

Chapter-5

(Influence of a combination of oxidation inhibitors in Al_2O_3 -SiC-C)

Influence of a combination of oxidation inhibitors in Al₂O₃-SiC-C

5.1 Motivation

Carbon, in Al₂O₃-C refractories, is oxidized in two ways: direct oxidation and indirect oxidation. Direct oxidation occurs at 1400 °C when carbon is oxidized directly by the oxygen from the atmosphere. **(Eq. 5.1)** Indirect oxidation occurs above 1400 °C, where the oxygen from Al₂O₃ oxidizes carbon **(Eq. 5.2)** or slag reaction **(Eq. 5.3)**. The resulting Al gas oxidizes again and generates Al₂O₃ **(Eq. 5.4)** which is called the secondary oxide phase or the dense layer. It is claimed that the secondary oxide phase protects the brick against oxidation by preventing oxygen ingress.



Simultaneous additions of two antioxidants (termed as double addition) have also been introduced. The benefit of this type of addition is that it inhibits carbon oxidation more effectively than a single antioxidant and contributes to

the improved corrosion resistance, although the mechanism has not been specified. The present investigation attempts to formulate and evaluate the properties of three refractories containing double antioxidants viz. Al, Si and B₄C.

5.2 Formulation

RAW MATERIALS	AS	AB	SB
Tabular Alumina (0-6.3 mm)	84	84	84
Silicon Carbide (SiC)	10	10	10
Flake graphite (<250 μm)	4	4	4
Nano Carbon Black (20 nm)	1	1	1
Aluminum metal powder (Al)	0.5	0.5	0
Boron Carbide (B₄C)	0	0.5	0.5
Silicon metal powder (Si)	0.5	0	0.5
Liquid resin (Resol)	+3.50	+3.50	+3.50
Powder resin	+0.50	+0.50	+0.50

Table 5.1 Formulation Al₂O₃-SiC-C with a combination of different antioxidants

The formulation is designed in a manner to resemble the standard lining of a torpedo ladle. Its application area requires a stable and dimensional control. These linings are susceptible to expansion and which leads them to severe damage.

The *in situ* carbides and oxides are expansive in nature and need to be controlled for a successful life span. The amount and nature of antioxidants are the prime cause of this failure. So, three most commonly employed antioxidants are added in a lower amount than current industry trend, and their combination is studied. The sample series AS correspond to the aluminum and silicon metal as an antioxidant. Similarly, AB is aluminum metal powder added with boron carbide, and SB is silicon metal powder added with boron carbide. As obtained from the previous chapter the silicon carbide acts as an excellent reinforcing agent although it was not a good antioxidant. Hence, it is used in a high amount as a reinforcement.

5.3 Results and Discussion

The major phases were alumina, graphite and silicon carbide in all three compositions. These phases were compared with standard JCPDS charts whose numbers are depicted in the figure.

