Chapter-7

(A hybrid Al$_2$O$_3$–MgO–C refractory containing in situ and pre-formed spinel)

A hybrid Al$_2$O$_3$-MgO-C refractory containing *in situ* and

pre-formed spinel

7.1 Motivation

Alumina-magnesia-carbon bricks have been increasingly used as lining materials for steel ladles below the slag line, mainly due to their chemical properties and better thermomechanical behavior when compared to the alumina–spinel-carbon ones.

In our previous chapter, we have established that ideal spinel (MgAl$_2$O$_4$) content to ensure an optimized corrosion and penetration resistance is close to 21 wt%. However, according to the selected raw materials and the different reaction mechanisms, the residual expansion due to the formation of 21 wt% of *in situ* spinel may be excessive, and could then spoil the material's structural integrity as a result of crack generation. The *in situ* spinel (MgAl$_2$O$_4$) formation provides an enhanced corrosion and thermal shock resistance, the composition with pre-formed grains shows higher volumetric stability and do not have the inherent MgO hydration problems.

As some important properties of the alumina-magnesia-carbon could be affected by the micro crack coalescence resulting from excessive residual expansion due to spinel formation, pre-formed spinel additions would be a better path to control it. Nevertheless, the severe thermal cycles and the

constant chemical attack of the refractory lining in the steel ladle environment could easily decrease its working life if pre-formed spinel is used. Besides this, when using pre-shaped products, a designed expansion is desirable to inhibit slag and molten steel penetration at the lining joints. Considering these aspects, bricks containing only preformed spinel do not satisfy all requirements.

In this chapter, briquettes with optimized spinel content (21 wt%) were developed with a goal of attaining samples containing both pre-formed and *in situ* spinel with low residual expansion. In such a composition, the *in situ* spinel phase could enhance the thermal-shock and molten slag resistance whereas the preformed grains would ensure suitable volumetric stability.

7.2 Formulation

RAW MATERIALS	AMC_P	AMC_I	AMC_H
TA (0.2-3mm)	28	28	28
TA (74-44μ)	22	22	22
TA (<44μ)	16	31	22
AR78 (<44μ)	21	0	11
MgO (<44μ)	0	6	4
Flaky Graphite	7	7	7
Resol Resin	3.50	3.50	3.50
Powder Resin	0.50	0.50	0.50
Nano-Carbon Black	1.0	1.0	1.0
Al-Metal Powder	0.50	0.50	0.50
B_4C	0.50	0.50	0.50

Table 7.1 Composition table demarcating different spinel formulations

The present lining resembles a side-walls and bottom of a ladle refining furnace. The extent of spinel formation creates a volumetric instability and which then leads to the formation of surface and microstructural cracks thereby leading to deleterious conditions. A total number of three different compositions were formulated. AMC_I, AMC_P, and AMC_H. These subscripts I, P and H corresponds to the nature of spinel addition viz. *in situ*, pre-formed and a new hybrid type containing both respectively.

