

Effects of niobium oxide additive on the phase development and physico-mechanical properties of zirconia-clay ceramics composite

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The effect of niobium oxide additives and sintering temperature on the phase developments and physico-mechanical properties of zirconia-clay ceramic composite was investigated. The clay of known mineralogical composition was source from a large deposit in Ile-Ife, in Osun State Nigeria. The beneficiated clay, was milled to a particle size of 300 μm . The milled clay was blended with varied percentages of yttria stabilized zirconia and niobium oxide powders in a tubular mixer for 18 hours at a speed of 72 rev/min. From the blended powders, standard samples were produced by uniaxial compression. This was followed by sintering in an electric furnace at 1200 °C and 1300 °C for one hour. The sintered samples were characterized for various physical and mechanical properties. The phases developed in the sample during sintering were also investigated using X-ray diffractometer (XRD). Morphology and microanalysis of the sintered ceramic composite samples were determined using ultrahigh resolution field emission scanning electron microscope (UHR-FESEM) equipped with energy dispersive spectroscopy (EDS). It was observed that at 1200 °C the presence of niobium oxide in the samples favours the decomposition of zircon to silica phases and zirconia. It was also observed that the combined effects of increased sintering temperature to 1300 °C and addition of niobium oxide favour the formation of more sillimanite in preference to mullite. At 1200 °C niobium oxide additive inhibits the formation of mullite in preference to the formation of aluminum niobate and sillimanite. It also favours decomposition of zircon to the silica phases and zirconia. Increase in the niobium oxide content lead to increased bulk density at 1300 °C. It was concluded that the sample with optimum physico-mechanical properties is considered to be sample FT2 with 10% ZrO_2 , 0% Nb_2O_5 , 90% clay and sintered at 1300 °C held at the sintering temperature for 60 minutes

Key words: Niobium oxide additives, sintering temperature, phase developments, physico-mechanical properties, zirconia-clay, ceramic composite.

Introduction

Ceramic composite containing zirconia had received a lot of attention from various researchers due to the martensitic phase transformation which zirconia undergoes under applied stress. This phase transformation goes a long way in improving the property of the ceramic composite [1-5]. This is not unconnected with the superior physical and mechanical properties of zirconia (mostly when it is partially or fully stabilized) which includes high hardness, wear resistance, high melting temperature, elastic modulus to mention but few [6].

Clay is a composite of several important minerals like hematite, alumina, silica (which mostly occur as aluminosilicates like kaolinite) which have many useful properties, including high specific surface area and excellent adsorptive capacity. Many researchers have synthesized mullite through solid state reaction sintering using alumina and silica [7, 8]. Attention is shifted to the use of cheap and abundant available

natural raw materials such kaolinitic clays or kaolin for the production of mullite based ceramic composites that are economically viable for bulk refractory applications. Typically Al_2O_3 and SiO_2 containing reactants used for this purpose are clay minerals such as kaolinite, pyrophyllite, sillimanite group of minerals and bauxite [9]. Many researchers have made several attempts to improve the properties of ceramic based composites. Badiie et al. (2001) [10] investigate how the addition of CaO , MgO , TiO_2 , and ZrO_2 affects the mullitization process in Iranian andalusite located in Hamedan mines. They discovered that all the additives, except ZrO_2 favour the formation of mullite from andalusite.

Ebadzadeh and Ghasemi [11] synthesized zirconia-mullite composites by using α -alumina, aluminium nitrate, zircon powder and TiO_2 as additive. Aramide *et al.* [2] synthesized mullite-zirconia composites containing yttria as additive. Chandra et al. [12] synthesized zirconia-toughened ceramics with a mullite matrix based on the quaternary system ZrO_2 - Al_2O_3 - SiO_2 - TiO_2 in the temperature range 1450-1550 °C using zircon-alumina-titania mixtures. Aksel and Komieczny [13] studied the influence of zircon on the mechanical properties and thermal shock behavior of slip-cast

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alumina-mullite refractories. With the exception of Aramide et al. [2] little information is available on the reports of production of ceramics involving natural clay using additives like zirconia etc. The main aim of this research is to investigate the effects of niobium oxide on the phase developments in the zirconia-clay ceramic composite.

Materials and Methods

Materials

Clay samples used in this work were sourced from Ipetumodu, Osun State in the south western part of Nigeria. High purity oxides such as zirconia and yttria were supplied by F.J. Bodmann & CO, L.L.C. (The thermal spray materials and technologies source). Oakmere Business Park, 2072 Sussex Street, Harvey, LA 70058.

