A
Thesis
On

A Study on the Development of Refractories for Carbon Black Reactor

By

Tynee Bhowmick

Under the Supervision
Of

Dr. Ritwik Sarkar
Department of Ceramic Engineering
National Institute of Technology, Rourkela

Thesis submitted
in partial fulfillment for the Degree of
MASTER OF TECHNOLOGY
IN
CERAMIC ENGINEERING

Department of Ceramic Engineering
National Institute of Technology, Rourkela
Orissa-769008
2013

CERTIFICATE

This is to certify that the thesis entitled *"A study on the Development of Refractories for Carbon Black Reactor"* submitted by **Tynee Bhowmick (Roll No: 211CR1265)** in partial fulfilment of her requirements for the award of Master of Technology degree in Ceramic Engineering at **National Institute of Technology, Rourkela** is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied within this thesis has not been submitted to any other university/institute for the award of any other degree or diploma.

Dr. Ritwik Sarkar
Dept. of Ceramic Engg.
National Institute of Technology
Rourkela

Biswajit Ghosh
GM (Tech) (R&D)
TRL Krosaki Refractories Ltd
Belpahar

Acknowledgement

“Alone we can do so little; together we can do so much” – Helen Keller

My deepest regards to my guide and supervisor, Prof. Ritwik Sarkar, Department of Ceramic Engineering, NIT, Rourkela for his timely help and guidance. Without his kind guidance, this thesis would have remained incomplete. I should also thank Dr S. Adak, Vice President, Technology, TRL Krosaki Refractories Ltd. for permitting me to carry out the major part of my work at the premises of his esteemed company. Another important person who deserves mention is my mentor at TRL Krosaki Refractories Ltd., Biswajit Ghosh, GM (Tech, R&D). It was because of his constant guidance and the fact that he always managed quality time for me inspite of his hectic schedule that I was able to complete my project work on time. All the employees of TRL Krosaki Refractories Ltd., specially T.T. Tripathi Sir, Ambarish Ghosh (Manager, High Alumina Plant) and the workers at the High Alumina plant who helped me without complaining also deserve a special mention. I would also like to thank each and every employee at the R&D facility of TRL Krosaki Refractories Ltd. who went out of their way to help me with my work especially Tapas *dada*. I would also like to thank all the faculty members of Department of Ceramic Engineering, NIT, Rourkela for their constant encouragement. I thank my friends especially Aditya Prakash Shrimali, Subham Mahato and Uttam Kumar Chanda who stood beside me through thick and thin. Last but not the least, I wish to thank Prof. S. Pal and Prof. S. Bhattacharya, Department of Ceramic Engineering, NIT, Rourkela for believing in me even when failed to do so myself.

Dedicated to my parents

…without whose love and support I do not stand a chance in conquering the world…

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Abstract

High alumina refractories are manufactured with high quality raw materials and normally possess good hot properties and can be lined in operation zones with critical conditions. However, certain application areas require very high specifications. An example is the carbon black reactor which operates beyond 2000°C. Here, conventional high alumina refractories do not give good performance and life. In the present study, an attempt has been made to study the development of refractories suitable for use in carbon black reactor. Zirconia is added to high alumina refractories to improve its thermo mechanical properties and spalling resistance. Transformation toughening due to tetragonal to monoclinic phase change in zirconia is utilized for the improvement of properties. Zirconia can be obtained from many sources. The raw materials selected have an important bearing on the properties of the final product. Three different sources of zirconia were used to optimize zirconia. This was followed by optimization of reactive alumina. Reactive alumina has very fine particle size which helps to achieve better sintering and reduces porosity. Hot properties were further improved by the addition of chrome oxide. Physical, thermal and thermo – mechanical properties, critical to operating conditions in the carbon black reactor, were studied and reported in this thesis.

Keywords: High alumina refractory, carbon black reactor

CHAPTER 1
INTRODUCTION

1.1 Introduction to Refractories

Refractories are non – metallic materials that are suitable for the construction or lining of furnaces operated at high temperatures [1]. These are used to line kilns, incinerators and reactors and also used in the manufacture of crucibles. The definition of refractory according to ASTM C71 can be expressed as: "non – metallic inorganic materials having those chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000^{O}F (811 K; 538^{O}C)". These materials have high melting points and act as barriers between high and low temperature zones. Refractories are different from other building materials as these are required to meet certain pre – defined specifications. As the temperatures in modern industrial furnaces can be anywhere in between 1000 and 1800^{O}C, the refractories used in the lining of these furnaces should be able to withstand these high temperatures. Also, the importance of withstanding structural load can not be underestimated especially during setting up or construction of the structure. A refractory should also be able to take load from the charge. A refractory may undergo an increase in volume on firing at higher temperatures which may lead to cracks in the refractory (decrease in volume is a desired phenomenon and occurs as a result of sintering). Thus, another important property that a refractory must possess is volume stability at operating temperatures. On being exposed to temperature differences as a result of cycled heating and cooling of furnaces, a refractory may undergo thermal spalling which leads to crack formation. A refractory should therefore have high spalling resistance. High abrasion resistance is required to tolerate movement of furnace components. Mechanical strength is required in order to be able to withstand movement of furnace components. Also, a refractory should be chemically stable and should be able to cope with attack from heated solids, liquids, gases or fumes. The general properties of refractories that are monitored for the purpose of quality control are mentioned below:

- High refractoriness
- High melting point
- High crushing strength
- High refractoriness under load
- High modulus of rupture
- High spalling resistance
- Good resistance to slag (for refractories used in steel industry)
- Good erosion and corrosion resistance
- Good abrasion resistance

- Low porosity
- Low thermal expansion

1.2 Classification of Refractories

1.2.1 Classification on the basis of chemical nature

Refractories can be classified on the basis of nature into acidic, basic and neutral refractories.

1.2.1.1 Acidic Refractories

The major acidic refractory is silica (SiO_2). However, at high temperatures, alumina (Al_2O_3) assumes acidic character. These are easily attacked by basic materials. Fireclay refractories also fall within this category.

1.2.1.2 Basic Refractories

Basic refractories are used in basic environment. Examples are magnesia (MgO), dolomite (CaO.MgO) and mag – chrome ($MgO – Cr_2O_3$) refractories.

1.2.1.3 Neutral Refractories

These refractories are used in both acidic and basic environments. Common examples are alumina (Al_2O_3), chrome (Cr_2O_3), zirconia (ZrO_2) and carbon refractories.

1.2.2 Classification on the basis of manufacturing method

1.2.2.1 Shaped Refractories

Shaped refractories refer to those refractory bricks that have a definite size and dimension. Standard straight bricks are of dimension 230 mm X 115 mm X 75 mm. Other shapes include arch, wedge, key, neck, skew, split etc. Size tolerances on standard shapes as given by ASTM are ± 2 % on dimensions over 4 inch and ± 3 % on smaller dimensions **[2]**. Special shapes are used for specific applications such as coke oven bricks, baffle tile for boilers, checkers for blast furnace stove regenerators. Many times complicated shapes are submitted by customers to refractory industries with detailed design for specific operations.

1.2.2.2 Unshaped or Monolithic Refractories

These do not have any specific shape and assume shape only at application site after setting. The most important advantage of monolithic refractories is that these are joint - free and hence not prone to cracks. Monolithic refractories can be categorized into the following types **[3]**:

- Castable refractories
- Trowellable refractories
- Plastic refractories
- Ramming refractories
- Patching refractories

- Gunning refractories
- Injection refractories
- Vibratable refractories
- Free flow castable refractories
- Coating refractories
- Refractory mortars

1.3 High Alumina Refractories

1.3.1 Introduction

Refractories containing more than 45 % alumina can be classified as high alumina refractories. Raw materials that are used in the manufacture of high alumina refractories include the sillimanite group of minerals (sillimanite, kyanite, andalusite) with Al_2O_3:SiO_2 in 1:1 ratio, natural hydrated alumina (boehmite, gibbsite, diaspore), synthetic calcined alumina, bauxite, clay, and natural and electrofused corundum. High alumina products are subdivided into three categories based on their alumina content **[4]:**

- Class A (45 – 65 % Al_2O_3)
- Class B (65 – 75 % Al_2O_3)
- Class C (> 75 % Al_2O_3)

The Al_2O_3 – SiO_2 phase diagram (Fig 1) indicates that as the Al_2O_3 content of a mixture is increased, above 1545 or 1585^{O}C, the solid phase (mullite or corundum) increases and the amount of, liquid phase decreases. This leads to an increase in refractory properties. However, these conditions are invalid when a third component is present in the system and reacts with any of the components. Further deterioration of refractory properties may occur due to formation of liquid phase at lower temperatures. Purity of raw materials makes an important emphasis in case of three component systems in order to make the effect of increasing alumina persistent.

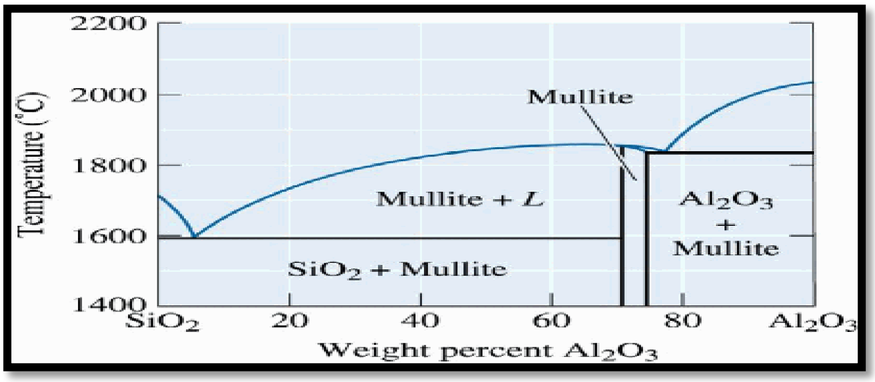


Fig 1.1: Al_2O_3 – SiO_2 phase diagram

Refractories which consist of less than 72 % Al_2O_3 have mullite as the only stable solid phase upto 1910^{O}C. Thus, regardless of the raw materials selected, mullite formation occurs at higher temperatures. On further increase of Al_2O_3 content, solid corundum (α - alumina) phase stabilizes which possesses better refractory properties. The unreacted silica occurs as cristobalite which liquefies at around 1595^{O}C. This liquid phase is visible in the interface between the formed mullite and free quartz [5]. Mullite formation increases and the amount of liquid phase decreases bringing about an increase in refractoriness. As the amount of alumina scales above 72 %, SiO_2 content decreases. Thus, the two phases at this point are mullite and corundum. Liquid phase should not occur below 1850^{O}C as per the $Al_2O_3 – SiO_2$ phase diagram provided impurities do not exist in the system. More amount of corundum in the corundum – mullite system leads to an enhancement in strength and thermal conductivity of the refractory which in turn improves its spalling resistance although alumina has a high linear thermal expansion. Also, resistance to acidic and basic slag greatly improves on increasing the amount of alumina.

1.3.2 Grades of high alumina refractories [6]

- Bricks with an aluminium phosphate bond: These bricks show increased resistance to melts, slags and dust. These bricks are either fired at 1000 – 1500^{O}C or heat tempered at 150 – 800^{O}C. Addition of heavy spar ($BaSO_4$) makes the bricks resistant to aluminium melts.
- Alumina (corundum) – chrome oxide materials: Manufacture of materials with 5 – 80 % Cr_2O_3 by addition of either chrome oxide or other raw materials containing chrome and zircon. During firing, the chrome oxide dissolves in corundum leading to a very good corrosion resistance.
- Alumina – zirconia – silica (AZS) bricks: These fused grain bricks are bonded in a matrix with high chrome oxide content. These are installed in electric melting furnaces and in glass melting furnaces.
- Impregnated high alumina bricks: The pores of the fired bricks are impregnated with pitch or sometimes with aluminium phosphate solution. This improves the corrosion and erosion resistance to molten metal and slag.
- Unfired pitch – bonded or resin bonded high alumina materials: A slag resistant carbon bond is created on heating up to 300^{O}C. The carbon content is < 7 % after coking.
- 45 – 55 % Al_2O_3 bricks: These bricks are a better version of fireclay bricks improved by the addition of high alumina raw materials. Low porosity and good creep

behaviour are advantages of these bricks. An example is the checker work of hot blast stoves.

- Bauxite based bricks: Proper selection of bauxite grain, type and amount of bond clay and firing temperature can help to control the expansion of bauxite bricks (due to mullite formation) during operation. Application areas include ladles, electric furnace roofs as well as rotary kilns in the cement industry.
- Andalusite and sillimanite bricks: These possess very good creep resistance as well as spalling resistance. Slag resistance is also good provided slag does not contain a large amount of lime or iron oxide. Application sites include furnace engineering, iron and steel industry, waste incineration and glass melting furnaces.
- Mullite bricks: High fired bricks of this type along with zirconia addition are used in combustion furnaces at temperatures up to 1750^{O}C and in the superstructure of glass melting tanks.
- Corundum products with mullite bond: These bricks contain approx. 90 % Al_2O_3 and are used in induction furnaces and as slide gate plates in continuous casting. Spalling resistance can be improved by zirconia addition.
- >95 % Al_2O_3 bricks: These bricks are resistant to CO and hydrogen at high temperatures. The major application areas are fertilizer industry, petrochemical industry, certain furnaces of chemical industry and **carbon black reactors**.

