

Phase and microstructural evolution of high TiO₂-containing Iranian bauxite at high temperatures in different atmospheres

R. Naghizadeh*, H. R. Rezaie and F. Golestani-fard

Department of metallurgical and materials engineering, Iran University of Science and Technology (IUST), Iran

Calcined bauxite is one of the components of alumina-magnesia-carbon refractories for steelmaking applications when in these refractories two types atmosphere at the surface and inside of the refractories exist in service conditions. In this study, Iranian bauxite powders were pressed with and without graphite additions, fired at 1300 °C and 1600 °C in air or reducing atmospheres. The phase evolution of samples was investigated using X-ray diffraction. It was shown that the samples fired at 1600 °C in an air atmosphere, contain corundum, 3 : 2 mullite, tialite, rutile and in a reducing atmosphere corundum, alumina-rich mullite (Al_{1.7}Si_{0.15}O_{2.85}), rutile and a reduced form of titanium oxide (Ti₂O₃) and titanium nitride (TiN) were present. For an explanation of alteration the 3 : 2 mullite to alumina-rich mullite and decomposition of tialite into the parent oxides, the microstructures of samples fired at 1600 °C were investigated. Also the effect of a reducing atmosphere at high temperatures on high purity TiO₂ and a mixture of high purity TiO₂ plus Al₂O₃ in the stoichiometric ratio of tialite were inspected. From these results, a new explanation for the mechanism of the alteration 3 : 2 mullite to alumina-rich type and decomposition of tialite were established.

Key words: Bauxite, TiO₂, Reducing atmosphere, Tialite, Mullite.

Introduction

Natural bauxites contain gibbsite (Al (OH)₃), bohemite or diaspor (AlOOH) along with other minor minerals such as kaolinite, quartz, titania and goethite (α -FeO(OH)) [1, 2]. Natural refractory bauxites are calcined at high temperatures and then used in different refractory products such as high alumina and Al₂O₃-MgO-C. Different types and amounts of impurities in bauxites result in the establishment of different microstructural features of calcined products. Calcined bauxite phases consist of corundum, mullite, glassy phases and sometimes tialite (Al₂Ti₂O₅). Iranian bauxites can be classified as diaspor-kaolinite or bohemite-kaolinite types with low or high TiO₂ contents [3]. Calcination of high TiO₂-containing Iranian bauxites results in the formation of corundum, mullite and tialite composites [3]. Corundum is the important phase in many traditional and modern ceramic bodies with a high melting temperature (2050 °C) and high strength [3, 4]. Mullite has a high thermal stability (Mp = 1830 °C), a relatively low thermal expansion ($4.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$) and a high creep resistance [5]. Mullite which is the only binary compound in the Al₂O₃-SiO₂ system displays various Al to Si ratios referring to the solid solution Al₄(Al_{2x}Si_{2-2x})O_{10-x} ($0.18 \leq x \leq 0.82$). With substitution of 2Al³⁺ cations instead of 2Si⁴⁺ at tetrahedral sites, one oxygen vacancy is formed [5, 6]. The concentration of oxygen vacancies

corresponds directly to the x-value in the general formula of mullite. Two stable solid solutions of mullite are 3Al₂O₃·2SiO₂ ($x = 0.25$, Al₂O₃ = 72 wt%) and 2Al₂O₃·SiO₂ ($x = 0.40$, Al₂O₃ = 78 wt%) that are referred to as 3 : 2 and 2 : 1 mullite respectively [7, 8].

Aluminum titanate (Al₂TiO₅, tialite) has a relatively low thermal expansion coefficient ($0.2 \times 10^{-6} \text{ }^{\circ}\text{K}^{-1}$), a high melting point (1860 °C) and excellent thermal shock resistance ($\sim 500 \text{ W.m}^{-1}$) [9]. The structure of tialite consists of distorted oxygen octahedra of Al³⁺ or Ti⁴⁺ cations (AlO₆ or TiO₆) that form double chains weakly bonded by shared edges [10]. Al₂TiO₅ is stable above 1280 °C and undergoes a eutectoid like decomposition to α -Al₂O₃ and TiO₂ (rutile) within the temperature range 700-1280 °C [11].

Even though considerable studies have been carried about the phases and microstructure of calcined or fired high grade refractory bauxite in an oxidizing atmosphere but the effect of high temperature on high titania bauxite in two different oxidizing and reducing atmospheres has not been completely studied. Bauxite is one of the raw materials in the matrix of Al₂O₃-MgO-C bricks and therefore in this study the effects of the ingredients and atmospheres in the matrix of these types of refractories are investigated.

