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Improved Refractory Aluminosilicate Bricks Through Nano Zirconia Additions

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Abstract: The physico-mechanical and refractory properties of refractory bricks, prepared from 50 wt.% kaolin and 50 wt.% alumina, were improved through the addition of different contents (2, 4, 6, 8 and 10 wt. %) of nano zirconia powder. The densification parameters (bulk density and apparent porosity), mechanical properties (cold crushing strength) and refractory properties (thermal shock resistance) were tested for the prepared refractory bricks fired at 1500 ºC. The mineralogical composition of the prepared zirconia and the refractory bricks were followed by X-ray diffraction analysis (XRD) whereas while their microstructure and chemical constituents were depicted using scanning electron microscope attached with energy dispersive x-ray unit (SEM + EDAX). The refractory brick samples containing 8 wt. % of nano zirconia was considered as the optimum among the investigated samples as it shows the best sintering, mechanical and refractory properties, these were correlated with their recognized assemblage of minerals; mullite-cristobalite-zirconia.

Keywords: nano, zirconia, refractory, bricks, sintering.

1 Introduction

Refractory materials are one of the most interesting class of ceramics that used in huge quantities as linings of industrial furnaces used for manufacturing other products, e.g. Iron and steel, cements, ceramics, glass and different metals.

The refractory materials are classified into several classes according to;

(a) The application method; shaped and unshaped refractories.
(b) The chemical nature; acidic, basic and neutral refractories based on their chemical composition.
(c) Manufacture; fused and sintered.
(d) Porosity; dense and porous.

These materials should be able to resist the severe conditions at the manufacturing process including; high temperatures, mechanical abrasion, stress and strain as well as chemical corrosion by gases and molten metals [1-9]. Using different processes for different raw materials many types of refractory materials can be synthesized and their application will depend on their compositions and hence characteristics. In fact, the performance of a refractory is related directly to its texture and richness of the refractory minerals, such as mullite, corundum, periclase, doloma, spinel and alumina [10, 11]. Among the metallurgical industries, basic industries especially Iron and Steel is the most consumer of refractories since it consumes alone about 60% of the total refractory productions used in basic oxygen furnaces (BOF) due its capability to resist molten slag (basic) [12]. The requirements of the refectories are entirely different in the aluminum and other metallurgical industries compared with steel making due to the relatively lower refining temperature. Therefore, the design of refractories should be adequate to nonwetting characteristics of molten aluminum [3]. Similarly, in

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hydrocarbon industries, the refractories are subjected to a high rate of abrasion as a result of continuous flow rate of high-velocity particles. So, the refractory properties should be such that it should be capable of resisting the abrasion [12]. In the process of glass industry non porous refractories are widely used to avoid penetration of the molten glass through the pores of the refractory lining [2, 7, 9]. Among the refractories the silica-alumina refractories are materials which are increasingly demanded and whose manufacturing involves, necessarily the synthesis of mullite beside that of being relatively inexpensive compared to other bricks (special carbon refractories, zircon, zirconia, fused-cast refractory). In addition, silica-alumina refractory can be used in several applications: coating of laboratory furnaces, refractory supports, thermal insulating, industrial ceramics and pottery, pulp and paper, food production-related industries and generally any materials required heat for its production. Aluminosilicate refractories can be manufactured from refractory clays, sillimanite minerals, bauxite, and mixtures of alumina and silica sand. Refractories generally refer to materials that can withstand at least 1500 ºC [3]. Alumina and/or silica-based products are the major categories of traditional refractories. Balancing between the cost and performance (lifetime) is the driving force for the choice of refractories either for traditional or advanced applications.

Recently in the last five years, several works have come out by various researchers to produce high quality aluminosilicate products by controlling either the components of the starting materials in the method or synthesis process [13-15].

Much interest has been given to nano-materials in recent years for scientific researchers as well as for industrial reasons. These materials show a good result in the field of refractories.

