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Effect Nano-SiC Additives on Physical and Mechanical Properties of Bauxite Refractories Used in Oil Treatment Units

Abstract-Refractory mixtures were prepared from: bauxite raw materials, grog and Kaolin. Different weight percentage of micro-SiC (5, 10, 15 and 20 wt%) and nano-SiC (2.5, 5, 7.5 and 10 wt%) was added to bauxite mixture to improve the refractories characteristics to suit the lining of oil treatment units. Semi-dry pressing used to forming cylindrical specimens with load (7 ton) and 25 mm in diameter after mixing the powder with 10 wt% Sodium Silicate as a binder. The specimens dried at (110 °C) for (2 h) and fired at (1400 °C) with soaking time (2 h). During firing process, some of nano-SiC powder oxidants and transformed to SiO₂ glass phase with increasing mullite phase. Therefore; the bonds with bauxite increases as a result glass phase generated and lead to decreasing the porosity and increasing the shrinkage, density and mechanical properties compared with micro-SiC additives.

Keywords- Refractory, Nano-Ceramic, Silicon carbide, Kaolin and Bauxite. .

How to cite this article: S.A. Zaidan, H. H. Jasim, "Effect Nano-SiC Additives on Physical and Mechanical Properties of Bauxite Refractories Used in Oil Treatment Units" *Engineering and Technology Journal*, Vol. 35, Part A, No. 10, pp. 992-998, 2017.

1. Introduction

A refractory material is a type of engineering ceramic called an "industrial ceramic". Refractory materials, however, have coarser grain sizes and higher porosities than engineering ceramics, and consist of aggregate particles, held together by a bonding (matrix) phase, where both the aggregate and the bond can be multiphase. The particle size distributions are carefully controlled in order to control the microstructure, which directly influences porosity and density, strength, corrosion resistance and thermal shock resistance. Refractory materials are mostly oxide based materials, but they are becoming increasingly composite materials, which also contain non-oxide components such as graphite, SiC [1,2]. Nanotechnology aims to achieve enhanced material properties and functionality by dealing with matter on the atomic and molecular scale [3]. The use of highly reactive nanoparticles open up a vast range of possibilities as sintering agents and participants in matrix phase formation through in situ reactions. Problems associated with these nanoscale materials are related to their cost, availability, handling, dispersion and mixing, as well as health and safety aspects related to the handling of these very fine materials [4]. Ceramic forming techniques transform the raw material into a green product having a controlled size, shape, density and microstructure, porosity. The careful control of the density and microstructure of the green ceramic is necessary to obtain ultimate product performance, because the large defects introduced in the forming stage cannot normally be

eliminated when the product is fired. The difference in the packing density of ceramic powder will cause different shrinkage, which leads to non-homogeneous and generate cracks in the specimens during sintering. One of methods known in the manufacture of ceramic refractories is semi-dry pressing where biaxial pressing involves the compaction of powder into a mold by applying pressure along two directions [5]. This method is used because it make a product has homogeneous composition, fixed-dimensional and shape, has no deformations and high resistance to thermal shock [6], and it did not need a high proportion of binding material and reduce appearance of cracks during drying and burning [7].

2. Materials and Methods

The raw materials used in the experiments were subjected to different primary analysis steps in order to determine which extent those raw materials are suitable for the preparation of specimens. The chemical composition of the bauxite, fired bauxite (grog) and kaolin are shown in table (1). Then raw materials subjected to crushing and grinding processes to increase the surface area of particles, which lead to improve the physical and mechanical properties [8]. Selected particle sizes was depending on the characteristics of refractory product. The use of coarse particle size tends to reduce the surface area and also weakens the strength of the link between the granules. But when use fine particle sizes that will tend to increase the surface area and increase the binding material proportion [9]. The gradient has been used illustrated in Table 2.

Table 1: Chemical analysis of raw materials.

| Raw materials | L.O.I % | K ₂ O% | Na ₂ O% | MgO% | CaO% | TiO ₂ % | Fe ₂ O ₃ % | Al ₂ O ₃ % | SiO ₂ % |
|---------------|---------|-------------------|--------------------|------|------|--------------------|----------------------------------|----------------------------------|--------------------|
| Bauxite | 13.75 | — | — | 1.05 | 1.20 | 1.80 | 1.20 | 60.90 | 18.98 |
| Grog | 0.08 | 0.08 | 0.47 | 0.20 | 0.85 | 1.37 | 1.48 | 71.3 | 26.50 |
| Kaolin | 10.47 | 0.48 | 0.41 | 0.25 | 0.37 | 1.43 | 1.33 | 33.40 | 50.58 |

