SMELTING-REDUCTION OF BAUXITE FOR SUSTAINABLE ALUMINA PRODUCTION

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ABSTRACT

Bauxite ore is the main raw material for aluminum production, it is converted into alumina (Al_2O_3) to obtain a proper charge material for aluminum production in Hall-Héroult process. Bayer process is the main commercial alumina production method in which bauxite ore is first digested by NaOH at moderate hydrothermal conditions, followed by aluminum hydroxide ($Al(OH)_3$) precipitation from the obtained sodium aluminate solution. Calcination of the hydroxide to alumina yields a high purity alumina feedstock for aluminum production. One of the main by-products of the Bayer process is red mud, which is separated from the bauxite solution after digestion and contains significant amount of iron oxide. Red mud is one of the most important disposal materials in the world with no commercial use. Alternative sustainable process for bauxite treatment to alumina is Pedersen process, which was patented in 1920s. This process was run for 40 years on a commercial scale before it was closed down due to the high cost of the alumina produced. The Pedersen process is more sustainable compared to Bayer process regarding lower CO_2 emission and energy consumption. In this process, iron (the main impurity in bauxite) is removed from the ore through a smelting reduction process, which yields pig iron and high alumina containing slag. The slag is further hydrothermally treated to alumina through an economical process. In the present study, the carbothermic reduction of bauxite is studied at elevated temperatures through experimental work with lime addition as the flux. The effect of process temperature, slag chemistry, and type of carbon material on iron removal is studied. Moreover, the distribution of the elements such as Si, Ti, Al, Ca, … and so forth is investigated under different process conditions. The chemical, physical, and microstructural properties of the produced slags are also studied.

INTRODUCTION

Alumina production from a variety of raw materials is possible and there are significant publications in this area. The main commercial process for alumina production, and an alternative process are described in details as follows.

BAYER PROCESS

Alumina is mainly produced from bauxite ore through the well-known Bayer process, a hydrometallurgical process invented by Carl Josef Bayer in 1888-1892.[1] In this process bauxite ore is the main raw material and it is digested together with lime addition by a solution of caustic soda (NaOH). This causes a saturated solution of sodium aluminate with insoluble impurities. The suspended solid particles are separated in a clarification step, which is called red mud, is discarded. Aluminum hydroxide ($Al(OH)_3$) crystals are precipitated from the sodium aluminate solution through the addition of fine $Al(OH)_3$ seeds and a caustic solution is reproduced, which is reused in the digestion step. The calcination of the produced aluminum hydroxide yields alumina product.[2] The main process byproduct is the red mud that contains significant amount of iron oxide, usually in the range 30-50% Fe_2O_3, and also significant amount of aluminum oxide, usually in the range 15-25% Al_2O_3.[3] The Red Mud production indeed represents an environmental problem because of its alkalinity and being stored in holding ponds.[4] In addition, red mud production causes a direct loss of the iron and aluminum units contained in the ore. Although there have been many research activities about red mud processing and minimizing its production, there is not still a global economic solution for red mud usage. In addition, red mud has shown significant negative environmental effects i.e. the red mud flooding several towns in Hungary in 2010.[5]

