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Microstructural characterization of alkali metal mediated high temperature reactions in mullite based refractories.

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Abstract. Two types of refractory bricks were used in reaction tests with slag from a production kiln for iron ore pellet production. Electron microscopy was used to characterize morphological changes at the slag/brick interface and active chemical reactions. Phases such as kalsilite, nepheline and potassium β -alumina form, in a layered structure, as a consequence of alkali metals migration in the brick. Larger hematite grains (50-100 μm) in the slag remain at the original slag/brick interface, while smaller grains dissolve and move through the partly dissolved brick bulk, and forms micrometer sized needle shaped crystals deeper in the lining material. Thermodynamic simulations predict the formation of a solid solution between hematite and corundum which is also observed in the reaction zone after extended time periods.

Keywords: Electron microscopy (**B**); Mullite (**D**); Al_2O_3 (**D**); Refractories (**E**).

Introduction

Refractories based on ceramic materials have been used in metallurgical processes since around 3500 B.C. when metals first were extracted from ores. Today there is an ongoing development of new refractories, but traditional alumina silicate refractories are still in

widespread use, especially in the iron- and steelmaking industry, which uses 70% of all refractories [1].

The pelletizing of iron ore as a burden material for blast furnaces was first patented 1912 by A.G. Andersson and the first commercial plant started in Minnesota, 1952. Two main processes are today used during such production: the traveling grate, and the grate-kiln process [2], where the grate is a roaster furnace and the kiln is a rotating furnace insulated with refractory bricks. Temperatures up to about 1350°C can be reached in the kiln [3]. The first iron ore pellet plant of grate-kiln type started 1960 and today there are globally 35 such Allis-Chalmers type pellet plants and a few of other types.

Refractory bricks wear and need to be replaced after some time when exposed to a corrosive atmosphere at high temperatures. In rotary kilns the wear situation is complex since several different mechanisms operates simultaneously. The main source for corrosion and wear is residues from the pellet production that together with fly ash from coal burned to heat the kiln forms a so called slag that accumulates in chunks on the bricks. This phenomenon with adhesion of deposits on the refractories is observed at different iron ore production sites and types of kilns, and it seems to be related to the quality and composition of the burner fuel [4].

Two common brick types used in such kilns have been used in this lab scale study. The dominant constituents in both brick types are alumina (Al_2O_3) and silica (SiO_2) in different amounts, but there are also traces of other oxides present. Al_2O_3 and SiO_2 in the ratio 3/2 form the mineral mullite during heat treatment, which has appropriate

refractory properties, among them high melting temperature, low thermal expansion and low thermal conductivity. Mullite is a solid solution where the amount of Al_2O_3 can vary between 55 and 90 wt%, but it is commonly expressed stoichiometric by the oxide formula $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ [5].

In general, the most harmful wear mechanism of refractory bricks in this application, is a combination of mechanical strength degradation caused by the slag and thermal shock [6]. The brick degradation is caused by concurrently active processes of chemical reactions and migration of grains from the refractory lining into flow of viscous molten slag [7].

During a chemical attack caused by alkali metal containing slag, mullite refractories corrode and some specific phase transformations occur. When alkali metal reacts with aluminosilicates, the feldspathoids nepheline ($\text{NaAlSi}_3\text{O}_8$), kalsilite (KAlSi_2O_6) and leucite (KAlSi_2O_6) are commonly formed [8], while the formation of the alkali feldspars orthoclase (KAlSi_3O_8) and albite ($\text{NaAlSi}_3\text{O}_8$) depend on time and presence of free SiO_2 , and jadeite ($\text{NaAlSi}_2\text{O}_6$) only forms under high pressure [9]. The formation of these phases are assumed to contribute to the degradation of the bricks. However, proper descriptions of the wear mechanisms are still lacking to facilitate improved life time through proper brick design. Thus, this paper gives detailed descriptions of the chemical reactions occurring at the interface between the brick and alkali metal containing slags. The reaction zone is characterized after different types of heat treatments by x-ray diffraction (XRD) and electron microscopy and spectroscopy (QEMSCAN and SEM), and the experimentally observed reaction products are compared to thermodynamic simulations of the same system.

