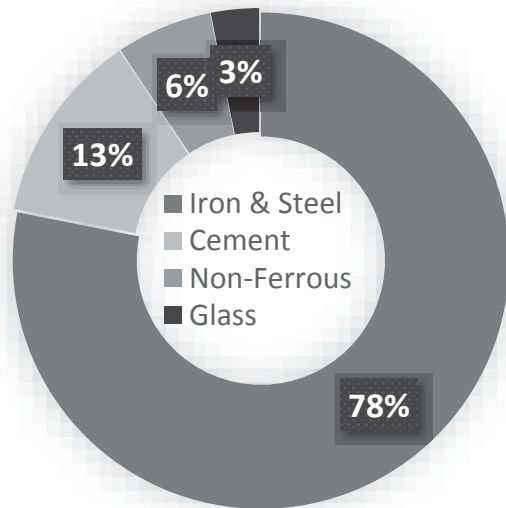


Figure 1.1 Industry-wise refractory consumption

world in 2013. India produced 81.2 MT crude steel production in 2013, and it is targeted to 300 million tons per annum capacity by 2025. The 12th plan has projected that the crude steel capacity in the country is

likely to be 113.3 million tons by 2016-17. The national steel policy had set a production targeted to 130 million tons by 2019-20 if all requirements are effectively met. The proposed assessment expansion plans are implemented according to the schedule; India may become second largest crude steel producer in the world by 2020. In the recent years, the production of refractory has also increased to reach the growing demand for steel production. The capacity utilization, however, currently stands at around 11.5-12 lakh tons per annum. Also, there has been an extraordinary change in refractory technology to fulfill the demand of high-quality steel production. From the global stock, steel industries (75%), cement industries (12%), non-ferrous industries (5-6%) and glass industries (3%) are the major consumers of refractories, which had been shown in Figure 1.1. Refractories are mostly used (70%) in basic metal industries whereas iron and steel industries are the primary consumers

of refractories. Therefore, refractory production is in tuned with the demand of iron and steel industries. In steel making furnaces, particularly basic nature refractories are using because of the basic reaction takes place during steel making process

To compete with the highest demands concerning performance, reliability and quality of steel castings lead to increasing pressure on both the metal-making and metal-using industry. In the light of above, refractory global demand is projected to expand at a 3.4 percent annual rate through 2016 to 46.3 million metric tons. Product sales will climb 5.3 percent annually in value terms to \$46.5 billion in 2016, not as strong as gains registered in recent years because of moderation in raw material costs and refractory prices. Increases in refractory demand will be stimulated by an acceleration in construction and other fixed investment activity as economic conditions continue to improve, leading to stepped up an output of steel, aluminum, cement, and other refractory-made goods.

1.2 Review of literature

Nothing happens unless first a dream. Incorporating carbon into refractories for iron and steel making applications has become in recent years an essential deed more than a dream. This is especially meaningful for hot metal pre-treatment and continuous casting and secondary steel making processes, where aggressive slag attack becomes the main concern to refractory linings. To improve slag resistance, especially penetration resistance, has become nowadays a focus of R&D work for iron and steel making applications, because

structural spalling caused by slag intrusion is, in many cases, the main wear mechanism. Several recent articles have pointed out the imperative of minimizing structural spalling and the meaningfulness and potential of carbon containing bricks.

Natural flake graphite, due to its availability and superiority in anti-oxidation and corrosion resistance, deserves the first choice as the carbon source. However, unlike other materials, its incorporation remains to be a hot potato, when taking a series of problems into consideration, such as poor wettability with the binder, much lower density than the oxide materials, lack of bonding with the oxides and oxidation at elevated temperatures. Elaborative work by taking effective countermeasures to minimize these adverse effects is very necessary to make a breakthrough in true graphite containing refractories.

Looking back on the evolution of refractories technology, we come to the consensus that introducing carbon into oxide based refractories is an epoch-making milestone in the past two or three decades. Since the late 1970's, carbon-containing refractories have been developed rapidly and have dominated many important application areas in metallurgy. Their widespread has led to a remarkable increase in service lives and reduction in specific consumption and specific cost of refractories (Ewais, 2004).

1.2.1 Carbon and graphite refractories

Elemental carbon is found in nature in the form of diamonds, graphite and above all as coal. For refractory purposes natural and artificial graphite (coke

from coking plants) are important for the manufacture of carbon bricks. The raw materials for carbon blocks should have ash content as low as possible as well as a high yield (Shaw, 1972). Because carbon or graphite refractories are both made up of the single element carbon, their distinction depends on upon the basis of their crystal structure.

Carbon Refractories generally do not have a well-ordered crystalline structure and may be considered amorphous, depending on the initial raw materials and

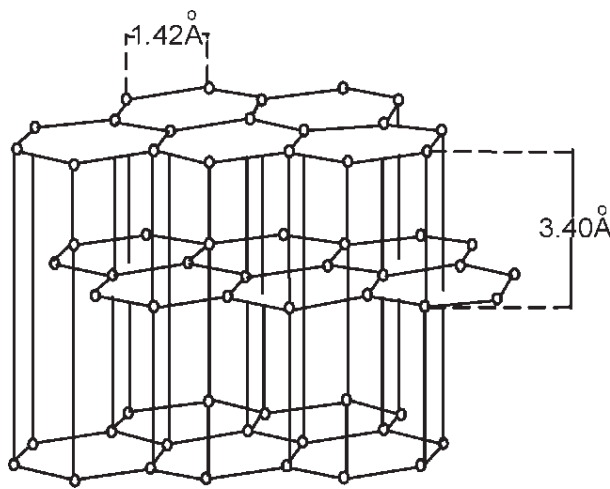


Figure 1.2 Crystal structure of graphite

the temperature that reached during the manufacturing. The graphite structure is well known (Cooper, 1980; Russel, 1982; Cooper 1982) planar structure with an infinite two-dimensional array of carbon atoms arranged in hexagonal networks in the form of a giant aromatic molecule. The

carbon-carbon bond (covalent) in the plane is strong as indicated by the interatomic distance of 0.142 nm where the bonding (Van der Waal type) between the planes is weak the interatomic planar spacing being 0.304 nm. Consequently, Graphite has a layered structure and may occur in flakes or show a preferred orientation of its crystallites because of the alignment of the crystallites in fabrication process i.e. the planar structure results has anisotropic properties.