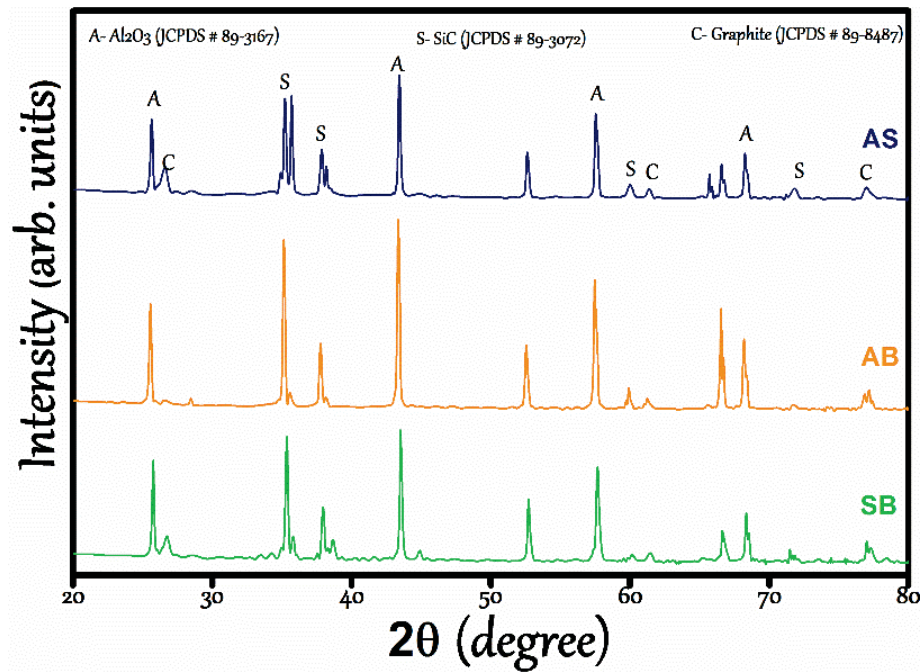


Fig 5.1 XRD plot of samples coked at 1400°C

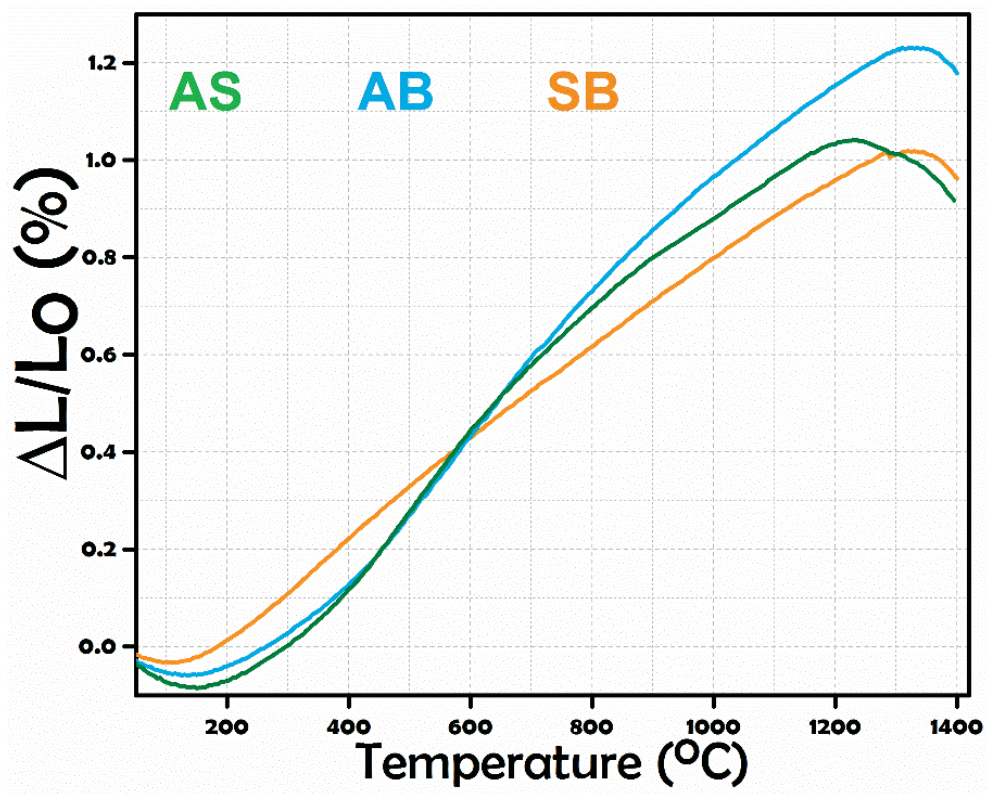


Fig 5.2 Dilatometric curve of specimens containing different antioxidants

All the expansion curve possesses a similar shape, although their slopes might differ. The formation of liquid aluminum borate triggers the expansion of AB above 800°C.

