CHAPTER 1

PRESENT STATUS
&
SCOPE OF RESEARCH
1.1 INTRODUCTION

Magnesia Carbon bricks which were first developed for Electric Arc Furnace (EAF) in the 1970s have been gradually applied to the Basic Oxygen Furnace (BOF) and Secondary Refining Ladle Furnaces with excellent results in the 1930s. Magnesia Carbon bricks are preferred because they possess high corrosion resistance and thermal shock resistance. The prime raw material used for manufacture of magnesia carbon bricks is magnesia and graphite. Resin or pitch is used as binder along with some antioxidants. The green mixture is moulded to shapes in high capacity presses to achieve high density and then dried at 150-200°C. After drying the bricks are ready for use. The magnesia used for making magnesia carbon bricks plays an important role for controlling the properties of bricks, since the magnesia component in the brick is 80-90%. The magnesia generally used for magnesia carbon bricks are either sintered or fused magnesia, which may be natural or synthetic.

During the initial period of development of magnesia carbon bricks sintered natural magnesia and synthetic sea water magnesia were used. Later on it was found that fused magnesia has higher corrosion and erosion resistance to basic slag than sintered magnesia but the cost of fused magnesia was higher than that of sintered magnesia. Therefore only part of the sintered magnesia was replaced by fused magnesia to enhance the corrosion and erosion resistance properties of magnesia carbon bricks.
Production of fused magnesia in different countries is shown in Table 1.

<table>
<thead>
<tr>
<th>Country</th>
<th>Company</th>
<th>Plant location</th>
<th>Magnesite source</th>
<th>Capacity (tpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>QMAG (Australian Magnesium Corp. Ltd.)</td>
<td>Rokhampton, Queensland</td>
<td>Magnesite mine, Kunwara, Queensland</td>
<td>30000</td>
</tr>
<tr>
<td>Brazil</td>
<td>Geral de Electrafusa Ltd-Elfuse</td>
<td>Saa Jao de Boa, Sao Paulo</td>
<td>Magnesite /brines</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>Refratec Productos Electrofundias Ltd</td>
<td>Contagem, Minas Gerais</td>
<td>Magnesite</td>
<td>18000</td>
</tr>
<tr>
<td>Canada</td>
<td>Baymag (Refratechnik GmbH)</td>
<td>Exshaw, Alberta</td>
<td>Magnesite, Mt Brussilaf, BC</td>
<td>14000</td>
</tr>
<tr>
<td>China</td>
<td>Dashiqiao City, New Type Refractories Ltd</td>
<td>Dashiqiao, Liaoning</td>
<td>Magnesite</td>
<td>160000</td>
</tr>
<tr>
<td></td>
<td>Liaoning Qunyl Group</td>
<td>Dashiqiao, Liaoning</td>
<td>Magnesite</td>
<td>100000</td>
</tr>
<tr>
<td>Israel</td>
<td>Tateha Dead Sea Fused Magnesite</td>
<td>Mishor Rotem</td>
<td>Brines at Mishor Rotem</td>
<td>13000</td>
</tr>
<tr>
<td>North Korea</td>
<td>Korea Magnesia Clinker Industry</td>
<td>Song Jin, Kimchae, North</td>
<td>Magnesite</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hangyong Province</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Russia</td>
<td>JSC Kombinat Magnezit</td>
<td>Satka, Chelyabinsk</td>
<td>Magnesite, Satka</td>
<td>24000</td>
</tr>
<tr>
<td>South Africa</td>
<td>Vereeniging Refractories (Pty)Ltd</td>
<td>Vereeniging, Gauteng</td>
<td>Magnesite</td>
<td>10000</td>
</tr>
<tr>
<td>South Korea</td>
<td>Sam Hwa Electromineral s Co Ltd.</td>
<td>Pohang</td>
<td>Seawater magnesia</td>
<td>7200</td>
</tr>
<tr>
<td>USA</td>
<td>Minco Inc</td>
<td>Midway, Tennessee</td>
<td>Magnesite /brines</td>
<td>20000</td>
</tr>
</tbody>
</table>
From the Table:1 it is seen that China is the biggest manufacturer of fused magnesia in the world. The price of fused magnesia gradually decreased with the increase of fused magnesia production. Presently magnesia component of magnesia carbon bricks wholly comprises of fused magnesia for cost effective products.

1.2 PREVIOUS WORK

A considerable work has been carried out on the production & evaluation of properties of fused magnesia and manufacturing of magnesia carbon bricks, which have been surveyed are mentioned below.

V A Bran et.al. (2) in their study have concluded that the main criteria for the high quality of fused magnesia are the purity of the raw materials and rational fusing cycle, ensuring migration of the impurities into the skin of the block. There is marked differentiation in the melt’s components and the various zones of the block are enriched with magnesia, while the impurities accumulate at the skin, the central zone, and the melter dust. The CaO and SiO₂ experience most redistribution in the block, least by the Fe₂O₃ and Al₂O₃. Increasing the cooling time positively affect the thickness of the single crystal zone and the size of the periclase crystals. Increasing the heating rate also yields fused periclase of adequately high quality. The impurity oxides like SiO₂, Al₂O₃, Fe₂O₃ and CaO in the fused periclase are detected as M₂S, CMS,
C₃MS₂, C₂S and C₃S, solid solutions of magnesioferrite and
magnesiowustite.

Yasuyoshi Oda, Chisato Ota, Youichi Takamiya (3) have reported
that electrofused magnesia having high purity and single crystal is
desirable. A number of factors are known to influence solid state
sintering. It is not necessary that the factors which affects densification
will coincide with the factors which influence the crystal growth. It has
been reported that crystal growth is a function of sintering temperature
and time.

Yu.M.Galkin et.al.(4) have carried out an investigation of the of
chemical purification of fused periclase. X-ray diffraction investigations
showed the impurity in Ca containing phases in the periclase are
primarily C₃S, C₂S, C₃MS₂ and CMS. In a crystallised piece of fused
periclase the impurity phases are localised to a large degree in the inter
granular boundary and the cleavages of the periclase crystals and to a
lesser degree in the volume of the grains. The size of the silicate phase
with inclusions vary from 0.10-0.01mm. As the result of differences in
the thermal coefficient of expansion of the impurities phases and the
periclase in crushing of the cold block and grinding of it the impurities
located in the interface boundaries are found primarily on the surface of
the periclase powder particles and in the fine fractions.

Liang xun Yu et.al. (5) have reported that the research work on
producing electrically fused magnesia began in 1960s in China. The
sintered magnesia was initially taken as starting material, later on the
high purity magnesite instead was directly fused in an electrical furnace which leads to simplicity of the process. The fused magnesia with high purity, high bulk density and especially with complete growth of crystals is opted for manufacturing super-duty basic refractories.

N N Novikova\textsuperscript{(6)} et.al. have reported that fused periclase and the products based on it have been finding ever increasing applications in high-temperature technology as efficient refractories. However, the specifications concerning the composition, the properties and the structure of periclase and high quality periclase products are not completely met by modern production technology because of the differences in the nature of the materials used, the specific features of the melting practice and the distribution of the products in the block. The particles of brucite and magnesite were heated to the temperatures of dehydration and were melted. Under the action of the forces of surface tension, they assumed spherical shape. From the high-temperature zone, the particles entered the quenching zone. When using brucite, the degree of spheroidisation was as high as 95%; in the case of magnesite it was lower.

D I Suvorova et.al.\textsuperscript{(7)} reported that the under fired material during the manufacture of fused periclase has high impurity content. Beneficiation was done for this under fired powder with hydrochloric acid followed by precipitation with sodium carbonate and then thermal decomposition of magnesium carbonate to get sintered magnesia. The
sinter magnesia obtained is subsequently used for fusion to produce fused magnesia.

Alberto Ross et. al.\(^{(8)}\) have studied the production of fused magnesia. Production is achieved through high technology process using Higgins electric furnace. Mexican fused magnesia is fused in an electric arc furnace where the furnace is fed with high grade Mexican magnesia. The shell of this furnace is protected by its own feed of MgO. After each melt, it is allowed to cool and the ingots are separated from the non-fused material and crushed to proper sizes. The Mexican fused magnesia has higher CaO:SiO\(_2\) ratio which helps in lower diffusion and penetration of iron from the slag. Boron is an important impurity that must be kept very low to avoid the deterioration of mechanical properties of the bricks used at high-temperatures and to minimise the corrosion against slag attack. It has been observed that the larger the crystal size, the lesser corrosion on the periclase.

P P Budnikov\(^{(3)}\) in his book on ceramics states that fused magnesia constitutes a purer material since the iron oxides and other impurities migrate to the periphery of the block during electrofusion. In fused magnesia the periclase grains are very large and have well developed cleavage cracks. Consequently the spalling resistance of refractories made out of this material is superior.