The properties of graphite, in particular, single crystal graphite, in terms of thermal expansion, thermal conductivity and compressibility are attributed to the structure (Cooper, 1982; Ho et al., 1972). Thermal expansion perpendicular to the planes is 200 times that parallel to the planes. Thermal conductivity paralleled to the planes is 200 times that perpendicular to the planes. Its compressibility is 104-105 times greater in the direction perpendicular to the plane. However, the degree of anisotropy decreases for the graphite components produced from a random array of graphite crystallites and the properties of such a body can't be readily inferred from orientation factors in the random structure. This is the case for manufactured carbon refractories as they contain amorphous carbon and/or well-ordered crystalline structure.

Interesting properties of this refractory class regarding the distribution of size pore, low porosity, low thermal expansion and zero permanent linear change at 1600°C, were reported, in particular, if this type is manufactured from anthracite calcined at very high temperatures (1600-1800°C), extruded, impregnated. This improvement in the properties was based on the proper distribution of the grain size and, in turn, minimizing the intergranular spacing of the product (Bauer et al., 1983; Piel et al., 1997).

Three groups of refractory bricks out of carbon have been reported: amorphous, part-graphite or semi-graphite and graphite bricks. In recent years two further types designated as "microporous" were developed from the first two groups by additions of additives to improve their wear resistance (Piel et al., 1997).

a. Manufacturing

Carbon and graphite refractories are naturally occurring graphite, coal, petroleum coke, coal tar pitch, artificial graphite, coke from mines, gas-calcined anthracite and electrically calcined anthracite. Tar-pitches, petroleum pitches, and other organic materials are used as binders. The raw materials are prepared, ground, sieved, classified, mixed to batches depending on the desired property values, heated to approximately 160°C based on the type of bond, and mixed with a binder to get the so-called "green batch" or "green mixture." Next, the mix is shaped. Vacuum vibration equipment, die presses, extrusion presses, isostatic presses, and ramming equipment are used to form the batch/mixture into the desired shape. After shaping the so-called "green" shape is subjected to a firing process up to approx. 1200°C. The binder converts to coke. It is possible to accomplish subsequent densification and compaction by impregnating the blocks with impregnation agents, which are similar to the binders about their composition. The impregnation agent, which has entered the pores, is also converted to coke during further firing (Piel et al., 1997; Elderfield et al., 1968; Chester, 1973).

b. Physico-chemical properties

Carbon and graphite are not wet by most molten materials because of the low interfacial tension between carbon or graphite and molten materials. They have excellent thermal shock resistance, and their strength increases when they are heated. At 2500°C, the tensile strength of graphite is roughly twice as great as its room temperature tensile strength, which is approximately 2000

psi (Shaw, 1972). Carbon and graphite have a range from good to superb electric conductivity, thermal conductivity, and low expansion coefficients. Their thermal shock resistance is sufficient for standard applications. Despite good thermal conductivity and thermal shock resistance, the application of carbon blocks is restricted because they are susceptible to be attacked by oxygen, steam and CO₂ in an oxidizing atmosphere above 400°C.

The wear mechanisms for carbon bricks lining the hearth and hearth wall of blast furnace were reported (Mortl et al., 1983). Six wear mechanisms are responsible for the damage of carbon bricks;

1. The dissolution of carbon in pig iron (Wilkening, 1979).
2. The pick-up of potassium oxide and migration of it into the brick to temperature zones of 900°C and reaction with the crystalline phases of carbon e.g. mullite, α -cristoballite and α -quartz under the formation of kalsilite (K₂O·Al₂O₃·2SiO₂) and leucite (K₂O·Al₂O₃·4SiO₂) (Miyamoto et al., 1981). These reactions are combined with a volume increase, which causes a destruction of the brick texture. Further pick-up of potassium and the formation of potassium- carbon compounds of the formula C₈K, C₂₄K, and C₆₀K causes a swelling of the carbon bricks and a complete disintegration of it.
3. MnO pick-up of the brick and its reaction with ash compounds at a temperature above 1200°C forming manganese aluminum silicates. This, in turn, reduces the modulus of rupture of the brick.

4. The reaction of picked-up ZnO with binding phases of the carbon bricks destroying it, the formation of zinc orthosilicate ($2\text{ZnO}\cdot\text{SiO}_2$) or zinc aluminate during shutdown of the blast furnace (Miyamoto et al., 1981).
5. Oxidation of carbon by water vapor (McKee et al., 1981; Krol et al., 1978).
6. Thermal stress due to the existing pressure within the lining (Wilkening, 1979).

c. Applications

Because their properties, graphite, and carbon refractories are serious contenders for applications in a reducing environment. Blast furnaces use appreciable quantities of carbon and graphite, particularly in the hearth, but carbon and graphite may also find application in the bosh and other places such as tapholes (Chester, 1978).

With water-cooled shells, cupolas have been lined with carbon in the wells. Because of its high electrical conductivity, graphite is used for electrodes in electric furnaces to generate the arc. Because graphite can be easily machined, complicated shapes can be cut from stock in the form of bars, slabs, or cylinders. To accomplish the reduction process at electric arc temperature for the production of Si, FeSi, FeMn, etc., carbon electrodes with various graphite additives are applied. In these furnaces, the bottoms are partially lined with carbon blocks.

Carbon bricks are also installed as lining in tanks for making phosphoric acid because carbon has an excellent resistance to acids. Wear resistant graphite plates are used as shaped bricks for the manufacture of fused cast corundum bricks.

It must be mentioned that there is no international standard for carbon and graphite refractories and properties depend only on the manufacturer according to the request of the consumer.

d. Carbon-containing materials

Graphite and carbon also are used in combination with other refractory materials to form a composite suitable for certain applications. The importance of carbon additions can be seen in the wear reduction by reducing infiltration depth and in the bond of the unfired bricks. Furthermore, thermal shock resistance is improved by increasing thermal conductivity and decreasing thermal expansion (Barthel, 1997).

The brick bond of unfired products in a coked operation state is based on the adhesion between the coke lattice and refractory particles as well as on the adhesion within the coke lattice with partial direct atomic bonds, secondary valence bonds, and van der Waal forces.

