

# **Chapter-3**

*(Studies on low carbon containing  $Al_2O_3$ -C refractory)*

### Studies on low carbon containing $\text{Al}_2\text{O}_3$ -C refractory

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#### 3.1 Motivation

Use of carbon mainly imparts advantages like non-wetting nature resulting in improved corrosion resistance; high thermal conductivity, low thermal expansion, low elastic modulus and thus results in a superior thermal shock resistance. These advantages initially attracted the refractory manufacturers to use more amount of carbon in the composition.

However, with time progress in knowledge and technological improvement has made it clear that higher carbon content in the brick imparts several drawbacks too:

- I. Carbon has the inherent disadvantage of oxidation during use in the steelmaking process, associated with oxygen lancing, at high temperatures. Oxidized refractory has a highly porous structure with nearly no bonding and strength. It is easily penetrated and corroded by slags. Use of antioxidants restricts and delays the oxidation of carbon, but it cannot be stopped entirely.
- II. Higher energy loss due to increased thermal conductivity of refractory, causing higher energy consumption per unit of steel produced.
- III. Poor wettability with binders, leading to dispersion, and higher resin demand problems.

- IV. The big density difference between graphite and refractory raw materials, resulting in segregation.
- V. Lack of bonding between graphite and refractory oxides, engendering strength problem.
- VI. Increase in shell temperature leading to damage and deformation of the shell/metallurgical vessel.
- VII. Chances of carbon pick-up from refractory become high, whereas steelmaking is a decarburization process and user industries are very stringent about the purity of steel.
- VIII. Releases more amount of the carbon dioxide or carbon monoxide gasses to the atmosphere.

Refractories with reduced carbon content without compromising with the beneficial properties is a challenge to the refractory technologists. Many researchers have demonstrated that nano carbon cannot replace graphite completely in MgO-C compositions as it has inferior oxidation resistance and thermal conductivity compared with graphite flakes.

Hence it is the demand of the day to produce refractories with reduced carbon content to avoid all such drawbacks of the conventional carbon-containing refractories. Research have already been started to develop a new kind of MgO-C refractory with low carbon content [Bag et al., 2012]. However, this may lead to a decline in corrosion and thermal shock resistances of the refractory. Some researchers [Bag et al., 2012; Bernard, BA, 2003] have obtained MgO-C compositions with excellent properties by adding nanometer-sized particles, as additives or carbon which play a role by filling up the interior pores and gaps

between the various particles. 1.5% nano carbon containing MgO-C refractories showed [Braulio, MAL, et al., 2011] thermal spalling resistance equivalent to that of conventional refractories containing 18% graphite. Some other studies [Xianhui L, et al., 2005; Xuejun, Y, et al., 2003] on the use of nanocarbon in MgO-C refractories showed improved spalling resistance as nano carbon suppresses the sintering of MgO and gradual improvement in mechanical properties with the increasing amount of nanocarbon. MgO-C bricks produced [Takanaga, S, et al., 2005] by applying a nanostructured matrix with less than 5% of carbon and found that thermal shock resistance and oxidation resistance of developed brick was remarkably superior rather than the conventional one whereas corrosion resistance was almost on a level. Nano-tech magnesia carbon bricks, utilizing the nano compound graphitized black (hybrid graphite black; HGB) having outstanding features like high thermal shock resistance, corrosion resistance, oxidation resistance were reported [Matsui, T, et. al., 2005] to provide excellent durability in RH degassers. The addition of nano-sized carbon black and hybrid graphite black in MgO-C brick resulted [Fujiwara, Y, et. al., 2004] improved spalling resistance due to the formation of a nanostructured matrix and excellent high-temperature oxidation resistance. MgO-C bricks containing both nano-sized carbon black and flake graphite were found [Hatta, M, et. al., 2004] to reduce the total carbon content with a reduction in heat loss and thermal stress on the steel shell. This addition also [Liu, B, et. al., 2010] improves the crushing and bending strengths before and after coking, oxidation resistance and thermal shock resistance of the low-carbon MgO-C composites.

Given these problems the strategy in this work is dictated to study the effect of increasing amount of NCB on the properties of Al<sub>2</sub>O<sub>3</sub>-C refractory keeping total carbon content below half of that of the conventional carbon-containing refractories. Compositions are also compared with the conventional Al<sub>2</sub>O<sub>3</sub>-C refractory composition (without NCB) processed under similar conditions.