1.4. What is carbon black?

Carbon black is virtually pure elemental carbon in the form of colloidal particles. Carbon black is different from other forms of carbon namely diamond, coke, charcoal and graphite. Its physical appearance is that of a finely divided pellet or powder, spherical in shape. Aggregates are the primary units of carbon black which are formed in the combustion zone of the carbon black reactor when smaller particles collide and fuse together. These aggregates may be bonded together by weak forces of attraction to form agglomerates. Agglomerates break down during mixing. This means that aggregates can be considered as the smallest dispersible unit of carbon black [7]. Primary particle, aggregate and agglomerate are differentiated in the figure below:

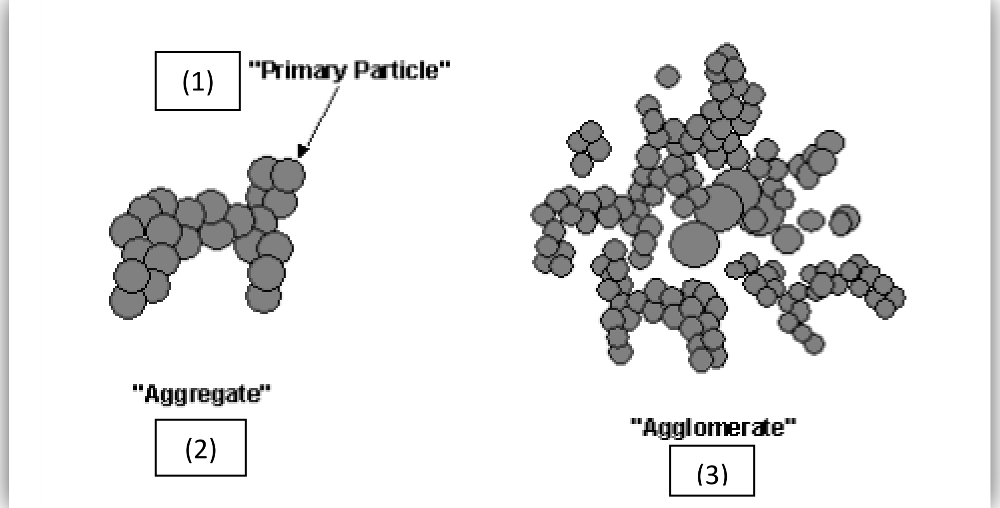


Fig 1.2: (1) Primary particle, (2) Aggregate, and (3) Agglomerate [7]

Carbon black is produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbons under controlled conditions, normally temperature and pressure.

$$C_xH_y + O_2 \rightarrow C + CH_4 + CO + H_2 + CO_2 + H_2O \quad [7]$$

Carbon black is used for strengthening of tyres, for making industrial bags and blow mold containers in the plastic industry. It is also used in printing inks and coatings where colour flexibility is required. Current worldwide production of carbon black is about 8.1 million metric tons per year [8].

1.4.1 Physical and chemical properties of carbon black [8]

Carbon black contains more than 97% elemental carbon arranged in aciniform (grape like cluster) particulate. Commercial carbon black contains organic contaminants such as polycyclic aromatic hydrocarbons (PAH) which can only be extracted under very rigorous laboratory analytical procedures (soxhlet extraction using organic solvents and high temperatures). These extracts differ from those of soot or graphite.

1.4.2 Manufacturing process of carbon black

There are two manufacturing processes for carbon black – the thermal black process and the furnace black process.

1.4.2.1 Thermal black process

Natural gas, consisting primarily of methane or heavy aromatic oils, is used as feedstock. The process uses a pair of furnaces that alternate approximately every five minutes between preheating and carbon black production [8].

1.4.2.2 Furnace black process

The furnace black process [8] is the most common method used for carbon black production. The reactor used here is cylindrical in shape similar to a very large burner [9]. The process uses heavy aromatic oils as feedstock. The reaction furnace consists of four zones or chambers [9]:

- **Combustion zone:** Pre – heated air can be added in this zone and also fuel is burnt to generate the necessary high processing temperature. The primary feedstock is added to the hot gas stream obtained by burning natural gas or oil (secondary feedstock).
- **Restriction zone:** A ring separates the combustion and restriction zones. The restriction ring raises the velocity of the gases as they enter the reaction ring chamber.
- **Reaction chamber:** Here, the primary feedstock vapourizes and pyrolyzes to form microscopic carbon particles. The size, shape and hardness of carbon black is controlled by temperature, velocity and various seed materials which were introduced along with the feedstock.
- **Quench zone:** The reaction rate is controlled by steam or water sprays. Water spray rapidly reduces the temperature and helps to conclude the reaction in the furnace. The carbon black particles are allowed into the reactor, after which these are cooled and collected via filters continuously.

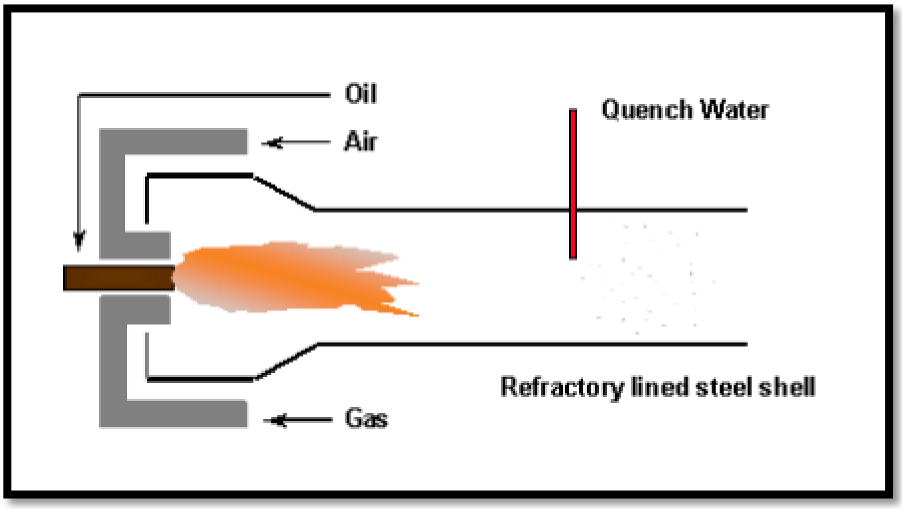


Fig 1.3: Schematic of oil furnace process [7]

The overall procedure of the carbon black manufacturing process can be summarized in the following schematic:

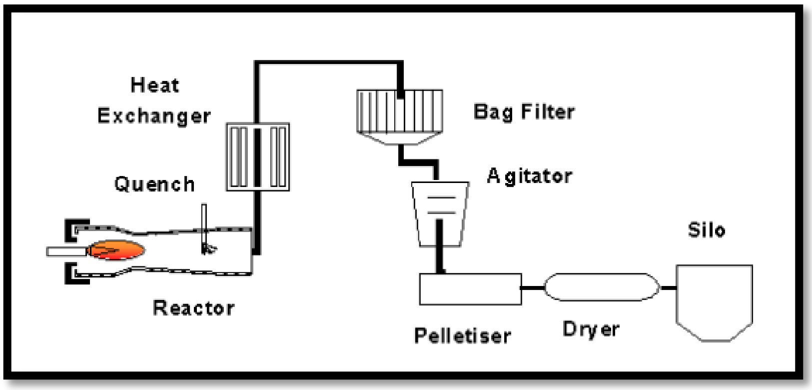


Fig 1.4: Carbon black manufacturing process [7]

Furnace black process involves two types of reactors:

- **Tread reactor:** Manufactures hard carbon black. Temperatures within these reactors reach beyond 1900^{O}C.
- **Carcass reactor:** Manufactures soft carbon black. Operating temperature range is between 1550^{O}C and 1750^{O}C.

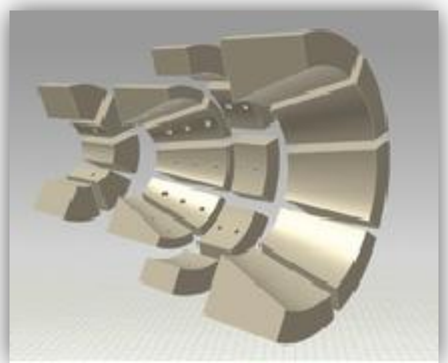


Fig 1.5 (a): Tread Reactor [10]

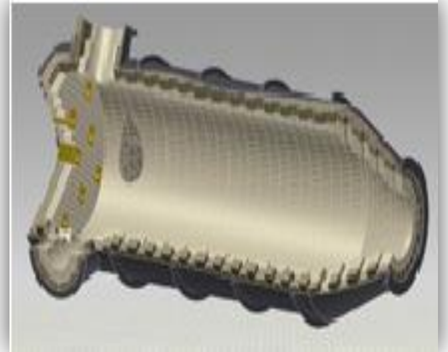


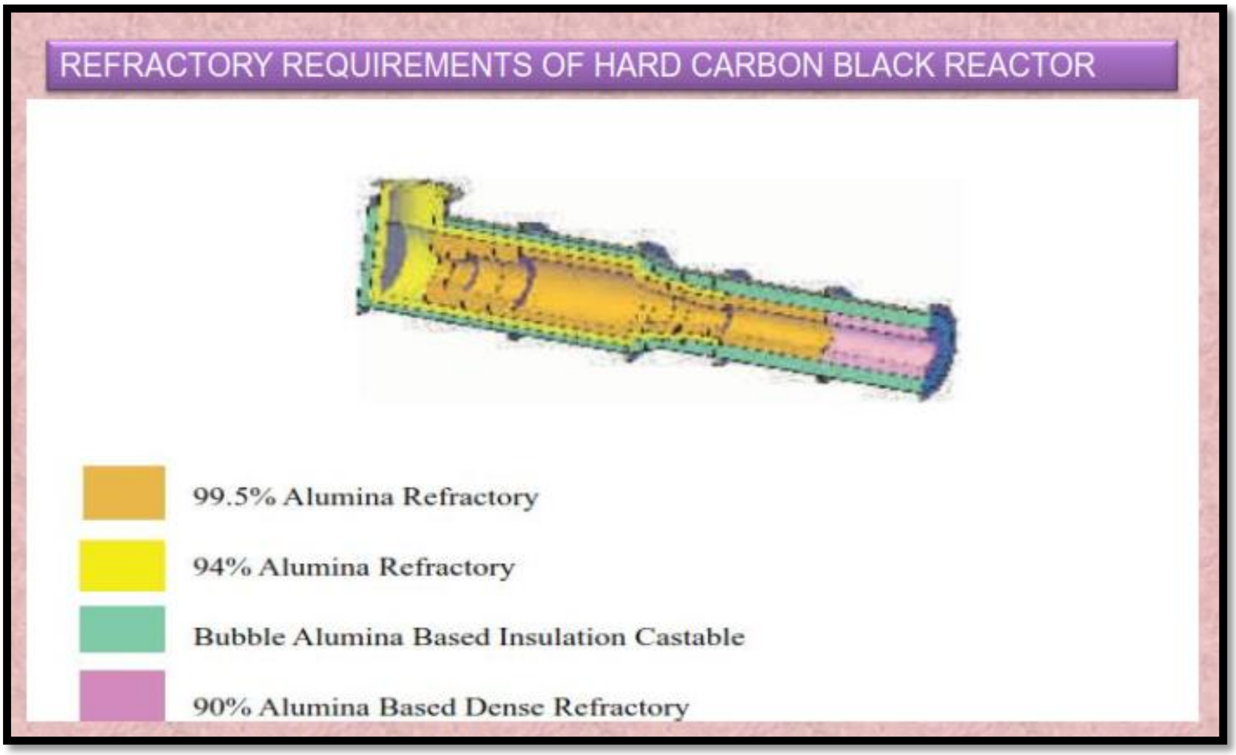
Fig 1.5 (b): Carcass Reactor [10]

1.5 Refractories used in carbon black reactor [9, 10]

- **Working lining:** High alumina bricks
- **Back up lining:** High alumina castables, high alumina or fire clay bricks
- **Lower operating temperature reactors (Carcass Reactor):** Operating temperatures lie within the range of 1550°C and 1750°C. These reactors pose a challenge due to the size and alkali additives. Mullite bonded corundum (90% Al_2O_3 – 10%SiO_2) bricks are generally used.
- **Quench chamber:** High purity 60% and 70% alumina bricks
- **High operating temperature (>1900°C) reactors (Tread Reactor):** Extreme temperatures, reducing atmosphere, quenching with water and gas velocities beyong the speed of sound require highest quality refractory materials like high performance mullite or corundum bricks. Refractories are zoned frequently.
- **Combustion chamber and quench chamber hot face:** 90% Al_2O_3 – 10% SiO_2 bricks
- **Restriction ring and reaction chambers (hot face):** 99% Al_2O_3 and thermal shock resistant 90% Al_2O_3 – 10% Cr_2O_3 bricks

1.6 Refractory requirements of carbon black reactor [9]

- **High refractoriness:** High refractoriness or melting point is desired because with increase in operating temperature, the operating rate and process efficiency also increase. Harder carbon black requires higher temperatures and even a minor operating problem can result in refractory melting.
- **Thermal shock resistance:** Changing production of carbon black grades results in temperature fluctuations. This can lead to thermal cracking and spalling of the hot face lining particularly in the combustion and restriction zones. Changing location of quench sprays also leads to the same problem. Quench chamber is the zone most susceptible to thermal shock.
- **Wear resistance:** The restriction ring has a small diameter. Even a small increase (5 cm) in diameter due to refractory wear can significantly change process conditions which may demand replacement of the entire refractory lining.
- **Corrosion resistance:** The restriction chamber involves the use of high ash and high vanadium oils which results in corrosion. Corrosive ash can result in severe damage.