PEDERSEN PROCESS

An alternative process for alumina production was patented in 1920s by Harald Pedersen[6], which was commercialized and had production of 17000 ton per year until 1969 in Høyanger, Norway. The process flowsheet is shown in Figure 1. In this process, bauxite ore is smelted with lime as the flux and is partially reduced by coke. As seen this yields pig iron due to the carbothermic reduction of the iron oxides to metallic iron, and a calcium-aluminate slag, which is further hydrometallurgically treated for alumina extraction. The slag is first pulverized and further digested by using a sodium carbonate solution. A non-soluble residue is separated from the produced sodium aluminate solution in the classification step, which is called grey mud. The precipitation of aluminum hydroxide from the solution is through carbon dioxide injection, which yields a sodium carbonate solution, and it is reused in the digestion step. Pedersen process is in principle a more sustainable process compared to Bayer process with regard to no red mud production, and the production of consumable by-products; pig iron and grey mud.[6,7,8 9,10]
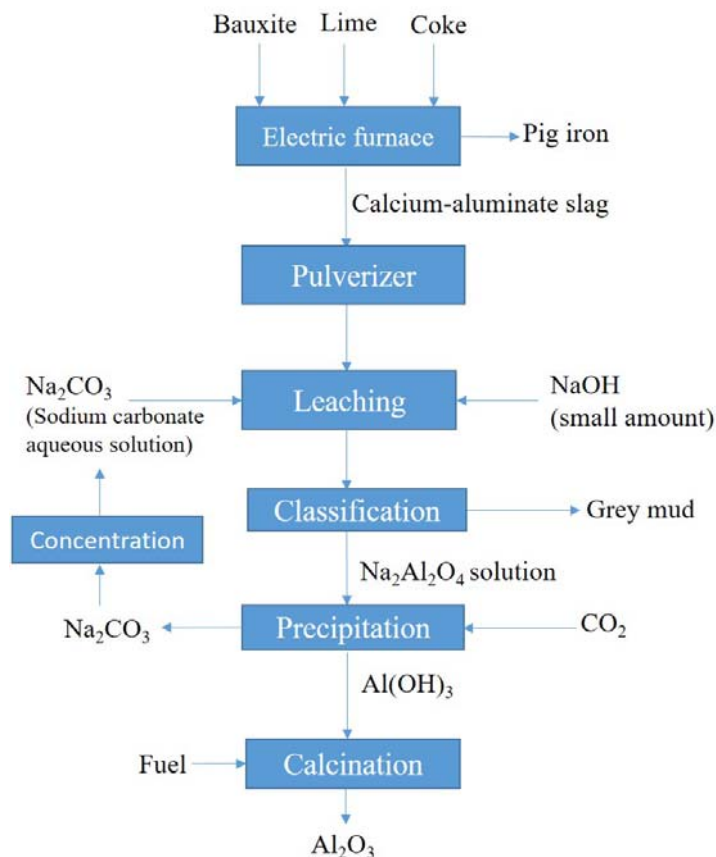
Figure 1: Flowsheet of material flow in Pedersen process for alumina production.

In the present research work, the pyrometallurgical part of the Pedersen process is studied through the smelting-reduction of bauxite and studying the distribution of the elements between the slag and metal phases.

EXPERIMENTAL PROCEDURE

A commercial bauxite ore was used in the present research which contained mainly Gibbsite $Al(OH)_3$, Kaolinite $(Al_2Si_2O_5(OH)_4)$, hematite (Fe_2O_3) and TiO_2. The structural moisture of the ore is removed in heating the ore to elevated temperatures and therefore the calcined form of the ore may be more important to be considered. The chemical composition of the calcined form of the bauxite is presented in Table I.

Table I: Chemical composition of the main components of calcined bauxite (wt%)			
Al_2O_3	Fe_2O_3	SiO_2	TiO_2
59.8	21.8	15.9	2.4

Calcium oxide with purity around 99% was added to the milled bauxite to obtain a CaO/Al_2O_3 ratio equal to unity with regard to the Al_2O_3 concentration in calcined bauxite. In addition, fine coke particles 50% more than the stoichiometric required for complete reduction of the hematite in the ore was added. The coke contained 97.1% fix carbon, 2.3% ash and 0.5% volatile matter. The powders of the materials were mixed and put in a graphite crucible for smelting.

Smelting of the bauxite+lime+coke sample was done in an induction furnace with a water cooled copper coil (Figure 2). The temperature of the sample was measured by a thermocouple type C located in an alumina insulating tube inserted into a graphite tube, which was fixed in the crucible. The furnace chamber was evacuated and filled out with argon, and the sample was