### 3.2 Formulation

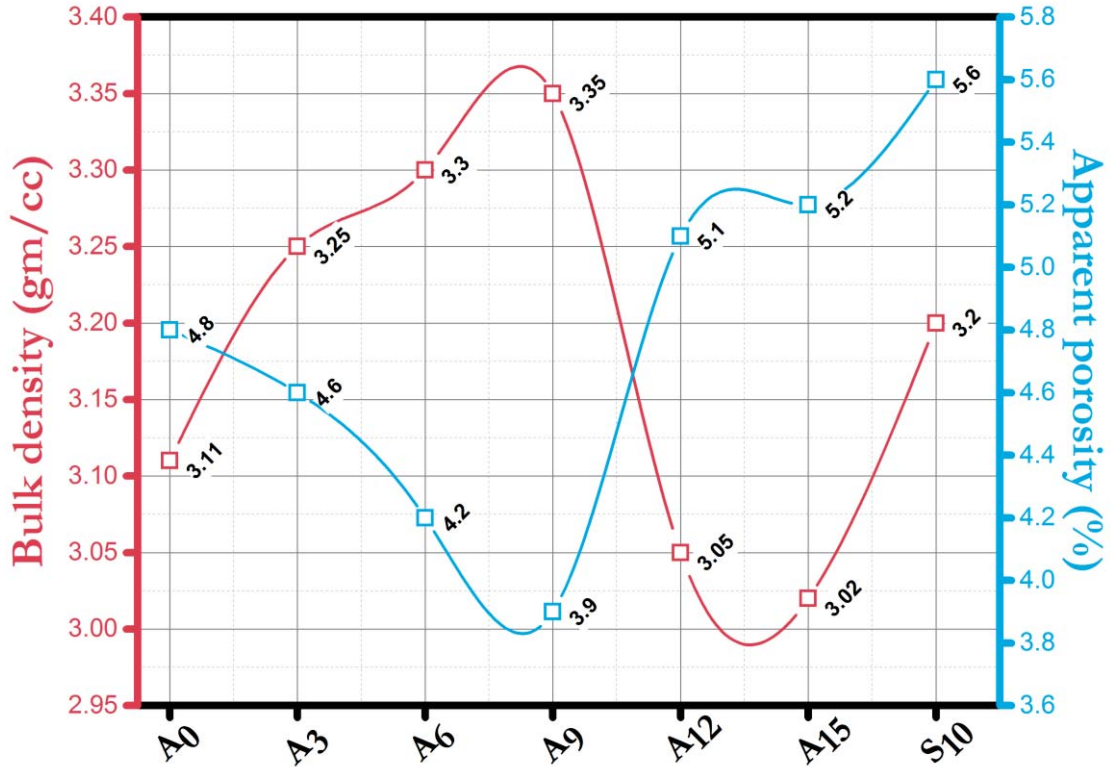
Raw Materials	A <sub>0</sub>	A <sub>3</sub>	A <sub>6</sub>	A <sub>9</sub>	A <sub>12</sub>	A <sub>15</sub>	S <sub>10</sub>
<b>T60 (0-3mm)</b>	96	95.7	95.4	95.1	94.8	94.5	89
<b>FC97</b>	3	3	3	3	3	3	10
<b>N220</b>	0	0.3	0.6	0.9	1.2	1.5	0
<b>Resol type Liq. Resin</b>	+3.50	+3.50	+3.50	+3.50	+3.50	+3.50	+3.50
<b>Powder Resin</b>	+0.50	+0.50	+0.50	+0.50	+0.50	+0.50	+0.50
<b>Al-Metal Powder</b>	0.50	0.50	0.50	0.50	0.50	0.50	0.50
<b>B<sub>4</sub>C powder</b>	0.50	0.50	0.50	0.50	0.50	0.50	0.50

**Table 3.1** Variation of nano carbon black and a standard conventional Al<sub>2</sub>O<sub>3</sub>-C product

### 3.3 Results and Discussion

The change in AP and BD with the increase in nano carbon content is shown in Fig. 3.1. Increasing nano carbon content up to 0.9 wt% reduces the AP value

due to increased filling of the inter-particle spaces of the refractory by much finer nanoparticles.



