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A study of the stabilization of aluminium titanate

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A tialite ceramics (Al_2TiO_5) was synthesized at a temperature of 1500 °C, incorporating CaF_2, La_2O_3, SiO_2 or kaolin and MgO additives. Its thermal stability was investigated by thermocycling in a reducing medium. The batches containing SiO_2 or kaolin additives underwent a decomposition to rutile and corundum. A stabilized ceramic with added MgO was produced. X-ray and electron-probe microanalysis established the presence of Mg/Al, Ti_z/O_4, $Al_{2-x-y}Ti_{1+x}Mg_yO_5$ and $Ca_{1-x}La_x/Al_{12-y-z}Mg_yTi_z/O_{19}$ solid solutions, which retained their chemical composition after thermocycling in a reducing medium.

1. Introduction

The aluminium titanate-based ceramic is characterized by a low coefficient of thermal expansion [1, 2] and a high melting temperature which assign it to the thermostable fireproof materials which have versatile applications [3–6]. A shortcoming of this ceramic is its tendency to decompose in the temperature range 750–1300 °C [7, 8]. As pointed out by many investigators [9–11], the temperature of maximal decomposition is in the range 1100–1300 °C. Aluminium titanate decomposition depends on the following more significant factors: the pressing and firing technology [12, 13], the atmosphere in which the ceramic is used and the size of its crystal grains [14, 15]. It is well known, that the thermal decomposition of Al_2TiO_5 may be controlled by adding lanthanides [16], SiO_2, MgO, MgF_2, Fe_2O_3, ZrO_2, etc. [17–19].

The thermal stability of the aluminium titanate ceramic is of importance due to its practical applications. It is related to the tialite solid solution formation, including oxide additives [20–22]. Many uncertainties still exist concerning the mechanism of stabilization and the degree of solubility of the introduced additives.

The object of the present work was to investigate the effect of CaF_2, La_2O_3, SiO_2, kaolin and MgO on the phase composition of the ceramic material, aiming to achieve its stabilization.

2. Experimental procedure

In order to eliminate the volumetric changes of the end product accompanying the tialite formation, a two-stage technology was applied. The investigated compounds are presented in Table I.

The oxides $\alpha - Al_2O_3$ (99.99%, particle size 1.8 μm) and TiO_2 (rutile, 99.92%, particle size 1.8 μm) were in stoichiometric ratio with the added CaF (99.9%) and initially were milled by the wet method for 12 h in a ball mill with corundum milling elements. The obtained batch was then dehydrated, plastified and bricketted under a pressure of 100 MPa, the brickets fired, holding the final temperature of 1400 °C constant for 4 h. The fired brickettes were then subjected to crushing and wet milling with the introduction of the corresponding additive. The homogenization was carried out in a plastic container, followed by drying, plastifying the pressed powder and semidry-pressing at 100 MPa. The samples were fired at 1500 °C, for 4 h, after which they were subjected to thermal treatment at a maximum temperature of 1370 ± 5 °C in a furnace in a gaseous medium CO–H_2 (8%–12%) with a cycle duration of 26 h. A number (28) and thermal treatment cycles were carried out. The apparent density and the water absorbtivity were determined by standard techniques. The phase composition of the samples was determined using a X-ray analyser "DRON-UM1" with a copper radiation source (CuK_α). The quantitative chemical analysis of the experimental samples was determined using a "Philips-505" scanning electron probe microanalyser. The distribution of the basic elements in the selected sections was determined by X-ray spectral microanalysis, using an energy EDAX spectrometer.

3. Results and discussion

The apparent density, ρ, and the water absorbability, WA, data, prior to and after the thermocycling are presented in Table II and the corresponding diffraction patterns of the separate compositions are shown in Figs 1 and 2.

After being subjected to thermal treatment, the experimental samples containing SiO_2 and kaolin, underwent a partial decomposition of the Al_2TiO_5 basic phase, which was indicated by the corresponding maxima for rutile ($d = 0.324$ nm) and corundum ($d = 0.347$ nm). The structure of the samples becomes looser, as indicated by the increase in the water absorbability and the decrease of the apparent density.

