Microstructural features of alumina refractories with mullite-zirconia aggregates

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Refractory materials are often subjected to high temperatures and loads and their performance depends on their microstructural evolution during use. In this context, microstructural changes were monitored in alumina-based refractories containing mullite-zirconia aggregates and heat-treated at 1400°C and 1500°C for 2, 6, and 18 days. With the purpose of inducing *in situ* mullite formation, bricks containing microsilica were also prepared and heat-treated at 1500°C for 6 days for the sake of comparison. These heat treatments allowed for an evaluation of the use of refractories from the standpoint of temperature and time. In this work, scanning electron microscopy and X-ray diffraction analyses were made to identify the phases in the materials. The Rietveld method was also used for quantitative phase analyses. Interfacial reactions occurred between alumina and aggregates and between alumina and microsilica, causing the system to become mullitized. The effect of *in situ*-formed mullite was particularly evident in the results of the modulus of rupture of the materials containing microsilica. Creep tests revealed a reduction in the creep rate of materials treated at 1500°C for 18 days.

Key words: refractories, microstructure, aggregate, Rietveld, creep

Aspectos microestructurales de los refractarios con alúmina conteniendo agregados de Mullita-Circona.

El comportamiento de los materiales refractarios, cuando sometidos a altas temperaturas y a grandes esfuerzos mecánicos, está íntimamente relacionado con la evolución microestructural, durante su uso.

En este contexto, fue realizado un estudio de la evolución microestructural de los materiales refractarios de alúmina conteniendo diferentes porcentajes de agregado de mullita-circona, sometidos a tratamientos térmicos por 2, 6 y 18 días, en temperaturas de 1400 y 1500°C. Fueron confeccionados, algunos ladrillos conteniendo microsilíce, con la idea de se introducir la formación de mullita *in situ*. Para la comparación de los ladrillos, fueron realizados tratamientos térmicos por un periodo de 6 días en 1500°C. Estos tratamientos térmicos permitieron una aproximación del refractario en uso, considerando apenas el efecto del tiempo y la temperatura. En este trabajo, fueron utilizados, la microscopía electrónica de barrido y la difracción de rayos-X para identificación y caracterización de las fases presentes. Se aplicó el método de Rietveld para el análisis cuantitativo de las fases. Ocurrieron reacciones interfaciales entre la alúmina y los agregados, y entre la alúmina y la microsilíce, como resultado de la mullitización del sistema. El efecto de la formación *in situ* de la mullita fue notado especialmente en los resultados del modulo de ruptura para los materiales que contienen microsilíce. Las pruebas de fluencia revelaron la reducción de la tasa de deformación de los materiales tratados térmicamente por 18 días a 1500°C.

Palabras-claves: refractarios, microestructura, agregado, Rietveld, fluencia.

1. INTRODUCTION

The steelmaking industry is the major consumer of refractories among the various industrial sectors. Changing metallurgical processes have influenced the demand for refractory products and the trend today is for high quality refractories with greater technological content. From this standpoint, therefore, microstructural design is particularly important.

Among the special refractories under development to meet the strict requirements of the metallurgical industry, carbon-bonded high-alumina refractories with added electrofused mullite-zirconia aggregates (MZ-aggregates) rank among the most important materials. These materials are used, for instance, in the production of plates for slide valves (1). The purpose of using MZ-aggregates to replace part of the coarse fraction of alumina is to promote a more intensive interaction between cracks and microstructure. Because the microstructure of this type of refractory is highly prone to microcracking and

porosity, the addition of small zirconia particles, even partially-stabilized one, does not significantly affect the toughening mechanism through additional microcracking, as could be done in the case of normal technical ceramics. That is the underlying reason for the use of MZ-aggregates.

The technical literature (2-8) contains reports on many processing routes to produce mullite-zirconia and alumina-mullite-zirconia (AMZ) ceramics. However, owing to raw material availability and production-related costs, the most common routes are reaction sintering (4-6) and solid-state reaction between oxides (7,8). Be that as it may, control of the final microstructure is a determinant in limiting the severity of critical defects. Moreover, the microstructure must be capable of adjusting to phase transformations and microcracking (9).