The clay samples were first soaked in water for three days to dissolve the deleterious materials in them and at the same time to form slurry. The slurries were then sieved to remove deleterious materials and other foreign substances. The sieved slurries were then allowed to settle down for three days after which the clear floating water was decanted. The dispersed fine clays in water (clay slurries) were then poured into plaster of Paris (P.O.P) moulds and left undisturbed for three days in order to allow the remaining water present to drain out completely. The resulting plastic clay masses were sun dried and subsequently dried in a laboratory oven at 110 °C for 24 hrs. The resulting dried clay samples were crushed and milled in a Rawwley Sussex grinder to an average particle size of 300 µm.

The mass percent of the composition below was computed using Eqs. (1) and (2) using the densities in

Table 2 and the individual powders volume fraction in each composition. The powders were weighed per batch of 50.00 g on a sensitive electronic weighing balance to five (5) decimal places. The individual (batch) composition was thoroughly mixed in a Turbula Mixer for 18 hrs at 72 rev/min. The compositions of the blended samples were shown in Table 1

If

$$M_t = V_{cl}\rho_{cl} + V_{Zr}\rho_{Zr} + V_{Nb}\rho_{Nb} \quad (1)$$

where V_{cl} , V_{Zr} , and V_{Nb} are respectively the volume fraction of clay, ZrO_2 and Nb_2O_5 , ρ_{cl} , ρ_{Zr} and ρ_{Nb} are respectively the volume fraction of clay, ZrO_2 and Nb_2O_5 , and M_t is the total mass contribution of all the components. And if M is the mass of each batch, then the mass contribution of each component could be calculated from:

$$M_c = \frac{V_{cpc} \times M}{M_t} \quad (2)$$

M_c is the mass contribution of a component in a batch (clay or ZrO_2 or Nb_2O_5), V_c , ρ_c the respective volume fraction and density of the component.

The resulting homogenous powder mixtures were compacted uniaxially into standard sample dimensions for cold crushing strength, bulk density and apparent porosity. The samples were compressed uniaxially using 750 MPa compaction load inside a standard stainless steel die. The resulting green compacts were fired at 1200 °C and 1300 °C in an electric furnace. The sintered samples were then characterized for various mechanical properties as described below:

Characterization

Test samples from each of the ceramic composites were dried for 12 hrs at 110 °C. The dry weight of each fired sample was taken and recorded as D . Each sample was immersed in water for 6 hrs to soak and weighed while been suspended in air. The weight was recorded as W . Finally, the specimen was weighed when immersed in water. This was recorded as S . The apparent porosity was then calculated from the expression:

$$p = \frac{(W-D)}{(W-S)} \times 100\% \quad (3)$$

The results obtained are presented in Table 5.

Cold compression strength test is to determine the compression strength to failure of each sample, an indication of its probable performance under load. The standard ceramic samples were dried in an oven at a temperature of 110 °C, allowed to cool. The cold compression strength tests were performed on INSTRON 1195 at a fixed crosshead speed of 10mm min⁻¹. Samples were prepared according to ASTM C133-97 (2003) and

Table 1. The compositions of various ceramic composite samples used for the experimental investigations.

Sample	Zirconium oxide ZrO_2 (2%yttria) (vol %)	Niobium oxide Nb_2O_5 (vol %)	Raw clay (vol %)
F	10	–	90
F1	8	2	90
F2	6	4	90
F3	4	6	90
F4	2	8	90
F5	–	10	90

Table 2. Densities of various components used.

Oxide/Clay	Clay ^a	ZrO_2 ^b	Y_2O_3 ^b	Nb_2O_5 ^b
Density (g/cm ³)	1.20	5.68	5.01	4.60

^aDetermined in the laboratory.

^bProvided by the supplier.

cold crushing strength, modulus of elasticity and absorbed energy of standard and conditioned samples were calculated from the equation:

$$CCS = \frac{\text{Load to Fracture}}{\text{Surface Area of Sample}} \quad (4)$$

The results obtained are presented in Table 5.

The test specimens were dried at 110 °C for 12 hrs to ensure total water loss. Their dry weights were measured and recorded. They were allowed to cool and then immersed in a beaker of water. Bubbles were observed as the pores in the specimens were filled with water. Their soaked weights were measured and recorded. They were then suspended in a beaker one after the other using a sling and their respective suspended weights were measured and recorded. Bulk densities of the samples were calculated using the formula below:

$$\text{bulk density} = \frac{D}{(W-S)} \quad (5)$$

where: D = weight of dried specimen, S = weight of dried specimen suspended in water, and

W = weight of soaked specimen suspended in air.

