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Research Article

Effect of SiO_2/TiO_2 Ratio on the Mechanical Behaviour at High Temperature of Refractory Bauxites

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Abstract

The effect of silica/titania ratio on the mechanical behaviour, compression test at high temperature (1550 ºC), of a series of synthetic refractory bauxites has been studied. The stress-strain test have shown that when alumina (Al_2O_3) and iron oxide (Fe_2O_3) are kept constant and the SiO_2/TiO_2 ratio is increased both the maximum load stress and toughness of samples is raised as a consequence of increasing mullite vol.% content and mullite/tiellitess ratio.

Introduction

Refractory–grade bauxites potentially have a high refractoriness on the basis of their two main constituents alumina and silica, however in practice their refractoriness is limited to 1500^0-1550 ºC to the presence of impurities, in particular alkaline oxides. Recently studied on refractory bauxites carried out by Qiang Ren et al. [1] have put in evidence that formation and presence of mullite ($3Al_2O_3.2SiO_2$) have a positive effect on the mechanical properties of materials obtained from low-grade refractory bauxites while Pereira AL et al. [2], concluded that the non-formation of tiellitess, ($Al_{2-x}TiFe_xO_5$), the absence of glassy phase together with mullite formation improve the properties of refractory bauxites [2]. Sepulveda P et al. [3], made a complete characterization and properties of refractory grade bauxites and reported that apart from alumina and iron oxide, alkaline and alkaline earth impurities together titanium compounds have an important influence on the mechanical properties and corrosion resistance at high temperatures.

Caballero A et al. [4,5] studied the constitution of calcined refractory-grade bauxites showing the heterogeneity of the samples and made an interpretation of their thermal behaviour at high temperatures and also they put in evidence the effect of processing on the mechanical properties at high temperature and how their fracture behaviour at high temperature, in the absence of liquid phase, is conditioned by the nature of the second solid phase, being tough when it is mullite and brittle when it is tiellitess. Taking into account that the nature of the second solid phase in refractory grade bauxites depends of SiO_2/TiO_2 ratio, as can be deduced from the Al_2O_3-SiO_2-TiO_2-iron oxide system in air [6,7], the effect of this relation on the mechanical properties at high temperature (1550 ºC) of three synthetic refractory bauxites has been studied.

Materials and Methods

Three synthetic bauxite (1A, 2A, 3A) were prepared from low-sodium alumina (99,998 wt. % Fluka), washed Belgium sand (99.9 wt. % of SiO_2) and A.R. grades TiO_2 and Fe_2O_3 (Merck). These starting oxides were ground to pass a 35um sieve before used. The selected composition were attrition–milled in water media, dried at 110 ºC during 24 hours and after sieving were isostatic pressed at 200MPa.The green samples were fired at 1650 ºC during 2h (heating rate 5 ºC) and were cooling in the furnace. The true density (Helium Picnometry), bulk density (Arquimedes Method) and total porosity of the compacts were determined. All calcined samples were studied by X-Ray and, before and after testing, by reflected light microscopy of polished samples. All polished sections were chemically etched for 30 s. in a continuous agitated solution of HF10% acid at room temperature.

Quantitative x-ray determinations have been performed for corundum, mullite and tiellite by matrix flushing method [8] using CaF_2 as standard. From quantitative x-Ray results and true density of α-alumina (3.98Mg.m^{-3}), mullite (3.16Mg.m^{-3}) and tiellite (3.72 Mg.m^{-3}), volume percent of each phase were determined. Cylinders of 10±0.1mm diameter and 10±0.1mm high were obtained from calcined samples. Compression tests, specifically stress-strain curves under compression, were obtained using an Instron universal testing machine to which a high temperature furnace was incorporated. The stress-strain curves under compression at 1550 ºC, five for each sample, were obtained for a constant load rate of 8.3x10^{-7} m/s.

