An investigation of microstructure and properties of magnesia-magnesium aluminate spinel refractory promoted with Titania for steel industries

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Abstract

Alkaline bricks, especially magnesia refractory products containing spinel, are the most important refractory materials that are used in many industries such as steel, cement and non-ferrous industries due to their special physical, chemical and mechanical properties. In this study, the effect of titania addition on the properties and microstructure of chrome spinel free magnesium alkali refractories was studied. After sintering of the product samples at two temperatures of 1500 °C and 1600 °C, different physical and mechanical properties such as density, apparent porosity, cold compressive and bending strength, load retardation and warm rupture modulus were evaluated according to ASTM standards. The results showed that with increasing Titania up to 6% by weight after sintering at 1600 °C compared to the reference sample without additive, density and apparent porosity due to the formation of spinel phases especially magnesium titanate increased and then decreased, respectively. Also, as the titania amount increased to 4% cold compressive and bending strength increased. To further increase, due to the increase in volume percentage of magnesium titanate and magnesium aluminate spinel phases, cold compressive and bending strength decrease and increase, respectively. The results also show that by increasing the Titania up to 6% by weight compared to the sample without additives, the modulus of warm rupture (thermomechanical properties) increases at 1000 °C and 1400 °C and on the delay under load by increasing the amount of titania to 2% by weight from temperature T_0 =1570 ºC is added to 1620 ºC under load 2 Kg / cm^2.

Keywords: Refractory materials, Magnesia-spinel refractory, Titania, Steel furnace.

1. Introduction

The production of refractory materials is of particular importance due to its widespread use and strong dependence on various industries, especially in infrastructure industries such as steel, cement, aluminum, copper and glass. Refractory materials are generally materials used in the lining of high temperature furnaces and maintain their physical properties at high temperatures (600 °C to 2000 °C) and the environmental conditions of the furnace. Obviously, the importance of a refractory material is not only in its thermal stability, but also physical and chemical stability against the destructive effects of high temperature work environment. In other words, refractories are materials with high melting and pasting points that are able to maintain the chemical, physical, mechanical and thermomechanical properties in high temperature application conditions [1-3].

In a comprehensive definition, refractories can be chemically divided into three categories: acid refractories such as zirconia and silica refractories, neutral refractories

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that have no cure for acidic or alkaline conditions, such as bauxite and alumina refractories and alkaline refractories that mainly contain base oxides such as MgO, CaO, such as magnesia, magnesia-chromite, magnesia-spinel, magnesia-graphite and dolomite refractories[4-7]. Magnesia-chromite refractories have been among the most widely used alkali refractories used in the steel, iron and cement industries for many years. But in recent years, chrome-free alkali refractories, including magnesia-spinel refractories, to reduce the environmental hazards of chrome-containing refractories widely replaced in the cement, iron, steel and non-ferrous metals industries, especially magnesia-chromite bricks [(8-11)]. Hexavalent chromium ions in waste bricks are highly toxic, highly soluble in water, and can enter groundwater. On the other hand, it is highly carcinogenic and leads to allergic skin lesions and respiratory diseases. Therefore, the production of such bricks in the world has been accompanied by a declining trend and as a result, in recent years, chromium-free bricks have been developed, including magnesia-spinel products. On the other hand, magnesia-spinel refractories are highly resistant to corrosion and chemical attacks due to the lack of spinel reaction with alkali materials and are very little affected by the furnace atmosphere. However, in order to improve the properties of magnesium refractories, some additives are usually added to it. These additives can improve coatability, increase strength and reduce corrosion in magnesia refractories [12-14)].

Iwadoh et al. investigated the effect of adding Fe_2O_3 and TiO_2 on magnesia-spinel refractories. They obtained results that show that the refractory laboratory sample produced, in addition to excellent corrosion resistance, also has a very good coatability. Meanwhile, when the brick contains some iron impurities, a solid or spinel solution consisting of ferrite-magnesia ($MgO.Fe_2O_3$) is formed with TiO_2 and Al_2O_3 this product not only has suitable resistance to high temperatures, but also increases resistance to hydration. It was also concluded that these refractories are not only suitable for use in rotary cement kilns it can also be used in iron, steel and non-ferrous metal refining industries [15, 16)].

Kimuro et al. examined a sample of magnesia refractory brick with titania and they concluded that the magnesium ortho-titanate phase formed between magnesium particles increases strength and also provides high resistance to the penetration of alkaline melt at high temperatures [17)]. Makin et al. also investigated chromium-free refractories in the $MgO-TiO_2-Al_2O_3$ three-component system. They concluded that it had a higher resistance to thermal shock than conventional magnesia-chromite and magnesia-spinel refractories. They also concluded that in the presence of TiO_2, the sintering process of bricks is accelerated [18)]. Kalapakli investigated the effect of adding TiO_2 on the properties of magnesia-chromite refractory bricks and concluded that by increasing TiO_2, cold compressive strength increases while porosity decreases. They also observed that in this system, monosilicate, periclass, ortho-titanate magnesium and magnesochromite phases are formed, which ultimately improves the microstructural properties [19)]. Lodha et al. investigated the alkaline refractories of chromium-free and magnesium-rich spinel bonds by substituting ions exchange instead of three-dimensional chromium ions and investigated the effect of adding TiO_2 and Fe_2O_3 on the properties. Investigating the effect of adding TiO_2 at the nanoscale and micron scale, the researchers concluded that in the presence of nanosize titanium, due to increased reactivity, spinel formation accelerated and density improved [20)]. Akira Kaneyasu also investigated the effect of adding TiO_2 on the properties of magnesia-spinel bricks and concluded that with increasing TiO_2 up to 2%, cold compressive strength and density increase and apparent porosity decreases [21)].Najafi et al. also investigated the effect of adding TiO_2 on the properties of alumina-spinel masses and concluded that increasing TiO_2 accelerates the sintering process and increases density and reduces porosity. Also, due to the improvement of stable linear changes (PLC) due to the addition of this material, the shockability of the parts is finally improved [22)].

In this paper to eliminate defects and improve various properties including physical (apparent porosity, density), thermomechanical (refractory under load and warm bending strength) and mechanical properties (cold flexural strength and cold compressive strength) as well as corrosion resistance and coatability, TiO_2 additive is used. The role of titania addition on the properties microstructure of chromium-free magnesium bricks was examined by analyzing its sintering behavior through warm and cold mechanical properties.

2- Materials and research methods

Magnesia is the most important refractory raw material of the samples studied in this article. Since this oxide is the main part of the formulation, in the design of refractory samples, the quality of magnesium used will have a very important effect on all properties and characteristics such as purity, c / s ratio, density and porosity, bonding phases and granulation distribution. In this study, Iranian zinc magnesia with a purity of more than 96% has been used. Table 1 shows the chemical analysis of consumed magnesia performed in a more chemical method.

Table 1. Chemical analysis and density of magnesium raw material.

Oxide	MgO	CaO	Al_2O_3	Fe_2O_3	SiO_2	L.O.I	B.D (g/cm^3)
Purity (wt %)	96.22	1.62	0.25	0.82	0.6	0.28	3.25

Spinel is the second component of the desired laboratory body. Depending on the amount of excess alumina or magnesium it contains, this substance will have a direct effect on the sintering behavior of the samples. Magnesite-rich sinter is a product of Alcoa USA with the code AR78 and purity higher than 99% and particle size range is 0- 0.5 mm. The chemical analysis of this substance, which has been done by wet chemistry method, is given in Table 2.

Titanium dioxide or titania is an important additive in the manufacture of chromium-free refractories. Titania has a significant effect on various properties, especially mechanical and thermomechanical properties of refractory materials. It should be noted that the purity, crystal structure and particle size of titanium oxide play an important role in terms of its properties. In this research, titanium dioxide of Merck which has a rutile structure has been used. The average particle size d (50) of consumed titanium oxide particles is 3 µm and the chemical purity is 99%. The chemical analysis and physical properties of this material are given in Tables 3 and 4 according to the technical specifications sheet of the manufacturer and also the X-ray fluorescence method.

Alumina is another major and relatively pure raw material used in the refractory industry that has several types. One of the most important types of alumina is plate-shaped alumina (alumina tubular), which is a type of high-purity aluminum oxide that produces alpha alumina crystals into large crystalline grains (corundum phase) through temperature control. Particle size range 0-0.05 mm is selected. Table 5 shows the chemical analysis of consumable alumina tubular.

Since porosity plays an important role in reducing the life of refractory bricks, it is always tried to make the bricks have the highest density. Therefore, the grain size of the product must be selected correctly to achieve the maximum density. Selection of samples in this study was based on previous studies in the field of magnesium refractories. Basically, the granulation of refractory materials has three components: large, medium and small to achieve maximum compaction. In this study, a large component of 1-4 mm, a medium component of 0.5-1 mm and a smaller component of 0.5 mm were selected. After preparing the raw materials and weighing them,

Table 2. Chemical analysis of consumed spinel.

Oxide	MgO	CaO	Al_2O_3	Fe_2O_3	SiO_2	L.O.I	B.D (g/cm^3)
Purity (wt %)	33.00	<0.01	64.00	<0.01	0.50	0.65	3.28

Table 3. Physical properties of consumable titania raw material.

Solubility at temperature 20 (ºC)	Melting point (ºC)	Molecular Weight (g/mol)	density (g / cm^3)	Bulk density (kg / m^3)
Solvable	1855	79.89	4.20	850

Table 4. XRF Chemical Analysis of Titania Consumption.