REFRACTORY REQUIREMENTS OF HARD CARBON BLACK REACTOR

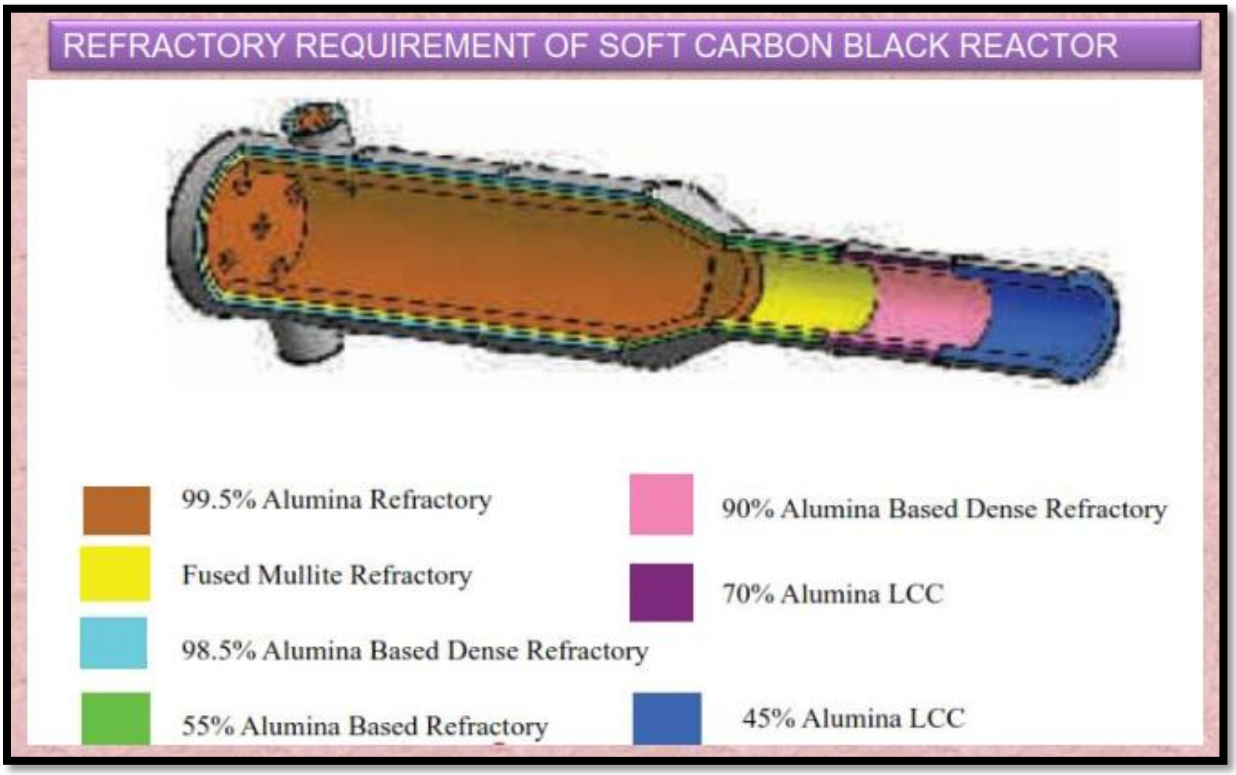
■ 99.5% Alumina Refractory

■ 94% Alumina Refractory

■ Bubble Alumina Based Insulation Castable

■ 90% Alumina Based Dense Refractory

Fig 1.6 (a): Refractory requirement of hard carbon black reactor



REFRACTORY REQUIREMENT OF SOFT CARBON BLACK REACTOR

■ 99.5% Alumina Refractory

■ Fused Mullite Refractory

■ 98.5% Alumina Based Dense Refractory

■ 55% Alumina Based Refractory

■ 90% Alumina Based Dense Refractory

■ 70% Alumina LCC

■ 45% Alumina LCC

Fig 1.6 (b): Refractory requirement of soft carbon black reactor

1.7 Importance of current project

Carcass reactors can be lined with mullite bricks as these can withstand temperatures up to 1750^{O}C. However, tread reactors require high alumina bricks which can provide undaunted operation even beyond 2000^{O}C under severe operating conditions. These are mentioned below:

- > 1900^{O}C operating temperature
- Reducing atmosphere
- Water quenching and gas velocities beyond the speed of sound
- Highest pressure differences

The above conditions make the development of a suitable refractory for the carbon black reactor very challenging. The refractory should be able to withstand higher temperatures as well have high thermal spalling resistance, high thermal conductivity, low thermal expansion, high bulk density and low porosity. High alumina refractories generally have good refractory properties. Hence, it may be justified that study of addition of zirconia and chrome oxide in alumina refractories is required for carbon black reactor applications.

CHAPTER 2
LITERATURE REVIEW

2.1 Raw materials

2.1.1 Alumina

2.1.1.1 White Fused Alumina (WFA)

WFA is produced by melting calcined alumina above 2040^{O}C in an electric arc furnace followed by slow solidification process. High temperature fusion results in good properties like high purity, high refractoriness and high abrasion resistance. WFA is also used because of its chemical inertness. WFA is white in colour, a dense mineral and consists of large crystals of alpha alumina. WFA contains very low amount of iron which makes it suitable for many refractory applications.

2.1.1.2 White Tabular Alumina (WTA)

White Tabular Alumina is made from $Al(OH)_3$ derived from bauxite by Bayer's process [11]. It can be used as aggregates or as fine addition to the matrix. Its properties include volume stability at higher temperatures, high refractoriness, excellent thermo – mechanical properties, high density, low permeability, high chemical resistance, high purity, high mechanical stability, high wear resistance and high spalling resistance mainly due to the presence of large crystals of alpha alumina. Fine WTA optimizes the particle size distribution and refractoriness of the refractory matrix. Closed pore distribution in the microstructure of tabular alumina results in 0.5% water penetration which helps to prevent slag infiltration and provides high erosion resistance. Low amount of impurities (SiO_2, TiO_2, Fe_2O_3) helps to retain the higher hot strength. Lower bulk density as compared to fused alumina helps tolerate increased toughness and this leads to a higher abrasion index even at higher temperatures. [12].

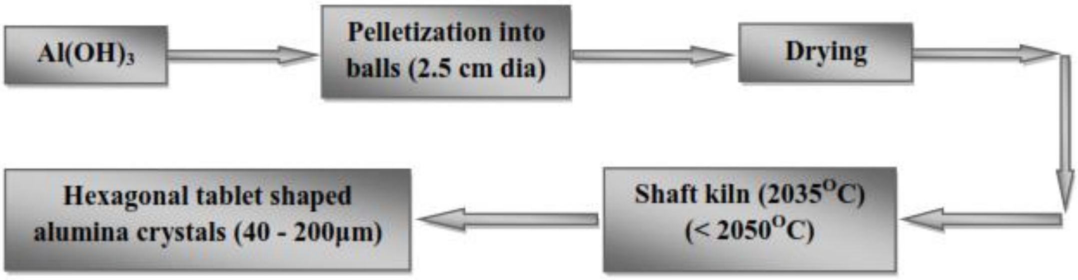


Fig 2.1: Manufacturing process of tabular alumina [11]

2.1.2 Zirconia

Zirconia has high melting point, superior corrosion resistance, non – wetting to molten metals, low vapour at high temperatures and low thermal conductivity **[13].** It is also hard and has high fracture toughness at room temperature.

2.1.2.1 Fused Zirmul

Fused zirmul is manufactured by the electric furnace fusion of Bayer process alumina and zircon sand. During melting, the zircon and alumina react to yield a mixture of mullite and zirconia. Fused zirmul is highly resistant to chemical attack and has low and unusual reversible thermal expansion coefficient which improves thermal shock resistance by producing a crack stopping mechanism. Fused zirmul also has high corrosion resistance.

2.1.2.2 Zircon flour

Zircon flour is manufactured by vibro grinding zircon sand in an alumina lined jet mill. It is highly resistant to high temperature abrasion. Zircon flour dissociates into zirconia and silica on being heated to 1700°C. therefore, when zircon sand or zircon flour is added to alumina, the liberated silica reacts with the alumina forming mullite and releasing zirconia **[14]**. This mullite – zirconia aggregate possesses superior properties like refractoriness, chemical inertness, mechanical strength at elevated temperatures and low thermal expansion **[15]**.

2.1.2.3 Stabilized zirconia

Zirconia is stabilized with magnesia, yttria or calcia to bring about transformation toughening. Cubic structure is induced because of this along with the tetragonal phase which remains in a metastable state during cooling. Upon impact, the tetragonal precipitates undergo a stress induced phase transformation near an advancing crack tip. This leads to high toughness in the material.

2.1.3 Binder

2.1.3.1 Dextrin

Dextrin is a polysaccharide of amylose (20 – 30% starch) and amylopectin (70 – 80% starch). It is produced by the oxidative decomposition of starch. The chemical formula of dextrin is $(C_6H_{12}O_6)_n$. Dextrin goes off between 800 – 1000^{O}C **[3].**

2.1.4 Chrome oxide

Chrome oxide contains about 95% chrome. It is a dark green powder and crystallizes in the hexagonal structure. Chrome oxide does not dissolve in acid or base and shows extreme stability to light, air, sulphur dioxide and hydrogen sulphide **[16]**. It improves corrosion resistance and spalling resistance of refractories significantly. Sintering of chrome containing refractories highly depends on the partial pressure of oxygen. Oxidizing conditions lead to abnormal grain growth and pore gathering which makes densification hard to achieve **[17]**. Therefore, additives such as TiO_2 or clay minerals are added. This problem can also be solved by hot pressing chrome, the microstructure of which shows better sintering. Slag corrosion resistance of chrome is affected by the size and form of the grains **[18]**.

2.2 Study of alumina refractories

High alumina bricks, as mentioned earlier, refer to those refractories that contain > 45% alumina. These refractories are mainly composed of α – alumina and mullite and the major properties of these bricks depend on the properties of these two phases. The main characteristics of α – alumina are (a) linear thermal expansion (moderate value), (b) high mechanical strength, (c) high thermal conductivity than mullite, (d) good corrosion resistance and (e) high specific gravity. High alumina bricks are used in iron and steel industry, glass, cement, lime, incineration and others **[11]**. High alumina bricks are used in the blast furnace and it has been found that bricks containing 92% alumina and 6% silica show good corrosion and alkali resistance as compared to that with 99% alumina and 0.15% silica **[11]**. The corrosion ratio of high alumina bricks increases with increasing alumina content but slag penetration increases. This leads to spalling which is improved by the addition of SiC, C and other components. Structural spalling is also effected in the side walls and bottom of VAD ladles due to slag penetration. Three types of high alumina bricks (phosphate bonded unburnt high alumina, burnt high alumina and an improved burnt high alumina brick) were used in the VAD ladle and their spalling properties were studied **[19]**. The third type involved the effective arrangement of $Al_2O_3 – SiO_2$ coarse grains as well as modifying matrix composition and texture to improve structural spalling. It has lower porosity and higher strength than the first two, lower coefficients of thermal and residual expansion, excellent volume stability and low modulus of elasticity. Hegde and Chaturvedi **[20]**, studied the performance of used high alumina bricks in EAf's and ladles. They found that alumina content reduced to about 64 wt% in the cold faces. Fe_2O_3 content increases in both the cold and hot faces to a maximum of 4.33 wt%. Microscopic study indicated similarity in mineralogy for cold face bricks and unused bricks. XRD of cold face used bricks showed high presence of cristobalite as compared to that of hot face. Structural spalling results due to porosity of bricks.

Corundum – mullite refractories **[21]** have high melting point, high hardness and good chemical and slag attack resistance. Mullite also has good spalling resistance. If the Al_2O_3/SiO_2 ratio can be maintained to 2.55, high creep resistance and spalling resistance can be obtained for corundum – mullite refractories. To improve the reaction sintering, good matrix texture must be optimized.

2.3 Effect of addition of zirconia on alumina refractories

High alumina refractories have high hardness, good hot strength but poor toughness as well as poor thermal shock resistance. These problems can be addressed to by the addition of a certain amount of zirconia. Naturally occurring zirconia is in monoclinic (m) form. Certain applications however require the more unstable phases of zirconia – the tetragonal or the cubic phase. These phases are stabilized by the addition of stabilizer normally calcia (CaO), yttria (Y_2O_3) or ceria (CeO_2). On heating, the monoclinic phase which is stable at room temperature converts to the tetragonal (t) phase at $1100^{O}C$ over a $100^{O}C$ temperature range. The tetragonal phase converts to the cubic (c) phase at $2370^{O}C$ and zirconia melts near $2700^{O}C$. Cooling results in the t ↔ m transformation which is accompanied by a massive volume expansion of 4%. This t ↔ m transformation can be utilized in increasing fracture stress and toughness of zirconia and zirconia containing ceramics **[22]**. The tetragonal grains are dispersed in the matrix of m – ZrO_2. If these tetragonal particles are fine enough, the surrounding matrix can constrain the transformation of these particles into a metastable tetragonal phase. This transformation at the vicinity of the crack front results in appreciable increment in strength and fracture toughness.