In recent years, nanotechnology has contributed strongly in the development of properties and functionality of the materials in various scientific areas, the field of refractories was not far from that. The Japanese have already supplied refractories in which nanotechnology is applied [16,17]. The first trial of employing nanotechnology to the service of refractories was represented in UNITECR 2003 which gained a wide interest from the specialists in this field [16, 17].

After that the works in this area has been expanded to cover different classes of refractories. This occurs either through creating a nono structured matrix e.g Mg-C, ZrO_2-C, Al-C or through addition of one or more refractory oxide or spinel powder e.g; Al_2O_3, Cr_2O_3, MgO, MgO. Al_2O_3 during manufacturing of the refractory products. The role of nano particles depends on its very small scale which improve the microstructure and assist the sintering and hence the other technological properties of refractory materials [16-20].

The complication faced the use of the nanoscale materials are related to their availability, cost, handling as well as safety and healthy aspects associated with their handling.

This work aims to make and directing the nanotechnology for the service of refractories through preparation of nano zirconia powder via sol-gel technique and using it as additives for aluminosilicate bricks to improve their Physico mechanical and refractory properties to expand their service life during industrial applications.

2 Experimental Procedures

2. 1 Materials

Raw kaolin and bauxite were used to prepare aluminosilicate bricks. Zirconium oxy chloride ($ZrOCl_2$) and ammonia solution (NH_4OH) were used to prepare nano zirconia (ZrO_2) powder.

2. 2 Experimental

2. 2. 1 Preparation of Nano Zirconia Powder

Fresh paste of zirconium hydroxide was prepared by the neutralization of zirconium oxychloride octahydrate ($ZrOCl_2$-$8H_2O$) solution (2M) and ammonia solution (2M) in a buffer (pH 8). The precipitate was filtered and washed with DI water, diluted ammonium bicarbonate solution, again with water for several times until chlorine-free (confirmed by $AgNO_3$ test), then firing at 900 ºC for one hour. The phase composition of the fired sample was investigated using X-ray diffraction analysis (XRD instrumental D8 ADVANCE, Bruker, Germany; monochromatic beam with Kα1 Cu, Bragg Brentano geometry θ. 2θ and linear detector LYNX EYE 174 channels 2 s/channel, total time = 348s).

The crystal size of the prepared zirconia particles was deduced from the XRD patterns using the following Scherer equation;

$$d = \frac{B\lambda}{\beta\ Cos\theta}$$

Where B is the Scherrer constant (B = 1), β is the full-width half maximum (FWHM) of diffraction and θis the Bragg's angle, λis the wavelength of X-ray beam used, d is the average crystallite size of the phase under investigation.

Scanning electron micrographs (SEM) were recorded on SEM-JEOL JAX-840A electron microanalyzer (Japan). Energy dispersive X-ray (EDX) analysis was carried out on Hitachi S-800 electron microscope with an attached kevex Delta system (accelerating voltage 20 kV, accumulation time 100s, window width 8 μm).

2. 2. 2 Preparations of Aluminosilicate Bricks

Based on one of my previous studies [21] aluminosilicate brick samples were prepared from 50 wt. % kaolin and 50 wt.% bauxite. In this work several similar batches were prepared, but with different contents (0, 2, 4, 6, 8, 10 wt. %) of nano zirconia additives (Table 1). The prepared batches were subjected to different firing temperatures

(1100 ºC, 1200 ºC, 1300 ºC, 1400 ºC, 1500 ºC and 1600 ºC) for 1 hr soaking time. The fired bodies were investigated through their sintering parameters (bulk density and apparent porosity), mechanical (cold crushing strength) as well as refractory properties (thermal shock resistance). These tests were carried out according to the International Standard Specifications [22-24]. Solid phase composition and microstructure of some selected samples were investigated using XRD and SEM attached with EDAX unit.

3 Results and Discussion

3. 1Characterization of the Prepared Nano Zirconia

Fig. (1) shows the XRD data of the prepared zirconia (ZrO_2) powder. All lines characterizing zirconia

Table 1: Composition of the prepared batches.