The infiltration depth is changed substantially by carbon from centimeters to millimeters. Consequently, the wear mechanism of the bricks is changed drastically. Two factors are responsible for this:

1. The reduction of iron oxide in the liquid infiltration by metal. The eutectic temperature of the infiltrate is increased to its solidification point (with CaO/SiO_2 molar >2 if infiltrate contains FeO).
2. Non-wetting between the oxide infiltrate and carbon of the brick at a contact angle $\varphi > 90^\circ$ (with CaO/SiO_2 molar <2 if infiltrate doesn't contain FeO).

In addition to the FeO content, the CaO/SiO_2 molar ratio is a decisive in determining which of the two effects take place. The CaO/SiO_2 molar ratio regulates itself on the hot face side directly in the front of the carbon-containing brick zone. With magnesia and magnesia-doloma brick, the CaO/SiO_2 molar ratio always stays >2 because of the high CaO content in the brick. Consequently, the reducing effect is always active with these bricks if the slags contain FeO . For magnesia bricks, however, this ratio can drop below <2 as a result of the different precipitation during infiltration. The periclase absorbs the iron ions of the infiltrate (MgO by the chemical balance of the solution). Consequently, the melt losses iron before it reaches the carbon in the brick. Due to the CaO/SiO_2 molar ratio dropping <2 , the infiltrate remains liquid and agile despite its loss of iron. In this case, the non-wetting effect prevails. The same applies for slags without FeO .

The decisive factor for effective utilization and application of C-containing bricks is the burnout speed of carbon. In pitch or resin-bonded bricks, a cracked carbon lattice forms the brick bond. This means that carbon burnout leads to a decisive bond loss. Consequently, C-containing bricks can and should be used where reducing gasses, that is a furnace atmosphere with low oxygen

partial pressure, are predominant. Examples are converters, electric arc furnaces or the metallurgical ladle. To lower speed, additives for retarding oxidation are also used.

Carbon-containing materials are divided into carbon-based basic refractories and carbon based nonbasic refractories. Each type also can be classified according to the binders used. This means that the carbon to refractories carries out via different techniques to manufacture these types.

e. Manufacturing

The bricks or the blocks of these types of refractories are manufactured by grinding the raw materials, sieving, classification, mixing to batches depending on the desired property values, heating to approximately 100-200°C depending on the type of bond, and mixing with binder to get the so-called "green batch" or "green mixture." However, the bricks bonded with synthetic resin are manufactured cold or hot <100°C with liquid and a hardener. Next, the mix is shaped. Vacuum vibration equipment, die presses, extrusion presses, isostatic presses, hot pressing and tempering, and ramming equipment is used to form the batch/mixture into the desired shape. After shaping, the so-called "green" shape is subjected to a firing process up to approx. 1200°C. The binder converts to coke. Accomplishing subsequent densification and compaction is possible. It is possible to accomplish subsequent densification and compaction by impregnating the blocks with impregnation agents, which are similar to the binder regarding their compaction. The impregnation agent, which has entered the pores, is also converted to coke during the further firing cycle.

1.2.2 Binder – Phenolic Resin

The binding materials for carbon-based refractory materials should have an ash content as low as possible as well as a high yield. Tars, coal-tars or coal-tar pitches are the commonest types of materials used as carbon sources and binders for refractory bricks. They have long been used in practice. The physical properties of the tar or pitch influence the processing behavior greatly during manufacture. Conversely, the choice of binder is also determined by the particular processes in use (Blakeley, et al. 1957). The softening point of the residual binder should not be exceeded before carbonization for any given bricks to prevent spalling (Hughes, et al. 1980).

Because of the potential health hazards in the handling of such materials and the evolution of hazardous pyrolysis products, there is a tendency to use polymers to replace tars, coal tars and pitches (Bowman, et al. 1974; Gardziella, et al. 1992; Geber et al. 1992; Geber et al. 2000).

Phenolic resins, both novolak and resol are favored because they are or can become thermosetting and because they can be pyrolyzed during coking to achieve a high carbon yield. In addition to favorable pyrolysis and carbonization behavior, they are available in various forms, such as solutions, powder resins, solid materials, and melts. They also serve as binders and impregnating agents for carbonaceous materials and refractory products. Synthetic resin bonded bricks offer the following basic advantages (Suren et al., 1990; Zoglmeyr et al. 1988):

1. Their production and processing are environmentally acceptable.

2. Their production using the cold mixing method conserves energy.
3. The products can be processed in uncured conditions.
4. The products have no plastic phase when heated up, in contrast to tar-pitch binders.
5. The carbon content (more graphite or soot) can increase to augment resistance to abrasion and slag attack.

The control in the cure of the resins is a crucial factor where some resins tend to harden in a comparatively short time. This, in turn, reduces the time that mix can be retained before it must be shaped into bricks or other desired shapes. Layer and Shah et al., 1988, contributed in solving this problem by the control in pH in the presence of a catalyst.

During heating of this product in the operation state, the pitch forms elementary carbon (coking) at 300-600°C by pyrolysis in the liquid state leading to a separation of the volatile constituents (cracking) (Barthel, 1997). Laminated carbon packages form the proper structure at the hexagonal base plane. These carbon packages are easy to graphitize and possess excellent optical anisotropy. However, in the c direction the carbon planes stay shifted and twisted, with varying degree of distance, even at the highest operation temperature. This intense degree of one-dimensional imperfection corresponds to a polycrystalline graphite lattice (the three-dimensional graphite structure is not obtainable until >2000°C). In contrast to pitch, the pyrolysis of phenolic resins, which are synthetic polycondensation products occur in the solid state. The strong space interlacement of the molecule chains and, as a consequence, missing agility prevents an oriented deposit of

hexagonal carbon layers. A poorly arranged and strongly interlaced lattice is the result. This prevents gliding and cleavage. Therefore, these cokes are hard and very sensitive to oxidation due to the large inner surface (Barthel et al., 1983).