6.3 Results and Discussion
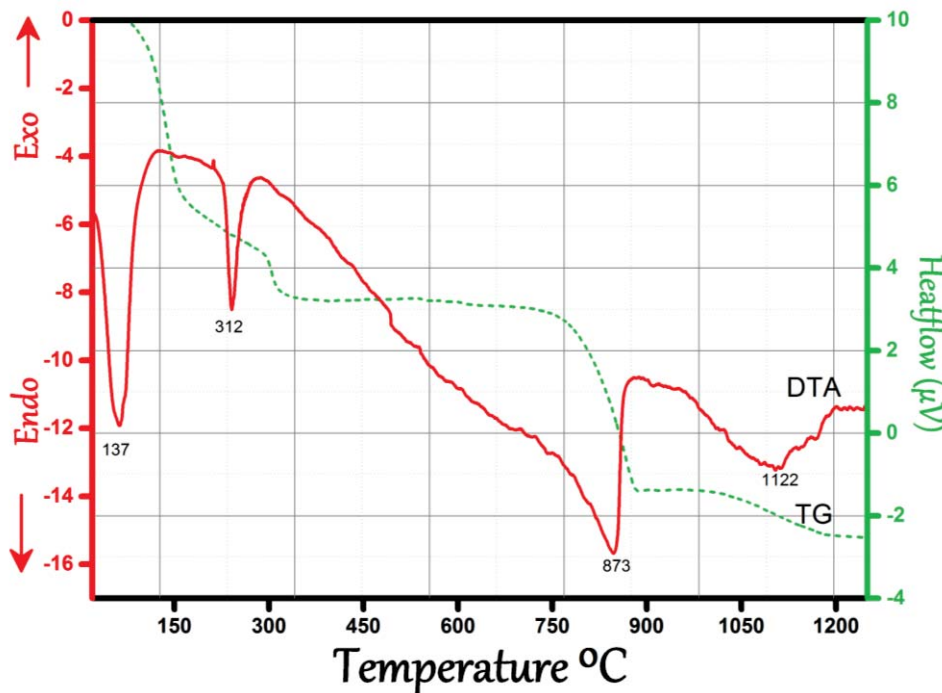
Fig 7.1 DTA-TG of dried spinel gel precursor

A fine spinel prepared by gelation and precipitation method was processed for incorporating in the bricks as pre-formed spinel containing bricks. Above is the thermal evolution of the dried gel powder. The loss of water of crystallization occurs below 312°C, and the spinel formation starts to occur around 873°C. Considering this, the calcination temperature was kept 900°C.
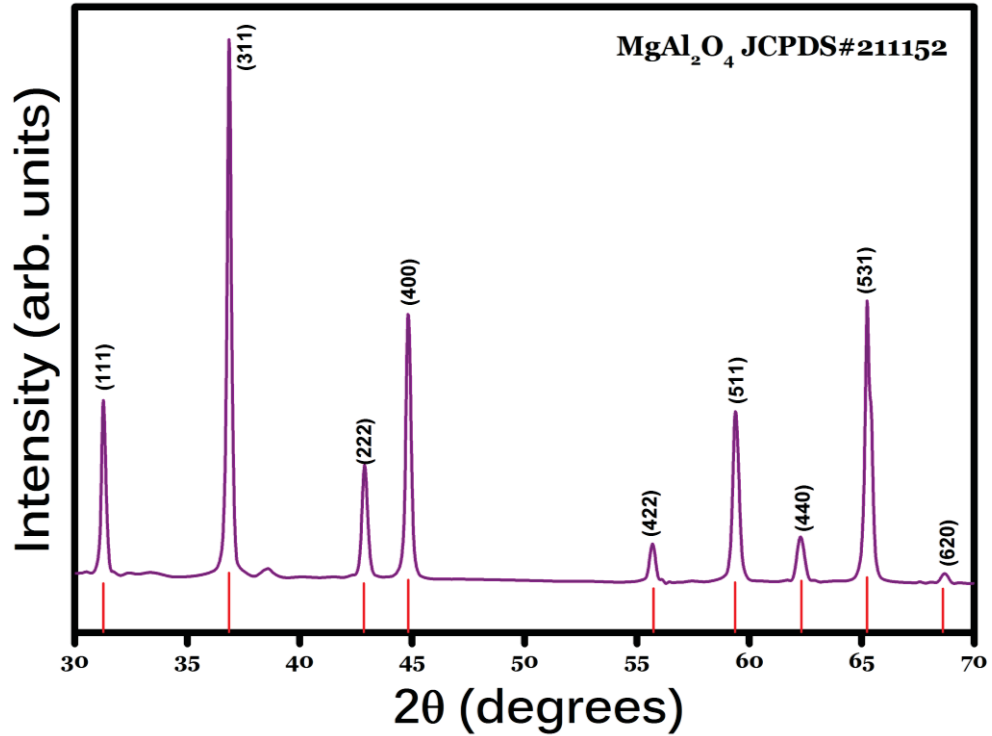
Fig 7.2 XRD plot of gelation and precipitation processed spinel at 900°C

Applying the Scherrer's formula, crystallite size from the {311} diffraction plane is evaluated to be 36 nm.

	Bulk density (gm/cc)	Apparent porosity (%)
AMC$_I$	2.79	20.9
AMC$_P$	2.85	18.5
AMC$_H$	2.92	13.4