Batch no.	Clay/alumina mix, wt. %	Nano zirconia additive, wt. %
1	100	0
2	98	2
3	96	4
4	94	6
5	92	8
6	90	10

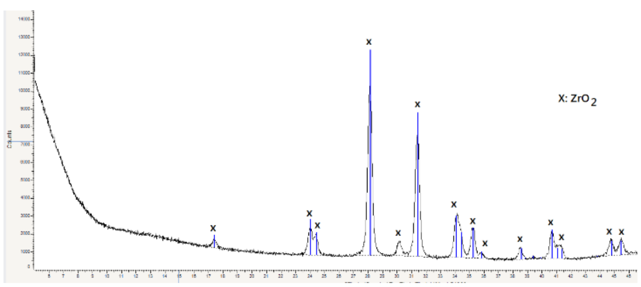


Fig .1: XRD patterns of the prepared nano zirconia powder.

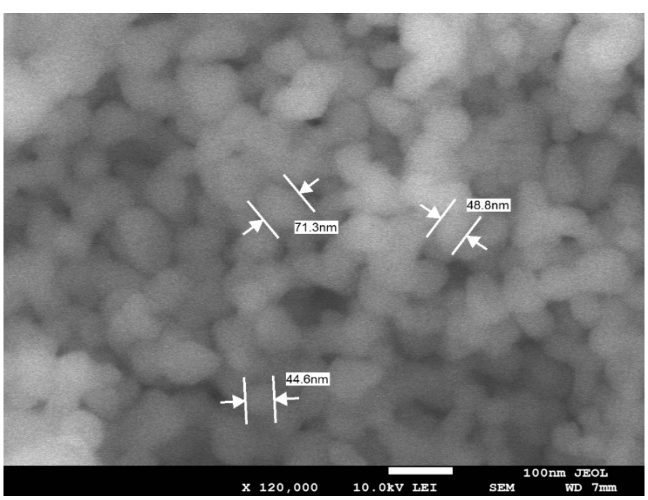


Fig .2: Scanning electron microscope photomicrograph of the prepared nano zirconia powder.

could be detected according to JCPDS card no 00-002-0464, no other lines could be detected which indicate the high purity of the obtained zirconia. The crystal size calculated from the XRD patterns using Scherrer equation was in the range 25-40 nm which proves that the obtained powder belongs to the nano materials. Fig. (2) shows the scanning electron microscope photomicrographs of the prepared zirconia powder. Rounded crystals characterizing zirconia particles are recognized, the diameter of the particles is always less than 100 nm, the measurements of the grain size of some randomly selected particles are; 34.8, 71.3 and 44.6 nm which confirms that the prepared zirconia particles belong to the nano powder class of materials. The EDAX analysis shown in Fig. (3) and Table (2) indicates that the rounded crystals are composed of zircon (67.59 %) and oxygen (19.23 %), no other elements, other than the residual carbon (13.18 %) presents during the sample preparation, could be detected which confirming the high purity of the prepared nano zirconia powder.

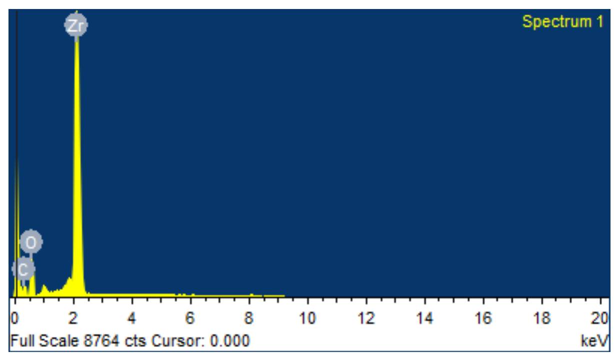


Fig .3: EDAX analysis chart of the prepared zirconia.

