LOW CEMENT CASTABLE WEAR MECHANISMS IN DRI ROTARY KILNS

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ABSTRACT

Production of sponge iron, via the direct reduction route using rotary kilns, continues to experience significant growth in countries such as South Africa and India. The vast majority of these DRI kilns are lined with monolithic castables and there is a need to improve the durability of low cement castables for this specific application. To a large extent, the refractory life of a DRI kiln is determined by the build up of accretions within the kiln. The accretions must be removed to maintain production levels, but removing them not only results in lost production due to downtime but the refractory lining is often also damaged in the removal process. A post-mortem analysis of used DRI kiln refractories has been performed in order to provide a clearer understanding of the underpinning refractory wear mechanisms. Used samples of a low cement castable have been recovered from two direct reduction rotary kilns. Samples were taken from areas where severe accretion formation was observed as well as areas where there was no sign of build up. Chemical and physical analysis has been carried out using XRF and XRD and this data has been coupled with an analysis of microstructures by SEM and EDS. The investigation reveals a number of mechanisms which account for the accretion build up and lead to premature castable wear through the removal of the refractory hot face during removal of the accretions from inside the kiln.
Introduction

DRI (Direction Reduced Iron or Sponge Iron) is being produced in increased quantities in numerous countries around the world. World DRI production in 2007 for the countries reporting to the International Iron and Steel Institute is estimated to be 54.433 million tonnes, up by 9.1% YoY as compared to 49.460 million tonnes in 2006.

The largest national producer of DRI is India. India maintained the position of global leader by producing 17.820 million tonnes of DRI in 2007 and accounting for 32.7% of total global DRI production. Indian production of DRI has grown rapidly over the last 10 years jumping from 4.8 millions tonnes in 1996 to 15.4 million tonnes in 2006 at an annual growth rate of 33% per annum. The growth of production continues on a monthly basis as evidenced by figures for January 2008. The International Iron and Steel Institute production figures for direct reduced iron for the month of January 2008 show the global production of DRI in January 2008 was 4.966 million tonnes, up by 10.9% YoY and up by 3.8% MoM as compared to December 2007. And India retained the top slot, producing 1.6 million tonnes and accounting for 32.2% of the total global DRI production.

The national steel plan in India foresees DRI increasing to 30 million tonnes by 2010, an approximate two fold increase over volumes produced in 2007. This assumes an annual growth rate of 20% in DRI production. Since DRI production consumes a significant amount of refractories, growth in DRI production should stimulate refractory demand. A survey [1] of this market was undertaken to understand the impact of this growth in DRI production on refractories and, more specifically, the refractory demand linked to monolithics and the consequential demand for calcium aluminate cement. As part of this survey it was necessary to study refractory wear mechanisms within DRI production units to better understand potential opportunities for technological progress and ways to reduce the specific refractory consumption through improved refractory performance.

DRI Production and Market Statistics

The primary use of DRI is as an alternative source of metallics for steel making. There is also a second and allied product, namely hot briquetted iron (HBI), which does not generate fines as readily and is less susceptible to oxidation, making HBI the preferred product to export around the world. DRI is primarily used as a cheaper substitute for HBI and is added to supplement the scrap charge for steel making via the EAF route. This is especially relevant in India due to scrap sourcing issues - both in terms of scrap quantity and scrap quality. The chemical composition of DRI is far more stable than that of steel scrap, the latter being prone to high and varying amounts of tramp elements e.g. Cu, Pb, Zn etc. In addition, DRI is generally predictably available, although this is not always true in India.

Other applications for DRI are as a coolant in the BOF steel making route (replaces scrap), and as charge mix to Blast Furnaces to economise coke consumption and increase furnace productivity.

DRI is produced by the direct reduction of Iron ore by CO gas. The reduction reactions are performed in either a rotary kiln or vertical shaft furnace and the energy required is supplied by either gas or coal as shown schematically in Figure 1 (which illustrates the rotary kiln process).
There is a plethora of DRI production processes, with more than 15 different process types existing in the world. The majority of the world's DRI is produced by Midrex/Hyl processes using gas fired vertical furnaces. 60% of world production is through Midrex units and an additional 20% of world’s production is via other vertical shaft furnaces. Notable exceptions to producing DRI by gas fired vertical furnaces can be found where there is currently limited gas supply e.g. in India and in South Africa. This has led to 60% of DRI production in India employing a variety of indigenous and imported technologies that are coal fired - essentially rotary kilns with an average throughput of 100t.p.d. The remaining 40% of DRI production in India is gas fired, and both shaft kilns and rotary kilns are in operation. Shaft kilns tend to be large units with an average of 1500 to 4000 t.p.d.