Experimental Procedures

The main starting materials were Iranian high TiO₂ bauxite (Bigglar). The main minerals of natural Bigglar bauxite are diaspor (AlO(OH)), anatase (TiO₂), kaolinite (Al₂Si₂O₅(OH)₄) along with small amounts of orthoclase (KAlSi₃O₈), rutile (TiO₂) and iron hydroxide (FeO(OH)). The Bigglar bauxite was calcined at 1000 °C/5 h in an

*Corresponding author:
Tel : +98-21-77459151
Fax: +98-21-77240480
E-mail: rnaghizadeh@iust.ac.ir

electrical furnace in a normal atmosphere with a heating rate of 10 K h^{-1} to remove the water of constitution. The pyrometric cone equivalent of this bauxite is above 1730°C . The particle size of calcined bauxite was less than $70 \mu\text{m}$ with a mineral content of corundum, rutile, and an alumina-silica spinel. The calcined Bigglar bauxite has the chemical composition of $\text{Al}_2\text{O}_3 = 64.8 \text{ wt\%}$, $\text{SiO}_2 = 21.7 \text{ wt\%}$, $\text{TiO}_2 = 12.15 \text{ wt\%}$, $\text{Fe}_2\text{O}_3 = 1.13 \text{ wt\%}$ and 0.54 wt\% alkalis. The additive raw material in this study was Chinese flake graphite ($\text{C} \geq 96.5 \text{ wt\%}$). Two batches from calcined Bigglar bauxite with or without an additive were prepared. Samples without any additive are identified as the B series and samples with 10 wt\% graphite additive are labeled with BG.

The raw materials of each series were mixed with suitable binders. The binder for the B series were a water solution of (3 wt\%) polyvinyl alcohol (PVA) and for the graphite-containing series were 3 wt\% Turkish novalak liquid resin with 0.3 wt\% hexamethylene tetramine powder (hexamine). The prepared mixes were aged for 24 h and then were uniaxially pressed into a cylindrical shape (50 mm height and 50 mm diameter) under a pressure of 140 MPa . The PVA containing samples were dried at 110°C for 24 h and the resin bonded samples were cured at 200°C for 12 h . The samples were fired in an electrical furnace at 1300°C and 1600°C (soaking time 3 h) with a heating rate of $5 \text{ K} \cdot \text{minute}^{-1}$ in air or in a coke environment and furnace cooled. The samples which were fired in a coke environment are identified with the suffix E. For some description of the results TiO_2 ($> 99\%$, Merck) and $\alpha\text{-Al}_2\text{O}_3$ ($> 99\%$, Fibrona, India) were used. Crystalline phases of different samples were analyzed using X-ray diffraction (XRD, $\text{CuK}\alpha$, Philips-D80). Microstructural observations of polished and coated samples were made by a Cambridge S360 scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS). Also backscattered electron imaging (BEI) was used.

Results and Discussion

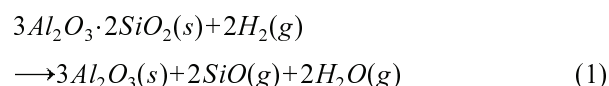
Figure 1(a) shows the XRD patterns of the B formula containing 100% Bigglar bauxite after firing at 1300°C and 1600°C in air and reducing (coke bed) atmospheres. The XRD pattern of B samples revealed that the major existing crystalline phase was corundum ($\alpha\text{-Al}_2\text{O}_3$) and the minor phases were mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), tialite ($\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$) and rutile (TiO_2) at firing temperature of 1300°C and 1600°C in an air atmosphere. In reducing conditions at 1600°C some of the rutile was reduced to the Ti_2O_3 phase. Reducing conditions at 1600°C results in the removal of oxygen and silicon atoms from the mullite structure leading to oxygen and silicon vacancies and finally transformed the mullite to an aluminium-silicate phase ($\text{Al}_{1.7}\text{Si}_{0.15}\text{O}_{2.85}$).

The XRD patterns of samples containing 90 wt\% Bigglar bauxite plus 10 wt\% graphite (BG formula) are shown in Fig. 1(b). The patterns show similar phases in an air

atmosphere but in a coke bed condition at 1300°C graphite and Ti_2O_3 and at 1600°C graphite, titanium nitride (TiN) and silicon carbide (SiC) as new phases were detected.