2.3.1 Effect on mechanical properties of alumina refractories

M. Szutkowska **[23]** studied the fracture resistance behaviour of alumina – zirconia composite. The composites were fabricated using commercial alumina powder (Alcoa). MgO was used as sintering additive to inhibit grain growth. Fracture toughness was measured by two methods – 1) conventional three point bending of SENB (single edge notched beam) and 2) post indentation crack length. The R – curve showed increasing dependence on fracture toughness with crack extension co-efficient for alumina – 10wt% zirconia composite with unstabilized zirconia higher in comparison to alumina – 10wt% zirconia composite with 3mol% yttria stabilized zirconia. Vicker's crack growth measurement showed that the fracture toughness of Al_2O_3 – 10wt% ZrO_2 composite with unstabilized zirconia exhibits higher value of (about 20%) in comparison to Al_2O_3 – 10wt% ZrO_2 composite with 3mol% yttria stabilized zirconia and pure alumina. I. Rafols *et al* **[24]** also studied the fracture toughness of alumina – zirconia composites. Zirconia toughened alumina's with volume additions of 5%, 15% and 30% t – ZrO_2 stabilized with 3mol% Y_2O_3 were studied. 99.7%

pure alumina matrix was also studied. The fracture toughness was measured by testing pre – crack SENB and SEVNB (single edge V notched beam) specimens to failure with a loading rate of 200 N/s. In ISB method, indentation load was kept constant at 392 N. In SCF (surface crack in flexure) method, crack depth varied from 230 - 470µm. Indentation based methods produced lower K_{IC} values. SCF method produced K_{IC} values similar to SENB and SEVNB methods. Heat treatments produced up to 20% increases in fracture toughness in ZTA15% and ZTA30%, but in ZTA5%, nothing much was observed. Addition of zirconia particles hinders the matrix grain growth. Larger the zirconia content, smaller the alumina matrix grain size. No abnormal grain growth was observed at 1600^{O}C. In ZTA5% however, a few grains do lead to abnormal grain growth. Zirconia particles grew faster in composites ZTA15% and ZTA30%. Zirconia particles tend to grow in clusters with no total coalescence. J.Chevalier et al **[25]** studied the creep behaviour of ZTA. Alumina, zirconia and Zirconia Toughened Alumina (ZTA) were prepared by C.T. Demarquest method by mixing the raw materials in water with a deflocculant. Creep rate decreased as grain size increased for alumina. Finer grain sized alumina showed low creep resistance and quasi – state creep rate was higher when purity was lower. Tetragonal Zirconia Polycrystal (TZP) showed poor creep resistance. High purity and coarse microstructure implied high creep resistance for similar grain size. Also, creep resistance is favoured by large grain size. ZTA did not show very good creep resistance. V.C. Pandolfelli et al **[26]** reported that addition of 20wt% mullite – zirconia (MZ) aggregate to high alumina refractories leads to development of glassy phase at the junction between MZ aggregate and alumina matrix which enhances the physical and thermo - mechanical properties. The effect of microcracking due to coalescence was evident in samples with 20wt%, 30 wt% and 40wt% MZ aggregate. The sample with 10wt% MZ aggregate showed increased mechanical strength up to 800^{O}C due to additional glass formation. Beyond this temperature, glass viscosity decreases allowing grain sliding and eventually mechanical strength decreases. X.C. Zhong et al **[27]** also investigated the thermo – mechanical properties of corundum – mullite – zirconia materials. HMOR (at 1100^{O}C, 1300^{O}C, 1500^{O}C) values show that 25:75 CM and 75:25 CM possess better hot strength than individually corundum or mullite and also, mullite is better than corundum. Specimens with two crystalline phases normally show high creep resistance as well as superior hot strength. Corundum showed lowest creep resistance.

2.3.2 Effect on sintering behaviour of alumina refractories

C. Zhiqiang and Q. Feng in their paper [28] reported the sintering behaviour of zirconia – alumina ultrafine composites. ZrO_2 grains and alumina grains can inhibit each other's growth during sintering process. ZrO_2 – Al_2O_3 composites have higher sintering temperatures than single Y – ZrO_2 or Al_2O_3 materials. Proper zirconia addition can reinforce and densify alumina ultrafines as well as improve thermal spalling resistance. The authors reported that with rising temperature, sintering shrinkage becomes higher and gradients get smaller. The alumina – zirconia samples showed highest density after sintering at $1600^{O}C$. Alumina sample, however, achieved highest density at $1500^{O}C$. Alumina with high modulus of elasticity can prevent t ↔ m transformation which is beneficial to spalling resistance. Kiyoshi Itatani and Masanori Kasai in their paper [29] reported the benefit of two step sintering of TZP's. They found that in single step sintering, grain growth accelerated as relative density approached full density and in two step sintering, grain size were always as low as 0.25 – 0.3µm and relative density approached full density. Grain growth in two step sintering was inhibited by grain boundary pinning. Grain boundary mobility which leads to grain growth may be slowed by lowering firing temperature. Higher flexural strength was obtained for TZP sintered via two step sintering technique.

2.3.3 Effect on spalling resistance of alumina refractories

M. Saito et al [30] studied the influence of microstructure of alumina –zirconia grain on spalling resistance. Grain A was prepared with 30mass% ZrO_2 and grain B with 25mass% ZrO_2. Microstructure studies showed agglomerates of large alumina crystals precipitated within eutectic domains of alumina and zirconia within grain A and in grain B, primary alumina crystals were dispersed in the matrix. Individual spalling tests showed that grain A had a smooth fracture surface whereas grain B had a rugged fracture surface. Also, pressed samples of A showed higher reduction in MOE as opposed to B which implies that B has better spalling resistance. S. Fukai et al [31] investigated the effect of improved spalling resistance of A – Z refractory suitable for use in slide gate nozzles. Alumina – zirconia systems with various compositions of alumina and zirconia were made in which both alumina and zirconia were varied between 0 and 99%. Zirconia was either in cubic or tetragonal form. A particular composition (39% ZrO_2; 59% Al_2O_3; 100% m – ZrO_2) in which primary crystals of alumina were dispersed in an eutectic of Al_2O_3 – ZrO_2, exhibited abnormal thermal expansion originating in the zirconia phase transformation at around $1100^{O}C$. This produced microcracks which led to improved spalling resistance. T. Xiaoli et al [32] also made a similar investigation in which alumina – zirconia (ZA) composite powder was pressed into samples and then characterized. Apparent porosity (AP) and bulk density (BD) measurements showed that with increasing ZA content, AP decreased and BD increased until a particular ZA content, when further change was not noticed. Excessive ZA addition is detrimental to the strength of zirconia sizing nozzle.

2.4 Effect of addition of chrome to alumina refractories

Alumina – zirconia refractories show good hot strength but spalling resistance could be further improved by the addition of chrome oxide. Alumina – zirconia – chrome refractories can survive in difficult operating conditions as well as high temperatures due to improved mechanical and hot properties. Corresponding literature has been summarized below. The addition of Cr_2O_3 to Al_2O_3 [33] results in the formation of a solid solution, the melting temperature of which rises with increase in chrome content. This results in a high corrosion resistance. Alumina – zirconia – chrome refractories are used in a variety of applications, the major ones being incinerators and waste melting furnaces. A composition of 35 – 50 wt% alumina, 20 – 35wt% chrome oxide and 25 – 30wt% zirconia is generally used in sewage sludge melting furnace [34]. Addition of chrome alone gave high corrosion resistance as well as slag resistance to alumina refractories. However, addition of both zirconia and chrome lead to better corrosion resistance. Normally, zirconia present in the grain boundaries is attacked by slag. To avoid this problem, chrome is added. In alumina – chrome ceramics, chrome addition helps to improve the share of grain boundaries that cannot be wetted by either slag or any other silicate based melt as emphasized by K.Uibel et al in their paper [35]. These refractories are also resistant to fly ash which is an important requirement when it comes to carbon black reactor [36]. Alumina – chrome refractories have also been used in industrial waste melting kilns. It was found that the erosion resistance of these bricks is very good and improves with increasing chromia content [37]. Alumina – chrome bricks are also superior in corrosion resistance as compared to MgO – Cr_2O_3 bricks [38]. The corrosion resistance improves further when coarse grained microstructure is present. The stress relaxation for this type of brick is also good due to presence of microcracks. This type of brick was installed in a waste melting kiln for 457 days and it lasted three times longer as compared to the brick without coarse microstructure [39].

2.5 Refractories for carbon black reactor

High alumina refractories, alumina – zirconia refractories and alumina – zirconia – chrome refractories are suitable for use in the carbon black reactors. V.V. Primachenko et al reported that yttria stabilized zirconia pressed using semi dry pressing showed greater density and mechanical strength but low spalling resistance. Samples manufactured by the vibratory casting process possessed better spalling resistance. Zirconia present in monoclinic form when added to samples pressed using the first method highly improved the spalling resistance **[40]**. David V. Stiles et al of Harbison – Walker Refractories developed three different categories of bricks intended for carbon black reactor applications. Mullite bonded 90% alumina brick were developed for use in quench chamber of lower temperature reactors. These ran for longest life for five years. Alumina bonded alumina brick led to an extended service life. Chrome – alumina bonded 70% Cr_2O_3 – 25% Al_2O_3 brick was successfully installed in restriction chamber of carbon black reactor and exhibited exceptionally high corrosion resistance **[9]**.

CHAPTER 3
OBJECTIVES OF CURRENT WORK

3.1 Objectives

The objective of the current project was to study the development of refractories suitable for use in the carbon black reactor by

- Optimization of source and amount of zirconia in zirconia containing alumina refractories
- Optimization of sintering temperature and reactive alumina content in zirconia optimized alumina refractories
- Addition of chrome oxide to the optimized alumina – zirconia refractory in order to improve the spalling resistance of the refractory

CHAPTER 4
EXPERIMENTAL WORKS

4.1 Chemical analysis of raw materials

Raw materials were selected on the basis of the properties desired in the final product. Chemical analysis of raw materials was performed in order to determine the amount of Al_2O_3, SiO_2, Na_2O, Fe_2O_3, ZrO_2 and Cr_2O_3 in accordance with Indian Standards.

4.2 Fabrication of refractory brick

The raw materials are taken and granulometric calculations are done in order to determine the highest packing density. Batch trials are designed on the basis of granulometry.

4.2.1 Determination of maximum packing fraction

Refractory shapes normally contain particles ranging from about 1 cm to submicron size. These are formulated with varying sizes so that a high packing density can be achieved. Packing fraction (PF) and packing density (PF%) can be defined as the fraction and the percent of the bulk volume occupied by uniform spheres. The larger particles are in contact and the smaller particles fill the pores or interstitial spaces between these particles. This is in accordance with Furnas model. The maximum packing fraction (PF_{max}) for a mixture of coarse (c), medium (m) and fine (f) particles, when the large particles are in contact, is given by [41]:

$$\boldsymbol{PF_{max} = PF_c + (1 - PF_c)PF_m + (1 - PF_c)(1 - PF_m)PF_f}$$

4.2.2 Batch formulation

Initially, trials are designed to optimize the source of zirconia as well as the firing temperature. A conventional composition is also included for comparison. The conventional composition (99% alumina) does not contain any zirconia. The other compositions include three different sources of zirconia – zirmul, zircon flour and stabilized zirconia. Optimization of firing temperature and source of zirconia is succeeded by trials for optimization of reactive alumina. Two reactive aluminas, RA1 and RA2 which work in good tandem with high alumina refractories are used for trial. Following this, chrome oxide trials are designed to achieve the aim of refractory production for carbon black reactor.

Raw material	Trial 1 (wt %)	Trial 2 (wt %)	Trial 3 (wt %)	Trial 4 (wt %)	Trial 5 (wt %)	Trial 6 (wt %)	Trial 7 (wt %)	Trial 8 (wt %)
WFA	55.0	55.0	55.0	55.0	55.0	55.0	55.0	55.0
WTA	45.0	42.0	40.0	44.0	42.0	40.0	44.5	44.0
Fused Zirmul	Nil	3.0	5.0	Nil	Nil	Nil	Nil	Nil
Zircon Flour	Nil	Nil	Nil	1.0	3.0	5.0	Nil	Nil
Stabilized Zirconia	Nil	Nil	Nil	Nil	Nil	Nil	0.5	1.0
$MgSO_4$ Solution	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Dextrin	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0

Table 1: Batch composition for trial with zirconia source and 99% alumina brick

Raw material	Trial 9 (wt %)	Trial 10 (wt %)	Trial 11 (wt %)	Trial 12 (wt %)
WFA	55.0	55.0	55.0	55.0
WTA	37.0	35.0	37.0	35.0
FZ	5.0	5.0	5.0	5.0
RA1	3.0	5.0	-	-
RA2	-	-	3.0	5.0
Magnesium Sulphate Solution	0.5	0.5	0.5	0.5
Dextrin	2.0	2.0	2.0	2.0

Table 2: Batch composition for trial with reactive alumina

Raw material	Trial 13 (wt %)	Trial 14 (wt %)
WFA	55	55
WTA	32	27
FZ	5.0	5.0
RA2	3.0	3.0
Chrome Oxide Green	5.0	10.0
Magnesium Sulphate Solution	0.5	0.5
Dextrin	2.0	2.0

Table 3: Batch composition for trial with chrome oxide green

4.2.3 Mixing

Different raw materials were weighed as per batch compositions and then mixed as per the following mixing sequence. During mixing, water is added to improve workability of the mixture. The mixing equipment employed was an Eirich pan mixer. Total mixing time was no more than 20 minutes for a single batch.