Experimental procedure

Two different types of bricks were used in this study, one based on bauxite (product name: Victor HWM, Höganäs Bjuf) and on andalusite (product name: Silox 60, Höganäs Bjuf). The chemical compositions of the bricks, based on datasheets from the producer, are shown in Table 1. Their porosity is between 15 and 20 % and their density 2500-3000 kg/m³. The slag used in this study was collected at the outlet of a production kiln located in Svappavaara (LKAB), Sweden, during a production stop. Additives used were K₂CO₃ and Na₂CO₃ (both from Merck, 99.9 wt% purity).

The reactions between brick material and slag were conducted through a series of crucible/slag reaction tests. Crucibles were machined from both brick types in their as fabricated condition, with dimensions of 40x40x50 mm³. The diameter of the cavity was 16 mm, with a depth of 25 mm. Each cavity was filled with a milled 8 g powder mixture comprised of slag, 5 wt% sodium and 5 wt% potassium, both in the form of carbonates. The crucibles were heated to different temperatures near the process temperature in the kiln for different holding times. After heat treatment, the crucibles were cut in two parts along the center of the cavity, to facilitate investigation of the slag/brick interface. The interfaces were polished and carbon sputter deposited prior to electron microscopy.

The chemical composition of the slag were determined by x-ray fluorescence spectroscopy (XRF) using rhodium x-ray radiation, a flow proportional counters for Na, Mg and Al and a scintillation counter for all other elements over a 2 θ -interval of 22 to 145°, using a PANalytical MagiX instrument.

The x-ray diffraction experiments were conducted on as fabricated bricks, milled to a powder, with a Philips X-ray diffractometer (MRD) instrument, using Cu K α radiation. The diffractograms were recorded over an interval 10 to 90° of 2 θ . Scanning electron microscopy (SEM) studies were carried out in a JEOL JSM-6460 (software INCA), equipped with energy dispersive spectroscopy (EDS). To map the location and chemical composition of the minerals present in the sample, quantitative mineralogical evaluations using a QEMSCAN[®] system were performed. The system is based upon a Zeiss E340 scanning electron microscope with four energy dispersive x-ray spectrometers (EDS). The resulting x-ray and backscattered electron signals (BSE) are compared with a database of known minerals and amorphous phases to produce a mineralogical identification [10-12]. Species with similar EDS-spectrum such as magnetite and hematite, can be differentiated by different BSE signal, while it is still difficult to separate magnetite and wüstite, since the software does not differentiate crystal structures [13]. Several studies have been performed using this type of instrument, for different mineralogical systems, such as aluminosilicates in fly ash [14], kimberlite ores [15], and gold-bearing ores [16]. In this study phase maps were recorded based upon point analysis with a step size of 7 μ m.

A mineral database – Species Identification Protocol (SIP) – was used in the QEMSCAN[®] studies for phase identification. The SIP is built by the user to describe the different minerals and slags. These include amorphous phases, boundary phases and minerals with impurities. In this work special attention was given to the definitions of complex slag phases, hematite, corundum and mullite, all with variable composition. The SIP was built using detailed x-ray spectra which were collected at different sample areas of interest. For phase identification, the software works through the SIP from top

to bottom and defines the measurement according to first match. The SIP is sorted with the minerals first, followed by defined slags and other undefined groups. Table 2 gives the compositions of the modified SIP-entries used in this study.

Thermodynamic simulations were carried out with the software Factsage, version 5.5 (Thermfact/CRCT, GTT-Technologies) using the equilibrium package. A complex system such as a refractory-slag system never reaches equilibrium, but simulations were performed to give an indication of which phases that represent the end points of the reactions. The simulations were performed in the temperature range between 500 and 1400°C, in inert atmosphere at ambient pressure.

Results

The composition of the slag used in the tests is presented in Table 3. The slag is assumed to be fully oxidized, thus its composition is presented as oxides (in wt%).

The x-ray diffractograms of powders of milled bricks Victor HWM and Silox 60 in their as received condition show that mullite and corundum are present in both brick types (Fig. 1). In addition both bricks contain traces of other oxides, including quartz.

Figure 2 depicts graphically the minerals assays detected by QEMSCAN of the investigated samples and the minerals concentrations. The color codes used in Figure 2 is also used in the field images (Fig. 3 and 4). Abbreviations used in the figure are: V=bauxite based brick and S=andalusite based brick, e.g. S(24)1400 should be read as crucible made from the andalusite based brick tested at 1400°C for 24 hours.