The XRD patterns of B and BG samples after firing in a reducing condition showed an aluminium silicate phase with $\text{Al}_{1.7}\text{Si}_{0.15}\text{O}_{2.85}$ ($0.85\text{Al}_2\text{O}_3 \cdot 0.15\text{SiO}_2$) formula, that as compared with a general solid solution series of the mullite formula ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$ $x = 0.18\text{--}0.82$) fits with $x = 0.76$. This shows that due to the removal of oxygen atoms in the reducing atmosphere and substitution of Al^{+3} instead of Si^{+4} in the tetrahedral sites, $3:2$ mullite ($x = 0.25$, $\text{Al}_2\text{O}_3 = 72 \text{ wt\%}$) converted to Al-rich mullite ($x = 0.76$, $\text{Al}_2\text{O}_3 = 90.6 \text{ wt\%}$) that in turn has a higher alumina content than $2:1$ mullite ($x = 0.4$, $\text{Al}_2\text{O}_3 = 78 \text{ wt\%}$). The structure of the mullite solid solution with $x \geq 0.67$ is assigned to a pseudo-tetragonal phase that has the symmetry of the orthorhombic structure of mullite with $x < 0.67$ [12].

Other authors found that heat treatment of mullite and other alumina-silicate minerals at high temperatures under a reducing atmosphere causes the decomposition of these minerals. Tso and Pask [13] stated that mullite under a hydrogen gas atmosphere at high temperatures decomposes with the following reaction:



Krönert and Buhl [14] studied the behavior of mullite in a $\text{CO}(\text{g})$ atmosphere and noted that the following reaction occurs:

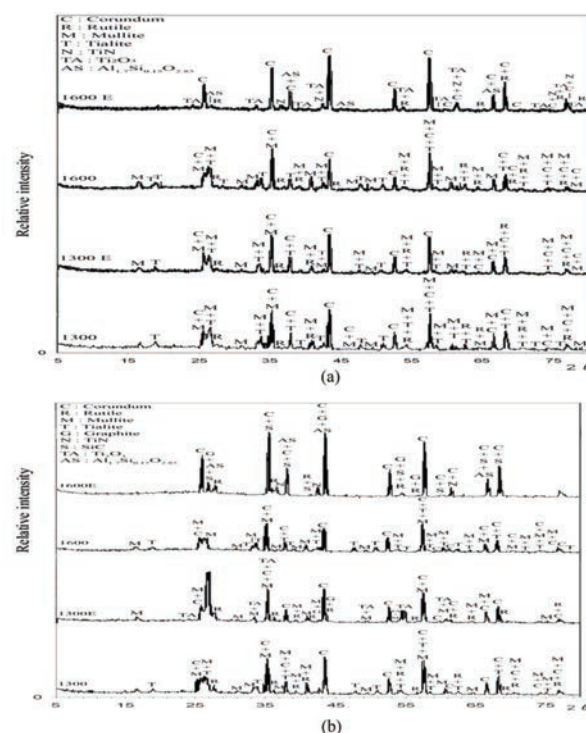
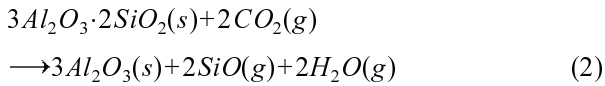


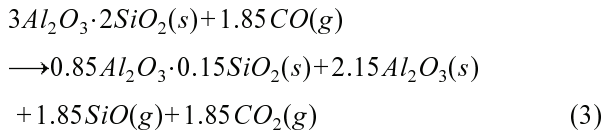
Fig. 1. XRD patterns of samples fired at 1300°C and 1600°C for 3 h in an air atmosphere or coke bed. (a) B sample (b) BG samples.



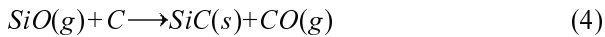
In this text S, L and g stand for solid, liquid and gas respectively.

Near to the surface of the sample or in a mild reducing atmosphere reoxidation of SiO(g) to SiO₂(g) and the subsequent precipitation to SiO₂(l) or SiO₂(s) or reactions with other constituents of the specimen can occur. In the carbothermal reduction of kaolinite (Al₂O₃·2SiO₂·2H₂O) SiO reacts with other components and establishes SiC, Sialon (Si_{6-z}Al_zN_{8-z}O_z), and Si₃N₄O phases [15].

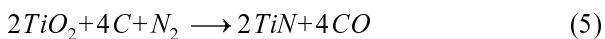
According to the XRD patterns in Fig. 1(a) and Fig. 1(b), the following reactions may occur in B and BG samples in reducing conditions.