**Fig 3.1** BD-AP as a function of NCB addition

Increasing NCB content up to 0.9 wt% reduces the AP value of nano carbon due to increased filling of the inter-particle spaces of the refractory by much finer nanoparticles. Nanoparticles can disperse evenly in a better way among the tiny spaces between coarse, medium and fine alumina particles thereby filling of interior pores and gaps. However, its further increase is deleterious as the value of AP is even greater compared to the batch without nano carbon (A<sub>0</sub>). An excess amount of nanoparticles does not enter into the inter-particle voids and remains as free thereby increasing AP.

Similarly, the increased bulk volume due to the excess amount of fine particles present reduces BD values in A<sub>12-15</sub>. The BD without the nano carbon is 3.11 g/cm<sup>3</sup>, which increases with the increase in nano carbon content for better pore filling and reaches a value of 3.35 g/cm<sup>3</sup> for 0.9% nano carbon. Further increase in the nano carbon content does not result in the further filling of the pore volume, but the bulk volume has grown due to the excess amount of fine particles present, thereby reducing the BD values.

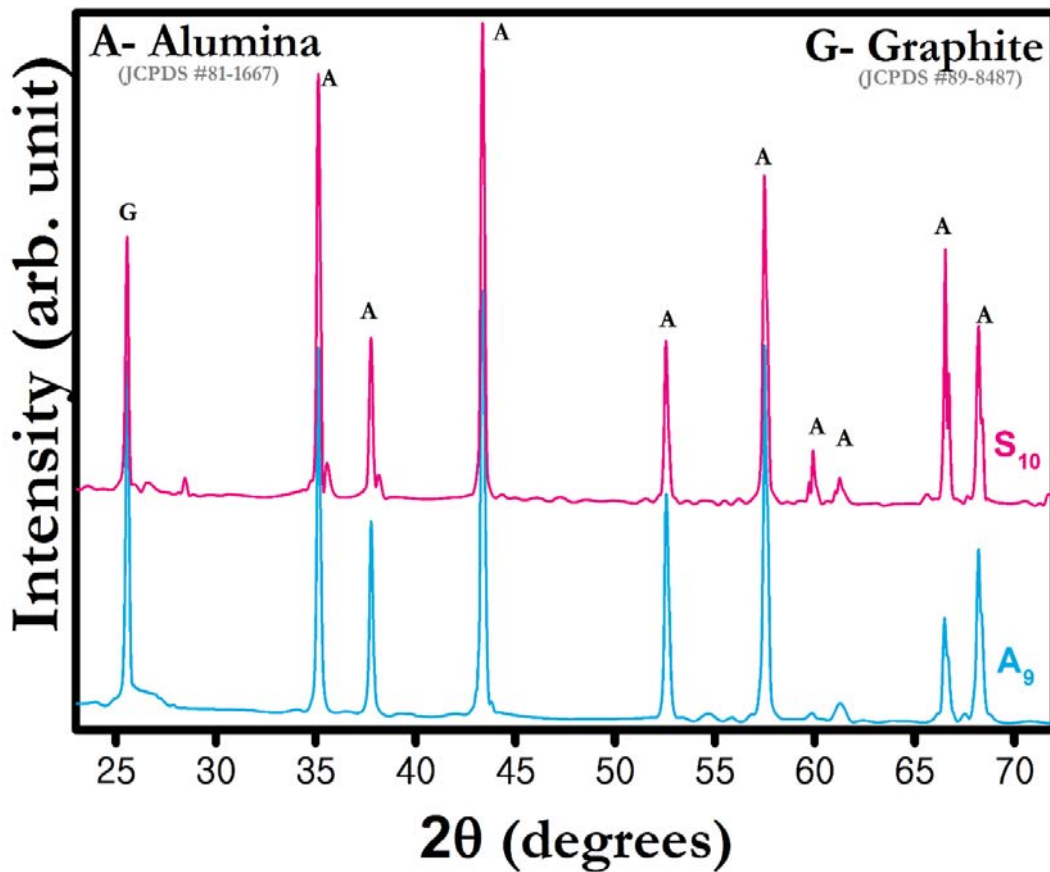


Fig 3.2 XRD patterns of A<sub>9</sub> and S<sub>10</sub>

Added NCB decreases the sinterability of alumina particles, which is evident by the reduced relative diffraction counts as compared to the standard sample. It reduces ceramic brittleness and is expected to increase the modulus of

elasticity of the structure. NCB being non-graphitic does not contribute to its intensity values.