An earlier publication (7) reported that high-alumina refractories containing MZ-aggregates did not present a balanced microstructure immediately after sintering, but that

transformations towards equilibrium during the use of the refractory promoted improved creep resistance and thermal shock damage resistance, which are both qualities of major interest for technological applications. It was also observed (7) that, after electromelt cooling, the aggregates showed a small content of vitreous phase, which caused some degradation of the creep resistance of the as-received refractory. A 10-day heat treatment at 1400°C led to an increase in mechanical strength, which was attributed to the *in situ* formation of mullite. This increase was possible because, during heat treatments, the system tends toward equilibrium and a reaction occurs between the alumina matrix and the aggregate particles.

In order to better understand the mechanical and thermomechanical behavior of this type of material, this study investigated the microstructural evolution of high-alumina refractories containing different MZ-aggregate contents, heat treated at distinct temperatures and for different durations.

The chemical composition of the chosen aggregate differed from those of previous studies (7). Therefore, its crystallization during fabrication also differed and, as a consequence, no vitreous phase was formed in the aggregate used. From the mechanical standpoint, greater creep resistance would be expected when using a more refractory aggregate.

2. EXPERIMENTAL

2.1. Preparation of the refractory bricks

A mixture of tabular alumina, Alcoa T-60, calcined alumina, Alcoa APC-2011SG, electromelted MZ-aggregate, Elfusa TP-35, and microsilica, Elkem 971D, was prepared in a planetary device. Water and dextrin (additive) were added to the mixture, at concentrations of 2 wt-% each. Table I shows the compositions of the bricks produced. Considering the granulometry of the raw materials, two types of bricks were prepared: the first, called GF, for the fine granule material and the second, called GG, for the coarse granule material. The idea was that, in the GF-type, the interfacial reaction between the different raw materials would be easier, facilitating observation of the phase transformation. On the other hand, the GG-type results in a real brick.

The GF-type material presented a granulometric distribution in which particle sizes varied from less than 45 µm to 297 µm and, in this case, the MZ-aggregates constituted the coarse part of the brick (particle sizes of less than 297 µm). A granulometric range of less than 45 µm up to 6300 µm was imposed for the GG-type brick and, in this case, the coarse part of the brick consisted of tabular alumina (particle size smaller than 6300 µm).

Considering the granulometric distribution, the GG-material was designed to provide the greatest possible particle compactness.

The mixed powder was pressed into 40 mm x 40 mm x 160 mm shapes and sintered at 1510°C for 12 hours. Several samples were then heat treated at 1400°C and 1500°C for 2, 6 and 18 days. The following notation will be applied to distinguish between the samples: n%(x/y)-z, where n% indicates the aggregate content, x is the duration and y the temperature of the heat treatment, and z the granulometry (GF or GG), e.g., 20%(6/1500)-GG. The letter "S" will replace "x/y" to designate a brick which has been sintered but not heat treated, such as 20%(S)-GG.

2.2. Characterization

TABLE I: COMPOSITION AND DESIGNATION OF THE REFRACTORY BRICKS STUDIED

Raw materials	Composition designation			
	0 wt-%	20 wt-%	40 wt-%	(20+5) wt-%
Tabular alumina, Alcoa T-60	90	70	50	65
Calcined alumina, Alcoa APC-2011SG	10	10	10	10
Electromelted MZ-aggregate, Elfusa TP-35	-	20	40	20
Microsilica, Elkem 971D	-	-	-	5

Diamond-polished samples were observed by scanning electron microscopy (SEM) using a Cambridge Stereoscan S4000 microscope.

X-ray diffraction associated to the Rietveld method was applied to quantitatively identify the phases. Diffractograms were obtained by a step-by-step procedure, in a Siemens D5000 machine, using K α -Cu radiation and 3 second steps of $\Delta 2\theta = 0.033^\circ$. The recorded 2θ -angles ranged from 15° to 60° . The DBWS-9411 (10) software was used for the quantitative Rietveld analysis.