The difference between fused magnesia and sintered magnesia has been studied for corrosion resistance. K V Simonov\(^{(10)}\) et.al. concluded that the specimen made from fused periclase have higher...
density and the dimensions of the crystals of fused periclase are higher than sintered. Since the coarse crystalline fused periclase has fewer boundaries the corrosion resistance is higher in fused periclase body than in sintered periclase.

Dr. Hagen Schuites\textsuperscript{(11)} has concluded that fused magnesia is characterised by purity, CaO:SiO\textsubscript{2} ratio, bulk specific gravity and the average primary crystal size. Fused magnesia has large crystal size combined with higher bulk specific gravity and therefore lower porosity, which means in every unit of refractory lining, less area is available for any kind of chemical attack, may be through liquid or gaseous infiltrations. In the case that the CaO:SiO\textsubscript{2} ratio lies below 2:1, C\textsubscript{3}MS\textsubscript{2} and/or CMS are formed both having melting point around the 1500°C mark. In the case of a CaO:SiO\textsubscript{2} ratio above 2, C\textsubscript{2}S & C\textsubscript{3}S are formed which have melting point or decomposition temperatures around 2100°C. One ought not to go by the vertically calculated CaO:SiO\textsubscript{2} ratio alone since fused magnesia being the substance which crystallised from a high-temperature melt, noticeable amounts of CaO can be in solid solutions with MgO and therefore not available to form the above discussed Ca-or Ca-Mg silicates. Therefore, a CaO:SiO\textsubscript{2} ratio of well above 2:1 is a must to ensure highest refractoriness of fused magnesia.

F Golestani-Fard et al.\textsuperscript{(12)} studied Iranian Magnesite in detail by x-ray diffractometer and scanning electron microscope. In M-96 grade, the impurity constituents are low and diffractometer is not able to reveal their presence. In M-93, the existence of CMS and C\textsubscript{3}MS\textsubscript{2} were
found to be believed possible. Under scanning electron microscope the average MgO particles size is about 60 to 70 μm. A primary silicate bonds exists between main periclase particles. Despite being fired at 1850-1900°C, direct bonding was not observed in the sample. It is well established that when periclase, monticellite and forsterite are present simultaneously, the liquid formation is very likely to happen at low temperatures of 1500°C. The RUL of that test sample with M96 demonstrated 1500°C for T1 value at which shrinkage commenced.

Kunio Matsui and Fusao Kawano(13) measured the weight loss of electrofused magnesia at the temperature of 1500-1750°C and showed that the weight loss of electrofused magnesia is higher than the sintered magnesia in the temperature range of measurements. This is assumed to be the higher content of CaO and B₂O₃ in electrofused magnesia compared of the sintered one. It is also apparent that CaO in magnesia accelerates the reaction of magnesia and graphite. The evaporation of CaO and MgO proceeds at an identical rate, judging from the evidence that the CaO content of both magnesia species does not differ in the reaction before and after. Further, the reaction of magnesia clinker and carbon was largely influenced by the chemical composition rather than the physical factors such as crystal size of magnesia clinker.

A M Ryder et.al. (14) studied the influence of crystal size and purity of sintered magnesia with BOF slag. Small holes were drilled in MgO sample, which were filled with slag and subjected to a controlled time temperature regime. In all eight samples were taken for study
which consisted of fused and sintered magnesia of different crystal size and different purity. The crystal size of the samples taken varied from 80-1000\(\mu\)m. Fe diffusion through MgO crystals was similar for all materials tested, including electrofused magnesia. The low penetration in high purity materials is assumed to be a consequence of the narrow boundaries and direct MgO-MgO contact. With high-grade fused materials, boundaries reachable by the slag are observed, but the number of such boundaries is small. It is generally accepted that larger crystal size is beneficial with high quality fused magnesia giving best performance. In summary, high purity periclase inhibits slag penetration whereas large crystal tolerates it.

Uong Chon et.al.\(^{(16)}\) studied sintered seawater magnesia with bulk density 3.45gms/cc which showed sudden strength degradation after quenching from 600°C to vacuum oil at 22°C. The magnesia single crystal showed higher chemical wear resistance against molten slag, compared to that of sintered magnesia. Also it was found that bulk density and grain size are the most important factor affecting its chemical wear resistance in the case of magnesia with over 98% purity. It was found that the larger the grain size, the higher the wear resistance against molten slag.

The use of fused magnesia for manufacturing magnesia carbon bricks have been extensively studied. Tanezo Ishibashi et.al.\(^{(16)}\) investigated the effect of crystal size on the specific surface area of the
periclase particles. Weight loss in magnesia carbon refractories in Ar & CO atmosphere was conducted and found that the magnesia with lower CaO:SiO$_2$ ratio lose more weight because SiO$_2$ and B$_2$O$_3$ are more likely to be reduced by carbon. It is presumed that the volatilisation of SiO$_2$ and B$_2$O$_3$ causes the key surfaces to be activated, promoting magnesia carbon reaction. Magnesia with high CaO:SiO$_2$ ratio containing larger crystals and among them, those containing less B$_2$O$_3$ are less likely to lose weight.

Shigeo Yoshino et al.\textsuperscript{(17)} in their study of wear of magnesia carbon refractories concluded that magnesia carbon bricks with electrofused magnesia are very effective in increasing corrosion resistance. With electrofused clinker, periclase crystals are so large as to be less affected at the space between the grains. Almost same conclusion is drawn by Yoichi Naruse et al.\textsuperscript{(18)} after their investigation on magnesia carbon bricks used in converter. It has been emphasised that magnesia carbon bricks containing electrofused magnesia and high purity graphite serve favourably under more severe conditions of continuous casting and rising tapping temperature.

MgO grains in magnesia carbon brick usually blackened after being used at high temperature. Akira Yamaguchi\textsuperscript{(19)} investigated the cause and the mechanism of blackening of magnesia oxide grains. Fused MgO crystal grains, which are generally used in magnesia carbon bricks, contained many micropores below 1\textmu m in size. When the MgO grains with micropores is heated in an atmosphere with high partial
pressure of Mg i.e., with low partial pressure of O₂, Mg diffuses from the grain surface to the micropores and excess Mg condenses during cooling. Blackening of MgO grains caused mainly by condensation of Mg in the microdefects - in particular, in the micropores.

Takehiro Horio et al. (20) studied the corrosion test results of magnesia carbon brick in which electrofused clinker was used in different ratios as the replacement of sintered clinker. The result confirmed that larger the amount of electrofused magnesia mixed, the more corrosion resistance of magnesia carbon brick. The study concluded that
- wear rate increases with the increase of the amount of graphite mixed in the brick,
- wear rate is decreased by mixing highly pure graphite,
- wear rate is decreased by mixing electrofused magnesia

S A Suvorov et al. (21) conducted studies on three types of magnesia with different purity level viz., two types of sintered and one fused magnesia indicate that the ratio of the reduction rates of MgO and SiO₂ is a decisive factor. The oxidation-reduction reactions lead not only to an increased amount of silicates, but also to a change in their chemical composition. While CMS forms the main constituent after coking at 1000°C, it becomes progressively enriched with M₂S as the temperature of reduction firing increases. The changes in the silicate phases of periclase during reduction are depletion of MgO from the
material and removal of Si from the silicate constituents into the condensed oxygen free phase.

Z. Foroglou et al.\cite{22} have reported that in a number of European converter steel plants, remarkable improvement of lining life has been achieved with magnesia carbon refractories based on sintered magnesia. Authors concluded from the study of used magnesia carbon bricks that the lining performance depends more on the physical characteristics and related properties such as shape, size and structure of MgO crystallites, rather than the absolute purity of the material, example its MgO content. The tests on sintered and fused grains concluded that the microstructures of the clinker derived from microcrystalline magnesite, built-in resistance to structural changes as expressed by MgO crystallites, size and shape, its low porosity and the composition of secondary phases greatly decreases the rate of brick wear.

Kashio Shiotani et al.\cite{23} conducted a study with 4 different types of magnesia carbon bricks and one dolomite added type. Of these, one quality was with the use of fused magnesia with metal. When the bricks having high corrosion resistance have come to be required as the material for repairing for the extension of the furnace service life, at present the unburnt magnesia carbon brick added with Al alloy is used basically and fused MgO is further added to it for the preferential application to the worn parts in order to make the wear balance uniform.
Tadashi Morimoto\textsuperscript{(24)} studied the effect of fused magnesia mixing ratio, graphite mixing ratio, and graphite purity on the corrosion resistance of magnesia carbon brick by lining a high frequency induction furnace and measuring the amount of wear by slag with \textit{CaO:SiO}_2 \textit{ratio} = 2.3:1 and the total \textit{Fe} = 16\%. It was evident from the test that the corrosion resistance of magnesia carbon brick is improved by increasing the amount of fused magnesia as well as by using less graphite. Based on these results, unburnt magnesia carbon material consisting of 80\% fused magnesia and 20\% high purity graphite blended together was chosen for bottom blowing tuyere material.