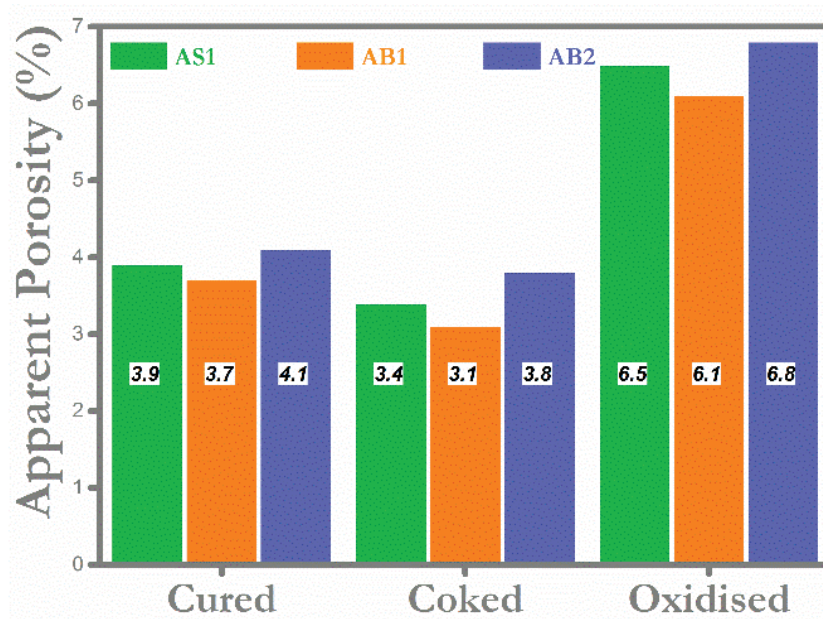


Fig 5.3 Apparent porosity of samples

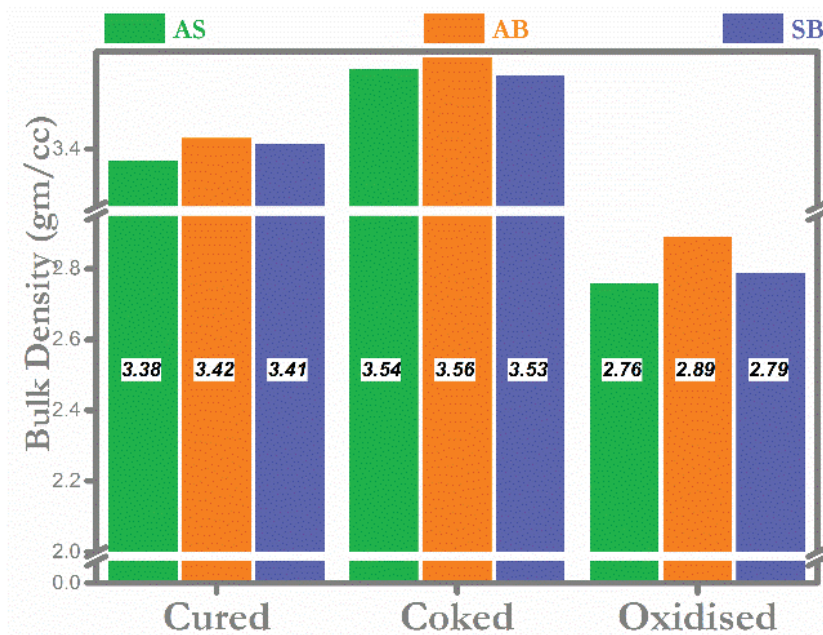


Fig 5.4 Bulk density of samples

The Al-B₂O₃ containing samples achieved maximum coked density due to predominant liquid phase sintering. Phenolic resin is converted to amorphous carbon at elevated temperatures, and the conversion is accompanied by the release of gaseous species such as CH₄, CO, and CO₂ being the primary cause of increased oxidized porosity.

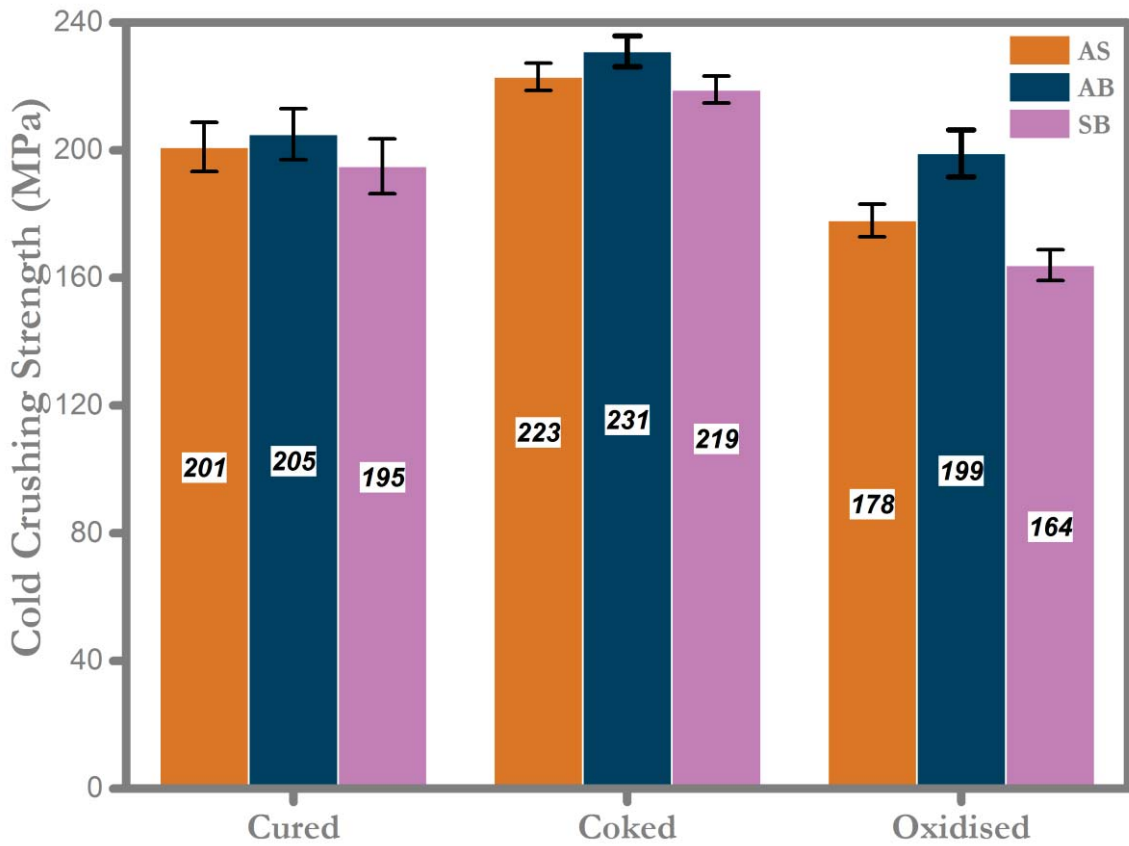


Fig 5.5 Variation in crushing strength with heat treatment

The sufficient strength is mainly associated with the *in situ* formation of carbides in the matrix. At the curing and coking temperatures, no noticeable difference in different compositions is observed as it is bonded only to carbon derived from the phenolic resin. With the oxidation taking place the SiC phase oxidizes and regenerates with the escaping CO gas phase reaction. Formation

of this reticulated SiC is promoted by liquid phases generated from oxidation inhibitors which trap the escaping gasses by surface coating mechanism.