heated while there was a continuous argon flashing through the furnace. The heating was slow with around 15˚C/min to 1000˚C to have proper calcination of the bauxite, and then it was heated faster with around 30 ˚C/min to 1600˚C. The sample was completely molten after a while and sample was hold at 1600˚C for 20 minutes. Then the sample was cooled down with a moderate rate of 20˚C/min to the room temperature.
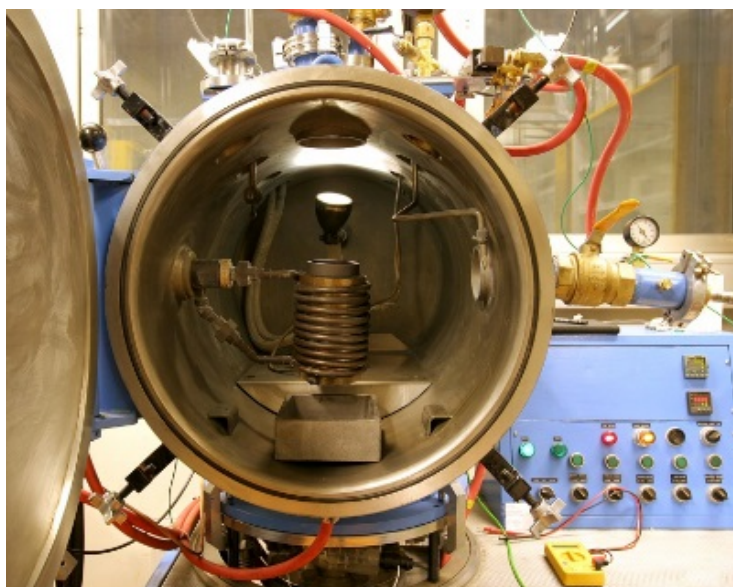

Figure 2: Induction furnace used for smelting-reduction experiment.

After smelting-reduction experiment, the crucible was crushed and metal containing particles were separated from the slag phase by magnet. Metallography samples were prepared through mounting in resin and polishing. Then the structure and composition of the phases were studied by Electron Probe Micro-Analyzer (EPMA) supported by Energy Dispersive Spectroscopy (EDS) and Wavelength Dispersive Spectroscopy (WDS) technique.

RESULTS AND DISCUSSION

The results of the microstructural analysis are presented and discussed as follows.

Reduced slag analysis

The coexisting phases in the two samples are presented in Figure 3 in low magnification. As we see the slag contains four main phases with regard to the shape and structure; a grey phase (1) with mostly angular shape, more bright grey phase (2) with porous structure, granular grey phase (3) with small size, and bright phase (4) with irregular shape.
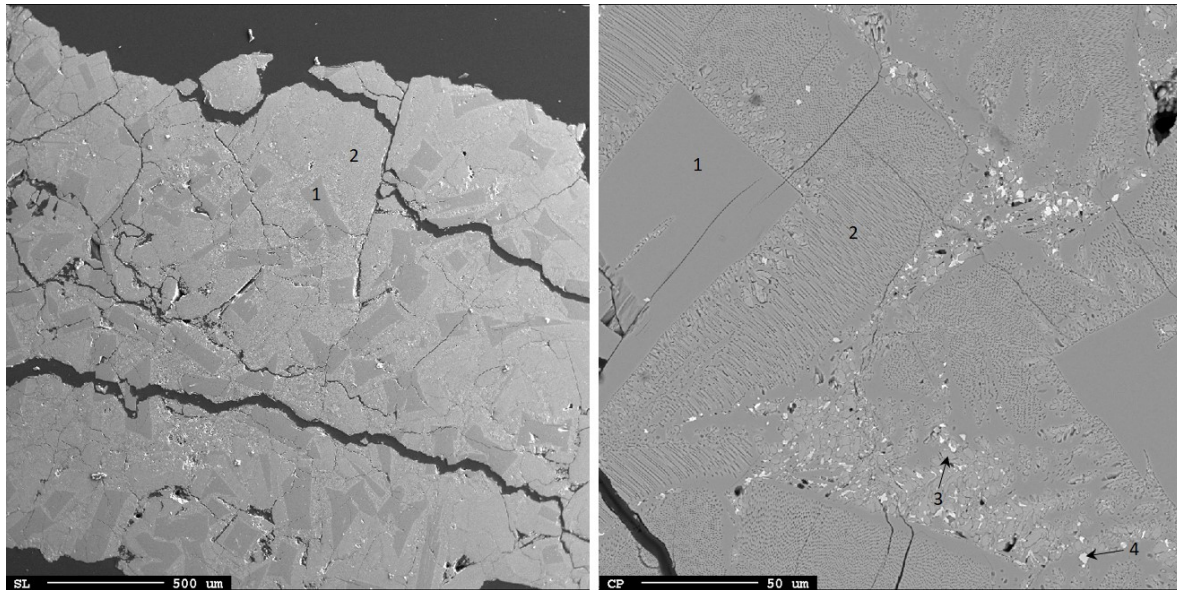
Figure 3: Electron microscopy images of reduced slag at different magnifications and the coexisting phases (1) to (4), left: SE mode, right; BSE mode.