J. Karja\textsuperscript{(25)} in his study on the refractory performance in Rautaruukki's LD-KG converter have concluded by comparing wear rates and laboratory tests that best result with wear rates less than 0.5\textit{mm} per charge is achieved with a magnesia-graphite brick containing 18\% C, 75\% fused magnesia and metallic additives.

The importance of periclase crystal size in restricting corrosion resistance has been studied by Yan Xingjian and Zhang Wanchun\textsuperscript{(26)}. The larger the crystal size, the lesser is the wear rate. The infiltrated slag reacts with the magnesia or more exactly with the inter crystalline silicate phases to give a compound with a low melting point. The destruction of the silicate bonds and/or direct bonds leads to the elimination of crystallites and their dissolution in the slag. The elimination of crystallites is all the more difficult if the size is large. In fact, besides the large size of the crystals, fused magnesia aggregates
have the following advantages: excellent chemical stability, low activity with slag, low volatility of magnesium depending on the reaction

\[
\text{MgO} + \text{C} \rightarrow \text{Mg} + \text{CO}.
\]

S V Kazakov et al.\(^{(27)}\) reported that at high-temperature, the structure of the magnesia carbon brick system forms as a result of the sintering process of the mineral filler under the conditions of varying volumetric ratios of the oxides and the carbonaceous phases due to the oxidation reduction reaction. In the oxides constituent, periclase and graphite ash, the MgO content decreases and the content of silicates increases due to the occurrence of the following reaction:

\[
\text{MgO(sol)} + \text{C(sol)} = \text{MgO(gas)} + \text{CO(gas)}.
\]

Israel Peretz et al.\(^{(28)}\) studied the effect of addition of fused magnesia properties of twenty magnesia graphite refractory brick, based on four different sintered magnesia in combination with fine and coarse fractions of two fused magnesia aggregates. Addition of fused magnesia resulted in an improvement of the following properties: strength after tempering, strength at elevated temperatures, and strength after coking and thermal shock resistance parameters. It has been concluded that the addition of fused grains to the magnesia carbon brick significantly improved the cold strength, as long as fine fused grains fractions is used. Also thermal shock resistance improves when part of a sintered is replaced by equivalent amount of fused grains.

Hiroaki Ishii et al.\(^{(29)}\) studied magnesia carbon brick after use and observed this to have metal precipitated on the magnesia clinker. Such
precipitates are the results of reduction and metallization of impurities in the magnesia clinker. By observing a number of magnesia carbon bricks it could be concluded that the specimen containing high purity graphite and Al showed metallic precipitation in the magnesia clinker and their disappearance of grain boundaries of magnesia clinker.

Kohei Shimada et.al. (30) studied the use of metallic additive in magnesia carbon refractories made out of fused magnesia to improve the wear resistance. The results of investigations of the physical properties showed that the wear resistance improved when high purity seawater MgO clinker is combined with high purity graphite. Further wear resistance improved more when fused magnesia clinker is added to high purity seawater MgO clinker. This durability becomes significantly higher when a small amount of fused magnesia is added to seawater MgO clinker with a low content of impurity boron. Hiroyuki Kokumai et.al.(31) also reported that magnesia carbon bricks manufactured out of fused magnesia is superior for taphole bricks which are subjected to heat shock from molten steel, slag and abrasion from molten steel and oxidation from the atmosphere and slag.

C.Baudin and C.Alvarez (32) have tried to study the influence of thermal history on stress-strain relations, Young's modulus and HMOR of magnesia carbon and magnesia carbon brick antioxidants at high-temperature. Elastic and mechanical behaviour of magnesia carbon and magnesia carbon with Al bricks at 1000, 1200 and 1450°C in inert atmosphere were studied. In magnesia carbon samples carbon
oxidation takes place at all temperatures and carbothermal reduction of magnesia accompanied by the dense magnesia formation takes place at 1450°C. A decrease in Young's modulus as well as modulus of rupture occurs as testing temperature increases. In magnesia carbon-Al samples treated at 1000 and 1200°C, Al₄C₃ and the MgO.Al₂O₃ spinel were formed. No differences were found between samples treated at these two temperatures in terms of hot modulus of rupture and hot Young's Modulus. In magnesia carbon-Al samples treated at 1450°C, Al₄C₃ reacts forming MgO.Al₂O₃ spinel in the bulk. The carbothermal reduction of magnesia and related dense magnesia zone formation are responsible for this elastic and mechanical behaviour.

Robert E. Moore et al. (33) studied eight different specimen, all consisting of different proportions of fused magnesia, graphite and different types of metallic additives. Dense MgO layer formation was observed in all specimens. In each case the layer seems to be associated with impurity materials. It is plausible that the impurities aid in sintering and densification of the secondary magnesia. Significant amounts of magnesium metal were observed at the cold phase of the most of the specimen. These magnesium metal deposits were formed by condensation of Mg(gas) in the coldest region of the specimen.

L. l. Andievskikh et al. (34) carried out a study with the incorporation of various complex additives-barium, flourine, boron, phosphorous containing materials. The amounts varied in the range of 0.5-5%. Complex thermal analysis showed the following: the first
endothermic effect is connected with the removal of the adsorbed moisture at 130°C, the second with the oxidation of the organic matter at 510°C. Heating at 1350°C is accompanied by the mass loss from the specimen. A number of exothermic effects with steep maximum at 880°C and 1140°C were clearly connected with oxidation of deep layers of carbon. At 1330°C there was a sharp endothermic effect with an increase in mass, which was apparently due to the oxidation of Fe and Al. The total mass loss is 12.1%.

C.Baudin and C.Alvarez\(^{(35)}\) have tried to study the influence of graphite flake orientation on the textural modifications of magnesia carbon bricks. The effect of pressing on magnesia carbon and magnesia carbon-Al brick texture is that of orientation of graphite flakes with their maximum surface vector parallel to the pressing direction. There is no effect of pressing direction on porosity of Magnesia carbon and Magnesia carbon-Al bricks. In Magnesia carbon-Al, Al\(_4\)C\(_3\) is formed in the bulk of the samples at 1200°C and spinel is formed in the bulk as well as at the surface at 1200 and 1450°C. In Magnesia carbon-Al, Al\(_4\)C\(_3\) acts as bonding between graphite flakes and the matrix and no orientation effect of internal strength degradation exist.

Masato Tanaka and Tsuneo Kitai\(^{(36)}\) studied the influence of particles size distribution of magnesia particle on thermo-mechanical properties. Magnesia particle size distribution was varied in accordance with Andreason's equation: 
\[
F = 100 \times \left( \frac{D_p}{D_{\text{max}}} \right)^q;
\]
where \(D_{\text{max}}\) is the maximum particle size (mm), \(q\) = distribution coefficient, \(F\) = Accumulation percentage.
under Dp(mm). Maximum grain size is set to 3 mm or 5 mm in diameter, the distribution coefficient of grain size (q value) ranged from 0.3-0.6. For getting the optimum proportion of thermo-mechanical properties 4% of Al-Mg alloy with 0.6 distribution coefficient (q value) and 5 mm particle size was chosen for application in the converter.

Kunio Matsui et.al.\(^{(37)}\) have concluded that the magnesia employed for the magnesia carbon brick should be highly pure and should have large crystals. The probable reasons that the bricks of electrofused magnesia has a higher slag resistance than those of sintered magnesia are (1) electrofused magnesia has fewer grain boundaries such that slag penetration is less and falling of crystal grains into slag does not occur and (2) the density of electrofused magnesia is higher than that of sintered magnesia and thus the pores which allow room for slag penetration are fewer. Furthermore, there is an indication that electrofused magnesia does not easily react with carbon.

Kenji Ichikawa et.al.\(^{(38)}\) have reported that in general, magnesia carbon brick is the material with excellent thermal spalling resistance because of its high thermal conductivity and is extensively used in refining furnaces. An experiment has been designed to test thermal spalling of magnesia carbon bricks using high purity seawater magnesia oxide. Al metal of 3% was added in all the compositions. The heat source was by a high frequency induction furnace and was maintained at 1650°C. Sample size of 40x40x270mm was immersed halfway into
the hot metal, maintained for 60 seconds and discharge from the hot metal for cooling. The results are as follows

1. Higher graphite content leads to higher thermal spalling resistance
2. The thermal spalling resistance decreases with an increase in metal content.

In addition, the quantification of generated cracks was attempted and the correlation with various theoretical thermal shock resistance parameters was investigated. As a result, the resistance parameters show a strong correlation with the results of this method.