The variation of CCS of the batches with the change in nano carbon content is shown in Fig. 3.3. A calculated 7% increment in the crushing strength is observed as compared to S<sub>10</sub>. A further increase in nano carbon content resulted in nearly the similar CCS values. This may be explained as pore filling is achieved nearly the optimum for 0.9% nano carbon and a further increase in nano carbon do not affect the filling and also the strength behavior.

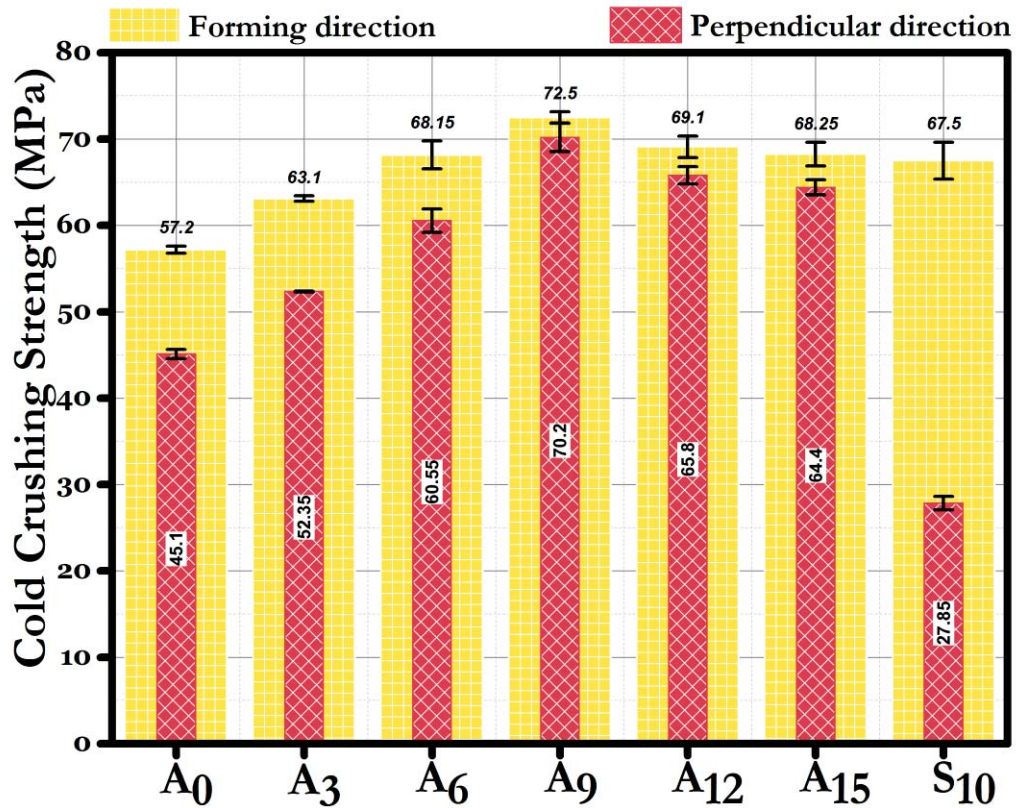


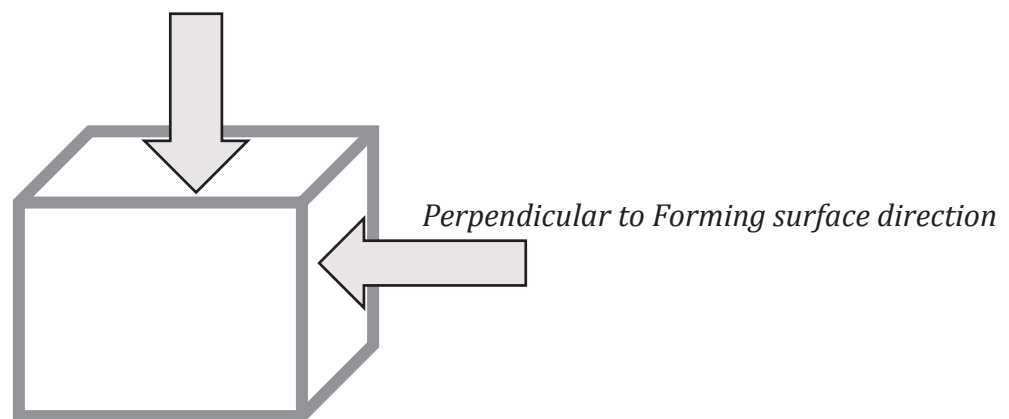
Fig 3.3 CCS of samples coked at 1400°C

The inherent anisotropy of flake graphite has significant effects on physical properties of the briquettes. During applications, the anisotropy and plastic