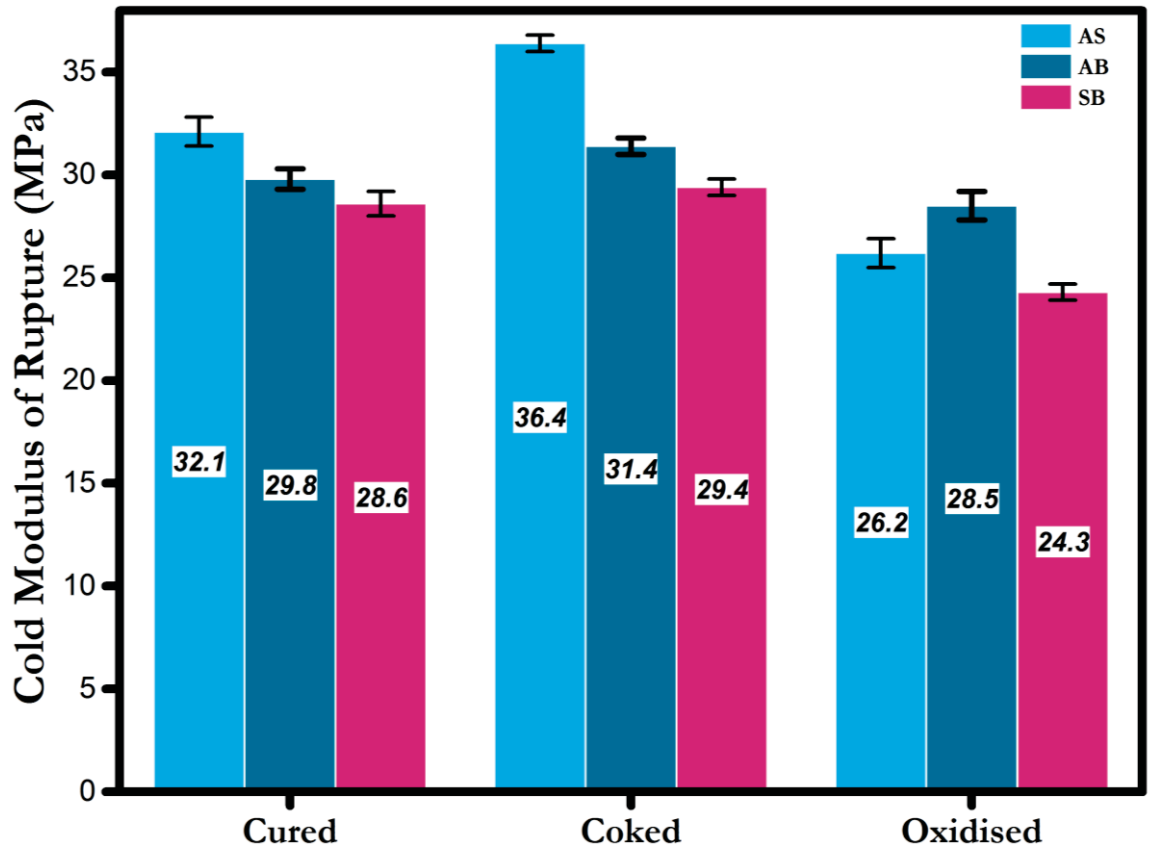


Fig 5.6 Variation in bending strength with heat treatment

Two possible explanations may be given to the enhanced rupture strengths of coked specimens:

- ❑ First, the sliding mechanism is operating between graphite layers and leads to the apparent tortuosity of cracks. Consequently, a larger specific surface area would be generated, and the load transfer mechanism would be enhanced.
- ❑ Second, mechanical properties of refractories are affected by the quantity and morphologies of SiC and Al_4C_3 . Based on the toughening

mechanisms of ceramic materials, including crack deflection, whisker bridging, whisker fracture and pull-out, whiskers are found to be more positive than particles for improving mechanical properties due to their large aspect ratio.

The presence of Al-Si containing samples achieved maximum coked strength due to *in situ* whisker formation although they could not beat the oxidized AB samples.