A. Wolfert et al. (33) reported by way of thermogravimetric study to know the reaction between magnesia and graphite at 1700°C have reported that solid solubility of SiO₂ in magnesia is very low. SiO₂ is usually present as one of the constituents of impurity phases in the material. Amount of SiO₂ determines to a great extent the amount of impurity phases. The thermogravimetric experiment indicates that the stability of magnesia towards carbon is influenced by the SiO₂ content. Therefore, it is concluded that the impurity phases in the magnesia play an important role in the reaction mechanism.

Shi Gang et al. (40) have studied the fused magnesia quality focusing on reducing impurity levels, optimising their CaO:SiO₂ ratio and increasing the primary crystal size of the material. Studies also showed that the contribution of higher chemical purity and larger primary crystal size in fused magnesia for the quality of magnesia carbon bricks is very significant. The carbon reinforced fused magnesia has been
developed and the thermal shock resistance as well as hydration resistance of this material was found to be better.

Sunayama Hirtoyuki et.al. \cite{41} studied the mechanism of corrosion of magnesia carbon brick in molten slag under high oxygen partial pressure. Experiment was conducted with sintered and electro fused magnesia. The specimen was immersed into the slag after homogenisation and was rotated at 5rpm for 20 minutes at 1673°C. The small quantity of slag was sampled from the molten slag at every required time. The decrease of radius of the specimen was determined by the calculation of concentration of MgO which dissolved in the slag. Further the diameter of the specimen after experiments was measured with a slide caliper. There was linear relationship between the decrease of radius and the immersion time. The corrosion rate of the brick was decreased with the decrease of the content of carbon from 13% to 4.8% in the magnesia carbon brick. Further the sample with electrofused magnesia had lower decrease of radius as compared to sintered magnesia brick.

J M Robin et.al. \cite{42} in their study of thermo-mechanical behaviour of magnesia carbon refractories have clearly differentiated between natural sintered magnesia, sea water magnesia and fused magnesia and have concluded that best mechanical and chemical properties of magnesia carbon refractory are obtained with electrofused magnesia grains, which are obtained by slow solidification of molten magnesia.
allowing growth of larger crystals (>500\(\mu\)m). The impurity content of this material is very small and the grain structure is of high quality.

L M Aksel'rod et al.\(^{(43)}\) evaluated periclase carbon refractories based on fused periclase with an additive of Al in service in 370 ton converter. A petrographic study of the used bricks showed that the zone formation in service is accompanied by the change in the phase composition of the refractory. The coarse periclase grains are represented either by single crystals or by intergrowths of fine polygonal grains separated by silicate layers. The silicate phase consists dominantly of monticellite and more rarely forsterite. The binder bears fine crystallised grains of alumina magnesia spinel that seems to have formed due to the interaction between metallic Al and periclase. The structure of the specimen is dense and pores are rare, mostly isolated, and of isometric shape and have size of 0.1-0.15 mm. The reaction zone contains no graphite. The main crystalline phase is periclase which is saturated with iron oxide from the slag. The saturation of the periclase increases with passage from the reaction zone to the slag crust.

In-Kyung Bae et al. \(^{(44)}\) studied the effect of stainless steel fiber, kinds of metal additive and particle size distribution for the purpose of the improvement of magnesia carbon bricks toughness by using fused magnesia clinker with 98% purity, flake graphite with 98% purity, Al and SiC and stainless steel fibers. The results of the study indicated that toughness of magnesia carbon bricks improved by the addition of
stainless steel fibers, the decrement of Al metal and enlargement of particle size distribution.

L.B.Khoroshavin and V.A.Perepelitsyn\(^{(46)}\) studied the use of carbon with manufacture of magnesia carbon bricks. They reported that carbon possesses a highly melting point, is not vetted by most liquids and merits, and is inert to slag and other corrosive media except oxidants. The unique combination of these physio-chemical properties determines the extensive use of periclase of carbon as an alloying additive for various types of refractory materials. The authors in order to improve the quality of periclase powders for increasing the hydration and slag resistance carried out alloying the carbon in an atmosphere of propane-butane at 800°C with 30 minutes soaking.

L.V.Ivashchenko et. al\(^{(46)}\) studied the use of graphite from the waste product of metallurgical industry which was used in magnesia carbon refractories to study its effect on the thermal shock resistance. The positive effects were the presence of antioxidants in the composition, intensified evolution of a dense structure of the products during the process of heat treatment, and the decreased degree of the decarburisation.

L.M.Demidenko et al.\(^{(47)}\) have reported that amorphous, cryptocrystalline and crystalline graphite may be used as the carbon component in periclase carbon refractories. The highest resistance in services is shown by periclase carbon with crystalline graphite. Investigations were carried out to know the suitability of crypto-
crystalline graphite. Study on the evaluation of the trial brick was done with respect to the specific wear comparing with the wear of the brick made from foundry graphite. It indicated that crypto-crystalline graphite containing periclase carbon refractories had more wear resistance.

P.O.R.C. Brant and V.C. Cruz\(^{(48)}\) have reported that graphite shows non-wetting behaviour in contact with molten steel and slags and it is also flexible, resulting to high-density products. Its ability to react with metallic powder has rendered carbide bridges, which reinforce the refractory matrix. Its higher thermal shock resistance is one of the most important features of carbon containing refractories. Graphite has a played like morphology with the pronounced cleavage in the basal planes, accounting for its efficacy as a lubricant. The structure is planer and consists of stacks of layers in which carbon atoms are covalently linked in hexagonal array forming a large condensed aromatic structure. The carbon carbon bond in the plane is strong, as indicated by the interatomic distance of 1.42 angstrom, whereas the bonding between the planes is weak, the interplanar distance being 3.354 angstrom. The surface of the graphite flake has a very low energy, which renders its very low reactivity and the surface is not easily wetted by aqueous or organic materials, or slags. Because of the strong binding of carbon atoms in the same sheet, and of the and binding forces between successive sheets, including Van der Waals forces, the planar structure results in marked anisotropy in the properties of the graphite which is very important in the refractory
application. Among the properties, the most important ones for the refractory point of view or coefficient of thermal expansion, thermal conductivity, compressibility and rate of oxidation. Trials on Magnesia carbon bricks were carried out and special emphasis was given with the ash behaviour for systems containing metals. The impurities reduced the potential of the metal to form carbide and they introduce low melting compounds at high temperatures, resulting in low corrosion and erosion resistance as well as lower HMOR at 1400°C.

Further Masayuki Sakaguchi(49) et.al. made a study on three types of graphite viz., <1 mm, <0.15 mm and <0.03 mm and Magnesia carbon bricks were manufactured. After various tests it is concluded that the use of graphite with greater particles size increases the reduction of strength by heat treatment. In the case of graphite with large particles size, the changes in modulus of rupture by heat treatment are great probably because graphite is distorted in brick moulding and the stress is relieved by heat treatment. It is surmised that these deformed graphite particles tried to restore the original shapes, thus increasing the coefficient of thermal expansion and reducing strength. Excellent oxidation abrasion resistance and corrosion resistance in the case of using fine graphite is probably caused by low permeability, which regards the oxidation of the brick textures and chemical reactions with slag.

Yasuhiro Hoshiyama et.al. (50) studied the effect of pitch addition in the magnesia carbon bricks with fused magnesia of 99.2 % purity with
A particles size of less than 5 mm and natural crystalline graphite of 98.7% purity with the particles size of less than 1 mm. The result showed that the strength of the bricks increased with the decrease in pitch softening temperature and thermal shock resistance improved with the increase in pitch softening temperature. The lower softening temperature of pitch powder melted and dispersed into the matrix of the brick. This is found to be more effective in strengthening carbon bond in the brick.

Antioxidants are needed for manufacture of magnesia carbon bricks to resist the oxidation during application. Hironobu Toritani et al. investigated the use of metallic additives on the oxidation-reduction reaction in magnesia carbon bricks using fused magnesia. Magnesia carbon bricks with metallic additives exhibited greater weight loss in brick composition when heated to more than 1400°C in Ar gas. Metallic Al added to magnesia carbon bricks reduces MgO and volatilizes Mg at temperatures between 800°C-1300°C due to the following reaction:

$$2Al + 3CO(g) \rightarrow Al_2O_3(s) + 3C(s)$$

Si metal powder in the magnesia carbon bricks scarcely changes until the temperature reaches 1200°C. Beyond 1300°C, Si reacts with C, CO and MgO to form SiC, SiO₂, SiO, and Mg. SiC and SiO₂ remained in the brick but SiO and Mg volatilises, accelerating the weight loss.
Satoshi Sakamoto et.al.\textsuperscript{(62)} studied the improvement of MgO-C brick for steel making. The study concluded that metallic Al is effective for the improvement of oxidation resistance. The addition of 3\% to 4\% was appropriate for balanced corrosion and oxidation resistance. The use of ceramic fibre successfully prevented the loosened structure after extended use.