Element	Ti	As	Fe	Pb	Sb	Zn	Other heavy metals
Purity	99% ≥	≤0.0005 ppm	≤0.005 ppm	≤0.001 ppm	≤0.01 ppm	≤0.005 ppm	≤0.002 ppm

Table 5. Chemical analysis of consumable tabular alumina.

Oxide	Na_2O+K_2O	CaO+MgO	Al_2O_3	B.D (g/cm^3)
Purity (wt%)	<0/5	<0/4	99/5	3/55

according to the above, the granulation of the formulations according to Table 6 and the formulations of different samples with their additives and codes are given in Table 7.

In order to prepare the samples, for each formulation, large and medium particles were first mixed together for 5 to 7 minutes. At this stage, while mixing, 3% of $MgCl_2$ binder was added and mixing was performed for another 5 minutes. Then the powder component was added and mixing continued for another 5 to 7 minutes. The total mixing time for each formula was 15 to 20 minutes and the amount of batches was equal to 20 kg. The total preparation time of the samples was about 45 to 60 minutes. Mixing was done manually in plastic containers. Also, since the additives in question are usually very fine-grained and are generally used in very small amounts compared to other refractory materials in the sample formulation. Therefore, in order to achieve their better dispersion in the field of refractory materials, additives were mixed with fine-grained components of the formulation.

The samples were formed by hydraulic press with a pressure of 1200 kg / cm^2. For this purpose, a number of samples were made in the form of bricks in dimensions close to the actual size of the bricks used in the rotary cement kiln. Also, for more detailed studies, a number of samples were pressed into small cylinders. The mold intended for making brick samples had dimensions of 198 * 200 mm and the mold used for making cylindrical specimens had dimensions. Figure 1 shows a number of bricks and Figure 2 shows a number of pressed tablets.

Table 6. General formulation and granulation of different components in the composition of samples.

Material	Grading	Wt.%
MgO	1-4 mm	40
	0.1-5 mm	15
	0-0.5 mm	32 ،34،36 ،38
Spinel	0-0.5 mm	5
Al_2O_3	0-0.5 mm	2
TiO_2		2 ،4،6

Table 7. Formulation and coding of samples containing various additives.

Code Sample	Magnesia	Spinel	Alumina	Titania	**Sintering temperature ° C**
T2-1500	36	5	2	2	1500
T2-1600	36	5	2	2	1600
T4-1500	34	5	2	4	1500
T4-1500	34	5	2	4	1600
T6-1500	32	5	2	6	1500
T6-1600	32	5	2	6	1600
C2-1600	36	5	2	2	1600
C4-1500	34	5	2	4	1500
C4-1600	34	5	2	4	1600
C6-1500	32	5	2	6	1500
C6-1600	32	5	2	6	1600

Fig. 1. Some of pressed brick samples.

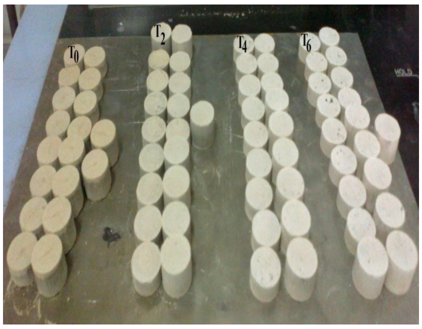


Fig. 2. Some of pressed tablets.

After pressing and shaping the samples, drying was performed for 24 hours at a temperature of 110 °C. The drying step is very important and sensitive, as some moisture is always added to the formulation in order to better shape the samples as well as to process the binder. If the moisture along with the formulation after pressing is not removed carefully at this stage, there is a possibility of cracking of the samples, especially for larger samples, in the early stages of sintering and during a sharp rise in temperature. An electric dryer was used to dry the samples.

The sintering and baking stage is one of the most important and sensitive stages in the production of ceramics and refractory materials, and it is possible for different types of defects to be present in the production parts after this stage. Therefore, the correct choice of cooking temperature and storage time at maximum temperature, along with the correct design of the entire heating regime and the selection of the optimal heating rate, have a significant effect on achieving flawless samples and fully sintered. In order to achieve bodies with suitable density of the selected formulations, two different maximum firing temperatures were selected according to the study sources and what is commonly used in the industry in the production of magnesia refractory bricks and magnesia spinel. For this purpose, the samples were sintered at 1600 and 1500 °C in a shuttle oven. The samples were stored at a maximum temperature of 6 hours and the whole cooking process took about 55 hours.

Determining the properties of samples

In this paper, the density and apparent porosity of the samples were measured by immersion method according to ASTM-C830 standard. In order to perform the strength test according to ASTM-C133 standard, first samples of brick-shaped parts were cut into cylindrical bodies with a diameter of 60 mm and a height of 60 mm. In addition, the load-bearing surfaces must be perfectly parallel to each other. In this experiment, measurements were taken from at least 3 samples and the average results were reported. The cold compressive strength measuring device is made by EKO company in Japan and is a 522TSA-model. ASTM-C583 standard has been used to evaluate the cold flexural strength. First, samples with dimensions of 140 * 40 * 25 mm are cut from bricks and then subjected to loading at a certain speed. For this purpose, in order to apply the load, it must be done in the direction perpendicular to the direction of the sample press. In this experiment, measurements were taken from at least 3 samples and the average results were reported. Cold flexural strength measuring device is made by EKO company in Japan and the model is JAN-1992. ASTM-C64 standard was used to measure hot flexural strength. For this purpose, the samples were cut from the main brick into pieces with dimensions of 25 * 40 * 140 mm and tested at two temperatures of 1000 and 1400 °C. In this experiment, measurements were taken from at least 3 samples and the average results were reported. The hot flexural strength measuring device is made by the Japanese company EKO and model TSA- 522. The amount of refractory under load is done according to ASTM-C113 standard. For this purpose, first the brick was cut into cylindrical pieces with dimensions of 50 * 50 mm with a diamond blade. Then the sample is placed under a certain load of 2 kg / cm^2 in the device and the temperature gradually increases. Temperature T0 is defined as the temperature at which contraction of the specimen begins under load, and temperature T2 is defined as the temperature at which the specimen exhibits a 2% contraction. In this experiment, measurements were taken from at least 2 samples and the average results were reported. The model of RUL device used was TSAR- 612 and made in Japan. Samples were studied by scanning electron microscopy (SEM) to study the developments and the type of connection between the grains and the ground phase after the sintering process and the type of phases formed in the grain boundaries to better understand the sintering mechanisms. In order to perform microstructural studies, first the cross-sectional area of the sample is carefully cut by a diamond blade. The prepared small samples were then cooled and then polished. The samples were polished first with silicon carbide powder and then with diamond paste. After the polishing process, the surface of the samples was covered with a gold spatter coating machine model SCDOOS made by BAL-TEC company in Switzerland to be prepared for microstructural studies. To study the microstructure of the samples, a scanning electron microscope made by the Czech company TESCAN VEGA was used. In order to study the phase changes of the samples after sintering, the samples were first crushed by a laboratory crusher and milled separately by a mortar. Finally, the prepared powders were subjected to phase analysis using X-ray diffractometer made by PHILIPS model 3710 PW. In order to study the chemical analysis of some of the raw materials used in this research, the method of chemical analysis by X-ray fluorescence (XRF) using XRF device made by PHILIPS company was used.

3. Results and Discussion

Stable linear changes

Figure 3 shows a diagram of stable linear changes in samples containing titanium additive after curing at 1500 °C and 1600 °C. As can be seen, as the amount of titanium additive increases, at 1500 °C the amount of linear change first increases slightly and then decreases. Due to the effect of titania additive on spinel phase formation, the linear expansion of these samples has increased compared to the sample without additive. However, with the increase of titanium additive, this expansion is accompanied by a decrease. One of the reasons for the decrease in linear expansion can be attributed to sintering in the vicinity of the liquid phase and increasing the density of the samples. At 1600 ° C, no expansion is generally observed due to the increase in spinel phase formation compared to the sample without additives. At this temperature, with increasing density and formation of temperature phases lower than spinel, the sample seems to be sintered and linear shrinkage behavior is observed with increasing titanium additive.

Density and porosity

Figure 4 shows the trend of changes in density and apparent porosity of the titanium-containing sample by increasing the percentage of additive at different sintering temperatures. As can be seen in these diagrams, there is a clear difference between the density and porosity of the samples containing the additive and the reference sample, which indicates the effect of increasing the amount of this additive in the sintering process. According to these graphs, with increasing titania up to 6% compared to the sample without additive, the density increases and the apparent porosity decreases.

In general, refractory systems contain ceramic bonds such as magnesia-spinel refractories, the apparent porosity and density of one part is a function of the particle size distribution as well as the density of each component. On the other hand, these parameters also depend on the sintering process and the reactions performed during cooking, which are accompanied by volume changes. It seems that in the system containing titania additive, the formation of phases such as magnesium titanate (MT, MT2 and M2T), aluminate-magnesium spinel and iron-calcium titanate and calcium titanate is caused by the reaction of titania and magnesium additive in the combination with an expansion.

Therefore, it is expected that with increasing the amount of titanium additives in the field of refractory and the formation of the above phases, the porosity will decrease and the density will increase compared to the sample without additives.