Table 7.2 Bulk density and apparent porosity of AMC briquettes

Hybrid samples present superior BD and AP values as compared with other two due to a better interlocking and pore filling tendency.
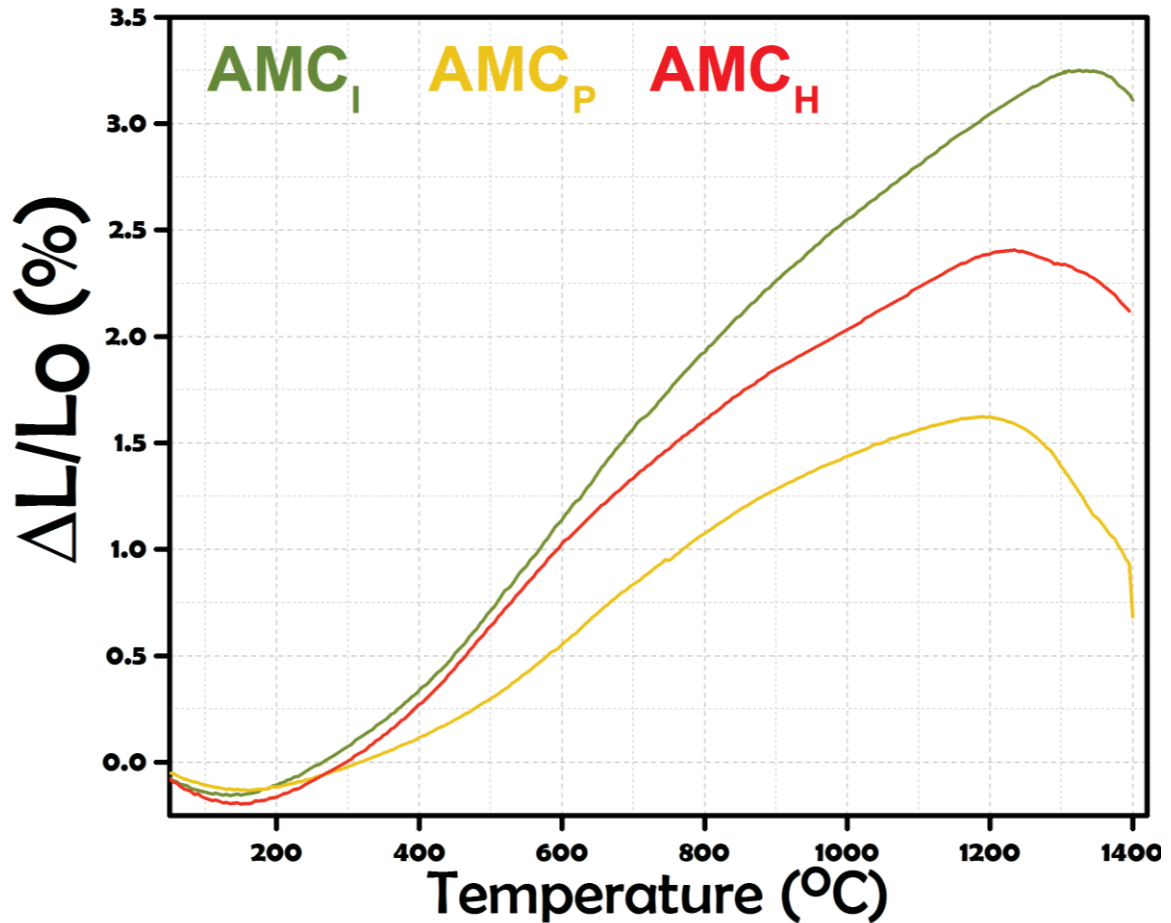
Fig 7.3 Expansion curves of AMC blocks

Two different mechanisms sintering shrinkage and *in situ* spinel affected the linear change behavior when increasing the temperature. Sintering shrinkage is totally hidden by the spinel expansion in AMC_I, and it was progressively highlighted in other two as the *in situ* spinel content decreased. Furthermore, the compositions did not have the same shape and intensity temperatures, indicating the role played by the particle size and carbide formations.
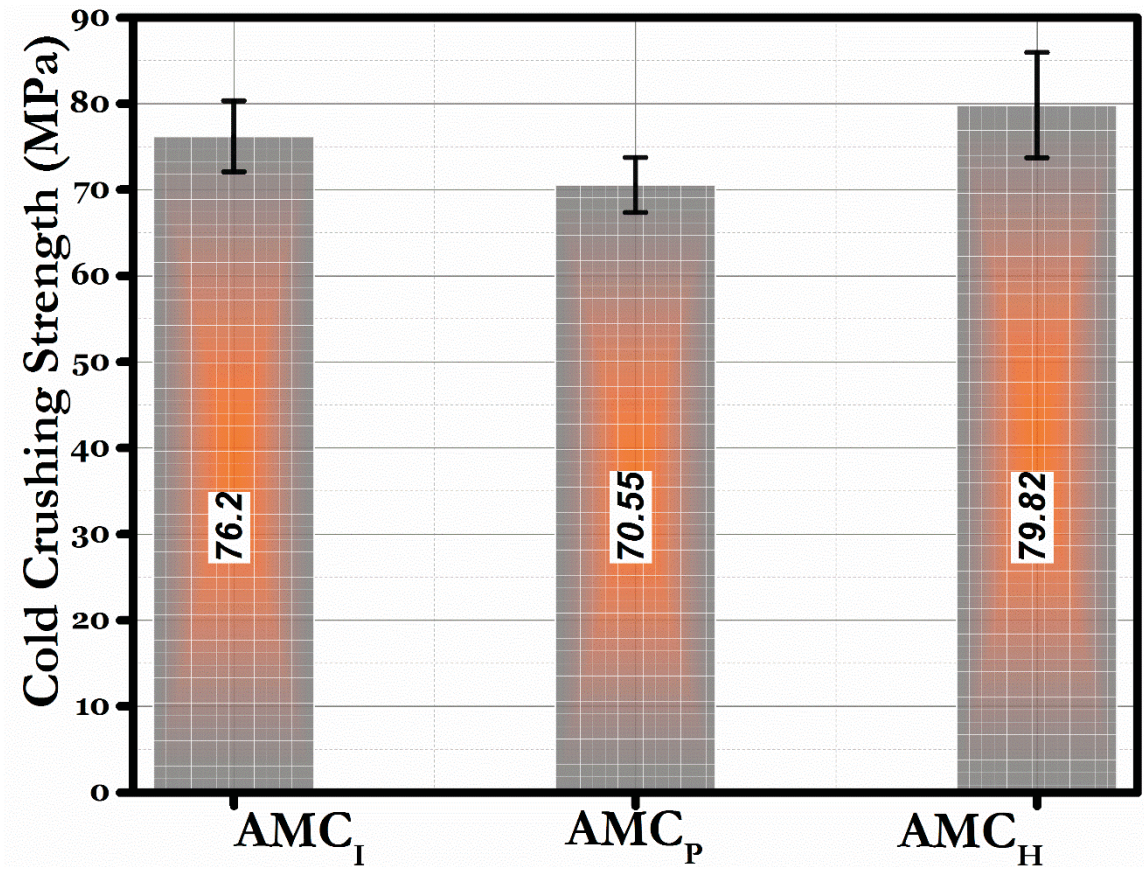
Fig 7.4 Cold Crushing strengths of samples coked at 1400°C