Akira Watanabe et.al.\textsuperscript{(53)} tried to correlate the brick properties with the complicated behaviour of metals. The behaviour of Al, Al-Mg and Ca- Si-Mg alloys added to magnesia carbon bricks were studied. When heated in Ar atmosphere, the crystal phases of Al and Si change to \( \text{Al}_4\text{C}_3 \) and SiC, while Mg and Ca have no crystal phase change but easily remained in the vapour phase. Mg volatility is less with Ca- Si-Mg alloys than with Al-Mg alloy.

A Ohte et.al.\textsuperscript{(54)} after many examinations of oxidation resistance using additives of various kinds of metals came to the conclusion that Al additive is the most effective for the improvement of oxidation resistance of magnesia carbon bricks. ZrB\textsubscript{2} additive affects an excellent improvement of oxidation resistance and maintains corrosion resistance. According to their tests and observation of the microstructures after thermal cycles(1500\(^\circ\)C to room temperature, 10 cycles), the space between the MgO grains and the matrix decreased by 30\% through the adoption of ceramic binders. Thereafter nine different types of bricks were subjected for three different types of corrosion resistance test methods. Of the methods so adopted the first one was with induction
furnace type and second with rotary type. From his authors also concluded that the rotary type of corrosion resistance was more nearer to the field test.

I.D.Kashcheev et.al.\(^{(55)}\) evaluated the effect of metallic additives (1,2, and 3% Cr, Al and Ferro silicon) on the properties of the unfired magnesia carbon refractories containing 10% graphite. The oxidation resistance of the magnesia carbon products containing Al additive is better than that of the additive-less products and the products containing Cr and Ferro silicon owing to the decreased gas permeability because of the formation of Al\(_2\)O\(_3\) and the due to the formation of Al\(_4\)C\(_3\) in the zone having the minimum degree of oxidation.

K.V.Simonov et.al.\(^{(56)}\) studied different antioxidants in use for the manufacture of magnesia carbon bricks with different antioxidants. The strongest oxidation resistance occurs with the addition of B\(_4\)C in a quantity of 3.5-6.%. This effect is related to formation of low melting B\(_2\)O\(_3\) and MgO.B\(_2\)O\(_3\), which melt and cover the graphite particles with protective films.

Yasuaki Jitsumori etal.\(^{(57)}\) tried to establish the effect of Al metal with various grain size and rate proportion for characterising magnesia carbon refractories. Specimens were made using fused magnesia clinker with purity of 98.5%. Two different kinds of grain size were used for Al mainly 1045\(\mu\)m and below 10\(\mu\)m with the same purity of 99.5%. In oxidised condition at 1000°C, Al addition less than 3% hardly shows oxidation preventing effect but a small effect appears by 5% and more.
On the other hand, at 1400°C even by 1% addition brings about a considerable effect, and increases gradually to 3%, leaving very remarkable effect by 5% and more. After firing at 1400°C, in all the specimen's with Al addition, spinel formation was observed, showing more spinel with increased Al addition. A satisfactory effect of oxidation prevention is by 5% and more of Al addition but by means of coating of Al on magnesia coarse grain, the effect is obtained by 3% of Al. Moreover, as to the grain size, the finer size is more effective.

Ichiro Tsuchiya et al. (58) studied the effect of antioxidants on the reaction between magnesia and carbon under reducing pressure has been studied by using the fused magnesia, natural graphite and fine powder of Al, B₄C, ZrB₂, MgB₂ and CaB₆. CaB₆ and MgB₂ were comparatively effective.

Zhu Dezhi and Cui Shuxian (59) studied the effect of four groups of additives, Al, Al+Ca-Si, Al+Cr and Al+B₄C on the properties and formation of MgO dense layer in magnesia carbon samples. Among the additives, the addition of B₄C obtained the best result in physical property test. High-temperature MOR and antioxidation ability of samples increased with the increase of metallic Al addition but though much metal Al addition will give reverse affect. Al, Al+Ca-Si, Al+Cr and Al+B₄C additives increase the strength and antioxidants ability of samples. With respect to the formation of MgO dense layer, metallic Al additive gives the best result, Al+Cr comes second, Al+Ca-Si comes the third and Al+B₄C is the worst.
Aloyso O. Figueiredo et al.\(^{(60)}\) attempted to evaluate magnesia carbon bricks with respect to type and amount of antioxidant, level of carbon, graphite purity and firing atmosphere. When Magnesia carbon bricks are heated up, the antioxidants react with the carbon of the bricks according to the reaction:

\[
\text{Si(s)} + \text{C(s)} \rightarrow \text{SiC(s)} \quad (1)
\]

\[
4\text{Al(s,l,vap)} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3(s) \quad (2)
\]

As oxygen diffuses into the structure of the bricks, the carbides formed by the reactions shown above are oxidised according to the reactions:

\[
\text{SiC(s)} + \frac{3}{2} \text{O}_2 \rightarrow \text{SiO}_2 + \text{CO(g)} \quad (3)
\]

\[
\text{Al}_4\text{C}_3 + \frac{9}{2} \text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{CO(g)} \quad (4)
\]

As temperature increases, the \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\) formed by the reactions above react with the \(\text{MgO}\) of the bricks in order to form \(\text{M}_2\text{S}\) and spinel, respectively, according to the reaction

\[
2\text{MgO(s)} + \text{SiO}_2(s) \rightarrow 2\text{MgO.SiO}_2(s) \quad (5)
\]

\[
\text{MgO(s)} + \text{Al}_2\text{O}_3(s) \rightarrow \text{MgO.Al}_2\text{O}_3(s) \quad (6)
\]

For the specimen fired under reducing atmosphere, higher values of strength are achieved by using higher Al level, low of carbon level and high purity graphite. This is due to the formation of \(\text{Al}_4\text{C}_3\) or \(\text{SiC}\). Under the same conditions, the formation of \(\text{Al}_4\text{C}_3\) is more intense than the formation of \(\text{SiC}\) because the kinetics of reaction number 2 is more favourable than that one of reaction number one. The higher Al content, the higher the formation of \(\text{Al}_4\text{C}_3\). So, the higher the strength of magnesia carbon bricks. For a specimen fired in the oxidising
atmosphere, the higher strength is achieved by using higher SiO₂ level, low of carbon content, no matter the graphite purity. This facilitates the formation of M₂S, which affects to a greater extent than the formation of spinel. That is why bricks containing Si presents higher strength than bricks containing Al. The lower the carbon content, the lower the porosity of the bricks after the burnout of the graphite and hence the higher the strength of magnesia carbon bricks. So, when developing magnesia carbon brick, the variables should be combined to improve a specific property. This point out the necessity to know the environment where the brick is going to be applied, and consequently, the properties that is required for the brick.

Kosuke Kurata et.al. (61) studied magnesia carbon bricks with metal Al and the glass added in order to prevent oxidation of the brick and lower the production cost. It improved the durability by 10%. The glass added to magnesia carbon brick should contain as little of SiO₂ and B₂O₃ as possible. In terms of amount to be added, Glass:Al ratio should be between 0.2-0.4. The improved brick has a better adhesion to the slag. The metal Al and the glass function as not only oxidation preventing but also sintering.

K Watanabe et.al. (62) evaluated the effect of various additives on oxidation behavior of magnesia carbon brick made out of fused magnesia. Five types of bricks with different additive such as Al, Si, B₄C and CaB₆ were studied. The test specimen were buried in coke powder and heated at 1000°C for three hours in an electric furnace. In
magnesia carbon bricks with Al & Si metal powder additives, oxidation depression effect is recognised at temperatures above 1130 and 1100°C respectively. The effect in the brick with Si metal powder is larger than that of the brick with Al. These additives densify the bricks and prevent diffusion of gas resulting in depression of oxidation. The brick with Si metal powder has larger densification effect. The bricks with Al and Si metal powder as additives have high strength at room temperature, 900°C and 1400°C. This is caused by strengthening of bond due to production of carbide and densification in the bricks. On the other hand magnesia carbon bricks with B₄C and CaB₆ additive have high strength at room temperature and 900°C, but low strength at 1400°C. The large amount of molten oxide produced at 1400°C decreases bonding force in particles, resulting in low strength.