On the other hand, the magnesium titanate phase formed due to the reaction of titania particles with magnesia in the field is able to increase the strength by creating a strong bond in the refractory field between the magnesia and spinel particles as well as the magnesium field [20]. This is while the pre-synthesized spinel phase in the system creates cracks due to the mismatch of the thermal behavior with the magnesia around it, which prevents a strong connection. As a result, the amount and type of magnesium titanate phase structure play a key role in the amount of porosity and strength of magnesia-spinel

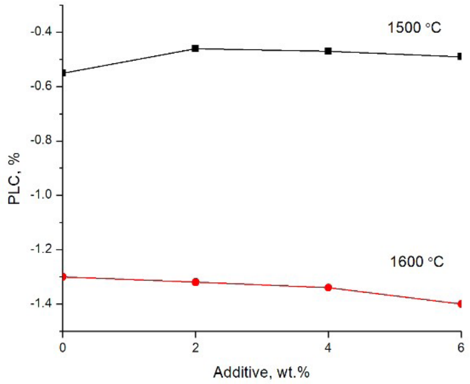


Fig. 3. Diagram of stable linear changes of the sample containing titania additive after curing at temperatures of 1500 °C and 1600 °C.

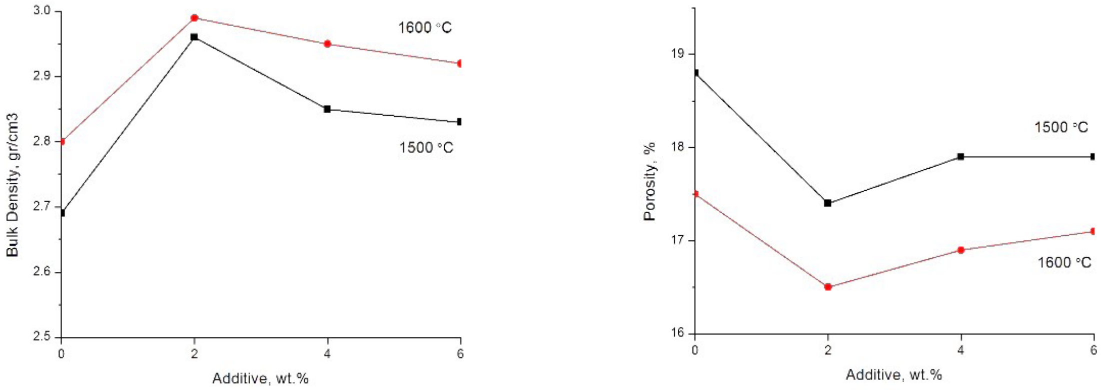


Fig. 4. Density and porosity diagrams of titanium-containing samples after curing at 1500 °C and 1600 ºC.

refractories. In this case, important factors to reduce porosity based on the formation of magnesium titanate phase and the formation of microcracks due to non-compliance of the thermal behavior of spinel and magnesia are effective in this regard.

On the other hand, naturally the density of refractory samples is also a function of the density of each component of the system. Therefore, it is expected that with increasing the amount of titanium oxide fine-grained additives in the field of refractory, compared to the reference sample without additives, porosity will decrease and density will increase. However, the cause of increasing porosity and decreasing density with increasing the amount of oxide additives from 2 to 6% depends on the volume percentage of the expansion phases. In other words, increasing the phases associated with volumetric expansion has reduced the density and increased the porosity compared to samples with 2% additive.

On the other hand, according to reaction 1, with the dissolution of titanium oxide additives in the periclass network, due to the difference in the capacity of Ti + 4 ion with Mg + 2, replacing Mg + 2 with a 4Ti + ion, an Mg + 2 ion must be removed that this causes a cationic hole in the network. The formation of these cavities increases the diffusion coefficient and ultimately encourages the mass transfer and sintering process. Therefore, it is expected that as the amount of titanium oxide additives increases, the density of the body increases and the porosity decreases [23, 24].

$$TiO_2 \xrightarrow{2MgO} Ti_{Mg}oo + V''_{Mg} + 2O_o \qquad \text{Eq.(1)}$$

In addition, dissolution of TiO2 oxide in the spinel network and removal of Al from the network in stoichiometric composition can also improve sintering. In fact, the dissolution of titania in the magnesia and alumina phases and the creation of atomic voids encourage the formation of a spinel phase.

In this case, in the presence of other impurities such as Fe_2O_3 and CaO due to the formation of liquid phases, the presence of these phases, in addition to encouraging the sintering process, can crystallize the iron-calcium titanate phases and the simultaneous formation of magnesium and spinel titanate phases. Magnesium aluminate from the melt, a phenomenon shown in reactions 2 and 3.

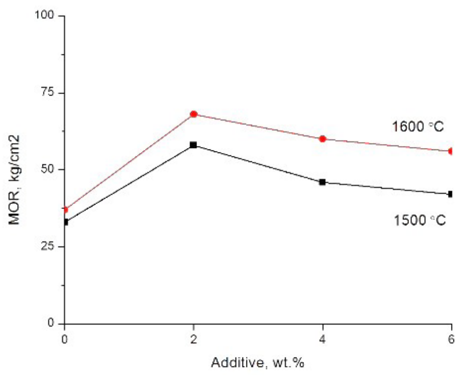
$$TiO_2 \xrightarrow{2CaO} Ti_{Ca}oo + V''_{Ca} + 2O_o \qquad \text{Eq.(2)}$$

$$Ca^{2+}\left(Fe^{3+}\right)_2O_4 \rightarrow V_ooo + Fe_{Ca}o + V''_{Fe} + 0.5O_2 + Fe_{Fe} + 3O_o \qquad \text{Eq.(3)}$$

Mechanical Properties

Figure 5 shows the cold compressive and flexural strength diagrams of titanium-containing specimens after sintering at different temperatures. At both curing temperatures, with increasing titanium additive, the values of cold compressive strength and flexural strength increase compared to the reference sample without additive. But with increasing the amount of additives to 4 and 6%, the values of these parameters have decreased slightly. This is true for all samples containing titania. It seems that the strength and mechanical properties of these specimens are strongly dependent on how they are compacted and compacted. In other words, as the porosity increases, the strength values decrease. Basically, a set of different factors can affect the mechanical strength of samples.

According to study sources, one of these factors is the formation of microcracks and especially the degree of porosity, which has led to small amounts of MOR and CCS in the reference refractory sample without additives. However, cracks due to the formation of spinel phases and phases that are formed due to the mismatch of the spinel's thermal behavior with magnesia with volumetric expansion, can be effective in increasing the strength and strengthening the mechanical properties of the body [20, 23] Therefore, it seems that the mechanism of micro-crack formation is dominant here. As the amount of titania increases, the formation of spinel phases has increased, which is further discussed in the microstructure study section.



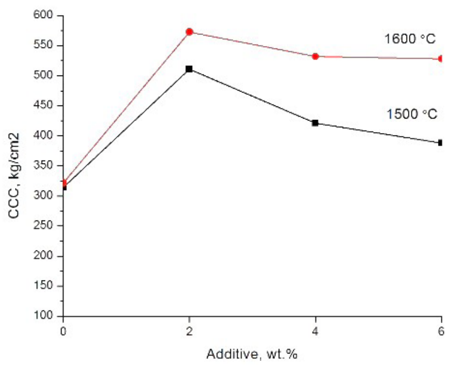


Fig. 5. Diagram of cold compressive and flexural strength of titanium-containing specimens after firing at 1500 and 1600 ºC.

In general, according to Figure 5, the strength increases with increasing amount of oxide additives. Various factors increase the strength, including higher density of the body with increasing amounts of titanium, as well as their interaction with the micro cracks around the spinel particles. In addition, these two oxides, due to the help of sintering, cause the critical cracks to deviate due to the difference in the coefficient of thermal expansion of magnesia and spinel, which also increases the strength.

Another reason for the increased strength of titanium-containing specimens is the dissolution of the tetravalent ions of titanium and the withdrawal of the trivalent Al ion from the spinel lattice, which causes the spinel structure to expand. As a result of this phenomenon, the field density increases, and the porosity decreases as much as possible, and eventually the cold strength of the samples will increase. It should be noted, however, that the presence of titanium ions in the composition also delays the dissolution of Al^{3+} ions within the spinel network. Because the dissolution of Ti^{4+}, according to Hume-Rotary theory, occurs faster inside the spinel lattice than the Al^{3+} ion, which will result in a further expansion of the lattice with a constant increase in lattice. Therefore, it should be said that what affects the properties of the bodies, especially the mechanical properties, is a set of factors mentioned above.

Thermomechanical properties

Hot Flexural Strength (HMOR)

Figure 6 shows a graph of hot bending strength changes (HMOR) of a sample containing titanium additive. As can be seen, with the addition of titania, the hot flexural strength of the specimens is increased by up to 6% compared to the reference specimen without additives at 1000 and 1400 °C. It can be said that this is due to the strong bonds that these oxides have created in the field. The formation of phases such as spinelite phases of titanate-magnesium and aluminate-magnesium can also be effective in this regard. Another reason for the increase in hot flexural strength by increasing oxide additives by up to 6% is the dissolution of Ti^{+4} in the periclass network by the direct reaction of magnesia with tubular alumina. In other words, in this case, the simultaneous formation of magnesium titanate and magnesium aluminate spinel phases occurs.