Phenolic resin has been widely used for its excellence kneading properties, molding properties and economy for carbon containing bricks. Although this binder has superior properties it has some drawbacks. Firstly, a phenolic resin generates gases such as water, hydrogen, ethylene, phenol, cresol and xylene when carbonized in temperature range of from 350-650°C causing air pollution and odor, etc. (Itotagawa et al., 1994; Itotagawa et al., 1995; Torigoe et al., 1996). Secondly, where a phenolic resin is used as a binder, the resulting structure is dense and has insufficient open cells. Therefore, the structure is liable to destruction due to the evolution of decomposition gas on heating. Thirdly, carbon produced from a phenolic resin is a glassy carbon inferior in resistance to spalling. Although the phenolic resin has a high residual carbon on burning, the resulting products have poor spalling resistance. Yamamura et al., 2000, proposed the using saccharify starch of a non-aromatic organic high-molecular compound to overcome the disadvantages of the pitch-bonded type and using a hexahydric alcohol as well as the first to the third drawbacks associating the use of a phenolic resin.

The properties of graphite, in particular, single crystal graphite, in terms of thermal expansion, thermal conductivity and compressibility are attributed to the structure. Thermal expansion perpendicular to the planes is 200 times that parallel to the planes. Thermal conductivity paralleled to the planes is 200

times that perpendicular to the planes. Its compressibility is 104-105 times greater in the direction perpendicular to the plane. However, the degree of anisotropy decreases for the graphite components produced from a random array of graphite crystallites and the properties of such a body can't be readily inferred from orientation factors in the random structure. This is the case for manufactured carbon refractories as they contain amorphous carbon and/or well-ordered crystalline structure.

1.2.3 Recent works on Al₂O₃-C refractories

Recently, a dramatic reduction of refractory consumption per ton of steel has been achieved in the iron and steelmaking industries. It is attributed to improving operations specifically in process control and hot gunning repair. It also results from the development of continuous casting processes. The quality of refractories, specifically carbon containing or based refractories, truly advanced composite materials, also played a major role in achieving a reduction in refractory consumptions.

Javadpour J. et al., 2006, have studied the effect of Al and Si additions on the properties and microstructure of Al₂O₃-C refractories. It has been observed that the strength increases and porosity decrease with increase in the Al as well as Si content in the samples. This improvement was due to the formation Al₄C₃ and AlN phases in the Al-containing samples and SiC formation in the case of Si-containing samples. It has also been reported that the improvement in the properties is sensitive to firing temperature in the case of Al additive but not

for Si additive. For example, the strength was found to decrease with increase in firing temperature in the case of Al containing the sample and the same was found to increase in Si-containing specimens. The lowering in strength with increase in firing temperature in Al-containing sample has been attributed to the decrease of Al_4C_3 phase with the increase in the firing temperature. The oxidation resistance was reported to improve with both Al (0-5 wt%) as well as Si (0-5wt%) additives. However, the formation of SiO_2 layer at the surface limits the improvement in the oxidation resistance at a higher percentage of Si addition.

The effect of combined addition of aluminum and silicon metal powder on the performance and properties of alumina-graphite composite refractories have been studied by Guoqi, Liu. et al., 2007, It has been reported that the weight loss for the sample without metal additive was less than that with metal additive when heat-treated at the same temperature. The weight loss of the sample with metal additive was found to decrease with heat treating temperature. The strength of sample with additives was higher than that without additives and was found to decrease slowly above 1200°C . The bulk density of the sample with additives was greater (lower apparent porosity) than that of the sample without additives which were found to increase with an increase in temperature. This is due to the in-situ AlN and a little Al_4C_3 formation when the heat-treated temperature above 1200°C . The formation of Al_4SiC_4 in the samples containing both the additives leads to the increase in strength when fired above 1300°C .

Gurcan, C et al., 2008, have studied the behavior and effects of antioxidants like $\text{Al}_8\text{B}_4\text{C}_7$ and Al_4SiC_4 on the carbon-containing Al_2O_3 -C refractories. It has been reported that $\text{Al}_8\text{B}_4\text{C}_7$ and Al_4SiC_4 showed an excellent oxidation resistance. This is because when $\text{Al}_8\text{B}_4\text{C}_7$ added to carbon-containing refractory, it reacts with $\text{CO}(\text{g})$ to form Al_2O_3 and B_2O_3 which further react with each other to form liquid phase at low temperatures. The liquid phase forms a protective layer on the surfaces of the refractory and thus inhibits the oxidation of the refractory. However, this effect of $\text{Al}_8\text{B}_4\text{C}_7$ as an antioxidant decreases at high temperature, owing to the evaporation of B_2O_3 . On the other hand, Al_4SiC_4 forms protective layer (Al_2O_3 - SiO_2) on the surfaces of the refractory as Al_4SiC_4 reacts with $\text{CO}(\text{g})$ and thus inhibits oxidation.

Bernard Argent B. et al., 2003, have studied the effect of additives (5% Al, 10% Si, 5% B_4C & 5% BN, 5% B_2O_3 , and 15% Si_3N_4) on the slag resistance of Al_2O_3 - SiO_2 - SiC -C refractories in air. Quite a good wear resistance was observed with the predicted content of SiC in the refractory in the as-fired condition. The most effective additives were found to be silicon and B_4C , while the most deleterious was B_2O_3 as slag resistance is concerned. These results were interpreted regarding the thermochemical predictions, including the variation in oxygen potential with slag attack. This study enables one to rank the refractories in order of likely resistance to attack significant amounts of liquid in the as-fired state favoring attack and reported that large quantities of SiC associated with Si additions and large quantities of BN associated with B_4C additions favored resistance to attack. Although the predictions about the order of oxidation of C and SiC were found correct for iron oxide-free slag, they were deemed wrong

for refractories other than those with silicon-containing additions exposed to iron oxide-bearing slag. This was due to the slow rate of oxidation of SiC at low oxygen activities.

The effect of ZrO₂-SiC composite on the oxidation resistance of Al₂O₃-C refractory have been studied by Jingkun, Yu. et al., 2007. The phase composition and microstructure of the synthesized composite were investigated by XRD and SEM. It has been found that the increase in heat treatment temperature promotes the synthesis of ZrO₂-SiC composite. The optimized temperature to synthesize the composite was 1873 K. It has been reported that the addition of synthesized composite had improved the oxidation resistance of the Al₂O₃-C refractory and the refractory with 6% (ZrO₂-SiC) addition had the best oxidation resistance.