Table 2: Particle size distribution.

| Grain size | mm | U. S. Mesh |
|------------|-----------|------------|
| Coarse | 0.5 - 2 | 35 - 10 |
| Medium | 0.1 - 0.5 | 140 - 35 |
| Fine | < 0.1 | > 140 |

The main refractory mixture was prepared from different Iraqi raw materials, and this mixture consists of (70 wt%) grog, (20 wt%) kaolin and (10 wt%) bauxite. The grog is prepared from firing bauxite in (1400 °C) and soaking time (4 h), its contain three particle sizes; (40%) coarse particles, (20%) medium particles and (40%) fine particles illustrated in Table 2, this grog will be used in the mixtures to reduce shrinkages, cracks, deformations, increase bulk density and decrease porosity. Ceramic powder (SiC) in micro and nano sizes and in various ratios have been used as additives to the prepared mixture, micro (SiC) in ratios (5, 10, 15 and 20%) and nano (SiC) in ratios (2.5, 5, 7.5 and 10%). There is two groups beside the first one (Mix.1) which have no additives, they are illustrated in Figure 1, and it will be illustrated more in the Table 3 of the ceramic additives amounts. Then Sodium Silicate added to the mixture ranging (9 – 10 wt %) and mixing them in a porcelain mortar, and they are ready to the next stage which is (Forming process).

Table 3: Composition of specimens.

| Specimens | Mix. (wt%) | Additive materials (wt%) | |
|-----------|------------|--------------------------|------------|
| | | β - SiC μm | β - SiC nm |
| Group (1) | A0 | 100 | - |
| Group (2) | A1 | 95 | 5 |
| | A2 | 90 | 10 |
| | A3 | 85 | 15 |
| | A4 | 80 | 20 |
| Group(3) | a1 | 97.5 | 2.5 |
| | a2 | 95 | 5 |
| | a3 | 92.5 | 7.5 |
| | a4 | 90 | 10 |

The samples are formed in a cylindrical shape, and in various dimensions according to ASTM. The applied load is (7ton) by using hydraulic press.

In this case, the specially prepared dry powder is placed in a die and pressed under high biaxial force to make green compact specimens, relatively only small parts can be made by this way.

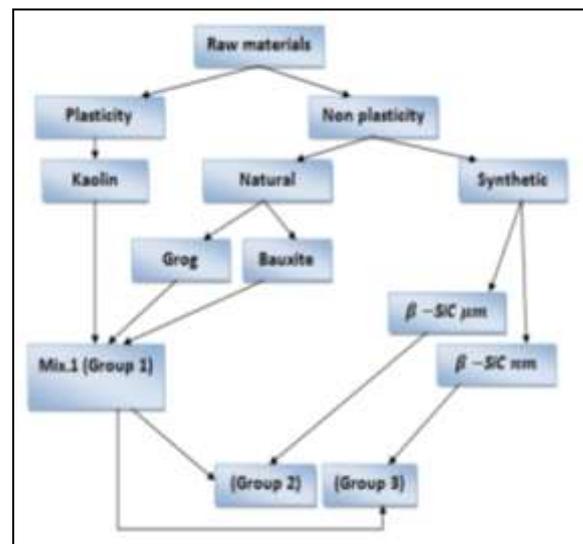


Figure 1: Diagram of prepared mixtures.

After forming, ceramics must be dried; drying must be carefully controlled to balance between minimizing drying time and avoiding differential shrinkage, warping, and distortion. An alternative to air drying is radiation drying in which microwave or infrared radiation is used to enhance drying. Amount of moisture in specimens varies according to the type of clays and depending on the quality of the molding, the samples were dried in (110 °C for (2 h) to remove moisture and configured to firing stage. The specimens were fired at (700, 1200 and 1400°C with soaking time (2 h) for each temperature.

3. Measurements

I. Microstructure

The scanning electron microscopy (SEM) has been taken by (Tescan Vega II XMU Variable Pressure SEM), this test available in Iran-Tehran-Razi Metallurgical Research Center.

II. Linear shrinkage

For linear shrinkage measurement we should take the specimens dimensions before and after firing with use of vernier caliper, and use the following equation:

$$L. Sh. \% = \frac{L_1 - L_2}{L_1} \dots (1)$$

Where (L_1) and (L_2) Specimen height before and after firing, respectively.