According to these diagrams, it can be seen that the hot flexural strength of the sample at 1400 ºC has decreased compared to 1000 ºC. This is due to the growth of micro cracks and the formation of possible pre-melting phases in the grain boundary regions such as titanate-calcium, titanate-iron and calcium-iron phases, due to the reaction of titania with iron and calcium oxide in the magnesia raw material. By increasing the titanium content by up to 6%, the pre-melting phases in the grain boundary regions are reduced, which increases the hot flexural strength of the sample containing 6% additive at 1400 ºC.

According to the reactions of 4 and 5 phases, iron-calcium titanate reduced the hot flexural strength of the sample at 1400 ºC. Because at high temperatures, it is possible to decompose this phase into two phases, iron titanate and calcium titanate, or the iron-calcium phase. Therefore, on the one hand, hot strength is expected to decrease, and on the other hand, it is possible that at high temperatures, the grain morphology changes due to the reaction of magnesia with titanium, which affects the strength of sintered products.

$$TiO_2 \xrightarrow{2CaO} Ti_{Ca}oo + V''_{Ca} + 2O_o \qquad \text{Eq.(4)}$$

$$Ca^{2+}\left(Fe^{3+}\right)_2 O_4 \rightarrow V_o oo + Fe_{Ca}o + V''_{Fe} + 0.5O_2 + Ca + 3O_o \qquad \text{Eq.(5)}$$

$$Fe^{3+}{}_{2x}Ca^{2+}{}_{1-x}Ti^{4+}{}_{1-x} \rightarrow Ca^{2+}Ti^{4+} + (1-x)Ca^{2+} + xCa^{2+} \qquad (0 \le x \le 1) \qquad \text{Eq.(6)}$$

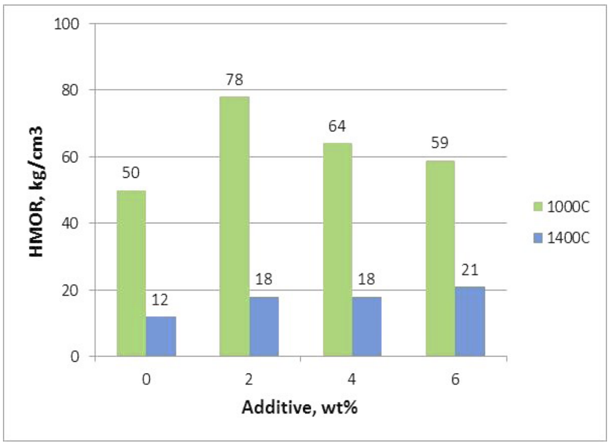


Fig. 6. Graphic flexural strength diagram of a titanium-containing sample at 1000 °C and 1400 ºC.

However, higher values of hot flexural strength of the titanium-containing sample than the reference sample indicate the positive effect of this additive on the properties of alkaline refractories of spinel joint.

Refractoriness under load (RUL)

In order to investigate the refractoriness under load, due to access restrictions and high costs of this test, only the sample containing 2% titanium additive and the reference sample were selected for this test and to evaluate and compare the behavior of the studied system. Figure 7 shows the refractory behavior under load (RUL) of these two samples under a load of 2 kg / cm^2. As can be seen, the starting point of softening of the phases of the titanium-containing sample is greater than that of the reference sample. refractoriness under load, is the applied force compressive and it is obvious that in this case the amount, type and distribution of intergranular phases with high or low melting point have an important effect on the defrost behavior under load.

The reason for the higher refractoriness under the load of the titanium-containing sample is T_0=1620 ºC formation of the cubic phase Mg_2TiO_4 at the Magnesia-Magnesia and Magnesia-Spinel grain boundaries. The melting point of this phase is higher than 1700 .C, while the softening point of the intergranular phases of the reference sample without additive (T_0= 1570 ºC) is much lower due to the formation of magnoliophyte and calcium-iron phases.

Phase analysis

Figures 8 and 9 show the X-ray diffraction patterns of the reference sample (without additives) cooked at 1500 °C and 1600 °C, respectively. As can be seen, the phase analysis of this sample at a lower cooking temperature consists of periclase (MgO) and spinel ($MgAl_2O_4$) phases. It is also observed that no traces of the remaining phases contain alumina and it can be concluded that the reaction of alumina with magnesia and the formation of the spinel phase at 1500 °C. However, given the peak intensity of the phases shown in Figures 8 and 9, it appears that the spinel grain size has grown relatively more at 1600 °C.

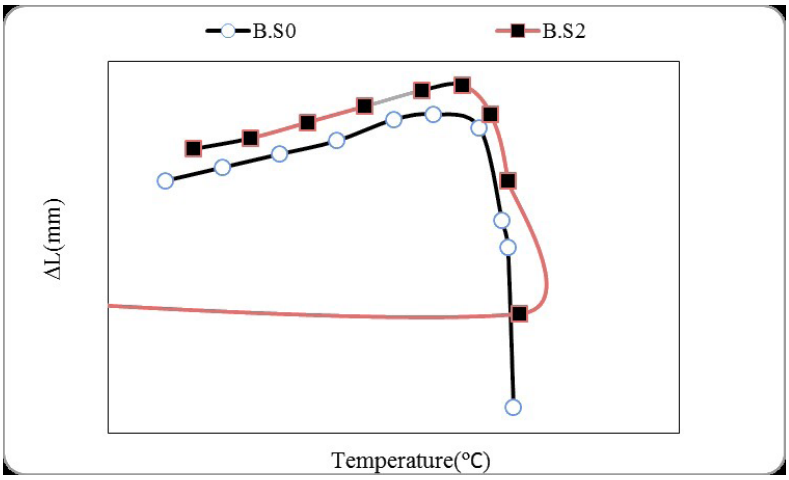


Fig. 7. Refractory behavior curve under load of reference sample (BS0) and sample containing 2% titania (BS2).

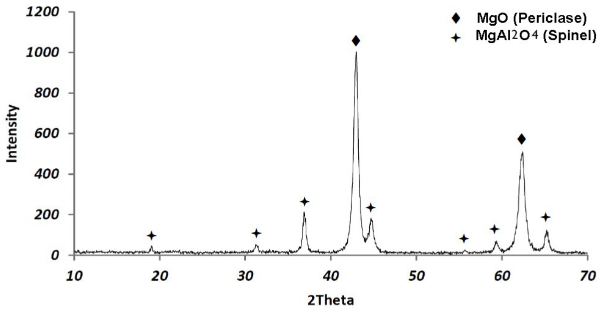


Fig. 8. X-ray diffraction pattern of the reference sample cooked at 1500 ° C.

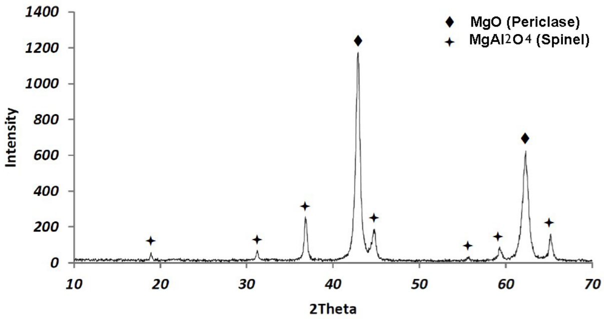


Fig. 9. X-ray diffraction pattern of the reference sample cooked at 1600 ° C.

Figures 10 and 11 show X-ray diffraction patterns of samples containing 4% titanium additive after cooking at 1500 ° C and 1600 ° C, respectively. As shown in Figure 10, the sample cooked at 1500 ° C has the main phases of periclase and spinel. Also, the presence of a new phase of solid solution (Mg, Al, Ti, O) with lower intensity was observed in this sample.

According to study sources, in the presence of the combination of Mg_2TiO_4 and the reverse spinel phase of Mg_2TiO_4, a solid solution phase is formed which has a spinel structure. Depending on the fraction of solvent and solvent, the main peak of this phase will be between the main peak of the spinel phase and the main peak of the Mg_2TiO_4 phase. The location of this phase is exactly within the 50% composition range as shown in the figure. Also, a small amount of spinel phase deviation is seen to the right, which in turn indicates the creation of empty spaces in the spinel network and the contraction of its network relative to the reference sample. As can be seen, the formation of this phase has occurred more at 1600 ° C.

Microstructure

In this section, the microstructure and context of the titanium-containing sample are discussed in this paper by electron microscopy (SEM.EDS). First, the microstructures of the reference sample are given and then the microstructures of the sample containing the titanium additive are examined.

Figure 12 shows the microstructure of the reference sample (no additive) sintered at 1600 ° C. Figure 13 also shows the microstructure and elemental analysis (point) of the four specified points of the reference sample microstructure. As can be seen, in grain boundaries (grain boundaries of Magnesia-Magnesia and Magnesia-Spinel particles), the calcium silicate phase is formed together with the magnesium ferrite phase (gray spots) which has a direct effect on the density and porosity of the bodies.

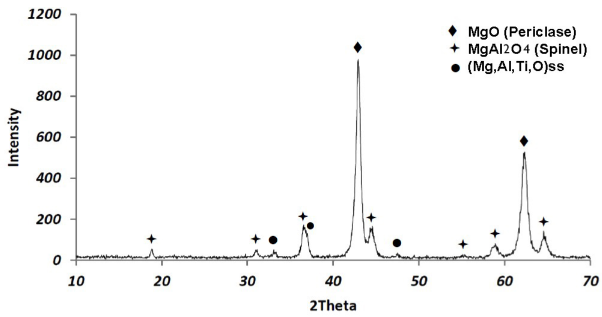


Fig. 10. X-ray diffraction pattern of a sample containing 4% of titanium cooked at 1500 ° C.