AMC_I and AMC_H show similar PLCR values, which show a clear tendency to increase the number of cycles increases.

PLCR values for AMC_P, however, remained practically unchanged at 0.26% during the entire cycles. The primary contributor to residual expansion at 1400 1C is spinel formation, which continues to increase as temperature and heating time increase
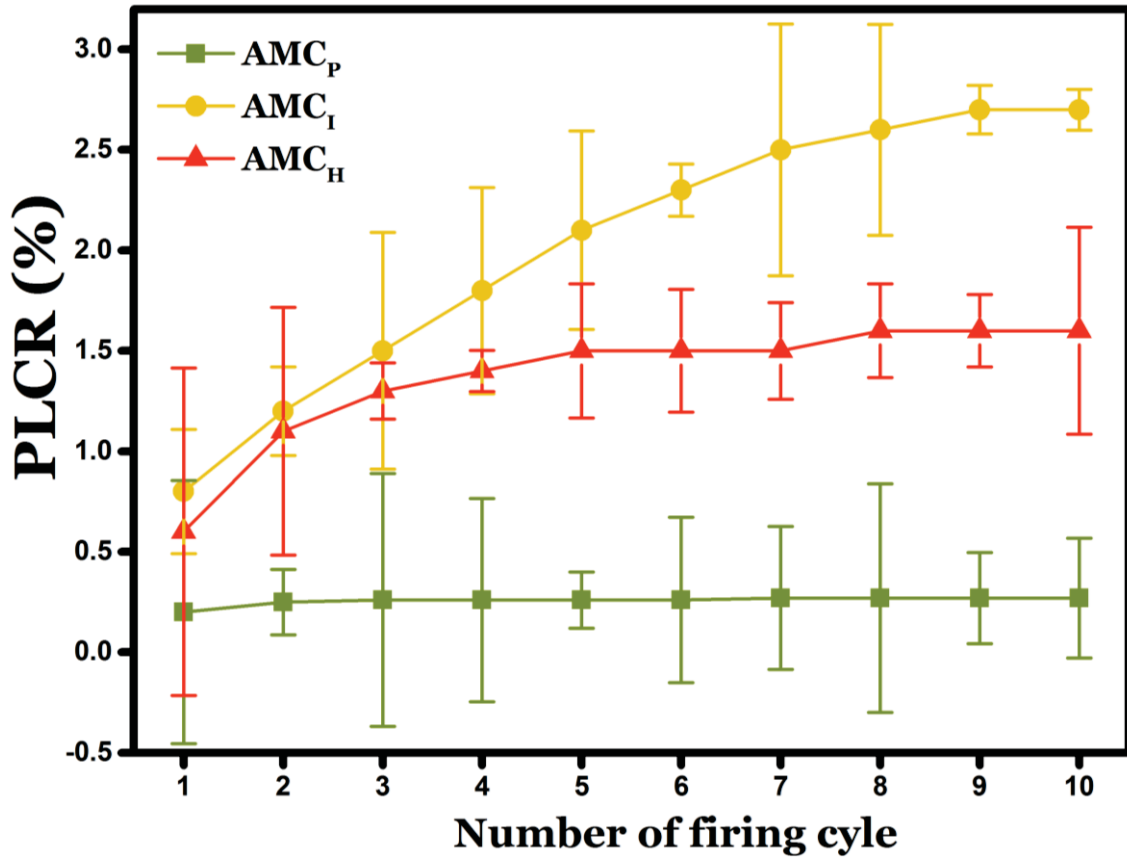
Fig 7.5 PLCR (%) of samples coked at 1400°C/3h for multiple cycles