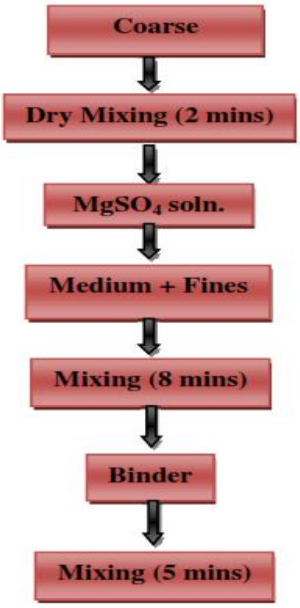


Fig 4.1: Mixing Sequence for high alumina bricks

4.2.4 Pressing

The mixtures prepared were pressed in a SACMI (Italy) press which has a maximum capacity of 1600. SACMI press requires volumetric feeding of material. Therefore, the volume of the mixture to be pressed was calculated and the mixture was slowly allowed into the mould. Normally, for testing, bricks of standard dimension (230mm × 115mm × 75mm) are pressed. Kerosene was used as a lubricating agent between the mixture and the mould. Poking was done to ensure uniform pressing and attainment of good green density. Initial pressing was done uniaxially with a pressure of 0.5 ton/cm^2 and then held for 60 seconds to remove any entrapped air. After this, the mixture was pressed maintaining a specific pressure of 0.9 ton/cm^2 with 5 dearing strokes. The pressed bricks were inspected for lamination, crack, etc.

4.2.5 Drying

High alumina bricks contain moisture. This moisture must be removed prior to firing to avoid cracks in the fired body. Bricks are first dried in open air for 24 hours followed by oven drying at 110^{O}C, again for 24 hours.

4.2.6 Sintering

Drying removes most of the moisture and if there is any moisture still left, it goes off during the initial stages of sintering. High alumina bricks are made from high purity raw materials which ensures that sintering can take place only at a very high temperature (> 1500^{O}C). Sintering is carried out at two different temperatures – 1680^{O}C and 1730^{O}C with a soaking period of 4 hours in a high temperature tunnel kiln. The temperature schedule (for 1730^{O}C) of the kiln is given below.

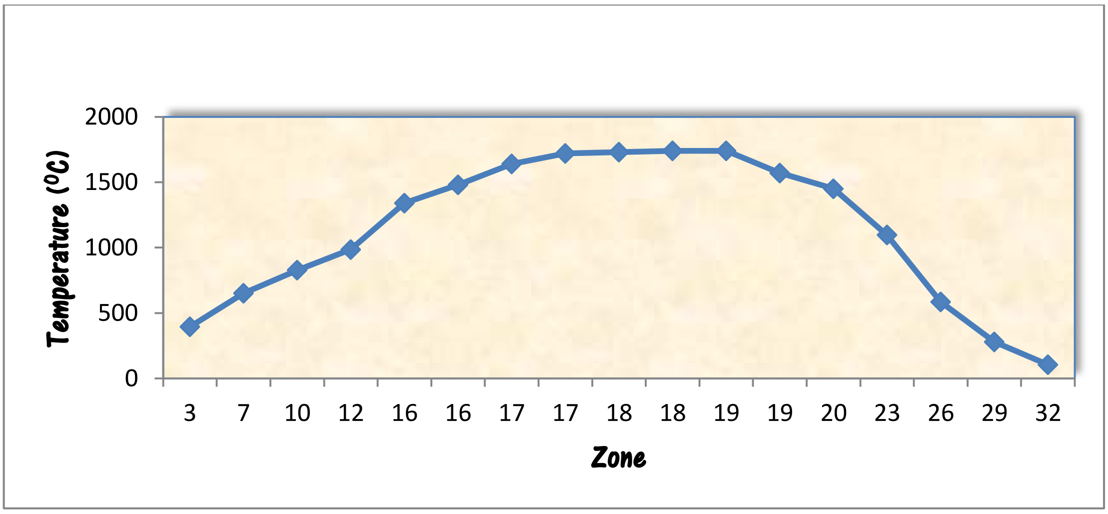


Fig 4.2: Temperature schedule of high temperature tunnel kiln for 1730^{O}C

4.3 General characterization

4.3.1 Physical Properties

4.3.1.1 Apparent porosity (AP) and Bulk Density (BD)

Apparent porosity is defined as the ratio of the total volume of the open pores or the surface pores of a material to its bulk volume and expressed as a percentage of the bulk volume. Pores are of two types – open and closed. Only open pores are penetrated by the immersion liquid. Apparent porosity (AP) and bulk density (BD) were measured according to IS: 1528, Part 8 (1974) for the fired bricks in tandem with the Archimedean Principle. Test specimens of 65mm × 65mm × 40mm were cut by wet cutting. After drying at 110^{O}C, dry weight (W_1) of the samples was taken. Following this, the samples were placed in a desiccator and subjected to vacuum of less than 25mm of Hg column for 30 minutes. Water was allowed to enter the desiccator maintaining vacuum all the while and 20 more minutes of vacuum was maintained. This method ensured that all the open pores had been filled up with water. The suspended weight (W_2) and soaked weight (W_3) were then taken. From the above weights, apparent porosity (AP) was calculated from the formula mentioned below:

$$\boldsymbol{AP = \frac{W_3 - W_1}{W_3 - W_2} \times 100}$$

BD is the ratio of the mass of the dry material of a porous body to its bulk volume expressed in g/cm^3 or kg/m^3, where bulk volume is the sum of the volumes of the solid material, the open pores and the closed pores in a porous body. BD was measured according to IS: 1528, Part 12 (1974) for all the samples.

$$\boldsymbol{BD = \frac{W_1}{W_3 - W_2} \times density\ of\ liquid\ at\ temperature\ of\ test}$$

4.3.1.2 Cold Crushing Strength (CCS)

The cold compressive strength of a refractory material is an indication of its suitability for use of refractories in construction. It is a combined measure of the refractory for the strength of the grains and also of the bonding system [27]. CCS was measured as per ASTM C – 133. Test specimens of 65mm × 65mm × 40mm were cut and dried at 100^{O}C. Cold crushing strength of the refractories are measured by placing the sample on flat surface followed by application of uniform load to it through a bearing block in a standard mechanical or hydraulic compression testing machine. The load at which crack appears in the refractory specimen represents the cold crushing strength of the specimen. The load is applied uniformly on the sample in a flat position. It is expressed in kg/cm^2.

$$\boldsymbol{CCS = \frac{Load}{Area}}$$

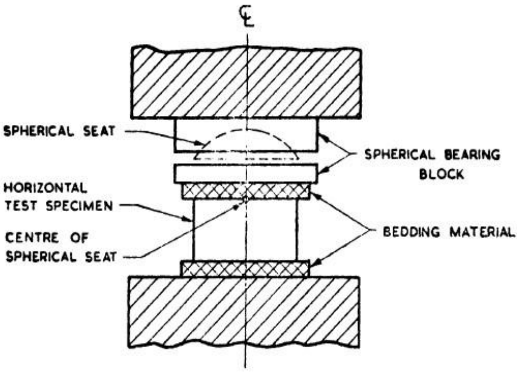


Fig 4.3: Schematic for testing of CCS

4.3.2 Thermo – mechanical properties

4.3.2.1 Hot Modulus of Rupture (HMOR)

The hot modulus of rupture provides information regarding the flexural strength of a refractory material at elevated temperatures. It is the true indicator of the suitability and performance of a refractory at elevated temperatures. HMOR was determined as per ASTM C 133 – 7 with a NETZSCH, 422 (Germany) apparatus. Samples of dimension 150mm × 25mm × 25mm were cut and then dried at 110^{O}C. The samples were then placed on the bearing edges of the testing machine 12.5cm apart. The apparatus was raised to a temperature of 1500^{O}C with a heating rate of 5^{O}C/min. At this temperature, the load of fracture was determined via the 3 point bending method. The working formula for HMOR is given below.

$$\boldsymbol{HMOR = \frac{3PL}{2bd^2}}$$

Where,

P (kg) = maximum load at which fracture appears

L (mm) = span length between the lower supporting points (fixed at 125mm for all tests)

b (cm) = breadth of the specimen

d (cm) = height of the specimen

4.3.2.2 Refractoriness Under Load (RUL)

RUL is measured as a combined effect of heat and load. Samples of dimension 50mm dia × 50 mm height were cut and dried at 110^{O}C. The sample was placed between two graphite cylinders as graphite has a very high melting point (> 3000^{O}C). A load of $2kg/cm^2$ is then applied to the sample through these cylinders. Heating rate was maintained at 15^{O}C/min up to 1000^{O}C and from there on it was lowered to 8^{O}C/min. Sample expands due to the applied heat up to a certain point but begins deforming after that point due to the formation of liquid phase. The change in height of the sample is plotted against time on a 10:1 scale to represent the temperature deformation curve. The temperature of appearance (t_a) at which the deformation of the sample is 0.6% of the total length (sample height + extension due to heat) is reported as the RUL of the sample.

4.3.3 Thermal Properties

4.3.3.1 Thermal Spalling Resistance

Thermal spalling or thermal shock is experienced by a refractory when it is exposed to rapid heating and cooling conditions. Both refractory grains and the bonding system expand while being heated and contract on cooling. Spalling resistance depends on many parameters like thermal expansion coefficient, thermal conductivity, modulus of elasticity, porosity and strength of the sample. It also depends on the type of matrix bonding the grains. Thus, samples which have inherent microcracks provide better spalling resistance as compared to rigid samples. Thermal spalling is generally determined by heating the sample at a particular temperature for a particular time followed by quenching the sample either in air or water. The number of cycles that a sample can undergo without development of crack gives a measure of its spalling resistance. Spalling resistance was determined as per DIN: 41058 specifications. Cylindrical samples of dimension 50mm × 50mm are heated at 950^{O}C for 15 mins and then quenched in running water for 3 mins at room temperature. Then the sample was placed in a drier at 110^{O}C for 30 mins. This constituted one complete cycle.

4.3.3.2 Thermal expansion

Thermal expansion of a refractory sample measures its linear stability when it is exposed to different ranges of high temperatures and then cooled to room temperatures. Refractories are installed at room temperature but on heating, the entire structure tightens up. If the temperature reaches beyond the softening point of the refractory, the bonding system may be disrupted. Thermal expansion was measured in a dilatometer (NETZSCH, Germany) with samples of size 50mm. The sample is placed in contact with an alumina tube and slowly heated. Both the sample and the alumina tube heat up and the thermal expansion is measured as the difference of expansion between the two.

4.3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) gives the topography and grain morphology of sintered samples. A scanning electron microscope images the sample surface by scanning it with a high energy beam of electrons in raster scan pattern. This is the regular pattern of image capture and reconstruction that a television uses. Raster graphics involves the pattern of image storage and transmission used in most computer bitmap image systems. The types of signals that are produced in SEM are secondary electrons, back scattered electrons, characteristic X – rays, light (cathodoluminescence), specimen current and transmitted electrons. Microstructure inspection of refractory samples were observed using JEOL T – 330 scanning electron microscope.

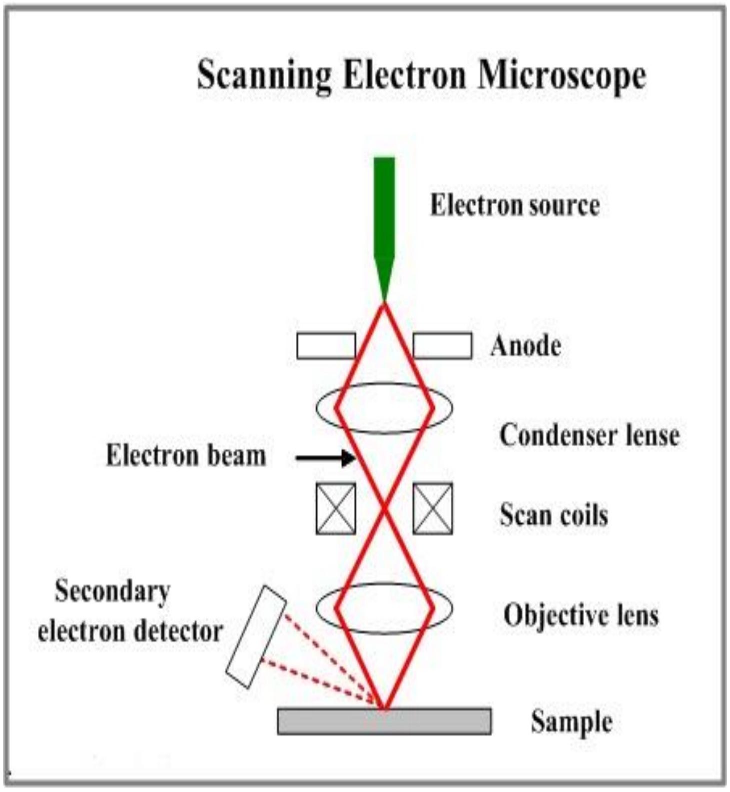


Fig 4.4: Schematic diagram of scanning electron microscope

CHAPTER 5
RESULTS AND DISCUSSIONS

5.1 Characterization of raw materials

The chemical analysis data is presented in the table below. All values are in weight percentages.