The effect of TiO₂ and TiO₂/Al addition in MgO-C refractories has been investigated by Hub'alkov J. et al., 2007. The formation of TiCN and TiC compounds in the samples containing TiO₂ and TiO₂/Al additives was reported to be responsible for the improved oxidation resistance, mechanical strength as well as the abrasion resistance of the bonding matrix. The addition TiO₂ in carbon-bonded refractories with Al as an antioxidant contributed to the formation of mainly crystalline Al₄C₃, Al₂OC and Al₄O₄C dumbbell shaped whiskers. These whiskers have a higher oxidation resistance in comparison to amorphous whiskers containing Al, C and O and increase the thermal shock resistance due to interlocking in the bonding matrix. The microstructural study revealed the presence of AlN only at the interface carbon matrix/Al-grain.

Gurcan, C. et al., 2008, have studied the effect of various antioxidants namely Al, Si, SiC and B₄C on the oxidation resistance of magnesia–carbon bricks in the temperatures ranges 1300- 1500°C. B₄C was found to be the most efficient and SiC was found to be least effective antioxidants in the studied temperature range. The formation of the impermeable dense Mg₃B₂O₆ layer on the brick surface was found when fired at 1500°C. Magnesium–borate, which is in a liquid state above 1360°C, had an excellent effect on the oxidation resistance of the bricks by filling up the open pores and forming a protective layer on the surface. Forsterite (Mg₂SiO₄) and Spinel (MgAl₂O₄) provided similar effects when metallic Si and Al added as antioxidant respectively. Volume expansion and cracks were observed in MgO–C refractories containing 3% Al, oxidized at 1300°C, but were rarely seen in the Al added specimens oxidized at 1500°C. These physical changes were the results of hydration of Al₄C₃. The SiC added specimens had similar phases with Si added specimens, but least effective one as because of the formation of a lower amount of forsterite phase in the SiC added bricks compared to the Si added bricks.

Nemati Z, 2003, has studied the effect of ferrosilicon-silicon antioxidant on the properties of magnesia-graphite refractory. It has been observed that the ferrosilicon-silicon containing specimens showed the least apparent porosity with an increase of temperature in comparison with samples containing silicon or ferrosilicon alone. The ferrosilicon-silicon containing specimens showed more CCS and MOR with an increase of temperature than silicon or ferrosilicon containing specimens. The formation of phases such as forsterite and magnesioferrite and their volume expansion (in the ferrosilicon-silicon

containing specimens) are the main reasons for more compact structure, filling of the pores, decrease of porosity and permeability. Consequently, oxidation resistances of the ferrosilicon-silicon containing samples are more than silicon or ferrosilicon containing specimens. The best results were obtained for the samples containing 1-3 wt. % silicon and 2-4 wt. %. ferrosilicon.

Krivokorytov, E. V. et al., 1999, have studied the effect of antioxidants on the properties of unfired carbon bearing refractories i.e. periclase-carbon and aluminum-periclase-carbon refractories. It has been observed that the introduction of aluminum and crystalline silicon into the composition of the refractory mixture decreased the degree of burning-out in 3h heat treatment at 1200°C. The thermo-reactive binder based on a resorcinol oligomer used for the production of refractory specimens was found to have a favorable effect on the preservation of carbon in the refractory due to the activation of the oxidation of the coke formed in the polymerization of the oligomer. The study suggests that these factors should improve the slag- and metal resistance of the refractory.

The behavior of Al_4SiC_4 addition to the MgO-C refractories has been studied by Hoshiyama, Y. et al., 2007, It been observed that the density increases and the porosity decrease in the MgO-C brick on the addition of Al_4SiC_4 powder above 1000°C. The apparent porosity after heating at 1500°C was found 2% lower than that after heating at 800°C. The brick strength was increased gradually above 1000°C by the addition of Al_4SiC_4 powder. The Al_4SiC_4 powder has improved the oxidation resistance of the bricks. The bricks containing Al_4SiC_4 had high slaking resistance after heating. The Al_4SiC_4 reacts with CO gas to form

spinel (MgAl_2O_4) and SiC above 1200°C . The formed SiC also reacted with CO gas and MgO to form forsterite (Mg_2SiO_4) above 1400°C . The Al_4C_3 and AlN were not formed in these reaction processes.

Kryvoruchko P. et al., 2007, have made a comparative study of the properties like apparent porosity, bulk density, cold crushing strength, refractoriness under load, linear shrinkage, creep and thermal shock resistance between different alumina i.e. fused and sintered. They found that the sintered and white fused alumina is practically equivalent materials for the production of alumina refractories with good properties of purity, open porosity, apparent density, cold crushing strength and refractoriness under load. However, the refractory of sintered alumina has higher thermal shock resistance, whereas refractory of white fused alumina has higher creep resistance. Both types of refractories have similar interaction with melted steel.

The dissolution and settling of spherical alumina particles into the synthetic slag of various compositions in the temperatures 1200 and 1400°C have been studied by Sridhar S. et al., 2009. It was observed that the surface remains smooth and no reaction layer was formed when the slag was without or contains low FeO_x . The dissolution curves indicate that the dissolution process was controlled by the diffusion of species. The total dissolution times of spherical particles in slag A (0 % FeO_x), B (5% FeO_x) and C (9% FeO_x), at 1400°C , are 3150, 1440 and 944s, respectively. At 1200°C , there is no appreciable dissolution observable due to the fact that the slag was saturated with Al_2O_3 .

Sunayama, et al., 2005 have studied on the dissolution of alumina spheres in a synthetic CaO–Al₂O₃– SiO₂ (CAS) slag in the temperature range between 1470 and 1630°C. It has been observed that the use of spherical particles was shown to increase the experimental resolution of the dissolution phenomenon, and consequently the determination of the dissolution mechanism was more convincing. The driving force for Al₂O₃ dissolution was related to the concentration difference of Al₂O₃ between the particle/slag interface and the bulk of the slag. Mathematical simulations showed that the dissolution mechanism was diffusion controlled, yielding an excellent agreement with the experimental data. The diffusion coefficients have been obtained ranging from 2.4×10^{-11} to 9.7×10^{-11} m²/s in the temperature range between 1470 and 1630°C.