Results and Discussion

Specimen characterization

Table 1 shows the chemical composition of samples studied. Alumina, silica and iron oxide content were chosen to be similar to the raw refractory bauxites. Silica/titania wt.% ratio varies between 0.44 in sample 1A to 2.0 in sample 3A. The titania content in samples 2A and 3A was greater than the usual in refractory bauxite to get a better understanding of its effect. X-ray results show that all samples were constituted by α-aluminass, mullitess and tiellitess, in accordance with the location of the samples in the quaternary system Al_2O_3-SiO_2-TiO_2-Iron oxide in air [6,7] (Figure 1). Table 2 shows the quantitative x-ray mineralogical analysis in wt. % and recalculated to vol. %. To point out that mullite$_{ss}$/tiellite$_{ss}$ ratio changes significantly from 0.90 to 6.34 if wt. % is considered, or from 1.05 to 7.44 when vol.% is used. This is a relevant point since silica/titania ratio plays an important role on the mineralogical constitution of samples given that moderate increasing of silica/titania ratio have an relevant influence in the proportion and ratio of mullite$_{ss}$ and tiellite$_{ss}$ phases. Table 3 shows the true density, bulk density and total porosity of the samples. No relevant differences were found among them.

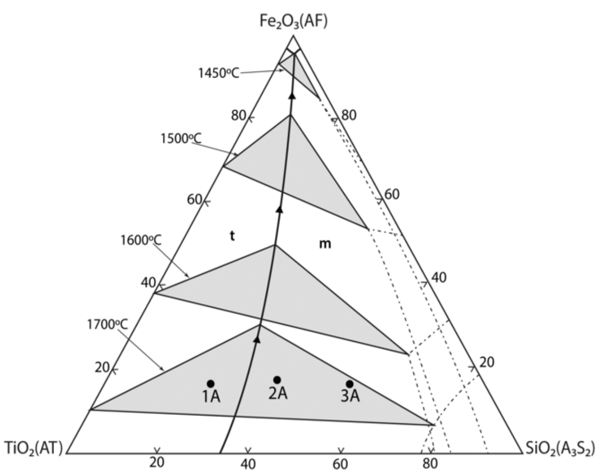

Figure 1: The Al_2O_3-SiO_2-TiO_2-Iron oxide quaternary system in air. Location of synthetic refractory bauxites on the projection (86 wt. % Al_2O_3 plane) of the primary volume of alumina and tie-tetrahedroms at 1450⁰, 1500⁰, 1600⁰ and 1700 ⁰C where alumina$_{ss}$-mullite$_{ss}$-tiellite$_{ss}$ and liquid phase coexists in equilibria at indicated temperature. Tie-tetrahedroms determine the temperature of liquid formation, 1700⁰ for studied sample.
t - Secondary crystallization field of tiellite$_{ss}$
m - Secondary crystallization field of mullite$_{ss}$
AT = $Al_2O_3.TiO_2$ = Al_2O_5Ti = Tiellite; A_3S_2 = $3Al_2O_3.2SiO_2$ = $Al_6O_{13}Si_2$ = Mullite
AF= $Al_2O_3.Fe_2O_3$

Table 1: Chemical composition of synthetic refractory bauxites (wt. %).

Sample	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	SiO_2/TiO_2 Ratio
1A	86.0	3.6	8.1	2.3	0.44
2A	86.0	5.9	5.8	2.3	1.01
3A	86.0	7.8	3.9	2.3	2.0

Table 2: Mineralogical composition of synthetic refractory bauxites.

Sample	α-Alumina	Mullite	Tiellite	α-Alumina	Mullite	Tiellite
	wt. (%)			vol. (%)		
1A	67.4±0.2	15.5±0.2	17.1±0.3	64.0±0.2	18.5±0.2	17.5±0.3
2A	63.9±0.2	25.4±0.2	10.6±0.3	59.6±0.2	29.8±0.2	10.6±0.3
3A	61.1±0.2	33,6±0.2	5.3±0.3	55.9±0.2	38.7±0.2	5.2±0.3

Table 3: True and bulk densities and total porosity of synthetic refractory bauxites.