Details of sample	Source	SiO_2	Al_2O_3	Na_2O	Fe_2O_3	ZrO_2	CaO	Cr_2O_3
WTA (coarse)	ALMATIS ALUMINA	0.1	99.5	0.32	0.02	-	-	-
WTA (fines)	ALMATIS ALUMINA	0.25	99.3	0.35	0.03	-	-	-
WFA (coarse)	CERAMIC INT.	0.22	99.24	0.43	0.03	-	-	-
Fuzed Zirmul	LIAN HAI RESOURCES	16.13	45.3	0.07	0.3	37.6	-	-
ZIRCON FLOUR	M. MINERAL	30.73	2.04	-	0.21	65.05	-	-
STABILIZED ZIRCONIA	POOJA ENTERPRISE	0.38	0.2	-	0.15	95.55	3.22	-
RA1	ALMATIS	0.03	99.61	0.07	0.02	-	-	-
RA2	ALMATIS	0.03	99.11	0.22	0.02			-
CHROME OXIDE	SIDDHARTH	-	-	-	-	-	-	95

Table 4: Chemical analysis of raw materials in weight percentages

5.2 Packing fraction of mixture

Furnas model emphasizes that the volume fraction of particles required decreases with particle size. The maximum packing fraction is attained when the ratio between the nearest sizes is greater than about 7 and the finer particles are dispersed uniformly. The maximum packing fraction (PF_{max}) increases as the size ratio increases and comes to 70.6% for 30wt% coarse, 40wt% medium and 30wt% fines in all the mixtures used. This value of packing density is consistent with most heavy refractories as reported by **[41].**

5.3 Properties of 99% alumina bricks and zirconia added bricks

5.3.1 Physical properties

5.3.1.1 Bulk Density (BD) and Apparent porosity (AP)

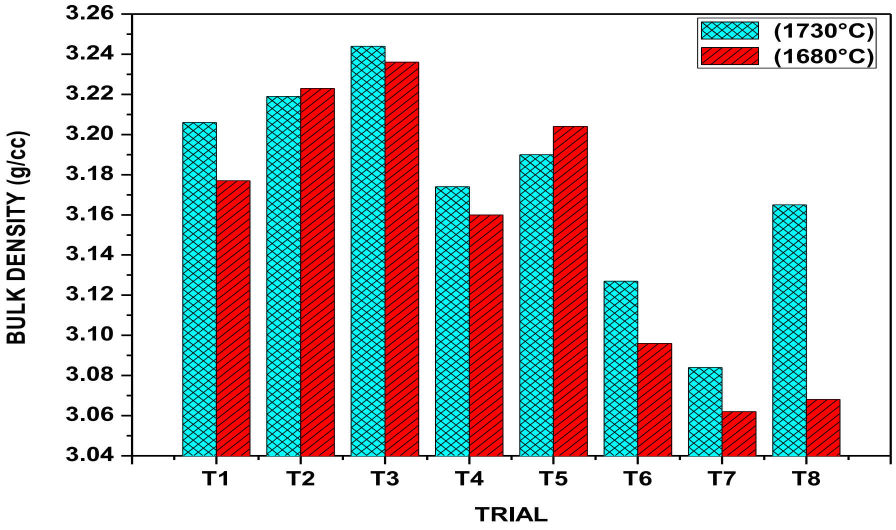


Fig 5.1: Bulk density variation of 99% alumina brick and zirconia added alumina bricks

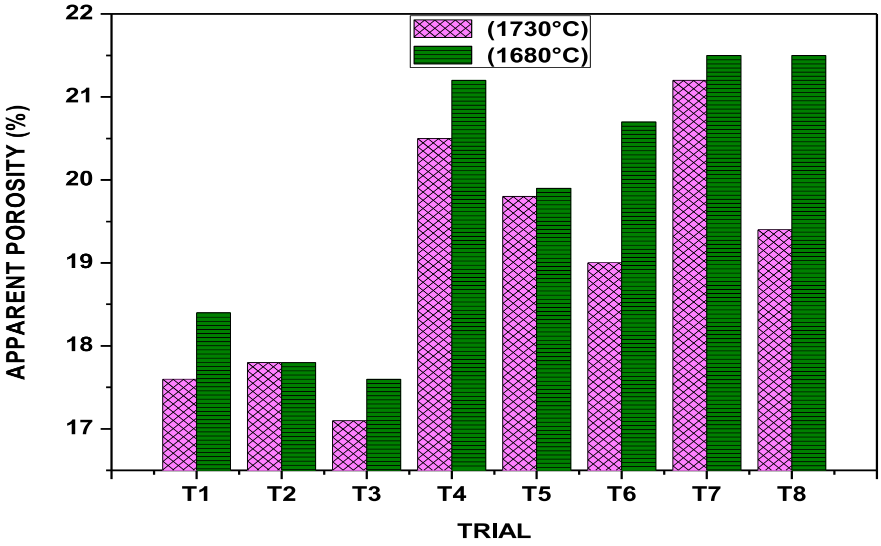


Fig 5.2: Apparent porosity variation of 99% alumina brick and zirconia added alumina bricks

In general, densification improved with increasing temperature (Fig 5.1). Presence of fines in the matrix phase helps in better sintering. But addition of zircon sand, especially T5 batch, has resulted in a lower density at higher temperature. This may be due to dissociation of zircon to its oxide components and reaction between free silica and fine alumina forming a low density mullite phase. This effect is pronounced in T5 batch having higher amount of zircon resulting in a higher extent of mullite formation.

5.3.1.2 Cold Crushing Strength (CCS)

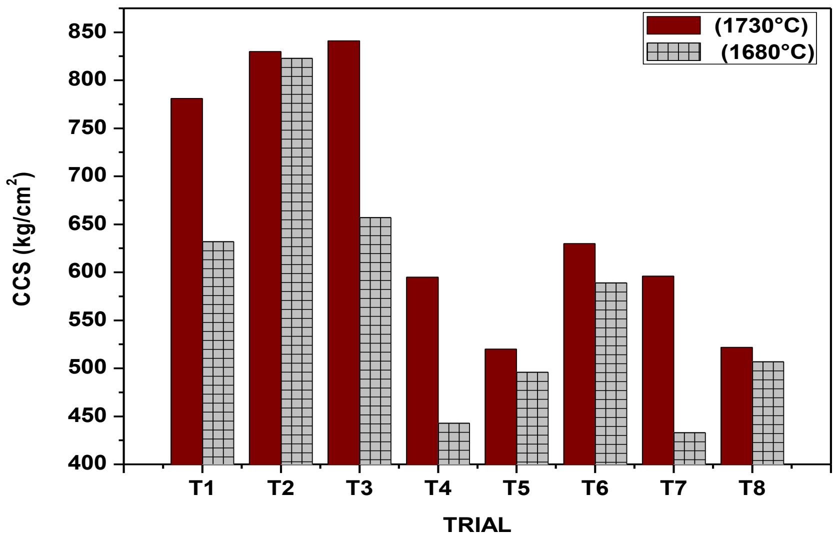


Fig 5.3: CCS variation of 99% alumina brick and zirconia added alumina bricks

CCS depends highly on the forming process and densification of the composition. CCS values are normally higher when fired at 1730°C due to the strength of the grains and also bonding between the grains at this high temperature leading to better sintering and hence better densification [42]. It is observed that zirmul containing batches resulted in better densification. AP values are firmly in support of densification character. Lower AP values are found for batches containing fuzed zirmul as additive.

5.3.2 Thermo – mechanical properties

5.3.2.1 Hot Modulus of Rupture (HMOR)

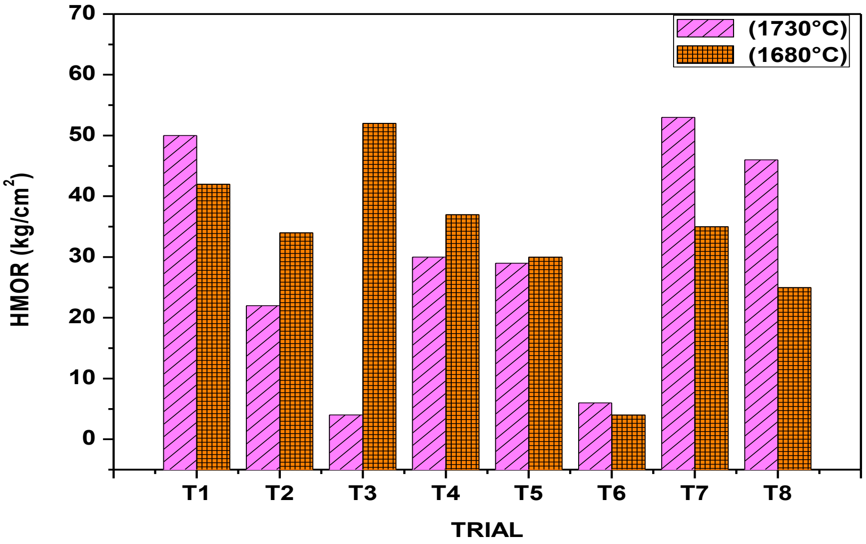


Fig 5.4: HMOR variation of 99% alumina brick and zirconia added alumina bricks

T1 batch containing zero additive shows good HMOR values and higher hot strength at 1730°C sintering temperature. Direct bonding without formation of low melting phase leads to good bonding between grains, low porosity and increase in strength, which in turn is responsible for higher HMOR. Zirmul containing compositions T2 and T3 showed decrease in HMOR at high firing temperature. The fall is drastic for higher zirmul containing T3 batch. This may be due to presence of impurity phases and formation of liquid. Zircon sand containing compositions resulted in lower HMOR values. In situ reaction and mullite formation has resulted in structural expansion causing internal voids or cracks which might have resulted in lower strength values. T7 and T8 contains very less amount of zirconia and alumina content is almost 98% which requires higher temperatures for complete densification and hence the HMOR values.

5.3.2.2 Refractoriness Under Load (RUL)

High alumina bricks are of very high quality as pure and good quality raw materials are used in the manufacture of these refractories. RUL values are > 1700°C for most high alumina materials as alumina has a lower coefficient of thermal expansion and low impurity content reduces the chances of liquid phase formation.

5.3.3 Thermal properties

5.3.3.1 Thermal Spalling Resistance (TSR)

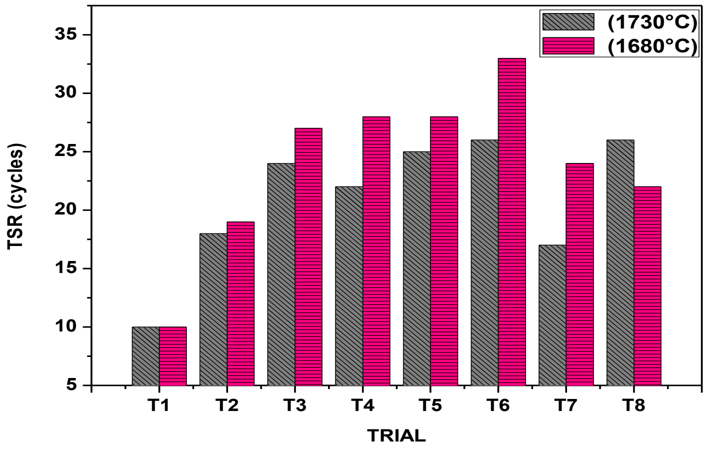


Fig 5.5: TSR variation of 99% alumina brick and zirconia added alumina bricks

Variation of TSR of different batches is plotted in Fig 5.5. It can be seen that T1 batch having no additive shows minimum TSR property. Other batches showing better spalling resistance may be due to the presence of microcracks, which are generated because of zirconia addition. Microcracks lead to the development of a stress gradient within the refractory which does not allow propagation of cracks. **[43].** Zirconia normally increases the spalling resistance of refractories.