Peter Artelt⁶³ have reported that metals such as Al, Si and Mg or mixtures and alloys of these matters react more aggressively with the oxygen in the air than graphite or the binding carbon in the magnesia carbon brick. This is the basis for the protection effect of the metal additions. Metal additions lead to the formation of carbides such as Al₄C₃, for example, which improve the mechanical properties. However, it is also known that Al added to magnesia refractories, that is, the Al₂O₃ which is produced, forms melts with the silicate impurities in the magnesia at temperatures as low as 1400°C, which has a negative impact on the lifetime when placed in service. In addition, it is better known that Al₄C₃ hydrates at low temperatures according to the reaction
AI₄C₃ + 12H₂O→ 3CH₄ + 4Al(OH)₃, which leads to significant crack formation, especially during operational shutdowns.

Michel Rigaud et al.⁶⁴ compared the roles played by B₄C and Al metal. After firing the magnesia carbon brick with 15% graphite for 5 hrs in air, at different temperatures it is clearly seen that the rate of decarburisation is determined by their initial porosity of the sample. In every case, at a given temperature, the greater the porosity, the greater the weight loss, and of course the higher the temperature, the greater the weight loss, at least up to 1400°C.

Dr. Hunold Klaus⁶⁵ experimented the resin bonded specimen of magnesia carbon with 14% carbon after by dipping in molten steel and ladle slag in order to test the protection to corrosion offered by different antioxidants. The antioxidants used were Al, B₄C, CaB₆, ZrB₂ and combinations thereof. B₄C is highly stable compound. The analysis performed after experiments showed that it was still present in the brick microstructures. However, it did react to a certain extent with the Fe₂O₃ in the slag to form a borate melt and additional carbon monoxide. B₄C thus failed significantly prevent corrosion. It is considerably more effective at preventing oxidation of carbon under at atmospheric conditions. All the CaB₆ reacted with the brick to form borate melt. No CaB₆ could be detected in the microstructures of the specimen after the experiments. ZrB₂ reacted as soon as the specimen is heated to 900°C with the formation of ZrC and B₄C. Both carbides are stable over the relevant temperature range. As a result, ZrB₂ also failed to significantly
prevent corrosion. Although the formation of magnesium vapour was not significantly affected by the boron compounds, the formation of spinel was. In addition the stability of MgO is enhanced by ZrB₂, because the amount of liquid slag drops significantly.

Dr. Hunold Klaus⁶⁶ further studied the effect of antioxidants on magnesia carbon bricks with and without boron compounds. Oxidation tests showed that oxidised layer of the refractories is less with B₄C and CaB₆ additions than Al or no additions.

R.J. Sarkkinen and J.J. Harkkō⁶⁷ have attempted to study the magnesia carbon brick under process conditions. This was done by means of more dynamics and thermodynamic relations. Under the condition of Al being antioxidants and when there is no oxygen in the system Al react with carbon in the temperature is below 1500°C and the reaction product is Al₄C₃. This reaction is a solid-liquid reaction and this reaction can also happen to the gas phase. Magnesia begins to react at 1500°C with Al, forming spinel which is also a good refractory material and the increases the density of the refractory product. Beginning at a temperature of the 1100°C Mg vapour will come from magnesia. Mg vapour ratio will increase exponentially at temperatures over 1700°C. At temperatures between 1700-1800°C magnesia and carbon react together forming Mg vapour and CO. The consequence is that refractory material disappears into the gas phase. In that case Si reacts the carbon producing SiC and above 1700°C Si anti oxidant react with magnesia to produce forsterite. At temperatures from 1700-1800°C the
reaction product is SiC and about 1800°C SiO gas. Solid carbon reacts quickly with gaseous oxygen producing gases CO, which diffuses out of the refractory material.

Shigeki Uchida and Kenji Ichikawa(68) studied the high temperature properties of magnesia carbon bricks containing Al and Si powder with the use of fused magnesia, flake graphite and phenolic resin as raw materials. Specimen with heat treatment at 500°C shrank and exhibited higher AP than untreated specimen. The bending strength and elastic modulus at 500°C were much lower than those of untreated specimen and AP increased and the mechanical properties at 500°C decreased with each repeating heat treatment. It was predicted that when the volatile matter was no longer generated, microstructures shrinkage would stop and the mechanical properties would become constant. The bending strength and static elastic modulus at 800°C, 1000°C and 1300°C were higher than those at 500°C because of the binding effect of the reaction products i.e., Al₄C₃, SiC and MgO·Al₂O₃, although the AP was higher than at 500°C. Repeated heat treatment from room temperature for the respective temperatures, however degraded the properties to nearly the same level as at 500°C because of the increased AP and the cracks generated in the magnesia particles by the reaction products.

Carmen Baudin et.al.(69) studied the mechanical behavior of magnesia carbon and magnesia carbon-Al bricks fabricated with systematic variations of Al (0-5%) and graphite (8 -15%) contents.
Porosity development caused by Al related reactions in particular to the formation of Al₄C₃ in the bulk of the specimen tested at 1200°C, MgOₐl₂O₃ spinel in the bulk and the surface regions of specimen tested at 1200°C and 1450°C, and a dense MgO zone in the surface regions of specimen tested at 1450°C. Young’s modulus decreased with increased porosity and newly formed phases in Al containing specimen generated stiffening effect for Al₄C₃ and a smaller stiffening effect for spinel formed in the bulk of the specimen were found. In this temperature range, modulus of rupture was parallel to that of Young’s modulus.

Further study by the same author evaluated the effect of Al and graphite content on magnesia carbon refractory. Comparison was done with magnesia carbon bricks prepared with sintered and electrofused magnesia with a wide range of graphite contents (~10-16.4 wt%), Al contents (0-5.2 wt%). The mechanical characterisation at high-temperature (1000°C, 1200°C & 1450°C) was done in terms of Young’s modulus and MOR in an Ar atmosphere (<1000 ppm O₂ at 1000°C). MOE values ranged from 4-16GPa, and their evaluation with temperature was determined by the evolution of microstructures in the bulk of the specimens. A strong effect of Al metal concentration on Young’s modulus overrode other micro structural differences among the materials.

Tianming Wang and Akira Yamaguchi conducted studies with fused magnesia and Al₈B₄C₇ in the magnesia carbon refractories. Al₈B₄C₇ was found to react with CO gas to form Al₇O₉(s), B₂O₃(l) and
C(s), at temperatures greater than 1100°C. The Al₂O₃ reacts with MgO in the form of MgO·Al₂O₃ spinel near the surface of the material. At the same time, B₂O₃(l) evaporates and reacts with MgO to form liquid phase at greater than 1333°C. The combined resistance of the liquid and of MgO·Al₂O₃ makes the protective layer denser, thus inhibiting oxidation of the refractory.

S Zhang and W E Lee⁷² studied the influence of additives on corrosion resistance and corroded microstructures of magnesia carbon refractories manufactured out of Australian Fused Magnesia (40 wt %), sintered magnesia (40 wt %) and Chinese graphite flake (20 wt %) and containing various antioxidants with electric arc furnace slag (with CaO: SiO₂ = 1.38:1) after 30hr at 1650°C. The study concluded with double addition of Al+B₄C, a boron-containing liquid formed which not only inhibited carbon oxidation, but also accelerated formation of MgO·Al₂O₃ crystals between graphite in the matrix. In this case even though MgO dissolution was accelerated to some extent, graphite in the matrix was effectively protected from oxidation and held in place by MgO·Al₂O₃ crystals and so was not easily eroded by slag. This addition showed the best corrosion resistance. They further studied⁷³ the thermochemistry and microstructures of magnesia carbon refractories consisting of fused magnesia, sintered magnesia and graphite flakes and containing additives such as Al, Si and B₄C. At 1200 and 1500°C, addition of Al leads to the generation of Al₄C₃, AlN, Al₂O₃ and MgO·Al₂O₃. At 1200°C, addition of Si leads to the formation of SiC,
Si$_3$N$_4$, SiO$_2$ and M$_2$S. These phases are still present at 1500°C except for Si$_3$N$_4$, which is not thermodynamically stable. Thermodynamic conclusions predicted that at 1200 and 1500°C B$_4$C reacts with N$_2$ from the atmosphere to form BN and the CO from the atmosphere to form B$_2$O$_3$ which further reacts with MgO to form low melting 3MgO.B$_2$O$_3$. M$_3$B becomes liquid >1350°C and takes up impurities from MgO and/or graphite from materials, forming more liquid, which will be detrimental for the refractory’s corrosion resistance.

J P Guha and J D Smith$^{(74)}$ studied the phase formation and their stability during firing magnesia carbon refractories with minor additions of Al metal at temperatures between 600°C and 1200°C in an atmosphere of argon. Authors have concluded that a small amount of Al metal to magnesia carbon refractories results in the formation of Al rich intermetallic Al-Mg phase at a temperature below the melting point of Al (660°C). The molten Al rich intermetallic phase, thus formed coexists with MgO upto 850°C and then dissociates into Al and Mg. At temperatures above 850°C Al reacts with C to yield Al$_4$C$_3$, whereas Mg-vapour moved towards the cold surface of the refractory where it re-oxidises to MgO. With increase in temperatures, an interaction between Al$_4$C$_3$ and MgO leads to the formation of spinel MgO.Al$_2$O$_3$.