The third series of compositions, incorporating MgO, is of particular interest, because as the samples contain several phases, which remain unchanged after thermocycling in a reducing medium (Fig. 2). Insignificant variations are established for the water absorbability and the apparent density after thermocycling.

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TABLE I

Additives		Compositions								
		1	2	3	4	5	6	7	8	9
CaF_2	(%)	3	3	3	3	3	3	3	3	3
La_2O_3	(%)	2	2	2	2	2	2	2	2	2
SiO_2	(%)	5	10	15	–	–	–	–	–	–
Kaolin	(%)	–	–	–	5	10	15	–	–	–
MgO	(%)	–	–	–	–	–	–	5	10	15

TABLE II

Property	Compositions								
Property	1	2	3	4	5	6	7	8	9
WA, cycle 0 (%)	2.13	1.34	1.36	1.90	1.35	1.32	1.85	1.75	1.24
ρ, cycle 0 ($g\,cm^{-3}$)	3.14	3.05	2.97	3.17	3.28	3.24	3.14	3.27	3.25
WA, cycle 28 (%)	7.54	5.87	2.68	4.39	7.30	9.20	4.08	2.61	1.62
ρ, cycle 28 ($g\,cm^{-3}$)	2.82	2.84	2.90	2.94	2.85	2.64	3.01	3.06	3.17