The modulus of rupture (MOR or σ_r) at room temperature was used to mechanically characterize the GG-type material. The MOR was measured by subjecting unnotched samples to the 3-point bending test and measuring the maximum load at the point of catastrophic fracture.

The mechanical behavior at high temperature was characterized by creep test. The longest and shortest heat-treated samples were chosen for this test in order to reveal the effect of the microstructure. 30 mm x 30 mm x 40 mm samples having 40%(S)-GF and 40% (18/1500)-GF were tested at 1400°C under 1 MPa and 3 MPa compressive stress.

Porosity was characterized by immersion in water and pore size distribution by quicksilver intrusion (Micromeritics Porosizer 9320) to physically characterize the samples.

3. RESULTS AND DISCUSSION

3.1. Quantitative phase analysis of MZ-aggregates

A Rietveld analysis of the as-received MZ-aggregates showed the following composition: 70.3 wt-% mullite; 26.1 wt-% zirconia, and 3.5 wt-% alumina (11).

Figure 1 shows the liquidus-projection of the alumina-silica-zirconia equilibrium phase diagram, where point A represents the composition calculated as described in the previous paragraph. That diagram is based on propositions of Sorrell and Sorrell, Aramaki and Roy, Buttermann and Foster, and Alper. It is supposed that the eutectic temperature of the invariant reaction inside the alumina-mullite-zirconia compatible triangle is between 1700 °C and 1710 °C. The nominal composition given by producer (60 wt-% mullite, 38 wt-% zirconia and 2 wt-% impurities), which is represented by point B, is also shown in Figure 1 for comparison. Point C indicates the composition of the aggregate studied in reference 7 (nominal composition: 67 wt-% mullite and 33 wt-% zirconia). The last composition is apparently a two-phase one, but is located inside the compatible zirconia-mullite-silica triangle, as shown and discussed by Pandolfelli et al. (12).

Based on the X-ray diffraction findings, the most probable

Figure 1: $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ phase equilibrium diagram (liquidus projection). MZ-aggregate composition quantitatively determined in this work (point A), nominal composition of the aggregate (point B), and composition of the material of reference 7 (point C) are shown in the diagram. See the text for points D, E, and F.

crystallization path for the melted aggregate used in this work is as follows: first the melt goes straight from point A to the liquidus valley which begins in the zirconia-mullite quasi-binary. The remaining melt then passes from the valley down to the eutectic ternary reaction point inside the zirconia-mullite-alumina compatibility triangle. Mullite and zirconia are formed along the first part of this path while mullite, zirconia, and alumina appear in the second part. Zirconia, mullite and alumina, in the proportion 8:24:1, would be the result of that process, justifying the small content of free alumina found in the aggregate.

3.2. Quantitative phase analysis of complete refractories without microsilica

Tables II and III show the resulting composition of refractories containing 20 wt-% and 40 wt-% aggregate, respectively. These tables also show the R-Bragg values (in parentheses), which are an indicator of the quality of the structural data used for the Rietveld calculation.

Silica phase was considered in the Rietveld calculation due to its possible presence in the end materials owing to impurities in the raw materials, particularly in the MZ-aggregate. However, the results given in tables II and III did not corroborate this hypothesis, since the content found in the silica was too small and the corresponding R-Bragg-values were too high. Values of 30 and 40 were found for materials containing 20 wt-% aggregate and 40 wt-% aggregate, respectively.

As for heat treatment after sintering, tables II and III show, from left to right, the effect of treatment duration and temperature. It was impossible to identify a trend for the reactions between different pre-existing phases in the bricks or between these phases and impurities. This means that either no thermally activated reaction took place during the heat treatments or that the Rietveld method was not

TABLE II: PHASE CONTENTS (wt-%) IN REFRACTORIES CONTAINING 20 wt-% AGGREGATE, DETERMINED BY THE RIETVELD METHOD

Phases	Composition, heat treatment, and granulometry			
	20% (S)-GF	20% (2/1400)-GF	20% (6/1500)-GF	20% (18/1500)-GF
Alumina	86.8 (5.56)*	88.4 (4.04)	85.0 (4.61)	86.2 (3.06)
Mullite	8.3 (16.71)	4.6 (16.51)	7.3 (15.70)	7.2 (20.50)
Zirconia	4.8 (8.06)	6.7 (12.71)	7.7 (10.78)	6.3 (8.85)
Silica	-	0.3* (29.00)	-	0.2* (23.35)