It is thought that DRI production in coal fired rotary kilns will remain dominant and continue to grow in the future in India largely due to limited gas availability (gas is really only available in Western India). The reasons for a preponderance of coal fired rotary kilns producing DRI in India is believed to be related to:

1. Low investment cost using local technology– I lakh (1800€) per tonne produced which is half the world standard
2. Coal is readily available – low grade local coals can be used
3. Iron ore is locally available.
4. Low cost alternative to the Blast Furnace integrated steel making route – relatively low capital investment
5. Coal fired DRI plants can be configured for a wide range of production throughputs - from small scale of <50tpd to more than 500tpd
6. Gas fired plants are limited to Western India where gas is available – generally large capacity plants
7. Availability of scrap and poor scrap quality
8. Existence of “Mountains” of Iron ore fines

Due to these factors, DRI production in India has blossomed and is forecast to grow at a rate of 20% per annum over the next few years to 30 million tonnes by 2010. According to the association [2] of Indian DRI producers, there are currently capacity expansions at 77 plants, 58 new plants are being constructed and an astonishing 167 additional plants are in the planning or early construction stages. Current capacity utilisation is around 65% today.
Thus the target of 30 million tonnes based on an installed capacity of 44 millions over the next 5 years appears achievable. Medium term plans show an estimated 56 million tonne capacity with more than 40 millions tonnes produced by 2020.

### 3 DRI Production and Market Statistics

A market survey [1] of DRI producers and refractory producers showed that the refractory environment depends upon the process type as well as the size of the unit. Generally speaking the refractory life span of gas fired plants (e.g. Midrex) is much longer than coal fired units. This is largely because there is less wear in gas fired furnaces since gas contains a low level of elements which cause melt formation at low temperature (e.g. SiO$_2$, alkalis) unlike coal. ‘Abrasion’ is also lower since gas fired units are static furnaces.

Coal fired rotary kiln units tend to have two basic refractory lining configurations:
- Combination linings of phosphate bonded + 80% Alumina brick combined with bauxite/mullite based LCC Monolithics. This is quite commonly found in very large +500 t.p.d. units.
- 100% LCC Monolithic is the lining configuration adopted mainly by Indian producers. The linings are zoned with 60%, 70% and 80% Alumina material and LCC’s are used in the entire length of the kiln.

Rotary kilns are an ‘ideal’ application for monolithics as these refractories are usually quicker to install than bricks in this case and less complicated (no need for jacking and specialised equipment). In addition, partial repair of sections can be carried out more easily with monolithics than with bricks.

Refractory wear is very dependant upon kiln size, iron ore feedstock quality and coal quality. The coal fired units suffer from the build up of accretions which can grow to such a size that they impede kiln throughput and force the kiln to be shut down so they can be removed. The accretions themselves damage the refractory lining as they lead to the lining tearing out during the mechanical accretion removal and lining cleaning.

The basic usage characteristics and qualities required for Refractories for DRI Rotary kilns are estimated to be:
- Limit the build up of accretions (iron aluminate spinels/CAS glasses) inside the kiln due to adhesion between charge and refractory [3]
  - Limit CaO% which forms CAS2/C2AS low melting compounds and CAS glasses but, at the same time, ensure sufficient strengths.
  - Smooth homogeneous lining surface
- Resistance to Alkalis
- Resistance to CO gases
- Mechanical strength and hot abrasion resistance at 800 to 1100°C
- Limit the density of the refractory castable to reduce the thermal conductivity and avoid excessive heat loss

The LCC monolithic solution is preferred in India as it is better able to resist the low quality coal with high alkali loading which tends to promote penetration into the refractory and build up of accretions. However, due to the extreme climatic conditions, excessive water is often used during the installation of the castables and, high water additions in conjunction with poor consolidation of the placed concrete can lead to more rapid wear.