The samples were prepared for XRD analysis using a back loading preparation method [14]. They were analyzed using a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and receiving slits with Fe filtered Co-K α radiation. The phases were identified using X'Pert Highscore plus software. The receiving slit was placed at 0.040 °. The counting area was from 5 to 70 ° on a 2 θ scale. The count time was 1.5 sec. The temperature-scanned XRD data were obtained using an Anton Paar HTK 16 heating chamber with Pt heating strip. Graphical representations of the qualitative result follow below. The relative phase amounts (weight %) were estimated using the Rietveld method (Autoquan

Program) as reported by Young et al [15]. Amorphous phases, if present were not taken into consideration in the quantification.

Morphology and microanalysis of sintered ceramic composite samples were determined using ultrahigh resolution field emission scanning electron microscope (UHR-FESEM) equipped with energy dispersive spectroscopy (EDS). The pulverized clay samples/sintered ceramic composite samples were previously gold coated. Particle images were obtained with a secondary electron detector.

Results and Discussion

Figs. 1 and 2 with Table 3 show the crystalline phases developed in the various samples under consideration, while Figs. 3 to 7 with Table 4 show the effects of sintering temperatures on the physico-mechanical properties of the various samples.

Effect of sintering temperature on the phase development in the sample F.

From Figs. 1 and 2 with Table 3 the effect of sintering temperature on the phase developed in the samples is clearly depicted. From the figures it could be seen that when the samples were sintered at 1200 °C, the phases developed in sample F (10% ZrO₂, 90% clay) are 8.16% quartz, 4.72% hematite 7.37% mullite, 16.07% sillimanite, 1.26% pseudobrookite, 0.42% iron (II) niobate [FeNbO₄], 0.45% rutile, 1.91% aluminum niobate [AlNbO₄], 4.12% zircon, 42% monoclinic zirconia [m-ZrO₂] and 13.52% cristobalite. From the XRD results of the raw Ipetumodu clay [10, 13], it contains 23.84% quartz, but on firing with 10% ZrO₂ to 1200 °C bulk of the quartz had transformed to cristobalite phase (13.52%) while only 8.16% quartz remained. Moreover, it is also observed that the raw Ipetumodu clay contains 23.74% kaolinite, 15.02%

Table 3. XRD results of the various samples showing the identified.

Samples	Quartz	Hematite	Mullite	Sillimanite	Pseudo brookite	Iron (III) Niobium Oxide (1/1/4)	Rutile	Aluminium Niobate (V)	Zircon	m-ZrO ₂	Cristobalite
FT1	8.16	4.72	7.37	16.07	1.26	0.42	0.45	1.91	4.12	42	13.52
FT2	1.96	3.96	10.97	18.38	1.12	0.78	1.39	2.53	23.19	28.8	6.92
F1T1	9.89	2.63	9.07	16.41	0.21	9.72	0.3	2.38	2.34	32.4	14.64
F1T2	3.16	0.79	8.56	18.63	0.21	9.59	3.13	3.69	23.61	18.61	10.01
F2T1	10.97	2.84	0	14.82	3.72	13.73	2.49	9.44	0.44	25.79	15.76
F2T2	3.49	1.57	4.65	23.21	3.84	16.5	0.05	2.33	10.84	19.99	13.53
F3T1	13.43	1.98	0	14.71	2.56	18.94	0	15.88	0.17	14.7	17.62
F3T2	2.1	0.67	1.18	16.12	2.23	29.49	0	16.1	3.96	12.65	15.52
F4T1	12.88	2.3	6.65	19.02	0	16.54	0.84	23.61	0	3.48	14.7
F4T2	3.16	1.2	3.06	16.4	0	30.79	0	23.29	0	4.95	17.14
F5T1	13.71	4.32	12.03	14.21	1.19	5.99	0	32.71	0.31	0.83	14.7
F5T2	3.86	1.76	15.98	12.2	2	6.21	0	41.35	1.02	0	15.62

muscovite/illite, 11.28% plagioclase/albite and 26.12% microcline (a feldspar mineral), this explain the sources of mullite (through the process of mullitization of kaolinite to mullite and excess silica) [2, 10], and sillimanite [11] when the samples were sintered to 1200 °C. The 1.26% pseudobrookite is an iron titanium oxide mineral with formula: Fe_2TiO_5 , as could be seen from the x-ray fluorescence (XRF) and atomic absorption spectrometry analysis (AAS) of the raw clay sample that it contained some oxides of iron and titanium [10, 13]. During the process of sintering, the some of the iron and titanium oxide (rutile) acquired enough energy to undergo solid state reaction which resulted in the formation of the pseudobrookite. The zircon content (4.12%) originated from the reaction of some of the zirconia additive with the silica (quartz) content of the clay to form zircon. 42% zirconia is from the 10% (vol.) zirconia that was added as additive to the raw clay. The niobate constituents of the sample which are in traces are from niobium oxide used as additive for other samples which will be discussed later.