3.2 Mineralogical Composition of the Fired Bodies

Fig. (4) shows the solid phase compositions of the fired batches (1500 ºC) containing different contents (0, 2, 4, 6 , 8 and 10 wt. % of nano zirconia powder). The figure shows that the prepared bricks are composed mainly of mullite ($3Al_2O_3$. $2SiO_2$) and cristobalite (SiO_2) minerals, the lines of zirconia (ZrO_2) could also be recognized in batches containing relatively higher contents of zirconia (8 wt. %).

Table 2: Elemental analysis data of the prepared zirconia.

Element	Weight, %
C	13.18
O	19.23
Zr	67.59
Total	100.00

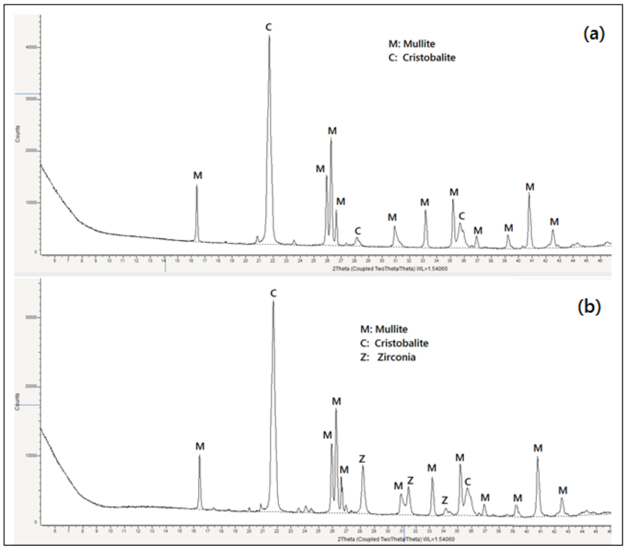


Fig .4: XRD patterns of the fired (1500 ºC) batches.

3.3 Densification Parameters

Bulk density (BD) and apparent porosity (AP) are good indicators of the refractories quality. Hence, the main goal in the refractory industry is to produce low porosity, and high-density refractories in order to resist chemical attack at elevated temperatures.

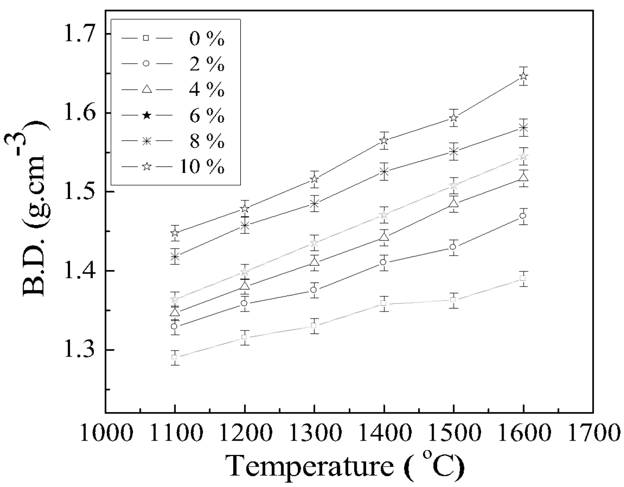


Fig .5: Bulk density of the prepared batches fired at different firing temperatures.

Figs. (5 & 6) show the bulk density and apparent porosity of the fired bodies containing different contents of the nano zirconia powder. The results in Fig. (5) show a steadily increase in the value of the bulk density of the non-modified refractory bodies (zero% zirconia) as the temperature rises from 1100 ºC (1.34 g/cm^3) up to 1600 ºC(1.55 g/cm^3). The bulk density increases also as the content of zirconia additive increases reaching its maximum value at 8 wt. % additive (1.45 g/cm^3 at 1100 ºC reaching 1.65 g/cm^3 at 1600 ºC) beyond which (at 10 wt. % zirconia