Refractory consumption varies significantly according to the size of the kiln and is governed by both the lining practice / configuration and the unit size. Linings tend to be 200 to 250mm thick and are generally repaired periodically as the need arises and replaced annually. The estimated refractory consumption by unit size is shown in Table 1.
Table 1: Estimated specific refractory consumption in rotary DRI units

<table>
<thead>
<tr>
<th>Specific consumption range Kg/t (DRI)</th>
<th>TPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 t.p.d.</td>
<td>2.8 to 6.2</td>
</tr>
<tr>
<td>100 t.p.d.</td>
<td>3.8 to 4.1</td>
</tr>
<tr>
<td>300 t.p.d.</td>
<td>3.1 to 3.4</td>
</tr>
<tr>
<td>500 t.p.d.</td>
<td>2.5 to 2.8</td>
</tr>
<tr>
<td>International benchmark</td>
<td>&lt;2.3</td>
</tr>
</tbody>
</table>

5. Operating Conditions: The reduction bed zone normally operates at 900-950°C, but this can go up to 1100°C (a third of the kiln cross section contains the feed material and this area is called the bed). Reducing atmospheric conditions are found in the reduction bed.

5 Examination procedures

Based on current expansion projects of either brown or greenfield plants, the current expansions in capacity should not materially affect refractory consumption as there is no discernable trend towards larger units. A significant refractory demand is expected to be pulled by the growth in DRI production capacity and, whilst specific consumptions will undoubtedly decrease, the overall effect on volume is expected to be positive. Therefore the DRI industry is expected to represent a significant growth potential for CAC bonded monolithics in the short and medium term.

In order to better understand the wear mechanisms of LC castables in DRI applications, a post mortem study of used castables was undertaken. It was hoped that this study would provide an insight into what opportunities existed for performance enhancement of calcium aluminate binders within this application.

4 Postmortem study

Samples were recovered from DRI (100tpd) plants having the following operating conditions:

1. Kiln: 3m diameter, with a 200mm thick 'as cast' refractory lining
2. Feed material: 6t/h iron ore lumps, 6t/h coal, 0.2t/h dolomite
3. Coal with a high ash content has been identified as a major contributor to accretion buildup [3]. The ash content of the coal used was estimated to be less than 25%.
4. Dolomite is used to partially desulphurise the iron.

Three samples were examined: Two samples of lining were taken from the reduction zone of a kiln after 180 days of operation and labelled Sample 1 and Sample 2 respectively. The bulk of each sample consisted of virgin uncorroded refractory identified as the original LC70 refractory that was cast; a dark layer of corrosion was visible over one surface of each sample. Sample 3 was a piece of an accretion layer from another kiln after 400 days of operation.

The samples were examined as follows:

1. For Samples 1 & 2, portions were chipped from both the reaction zone and from the virgin refractory. For Sample 3 portions from two layers in the sample of accretion were taken. Portions from each sample were analysed by X-ray diffractometry (XRD) to identify the phases making up different assemblages in each sample.
2. Sections from different parts of the samples (two sections from each sample) were mounted in resin, polished, and examined by scanning electron microscopy (SEM). The chemical compositions of discrete phases were measured by energy-dispersive spectrometry (EDS). The morphologies and the spatial arrangements of the discrete phases were observed and captured by backscattered-electron imagery.
3. The information uncovered by these techniques and interpreted by the theory contained in the phase equilibria of oxides and silicates in steelmaking allows
conclusions to be drawn about underlying phase-chemical reactions.

Discussions of the phase-chemical compositions of the samples falls into three parts, which reflect the three types of material in the samples received:

1. Un-corroded LC70 castable, the bulk of Sample 1 and Sample 2
2. The corrosion layer of products formed in reactions between castable refractory and charge to the kiln
3. The phase assemblages in accretions formed on the kiln lining

Virgin LC concrete

The castable refractory, after curing and firing, is a composite of two major phases as identified by X-ray Diffraction (namely, Al₂O₃ (corundum) and SiO₂ (quartz)) and three minor phases (namely, Al₂SiO₅ (sillimanite), CaAl₂Si₂O₈ (anorthite) and FeAl₂O₄ (hercynite)). Also present is a silica-rich phase containing 4–6% K₂O. These phases are distributed in angular particles ranging in size from coarse (aggregates) to fine. These features can be seen in Figure 2 which shows the un-corroded concrete from Sample 1 under different magnifications.