The EDS analysis of these phases show that phases (1) and (2) have relatively close chemical compositions and they contain mainly Ca, Al, Si and O elements. However, Al concentration in phase (1) is higher than that in phase (2) as seen in Figure 4 with a taller Al peak. WDS analysis of these two phases by EPMA indicates more accurate chemical analysis as presented for three analyzed points of each phase in Table II. Obviously, phase (1) has higher Al concentration compared to the phase (2). However, phase (2) shows higher concentrations of Ca and Si than Phase (1). It is worth noting that this difference is observed, while the oxygen concentrations in the two phases are almost the same. The data in Table II show that these two main phases are very low in Fe and Ti and therefore the produced slag is mainly a Al_2O_3-CaO-SiO$_2$ slag. The porous feature of phase (2) compared to phase (1), which has relatively close chemical composition is probably due to their formation through different reactions.

Table II: Chemical composition of phases (1) an (2) measured by WDS (wt%)						
	Al	Si	Ca	O	Fe	Ti
Phase (1)-1	18.85	9.38	27.85	37.2	0.03	0.037
Phase (1)-2	19.02	9.23	27.55	37.55	0.01	0.102
Phase (1)-3	18.86	9.32	27.76	37.51	0.02	0.096
Phase (2)-1	14.51	10.33	31.36	37.12	0.01	0.24
Phase (2)-2	14.68	10.21	31.20	37.25	0.005	0.20
Phase (2)-3	14.5	10.16	31.27	37.27	0.005	0.28