The mineral assays are generated from a frame size of a minimum of 0.5 cm². The mineral assays confirm that both brick types in their as received condition contain primarily corundum and mullite (*Corundum*, *Mullite* and *Mullite (Ca-K)*). The bauxite based brick has a higher Al₂O₃ content which is seen in Fig. 2 as a higher *Corundum* content. In the case of the reactions zones, the mineral assays should be read with some caution since the volume fractions of the formed phases are strongly related to the frame size. However, for the brick based on bauxite the major reaction products are: *Corundum (K)*, *Corundum (Fe)*, *Alumina silicate matrix*, *Mullite needles in alkali glass* and *Slag (Al-Fe)*, and for the andalusite based brick: *Alumina silicate matrix*, *Slag (Al-Fe)* and *Slag (Al-Si)*. Also some hematite from the added slag is found in the samples such as *Hematite* and *Hematite (Al)*.

Brick - slag interface characterization

Figure 3 shows Qemscan micrographs of the interaction zones between bauxite based brick and slag, after 5 (Fig. 3(a)) and 72 (Fig. 3(b)) hours at 1400°C. After 5 hours *Hematite* is dominating at the surface. Below the surface several layers have evolved, first two layers mainly consisting of *Hematite (Al)* and *Hematite (Al-K)*. Below the *Hematite* zone *Corundum (High Fe)* and *Slag (Al-Fe)* are present and even deeper layers of *Corundum (K)* and *Slag (Al-K)* are observed. A reaction layer has formed between the hematite and corundum zones. Deeper into the brick alkali metal has penetrated further and is found mainly as *Mullite needles in alkali glass*. The corundum grains are intact and some alkali metal has migrated along the grain boundaries. In addition, closely related to the alkali metal migration fronts the phase potassium β-alumina and the feldspathoid minerals kalsilite and nepheline are formed.

After heat exposure for 72 hours (Fig. 3(b)) *Hematite* is dominating together with needles of *Corundum (Fe)* at the surface. Further down, a *Corundum* and *Mullite* zone is present. Below a zone with *Corundum* and *Alumina silicate matrix* is present. The corundum and hematite solid solution, *Corundum (Fe)*, have increased in concentration compared to 5 hours test, seen as needle like formations at the surface. The reaction layer is here more diffuse. Much of the alkali metal is present in the *Alumina silicate matrix* which is distributed over a relatively large area.

Qemscan micrographs in Figure 4 shows the interaction zones between the andalusite based brick and slag, after 5 (Fig. 4(a)) and 72 (Fig. 4(b)) hours at 1400°C. At the surface in the 5 hours test, *Hematite* is dominating together with the *Slag (Al-Fe)*. Further into the reaction zone the *Slag (Al-Fe)* is still present together with *Hematite (Al-K)* and *Corundum (High Fe)*. Closer to the *Mullite* area a zone of *Corundum (K)* and *Slag (Al-Si)* is found. A distinct reaction layer has formed between the hematite and corundum/mullite. Below this reaction layer a crack is seen between the layer and the bulk of the brick material. Alkali metal penetration further into the bulk material is less pronounced with increasing depth, and mullite and corundum grains are intact.

At the surface in the 72 hours test, *Hematite (Al)* is dominating at the surface together with needles of *Corundum (Fe)*, below which a zone with *Corundum* and *Alumina silicate matrix* is present. A third and fourth layer are dominated by *Corundum* and *Mullite*, and *Corundum* and *Orthoclase*, respectively. The surface contains adhered hematite with corundum and hematite solid solution needles. The reaction layer is more diffuse in this test, compared to samples with 5 hours dwell time. A majority of the

alkali metal is present in the *Alumina silicate matrix* which is distributed across the entire reaction zone.

High resolution analysis performed by SEM/EDS shows the migration of hematite through the partly dissolved and porous brick bulk by capillary infiltration and diffusion. It appears as needle shaped formations deeper in the brick material. A typical image of the migration is illustrated in Figure 5(a) and is found in both brick types. Figure 5(b) shows needle like formations with stoichiometric proportions $K_2O \cdot 11Al_2O_3$ that are more profound in the bauxite based brick than in the andalusite based brick. The label used in the Qemscan analysis of this phase is *Corundum (K)* and it is referred to in the literature as potassium- β -alumina [17]. Secondary mullite is formed around the mullite grains in the presence of alkali metals in both brick types, shown in Figure 5(c). In the Qemscan images the secondary mullite is called *Mullite needles in alkali glass*.