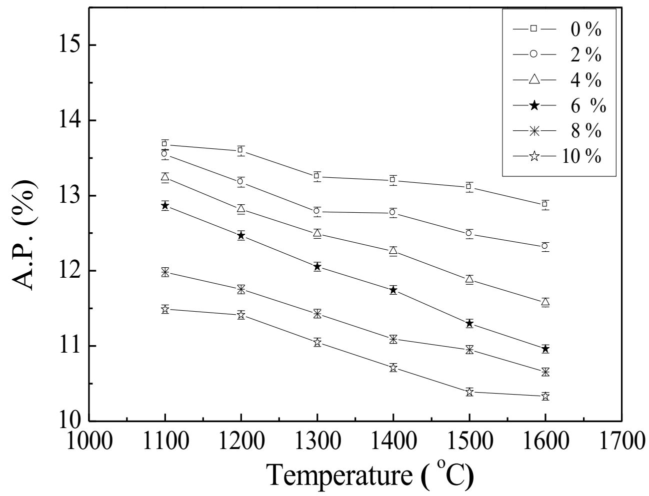


Fig .6: Apparent porosity of the prepared batches fired at different firing temperatures.

additive) the bulk density is noticeably decreased to 1.41 g/cm^3 at 1100 ºC and 1.58 g/cm^3 at 1600 ºC . The results of apparent porosity (Fig. 6) behaves adversely i.e. it gradually decreases as the temperature rises; in the non-modified bodies the apparent porosity decreases from 11.58 % at 1100 ºC to 11.24 % at 1600 ºC, the decrease is more noticeable in samples containing zirconia additives, the apparent porosity decreases as the content of added zirconia increases reaching their minimum value at 8 wt, % zirconia (11.49 at 1100 ºC and further decreases as the temperature rises reaching 10.33 % at 1600 ºC). The increase in the bulk density of the fired bodies containing nano zirconia additive is correlated with the relatively higher theoretical density of zirconia (5.68 g/cm^3) than mullite (3.05 g/m^3) or cristobalite (2.27 g/cm^3), in addition to the high surface area of the nano zirconia powder which fill intergranular voids, pores and cavities between mullite and cristobalite crystals resulting in a dense body. Also the existence of the ZrO_2 at the grain boundary controls the grain growth of mullite and cristobalite crystals by promoting the diffusion of the oxygen between the boundary [25-27] . The decrease in the densification parameters at relatively higher contents of zirconia (10 wt. %) is due to the generation of spherical voids by releasing high pressure oxygen which increases the apparent porosity. The improvement in densification parameters with the increase in the firing temperature is correlated with the enhancement in the mullitization process together with the grain growth of the mullite, cristobalite and zirconia (in samples containing zirconia additives) particles which eliminate voids, cavities and pores resulting in relatively higher dense matrices [27].

3.4 Mechanical Properties

Fig. (7) shows a noticeable increase in the cold crushing strength of the non-modified bodies as the firing temperature increases (110 kg/cm^2 at 1100 ºC reaching 136 kg/cm^2 at 1600 ºC). Samples containing zirconia additives