![Cross section of Sample 1](image1)

![Photomicrograph of un-corroded part (lower)](image2)

![Back scattered image of un corroded part](image3)

![BSE image of the detail in yellow box](image4)

Figure 2. Cross section and Photomicrographs of Sample 1 – portion of un-corroded / virgin refractory
Corroded LC concrete
At the hot face, virgin LC70 castable in contact with charge in the kiln has formed a layer of corrosion no more than 5 mm deep (see the photo of the castable cross section of Sample 1 in Figure 2). This zone of reaction, which was similar for both Samples 1 and 2 exhibits the following characteristics and changes compared to the virgin refractory:

- Aggregates persist, although reaction on their surfaces has diminished their sizes and rounded their shapes
- The matrix between aggregates forms channels for corrosion. This corrosion has introduced Fe^{2+} and Ca^{2+} into the refractory at the hot face
- Calcium is concentrated in CaAl_{2}Si_{2}O_{8} (anorthite) which is a major phase
- Iron occurs in two phases, FeAl_{2}O_{4} (hercynite, including a solid solution of similar composition) and Fe_{2}SiO_{4} (fayalite)
- SiO_{2} (quartz) is consumed in the reactions. Silica re-manifests in Fe_{2}SiO_{4} (fayalite) and in a melt phase—the residual liquid, solidified which contains CaO, FeO, Al_{2}O_{3} and SiO_{2}

This assemblage of phases is complex and not easily grasped by phase diagrams in the technical literature. Three diagrams do, however, explain the presence of phases observed in the refractory samples, and, by implication, hint at conditions in the kiln lining:

FeO-Al_{2}O_{3}-SiO_{2} diagram. The virgin refractory is represented by the point 70% Al_{2}O_{3} on the A_{2}O_{3}-SiO_{2} binary [4]. Its composition changes with the addition of FeO. Concomitant with the change is a drop in the solidus temperature: in the range 33–55% FeO, it drops to 1088°C. Recrystallisation under conditions of thermodynamic equilibrium produces an assemblage of FeAl_{2}O_{4} (hercynite), Fe_{2}SiO_{4} (fayalite) and Fe_{2}Al_{2}Si_{3}O_{18} (iron cordierite). The first two phases are present in the reaction zone of the refractory. The third phase which, beyond 44% FeO, would be the last phase to form during cooling, is prevented from forming by the “freezing” of the melt phase in the refractory matrix.

CaO-Al_{2}O_{3}-SiO_{2} diagram. The compositional change is represented by a tie-line extending from 70% Al_{2}O_{3} on the Al_{2}O_{3}-SiO_{2} binary to the apex CaO [4]. The addition of CaO to the refractory stabilizes CaAl_{2}Si_{2}O_{8} (anorthite), Al_{2}O_{3} (corundum) and Al_{6}Si_{2}O_{13} (mullite) under conditions of thermodynamic equilibrium, and it drops the solidus temperature from ~1600°C to 1512°C. CaAl_{2}Si_{2}O_{8} (anorthite) is present in the reaction zone of the refractory.

K_{2}O-Al_{2}O_{3}-SiO_{2} diagram. Some phases in the virgin refractory (Figure 2) contained almost 6% K_{2}O. Potassium has a deleterious effect on the solidus temperature of an aluminosilicate refractory: less than 0.7% K_{2}O in LC70 lowers the solidus temperature to 985°C [4]. The solidus temperature jumps to 1140°C in the range 0.7–1.0% K_{2}O, and jumps further to 1315°C when K_{2}O in the refractory exceeds 1.0%.

The following conclusions can be drawn from this analysis:
FeO and CaO do not have an immediately damaging effect on the refractory lining. Although they do lower the solidus temperature, the solidus remains above operating temperatures in the kiln (i.e., 1100°C maximum). K_{2}O may be damaging. It lowers the solidus temperature below higher operating temperatures (close to maximum), but the liquid phase that forms remains such a very small fraction of the refractory at the hot face as to have a minimal effect.