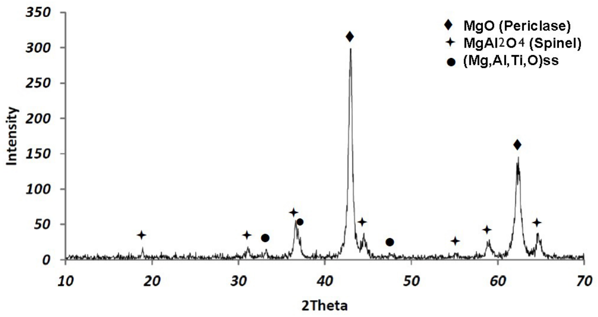


Fig. 11. X-ray diffraction pattern of a sample containing 4% titanium cooked at 1600 ° C.

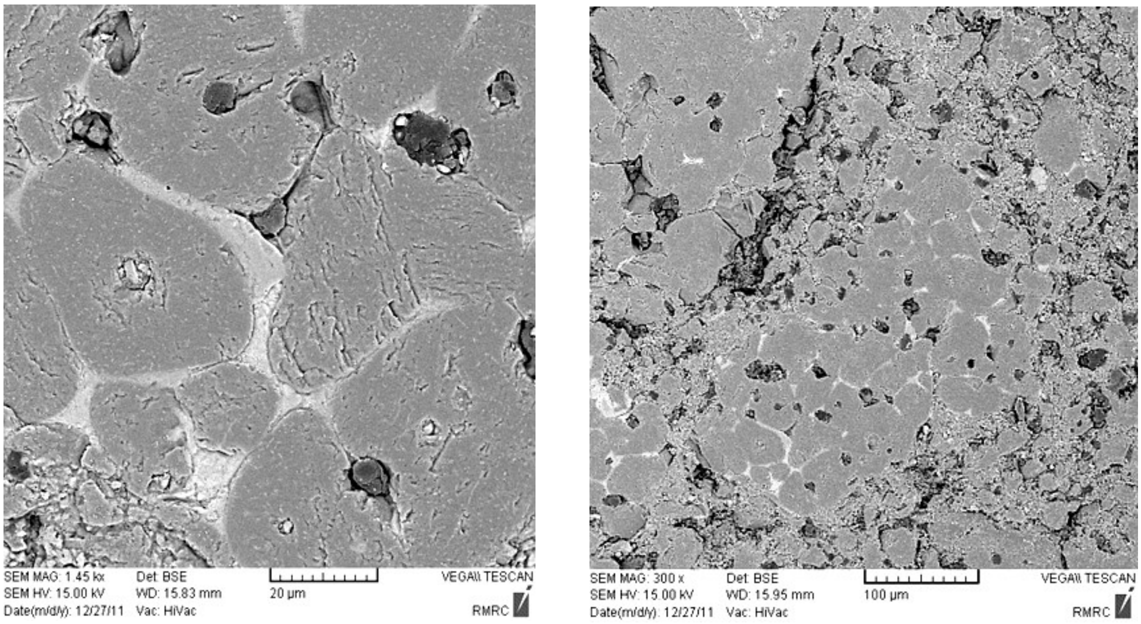


Fig. 12. Microstructure of a sintered reference sample at 1600 ° C.

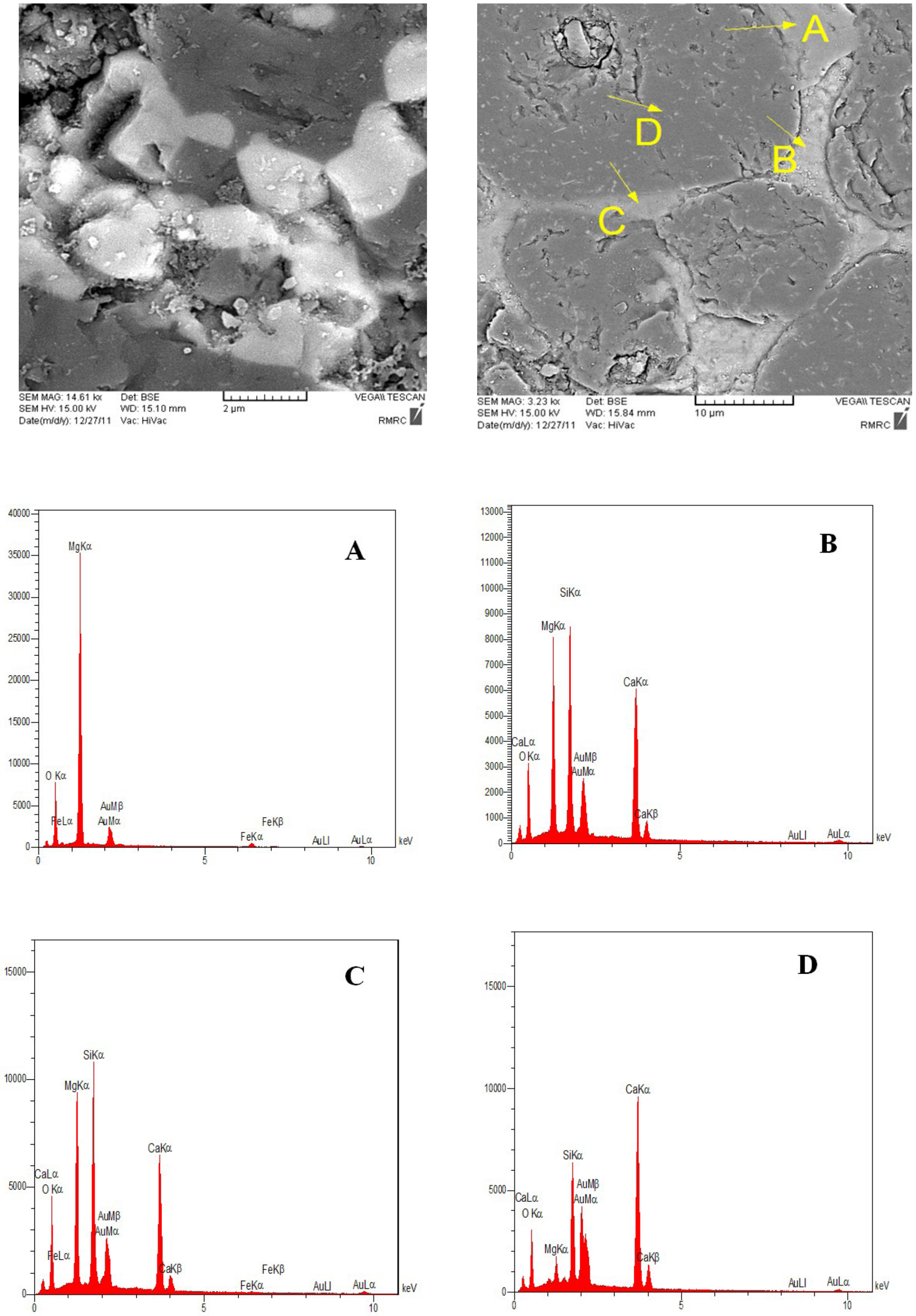


Fig. 13. Microstructure and elemental analysis of the four specified points of the sintered reference sample at 1600 °C.

Figure 14 shows the microstructure and elemental analysis of a sample containing 2% titanium sintered at 1600 ° C. In this picture the formation of magnesium titanate phases, magnesium aluminate spinel and iron-calcium titanates have been identified at the Magnesia-Magnesia and Magnesia-Spinel grain boundaries as well as within the Magnesia granules due to direct reaction.

As explained in the discussion of the results of the physical properties, given that the magnesium used in this study has a relatively high purity. Therefore, another effective factor in reducing porosity and increasing density can be the second mechanism, i.e. increasing voids and penetration coefficient. Also regarding the effect of TiO_2 grain size on the values of density and porosity can be said because d_{50} titanium particles are less than 3 µm, as a result, the intensity of particle dispersion increases, which makes Titania more uniformly located in the grain boundaries. As shown in Figure 14, TiO_2 also reacts with the CaO in magnesia to form the perovskite phase of calcium titanate at the grain boundary, which results in a stronger bond between the magnesia and the spinel. On the other hand, due to the fineness of the titanium used, the Ca^{2+} diffusion intervals are reduced, resulting in an easier titanate-calcium phase.

Figure 15 shows another image of the microstructure and elemental analysis of the sample containing 2% titania. In this figure, the formation of magnesium titanate, iron titanate, calcium titanate, and magnesium aluminate spinel phases is known to have established a strong bond in the field between Magnesia-Magnesia and Magnesia-Spinel particles.