Thermodynamically, more MgO addition means more spinel formation, which could result in more significant volume expansion (7.8% in volume and 2.6% linearly, based on molar volume calculation). If the MgO and Al_2O_3 reactants are powders rather than bulk solid materials, then the solid state reaction often yields linear expansion much larger than the predicted value simply from the molar volumes. Coarse MgO grains will not convert to spinel even at high temperatures (> 1400°C) in first cycle, due to dynamic restriction. This is confirmed by the increasing PLCR values of AMC_I. Even after eight firing cycles the linear expansion continues and reaches to a value above 2.6%. Although it seems to be stabilizing after eighth firing cycle. The rest other two samples do

not expand much and the permanent linear change after reheat retains a constant value less than 1.6% in AMC_H which is much desirable in lining to close the joint structure and form a monolithic interface. This value is less than 0.5% in AMCP which is slightly low for operating conditions as a gap might allow the liquid metal and slag to penetrate and destroy the structure.
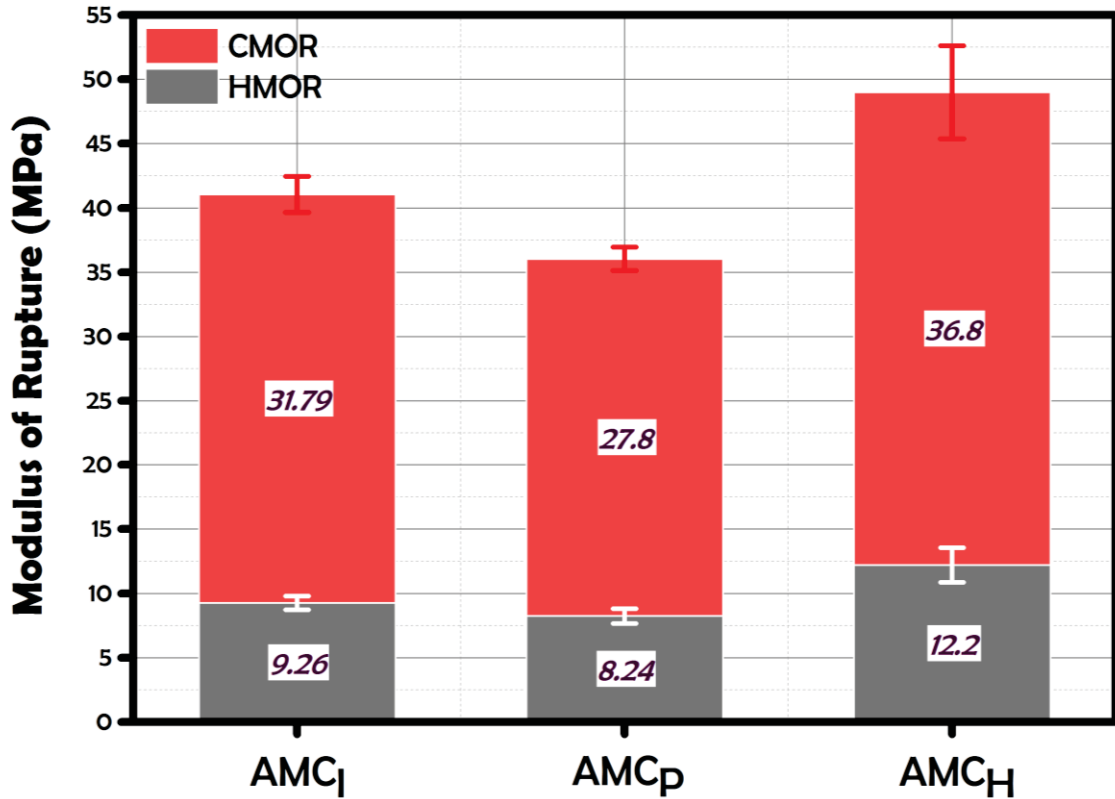

Fig 7.6 Cold Crushing strengths of samples coked at 1400°C

The lower strength results attained for, the higher *in situ* spinel containing compositions could be attributed to micro cracks generation in the matrix. The alumina-based refractories are known to exhibit superplastic behavior at high temperatures in the presence of ultrafine spinel grains.