R-Bragg-values, ♦ Not expected

TABLE III: PHASE CONTENT (wt-%) IN REFRACTORIES CONTAINING 40 wt-% AGGREGATE, DETERMINED BY THE RIETVELD METHOD

Phases	Composition, heat treatment and granulometry			
	40% (S)-GF	40% (2/1400)-GF	40% (6/1500)-GF	40% (18/1500)-GF
Alumina	63.6 (3.37)*	63.4 (4.16)	62.8 (4.32)	65.5 (3.11)
Mullite	24.9 (4.65)	25.4 (16.91)	23.8 (15.61)	23.1 (9.02)
Zirconia	11.3 (5.63)	10.6 (9.77)	12.6 (8.77)	11.2 (5.41)
Silica	0.2* (1.67)	0.7* (16.13)	0.8* (39.54)	0.7* (18.70)

R-Bragg-values, ♦ Not expected, * Average values based on the measurement of 3 samples of the same material.

TABLE IV: QUANTITATIVE PHASE ANALYSIS OF (20+5)%-GG REFRACTORY SUBJECTED TO SINTERING AND HEAT TREATMENT. UNITS IN wt-%.

Phases	Composition, heat treatment, and granulometry		
	Initial nominal composition	(20+5)% (S)-GG	(20+5)% (6/1500)-GG
Alumina	75.7	70.3 (4.26)	69.9 (4.40)
Mullite	14.1	22.9 (13.23)	21.2 (11.03)
Zirconia	5.2	4.5 (11.70)	5.9 (13.58)
Silica	5.0	2.3 (15.03)	3.3 (14.59)

R-Bragg-values are shown in parentheses.

sufficiently sensitive to detect them.

We are of the opinion that no reaction took place during the heat treatments and that the aggregate actually contained no free silica, corroborating our earlier analysis. Thus, the aggregate used in this study actually belongs the zirconia-mullite-alumina compatibility triangle and is more refractory than that of the composition shown at point C in Figure 1. In the same figure, points D and E represent the complete composition of the refractories with 20 and 40 wt-% aggregate, respectively.

3.3. Quantitative phase analysis of complete refractories containing microsilica

To promote the mullite formation reaction, a composition was prepared with 75 wt-% alumina, 20 wt-% MZ-aggregate, and 5 wt-% amorphous microsilica. This refractory was of the GG-type.

Table IV shows the quantitative phase analysis, with the corresponding R-Bragg-values shown in parentheses. The table reveals that the mullite formation reaction occurred as expected, since the content of alumina and silica was lower than the initial values. Point F in figure 1 represents the composition of that refractory.

Table IV also indicates that, even taking experimental errors into account, the heat treatment at 1500°C for 6 days did not contribute toward increased mullite content in comparison to the content already formed during sintering. A certain amount of silica failed to react and ended up becoming crystallized, indicating that the local fine alumina did not suffice to react with silica.

3.4. Mechanical characterization

The room temperature modulus of rupture was measured in GG-type refractories with 20 wt-% of aggregate and without aggregate. These measurements were taken from only sintered materials and from sintered and heat-treated materials. To observe the effect of *in situ* mullite formation, samples with 5 wt-% of microsilica ((20+5)%(S)-GG and (20+5)%(6/1500)-GG) were also characterized.

Figure 2 shows the results of the corrected modulus of rupture. For the sake of comparison, the results for materials containing 0 wt-% and 20 wt-% of aggregate from reference 7 are also shown. These materials were only in the sintered state and were produced with raw materials having particle sizes ranging from less than 10 μm to 2000 μm . The correction for different porosity-values was made according to equation 1 (13), using the porosity values shown in figure 3. The (20+5)%(S)-GG-refractory was taken as reference and all the MOR-values were normalized based on the porosity of this reference.

$$\sigma = \sigma_0 \cdot \exp(-b \cdot P)$$

[1]

In equation 1, P is the porosity, b is a non-dimensional constant, and σ_0 represents the MOR value of non-porous material. The value adopted for b was taken as 4 (14), which is the same value as that of alumina.