Zhang, S. et al., 2000, have investigated on the dissolution mechanism of commercial white fused alumina (WFA) and tabular Al₂O₃ (TA) grains into a model silicate slag. It has been reported that the dissolution of WFA grains in the slag was higher than the TA grains tested at a different temperature. The formation of CA₆ and hercynitic spinel layers was found at Al₂O₃/slag interfaces. Liquid present in the CA₆ layer adjacent to the WFA at 1450°C provides an easy transport path for ions and thus increases the extent of direct dissolution. However, a thick, continuous and liquid-free CA₆ layer was formed adjacent to the WFA at 1600°C. Thus the dissolution of WFA became fully indirect at this temperature, requiring mass transport through the CA₆ interlayer to access the Al₂O₃. The CA₆ and spinel layer that formed adjacent to the TA was not continuous at both temperatures, and hence TA dissolution was

never fully indirect. In these samples, the slag could penetrate readily to the grain interior via grain boundaries. Hence TA grains were directly corroded and disintegrated by the penetrating slag in these samples. After the formation of CA_6 and spinel, the remaining cations in the boundary layer formed low-melting phases, which dissolved into the slag at the high test temperature. These phases (anorthite solid-solution needles and hercynitic spinel dendrites) precipitate during cooling from the test temperature.

The corrosion resistance and microstructure of Al_2O_3 -C based refractories have been studied by Qingcai Liu et al., 2005, in smelting reduction melts by the quasi-stationary immersion and rotary immersion test. They reported that the corrosion rate of the Al_2O_3 -C (AC) based refractories was decreased with the addition of the graphitic carbon and ZrO_2 . The test results showed that the ZrO_2 containing bricks (AZ) had much better corrosion resistance than the ZrO_2 -free bricks. The ZrO_2 addition improved the oxidation resistance of the refractory and decreased the interaction rate between the melts and the refractory. The corrosion of the Al_2O_3 -C based refractories is caused by the interaction between melts and refractory, and the dissolution of the refractory constituents into the melts. The corrosion rate of both AC and AZ system refractories was found to increase with the iron oxide content of the melts and the temperature of the molten bath. The corrosion rate of the rotary test was 30% higher than that of quasi-stationary immersion test. The corrosion mechanism of AC refractories in the smelting reduction melts with iron bath was deteriorative layer formation followed by graphite oxidation. The interaction between melts and refractory and the dissolution of the refractory

constituents into the melts governs the corrosion for the AZ refractory. The microstructural study revealed that the new compounds FeSiO_3 , ZrSiO_4 , Ca_3FeO_4 , CaSiO_3 were formed in the deteriorative layer during the interaction between the melts and AZ refractory system.

Zhao, L. et al., 2003, have studied the interfacial phenomena during the interaction of liquid iron and graphite/alumina mixtures. It has been reported that the carbon dissolution strongly depends on the wetting/non-wetting behavior of the refractory/molten metal interface or in other words the contact angle of the liquid iron - refractory interface. It has been observed that during the graphite/iron interactions, the contact angle changed from 64° to the initial state to 38° at the final state and thus showed a good wettability between iron and graphite. However, the addition of different amounts of alumina into the graphite substrate caused the contact angle to increase. When the alumina in the substrate rose from 16.7 to 23.1%, the contact angle demonstrated a sharp change from good wetting to almost non-wetting. A relatively high rate of carbon dissolution was observed when the contact angle was low (at low alumina content) on the other hand it decreases sharply when the alumina in the substrate increased from 16.7 to 23.1%. This decreased rate of carbon dissolution had been attributed to the poor wetting behavior of graphite/alumina substrate.

The interaction between slag- Al_2O_3 -SiC-SiO₂-C refractory has been investigated by Hong, Lan. et al. The composition of the slag and refractory studied in this investigation were 45.4% SiO₂ - 36.6% CaO - 15.9% Al₂O₃ and 69.4% Al₂O₃ - 7.3 % SiO₂ - 10.6 % SiC - 12.7 % C respectively. The slag

refractory interaction has been studied in the temperature range 1773 to 1873 K. The XRD study confirmed that the formation of mullite when the refractory samples were maintained at high temperatures. The refractory/slag reaction has been evaluated from the carbon dissolution of the refractory. The time dependence carbon dissolution from the refractory was found to follow a two-step process. During the initial stage the carbon dissolution rate was high and then it is decreased. The high carbon dissolution from the refractory has been correlated with the evolved gasses. The gas chromatographic analysis study confirmed the evolution of both CO and CO₂ gasses during the initial stage however the latter disappeared as the time increased. The main in-situ reaction product was SiC rather than SiO. Slag showed a good wetting with the refractory and penetrated into the refractory through pores. The formation of low melting compounds like anorthite (CaAl₂Si₂O₈) and gehlenite (Ca₂Al₂SiO₇) was confirmed at the slag refractory interface when heated for a longer time.

The role of ash impurities in the depletion of carbon from the alumina-graphite refractory into liquid iron have been investigated by Khanna, R et al., 2007. Two natural graphite, containing 2.1% (NG1) and 5.26% ash (NG2) were used in this study. The carbon pick-up by liquid iron from alumina–natural graphite has been measured at 1550°C by a sessile drop arrangement. and was compared with the carbon pick-up from alumina–synthetic graphite mixtures. It has been observed that both natural graphite under investigation, showed a high level of carbon dissolution into liquid iron. The presence of up to 30% alumina had a negligible effect on carbon dissolution from alumina–natural graphite refractories with a carbon concentration in the melt reaching 5 wt%.

However, a significant reduction in carbon dissolution was observed for alumina in the concentration range 30 to 40 wt%. Further, it was observed that the significant differences in ash composition of the natural graphite used under this investigation lead to the difference in the nature of deposits observed in the interfacial region. While a small number of sporadic deposits were observed in the case of alumina-NG1 mixtures, a layer of fused ash appeared to cover the interfacial region in case of NG2. However, in both cases, EDS analysis of the interfacial region indicated the presence of Ca, Mg, Al, Fe, O and S in close vicinity. It was therefore confirmed that alumina in the refractory interacts with various oxides present in the ash impurities.