When the temperature was raised, and a tensile stress was applied, the grain boundary sliding might have occurred impeding the abnormal grain growth of alumina thereby increasing the hot rupture strength. The mismatch in the thermal expansion between alumina and magnesia induces micro-gaps or cracks in the matrix, this reduces the hot strength of AMC_I.
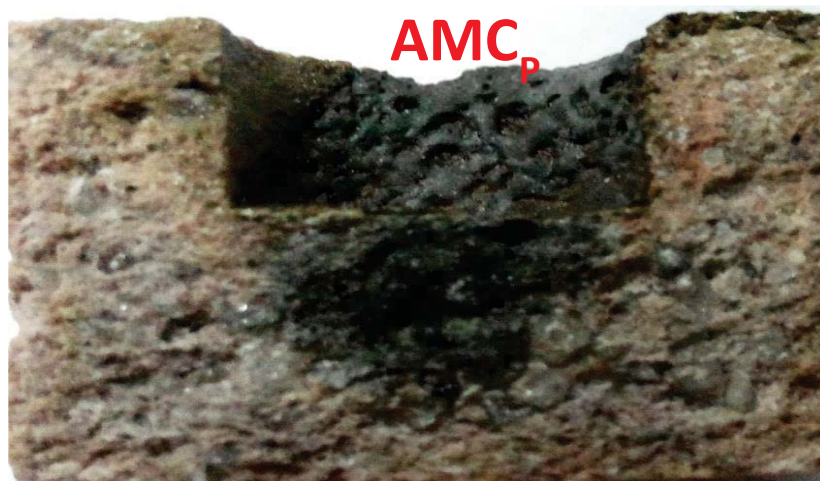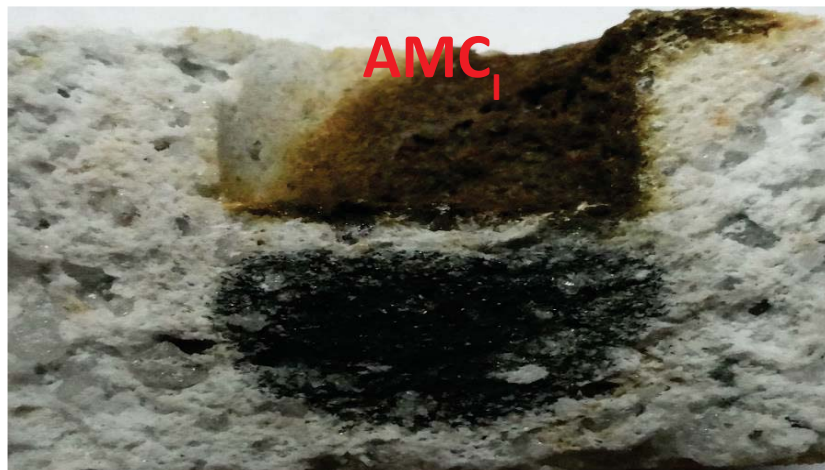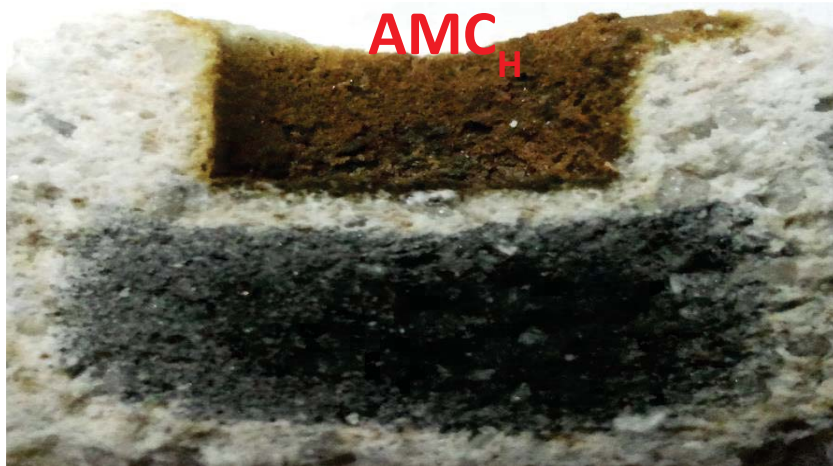
Fig 7.7 Slag corroded samples coked at 1400°C

Ladle slag (basicity index 3.0)	
Oxide	**wt%**
CaO	37.5
SiO_2	12.48
Al_2O_3	12.08
MgO	6.95
Fe_2O_3	30.0
MnO	0.99