III. Density, porosity, and water absorption

Bulk density and open porosity are determined by using Archimedes method using distilled H_2O . The mass of material in air is divided by its buoyancy (reduction in weight) when suspended in a liquid medium to give a measurement of density.

The density of material is:

$$Density = \frac{mass}{volume} \dots (2)$$

Where density, porosity and water absorption were calculated according to the ASTM (C 373 – 72).

IV. Hardness

Mohs scale of mineral hardness testing was used to measure the hardness of ceramic specimens. This test of minerals are among the easiest and most useful tests to perform, testing how easily one substance will scratch another. The hardness will refer to the surface resistance to abrasion as given by Mohs Scale.[10]

V. Compressive strength

The standard test to find the compressive strength in ASTM is (C-133) was used for cylindrical ceramic specimens.

VI. Diametrical strength

The diametrical strength test (Splitting Tensile Strength) can be derived by using the following equation(ASTM C 496/C):

$$\sigma_D = \frac{2F}{\pi Dt} \dots (3)$$

Where (σ_D) diametrical strength (MPa), (F) the applied load (N), (D) the disk diameter, (t) the thickness of disk. The stress field in the transverse direction is highly depended on the width of load application and becomes highly compressive. The disk test has therefore been used to attempt to study biaxial stress failure response [11].

4. Results and Discussion

At (1200°C) the growth of Mullite is complete with its columnar-like structure [12]. Figure (2) shows

SEM photographs for nano (SiC)specimens where it can be seen the large amounts of whiskers structure.

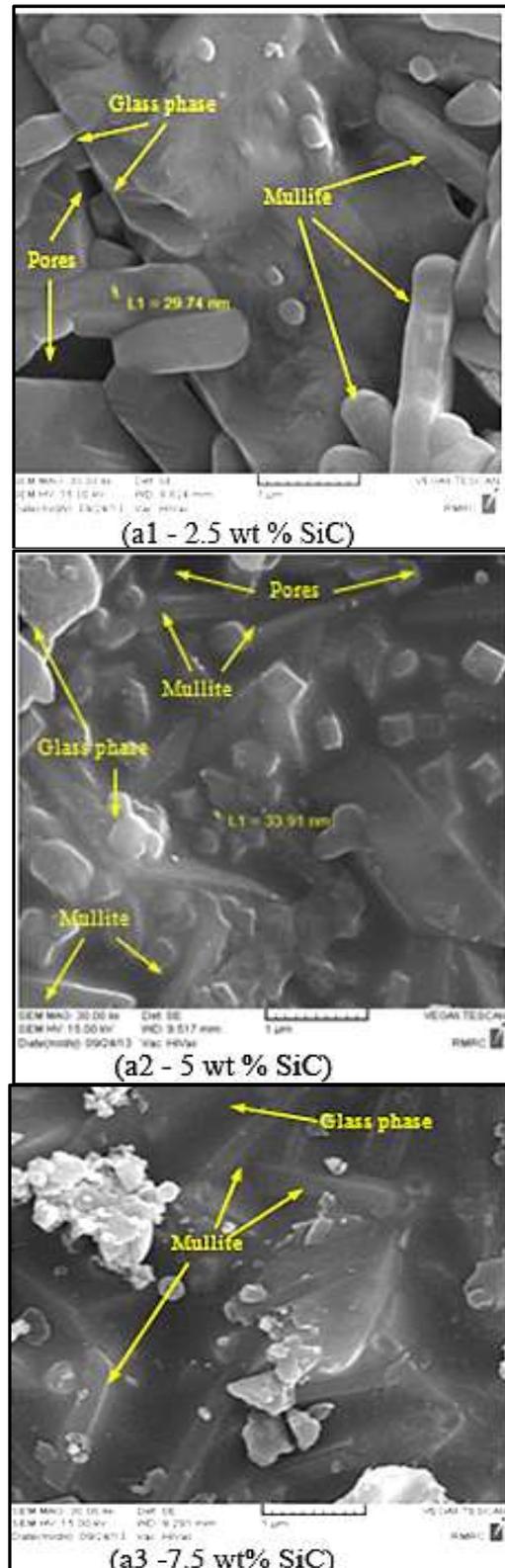




Figure 2: SEM images for Nano β –SiC specimens.

Figure 3 shows linear shrinkage of specimens when addition micro SiC. For (5 wt% SiC) addition, the linear shrinkage is (1.166%) as shown in Figure 3a, and this increase continuously to (1.491%) for (20 wt% SiC) addition compared with nano SiC addition Figure 3b, the increase in linear shrinkage where (1.329%) for (2.5 wt% SiC) addition, and this reach to (1.711%) for (10 wt% SiC) addition.