Furthermore, Fig. 2 shows the phases observed in the samples when the sintering temperature was increased to 1300 °C. From the figure it observed that the phases in the samples sintered at 1300 °C are; 1.96% quartz (reduction), 3.96% hematite (reduction), 10.97% mullite (increase), 18.38% sillimanite (increase), 1.12% pseudobrookite (reduction), 0.78% FeNbO_4 (increase), 1.39% rutile (increase), 2.53% AlNbO_4 (increase), 23.19% zircon (increase), 28.8% m- ZrO_2 (reduction) and 6.92% cristobalite (reduction). The reduction in the quartz, cristobalite and m- ZrO_2 with the corresponding

increase in the amount of zircon phase is due to solid state reaction of the silica phases (quartz and cristobalite) with the zirconia phase (m- ZrO_2) to form zircon [2].

Effects of addition of niobium oxide and sintering temperature on the phase development in the samples

From Fig. 1 and Table 3, the effects of addition of varied amount of niobium oxide to the sample is clearly depicted. It is observed that sample F1 (8 (vol.) % ZrO_2 , 2 (vol.) % Nb_2O_5) after sintering at 1200 °C contained the following phases; 9.89% quartz (slight increase when compared with F @ 1200 °C), 2.63% hematite (reduction when compared with F @ 1200 °C), 9.07% mullite (increase when compared with F @ 1200 °C), 16.41% sillimanite (increase when compared with F @ 1200 °C), 0.21% pseudobrookite (reduction when compared with F @ 1200 °C), 9.72% iron (II) niobate (large increase when compared with F @ 1200 °C), 0.3% rutile (slight reduction when compared with F @ 1200 °C), 2.38% aluminum niobate (increase when compared with F @ 1200 °C), 2.34% zircon (reduction when compared with F @ 1200 °C), 32.4% m- ZrO_2 (large reduction when compared with F @ 1200 °C) and 14.64% cristobalite (slight increase when compared with F @ 1200 °C). From the data extracted, it is seen that quartz and cristobalite phases slightly increased while zircon phase is observed to reduce as indicated. This could be that the addition of niobium oxide does not favour the formation of the zircon from the reaction of zirconia and silica. The slight increased observed in the silica phase could be explained by inferring that niobium oxide (at 1200 °C) favours the decomposition of zircon to silica and zirconia [21]. Although it is observed that m- ZrO_2 phases reduced in amount as indicated, the explanation could be due to the contribution of the 'large' increased amount of iron (II) niobate to the overall percentages of all the phases. Moreover it is also observed that the amounts of mullite and sillimanite also increased as earlier explained. Increasing the sintering temperature to 1300 °C, the observed phases in F1 are; 3.16 quartz (reduced when compared with F1 @ 1200 °C), 0.79% hematite (reduced when compared with F1 @ 1200 °C), 8.56% mullite (slightly reduced when compared with F1 @ 1200 °C), 18.63% sillimanite (increase when compared with F1 @ 1200 °C), 0.21% pseudobrookite, 9.59% iron (II) niobate (slightly reduced when compared with F1 @ 1200 °C), 3.13% rutile (increased when compared with F1 @ 1200 °C), 3.69% aluminum niobate (increased when compared with F1 @ 1200 °C), 23.61% zircon (largely increased when compared with F1 @ 1200 °C), 18.61% m- ZrO_2 (reduced when compared with F1 @ 1200 °C) and 10.01% cristobalite (reduced when compared with F1 @ 1200 °C). At 1300 °C the inhibitive effect of niobium oxide (which favours the decomposition of zircon to zirconia and

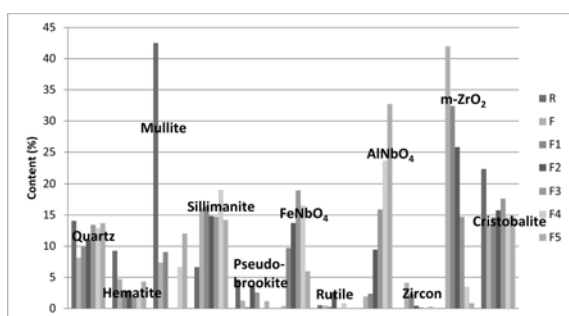


Fig. 1. Bar chart from the XRD result of the various samples, showing phases in the samples sintered at 1200 °C, soaked for 1 hr.