Sasai, K et al., 1995, have investigated the reaction kinetics between silica-containing alumina- graphite refractory and low carbon melted steel. The study suggested that the rate of reaction between the refractory and the molten steel was controlled by diffusion of the SiO gas and CO gas through the pores of the oxide film formed at the refractory-molten steel interface. The rate of the reaction between the refractory and the molten steel was found to be dependent on steel grade. For example, the reaction was found faster in the Ti-killed molten steel than in the Al- killed molten steel. This grade steel dependence had been ascribed to the differences in the gas permeability through the oxide film formed at the refractory-molten steel interface. In other words, the surface of the refractory immersed in the Al-killed molten steel was nearly covered with a relative dense oxide film present in both solid and liquid phases, whereas the surface of the refractory immersed in the Ti-killed molten

steel was discontinuously covered with a relative porous oxide film in the solid phase.

Sunayama, 2005, has studied the corrosion in magnesia carbon refractory, H. et al. rotating the cylindrical samples in molten slag at 1673K. It has been reported that the corrosion behavior was affected by the slag composition. The decrease in corrosion rate was found with a decrease in MgO content of the slag. The rotation speed did not have any significant effect on the corrosion rate. It has been suggested that the movement of CO bubble through the boundary layer strongly affect the dissolution rate of MgO grains. The study suggests that the reduced rate of CO bubble formation is effective to improve the corrosion resistance of MgO-C refractory in molten slag.

Uchida, S et al., 1998, have studied the behavior of MgO-C refractory with the slag-metal system. It has been reported that the reactions between MgO-C refractory with slag-metal was due to the dissolution of MgO and graphite in the refractory into slag and metal respectively. It has also been reported that the generation of gas bubbles was responsible for the corrosion. The local corrosion was regarded as due to the cyclic dissolution of MgO and graphite in the refractory into slag and metal phase respectively. The study suggests that gas bubbles formed mainly according to the reaction between (FeO) in slag film and C(s) in the refractory by the reaction $(\text{FeO}) + \text{C}(\text{s}) = \text{Fe}(\text{l}) + \text{CO}(\text{g})$. The corrosion rate was found to be influenced by the bubble generation position and the number of bubbles generated. Bubbles generated in the three-phase boundary restrain the local corrosion, while bubbles generated at the refractory metal interface enhance the local corrosion.

Zhang, S et al., 1997, have investigated the influence of additives on the corrosion resistance and corroded microstructures of MgO–C refractories in a model EAF slag (CaO/SiO_2 weight ratio = 1.38) for 30 h at 1650°C. It has been reported that Al additions improved C oxidation resistance at 1650°C only a little, but accelerated MgO dissolution resulted in a minor effect on corrosion resistance. Additions of Si or Al+Si was found to improve carbon oxidation resistance slightly but accelerated MgO dissolution more as compared to Al additions thus, resulted in worse corrosion resistance than Al addition and no addition. B_4C showed the worst corrosion resistance due to the formation of boron-containing liquid in the refractory which greatly accelerated MgO dissolution, resulting in C in the matrix, which easily eroded by the slag. With the double addition of Al+ B_4C , boron-containing liquid formed, which not only inhibited carbon oxidation effectively but also accelerated formation and growth of MgAl_2O_4 spinel (MA) crystals between graphite in the matrix at the test temperature. The formation of MA provides the integrity of the refractory texture and thus best corrosion resistance was observed in the Al+ B_4C containing refractory.

Lee WE et al., 2000 have studied on the penetration and corrosion resistance of high purity sintered and fused magnesia grain by model EAF ($\text{CaO}/\text{SiO}_2 = 1.38$) and BOF slag ($\text{CaO}/\text{SiO}_2 = 3.29$) at 1600 and 1700°C. It has been found that at the test temperatures, Fe and Mn ions from both model slag were diffused into the magnesia grain to form magnesio-wustite, $(\text{Mg, Fe, Mn})\text{O}$. The magnesio-wustite formed adjacent to the slag had a much larger crystal size than that of the bulk MgO far from the MgO/slag interface. The large magnesio-

wustite grains limit the potential for grain boundary penetration into the sintered magnesia. The magnesio-wustite layer formed with the EAF slag took up more Fe_xO from the slag than that formed with the BOF slag, which was partially responsible for a lower slag penetration into sintered magnesia grain since the remaining silica-rich local liquid was rendered more viscosity. It has also been reported that the EAF slag was not saturated with respect to MgO, so the magnesio-wustite which formed later reacted with Ca and Si ions remaining at the MgO/EAF slag interface to form low melting phases such as merwinite (C_3MS_2) and then dissolved into the slag, rendering the dissolution process essentially indirect.

Baldo, JB et al., 2000, have studied on the corrosion resistance of resin bonded alumina/magnesia/graphite refractories containing different kinds of aggregates subjected to the action of slag of several CaO/SiO₂ ratios. They also investigated the influence of alumina/carbon ratio and magnesia and silica contents on the refractories corrosion resistance. It has been observed that as the graphite content was high enough (6 wt%) to give excellent sinterability and small enough not to hinder the diffusion of ions responsible for the spinel formation. A lower concentration of the mullite phase resulted in a lower production of calcium aluminosilicates (eutectic composition anorthite-gehlenite MP.1265°C). Higher periclase/mullite ratios led to higher mullite consumption due to its reaction with periclase, producing the forsterite ($2\text{MgO}.\text{SiO}_2$) phase and alumina. This precipitated, highly reactive alumina was able to combine with the excess of periclase, forming initially magnesium aluminate and later magnesium-aluminum Spinel (MgAl_2O_4). The study

suggested that the combined effect of these reactions in the refractory microstructure creates barriers in the open porosity originating a concurrent mechanism of protection. The use of electrofused alumina in substitution to sintered alumina and bauxite in the formulations promoted an increase in the corrosion resistance as a consequence of the smaller rate of dissolution by the slag. In this case, the A/C ratio was 12.9.

The properties and corrosion of alumina-magnesia-carbon refractories have been studied by Pötschke, J. et al., 2003. The content of the mixture contains magnesia 5 - 35 % and the carbon content about 10 %. Coking of the “as delivered bricks” has resulted in an increase by about 6 % of porosity, and on firing at 1250°C, it was about 8 %. The burning-out of 10 % carbon has raised porosity by about 15 % in the samples. The porosities of the oxidized fired bricks at 1250°C have the range between 24-30 %. A post-firing expansion of the AMC refractory was observed due to the formation of spinel at high temperature. The post-firing expansion becomes stronger with higher contents of MgO and in a reducing atmosphere. The decarburization of AMC-refractories in the air was found to be controlled by the diffusion of oxygen in the open porosity. A slag layer on the refractory surface has been determined by laboratory tests and practically resulted in best protection for preventing oxygen diffusion. The metallurgical corrosion resistance of bauxite based AMC-refractories has been found to be poor as compared to alumina-based ones.