Figure 2 shows that the addition of 20 wt-% of MZ-aggregate to the alumina matrix increased the strength of the material of reference 7. However, the same addition produced a deleterious effect in the materials studied here. This comparison is reliable, since the materials made of only alumina in both studies presented very similar MOR-values, i.e., approximately 14 MPa.

It is probable that the particle size distribution of the raw materials limited the mechanical strength of the materials in this work. Table V shows the pore size ranges, which indicate that major flaws were generated in the materials containing aggregates. 20%-GG-type samples have pores ranging from 20 to 30 μm for equivalent diameters. In contrast, samples containing only alumina (0%-GG) presented pores with equivalent diameters of only 2-3 μm .

Hence, assuming that pores are the critical flaws and taking into account Griffith's equation (13), in its more general form,

$$\sigma_f = \frac{1}{Y} \cdot \sqrt{\frac{2 \cdot E \cdot \gamma_{\text{eff}}}{\pi \cdot a}} \quad [2]$$

where Y is a geometrical factor, γ_{eff} is the effective surface energy, E is Young's module, and a is half the length of the critical flaw, one can calculate that the strength of the complete refractory (containing aggregate) would be 0.3 of the one containing only alumina. This statement is confirmed by figure 2. In this evaluation, it was assumed that the ratio $\sigma_{r1} / \sigma_{r2} \cong \sqrt{a_2 / a_1}$ is valid. It is implicit in this ratio that the changes in Y, E and γ_{eff} are small considering the material with, 2, and without, 1, aggregate particles.

A 74.7 % increase in the MOR was obtained with the addition of 5 wt-% of microsilica to the material, taking as comparison the complete sintered refractory without microsilica (see figure 2). An increase of 64.3% was obtained after a 6-day heat treatment at 1500°C considering the porosity correction, which is evidence that microsilica contributes toward microstructural cohesion through the *in situ* formation of mullite, corroborating the phases determined and presented in table IV.

Figure 2: MOR values of the GG-type samples with porosity correction. The values correspond to samples without aggregate, with 20 wt-% aggregate, and with 20 wt-% of aggregate plus 5 wt-% of microsilica.

Figure 3: Apparent porosity values of the same samples shown in figure 2 obtained by water immersion.

TABLE V: PORE SIZE DISTRIBUTION IDENTIFIED BY QUICKSILVER INTRUSION POROSIMETRY.

Sample	Range of average pore diameter (μm)
0%(S)-GG	2-3
20%(S)-GG	20-30
20%(18/1500)-GG	20-30

Figures 4a and 4b show SEM micrographs of compositions with microsilica, (20+5)%(6/1500)-GG, and without microsilica, 20%(2/1500)-GG, respectively. Figure 4a shows large particles of MZ-aggregate and tabular alumina immersed in a matrix of fine alumina (tabular alumina and calcined alumina) plus microsilica. On the other hand, figure 4b, which shows the microstructure of the material without microsilica, reveals that the fine alumina matrix of that material was lost during cutting and polishing, providing evidence of the bond weakness between the large grains and the matrix of this refractory.

Thus, the material containing microsilica clearly has a more strongly bonded microstructure, as depicted in figure 4, and hence, greater mechanical strength. The use of the MZ-aggregate, though more refractory than that reported in reference 7 (since it belongs to the mullite-zirconia-alumina compatibility triangle), caused the mechanical strength to

(a)

(b)

Figure 4: Micrographs of cut and polished samples of composition (a) (20+5%)(6/1500)-GG and (b) 20%(2/1500)-GG obtained by SEM, using the secondary electron technique.

deteriorate due to the formation of a less strongly bonded microstructure. However greater aggregate/matrix cohesion is favored by the addition of a small amount of microsilica, which promotes the *in situ* formation of mullite during sintering and post-heat treatments (or use), resulting in a microstructure with enhanced mechanical strength.