5.3.4 Scanning electron microscopy

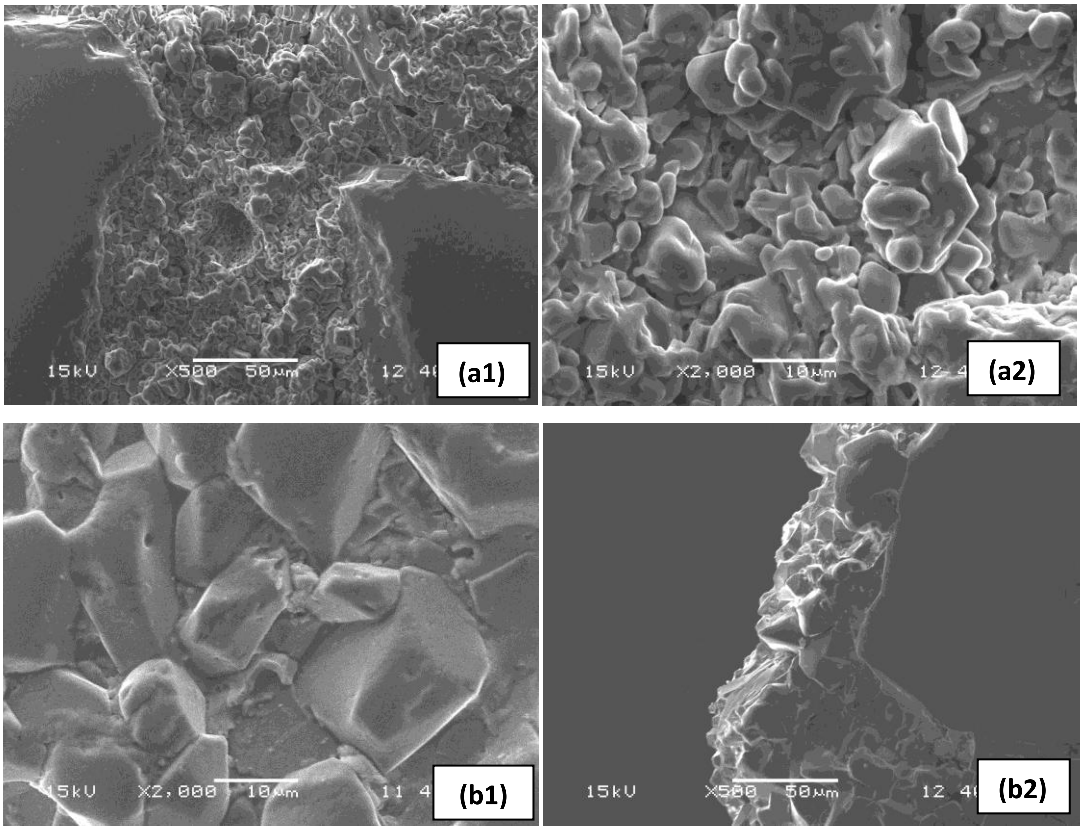


Fig 5.6: SEM micrographs of (a1 & a2) 99% alumina fired at 1680°C (T1), (b1 & b2) alumina – zirconia brick fired at 1680°C (T3)

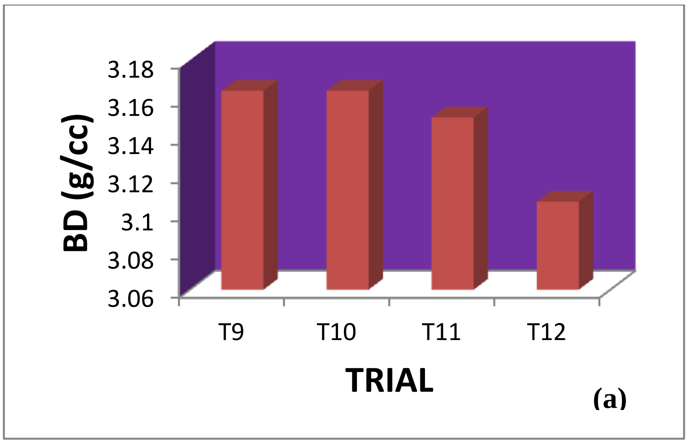
Secondary electron image through SEM shows compact and dense microstructure (Fig 5.6). Batch T1 is compared against T3. In T1 relatively smaller size grains are found compared to T3 and also some intergranular pores are observed. In both the batches, bonding between coarse grains and matrix is found to be good resulting in enhanced densification and strength values (Fig a1 and b1 for T1 and T3 respectively).

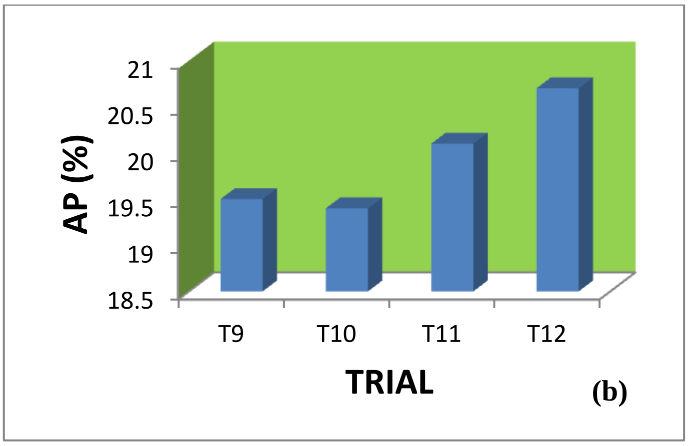
From the above study, it can be found that addition of zirmul has resulted in better properties and batch T3 sintered at 1680°C may be taken as the best batch. Hence 5% zirmul containing batch sintered at 1680°C is selected for further study.

5.4 Properties of bricks containing zirmul and reactive alumina

5.4.1 Physical properties

5.4.1.1 Bulk Density (BD), Apparent porosity (AP), and Cold Crushing Strength (CCS)





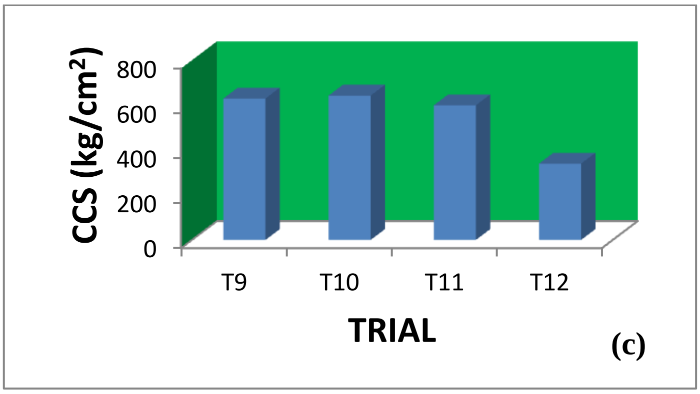


Fig 5.7: Variation of (a) bulk density on addition of reactive alumina to alumina – zirconia bricks, (b) apparent porosity on addition of reactive alumina to alumina – zirconia bricks, (c) CCS on addition of reactive alumina to alumina – zirconia bricks

Variation of bulk density, apparent porosity and cold crushing strength of reactive alumina added comparisons are plotted in Fig 5.7 (a), (b) and (c) respectively. RA1 containing T9 and T10 batches were found to have higher densification and low apparent porosity due to the variation in reactive alumina properties. RA1 has higher surface area, i.e., lower particle size which enables it to penetrate the pores easily, enhance the packing and decrease the porosity and also correspondingly increase the strength leading to high CCS values. RA2, on the other hand, has lower surface area as compared to RA1 and hence results in comparatively inferior AP, BD and CCS values. T12 batch containing higher amount of RA2 shows comparatively poor character.

5.4.2 Thermo – mechanical properties

5.4.2.1 Hot Modulus of Rupture (HMOR) and Refractoriness Under Load (RUL)

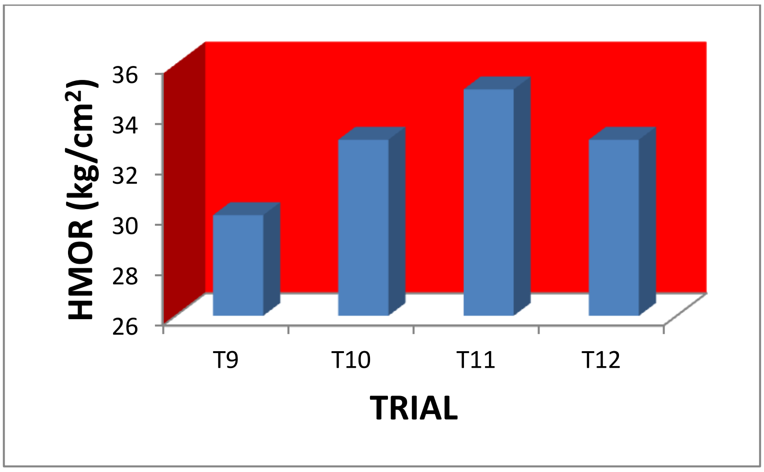


Fig 5.8: Variation of HMOR on addition of reactive alumina to alumina – zirconia bricks

Variation of reactive alumina was found to have negligible effect on hot strength properties. No appreciable change in HMOR values is observed with variation of RA and its amount. Reactive aluminas are helping in better sintering, even also during testing at high temperature, causing better bonding and strength.

5.4.3 Thermal properties

5.4.3.1 Thermal expansion

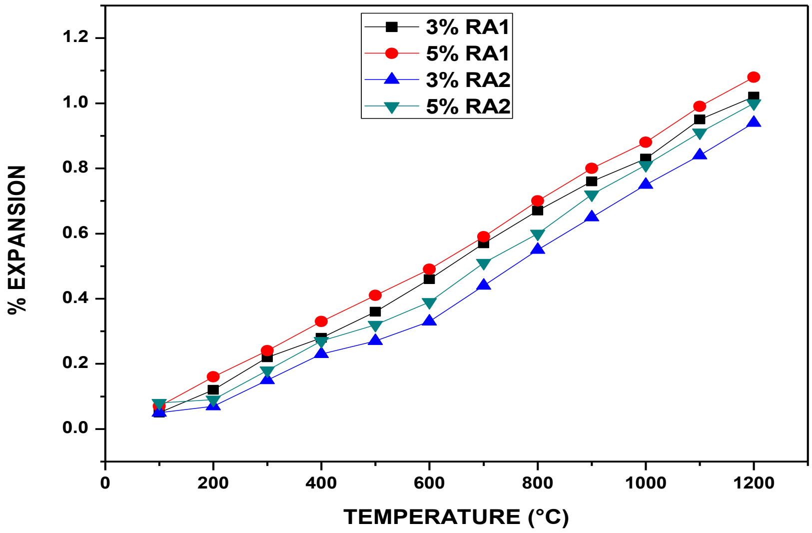


Fig 5.9: Variation of thermal expansion on addition of reactive alumina to alumina – zirconia bricks

Thermal expansion studies of reactive alumina containing samples are plotted in Fig 5.9. It can be seen that the expansion values increases linearly with increasing temperature. RA2 containing batches were found to have little lower expansion values may be due to higher porosity level in them.

5.4.3.2 Thermal spalling resistance (TSR)

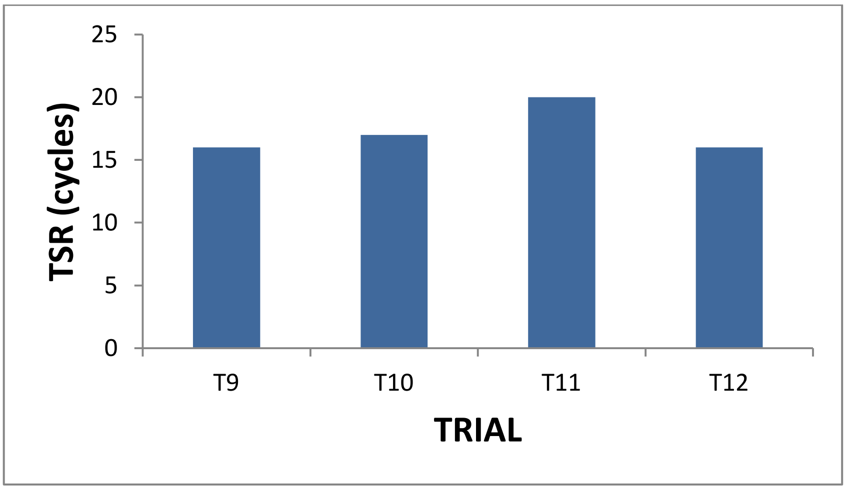


Fig 5.10: Variation of TSR on addition of reactive alumina to alumina – zirconia bricks

TSR study of the reactive alumina containing samples does not show wide variation among the batches. Marginally better resistance observed for the T11 batch may be due to little higher porosity and lower thermal expansion values with not much deterioration in strength properties.

5.4.4 Scanning electron microscopy

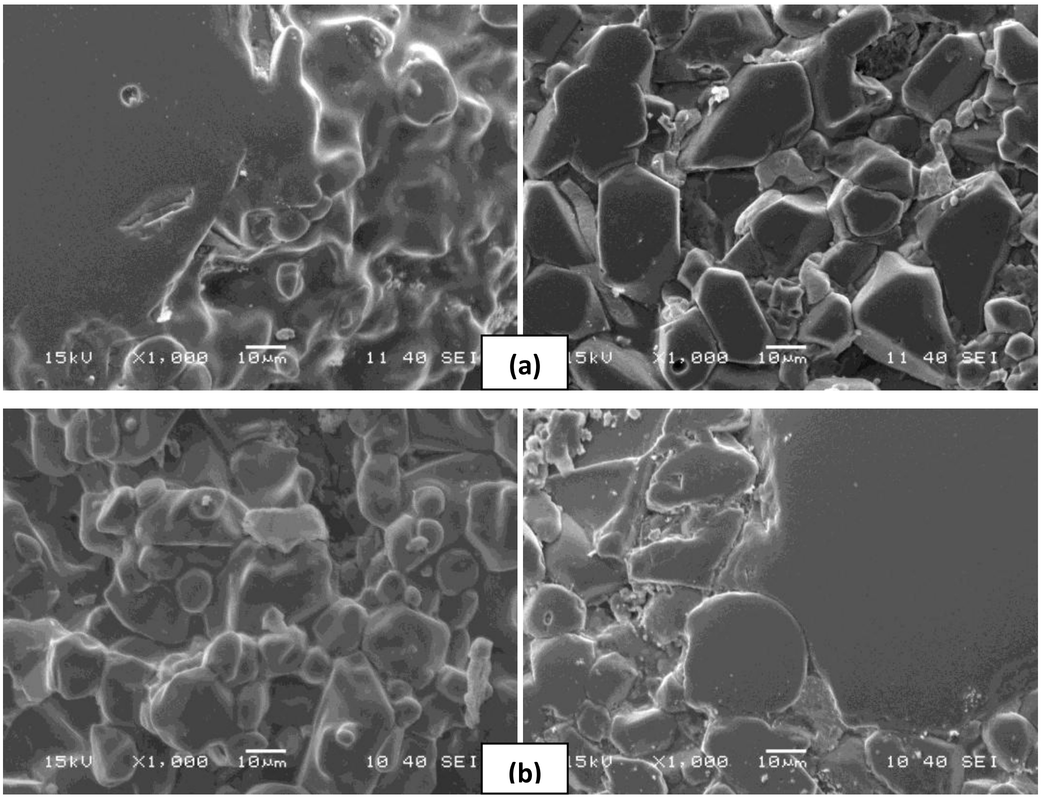


Fig 5.11: SEM micrographs of (a) 3% RA1 added alumina - zirconia brick (T9), (b) 3% RA2 added alumina – zirconia brick (T11)

SEM photomicrographs of the reactive alumina containing samples show similar microstructural character. Matrix portions were found to be compact and small zirconia grains are distributed randomly. Bonding or sintering between coarser grains and matrix phase can be observed for both the samples.