properties strongly intervene on the behavior of the material. In certain cases, under the influence of complex mechanical loading, the development of this anisotropy can lead locally to a critical stress state that can provoke a localized formation of micro-bands, local thinning or micro-cracks. Industrial applications always undergo various external loadings during fabrication and under service conditions. When they possess a heterogeneous microstructure, the usual mechanical properties do not allow appreciating the cracking risks and the rupture often occur throughout manufacture and service. In the plastic deformation studies, the microstructure is a basic factor deciding about the materials mechanical behavior. The microstructural homogeneities have to affect evidently the agreement achieved between predictions based on homogeneous deformations and the experimental observations. Strain and stress localization may conduct to a strong local reduction of the ductility then lead to material's rupture.

*Forming surface direction*



**Fig 3.4** Schematics of a brick sample

The plastic deformation of a crystalline material is essentially controlled by a nucleation/movement phenomenon of microstructural defects, particularly dislocations. When plastic deformation starts, the density of dislocations increases strongly inside the grains. The distribution of these dislocations rapidly becomes heterogeneous. One observes that gathering of dislocations increase and forms dislocation cell structure, often along privileged directions. During the deformation, there is accuracy in these walls, and the density of dislocations increases inside them with a formation of the cellular substructure. The cell size decreases when the deformation ratio increases. The disorientation between the cells increases too. The plastic anisotropy is in a strong relationship with the structural anisotropy.