Li Lin et al.$^{(75)}$ studied the in-situ formation of ZrB$_2$ in magnesia carbon bricks at lower temperature. Results reveal that 66.67% reactant had changed into ZrB$_2$ and the method of in-situ synthesis of ZrB$_2$
formed as antioxidant in carbon containing materials was one of the economy way.

Magnesia carbon bricks made out of fused magnesia have been used in various furnaces such as Electric Arc furnace, Converter, ladles etc. Study has been done worldwide to evaluate the properties of bricks vis-à-vis its application. Hiroshi Kyoden et.al.\(^{(78)}\) have reported that magnesia carbon bricks have been used extensively in the tuyere region of combined blowing converters because of their high spalling resistance. From different test results with different qualities magnesia carbon bricks with the carbon content of around 15-20% were found suitable for this application.

J.Karja\(^{(77)}\) studied four types of used magnesia carbon bricks in the three 80 ton converters. Comparing wear rates and laboratory tests it was concluded that one of the bricks which had the lowest wear rate, had the highest carbon content and the highest amount of fused MgO.

Izumi Ohishi et.al.\(^{(78)}\) have reported that magnesia carbon bricks with fused magnesia and higher purity graphite resist the vigorous conditions of steel making such as high temperature, longer duration and more vigorous stirring.

Tatsuo Matsumura et.al.\(^{(79)}\) have studied the use of magnesia carbon bricks in RH vessels. In RH vessels, direct bonded magnesia chromite bricks are widely used which have satisfactory durability. But
in RH due to vessels large internal temperature changes, the contribution to wear rate by thermal shock is large. So magnesia carbon bricks have been reported recently as a substitute for magnesia chromite bricks. The substitution has not been able to completely eliminate magnesia chromite bricks because the life of vessels is not stable for the reason that oxidation of cold phase carbon takes place.

Yukio Kiryu et.al.\(^{(80)}\) have reported that RH degassers use direct bonded brick but corrosion of the direct bonded brick magnesia chromite increased due to CaO-CaF\(_2\) system flux blown in by the RH injection method. The use of magnesia carbon brick has been developed for the operation to prevent that of penetration of impurities into the brick. To utilise the excellent properties of magnesia carbon brick such as spalling resistance, wear resistance and self absorption ability for stress it was used in RH degassers. This resulted in no structural crack or preceding wear out of joint and an improvement in wearing rate of about 60-70% over the magnesia chromite direct bonded brick.

Dr. Hisakazu Kawashima et.al.\(^{(81)}\) have mentioned that magnesia carbon brick has excellent hot strength and thermal spalling resistance and this is the reason why it has substituted MgO dolomite bricks. The success of the combine blowing processes for B. O. F owe much to the development of magnesia carbon bricks. Expansion absorption is not necessary brick MgO dolomite bricks lining because MgO dolomite bricks have the ability to absorb expansion through creep deformation over 1000°C. However, the creep deformation of magnesia
carbon brick is very low. Induced stress is maximum near the hot face, causing spalling damage in some cases. To decrease the stress caused by the thermal expansion of magnesia carbon brick, setting for expansion absorption is necessary.

Kenji Ichikawa et.al. (82) have mentioned that Electric arc furnaces with bottom tapping system, bottom bubbling process, direct current arc furnace are the new developments. Therefore, new types of refractories have been developed which optimise the performance of these new technologies. The factors which causes the wear of refractories for bottom bubbling are corrosion by slag, thermal spalling caused by temperature change during melting and scrap charging. Magnesia carbon bricks for such application needs the use of fused magnesia clinker because the corrosion resistance of magnesia carbon bricks made out of only seawater magnesia was not sufficient as excellent wear rate below 1 mm per heat is expected with the magnesia carbon brick with fused magnesia to which the special antioxidants was added.

Paul E. Scheerer and James W.Stendera (83) have reported that since 1980 BOF campaign life has tripled in the US and Canada. The trend in the use of magnesia grains in brick show the increase in the use of large crystal periclase grain, use of grain with lower and lower impurity contents like SiO₂, CaO, Fe₂O₃ and B₂O₃ and increase in use of fused magnesia. These developments in brick composition have led to
refractories with greater resistance to slag penetration, greater resistance to carbon oxidation and greater resistance to corrosion.

Shigeyuki Nabeshima et al. (84) have reported that improvements done in the top & bottom blowing converter (K-BOP) is addition of fused MgO and coarse grain fused MgO in the brick in order to improve durability. The use of fused MgO grains was for improving corrosion resistance and use of coarse grain fused MgO as a means of improving slag coating performance. It was found that in sintered magnesia, MgO grain separates at the grain boundaries and elute into the slag but with fused grains, elution into the slag occurs gradually from the brick surface. Authors believed that adding coarse grain fused MgO (10-15) mm brick would cause MgO grains to project out from the workings surface of the brick during use, and that this would firmly fix the slag coating over the workings surface of the brick.

P.O.R.C Brant et al. (85) summarised the success in the use of magnesia carbon refractories in BOF and concluded that the balance of properties for the each area has been achieved by optimum combination of sintered and/or fused magnesia associated with flake graphite, metals and additives and the binder source can be phenolic source or pitch. Study was conducted with sintered and/or fused magnesia, 4 different types of graphite, two different combinations of metals and with the boron compound addition. The outcome of the study is the presence of fused magnesia accelerates the corrosion resistance and oxidation resistance mainly due to the large crystal size. The
sintered magnesia, after EPMA results, is severely corroded by slag while the fused magnesia shows a little penetration of iron oxide in the periclase grain boundary.

Ritsu Ebizawa(86) studied the use of magnesia carbon in Combined Blowing Converter and found that there has been a wide change in the use of refractories in combined blowing converter. Slag resistance of MgO raw material is sensitively affected by impurities such as B₂O₃. Therefore it is desirable to use dense MgO clinker and to use MgO made from large size of periclase crystal as the raw material for magnesia carbon brick. Nowadays fused MgO is widely used as a raw material for magnesia carbon brick.

Shigeyuki Takanaga(87) have reported that the Oxygen Top Blown Converter process was introduced in Japan in 1957 and rapidly developed as the main steel making process. Now, almost all BOF are lined by magnesia carbon bricks. Magnesia carbon bricks compensated for the effect of the traditional basic bricks and increased corrosion resistance. The use of clinker comprising large size periclase is effective for corrosion resistance of magnesia carbon bricks. In the case of using small size periclase, clinker is easily dissociated due to slag penetration into much of the periclase boundary. It is found from the reports that the corrosion resistance of magnesia carbon bricks is highly increased by improving the characteristics of magnesia clinker.

N Sahoo et.al.(88) studied the nature of the destructive forces acting on the refractory lining at different places of LD converter. Rotary drum
erosion test has been developed from which corrosion, abrasion and oxidation properties of magnesia carbon bricks are studied. This test also gives textural properties of magnesia carbon bricks. The result obtained from this is correlated with service performance in a the converter.

Hideaki Nishio et.al. attempted to study the protection effect of Al, which is a the protective metal additive in magnesia carbon bricks for BOF has been studied based on the analysis of used magnesia carbon bricks and the results are

- almost all of the Al had changed to spinel at the hot face and the reaction was almost finished in magnesia carbon bricks used in actual furnace
- from the oxidation experiment modelled the hot face, it was confirmed that Al is effective against gas phase oxidation which forms the decarbonised layer
- the increment in oxygen consumption by the 3% Al addition was found to be from 2%-6%, so this was not the main factor for the phenomenon of oxidation protection observed in this experiment
- gas diffusion coefficient in the decarbonised layer decreases with the addition of Al. Therefore, the major cause of the oxidation protection effect is considered to be a decrease in the penetration rate of oxygen caused by densification of the decarbonised layer.
- Oxidation protection by adding Al is effective mainly under the conditions that the decarbonised layer is formed by gas phase oxidation.

Potschke Jurgen et.al.\textsuperscript{(90)} mentioned that carbon pickup of ULC steel by the magnesia carbon bricks in BOF and ladle has to be fixed as low as possible. This investigation explains the interaction of different brick qualities and steel melts with each other. Oxygen potential of the steel melts is decisive for carbon pickup from the refractory material: if the oxygen potential is high, a CO gas pad is built which separates the reaction partners and cuts short the carbon pickup of the melt. Parallel to this a highly oxygen potential leads to formation of the dense MgO layer prevents, in addition, further infiltration. If the melt is highly deoxidised or the refractory material contains for example metallic Al as antioxidant, only less or no carbon monoxide at all emerges, the steel melt infiltrates the brick and dissolves carbon. In practice metallic Al is converted into Al\textsubscript{4}C\textsubscript{3} during preheating. Al\textsubscript{4}C\textsubscript{3} builds the CO gas pad too, so that a preservation against decarburisation is maintained. The spinel which is formed inside the brick might close the pores to a certain degree and prevents infiltration.