EDS analysis of the phase (3), shows that it is a calcium-silicate phase containing low concentration of aluminum and other elements. While, the closely distributed phase (4) in the microstructure has Ti and Zr elements in addition to Ca, Al, Si, Mg and O. Figure 4 indicates clearly that all the co-existing phases are very low in Fe, which confirms that the iron oxide in the bauxite has been completely removed by the smelting-reduction and a slag in very low Fe concentration has been solidified. Based on the distribution of the phases, it may be concluded that phases (3) and (4) are formed at the end of the solidification of the reduced slag, while Al_2O_3-CaO-SiO$_2$ phases are crystallized from the melt.
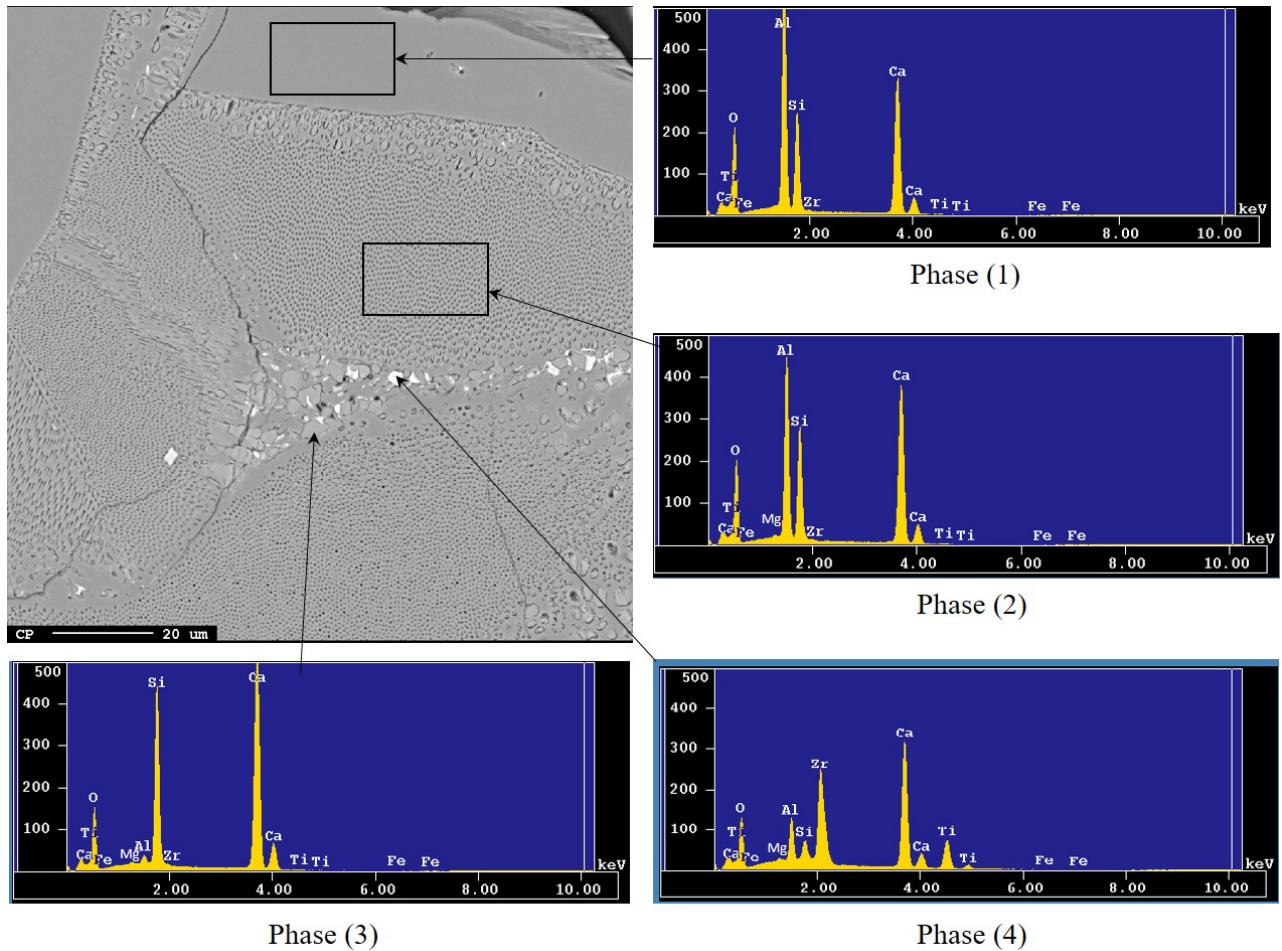
Figure 4: EDS analysis of the coexisting phases in the bulk slag phase after smelting-reduction.