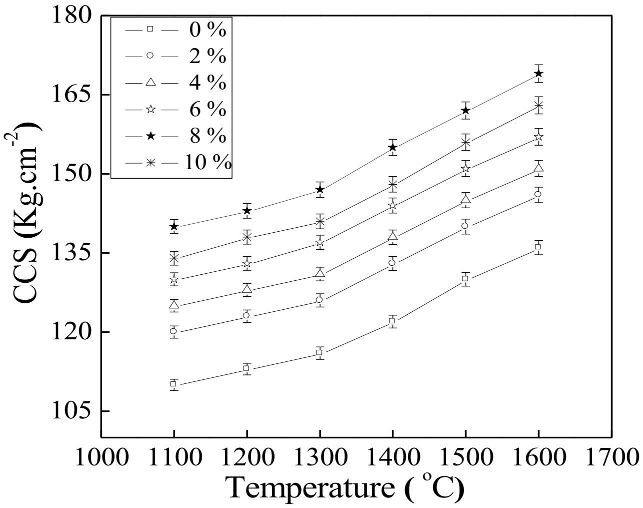


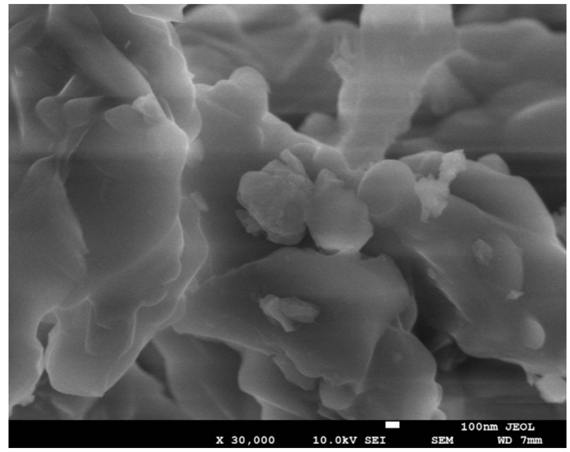
Fig.7: Cold crushing strength of the prepared batches fired at different firing temperatures.

show relatively higher values of cold crushing strength compared with the non-modified ones at each firing temperature, the increase becomes more pronounced as the content of zirconia additive increases reaching its maximum at 8 wt. % zirconia additive (140 kg/cm^{2}at 1100 ºC which further increases as the temperature rises, reaching 169 kg/cm^2 at 1600 ºC) beyond which (at 10 wt. % zirconia additive) the cold crushing strength decreases (134 kg/cm^2 at 1100 ºC and 163 kg/cm^2 at 1600 ºC). Samples containing 8 wt. % zirconia fired at 1600 ºC shows the maximum cold crushing strength value (169 kg/cm^2) among the investigated samples. This is correlated with the improvement in the densification parameters which results in a densified body with better resistance to vertical stress. This behavior is attributed to the thermal expansion coefficients (α) mismatch between mullite, cristobalite and zirconia (α mullite = 5.3×10^{-6} °C^{-1}, α cristobalite= 1.7×10^{-6} °C^{-1}, and α cubic zirconia = 10.5×10^{-6} °C^{-1}) this enhances the stresses on the body, resulting in the formation of interlinked micro-cracks which arrested across the large particles after a short distance of its propagation [28, 29].

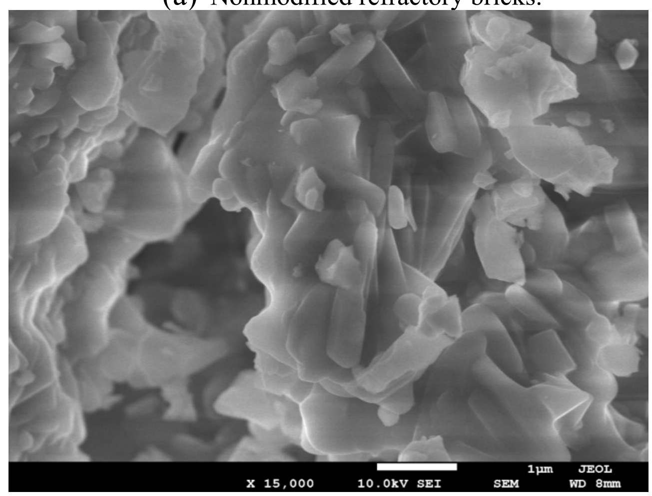
3.5 Refractory Properties (Thermal Shock Resistance)

All the fired bodies (1500 ºC) either with or without zirconia additives could withstand > 30 cycles of thermal shock test without any sign of cracking, however on measuring the loss in strength after thermal shock test, the samples behave differently. Table (3) indicates that the samples containing nano zirconia additives could retain relatively higher values of cold crushing strength than those containing no zirconia additives.

The value of retained strength (after thermal shock test) increases as the content of zirconia additive increases reaching its maximum with the sample containing 8 wt. % zirconia which could maintain 85 % of the initial strength



(a) Nonmodified refractory bricks.