Silica-rich mullite alumina-rich mullite

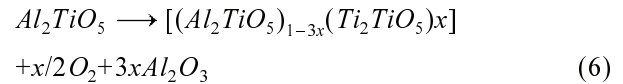


Formation of reduced forms of titanium oxide (Ti₂O₃), titanium nitride (TiN) and the decomposition of aluminium titanate particularly at 1600 °C were other phases are altered in reducing conditions in comparison with an oxidizing atmosphere in B and BG samples as shown in Fig. 1(a, b). In a reducing atmosphere, there is a wide composition range of titanium oxide such as TiO₂, Ti₃O₅, Ti₂O₃, TiO, and Ti₂O with metal and/or oxygen deficiency [16]. The volume per mole of TiO₂, Ti₂O₃ and TiO are 18.76 cm³, 15.63 cm³ and 12.96 cm³ respectively, therefore transition of rutile to the noted phases is accompanied with volume changes [17]. On the other hand, mullite incorporates titanium with a solubility limitation related to the cation radii, the alumina concentration of mullite and oxidation state of the ions that ranges between 2-6 wt% as a TiO₂ base [12]. Incorporation of Ti³⁺ (Ti₂O₃) occurs at two differently distorted octahedral sites with reciprocal dependence on Al₂O₃ concentrations in mullite [5]. Thus in a reducing atmosphere mullite may incline toward Al-rich types, due to the decreasing solubility of Ti³⁺ in it, then the formation of a low oxidation state of TiO₂ is promoted as shown in the phase composition of B and BG samples Fig. 1(a), (b). In BG samples Fig. 1(b), the formation of titanium nitride (TiN) occurred due to carbothermal reduction-nitridation of rutile or other titania-bearing phases. An atmosphere which is a mix of CO and N₂ is present in coke bed firing. It is reported that carbothermal reduction-nitridation also occurs in the TiO₂-bearing mixture of slag, silica fume, carbon black and bauxite as in the following reaction [18]:



In a reducing firing atmosphere for B samples at

1600 °C and BG samples at 1300 °C and 1600 °C Fig. 1 (a), (b) aluminum titanate was not observed. Tialite formation by a solid-state reaction route from fine powders occurs at above 1300 °C, but it has a tendency to decompose to Al₂O₃ and TiO₂ when cooled between 1280-700 °C [11, 19]. It is noted that the mechanisms of decomposition are poorly understood but observation led the authors to conclude that in all probability the decomposition reaction occurred via some metastable phases such as anosovite(Ti₃O₅) which has a complete range of solid solution with tialite and the following reaction is suggested for tialite decomposition [12]:



The rate of tialite decomposition depends on purity, types and amount of dopants (MgO, SiO₂, ...), grain size, temperature, annealing, internal or induced stresses, sintering time and types of atmosphere [20, 21]. In an argon atmosphere as compared with air the temperature range of thermal instability is not dependent on the atmosphere but the rate of decomposition at 1100 °C in an argon atmosphere is higher than in air [21].

It is postulated that in the presence of CO in the B and BG samples, along with the formation of the tialite at above 1300 °C some of the rutile transformed to a reduced form of titanium oxide and as a result, the rate and the amount of established tialite was decreased. On the other hand, when the specimens furnace cooled on

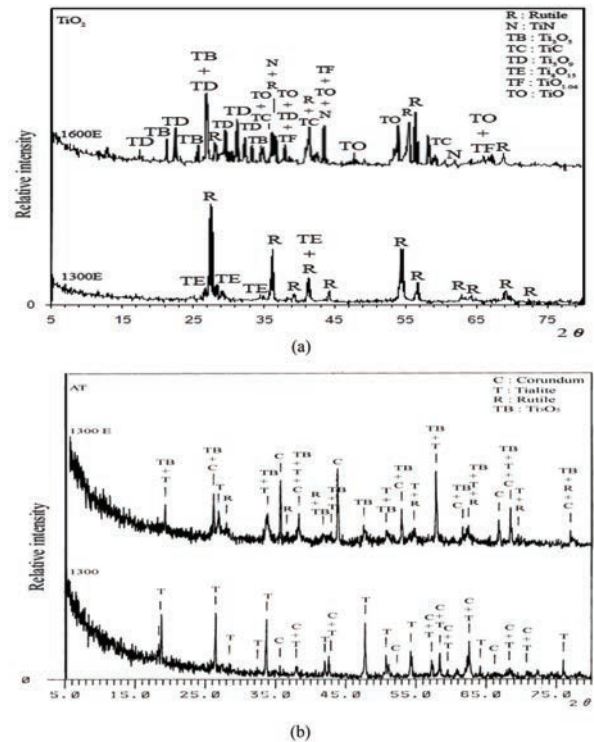


Fig. 2. (a) XRD patterns of TiO₂ after firing on a coke bed at 1300 °C and 1600 °C (b) XRD patterns of a Al₂O₃+TiO₂ stoichiometric mix after firing at 1300 °C in air and coke bed atmospheres.