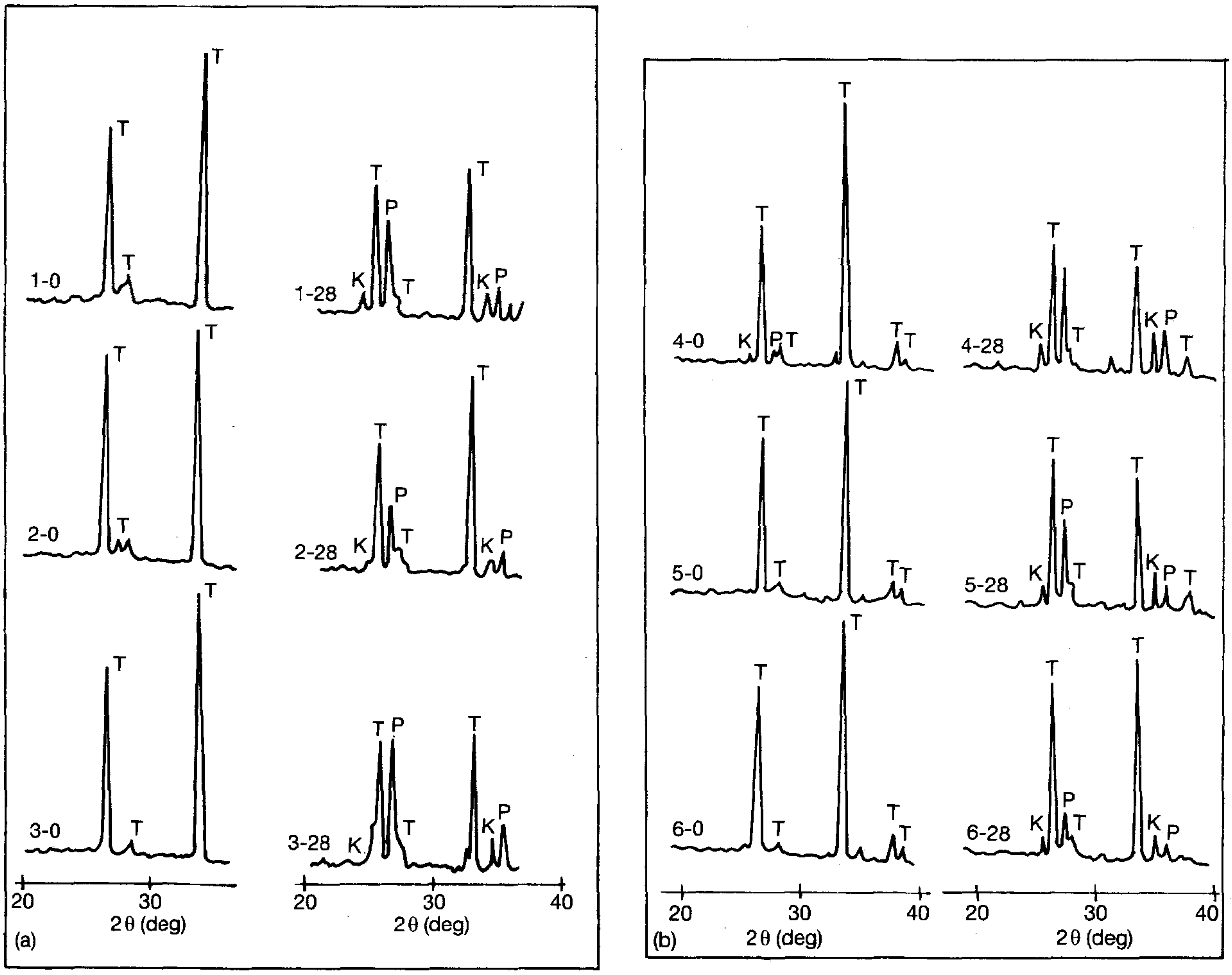

Figure 1. Diffraction patterns of the ceramic Al_2TiO_5 samples with (a) SiO_2 and (b) kaolin added prior to cycle 0 and after cycle 28 thermal treatment in a reducing medium. T, Al_2TiO_5; P, TiO_2 (rutile); K, Al_2O_3 (corundum).

Spinel, tialite and an Al_2O_3-enriched phase may be identified from the diffraction data.

When compared with standard $MgAl_2O_4$ data, the interplanar spaces for $Mg(Al, Ti)_2O_4$ show a close relationship. With increasing MgO content in the initial composition, a parallel increase in the diffraction pattern maxima was observed (0.284, 0.243, 0.201 nm), which is an indication of the higher amount of spinel phase in the experimental samples.

The spinel segregations are observed clearly in the micrographs, owing to the fact that they possess lower reflection ability (Figs 3 and 4). They are not uniform-

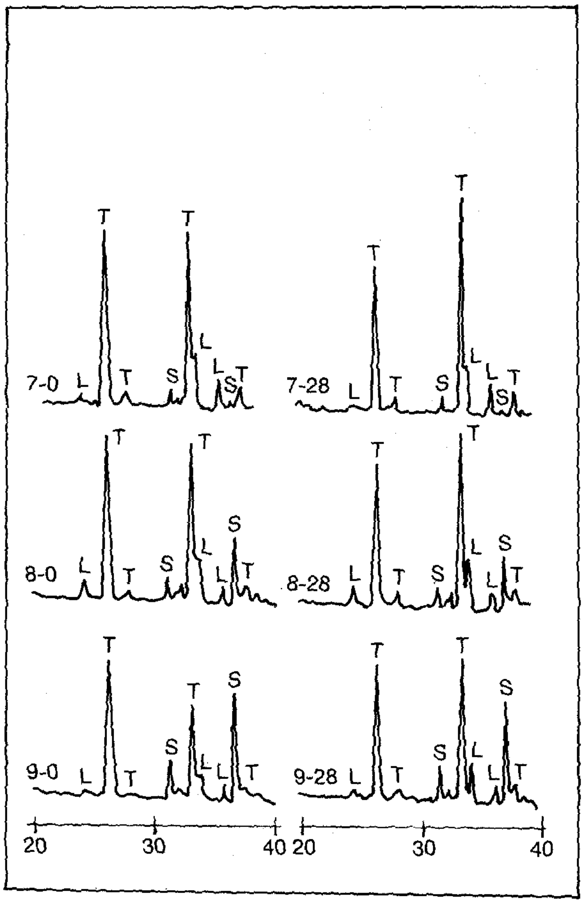

Figure 2. Diffraction patterns of the ceramic Al_2TiO_5 samples, with MgO added prior to (cycle 0) and after cycle 28 thermal treatment in a reducing medium. T, Al_2TiO_5; S, $MgAl_2O_4$; L, solid $Ca\cdot 6Al_2O_3$–$LaAl_{11}O_{18}$ solution.