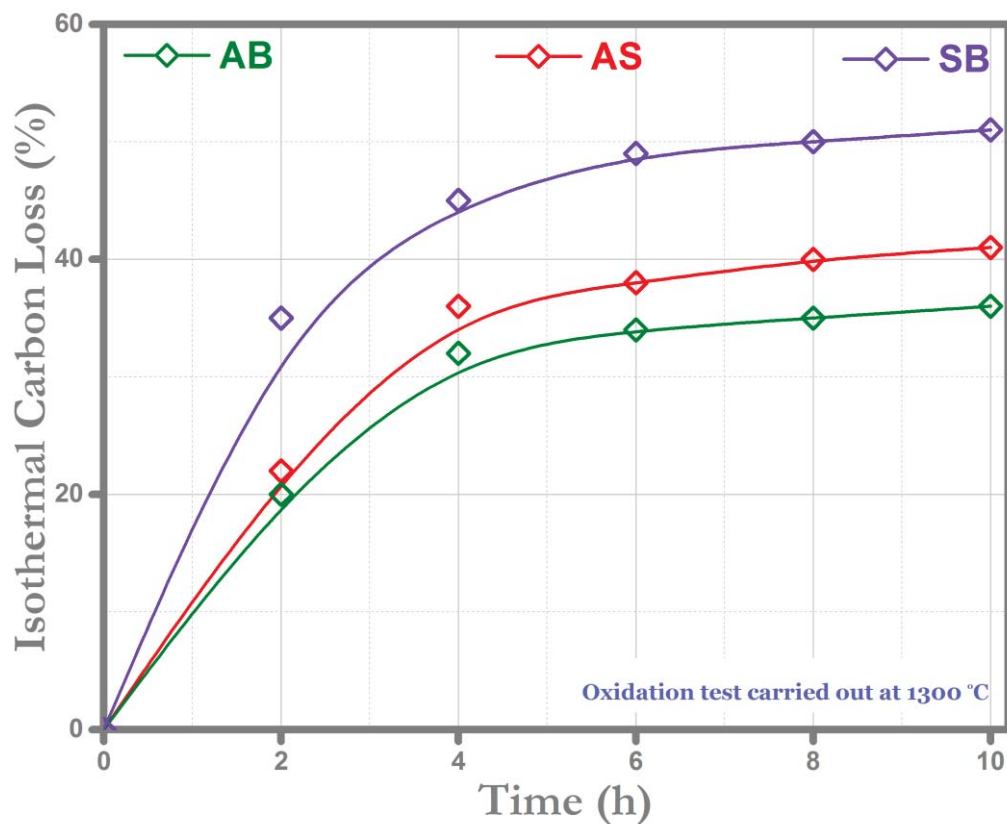


Fig 5.7 (a) Isothermal oxidation profile at 1300°C

The poor performance of the Al_4SiC_4 (AS) forming combination could also be related to the formation of small cracks on the fired samples surfaces, affecting the porosity results and increasing the deterioration process due to the greater oxygen infiltration in the refractory structure. These curves portray that impregnation with formation of secondary carbide although noteworthy, but not enough suitable technique for protection against oxidation of resin bonded refractory bricks. Surface coatings of the same materials, however, has proven to be more useful in retaining carbon losses.