Produced metal analysis

Figure 5 shows SEM images from the bottom of crucible which contains the produced metallic particles distributed in the slag. Obviously, the metal tiny drops are produced from the slag due to the carbothermic reduction and they move down due to their higher density. No formation of a large metal phase may be due to the short time of the experiment (20 min). The application of BSE mode as illustrated for a particle in Figure 5 shows that the produced metal contains three phases with specific form and distribution; a bright metal matrix, dark graphite flakes randomly distributed in the metal, and a grey phase spread on the metal surface. Qualitative EDS analysis of the bright metal matrix and the grey phase are shown in Figure 6. As we see the metal matrix contains mainly Fe and Si, while the grey phase around is consisted of Tin, V, Fe, Nb, Si and Al.
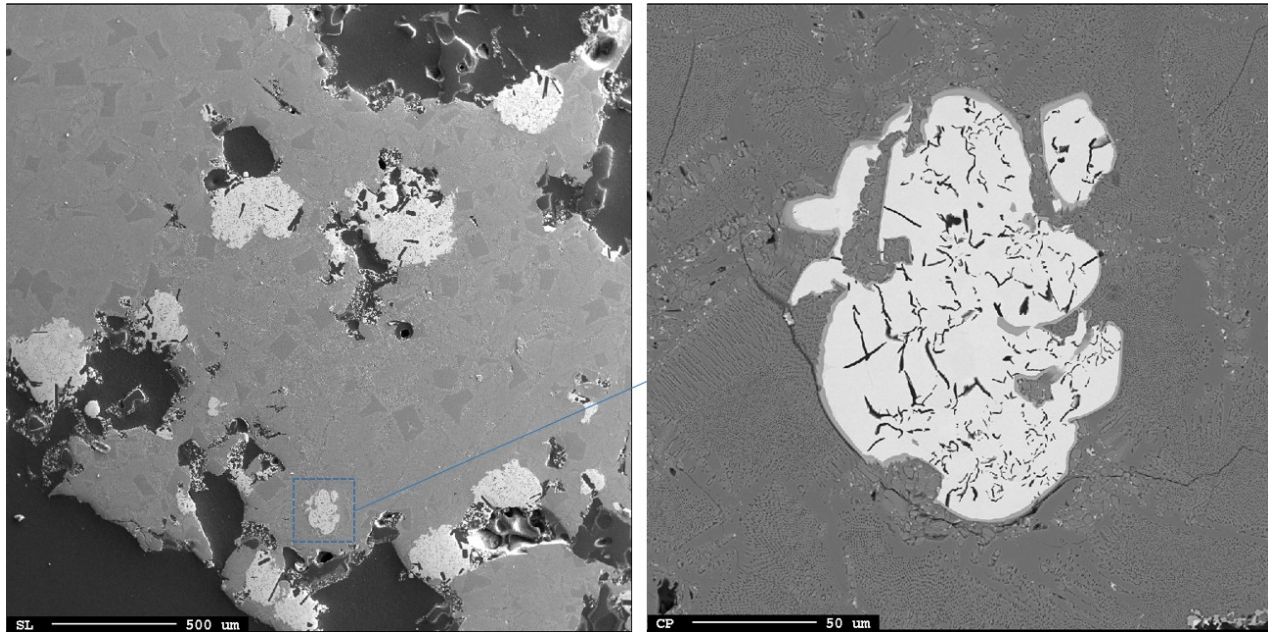
Figure 5: Electron microscopy images of reduced slag and produced metallic phases at different magnifications left: SE mode, right; BSE mode.
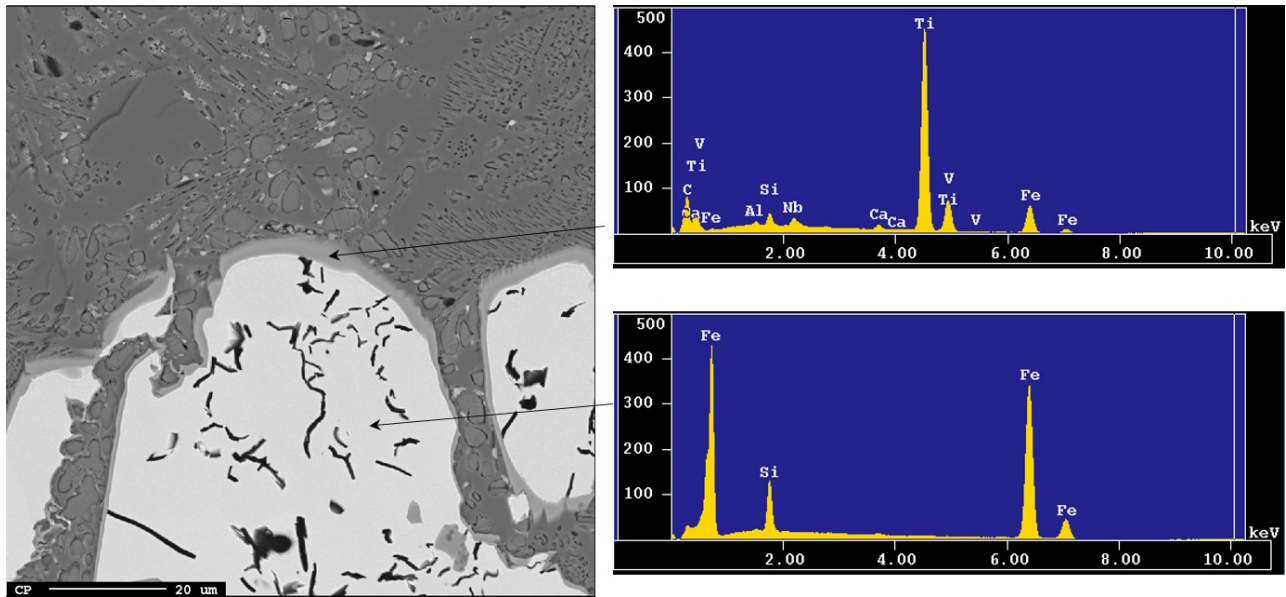