The tests show that the brick with higher corundum content (bauxite based) have a less distinct penetration front and the corundum grains stay more intact. The alkali metals have migrated along the grain boundaries in the high corundum brick, while the andalusite based brick create a reaction layer, shown in Figure 5(d). Such reaction layer is reported to prevent further slag penetration [17] and consists of nepheline [18] that forms a dense layer through a volume expansion, outside the layer of secondary mullite. Also observed, is that the slag adheres harder to the andalusite based brick.

From the reaction test with 72 hours dwell time at 1400°C, the corundum and hematite solid solution have further increased in concentration (Fig. 6), and appears as needle like formations in both bricks. The white regions adjacent to the needles are hematite

with the presence of titanium and without aluminium. Thus the corundum/hematite solid solution is Ti depleted while it retains Al. Most of the alkali metals have evaporated or migrated out of the slag and into the brick. The progression of the reaction zone is therefore affected by the lack of alkali metals to drive the zone further. Noteworthy is that the protective nepheline reaction layer observed in the andalusite based brick after 72 hours, is now lost and the penetration front looks similar in both crucible types.

Thermodynamic simulations

The composition of the system used for the first thermodynamic simulation was:

- 5 grams of $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (mullite)
- 1 gram of K_2CO_3
- 1 gram of Na_2CO_3

This is an approximation of the composition in the brick crucible tests when excluding hematite. The result of the simulation is shown in Figure 7(a) as phase fraction as a function of temperature. The simulation is based on reaching equilibrium at every temperature, which results in reactions between alkali metals, mullite and corundum at considerably lower temperatures than what is experimentally observed. Only solid phases and gaseous (not shown) are considered. The Al_2O_3 and the mullite are already disintegrated at 550°C when the simulation starts. Instead $\text{K}_2\text{Al}_{12}\text{O}_{19}$, NaAlSiO_4 , KAlSiO_4 , and Na_2CO_3 appear. At 700°C the Na_2CO_3 disappear, and KAlO_2 forms. The largest variation in concentrations is at 1100°C when $\text{K}_2\text{Al}_{12}\text{O}_{19}$ totally disappear to the benefit of $\text{KAl}_9\text{O}_{14}$.

In a second thermodynamic simulation 5 g of Fe_2O_3 (hematite) was added to the previous starting composition. The result of the simulation is shown in Figure 7(b).

The difference between the two simulations is that in the second case with Fe_2O_3 addition, Al_2O_3 and Fe_2O_3 forms a solid solution (labeled corundum) already at the starting temperature, which at most, incorporate ~10% Al_2O_3 . At temperature above 1200°C this phase transform to a spinel phase, which above 1250°C also incorporate Al_2O_3 from the $\text{KAl}_9\text{O}_{14}$, which then increase its amount.

Discussion

This work focus on the degradation of bricks serving as refractory liners in rotary kilns at iron ore pellet production; i.e. characterization of occurring chemical reactions and alkali metal migration in mullite based refractories. The observed reactions between brick and slag are as expected more enhanced by increased temperature compared to increased dwell time, both in terms of penetration depth of slag into the bricks, corrosion of the bricks, and how the slag adheres to the brick surface. Micrographs reveal that alkali metals react primarily with mullite, and secondarily with Al_2O_3 , forming $\beta\text{-Al}_2\text{O}_3$ which is expected based on the literature [17, 19]. The penetration front is less distinct in the bauxite based brick, where corundum exists in higher amounts. Corundum grains keep more intact than mullite grains but the grain boundaries corrode and the grains migrate into the slag. The slag adheres harder to the andalusite based brick that has a lower corundum concentration.