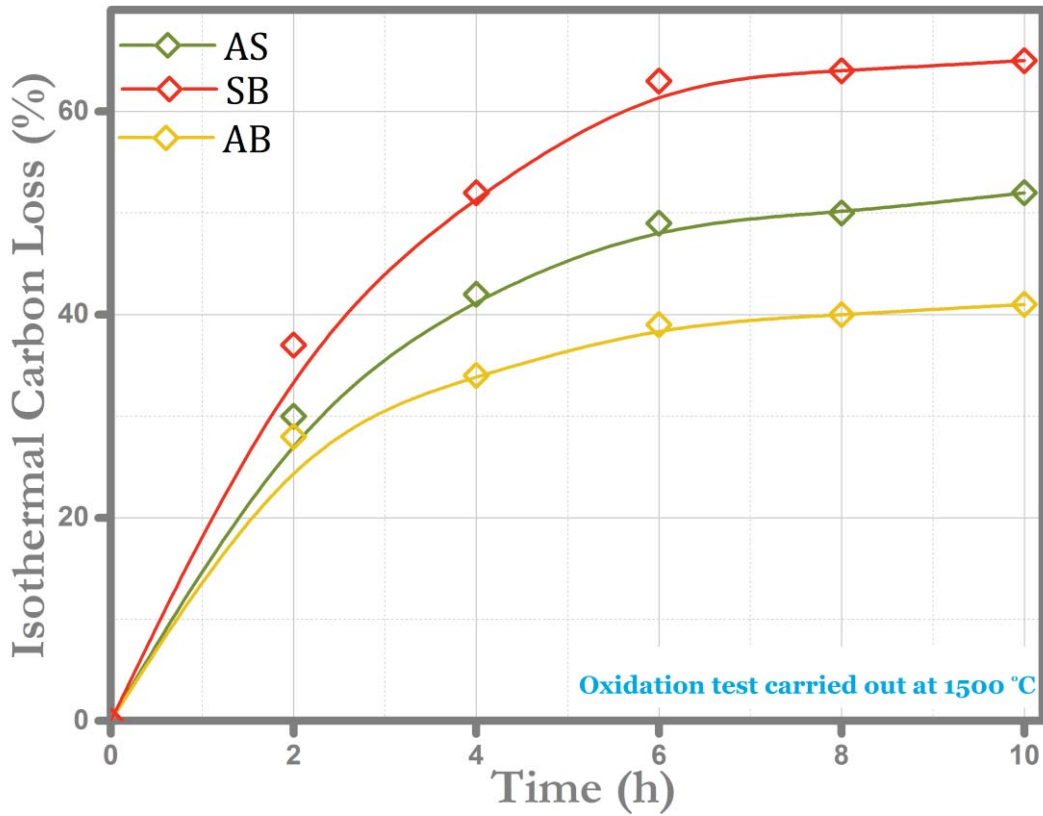


Fig 5.7 (b) Isothermal oxidation profile at 1500°C

The aluminum-silicon containing samples had limited oxidation protection through the maximum temperature evaluated. The formation of borosilicates (SB) also occur above the oxidation temperature of glassy carbon, and it failed miserably in protecting it. With the increase in the temperature the borosilicates result in the excessive liquid generation leading to the peeling-off of the surface coating.

The uncoated specimens (AS) also had a homogenous oxidation which reaches ~50%. The slope tendency of the curves changed with a gradual increase in its oxidation hours; initially being higher and then slowing down after four hours of oxidation. After the sixth hour the oxidation cure profile tends to being static.