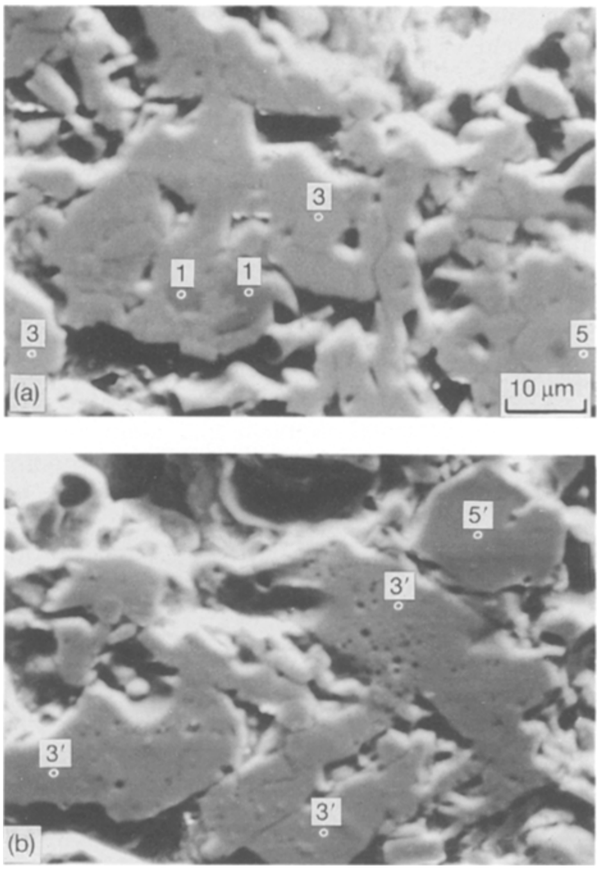

Figure 3. Scanning electron micrographs of the ceramic samples, including 5% added MgO, (a) prior to cycle 0 and (b) after cycle 28 thermal treatment in a reducing medium.

ly spread in the bulk of the ceramic body and their quantity is considerably greater when the amount of MgO added is 15%. An attempt was made to derive the cristallo-chemical formulae by the oxygen method, based on the data obtained from the quantitative chemical analysis of the spinel phase

5% MgO cycle 0 1 $Mg_{0.72}(Al_{2.14}Ti_{0.03})_{2.17}O_4$

5% MgO cycle 28 1' $Mg_{0.71}(Al_{2.13}Ti_{0.03})_{2.17}O_4$

15% MgO cycle 0 2 $Mg_{0.81}(Al_{2.09}Ti_{0.03})_{2.12}O_4$

15% MgO cycle 28 2' $Mg_{0.80}(Al_{2.10}Ti_{0.03})_{2.14}O_4$

The crystallo-chemical formulae correspond to the spinel-type $Mg(Al, Ti)_2O_4$ compounds. A significant Mg^{2+} insufficiency is observed in the composition of the spinel phase containing 5% added MgO, which may be attributable to an isomorphic Al^{3+} substitution for the Ti^{4+} ion, or to an inclusion of TiO_6 octahedra which causes the appearance of cation vacancies, thus retaining the electroneutrality of the crystal. The presence of Mg^{2+} in the compositions of the other phases should also de noted. The extent of cation difficiency is limited by the MgO content in the initial batch; it decreases when the quality of additive is increased. After thermocycling of the ceramic samples in a reducing medium, the data obtained indicate insignificant changes in the chemical composition of the spinel and in the values of the cation coefficients.