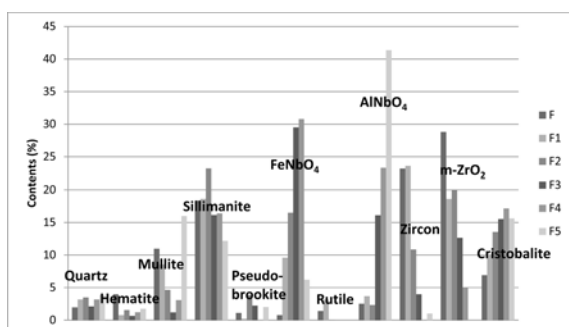


Fig. 2. Phases in the samples sintered at 1300 °C, soaked for 1 hr.

silica at 1200 °C) on the formation of zircon from the solid state reaction of silica and zirconia is overpowered. Reaction acquired more energy for the formation of zircon at 1300 °C; this explained the reduction observed in the amounts of quartz, cristobalite and zirconia together with the increase observed in the amount of zircon in F1 at 1300 °C. It is equally observed that the amount of sillimanite increased compared to what was observed at 1200 °C. It could be inferred that the combined effects of increased sintering temperature and addition of niobium oxide favour the formation of more sillimanite in preference to mullite.

Moreover, increasing the amount of niobium oxide additive in the sample to 4 (vol.) %; F2 with composition 6 vol.% ZrO_2 , 4 vol.% Nb_2O_5 90% clay. At 1200 °C, the phases observed in F2 are; 10.97% quartz (increased when compared with F1 @ 1200 °C), 2.84% hematite (slightly increased when compared with F1 @ 1200 °C), 0% mullite (largely reduced when compared with F1 @ 1200 °C), 14.82% sillimanite (slightly reduced when compared with F1 @ 1200 °C), 3.72% pseudobrookite (increased when compared with F1 @ 1200 °C), 13.73% iron (II) niobate (increased when compared with F1 @ 1200 °C), 2.94% rutile (increased when compared with F1 @ 1200 °C), 9.44% aluminum niobate (increased when compared with F1 @ 1200 °C), 0.44% zircon (reduced when compared with F1 @ 1200 °C), 25.79% m- ZrO_2 (reduced when compared with F1 @ 1200 °C) and 15.76% cristobalite (increased when compared with F1 @ 1200 °C). As earlier explained, the increase observed in the silica phases and the reduction in the zircon is due to the decomposition of the zircon to silica and zirconia. It is confirmed that at 1200 °C the presence of niobium oxide in the samples favours the decomposition of zircon to silica phases and zirconia [21]. There was no trace of mullite observed in the sample F2 at 1200 °C, this could be due to the explanation reported by Kong et. al. [14] that niobium oxide inhibit the formation of mullite. It can be inferred that at 1200 °C niobium oxide additive inhibits the mullitization process in preference for the formation of aluminum niobate and iron (II) niobate; as be seen that both iron and aluminum niobates increased in the sample at this temperature. Furthermore, when the sintering temperature is increased to 1300 °C, the phases observed in F2 are; 3.49% quartz (reduced when compared with F2 @ 1200 °C), 1.57% hematite (reduced when compared with F2 @ 1200 °C), 4.65% mullite (increased when compared with F2 @ 1200 °C), 23.21% sillimanite (largely increased when compared with F2 @ 1200 °C), 3.84% pseudobrookite (increased when compared with F2 @ 1200 °C), 16.5% iron (II) niobate (increased when compared with F2 @ 1200 °C), 0.05% rutile (largely reduced when compared with F2 @ 1200 °C), 2.33% aluminum niobate (reduced when compared with F2 @ 1200 °C), 10.84% zircon

(largely increased when compared with F2 @ 1200 °C), 19.99% m- ZrO_2 (reduced when compared with F2 @ 1200 °C) and 13.53% cristobalite (reduced when compared with F2 @ 1200 °C). It could be observed that at 1300 °C, the aluminum niobate formed in the sample was reduced compared to what was the case at 1200 °C. This accounts for the preferential formation of zircon from the solid state reaction of the silica phases with the zirconia. The reduction in the formation of aluminum niobate also accounts for the formation of some mullite at 1300 °C.