Sample	True Density ($Mg.m^{-3}$)	Bulk Density ($Mg.m^{-3}$)	Total Porosity
1A	3,78±0.05	3.36±0.05	11.1±0.2
2A	3.71±0.05	3.26±0.05	12.1±0.2
3A	3.63±0.05	3.13±0.05	13.8±0.2

Reflected light optical microscopy observations confirmed the presence of the previously mentioned phases and that the presence of glassy phase, was almost undiscernible. Sample 1A, (Figure 2a), with the lowest silica/titania ratio presented tiellitess as secondary phase while samples 2A, (Figure 2b), and 3A (Figure 2c) showed mullitess as secondary phase. All samples showed α-alumina as primary phase. Sample 1A showed a continuous α-alumina matrix where tiellitess was easily observed as secondary phase. In 2A sample mainly tiellitess but also mullita were observed between α-alumina matrix. Finally, in the case of sample 3A the presence of mullite in the matrix was relevant and the presence of tiellitess was barely visible.

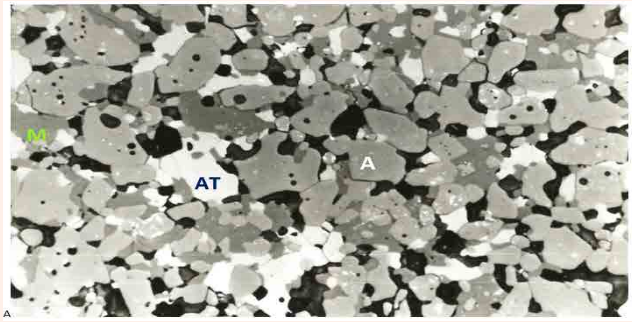

Figure 2a

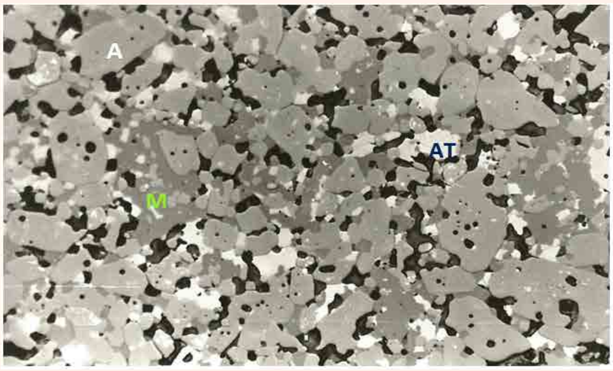

Figure 2b

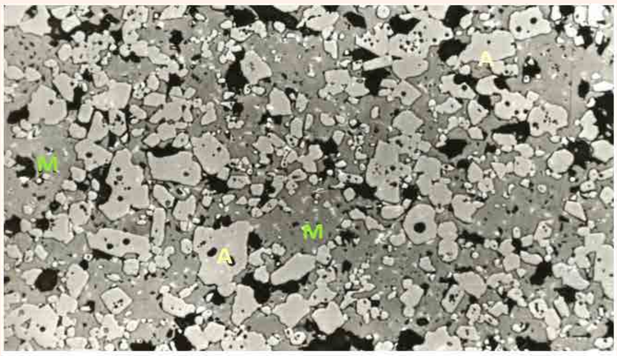

Figure 2c

Figure 2: Microstructural characteristics of studied samples 1A (figure 2a) 2A (figure 2b) and 3A (figure 2c) before testing. A=Alumina; M=Mullite; AT=Tiellitess; Black areas are pores. Reflected light microscopy (x310).