High shrinkage in nano SiC additives specimens caused by the transformation of SiC to SiO₂, this arises liquid phase. The transformation is according to the equation:

$$\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2$$

Where the oxidation of SiC increase with particle size decreases and leading to weight gain and the apparent density increasing for all specimens which firing at (1400 °C), and this increasing with the increasing of ceramics material addition. Figure 4 shows the increasing of apparent density according to (SiC) addition in (a) micro size and (b) nano size respectively, noting that both sizes are reach to the same apparent density with the half percentage of addition for nano size compared with micro size addition of (SiC). The clear increase in density due to addition of (SiC) in nano size, because the volume is reduce due to shrinkage and increase in mass because of oxidation.[13]

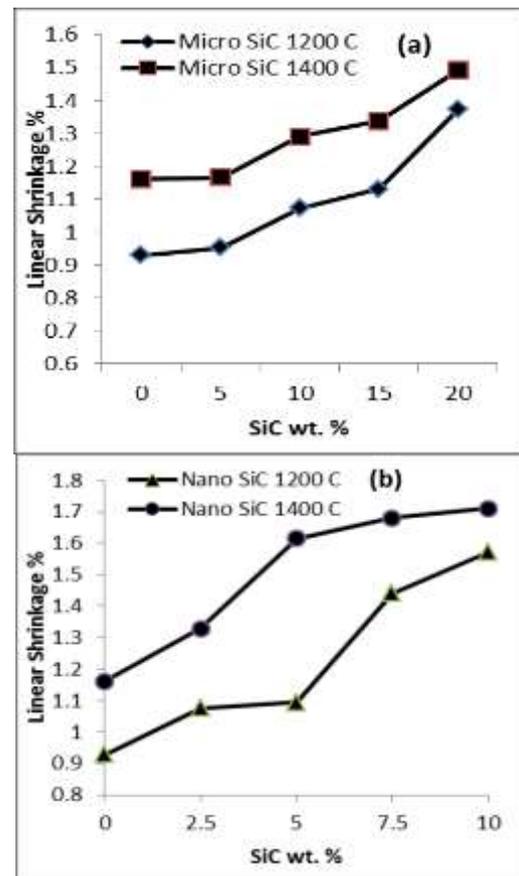


Figure 3: Linear Shrinkage of specimens with: (a) Micro β –SiC and (b) Nano β –SiC additions at sintering temperature 1200°C and 1400°C.

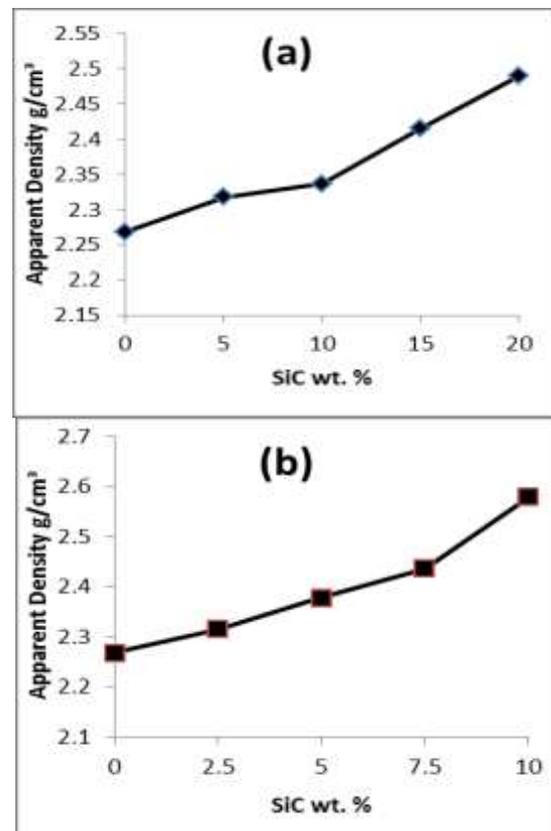


Figure 4: Apparent Density of specimens with: (a) Micro β –SiC and (b) Nano β –SiC additions at sintering temperature 1400 °C.