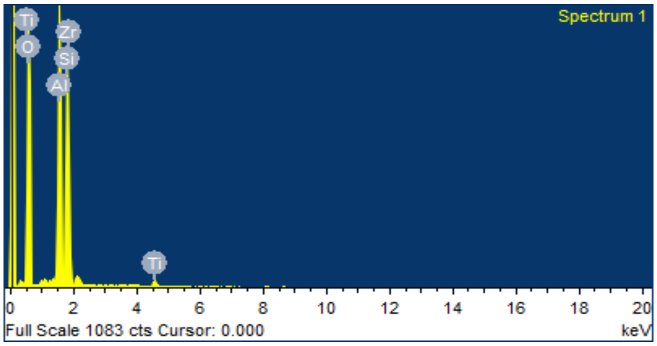
(b) Modified refractory bricks.

Fig.8: Scanning electron microscope of; (a) nonmodified (0 % zirconia) and (b) modified (8 % zirconia) fired (1500 ºC) bricks.

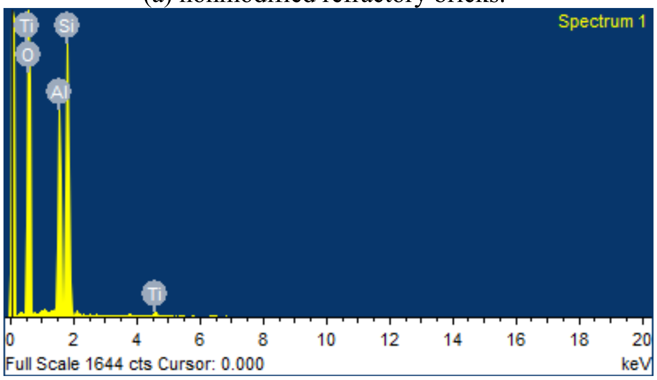
Table 3: Retained strength after thermal shock test.

Batch no.	Retained strength, %
1	65
2	69
3	74
4	79
5	85
6	80

compared with the non-modified sample (0 % zirconia) that could maintain only 68 % of the initial strength. This trend is reflected from the initial strength of the fired samples before the thermal shock test, i.e. samples with relatively higher cold crushing strength (8 wt. % zirconia) showed also the relatively higher value of retained strength. The outstanding behavior of this sample is attributed to its better densification parameters, good assemblage of minerals; mullite, cristobalite, zirconia as well as well compact microstructure shown in Fig. (8 b) compared with that containing no additives (Fig. 8 a). The main constituents of



(a) nonmodified refractory bricks.



(b) modified fired (1500 ºC) refractory bricks.

Fig. 9: EDAX patterns of; (a) nonmodified (0 % zirconia) and (b) modified (8 % zirconia) fired (1500 ºC) refractory bricks.

both samples are mullite and cristobalite minerals that could be confirmed through point analysis shown in Fig. 9 (a and b) and Table (2 and 3). In Fig. 9 (b) and Table (4) the presence of zirconia crystals could be recognized in addition to mullite and cristobalite crystals present in both samples (Figs. 9 (a), 9 (b) and Tables 2, 3) which assists in improving of microstructure and hence enhance the densification and mechanical properties as well as refractory properties as a result of the unique refractory properties of the added zirconia as well as the mullite mineral [33-36]. The improved properties of the modified brick samples are expected to increase their service lifetime while using in different metallurgical industries.

Table 4: EDAX analysis data of the non-modified (0 wt. % zirconia) and modified (8 wt. % zirconia) refractory bricks.

Element	Non-modified refractory bricks	Modified refractory bricks
	Weight %	Weight %
O	58.05	53.66
Al	15.52	19.98
Si	25.35	22.19
Ti	1.08	1.60
Zr	-	2.57
Totals	100.00	100.00

4 Conclusions

The properties of refractory bricks could be improved through nano zirconia additions. Refractory brick sample containing 8 wt. % nano zirconia is considered as the optimum among the investigated samples as it compromises good technological and refractory properties resulting from its good assemblage of minerals (mullite-cristobalite-zirconia) as well as its tight microstructure.

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