a coke bed between the instability temperatures ranges, the tialite formed decomposed with a high rate in comparison with air or argon atmospheres which were reported by Low et al. [21]. As evidence for the above description, TiO_2 samples were heated at 1300 °C and 1600 °C in a coke bed, also $\alpha\text{-Al}_2\text{O}_3$ after mixing with TiO_2 in the stoichiometric proportion of tialite were fired at 1300 °C in air and on a coke bed and furnace cooled. The XRD results of the above specimens are shown in Fig. 2(a), (b). In a reducing condition according to Fig. 2(a) at 1300 °C rutile and Ti_8O_{15} ($\text{TiO}_{1.875}$) and at 1600 °C Ti_5O_9 ($\text{TiO}_{1.8}$), Ti_3O_5 ($\text{TiO}_{1.66}$), TiO , TiN and probably TiC were present. As we can see in Fig. 2(b) the specimens which were heated and cooled in an air atmosphere mainly the tialite remained stable but on a coke bed the high amount of tialite decomposed to corundum, rutile and Ti_3O_5 phases.

Micrographs of B and BG samples fired at 1600 °C/3 h in air and reducing atmospheres are shown in Figs. 3 and 4.

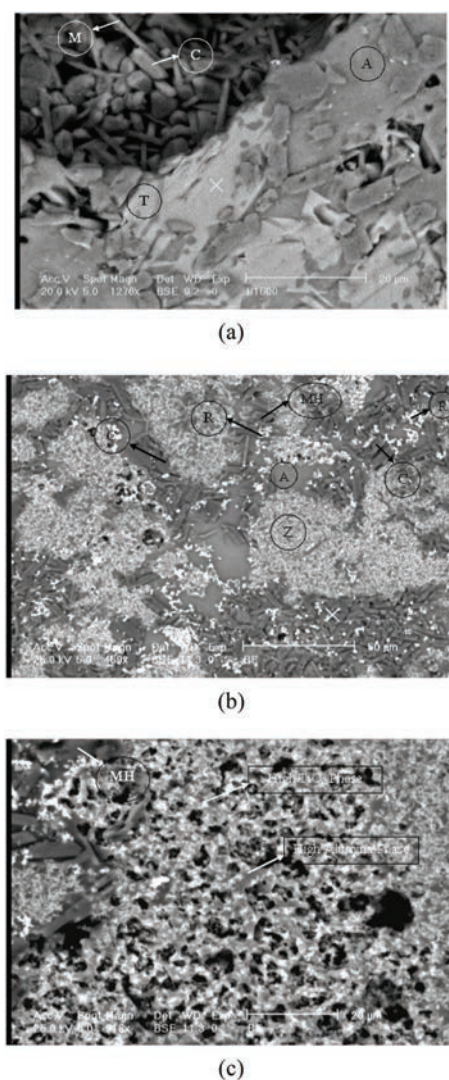


Fig. 3. SEM micrographs of B sample after firing in 1600 °C/3 h (a) In air atmosphere (b), (c) In a reducing atmosphere M = 3 : 2 mullite C = corundum A = Amorphous glassy phase T = tialite R = high TiO_2 phase MH = high alumina mullite.

Microstructural studies of these samples revealed that similar to other bauxites these samples also have a heterogeneous structure from the point of size, type, and distribution of the main and minor phases. The microstructure of the B sample after firing in an air atmosphere Fig. 3(a) shows elongated grains (M) as a solid solution 3 : 2 mullite with TiO_2 (4.45 wt%), cuboidal grains (C) of corundum with a trace amount of SiO_2 , white grains (T) of tialite with some SiO_2 content (1.04 wt%) and an alumina-silicate glassy phase (A) with some TiO_2 , MgO , Fe_2O_3 contents (9.9, 1.29, 1.75 wt% respectively). These results appeared by combining of energy-dispersive spectroscopy data (EDS) and XRD patterns. The microstructure of the B sample after firing in a reducing atmosphere Fig. 3(b) shows elongated grains (MH) as alumina rich mullite ($\text{Al}_2\text{O}_3 = 83$ wt%) that are richer in alumina than 2 : 1 mullite and poorer than $0.85\text{Al}_2\text{O}_3 \cdot 0.15\text{SiO}_2$ which proved the X-ray diffraction for this sample. It can be seen close to indicated mullite grains some high TiO_2 phases (R) existed due to the decreasing solubility of TiO_2