Mechanical properties at high temperature

In Figure 3 stress-strain curves obtained at 1550 ºC can be observed. Each line represents the average of results obtained for each sample. The results show that as silica/titania ratio increases, the maximum strength increases from 6.1±0.2 MPa in sample 1A to 9.2±0.2 MPa in sample 3A. Considering that differences in porosity are almost negligible and that the samples do not contain liquid phase, the rise in maximum strength is attributed to the increase of mullite content (Figure 4), since as the SiO_2/TiO_2 ratio increases mullitess/tiellitess also increases and furthermore, an increase in the mullite content (vol or wt %) in the samples produces a replacement of the continuous alumina matrix by a predominantly mullitic one. This fact is in agreement with those obtained by Dokko et al. [9], who found, in similar stress-strain test under compression at high temperature, that polycrystalline mullite bodies present maximum strength values more than double that pure polycrystalline alumina compacts. This behaviour of mullite phase can be understood taken into account the complexity of mullite crystal structure, which does not present any plastic deformation and, no dislocation glide [10] even at 1500 ^{0}C.

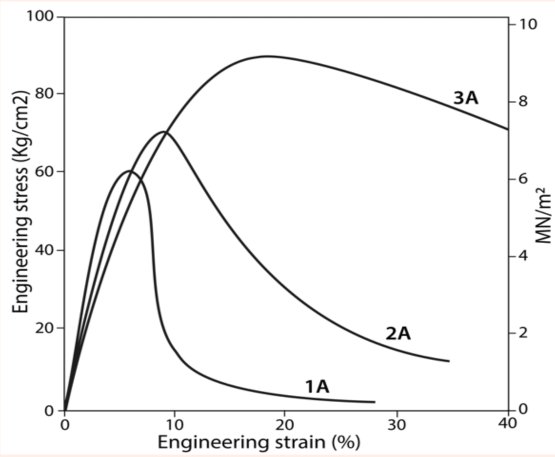

Figure 3: Stress-strain curves under compression test in air at 1550 ^{0}C.

Besides, as can be seen in Figure 3, a significant fact in relation to the samples tested could be observed: their difference fracture behaviour which changes from brittle to tough as the SiO_2/TiO_2 is increased. So that sample 3A, where mullite content is the biggest, presented a controlled fracture behaviour typical of tough materials, similar to that observed by several authors in composite matrix-fibre materials [11,12]. Unlike sample 1A where tiellitess is the secondary phase and the mullite content is the lowest one, presents a behaviour, once the maximum strength is reached, similar to that observed in brittle materials. The examination of the samples after testing by optical light microscopy allowed explaining this different behaviour. The sample 3A (Figure 5) showed a microstructure which maintain the continuous mullitic matrix and therefore, due to the high strength of mullite at high temperature, inhibits the crack propagation and consequently justifies the controlled fracture behaviour presented by that sample.

On the contrary, the sample 2A and particularly the sample 1A created, under mechanical stress at high temperature, an open microstructure which facilitated preferential ways to crack propagation (Figure 6) and consequently a lower strength and fracture behaviour similar to brittle materials were obtained. This different behaviour of samples 2A and 1A in relation to the sample 3A was attributed to the relative high content of tiellitess in both samples since tiellitess phase presents a low mechanical strength due to their grains are normally cracked due to its high dilatometry anisotropy [13] and consequently this samples, one the maximum strength of matrix is reached, did not present any impediment to the propagation of the cracks. Finally (Figure 7) shows the slope values of the stress-strain curves as a function of mullitess/tiellitess vol. % ratio, once the maximum strength has been reached. It is also indicated in this figure, the SiO_2/TiO_2 ratio at which takes place the change of secondary crystallization field from mullite to tiellitess according the information supplied by the Al_2O_3-SiO_2-TiO_2-Iron oxide phase equilibria diagram [6]. This figure it is possible to conclude that the toughness or brittleness of the samples, in the absence of glassy phase, is directly linked to the nature of secondary phase present. These results confirm those obtained in a previous work [5] on raw refractory bauxites, where it was concluded that the fracture behaviour of high temperature, in the absence of liquid phase, is conditioned by the nature of second solid phase, being tough when it is mullite and brittle when it is tiellitess.