The materials containing 40 wt-% of MZ-aggregate were subjected to constant-load compression creep tests under 1 MPa and 3 MPa at 1400°C. Materials with the fine microstructure and with and without 18-day heat treatments at 1500°C were used in these tests. Creep rate values were calculated from the resulting creep curves. Under 1 MPa compression the creep curve did not reach the stationary creep stage. So, the creep rate was calculated at 2% and 4% creep strains. Those results are shown on table VI. Pore influence correction was applied to the creep rate to permit comparison between materials with different total porosity values.

TABLE VI: CORRECTED VALUES OF CREEP RATE AT 2 % AND 4 % CREEP STRAIN VALUES FOR MATERIAL WITH 40 wt-% AGGREGATE. THE LEAST TOTAL POROSITY WAS TAKEN AS REFERENCE FOR RATE'S CORRECTION. THE CREEP TEST WAS CARRIED OUT UNDER 1 MPa AT 1400 °C.

Composition, heat treatment and granulometry	Total Porosity (%)	$\dot{\epsilon}$ at $\epsilon = 2\%$, corrected value (s^{-1})	$\dot{\epsilon}$ at $\epsilon = 4\%$, corrected value (s^{-1})
40%(S)-GF	34.95	4.0×10^{-7}	2.2×10^{-7}
40%(18/1500)-GF	25.16	4.5×10^{-8}	1.0×10^{-8}

Table VII: VALUES OF ϵ_{min} FOR 40 wt-% AGGREGATE CONTAINING MATERIALS OF THIS WORK AND FROM REFERENCE 7, INCLUDING 100 % ALUMINA MATERIAL AS REFERENCE. THE CREEP TEST WERE CARRIED OUT UNDER 3 MPa AT 1400 °C. IT IS ALSO SHOWN THE RANGE OF PARTICLE SIZE OF ALUMINA AND AGGREGATE FOR EACH MATERIAL.

Results' origin	Composition and heat treatment	Range of alumina particle size (mm)	Range of aggregate particle size (mm)	$\dot{\epsilon}_{min}$ (s^{-1})
ref. 7	100% alumina	0.044-2	-	1.1×10^{-7}
ref. 7	60% alumina + 40% MZ-aggr.	0.044-2	0.21-1	1.3×10^{-6}
this work	40%(S)-GF	< 0.045	< 0.3	8.0×10^{-8}
this work	40%(18/1500)-GF	< 0.045	< 0.3	3.0×10^{-7}

Compression stress of 3 MPa was also applied with the aim to compare the creep rate of the materials of this work and equivalent results from reference 7. Those results are shown on table VII.

For comparison, the creep rate was corrected by the effect of the total porosity on the creep process, based on the following equation (14,15):

$$\dot{\epsilon} = \dot{\epsilon}_0 \cdot \left[\frac{1}{(1-P^{2/3})^n} \right] \quad [3]$$

where n is equal to 1 and $\dot{\epsilon}_0$ denotes the creep rate for non-porous material.

From tables VI and VII it can be concluded that heat treatment exerted a remarkable influence on the creep rate of the fine-microstructure samples (type GF) of this work. Under 1 MPa compression, the creep rate reduction was of ninefold and twenty-twofold in comparison to the sample that was only sintered for 2% and 4% creep strain, respectively.

From table VII it can be observed that the MZ-aggregate addition caused an increase in the minimum creep rate of materials from both, reference 7 and this work. But, the heat treatment of 18 hours at 1500 °C almost recuperated the original value of creep rate of alumina from reference 7. The reduction in the creep rate caused by heat-treatment in comparison to the sample that was only sintered, is of twenty-sevenfold.

Tables VI and VII clearly show the influence of the heat treatment on the creep rate, even considering the corrected porosity values of the creep rate. This illustrates very well how microstructural transformations that occur during heat treatments towards equilibrium effectively influence the creep behavior of this type of refractory.

4. CONCLUSIONS

(i) Mullite, zirconia and a small amount of alumina deduced from the quantitative phase analysis by the Rietveld method were the phases present in the aggregate used in this

work. No vitreous phase was found. Therefore, the aggregate belongs to the zirconia-mullite-alumina compatibility triangle of the system $\text{ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$.