Similarly, increasing the niobium oxide to 6 vol.%; F3 with composition 4 vol.% ZrO_2 , 6 vol.% Nb_2O_5 90% clay. The observed phases in the sample at 1200 °C are; 13.43% quartz (increased when compared with F2 @ 1200 °C), 1.98% hematite (increased when compared with F2 @ 1200 °C), 0% mullite, 14.71% sillimanite (slightly reduced when compared with F2 @ 1200 °C), 2.56% pseudobrookite (reduced when compared with F2 @ 1200 °C), 18.94% iron (II) niobate, (increased when compared with F2 @ 1200 °C), 0% rutile, 15.88% aluminum niobate (increased when compared with F2 @ 1200 °C), 0.17% zircon (slightly increased when compared with F2 @ 1200 °C), 14.7% m- ZrO_2 (reduced when compared with F2 @ 1200 °C) and 17.62% cristobalite (increased when compared with F2 @ 1200 °C). The explanation is the same as explained in the preceding sections. Niobium oxide inhibits the formation of mullite in preference to the formation of aluminum niobate and sillimanite. It also favours decomposition of zircon to the silica phases and zirconia. On the other hand, increasing the sintering temperature to 1300 °C, the phases observed in F3 are; 2.1% quartz (reduced when compared with F3 @ 1200 °C), 0.67% hematite (reduced when compared with F3 @ 1200 °C), 1.18% mullite (increased slightly when compared with F3 @ 1200 °C), 16.12% sillimanite (increased when compared with F3 @ 1200 °C), 2.23% pseudobrookite (reduced when compared with F3 @ 1200 °C), 29.49% iron (II) niobate (increased when compared with F3 @ 1200 °C), 0% rutile, 16.1% aluminum niobate (increased slightly when compared with F3 @ 1200 °C), 3.96% zircon (increased when compared with F3 @ 1200 °C), 12.65% m- ZrO_2 (reduced when compared with F3 @ 1200 °C) and 15.52% cristobalite (increased when compared with F3 @ 1200 °C). All the samples concerned in this research work followed the same trend at the same temperature when it comes to phase development.

Effects of addition of niobium oxide and sintering temperature on the physico-mechanical properties of the samples.

Figs. 3 to 7 and Table 4 show the effects of niobium oxide additive and sintering temperature on the physical and mechanical properties of the samples.

Table 4. Results of various mechanical tests carried out on the samples.

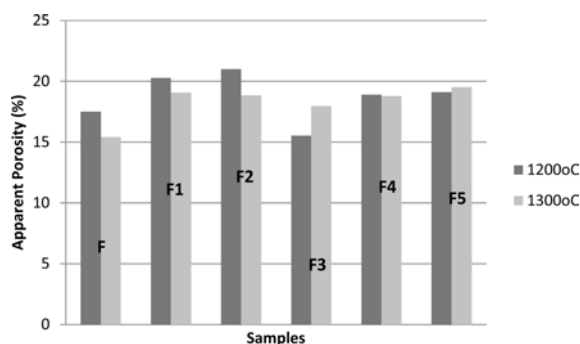
Samples	Apparent porosity (%)	Bulk density (g/cm ³)	Cold crushing strength (N/mm ²)	Absorbed energy (J)	Young's modulus (N/mm ²)
FT1	17.50	1.87	4409.00	1.2919	55208
FT2	15.40	2.06	8447.00	4.1753	64994
F1T1	20.27	1.63	8154.00	4.0575	71096
F1T2	19.07	1.97	2962.80	0.9567	19750
F2T1	20.99	2.26	6647.00	2.8648	50248
F2T2	18.85	2.23	4209.50	1.2604	29317
F3T1	15.54	1.58	3262.60	0.9631	38054
F3T2	17.96	2.17	1595.40	0.7104	17351
F4T1	18.89	1.57	3710.50	1.1623	34099
F4T2	18.79	2.28	5135.60	2.2875	39056
F5T1	19.10	2.04	1167.10	0.3349	11026
F5T2	19.52	2.25	994.00	0.3944	10029

Apparent porosity

Fig. 3 and Table 4 show the effect of sintering temperature and niobium oxide additives on the apparent porosity of the samples. From the figure, it is observed that at 1200°C sample F (10 vol.% ZrO₂, 0% Nb₂O₅ and 90% clay) had the porosity of 17.50%, increasing the niobium oxide content to 2 vol.% (F1) and at the same temperature, it porosity increased to 20.27%. Further increase in the amount of niobium oxide content to 4 vol.% (F2) leads to further increase in the apparent porosity to 20.99%. On the other hand, increasing the amount of niobium oxide content further to 6 vol.% (F3) and at 1200 °C, resulted in the apparent porosity being reduced to 15.54%. Moreover, increasing the

amount of niobium oxide in the samples to 8 vol. % (F4) at the same sintering temperature, it is observed that the apparent porosity of the sample increased to 18.89% and then increased further to 19.10% when the niobium oxide content of the sample was increased to 10 vol. (F5).