Takahiro Azuma et.al.\textsuperscript{(91)} made a study on the low carbon MgO-C brick with high thermal spalling resistance for tap hole sleeves. Study revealed that unburnt low carbon MgO-C bricks is excellent due to the large amount of micropores with a diameter of approximately 10
micrometer or less contained in the brick than the conventional MgO-C brick. This showed excellent corrosion and oxidation resistance.

N Sahoo et.al.\textsuperscript{(92)} have studied the replacement of magnesia chrome refractory bricks by magnesia carbon bricks in VOD ladles due to environmental pollution of hexavalent chromium compounds. Therefore, for VOD ladle special quality magnesia carbon refractory has been developed having 5-6\% graphite and special fused magnesite. The quality of magnesia carbon brick and its application in the slag zone of VOD ladle replaced magnesia chrome bricks and the campaign life becomes double and without facing any difficulty in producing low and extra low carbon stainless steel by using magnesia carbon bricks. This is quite in agreement with the laboratory wear index found in Induction furnace erosion test where the magnesia chrome bricks has double wear index than developed magnesia carbon bricks.

Masahiko Amano et.al.\textsuperscript{(93)} have reported that for LD-optimising refining process, the investigations were carried out on the effect of refractory and subsequent improvement needed was successfully accomplished based on the consideration of corrosion resistance and abrasion resistance under oxidation conditions as the main deterioration mechanisms. As for corrosion resistance, magnesia carbon brick is the best and significant improvement is possible by using purified magnesia aggregates and flakes graphite. As for the abrasion resistance under oxidation conditions, immediate improvement resulted from the addition of SiC and spinel, and the combined addition of both materials also
resulted in improved corrosion resistance. In actual furnace life, the performance was better for materials with improved abrasion resistance under oxidation conditions and as for the combined addition of SiC and spinel, the furnace life was about three times longer than the conventional magnesia carbon brick.

Gerald Buchebner and Hans-Jorg Junger\(^{94}\) summarized the change in process technology in BOF. Trials with slag splashing in BOF and introduction of slag gate closure system for BOF have been carried out. Special pitch bonded bricks are very successful in high wear area. There is dense matrix with a low porosity and permeability, the lower level of impurities and as a result a very redox resistance and excellent resistance against FeO rich slag. For magnesia carbon bricks with resin bonded, by using high purity fused magnesia, flake graphite with high purity in combination with dual metallic system the maximum corrosion resistance and hot strength can be achieved. The tendency of resin bonded bricks, especially those with addition of antioxidants, the spalling could be minimised by the addition of powder pitch.

Hiroaki Ishii et.al.\(^{95}\) has reported that for vacuum vessel in RH degassing units, magnesia carbon brick for working lining of RH lower vacuum vessel has been developed with fused magnesia. To secure oxidation resistance, carbon content is lowered to 3% along with metallic Si addition. To compensate the possible deterioration of thermal spalling resistance, in addition, graphite with large specific surface area is applied. The campaign of magnesia carbon re-lined...
vacuum vessel presented a quite satisfactory performance, 15% decrease of wear rate in comparison with conventional magnesia chromite brick.

Study is also made by S Parada et. al (96) on the use of magnesia carbon bricks in Vacuum-Oxygen Decarburisation (VOD). Best results with magnesia carbon bricks are obtained with large, fused magnesia grains. Although slag exposure is limited in the bottom parts of the ladle, dual CaO/MgO saturated slags should be targeted due to their low aggressivity towards the periclase phase and good desulphurising properties.

One more study by Steven Smets (97) et.al. reported that direct bonded magnesia chromite bricks are being used for VOD ladle. Various formulations for magnesia carbon bricks were made and studied. The study concluded that fused grains are preferable as the limit extent of the magnesia carbon reaction by restricting the surface area of contact. They also have a higher purity than sintered grain and hence show better corrosion resistance.

Tap hole sleeve is one of the major better to improve productivity of a converter. Magnesia carbon bricks with fused magnesia and 6% carbon content, 3% of metallic Al and 1% of metallic Si were manufactured and evaluated by K Koide et.al. (98). Strength of the magnesia carbon at different temperatures in reducing atmosphere was studied. The three different formulations had different grain size of metallic Al, which was large, small and fine. The formulations having
fine metallic Al showed highest strength for compressive strength and modulus of rupture at 800°C than the other formations. Also the abrasion resistance was maximum at 800°C for finer Al formulation. This is attributed to the formation of α-SiC and not the spinel, which is established by XRD. This is possible because the sample with finer metallic Al has broader surface area, which lowers the partial pressure of oxygen in the refractory thus paving the way for Si to be carbonized.

Atsushi Torigoe et al. (99) reported that magnesia carbon bricks have high thermal conductivity and hence decrease the insulating efficiency of the furnace. Study has been made to find the relationship between texture and thermal conductivity of the magnesia carbon bricks. Various formations were made with carbon 15% and fused magnesia. The magnesia carbon samples with several pore distribution was made by changing the mixing, pressing method, graphite grain size, and using different binders. The thermal conductivity and the pore size distribution of each of the sample was estimated out. The findings show that thermal conductivity changes when the brick has different pore size distribution even if the brick has the same properties and the carbon content. Further the pore size distribution and thermal conductivity show a definite correlation, especially, thermal conductivity diminished drastically with the increase in fine pore volume. The low thermal conductivity products applied in actual furnace, which had durability equal to the conventional products, and heat loss was reduced.
Eiichiro Hatae et al. (100) studies the spalling resistance of unburnt magnesia carbon and burnt pitch impregnated magnesia carbon bricks. For the study fused magnesia clinker with 98% purity and maximum particle size 5 mm, natural flakes graphite with approximately 98% and thin graphite with approximately 97% was used. Addition of thin graphite also improved the spalling resistance of burned and pitch impregnated bricks same as unburnt brick. Pitch impregnation after burning reduced mainly the volume of large size pore which is larger than $75\mu\text{m}$ radius and that of fine pore which is smaller than $0.1\mu\text{m}$.

From the above literature survey it is evident that fused magnesia is the ideal magnesia component of magnesia carbon bricks. There is still further scope to study on selection and combination of fused magnesia for manufacture of magnesia carbon bricks having balanced properties in oxidation, corrosion and thermal shock resistance.
1.3 AIM AND SCOPE OF WORK

Magnesia is the major constituent of magnesia carbon bricks. It constitutes 80-90% of the total ingredients of the bricks. Fused magnesia has higher corrosion and erosion resistance than sintered magnesia, therefore fused magnesia is predominantly used for manufacture of magnesia carbon bricks. Fused magnesia is produced in Australia, Brazil, Canada, China, Israel, North Korea, Russia, South Africa, South Korea and USA. China produces the highest quantity about 260000Mt of fused magnesia and dominates the world market. China is endowed with extensive deposits of high quality magnesite. Fused magnesia is produced by electrically fusing the natural raw or calcined magnesites. Chinese fused magnesia is comparatively cheaper than the fused magnesia available in other parts of the world. Therefore refractory manufacturers in India and abroad use Chinese fused magnesia for making magnesia carbon bricks.

A wide range of fused magnesia having different physical, chemical, thermal and mineralogical properties is produced in China. The magnesium oxide content of fused magnesia varies from 96-99% and periclase crystal size from 150-1000μm and sometimes to single crystal. The price of fused magnesia increases with the increase of magnesium oxide content and periclase crystal size. Fused magnesia having about 97% MgO is used for making cost effective magnesia carbon bricks.
The literature survey reveals that the properties of magnesia-carbon bricks is dependent on the properties of the fused magnesia used. The thermal, mechanical and corrosion properties of fused magnesia vary with variation of their chemical composition and mineralogical properties. Because of this reason it is difficult to achieve balanced physical, chemical, mechanical and mineralogical properties of magnesia carbon brick by using only one fused magnesia.

Considering the above it is felt necessary to carry out research work by using two fused magnesia having different chemical, physical and mineralogical properties for manufacture of magnesia carbon bricks so that the bricks will have balanced chemical, thermal, mechanical and mineralogical properties. For this purpose different compositions of magnesia carbon are formulated by using the two-fused magnesia keeping other constituents like graphite, binder and antioxidant unaltered. The physical, chemical, thermal, thermo-mechanical, corrosion and mineralogical properties are evaluated and attempt is made to correlate these properties with the properties of the two fused magnesia used in different formulation.

This research work will be helpful to refractory manufacturers for manufacture of cost effective magnesia-carbon bricks.