Figure 6: EDS analysis of the coexisting metallic phases produced in smelting-reduction.

In order to more precisely characterize the two phases, they were analyzed by WDS using EPMA and the results are presented in Table III. As we see the metal phase matrix contains around 93.5%Fe and 4.8%Si. It is worth mentioning that the coexisting graphite phase is formed due to the solidification of a molten iron containing carbon in saturation. Based on the thermodynamics of Fe-Si-C[11] we may estimate minimum 3.9wt% carbon solubility in the Fe-Si-C alloy. The carbon content can be, however, higher with regard to the existence of impurities in the molten metal such as Ti, V and Nb. The EDS analysis of the grey metallic phase surrounding the metallic particle shows the existence of significant amount of Ti followed by much smaller amounts of Fe, V, O and Nb. Applying X-ray mapping of the particle revealed that this phase is rich in carbon compared to the rest of sample. It is worth mentioning that the sample was coated by carbon for electron microscopy study. The X-ray mapping of the elements is shown in Figure 7 and it indicates that the grey phase is a carbide phase with regard to the high concentration of carbon and carbide forming elements Ti, V, Fe, Nb,… in it. Based on the shape of this phase which is almost all over the surface of the metal phase we may say that it is formed from the melt

during solidification. Hence, the molten metal phase is iron containing many impurities and during solidification graphite flakes are precipitated simultaneously with Fe-Si alloy solidification and a part of the dissolved carbon in the melt is then causes the formation of carbides (TiC, VC, Fe$_3$C,....).

Table III: Chemical composition of metal-containing phases by WDS (wt%)						
	Al	Si	Ca	Fe	Ti	C
Iron matrix-1	0.11	4.8	0.15	93.50	0.13	-
Iron matrix-2	0.05	4.71	0.09	93.68	0.08	-
Iron matrix-3	0.07	4.78	0.08	93.83	0.08	-
Carbide	0.25	1.28	0.61	13.22	48.26	Balance
Carbide	0.23	2.75	0.77	6.31	41.65	Balance
Carbide	0.22	0.44	0.65	4.04	62.79	Balance