Accretion
A cross section through Sample 3, the lump of accretion, shows layering (see Figure 4). The top, or outer, layer contains little or no metallic iron (see Table 2). Rather, it comprises three phases: an iron oxide (Fe_{1-x}O), a spinel (solid-solution members in the hercynite-magnetite series) and Fe_{2}SiO_{4} (fayalite).
Metallic iron occurs in abundance beneath this outer layer (Figure 4). It is associated with FeAl$_2$O$_4$ (hercynite) and CaAl$_2$Si$_2$O$_8$ (anorthite), two discrete phases in a silicate matrix (lower images in Figure 4). The composition of each layer is interpreted as follows:

- The chemical species making up phases in the inner layer are derived from the refractory (Al$_2$O$_3$ and SiO$_2$) and the charge to the kiln (FeO and CaO). Time under reducing conditions (i.e., low oxygen partial pressures at high temperatures) has reduced iron oxide to metallic iron. The solidus temperature of this assemblage of phases, namely Fe$_{1-x}$O (wüstite), FeAl$_2$O$_4$ (hercynite), Fe$_2$SiO$_4$ (fayalite) and metallic iron, is ~1150°C [1], which is above, albeit close, to higher temperatures measured in the kiln. Melting is, therefore, only partial.

- The chemical species making up phases in the outer layer (Layer 1) derive from the charge to the kiln i.e. from iron oxide in the lumpy iron ore and from the ash (SiO$_2$) in the coal. The iron oxide is partially reduced and the products are Fe$_{1-x}$O (wüstite) and Fe$_3$O$_4$ (magnetite).

The accretion, despite its porosity, is tough. This strength derives from the fusing and partial melting of particles, followed by recrystallisation at lower temperatures. The result is a continuous network of solid “bridges” (see lower images in Figure 4). Fusion also bonds the accretion tightly to the hot face of the refractory lining; and as chemical species diffuse across the accretion-refractory interface and phases re-equilibrate, so the accretion adheres ever more strongly to the lining. Partial melting and chemical phase re-equilibration support the mechanisms by which accretions, once formed on the kiln lining, can grow. These mechanisms do not in themselves, however, accelerate the erosion of the refractory lining. The immediate cause for accelerated erosion lies elsewhere.

### 6 conclusion

From the observations, FeO (from lumpy iron ore) and CaO (from dolomite) are constituents in phase assemblages in the reaction zone beneath the hot face of the refractory lining. Al$_2$O$_3$ and SiO$_2$ are major contributions from the refractory, and the refractory also contributes trace amounts of K$_2$O to assemblages.

In the absence of K$_2$O, the solidus temperatures of assemblages of the corrosion products lie above the range of operating temperatures (800–1050°C). In the presence of K$_2$O, the solidus temperature drops to 985°C, but rises as more K$_2$O is added. Assemblages with K$_2$O, therefore, form a liquid phase at temperatures at the high end of the operating range. The volume of this liquid fraction in the reaction zone fluctuates with rising and falling temperatures in the kiln. It nevertheless remains a very small fraction of any assemblage of phases. Although technically this liquid lowers the refractoriness of the kiln lining, it compromises the strength of the refractory only minimally, if not negligibly. It is unlikely, therefore, that corrosion reactions of the refractory at the hot face are the cause of a higher rate of erosion. However, the use of high alkali containing aggregates should be avoided. This is coherent with the recommendations of previous work [5].

The recovered samples, in common with other studies [5], all showed signs of a significant build up of accretions on the hot face. Accretions are formed in DRI kilns by the partial reduction of iron oxide and the partial

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**Table 2: Phases contained in Sample 3**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Layer 1 (top)</th>
<th>Layer 2 (below)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO (metallic iron)</td>
<td>—</td>
<td>M</td>
</tr>
<tr>
<td>Fe$_{1-x}$O (wüstite)</td>
<td>M</td>
<td>—</td>
</tr>
<tr>
<td>Fe(Al,Fe)$_2$O$_4$ (hercynite-magnetite)</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>Fe$_2$SiO$_4$ (fayalite)</td>
<td>M</td>
<td>—</td>
</tr>
<tr>
<td>CaAl$_2$Si$_2$O$_8$ (anorthite)</td>
<td>—</td>
<td>M</td>
</tr>
</tbody>
</table>