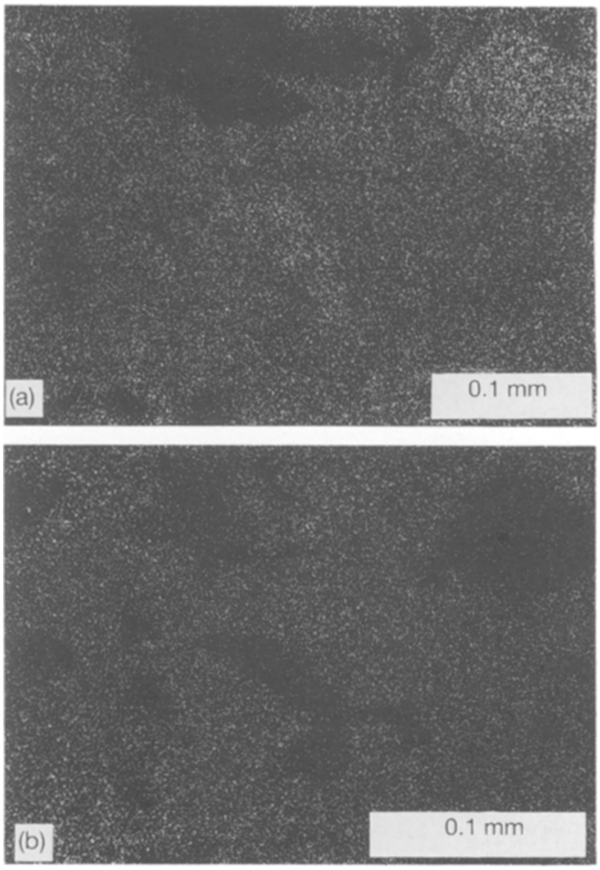

Figure 4. Scanning electron micrographs of the ceramic samples containing 15% added MgO, (a) prior to (cycle 0) and (b) after (cycle 28) thermal treatment in a reducing medium.

Consequently, the spinel is stable to thermal treatment.

Frequently the other two phases (tialite and Al_2O_3-enriched phase) are inhomogeneous, because they contain inclusions of pores and spinel, and are difficult to discern and detect through their reflection ability (Figs 3 and 4). They are closely associated and have intergrown into one another, because they were probably formed simultaneously. Both phases are successfully identified from the micrographs for the distribution of the two basic elements, because their aluminium content differs considerably (Figs 5 and 6). The tialite phase prevails with a relatively equal distribution of elemental titanium and aluminium; the tialite phase was identified with the help of the diffraction patterns (Fig. 2). From the scanning electron micrograph is seen that tialite consists of lamellar grains, whose size is 2–20 μm. The existence of some differences in the diffraction patterns and in the chemical composition data, obtained from the electron-probe mycroanalyses (EPMA), allows it to be treat as a phase of a variable composition $Al_{2-x-y}Ti_{1+x}Mg_yO_5$. It contains up to 2% MgO in the form of an isomorphic admixture. The tentative crystalo-chemical formulae of the tialite phase were derived by the oxygen method on the basis of the electron probe results

5% MgO cycle 0 3 $Al_{1.55}Ti_{1.28}Mg_{0.12}O_5$
5% MgO cycle 28 3′ $Al_{1.53}Ti_{1.30}Mg_{0.12}O_5$