Increasing the sintering temperature to 1300°C, it is observed that the porosity of sample F reduced (from 17.50% at 1200 °C) to 15.40%. This expected as more densification occurs with increased sintering temperature

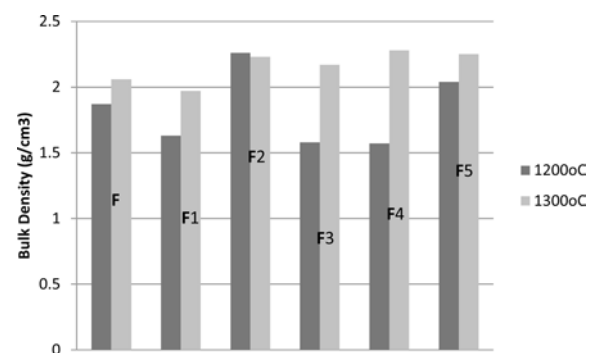
**Fig. 3.** Effects of sintering temperatures on the apparent porosity of the samples.

due to the presence of more liquid phases which fill more pores thereby reducing the porosity of the sample [2]. Addition of 2% niobium oxide to the sample (F1) at the same temperature (1300 °C) it is observed that the apparent porosity increased to 19.07%. Further increase in the amount of niobium oxide to 4% (F2), the porosity of the sample is observed to reduce to 18.85%. This means that

more liquid phases are available at this temperature (1300 °C) which filled more pores. Addition of more niobium oxide to the sample (F3: 6% niobium oxide) at the same temperature leads to further reduction in the porosity of the sample to 17.96%. But from this point it is observed that further increase in the amount of the niobium oxide leads to increase in the porosity of the samples.

Bulk density

Fig. 4 and Table 4 show the effect of sintering temperature and niobium oxide additives on the bulk density of the samples. From the figure, it is observed that at 1200°C sample F (10 vol.% ZrO₂, 0% Nb₂O₅ and 90% clay) had the bulk density of 1.87 g/cm³, adding 2% niobium oxide (F1) to it at same sintering temperature it is observed that the bulk density reduced

**Fig. 4.** Effects of sintering temperatures on the bulk density of the samples.

to 1.63 g/cm³, this expected because

at this particular point in the preceding section the porosity of the sample increased. Increased porosity in a sample means it has less matter (less weight), while still occupying the same space [17]. Moreover, increasing the niobium oxide content to 4% (F2) at the same sintering temperature of 1200 °C, it is observed that bulk density of the sample increased to 2.26 g/cm³. Further increase in the amount niobium oxide content to 6% (F3) made the bulk density of the sample to reduce to 1.58 g/cm³. Increasing the niobium oxide further to 8% (F4) lead to little reduction in the bulk density (1.57 g/cm³) of the sample. Subsequent increase in the amount of niobium oxide to 10% (F5) leads to the bulk density of the sample increased to 2.04 g/cm³.

Moreover, increasing the sintering temperature to 1300 °C the bulk density of sample F is observed to increase from 1.87 g/cm³ to 2.06 g/cm³. This is expected to be the case as its corresponding porosity reduced from 17.50% at 1200 °C to 15.40% at 1300 °C. Addition of 2% niobium oxide to the sample (F1) it is observed that its bulk density slightly reduced to 1.97 g/cm³. Further increase in the niobium oxide content to 4% (F2), it is observed that the bulk density of the sample increased to 2.23 g/cm³. It is also observed that the bulk density of the sample slightly reduced to 2.17 g/cm³ with further increase in the amount of niobium oxide content to 6% (F3). From the figure it could be broadly summarized that increase in the niobium oxide content lead to increased bulk density at 1300 °C.

Cold crushing strength (CCS)

Fig. 5 and Table 4 show the effect of sintering temperature and niobium oxide additives on the cold crushing strength (CCS) of the samples. From the figure, it is observed that at 1200 °C sample F (10 vol.% ZrO₂, 0% Nb₂O₅ and 90% clay) had the CCS of 4409 N/mm², adding 2% niobium oxide (F1) to it at same sintering temperature it is observed that the CCS increased to 8154 N/mm², this expected as it was explained in the preceding two section; putting all other factors into consideration, reduction in apparent porosity leads to increased bulk density which will lead