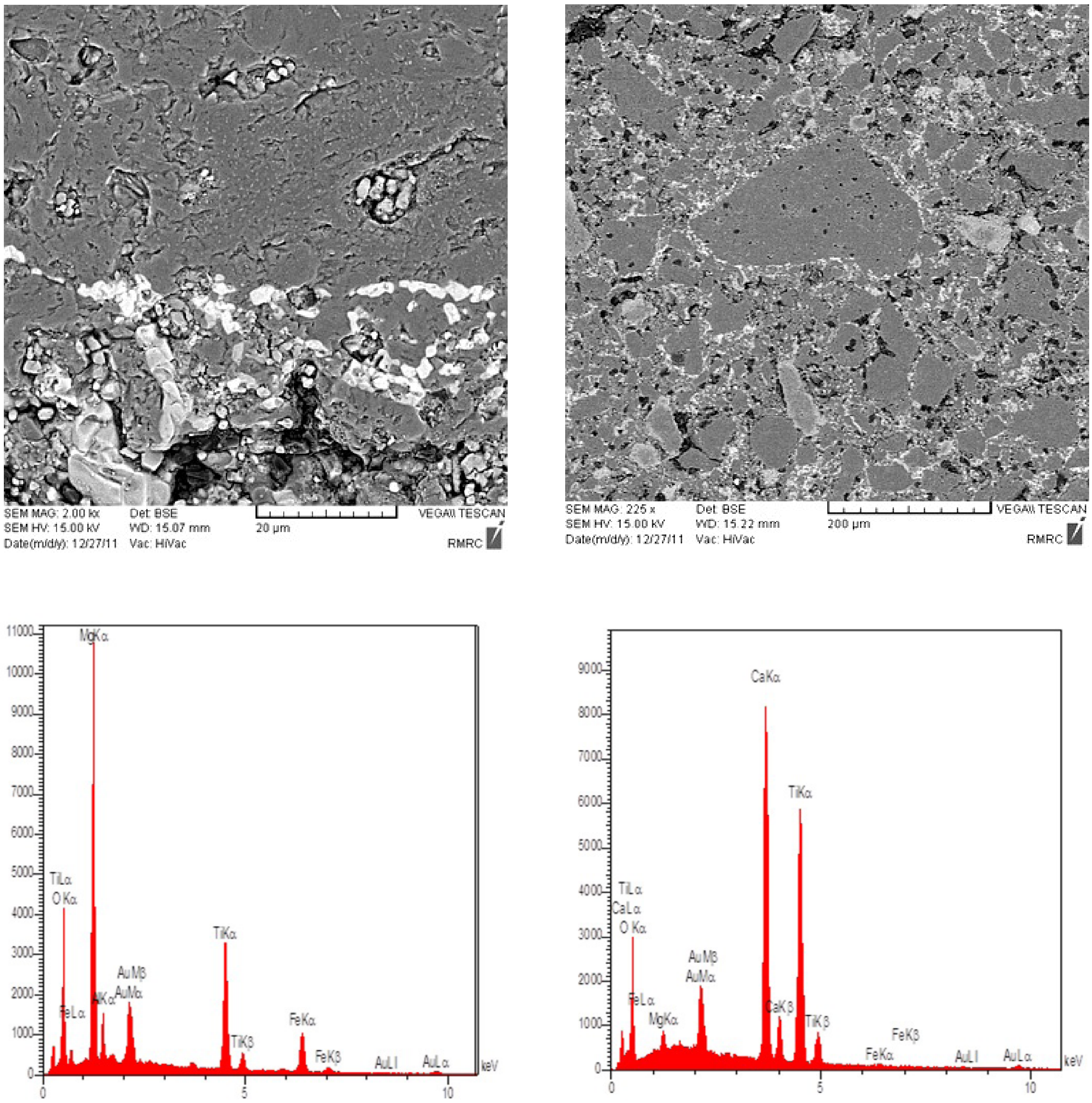


Fig. 14. Microstructure and elemental analysis of a sample containing 2% titania sintered at 1600 ºC.

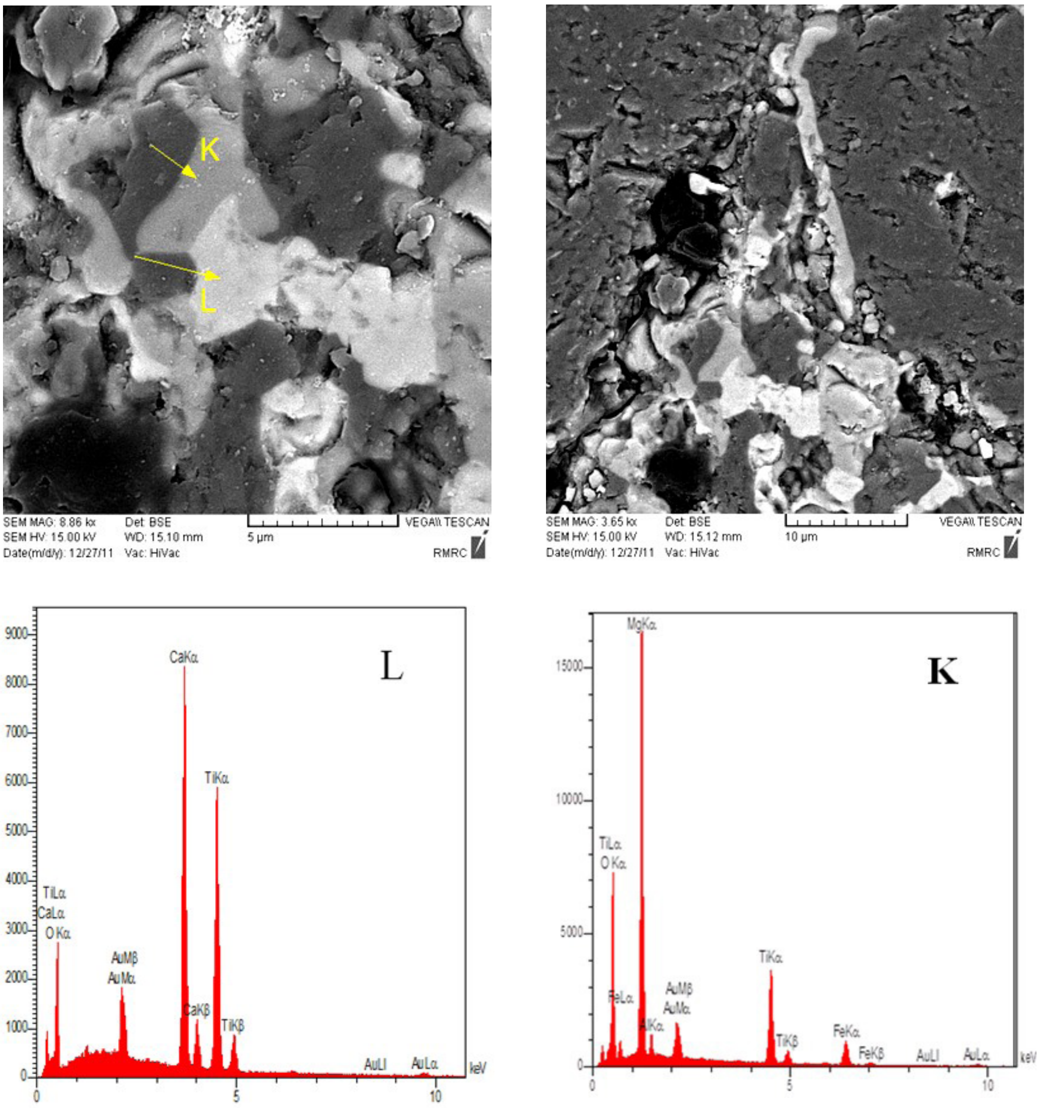


Fig. 15. Microstructure and elemental analysis of a sample containing 2% titania sintered at 1600 ºC.

Figure 16 shows another image of the microstructure and elemental analysis of the sample containing 2% titania. The reason for the higher refractory under the load of the sample containing 2% titania (T_0=1620 ºC) than the reference sample (T_0=1570 ºC), is the formation of the cubic phase of Mg_2TiO_4 at the boundary of Magnesia-Magnesia and Magnesia-Spinel grains. The melting point of this phase is higher than 1700 ºC, while the softening point of the intergranular phases of the reference sample is much lower due to the magnesiophyte and calcium-iron phases formed.

Figure 17 shows the microstructure of the sample containing 4% titanium cooked at 1600 ºC. In this image, the formation of phases containing titanium in the form of phases of magnesium titanate (light gray dots) and iron-calcium titanate (titanate-iron and titanate-calcium) as white dots at the Magnesia-Magnesia and Magnesia-Spinel grain boundaries and also to the form of sediment inside the cavities is obvious. This image also shows that titanium additive can play an effective role in increasing the density of the refractory body due to the ability to increase the cation vacancy. While in the reference sample, due to the lack of formation of high density phases, there is also high porosity. Reaction 6 to 8 shows the mechanism of solid solution formation of magnesium titanate and magnesium aluminate spinel. (S.S = Solid Solution)

$$MgO + Al_2O_3 \rightarrow MgO.Al_2O_3 \qquad \text{Eq.(7)}$$

$$2MgO + TiO_2 \rightarrow 2MgO.TiO_2 \qquad \text{Eq.(8)}$$

$$MgO.Al_2O_3 + 2MgO.TiO_2 \rightarrow [MgO.Al_2O_3 - 2MgO.TiO_2]_{S.S.} \qquad \text{Eq.(9)}$$