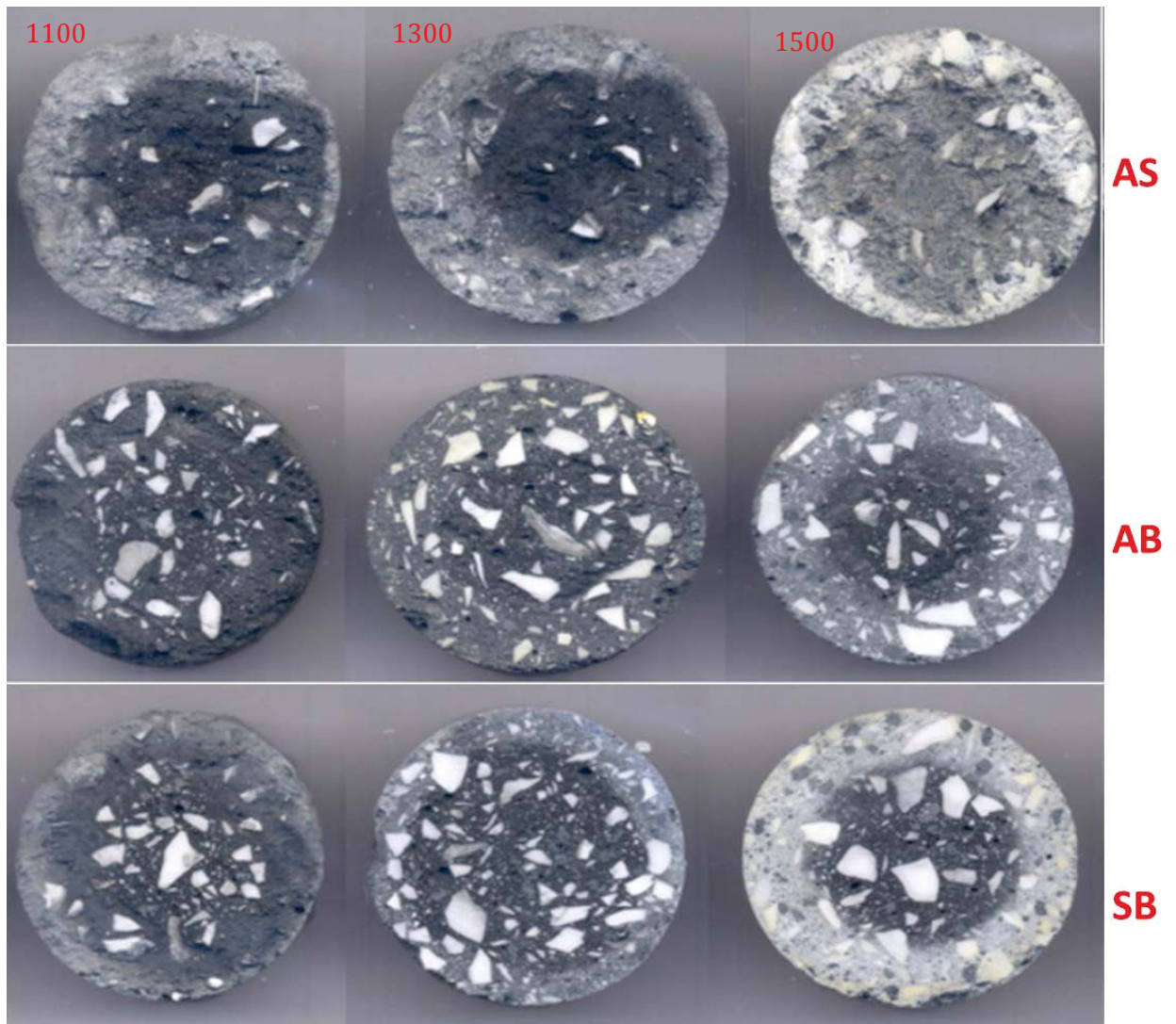


Fig 5.8 Non-isothermal oxidation samples at 1100, 1300 and 1500°C

The carbon oxidation took place at 1100°C, becoming more intense at higher temperatures. The AS sample showed lower oxidation resistance, as larger decarbonized areas were observed (white and gray regions). The antioxidant blend of Al-B₄C (AB) seemed to be more efficient in inhibiting the carbon oxidation as even a non-oxidized core area was detected in the inner part of these samples after firing at 1500°C.

Boron carbide reacts with O_2 and CO at temperatures above $450^\circ C$, resulting in C and B_2O_3 . Volume increase follows these phase transformations, inducing pore closure. Borosilicate glass (SB samples) can also form a glassy layer on the surface of the samples also reducing its porosity, but somehow this effect was not observed.

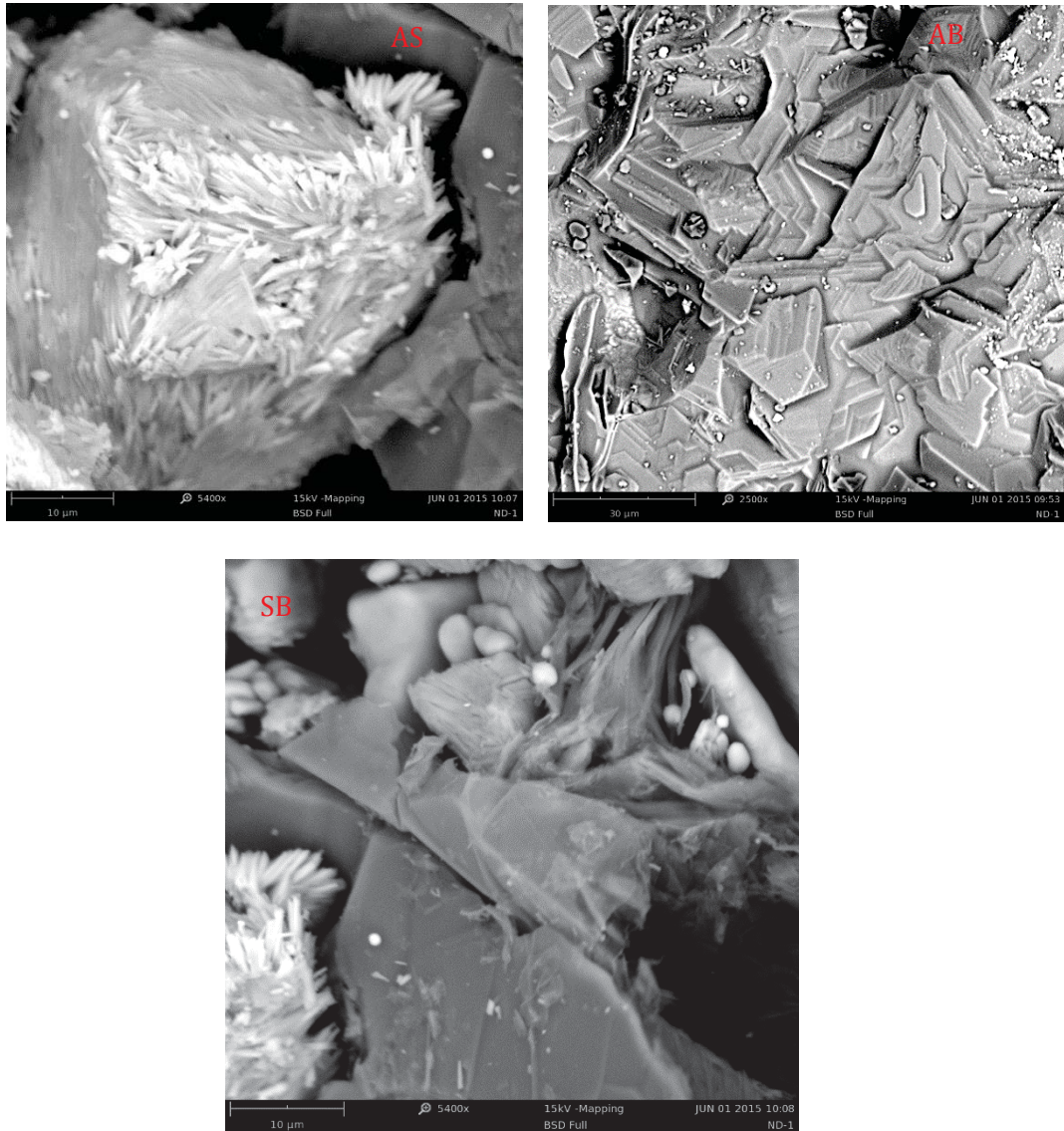


Fig 5.9 SEM of samples oxidized at $1500^\circ C$

The acicular morphology in AS is predicted due to mullite formation. The oxidation derived silica reacts with available alumina, and the acicular shape is promoted by the path created by escaping gasses.