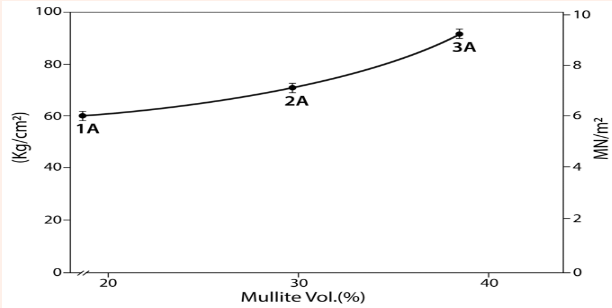

Figure 4: Maximum load supported by samples versus mullite vol.% content.

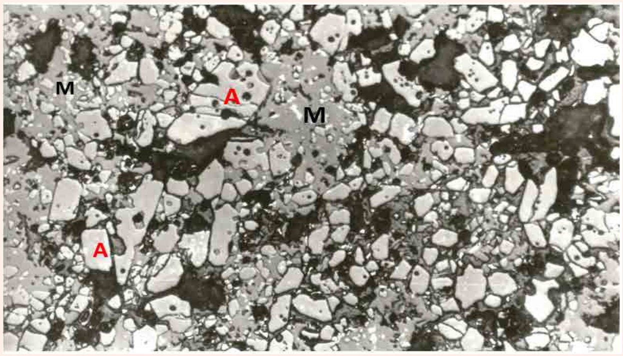

Figure 5: Microstructural characteristics of sample 3A after compression test at 1550 ^{0}C. Reflected light microscopy (x310).

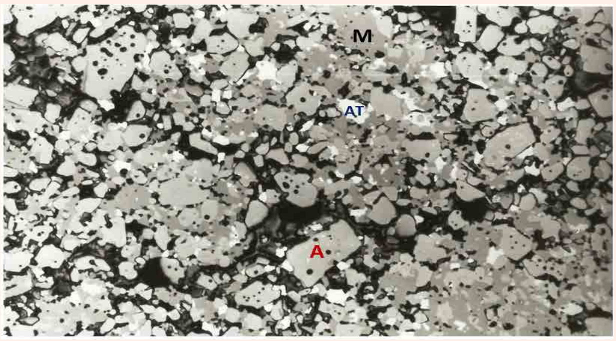

Figure 6: Microstructural characteristics of sample 2A after compression test at 1550 ^{0}C. Reflected light microscopy (x310).

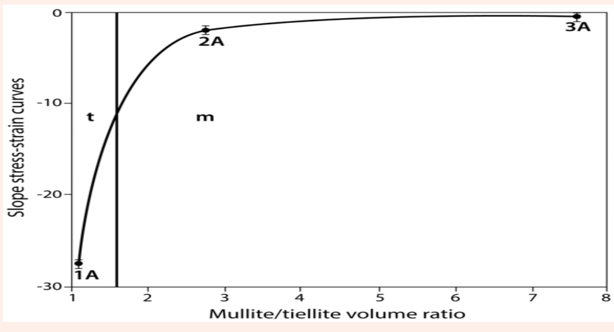

Figure 7: Slope of stress-strain curves after maximum load versus mullite/tiellite$_{ss}$ volume ratio. t- Secondary crystallization field of tiellite$_{ss}$; m- Secondary crystallization field of mullite$_{ss}$

Conclusion

The increase in SiO_2/TiO_2 ratio in synthetic refractory bauxites, keeping constant iron oxide and alumina content, involves an increase in the mullitess/tiellitess ratio and consequently an increase in both the maximum strength and the toughness at high temperature under compression test.

Acknowledgment

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