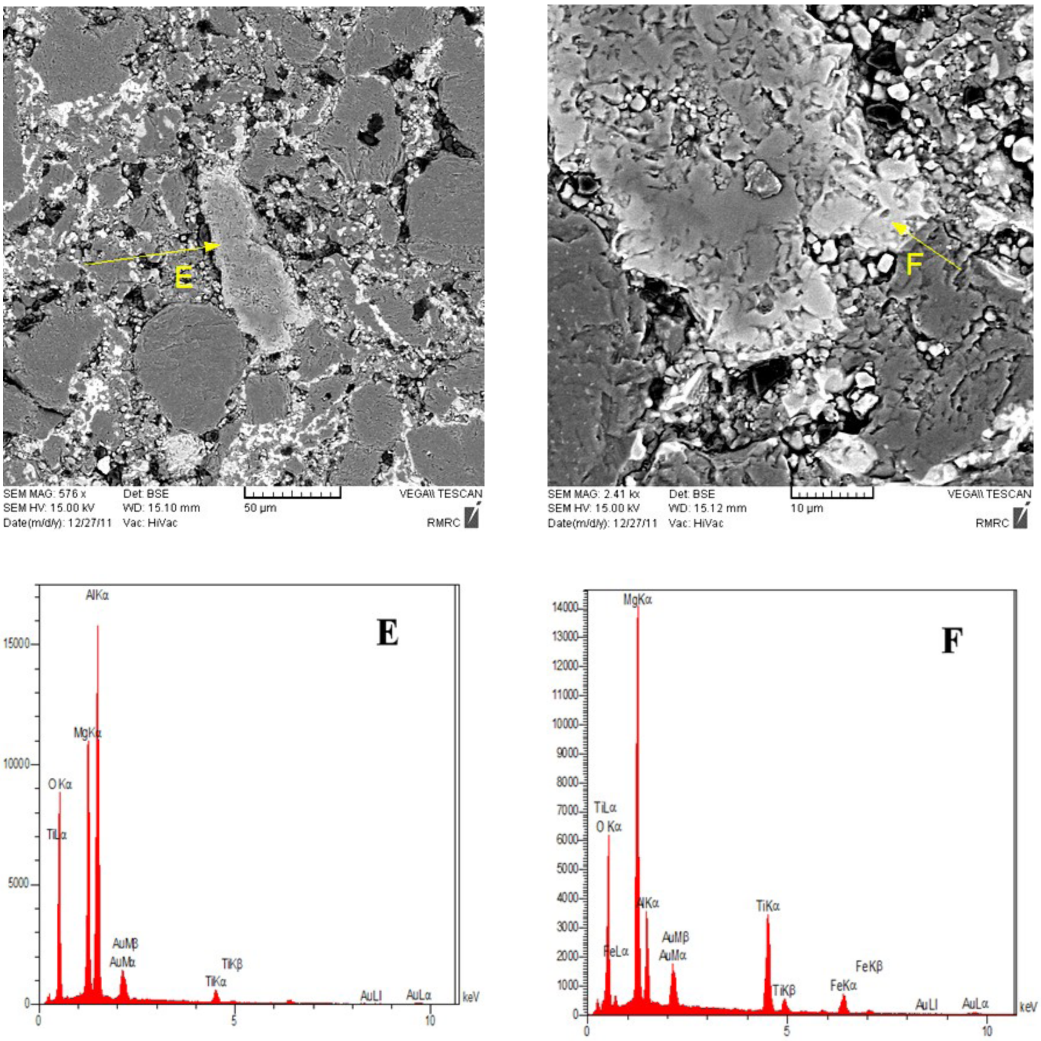


Fig. 16. Microstructure and elemental analysis of a sample containing 2% titania sintered at 1600 ºC.

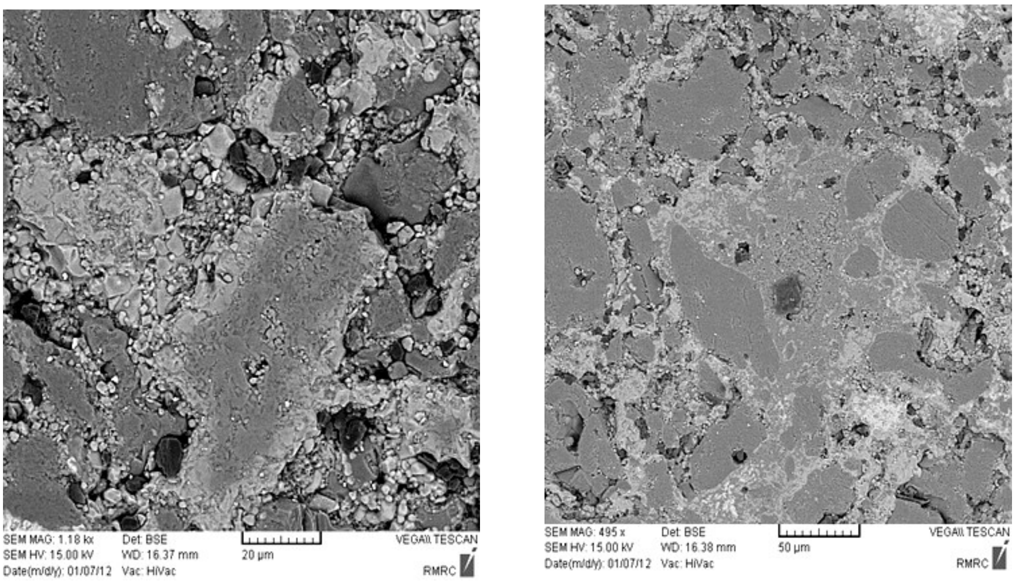


Fig. 17. Sample microstructure containing 4% titania sintered at 1600 ºC.

Figures 18 and 19 show other images of the microstructure and elemental analysis of the sample containing 4% titania. In these microstructures, the formation of magnesium titanate, iron titanate, calcium titanate, and magnesium aluminate spinel phases is known to have established a strong bond in the field between magnesia-magnesia and magnesia-spinel particles.

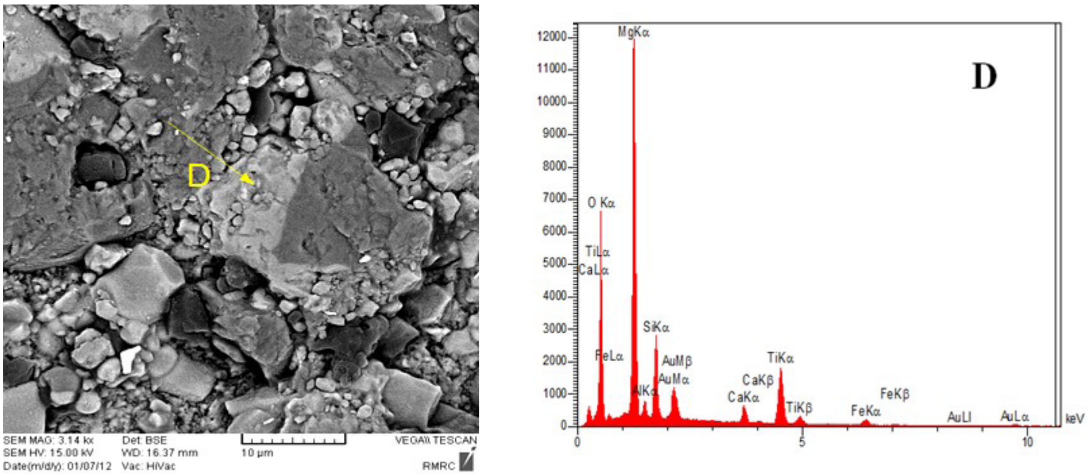


Fig. 18. Microstructure and elemental analysis of a sample containing 4% titania sintered at 1600 ºC.

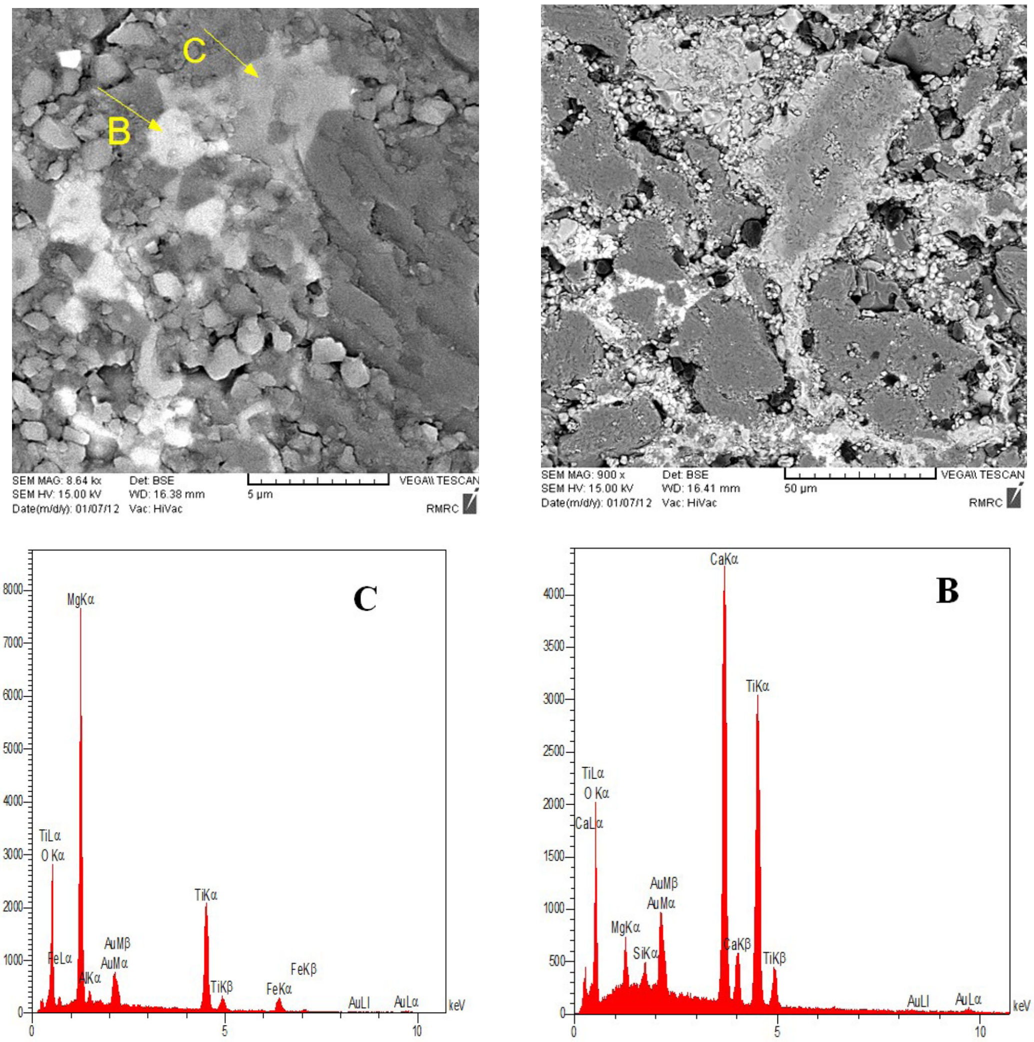


Fig. 19. Microstructure and elemental analysis of a sample containing 4% titania sintered at 1600 ºC.