Bavand-Vandchali, M et al., 2009, have investigated the effects of carbon, air and reducing atmospheres on microstructure and phase evolution of in situ MgAl_2O_4 spinel formation in the matrix of MgO-C refractories. It has been

reported that the formation of spinel was started under 1000°C in both air and reducing atmospheres. The study suggested that the solid-state reaction was the dominant mechanism of spinel formation in oxide atmosphere, while the gas–solid reaction was found to play a vital role in reducing atmosphere. The reaction of MgO and C in reducing atmosphere led to the formation of Mg(g) which was found to be partially controlling the in situ spinel formation in the carbon-containing samples fired in reducing environment. The in situ spinel formation was due to the reaction of reactive alumina and magnesia initiated around 1000°C in both reducing and oxidizing atmospheres. This reaction was completed above 1450°C where no signatures of the corundum peaks were found. The partial pressure of Mg(g) originated from MgO reduction was found to have a significant role on the in situ spinel formation. The intermediate phases such as CA₆ were clarified to be formed due to the reaction of MgO impurities with reactive alumina at 1450°C. The low-melting CMAS phases were also formed in the triple junction of spinel, which was believed to be responsible for corrosion resistance decrease at high temperatures. The nature of spinel in MgO–C refractories matrix produces an interlocking texture, which holds the graphite flakes within and improves the structural integrity. In this type of skeleton structure, the graphite and antioxidants can be confidently increased for getting better wear resistance and with less adverse effects on properties of MgO–C refractories.

Ghosh NK et al., 2001, have investigated on the oxidation mechanism of MgO-C refractories containing 20wt % graphite in air at various temperature (from 800C to 1600°C). It was found that the rate of decarburization increased with

the rise in temperature from 800°C to 1400°C and then remained more or less constant from 1400°C to 1600°C. The reaction rate was found to be controlled by diffusion of oxygen through the decarburized layer. At higher temperature (> 1400°C), oxidation of graphite takes place indirectly by the reaction $\text{MgO(s)} + \text{C(s)} \rightarrow \text{Mg(g)} + \text{CO(g)}$. The magnesium vapor thus produced is deoxidized at the outer surface and redeposited as MgO. This leads to a reduction in porosity in the decarburized outer shell and consequently a reduction in the rate of oxidation.

Guoqi Liu et al., 2005, have studied on the influence of heat-treatment atmosphere (argon, CO+N₂, and nitrogen) on Al₂O₃-C (AG) samples with metallic Al addition. The study suggested that none of these three heat-treating atmospheres can avoid the formation of Al₄C₃. However, different heat-treatment atmosphere can influence the hydration resistance of the samples containing metallic Al. The hydration resistance of the material heat-treated in N₂ atmosphere was found to be the best. The microstructural study suggests the formation of submicrometer whiskers shaped Al₄C₃ when heat treated under C+N₂ atmosphere. On the other hand, the formation of floccules, band-shaped and hexagonal coniform like whiskers and granular AlN was observed when the samples were heat treated under Ar and N₂ atmosphere respectively. Heat-treatment in C+N₂ and N₂ were found beneficial to increase the strength and decrease the apparent porosity of the samples with metallic Al addition.

The effects of resin type and content, as well as graphite content on physical and mechanical properties of MgO-C refractories, have been studied by Nemati, Z.A. et al., 2006. It has been reported that the low-viscosity resins improved

compressibility. However, the strength is degraded. Higher resin content was found to improve the compressibility, but it caused higher porosity after preheating at 600°C. The results also showed that the porosity and density of tempered samples were decreased on increasing the graphite content. It has been found that the porosity decreased when the resin content increases in the tempered specimens. This effect was due to the improvement of compaction during pressing as resin content increases. However, in the preheated samples at 600°C, the porosity was found to increase when the resin content increases, which reported being resulted from burning out of a total organic portion of resin (about 70 wt.%). On the other hand, cold crushing strength of the tempered (tempered at 240°C) samples was found to increase when their resin content increases, due to a decrease of porosity and improvement of resin bonds. Weight loss was found to increase with respect to time and temperature of oxidation test in the samples containing a high amount of graphite. Ivashchenko L. V. et al. have studied the effect of graphite on the properties of periclase- carbon composite using graphite flake and elementary carbon. It has been observed that the open porosity of the specimens held for 1 day after compaction was virtually independent of the type and the quantity of graphite. The ultimate compressive strength was found to decrease with increasing the graphite content and was 1.5-2 times higher in the case of the specimens containing graphite flake (have decreased gas permeability). The specimens containing flake graphite exhibit the best property after drying at 20°C for 24 h. A similar dependence of the open porosity, the strength, and the gas permeability of the specimens on the content and the type of graphite was

observed after heat treating at 1000°C. A comparison of the gas permeability of the specimens before and after firing at 1000°C showed that it was virtually identical, i.e., pores were evidently isolated (not interconnected) and decarburization (carbon burn up) occurs only on the surface of the specimens. The specimens containing graphite flake showed better properties on heat treating at 1000°C.

1.3 Objectives

The present work is set to tackle big challenges as carbon retention and structural integrity owing to spinelization. As an initial stage of such an endeavor, the aim and scope of the present work include:

1. Development of low-carbon refractories by dispersion of NCB for the production of ultra-low carbon clean steels.
2. Improve degradation of $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-C}$ based slide gate plates, nozzles using small quantities of mechanically activated oxidation inhibitors.
3. Minimize carbon oxidation in $\text{Al}_2\text{O}_3\text{-SiC-C}$ for BF iron/slag runner by studying three different combinations of antioxidants.
4. Optimization of *in situ* spinel formation in $\text{Al}_2\text{O}_3\text{-MgO-C}$ refractory and to minimize the crack and rupture through residual expansion.
5. Formulation of a new class of $\text{Al}_2\text{O}_3\text{-MgO-C}$ containing both pre-formed and *in situ* spinel. The *in situ* spinel phase enhances the thermal shock and molten slag resistance, whereas the pre-formed grains ensure suitable volumetric stability.