The porosity decreases for all specimens according to the ceramic materials addition, which firing at (1400 °C). This decrease of porosity was accompanied by decrease in water absorption as shown in Figure 5. Noting that the values of porosity and water absorption are decreased in nano size addition as shown in Figure 5b, more than it in micro size addition as shown in Figure 5a, because of nano size distribution lead to more diffusion for the addition ceramic materials, and that small size causes (nano size) reduction of porosity values with increasing temperature as compared to micro size, to form liquid phase resulted from the chemical reactions taking place among the components of the specimens (MgO, CaO, Fe₂O₃, Al₂O₃ and SiO₂). This glass phase fills the pores and vacancies among grains causes a compacting of the grains together at high temperature, then it solidifies after cooling causing increment in the density followed by decrement in porosity and water absorption.

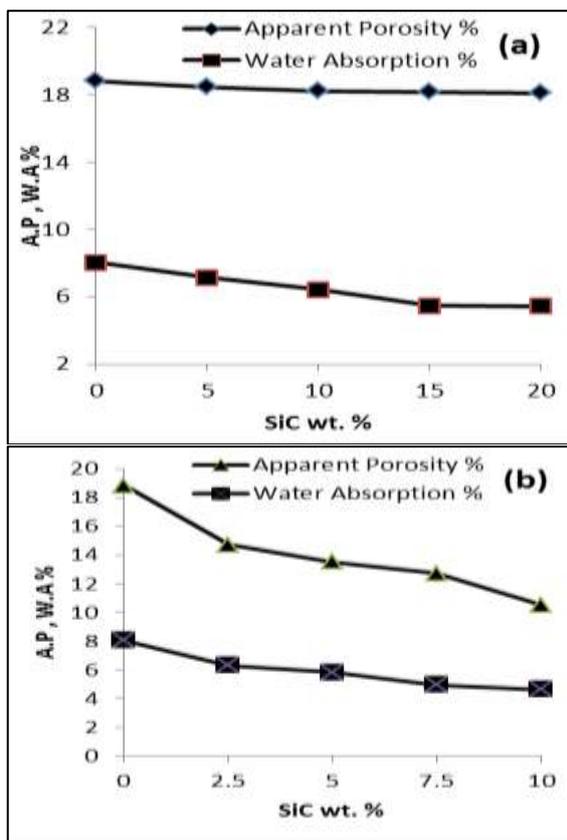


Figure 5: Apparent Porosity (A.P) and Water Absorption (W.A) of specimens with (a) Micro β-SiC and (b) Nano β-SiC additions at sintering temperature 1400 °C.

The results of compressive strength and diametrical strength for all specimens when fired at (1400 °C) in Figure (6), where these values are increased according to the increase the ratio of addition ceramic material. This increasing resulted from sintering process, during forming liquid phase at high temperatures which work on

reduction of porosity and closes pores, which lead to increase cohesion between grains, and this gives strength to the body and causes increase in compressive and diametrical strength values, this also depend on difference in mullite ratio in specimens [14].

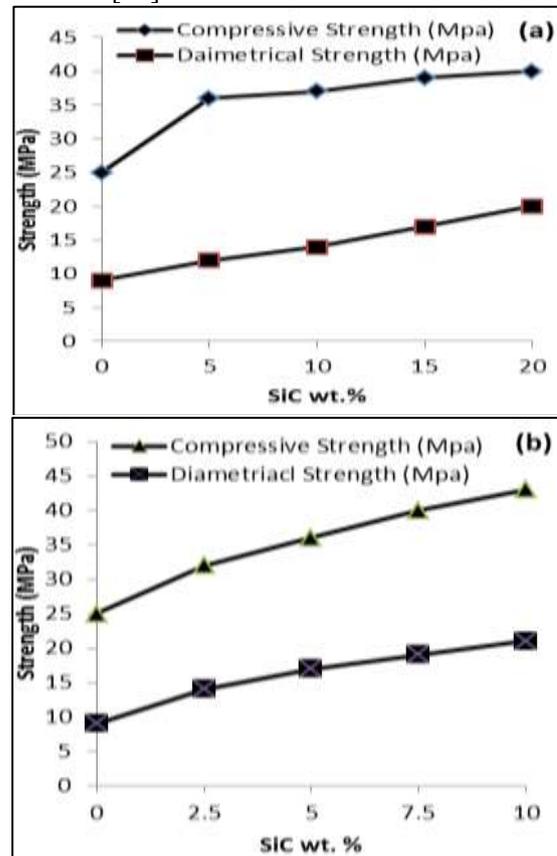


Figure 6: Compressive strength and diametrical strength of specimens with:(a) Micro β-SiC and (b) Nano β-SiC additions at sintering temperature 1400°C.