where M indicates a major constituent of the layer.
melting of the assemblage of products (temperatures in the kiln lie just below the solidus temperature of the assemblage of phases which are constituted from the charge to the kiln, fine iron ore, coal ash and the refractory itself). The accretion, despite its porosity, is tough. This strength derives from the fusing and partial melting of particles, followed by recrystallisation at lower temperatures. Fusion also bonds the accretion tightly to the hot face of the refractory lining, and as chemical species (Fe$^{2+}$ (Fe$^{3+}$, Al$^{3+}$)O$_4$, a spinel solid solution and Fe$_2$SiO$_4$, fayalite) diffuse across the accretion-refractory interface and phases re-equilibrate, so the accretion adheres ever more strongly to the lining. Partial melting and phase-chemical re-equilibration support the mechanisms by which accretions, once formed on the kiln lining, can grow. The result is a continuous network of solid “bridges”. There is no sharp boundary between accretion and refractory and the accretion is unlikely to slough off during normal operation.

These mechanisms serve to reinforce the adhesion to the lining. Because accretions are so tightly bonded to the lining, their removal by hammering is more likely to detach a layer, perhaps a few centimetres thick, of the lining. It can be imagined that this will shorten the life of the lining considerably. Rao [5] identified the formation and removal of accretions as a major cause for frequent downtimes and damage to refractory linings. The formation of accretions in DRI plants is unavoidable, but perhaps there are options that can be investigated to reduce their impact

- Ensure an installed refractory lining with good mechanical strength along the full length of the kiln and throughout the various temperature zones of the kiln. A necessary pre-condition is to ensure that the LCC’s are capable of being consistently field placed under extreme climatic conditions.
- Present a smooth surface to the kiln charge. Accretions are less likely to adhere strongly to the lining, and the lining is less likely to succumb to thermo-mechanical strains.

There is clear scope for LCC product optimisation through the use of a calcium aluminate cement. Selecting the correct calcium aluminate cement will assist with the easy installation of a homogeneous compact lining, with uniform hardening characteristics. In addition, the cement will aid the formation of a smooth lining surface. Once installed the refractory concrete should display high strength through out the operating temperature range of the kiln.

7 Acknowledgements

The authors would like to thank Mr. P. den Hoed of Mintek, South Africa, for the post mortem analysis. In addition the assistance, provision of samples and useful exchanges provided by IFGL, TRL, OCL, Maithan, Ceramics, Sharada, and Vesuvius refractories companies is gratefully acknowledged.

8 References

[1] Internal Kerneos market study
Photomicrograph of corroded hot face Sample 1

Back scattered image of corroded part

Enlargement of cross section show in fig.1

BSE image of detail in upper yellow box

BSE image of detail in lower box

- [1] Al$_2$SiO$_5$ (sillimanite)
- [2] 24.8% Al$_2$O$_3$, 47.1% SiO$_2$, 10.8% CaO, 15.5% FeO, 2.8% MnO, 1.6% K$_2$O and 0.4% TiO$_2$ (a quenched melt phase)

- [3] Fe$_{2+1.1}$Mn$_{0.1}$Fe$_{3+0.9}$Al$_{1.4}$Ti$_{0.1}$O$_{4}$ (Fe-Al spinel)
- [4] Fe$_{0.9}$Mn$_{0.1}$Al$_{2.4}$O$_{4}$ (hercynite)

- [5] Zr$_{0.7}$Si$_{1.2}$O$_{4}$ (zircon)
- [6] Al$_2$O$_3$ (corundum)
- [7] A melt phase approximating K$_{0.5}$Ca$_{0.6}$Fe$_{0.9}$Al$_{1.4}$Si$_{2.3}$O$_{8}$ (anorthite)
- [8] Fe$_{0.9}$Al$_{2.4}$O$_{4}$ (hercynite)
- [9] A melt phase approximating K$_{0.5}$Ca$_{0.6}$Fe$_{0.9}$Al$_{1.4}$Si$_{2.3}$O$_{8}$ (anorthite)

Figure 3: Cross section and photomicrographs of Sample 1 – corroded part at hot face
Figure 4: Photos of section through the accretion (Sample 3) and BSE images of the phase assemblage in the bottom half of the accretion (Layer 2)