From the above study, it was found that addition of reactive alumina did not have an appreciable effect on the properties of zirmul containing alumina refractory (T3). T11 is selected for further trials due to the fact that it gives maximum, although not much, spalling resistance among the four batch trials with reactive alumina.

5.5 Properties of alumina – zirconia – chrome bricks

5.5.1 Physical properties

5.5.1.1 Bulk density (BD), Apparent porosity (AP) and Cold Crushing Strength (CCS)

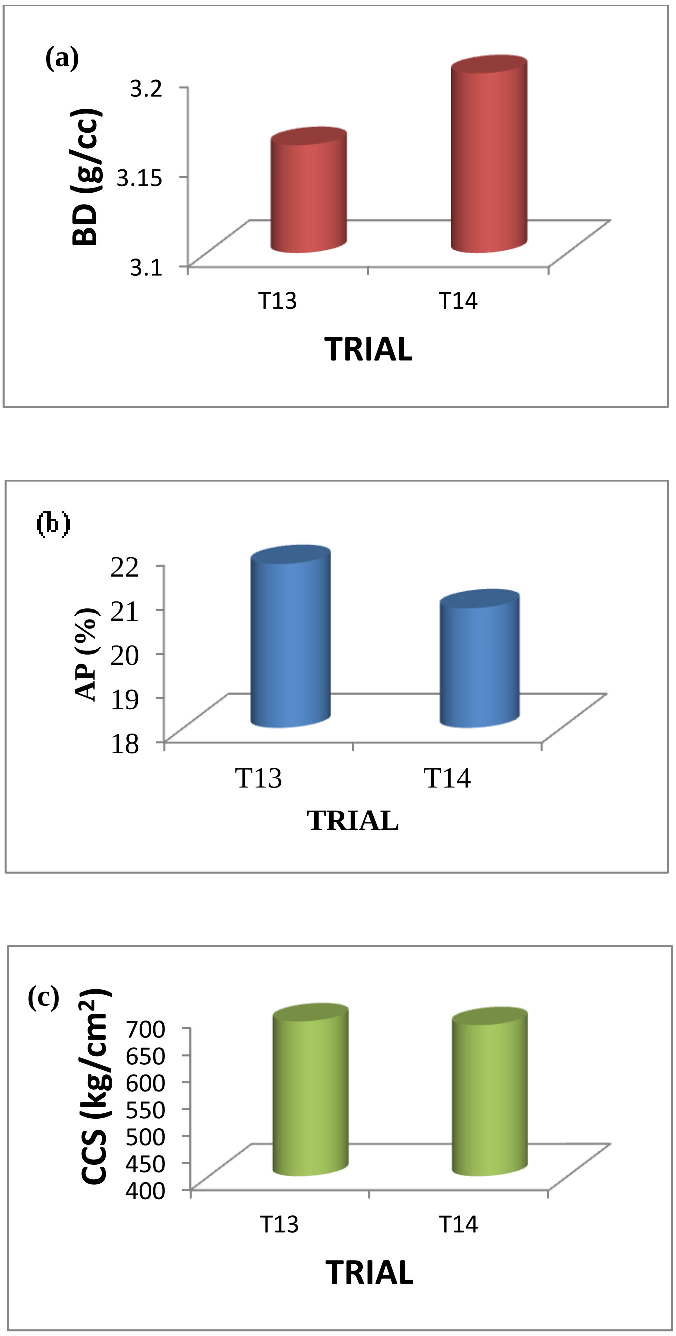


Fig 5.12: Variation of (a) bulk density on addition of chrome oxide to alumina – zirconia bricks, (b) apparent porosity on addition of chrome oxide to alumina – zirconia bricks, (c) CCS on addition of chrome oxide to alumina – zirconia bricks

Addition of chrome oxide to zirconia containing alumina refractories resulted in a decrease in densification. Chrome oxide has a high vapour pressure and vapour pressure increases with higher temperature resulting in removal of chrome oxide from the sample. This removal causes an increase in porosity and decrease in densification. But again, as we increases chrome oxide content from 5 wt% to 10 wt%, an increase in BD was observed. This may be associated with higher specific gravity of chrome oxide (5.2 g/cc) compared to substituted alumina (3.99 g/cc).

CCS values were found to improve in presence of chrome oxide. This may be associated with the formation of solid solution between alumina and chrome oxide causing a better bonding, resulting in high strength.

5.5.2 Thermo – mechanical properties

5.5.2.1 Hot Modulus of Rupture (HMOR) and Refractoriness Under Load (RUL)

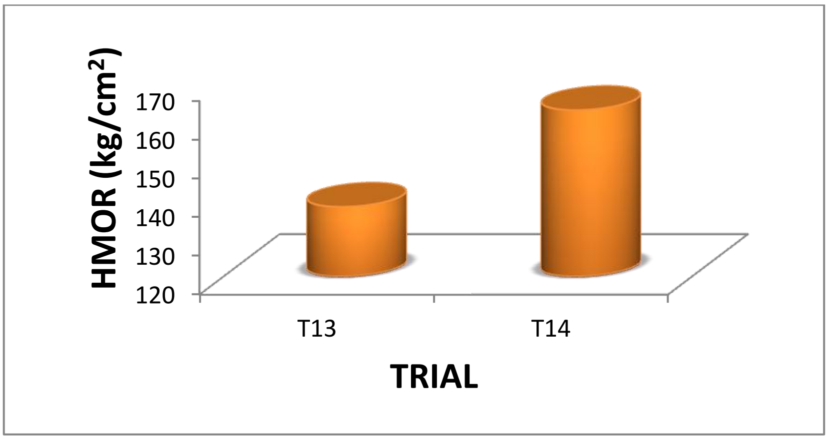


Fig 5.13: Variation of HMOR on addition of chrome oxide to alumina – zirconia bricks

HMOR values for chrome oxide containing samples were found to improve significantly than that of the other compositions having no chrome oxide. Chrome oxide in alumina system makes solid solution and the liquidus of the solid solution shifts to higher temperature with increasing chrome oxide content [33]. Thus, increase in the values was found with increased chrome oxide content in the batches. Highest HMOR of 170 kg/cm^2 was observed for the batch containing 10% Cr_2O_3.

5.5.3 Thermal Properties

5.5.3.1 Thermal expansion

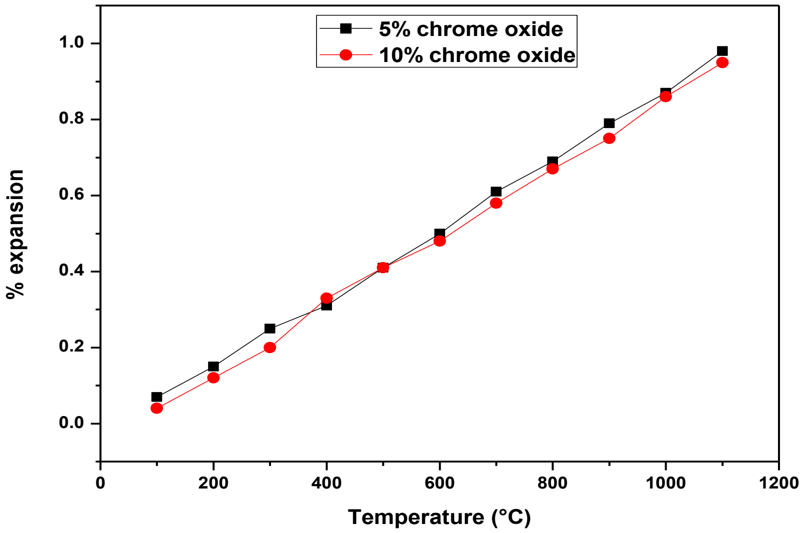


Fig 5.14: Variation of thermal expansion on addition of chrome oxide to alumina – zirconia bricks

Addition of chrome oxide does not alter the thermal expansion character of alumina – zirconia compositions which means that very high spalling resistance can be expected from this refractory. Thermal expansion coefficient, α, has been calculated to be 9.2×10^{-6} °C^{-1}.

5.5.3.2 Thermal spalling resistance

TSR values of chrome oxide containing compositions showed improvement over the batch T11 containing no chrome oxide. However, the TSR values obtained are lower than expected. Effect of high vapour pressure causing an escape of chrome oxide from the shaped products and very strong bonding (rigidity) resulting in poor flexibility might be the reasons for not obtaining the TSR as expected.

5.5.4 Scanning electron microscopy

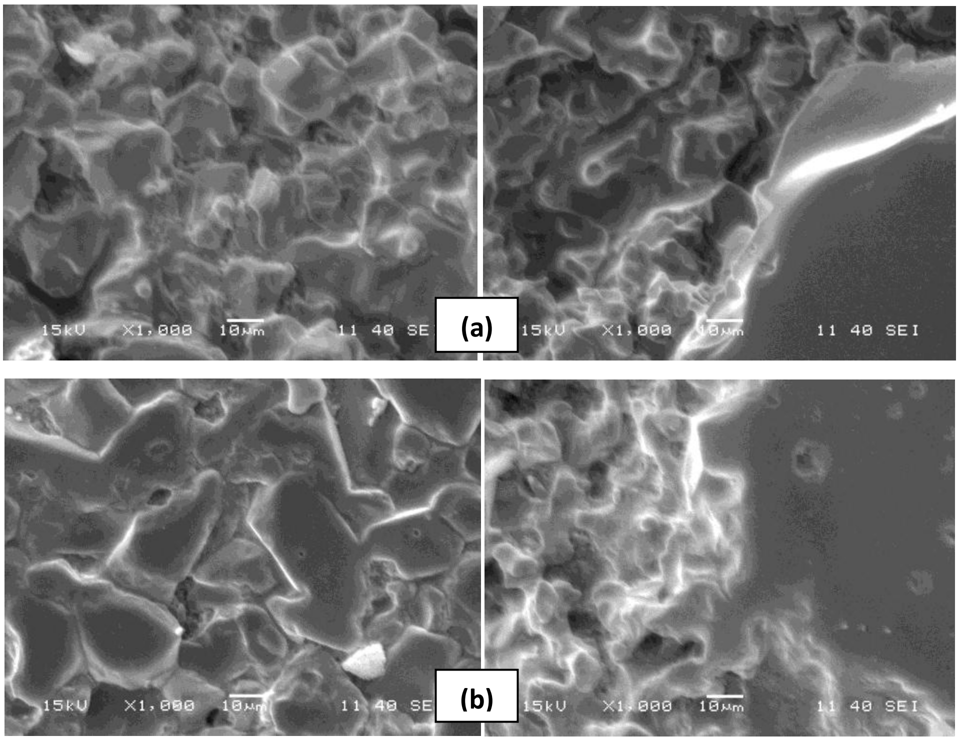


Fig 5.15: SEM micrographs of (a) 5% chrome oxide added alumina – zirconia bricks, (b) 10% chrome oxide added alumina – zirconia bricks

SEM photomicrographs of chrome oxide containing samples show nearly similar microstructural character, only 10% Cr_2O_3 containing samples were found to have little bigger grains in the matrix. Compact, angular, non – uniform grains were observed. Bonding between coarser grains and finer matrix phase is also found to be well bonded indicating good strength of the compositions.

CHAPTER 6
CONCLUSIONS

Thermal spalling resistance of high alumina bricks were significantly enhanced by addition of zirconia. This effected due to the tetragonal to monoclinic phase transformation of zirconia which led to toughening mechanisms and ultimately microcrack formation. Microcracks are stress absorbers and hence do not allow cracks to propagate thus resulting in an increased spalling resistance. Hot modulus of rupture also improved due to direct bonding between the grains as well as high firing temperature.

Reactive alumina addition, however, did not play any significant role in enhancing the hot properties. This may be due to less proportion of fines in the matrix that is essential in order that complete sintering may occur. Due to incomplete bonding, HMOR values were not obtained as expected.

Chrome oxide green, on being added to the zirconia optimized high alumina refractory significantly improves HMOR values due to the formation of solid solution between alumina and chrome oxide which imparts high strength to the refractory and also increases the CCS values.

SCOPE FOR FUTURE WORK

Carbon black reactor is a high corrosion zone which means that corrosion resistance of these samples need to be tested. Abrasion resistance should also be tested. High alumina bricks with varying amounts of chrome oxide can also be manufactured for different zones of the carbon black reactor. Alumina – zirconia bricks containing zirmul can be tailored to exhibit better hot properties my manipulation of sintering temperature as well as composition.

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