The complete reduction of iron oxide from the ore in short smelting and reduction time at the reaction temperature may indicate that the process is very fast. Since the slag is very low in iron (Table II), the usage of the slag in the leaching process yields a high purity alumina product, low in iron and also no red mud production.
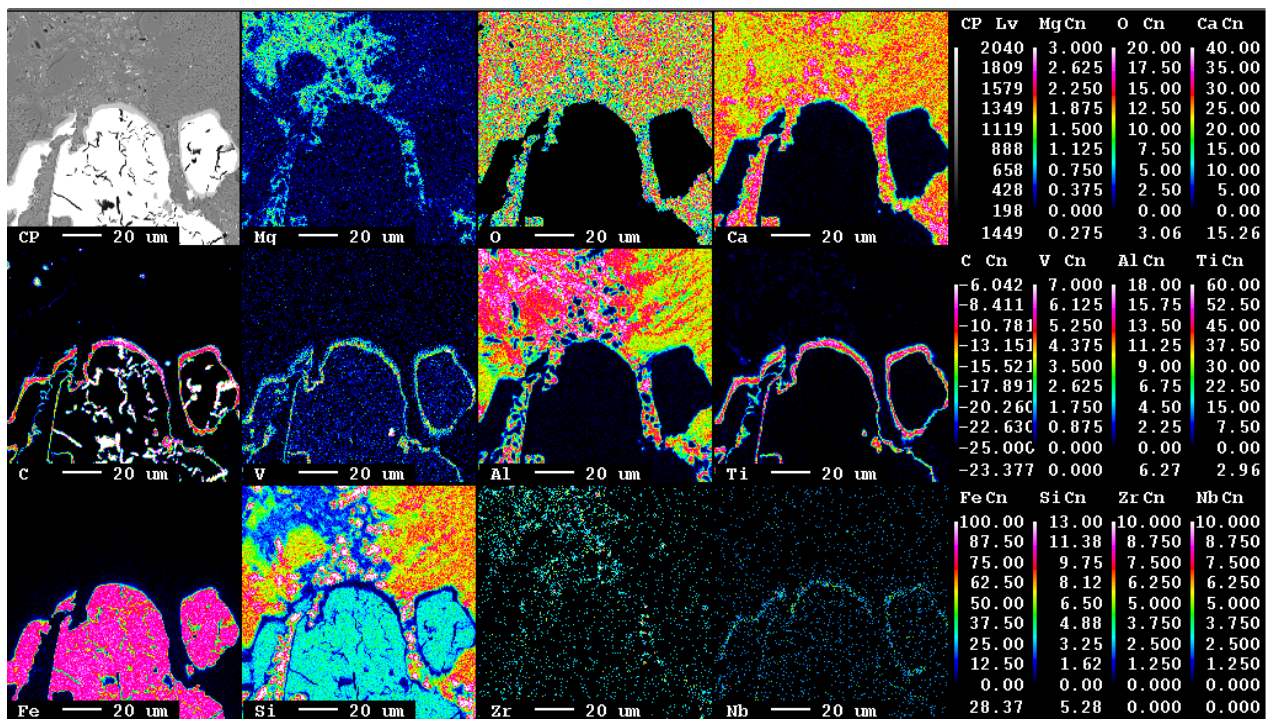

Figure 7: X-Ray map of the elements in different phases after smelting-reduction of bauxite.

Metallization of bauxite components

Based on the above results we may say that the smelting-reduction of bauxite by carbon causes the complete removal of iron from smelted bauxite. In addition, the process is affective for partial removal of the other impurities such as Si, Ti, V, Nb,…Based on the fact that silicon is distributed in the main metal phase and the slag, it is possible to calculate the extent of SiO$_2$ reduction by mass balance. This gives 10.6% SiO$_2$ reduction from the bauxite due to the application of smelting reduction process. This is an advantage of the process with regard to the fact that SiO$_2$ in the ore is always a problem in the extraction of alumina in the leaching step and lower SiO$_2$-containing ores are more favorable. The above results show also that TiO$_2$ is

significantly reduced in the smelting-reduction of bauxite and it is appearing mainly in the metallic/carbide form. This is in principle due to the very low chemical activity of Ti in molten Fe-Si-C-Ti alloy in low concentrations. In addition to Ti, other elements such as V and Nb are distributed in the metallic phases as clearly observed in Figure 7. All these results may be beneficial for producing high purity alumina from the produced calcium-aluminate slag by the smelting and carbothermic reduction.

CONCLUSIONS

The smelting-reduction of bauxite through lime addition and using coke as the reducing agent was carried out at 1600°C. Application of EPMA for studying the microstructure of the produced metal and slag phases indicated that:

- The smelting reduction yields a calcium-aluminate slag containing four different compositions with specific distributions and forms, and a metallic product containing solid solution of Fe-Si, graphite flakes and Ti-rich complex carbide phase.

- The complete reduction of iron oxide from bauxite occurs rapidly, which is beneficial from environmental point of view in further alumina production process.

- Stable carbide forming elements such as Ti, V, Nb,…will are distributed in the metal phase at high temperatures and they appear in the form of carbide in the solidified material.

- Significant reduction of TiO_2 has been qualitatively observed.

- SiO_2 is partially reduced from the molten slag and for the given process conditions in this study more than 10% SiO_2 reduction was determined.

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