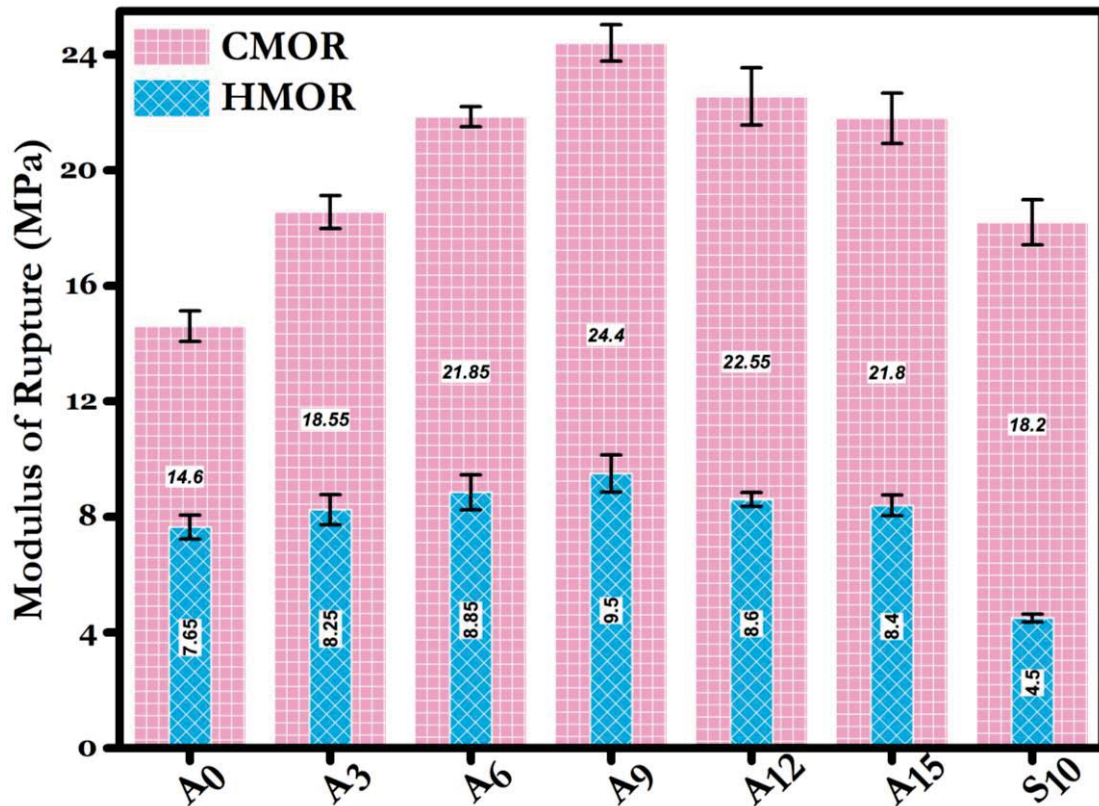
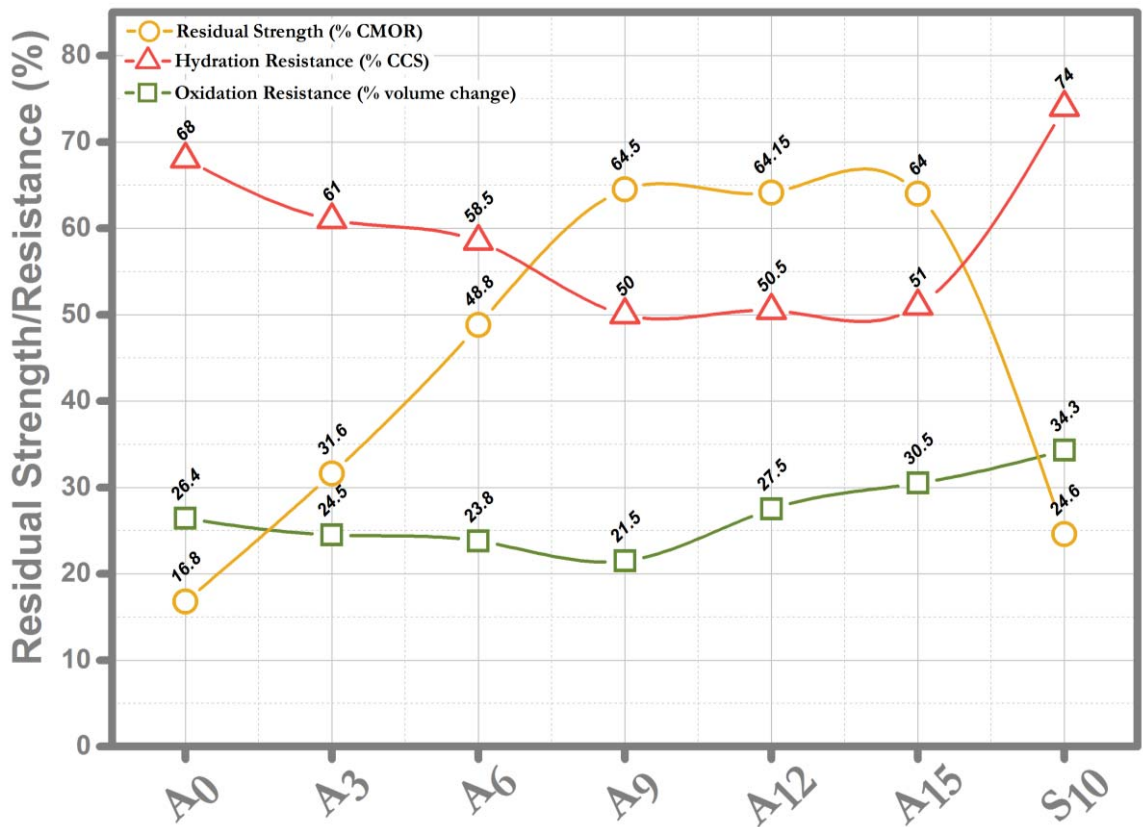


Fig 3.5 MOR of samples coked at 1400°C

The crushing strengths of standard sample S<sub>10</sub> evaluated from the Forming surface direction were about two and half times greater than that of the Pressing surface direction. Flake graphite in the forming direction must have been distributed without rules and quite a number of them become would have deformed, but in pressing direction most of them would have been layered distributed, perhaps this also help to explain why CCS is higher in forming direction. The use of zero-dimensional nano carbon black instead of anisotropic graphite helps overcome this problem.