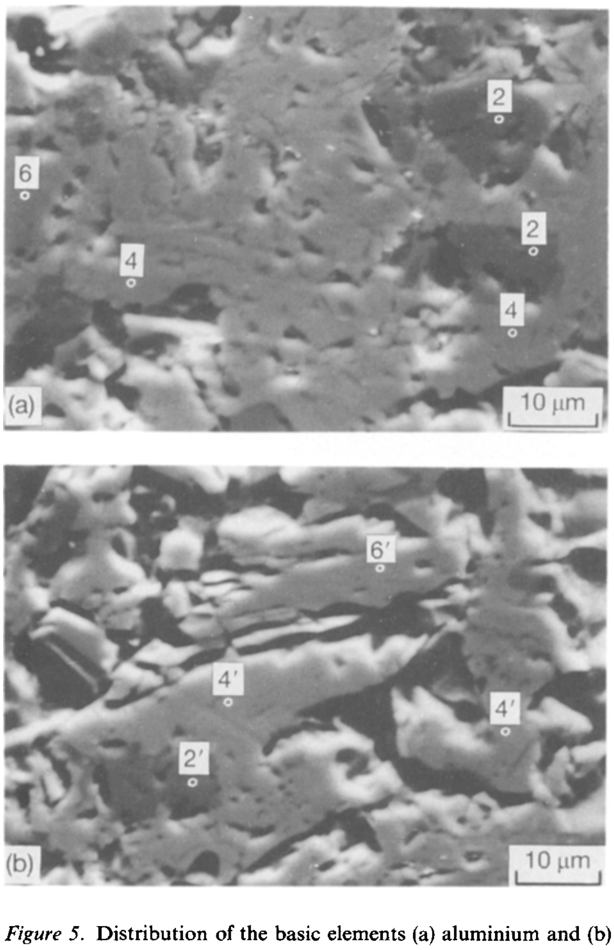

Figure 5. Distribution of the basic elements (a) aluminium and (b) titanium in the ceramic body, containing 5% added MgO after thermal treatment (cycle 28) in a reducing medium.

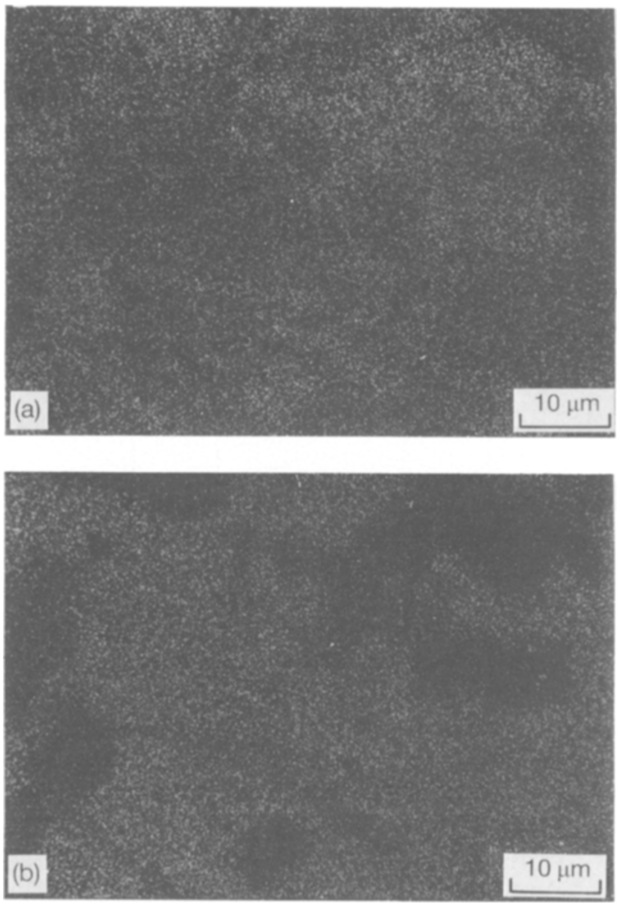

Figure 6. Distribution of the basic elements (a) aluminum and (b) titanium in the ceramic body containing 15% added MgO, prior to the thermal treatment in the reducing medium.

15% MgO cycle 0 4 $Al_{1.26}Ti_{1.41}Mg_{0.22}O_5$
15% MgO cycle 28 4′ $Al_{1.26}Ti_{1.42}Mg_{0.26}O_5$

The crystallo-chemical formulae illustrate well the complex composition of the mixed tialite, which may be treated as a solid anosovite solution with unrestricted solubility of the defined Al_2TiO_5 and $MgTi_2O_5$ compounds. The formation of a continuous solid solution is determined by the decreased crystal lattice deformation, mostly due to the distortion of the aluminium–oxygen octahedra. This is accomplished by substituting $Al^{3+}(R = 0.053$ nm) for Ti^{4+} ($R =$ 0.067 nm) and Mg^{2+} ($R = 0.078$ nm) ions [23]. This isomorphic substitution is not limited by the quantity in the initial batch. It should be underlined that the megnesium and titanium cations increase proportionally to the corresponding decrease of the aluminium cations, which proves the existence of the model, as pointed out. From the chemical composition analyses and the crystallo-chemical formulae obtained, it is stated that the solid $Al_{2-x-y}Ti_{1+x}Mg_yO_5$ solution retains its composition almost unchanged after thermocycling in a reducing medium.