Table 7.3 Slag composition

The non-crystalline phase (derived from the liquid formed at a high temperature) can be seen spread into the AMC_P matrix. The other two

seemingly resisted its penetration. The AMC_H also has a significant amount of residual carbon and lowest porosity.
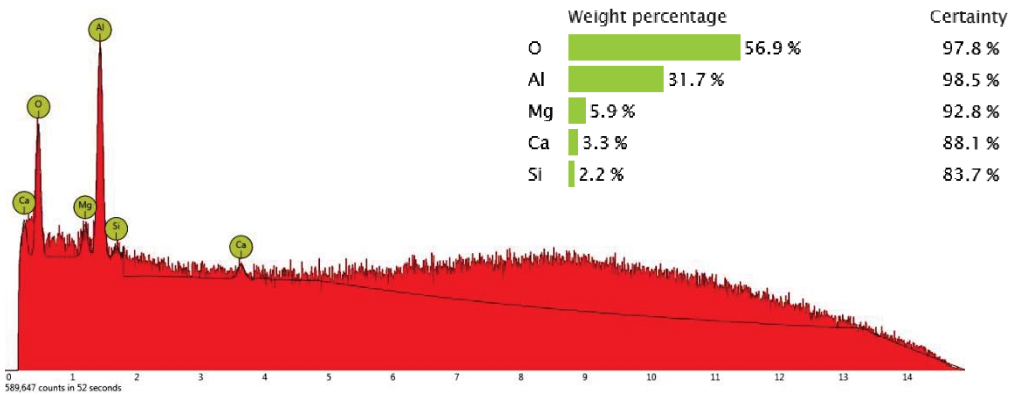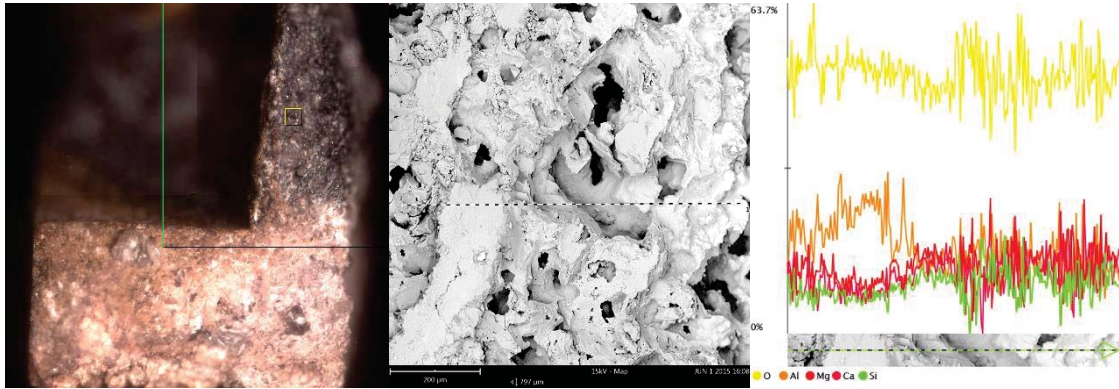

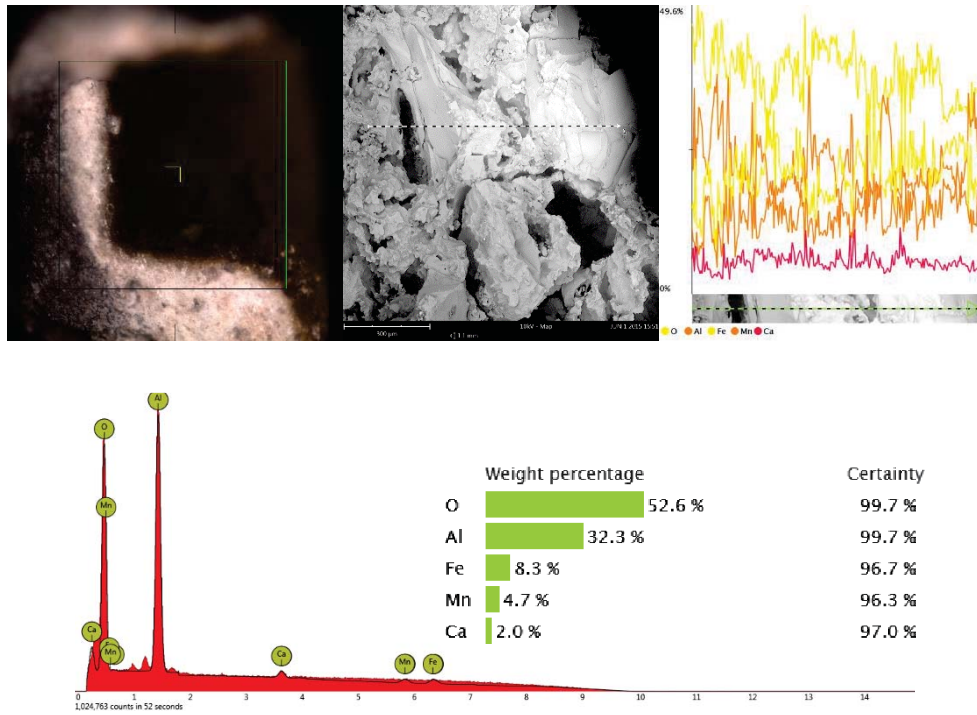**Fig 7.8** SEM, EDS and elemental line profile of AMC_I