Also, Formation high amounts of liquid phase in specimens contain SiC will decrease strength values of compressive strength and diametrical strength for specimens according to particle sizes, where nano (SiC) specimens; Figure (6b) have strength values higher than micro (SiC) specimens; Figure (6a), because the strength increased with the decreasing of particle sizes which more responsive to the sintering process than the coarse particles, also fine particles cause less fractures than coarse ones, where fractures increase in ceramic samples with the increase of particle size, and values of compressive strength and diametrical strength increase with the decrease of particle size [15,16]. Figure (7) shows the specimens damaged after applied diametrical strength test, at which shape of fracture gives a perception for the homogeneity of specimens and the amount of its fracture resistance. In most cases, the fracture into two halves, in other cases there will be a crush in the area of fracture as a result of high resistance due to presence the glass phases.

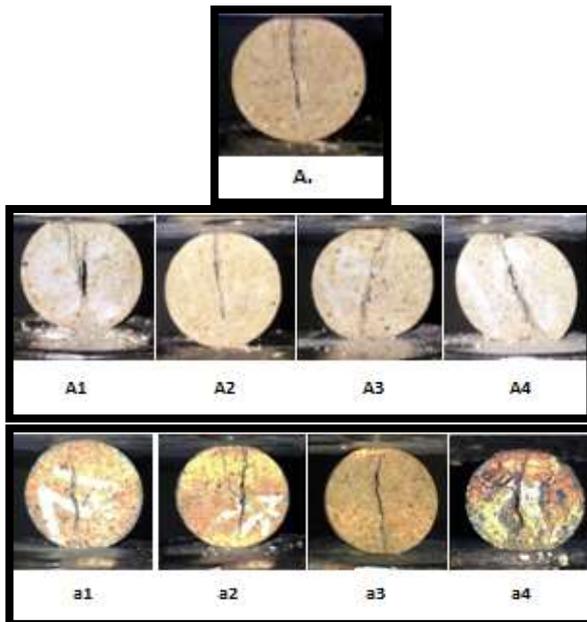


Figure 7: The fracture form resulting diametrical strength test.

Mohs hardness test results in Table (4) shows the values of hardness for the specimens firing at (1400 °C).

Table 4: Mohs hardness results for specimens, firing at 1400°C.

| Specimens | Contents | Mohs Hardness |
|-----------|-------------------------|---------------|
| A0 | Bauxite + Kaolin + Grog | 6.2 |
| A1 | A0 + 5 wt% μSiC | 6.4 |
| A2 | A0 + 10 wt% μSiC | 6.6 |
| A3 | A0 + 15 wt% μSiC | 6.8 |
| A4 | A0 + 20 wt% μSiC | 6.9 |
| a1 | A0 + 5 wt% nSiC | 8.5 |
| a2 | A0 + 10 wt% nSiC | 8.8 |
| a3 | A0 + 15 wt% nSiC | >9 |
| a4 | A0 + 20 wt% nSiC | >9 |

The hardness was approximately (6.2) for the specimen (A0) without any addition, and hardness values for other specimens ranged between (6.4 – 6.9) according to micro (SiC) addition, but it was (8.5 – > 9) according to nano (SiC) addition. These values are different depending on particle size, where the hardness increases with decreasing of particle size because the fine particles can be more responsive to melting process more than coarse particles, that leads to increase cohesion among particles and increase the hardness for specimens [15].

5. Conclusions

High shrinkage in nano SiC additives specimens caused by the transformation of SiC to SiO₂, this arises liquid phase.

Both sizes (nano and micro), are reach to the same apparent density with the half percentage of addition for nano size compared with micro size addition of SiC. The clear increase in density due to addition of SiC in nano size, because the volume is reduced due to shrinkage and little change in mass.

The values of porosity and water absorption are decreased in nano size addition more than it in micro size addition, because of nano size distribution lead to more diffusion for the addition ceramic materials.

Compressive and diametrical strength are increase according to the increase the ratio of addition ceramic material. This increasing resulted from sintering process, during forming liquid phase at high temperatures which lead to reduce porosity and close pores and increase cohesion between grains, and this give strength to the body and causes increase in compressive and diametrical strength values, whereas in nano SiC specimens, strength values higher than micro SiC specimens.

Hardness values for specimens have micro SiC addition, are less than values of nano. High values of hardness mean increasing in scratch and wear resistance, lead to increase resistance to external conditions.

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