Figure 20 shows the microstructure of the sample containing 6% titanium cooked at 1600 ºC. In this image, the formation of phases containing titania in the form of phases of magnesium titanate (light gray dots) and iron-calcium titanate (titanate-iron and titanate-calcium) in the form of white dots on the border of magnesia-magnesia and magnesia-spinel grains and also to the form of sediment inside the cavities is obvious.

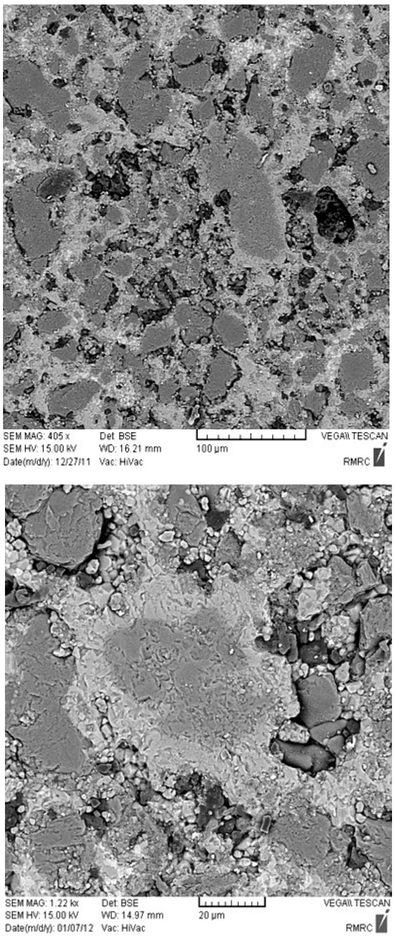


Fig. 20. Sample microstructure containing 6% titania sintered at 1600 ºC.

As stated in the discussion of the results of mechanical properties, a set of different factors can affect the mechanical strength of the samples studied in this study. According to the study sources, one of these factors is the formation of micro cracks and especially the porosity, which has led to a slight decrease in the values of MOR and CCS of the sample containing 6% titania. Especially in this case, cracks are formed due to the formation of spinel phases and phases whose formation is due to the mismatch of the spinel's thermal behavior with magnesia with volumetric expansion. Therefore, it seems that the dominant mechanism here that enhances the main mechanical properties is the formation of micro-cracks. As the amount of titania increases, the formation of spinel phases also increases. Figure 20 shows the microstructure of the sample containing 6% titania, the presence of these micro cracks. Figure 21 shows another image of the microstructure and elemental analysis of the 6% titania sample.

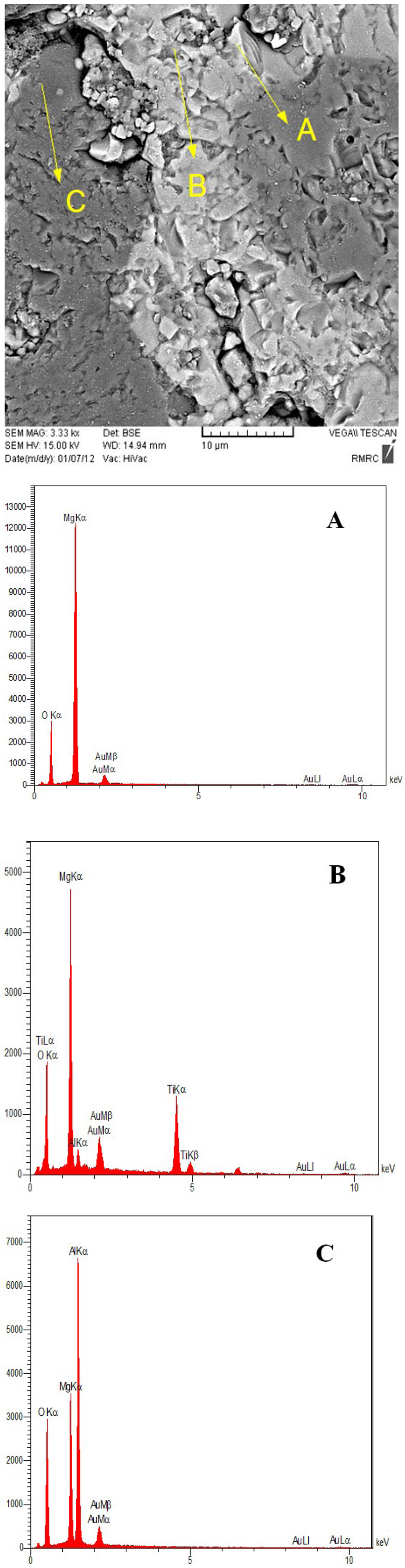


Fig. 21. Microstructure and elemental analysis of a sample containing 6% titania sintered at 1600 ºC.

As previously mentioned, in magnesia-spinel refractories, due to the large differences in the thermal expansion coefficient of magnesia (13.5 *10 $^{-6}$ ºC) and spinel (8.4 *10 $^{-6}$ ºC), often during cooling, the stress system is created and a network of microcracks is formed in the field of refractory. Increasing the temperature leads to the elimination of thermal stresses in the system and prevents the growth of cracks, thereby increasing the strength and improving the resistance to thermal shocks. In the present system, the addition of pre-synthesized spinel to magnesium refractories causes stress in the structure. But at high temperatures, the strength is increased by removing the stresses (releasing the stresses). On the other hand, with the formation of the titanate-magnesium phase due to the reaction of titania and magnesium in the system and the establishment of direct connections between magnesia-magnesia and magnesia-spinel particles and thus strengthening the microstructure of the brick, hot strength has increased.

4 . Conclusions

The use of magnesium alkali refractory bricks is very important in various industries of steel, iron and cement due to its remarkable physical and mechanical properties as well as high refractoriness and corrosion resistance against alkaline corrosive agents. However, due to the high coefficient of thermal expansion and low resistance to thermal shock, problems occur in the application of this type of refractory in the cement industry. One of the methods to solve these problems is to use some additives in small percentages that can reduce the above defects and increase the shock absorption of these refractories. In this paper, to eliminate the above disadvantages and also improve various properties such as physical properties (apparent porosity, density), thermomechanical (refractoriness under load and hot flexural strength), mechanical (cold flexural strength and cold compressive strength) and corrosion and coating resistance, TiO_2 additive is used. Due to the addition of titania, it was observed that the spinel phase of magnesium aluminate was synthesized through direct reaction of magnesia with tabular alumina at lower firing temperatures, which leads to the simultaneous formation of spinel phases of magnesium aluminate and magnesium titanate. The formation of these phases is temperature sensitive and usually occurs at temperatures above 1000 ºC. As the amount of titanium in the studied system increased, it was observed that the formation of a spinal joint increases the strength. This phenomenon is due to the creation of point defects resulting from the dissolution of titania in the periclass and spinel networks and thus increase the reactivity between the raw material and the additive. Increasing TiO_2 to 2% by weight increases the density and decreases the apparent porosity, and with further increase in titanium due to the volumetric expansion due to the formation of phases, the density and porosity decrease and increase, respectively. The mechanism of action of titania on mechanical strength (CCS, MOR) includes the creation of countervailing forces such as increasing the density of the body, microcracking and the mechanism of crack deflection. The combination of these factors increases the strength of the body by increasing the percentage of titanium. Therefore, cold compressive and flexural strength (mechanical properties) increases by adding TiO_2 up to 4% by weight compared to the titanium-free sample and decreases with further increase of titanium mechanical properties. It was also observed that in some cases, the presence of the low-temperature grain boundary phase improves the bond strength and increases the mechanical and thermomechanical properties of the samples. By increasing TiO_2 by up to 6% by weight, the modulus of hot rupture (HNOR) at 1000 and 1400 ºC increases relative to the titan-free sample and refractoriness under load also increases with increasing the amount of TiO_2 up to 2% of the temperature of 1570 ºC to 1620 ºC under load of 2 kg/cm^2. It seems that a combination of different factors such as high purity, titanium fineness and the formation of perovskite titanate-calcium phases, titanate-iron spinel and magnesium aluminate spinel together with the formation of titanium-magnesium-containing phases, with sedimentation in the grain and cavities and filling, enhance the microstructure of the samples.

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