(ii) The MOR values highlighted the importance of adding small amounts of microsilica to the refractory formulation, since the *in situ* formation of mullite results in improved microstructural characteristics. This microstructure possesses stronger interbonding among large tabular alumina grains and between the aggregate and the fine alumina matrix resulting, in turn, in a refractory with greater mechanical strength.

(iii) Densification, sintering, and microstructural accommodation are the transformation phenomena and microstructural evolution observed in the refractories containing only alumina and aggregate. In addition, a mullitization reaction was observed in the refractories containing microsilica.

(iv) The heat treatment applied effectively increased the refractory's creep resistance, suggesting that the performance of these refractories tends to improve during their service life.

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REFERENCES

1. Z. Xiangchong, S. Gengchen, L. Xinyu. «High Temperature Properties of Carbon-Bonded Corundum-Mullite-Zirconia Materials». pp.1803-1813, In: Proceedings of UNITCER, USA, 1, 1989.
2. M. Yoshimura, Y. Hanaue, S. Somiya. «Non-Stoichiometric Mullites From $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-SiO}_2$ Amorphous Materials By Rapid Quenching». Ceramic Transaction, 6 449-456 (1990).
3. J. M. Rincon, et al.. «Microstructure of Mullite/Zirconia and Mullite/Zirconia/Alumina Tough Ceramic Composites». Acta Materialia, 53 [5] 1175-1179 (1987).
4. E. Di Rupo, M. R. Anseau. «Solid State Reactions in the $\text{ZrO}_2\text{-SiO}_2\text{-aAl}_2\text{O}_3$ System». Journal of Materials Science, 15 114-118 (1980).
5. F. Cambier, et al.. «Formation of Microstructural Defects in Mullite-Zirconia and Mullite-Alumina-Zirconia Composites Obtained by Reaction-Sintering of Mixed Powders». British Ceramic Transaction Journal, 83 196-200 (1984).
6. R. Torrecillas, et al.. «Microstructure and Mechanical Properties of Mullite-Zirconia Reaction-Sintered Composites». Acta Metallurgica et Materialia, 41 [6] 1647-1652 (1993).
7. C. Wolf, et al.. «Effect of Mullite-Zirconia Additions on the Creep Behavior of High-Alumina Refractories». Journal European Ceramic Society, 15 913-920 (1995).
8. S. Prochaska, J. S. Wallace, N. Claussen. «Microstructure of sintered Mullite-Zirconia Composites». Communications of the American Ceramic Society, 66 [8] c-125 - c-127 (1983).
9. P. Boch, T. Chartier. «Tape-Casting and Properties of Mullite and Zirconia-Mullite Ceramics». Journal of the American Ceramic Society, 74 [10] 2448-2452 (1991).
10. R. A. Young, et al.. «Rietveld Analysis of X-Ray and Neutron Powder Diffraction Patterns». In: User's Guide to Program DBWS-9411, Atlanta, 1995, 60 p..
11. C. R. Ferrari, J. A. Rodrigues. «Refratários de Alumina Contendo Agregado Mullita-Zircônia: Aspectos Microestruturais». Cerâmica, 46 [298] 83-90 (2000).
12. V. C. Pandolfelli, V. R. Salvini, J. A. Rodrigues, H. Hübner, C. Wolf. «Evaluation of Thermomechanical Properties of Alumina Refractories Containing a Fused Mullite-Zirconia Aggregate». pp. 373-380, Proceedings of UNITECR'95, Kyoto, Japan, 2, 1995.
13. E. D. Zanotto, A. R. Migliore. «Propriedades Mecânicas de Materiais Cerâmicos: Uma Introdução». Cerâmica, 37 [247] 7-16 (1991).
14. E. Dörre, H. Hübner. «Mechanical Properties». pp. 74-103, In: Alumina. Springer-Verlag, 1994.
15. T. G. Langdon. «Dependence of Creep Rate on Porosity». Journal of the American Ceramic Society, 55 [12] 630-631 (1994).

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