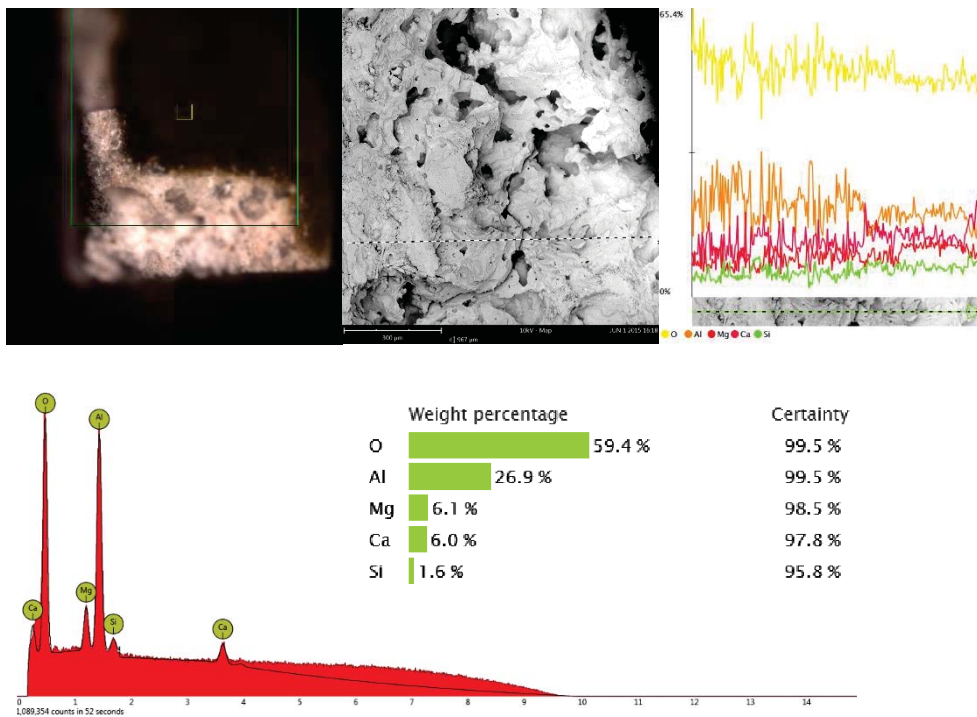**Fig 7.9** SEM, EDS and elemental line profile of AMC_P

Fig 7.10 SEM, EDS and elemental line profile of AMC_H

By static crucible slag test at 1600°C for 5h, using a basic steelmaking slag whose chemical composition is given in Table 7.3. The slag resistance of the specimens is compared, as shown by their photographed sections after slag attack in Fig. 7.7 and their microstructural evidences after the attack in Fig. 7.8, 7.9 and 7.10.

Clearly, the favorable role of an appropriate amount of spinel has been presented, as *in situ* addition increases, slag penetration increases. Although it also leads to carbon oxidation, which brings us to an understanding that spinelization is also accompanied by oxidation reactions. A much higher amount of residual carbon can be envisaged in AMC_H making it less penetrable.

7.4 Summary of Results

When the in situ/pre-formed spinel ratio decreased, this balanced expansive behavior suggested that the simultaneous use of pre-formed and *in situ* spinel was an interesting alternative to attain a suitable linear change without affecting the spinel content, when corrosion performance is the aim.

The attained results led to a proposed corrosion mechanism, in which the key factors that played a role in the basic slag corrosion behavior could be identified. The physical property measurements indicated that the pore diameter distribution is a key aspect of the penetration resistance, and better results were attained by using the hybrid system.

Furthermore, chemical and microstructural aspects (carbon distribution and the content of *in situ* spinel the matrix) also imparted a relevant role to the corrosion behavior and affected the mechanical integrity, to crack generation that would increase the slag infiltration driving force. Therefore, the proper design of the matrix and the selection of the most suitable raw materials are crucial to ensure a high basic slag corrosion performance.