The AB samples present a dense microstructure owing to an ion diffusion mechanism controlled by molten aluminum borate liquid. The microstructure of SB samples is similar in nature to AS samples, most probably due to mullitic existence.

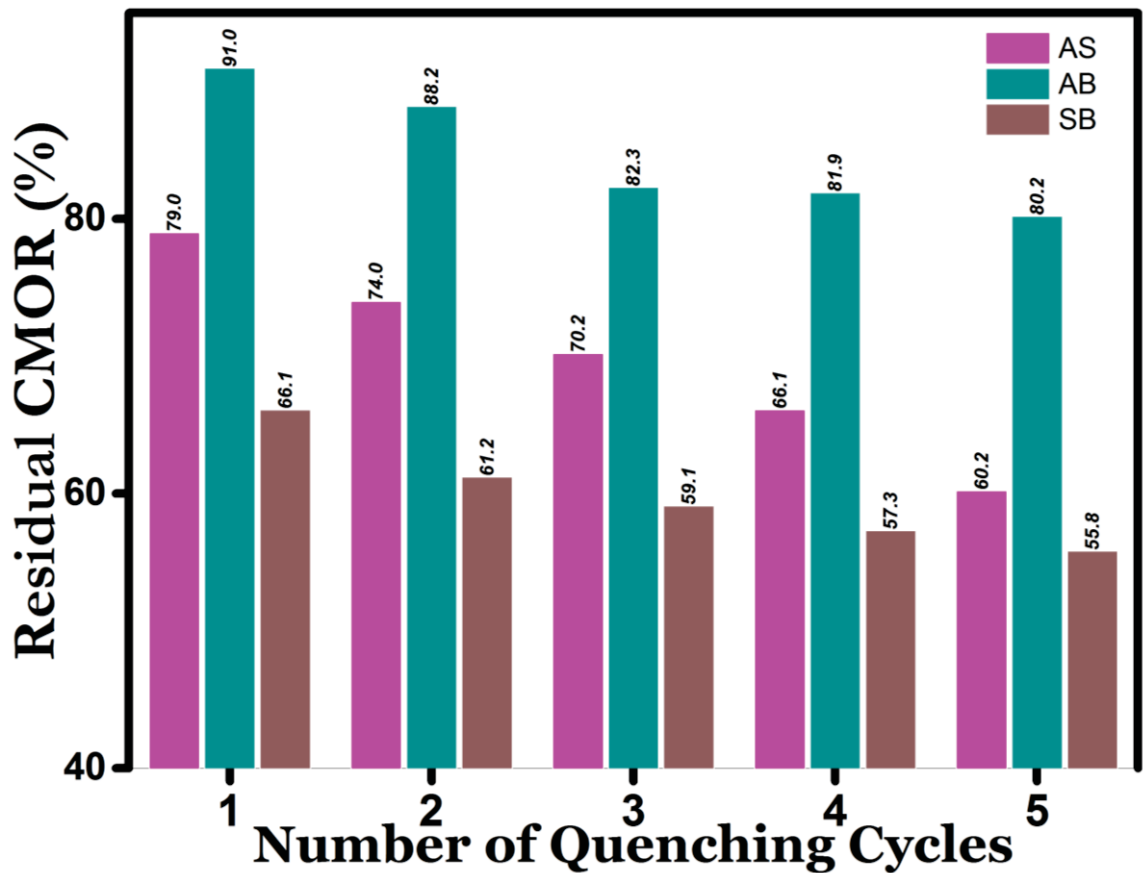


Fig 5.10 Spalling resistance as % CMOR retention

The formation of mullite by oxygen-derived silica melt as seen in microstructure play a major role, in improving spalling resistance. This residual silica and aluminum borate melt make enough room to accommodate

thermal strains leaving the whole structure intact. Quenching does not allow sufficient time to nucleate and recrystallize them in the melt and therefore added antioxidants in AB make the refractory self-repairing, thereby enhancing thermal shock resistance.

5.4 Summary of Results

Based on the results, the aluminum-boron carbide additive is pointed out as a promising antioxidant for refractory bricks; its performance proved to be outstanding to control the carbon oxidation of the designed $\text{Al}_2\text{O}_3\text{-SiC-C}$ refractory. Comparing to the other evaluated compositions, this addition was more efficient in mechanical strengths as no visible cracks were found on the samples' surface. The double addition of Al+Si, accelerated formation and growth of mullite, in the case of $\text{B}_4\text{C+Si}$, the SiC dissolution was accelerated to some extent leading graphite in the matrix get oxidized.