With the help of diffraction analysis and X-ray microprobe analysis, a third phase, enriched in Al_2O_3, is identified (Figs 2–6). Lamellar crystals, possessing a hardly distinguishable, but higher than the tialite phase reflection ability, are observed in the electron micrographs. The crystallo-chemical formulae were calculated, presuming the existence of solid $CaO \cdot 6Al_2O_3$ and $LaAl_{11}O_{18}$ solutions, because they possess close interplanar spaces and the most intensive of which are registered on the diffraction patterns (0.263, 0.248, 0.211 nm) in Fig. 2. The calcium content is relatively high, compared to that of lanthanum which was why a hypothetical crystallo-chemical formulae was proposed of the type $AB_{12}O_{19}$, where $A = Ca^{2+}, La^{3+}$, $B = Al^{3+}, Ti^{4+}, Mg^{2+}, Si^{4+}$, as follows

5% MgO cycle 0 5

$(Ca_{0.76}La_{0.30})_{1.06}(Al_{10.33}Mg_{0.55}Ti_{0.87})_{11.75}O_{19}$

5% MgO cycle 28 5′

$(Ca_{0.80}La_{0.31})_{1.07}(Al_{10.19}Mg_{0.58}Ti_{0.92}Si_{0.04})_{11.73}O_{19}$

15% MgO cycle 0 6

$(Ca_{0.71}La_{0.31})_{1.02}(Al_{9.52}Mg_{0.85}Ti_{1.28}Si_{0.06})_{11.71}O_{19}$

15% MgO cycle 28 6′

$(Ca_{0.71}La_{0.31})_{1.01}(Al_{9.76}Mg_{0.79}Ti_{1.20})_{11.75}O_{19}$

A complex phase of the solid solution type is formed: $Ca_{1-x}La_x(Al_{12-y-z}Mg_yTi_z)O_{19}$, where the isomorphic substitutions of the type $2La^{3+} \rightleftharpoons 3Ca^{2+}$ and $2Al^{3+} \rightleftharpoons Ti^{4+} + Mg^{2+}$ probably occur.

With batches containing 15% MgO, the magnesium and titanium contents increase, while that of aluminium decreases, where the precence of an isomorphic substitution, analogous to that for the tialite phase, is assumed. The results obtained show that after carrying out the decomposition test, the phase does not undergo any chemical change. Additionally, the coefficients of thermal expansion (CTE) of the experimental samples were measured prior to and after thermocycling. These data show that the values of the $CTE_{20-700\,°C}$ remain unchanged: $\alpha_{\text{cycle }0} = -0.5\,10^{-6}\,°C^{-1}$, $\alpha_{\text{cycle }28} = -0.56\,10^{-6}\,°C^{-1}$, for the batch with 5% MgO; and $\alpha_{\text{cycle }0} = +1.6\,10^{-6}\,°C^{-1}$, $\alpha_{\text{cycle }28} = 1.57\,10^{-6}\,°C^{-1}$ for the batch with 15% MgO proving that the ceramic materials is stabilized.

4. Conclusion

From the experiments carried out, it was established that when the prepared tialite materials, with SiO_2 and kaolin added, were treated under reducing conditions, they decomposed to Al_2O_3 and TiO_2 (rutile).

The batches containing added MgO were of particular interest. They exhibited good thermal properties, combined with decomposition stability. The stabilizing effect of the additive is related to the formation of the complex phases, $Mg(Al, Ti)_2O_4$, $Al_{2-x-y}Ti_{1+x}Mg_yO_5$ and $Ca_{1-x}La_x(Al_{12-y-z}Mg_yTi_z)O_{19}$, presenting solid solutions. The tialite phase is an anosovite solid solution of two defined isostructural compounds, which are formed by substituting Al^{3+} for Ti^{4+} and Mg^{2+}. The degree of isomorphic substitution is limited by the MgO content in the initial batch. An analogous substitution is established in the formation of the phase $Ca_{1-x}La_x(Al_{12-y-z}Mg_yTi_z)O_{19}$. The preservation of the chemical phase composition in the ceramic body after thermocycling in a reducing medium, indicates that the produced thermostable ceramic is a prospective candidate for the creation of fireproof material.

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