**Fig 3.6** Residual strengths of the samples

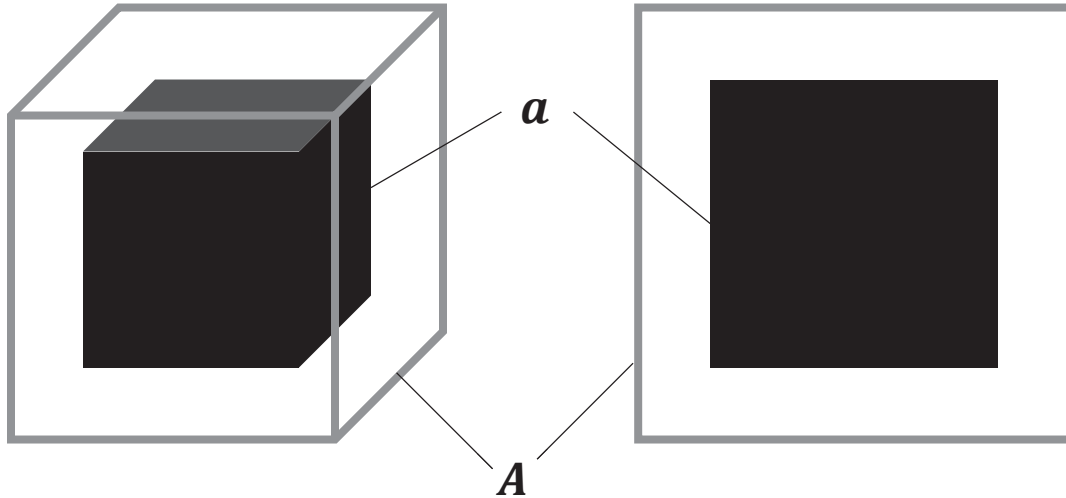
The Fig. 3.5 depicts that with the increase of NCB content a better filling as well as a better compaction has occurred, resulting in a better strength. NCB being

very reactive as a carbon source, forms carbide on reaction with aluminum additives at a higher rate, particularly in the high temperatures. Carbide formation results in better bonding and increased strength. The increasing amount of nano carbon enhances the extent of carbide formation and accordingly the strength too. These carbides have better oxidation resistance than free carbon, and it coats the surfaces of the carbon particles, carbide formation increases the oxidation resistance. Above 0.9% nano carbon no further betterment is achieved due to the growing oxidation of nano carbon when present at higher percentages, producing a porous structure and nullifying the beneficial effect for the greater extent of carbide formation.

The strength retention after a spalling test is dependent on the thermal conductivity of the briquettes. Nanomaterials not only absorb and relieve the stress due to thermal expansion and shrinkage of refractory particles but also reduce mal-distribution of thermal stress in the interior portion of refractories thus improving thermal shock resistance of A<sub>9-15</sub>. They also have maximum carbide formation, and Al<sub>4</sub>C<sub>3</sub> is unstable and prone to hydration at room temperature which leads to their self-destruction.

To quantify oxidation, the volume of the oxidized portion, normalized by the total open surface area (through which oxygen enters) of the refractory block was taken. The schematic portrays both the cross-sectional and isometric views of a partially oxidized refractory block. If 'A' is the length of each side of the cubic refractory block, and 'a' is the length of the un-oxidized cubic core, the oxidation diffusion depth (d, which is the volume oxidized normalized with the area of oxidation) can be calculated as follows:

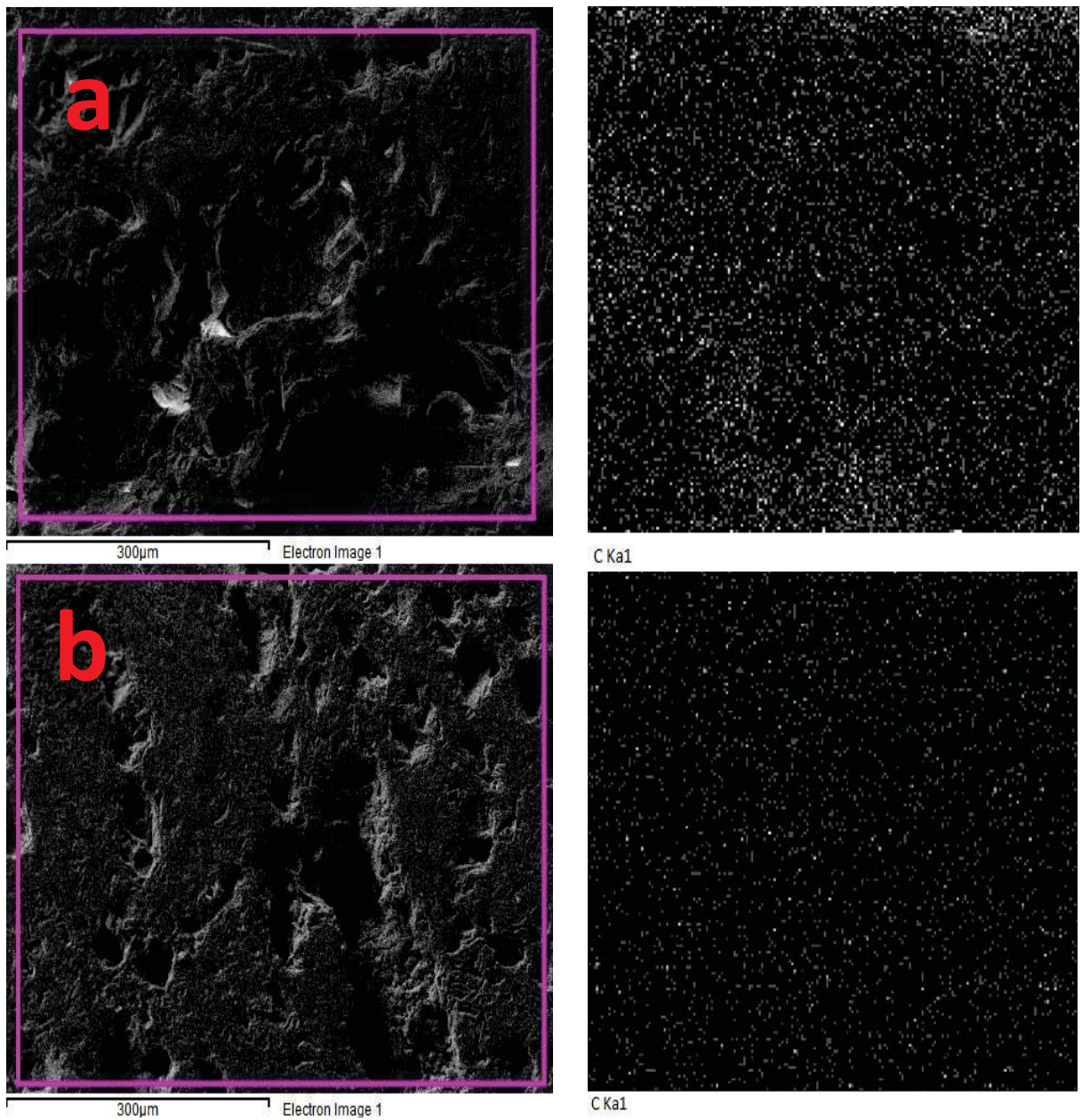
$$d = \frac{A^3 - a^3}{6A^2} \quad (3.1)$$



**Fig 3.7** Schematic of the specimen geometry for oxidation resistance calculation

Carbides have better oxidation resistance than free carbon, and it coats the surfaces of the carbon particles. Hence, carbide formation increases the oxidation resistance. However, above 0.9% NCB, the oxidation increases, as no further carbide formation occurs (due to fixed amount of metal additive) or a higher oxidation for a higher amount of nano carbon occurs, as similar in the case of HMOR.





**Fig 3.8** Distribution of carbon by elemental mapping, (a) A<sub>9</sub>, (b) S<sub>10</sub>

Distribution of carbon was checked by elemental carbon mapping for different compositions as shown in Fig 3.8. The S<sub>10</sub> samples have a relatively less uniform distribution of carbon particles in the matrix is envisaged even though

total carbon content is much higher. The large surface area of NCB helps to achieve a much better dispersion in A<sub>9</sub> sample.

### 3.4 Summary of Results

Low carbon containing Al<sub>2</sub>O<sub>3</sub>-C with total carbon less than half of the conventional refractories were fabricated with nano carbon black.

	<b>S<sub>10</sub></b>	<b>A<sub>9</sub></b>
<b>AP (%)</b>	5.6	3.97
<b>BD (gm/cc)</b>	3.20	3.35
<b>CCS [FD/PD] (MPa)</b>	67.5/27.85	72.5/70.2
<b>MOR [C/H] (MPa)</b>	18.2/4.5	24.4/9.5
<b>Spalling res (%)</b>	24.6	64.5
<b>Oxidation res (%)</b>	34.3	21.5
<b>Hydration res (%)</b>	74	50

**Table 3.2** Properties comparison table

Nano carbon being very fine and very reactive imparts the beneficial characteristics of carbon to a great extent even at a very low amount. This may also be associated with the occurrence of microcracks between the nano carbon black particles and matrix, and these micro cracks absorb energy, which results in obvious improvement of mechanical properties for nano carbon containing compositions.

Accordingly, the physicochemical and thermo-mechanical properties were improved significantly for an optimized quantity of 0.9 wt% NCB.