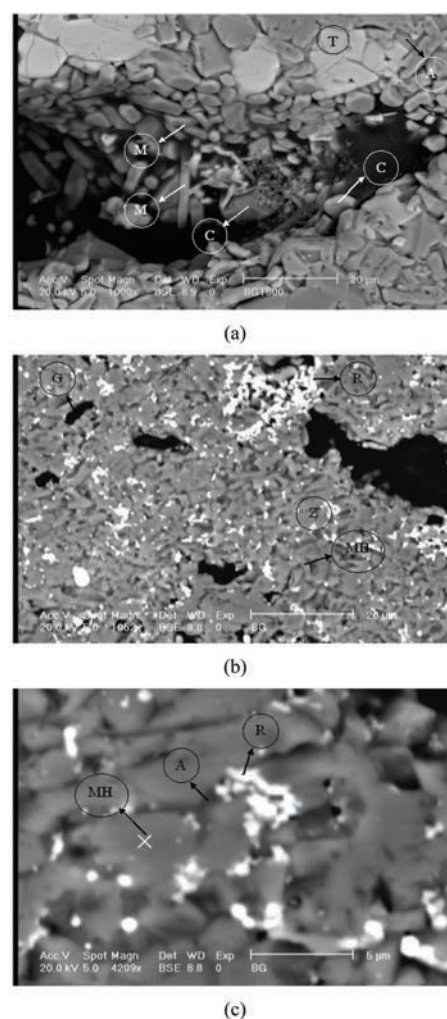


Fig. 4. SEM micrographs of BG sample after firing in 1600 °C/3 h (a) Air atmosphere (b), (c) In a reducing atmosphere M = 3 : 2 mullite C = corundum A = Amorphous glassy phase T = tialite R = high TiO_2 phase MH = high alumina mullite G = graphite.

in alumina-rich mullite. Corundum (C) and glassy phases (A) are also seen in Fig 3(b). light grey regions (Z) in Fig. 3(b) at higher magnification are shown in Fig. 3(c), revealed that there is a continuous porous skeleton light grey high alumina composition as a matrix with isolated high TiO₂ composition region in the matrix existed. It has been pointed out that porous α -Al₂O₃ grains after heat treatment of mullite at 1600 °C/1 h in CO atmosphere were formed [14], and probably this porous region established in the B sample results from a similar reaction but in the presence of TiO₂, Fe₂O₃ and alkalis intensive sintering or overfiring (partially softening) and recrystallization occurred.

Figure 4(a) shows the microstructure of a BG sample after firing in an air atmosphere. This Figure shows more porosity in comparison with the B sample Fig. 3(a) due to burning of the graphite content. The BG sample after firing in reducing conditions exhibits alumina-rich mullite grains (MH), corundum grains (C), graphite flakes (G) and high TiO₂ content phases (R) between mullite and/or corundum phases Fig. 4(b), (c). When compared with the microstructure of the B sample Fig. 3(b), (c) the porous skeleton zone was not detected. The BG sample had resin as a binder and thus had a lower porosity than the B sample so it seems that removal of the gaseous reaction products (reaction 3) occurred with difficulties.

Conclusions

On the basis of XRD and SEM+EDX results, the containing following may be concluded:

The mineral composition of specimens containing high TiO₂ bauxite with and without graphite after firing at 1300 °C and 1600 °C in an oxidizing atmosphere consisted of corundum, mullite, tialite and rutile. In a reducing atmosphere, specially at 1600 °C, 2 : 3 mullite converted to an alumina-rich form (Al_{1.7}Si_{0.15}O_{2.85}), tialite decomposed to parent oxides and some of rutile reduced to Ti₂O₃. It seems that when silica-rich mullite changed to an Al-rich form, corundum and the SiO(g) also formed and then some of the SiO(g) reacted with carbon in the graphite-containing specimen and produced SiC. In this condition, reduction-nitridation of TiO₂ occurred and as

a result, Ti₂O₃ and TiN were created. The establishment of Ti₂O₃ results from decreasing tialite formation and also promotes tialite decomposition and mulite transformation.

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