The interaction between slag and bricks observed in this study can be described as: grains of hematite with sizes between 50-100 μm remain at the original surface of the brick. Hematite species, migrates and penetrates through the partly dissolved and porous

brick by capillary infiltration and diffusion, and forms in needle shaped crystals deeper in the lining material. Hematite has an isomorphic structure to corundum and to some extent forms a solid solution according to the thermodynamic simulations, which is also seen experimentally as these needle-like formations. Below the layer of dissolved brick that contains these two types of hematite needles, another layer of β -alumina and feldspathoids are formed, seen experimentally and in accord with the thermodynamic simulations. This disintegration of mullite that results in formation of nepheline is associated with a volume expansion, observed by dilatometry to occur fastest between 650 and 750°C [18] and in some cases causing cracks in the tested crucibles. A third deeper layer with secondary mullite forms by the molten feldspar present during the heat treatment. Mullite in needle-like formations in an alkali metal rich glass is in accord with earlier observations [20-23], where nucleation of primary mullite occurred in an amorphous silica glass (sizes less than 0.5 μm), and the alumina richer secondary mullite started to grow from the primary mullite, in needle shaped formations (lengths above 1 μm) in the presence of an amorphous alkali-aluminosilicate melt. Potassium that causes this transformation is the element that migrates deepest into the brick. Scudeller et al. [8] suggested that K_2O reacts with SiO_2 , forming a glassy matrix. With time kaliophilite ($\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), the cubic form of kalsilite, is formed; and with longer time and depending on the presence of free SiO_2 , leucite ($\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$) is formed. At a dwell time of 72 hours a high concentration of a glassy *Alumina silicate matrix* is present, especially in the andalusite based brick, which further enhances the degradation of the brick [18].

Potassium beta-alumina ($\beta\text{-Al}_2\text{O}_3$) was observed as a reaction product in needle like formations, which is in agreement with thermodynamic simulations that predict the

presence of $\text{KAl}_9\text{O}_{14}$ with similar composition. $\beta\text{-Al}_2\text{O}_3$ containing sodium and/or potassium are observed in the literature in needle like formations [24] and with different molar ratios [8, 17, 24-26]; where the β' and β'' phases contain an increasing amount of alkali metals. The $\beta\text{-Al}_2\text{O}_3$ is no longer present after for 72 hours, to the benefit of the *Corundum (Fe)* solid solution and the *Alumina silicate matrix*. In order to improve the lifetime of the refractories primarily the penetration of potassium needs to be suppressed.

The corundum-hematite solid solution depleted of Ti formed after long dwell time at high temperatures (see in Fig. 6), has previously been observed [27-29] and is predicted by thermodynamic simulations (not shown). According to literature, the Hem(ss) can incorporate 8% Al_2O_3 , and the Cor(ss) can incorporate Fe_2O_3 8% at 800°C. At 1300°C the concentrations are increased to 12wt% and 15wt% respectively. Above 1318°C the phase AlFeO_3 is formed [30]. The maximum TiO_2 concentration in Fe_2O_3 at 1200°C is 12.3 mol%, while Fe_2O_3 maximum concentration at 1200°C in TiO_2 is 0.8 mol% [28]. The maximum TiO_2 concentration in Al_2O_3 is ~0.3 mol%, while Al_2O_3 is not soluble in TiO_2 [29]. Titanium is instead often included by the phase pseudobrookite ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$) on the form M_3O_5 , a solid solution that can include other cations (e.g. Al^{3+} , Mg^{2+}) [31-32], or have a higher iron concentration similar to our experiment. A pseudobrookite with aluminium is often referred to as $\beta\text{-Al}_2\text{TiO}_5$. Another phase observed in the system, with confirmed stoichiometry $\text{Al}_6\text{Ti}_2\text{O}_{13}$ and orthorhombic crystal structure were synthesized by Norberg et al. [33]. Among these solid solutions between phases, observed in the literature [27-32], what satisfies best with our observation (Fig. 6) is a hematite incorporating Al_2O_3 (large arrows in Fig.) and a hematite incorporating TiO_2 (small arrows in Fig.), both depleted of TiO_2 and Al_2O_3 respectively.

Conclusions

- The presence of alkali metals cause several types of chemical reactions that are detrimental to the lifetime of both types of brick investigated.
- Potassium is more detrimental than sodium since it penetrates deeper in to the brick.
- The alkali metals penetrate deeper in the high corundum bricks, forming β -alumina, nepheline and kalsilite accompanied with a volume expansion that causes brick degradation through cracking.
- The slag adheres harder to the brick with lower corundum concentration.
- A protective reaction layer is formed in the low corundum brick, which only stays intact at lower temperatures and short dwell times.
- Grains of hematite, with sizes between 50-100 μm , were observed to remain on the origin surface of the brick, while hematite species migrates through the partly dissolved and porous brick bulk by capillary infiltration and diffusion, and forms needle shaped crystals deeper in the lining material.
- At high temperature corundum and hematite forms a solid solution, which is depleted of Ti.

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Tables with captions

wt%	Victor HWM	Silox 60
Al ₂ O ₃	~73	~60
SiO ₂	~26	~37
CaO	0.2	0.1
TiO ₂	2.7	1.5
Fe ₂ O ₃	1.1	0.9
Alkalis	0.3	0.5

Table 1. Chemical composition of refractory bricks used in this study.

	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O
Alumina silicate matrix	25 ± 5	40 ± 5	10 ± 3.5	15 ± 6	10 ± 3.5
Slag (Al-Fe)	30 ± 5	25 ± 5	25 ± 3.5	10 ± 6	10 ± 3.5
Slag (Al-Si)	45 ± 5	30 ± 5	10 ± 3.5	10 ± 3	5 ± 3.5
Hematite (Al)	35 ± 5		50 ± 7	10 ± 3	
Hematite (Al-K)	45 ± 5		50 ± 3.5	10 ± 3	
Mullite needles in alkali glass	50 ± 5	30 ± 5	5 ± 3.5	10 ± 3	5 ± 3.5
Mullite	60 ± 5	40 ± 5			
Mullite (Ca-K)	65 ± 5	5 ± 5	7 ± 7	20 ± 6	5 ± 3.5
Corundum	100 ± 5				
Corundum (K)	70 ± 10	5 ± 5	10 ± 10	10 ± 3	5 ± 3.5
Corundum (Fe)	85 ± 5		15 ± 3.5		
Corundum (High Fe)	55 ± 5		40 ± 7	10 ± 3	

Table 2. Composition in wt % for modified entries in the Species Identification Protocol (SIP) used in the Qemscan analysis.

Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	CaO	FeO	TiO ₂	Na ₂ O	K ₂ O	V ₂ O ₅	MnO	P ₂ O ₅
92.45	3.11	0.99	1.38	0.58	0.54	0.29	0.128	0.102	0.19	0.09	0.053

Table 3. Chemical composition of the slag used in the experiments.

Figures with captions

Figure 1. XRD diffractogram of the original brick materials Victor HWM and Silox 60.

Figure 2. Mineral assay of different minerals and phases from the Qemscan analysis.

Figure 3. Phase maps generated by Qemscan field image scans showing Victor HWM and the interaction zone with the slag after 5 (to left) and 72 (to right) hours at 1400°C. Identified phases in different reaction zones are given to the right of the images.

Figure 4. Phase maps generated by a Qemscan field image scans showing Silox 60 and the interaction zone with the slag 5 (to left) and 72 (to right) hours at 1400°C. Identified phases in different reaction zones are given to the right of the images.

Figure 5. Back scattered electron micrographs that shows; (a) hematite migrated through the dissolved brick in needle shaped formations, (b) formation of potassium-beta-alumina, and (c) formation of secondary mullite; all from the Victor HWM crucible in the test at 1400°C (5h), and (d) the reaction layer between mullite and slag, from the Silox 60 crucible in the test at 1400°C (5h). Seen in image (d) is: (i) hematite in needle formations in the slag phase, (ii) formation of nepheline together with mullite needles, (iii) secondary mullite, and (iv) primary mullite.

Figure 6. Back scattered electron micrograph from the Silox 60 crucible test at 1400°C (72h). Large arrows to right mark the needle formations of the corundum-hematite solid solution, small arrows to right in the image mark the periphery of these needles that consists of hematite with Ti, depleted of Al, the circle marks hematite grains in snow flake formations, in an alumina-silicate matrix.

Figure 7. Thermodynamic simulation of a system consisting of (a): mullite, K_2CO_3 , and Na_2CO_3 , and (b): mullite, hematite, K_2CO_3 , and Na_2CO_3 ; both carried out between 500 and 1400°C in argon atmosphere at ambient pressure.