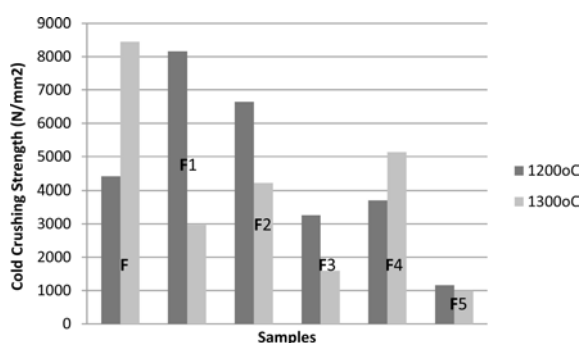


Fig. 5. Effects of sintering temperatures on the cold crushing strength of the samples.

to increased CCS [17-19]. Increasing the niobium oxide content to 4% (F2), it is observed that the CCS of the sample reduced to 6647 N/mm² this because the apparent porosity of the sample at this point increased. Further increase in the niobium oxide content to 6% (F3) at the same temperature of 1200 °C the CCS of the sample is seen to further reduce to 3262.6 N/mm². Moreover, increasing the niobium oxide content to 8% (F4) it is observed that the CCS of the sample slightly increased to 3710.5 N/mm². The CCS the reduced to 1167.1 N/mm², with further increase in the amount of niobium oxide content to 10% (F5).

However, as the sintering temperature is increased to 1300 °C, the CCS of the sample F is observed to increase from the value it was at 1200 °C to 8447 N/mm². The reason for this is that at this point as seen in the preceding sections, its apparent porosity at 1300 °C is lower than what it was at 1200 °C [17]. Addition of 2% niobium oxide to the sample (F1), it is observed that the CCS of the sample reduced sharply to 2962.8 N/mm². This due to increase in the apparent porosity of the sample from it was at FT2 to what it is now at F1T2. Further increase in the amount of niobium oxide in the sample to 4% (F2), it is observed that the CCS of the sample increased to 4209.5 N/mm², this is due to the same reason given above. Moreover, when the niobium oxide content was further increased to 6% (F3), it was observed

that the CCS of the sample was reduced to 1595.4 N/mm². Increasing the niobium oxide content further to 8% (F4) at the same temperature it is noticed that the CCS increased to 5135.6 N/mm², any other increase in the content of the niobium oxide to 10% (F5), made the CCS of the sample to be reduced to the minimum value of 994 N/mm². Moreover, from the Table 1, it could observed that all the samples have quartz and cristobalite (different polymorphs of silica) coexisting within their matrices. These phases have wide differences in their thermal expansion coefficients and the glass matrix. During cooling from the sintering temperature to room temperature, these differences in their thermal expansion result in internal residual stresses which adversely affect the strength of the sample [20]. Sample F3T1 has the highest amount of quartz and cristobalite, followed by FT1/1 while the least amount of the mentioned phases was observed in FT2. This explained why most of the samples have very low strength, when compared with the best sample, which is considered to be FT2.

Absorbed energy

Fig. 6 and Table 4 show the effect of sintering temperature and niobium oxide additives on the absorbed energy of the samples. From the figure, it is observed that at 1200 °C, the absorbed energy

value of sample F (10 vol.% ZrO₂, 0% Nb₂O₅ and 90% clay) is observed to be 1.2919 J. The absorbed

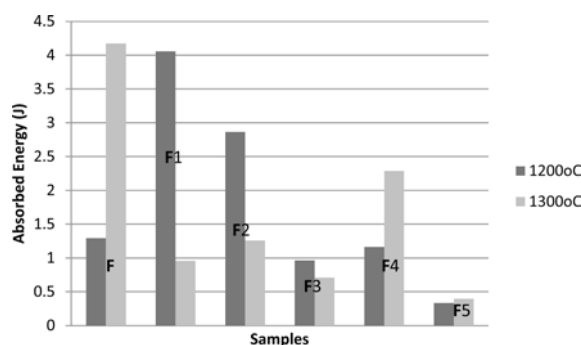


Fig. 6. Effects of sintering temperatures on the absorbed energy of the samples.

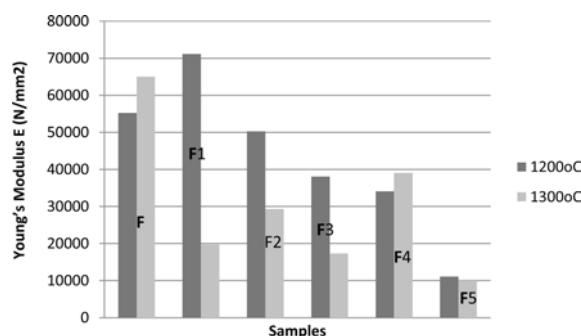


Fig. 7. Effects of sintering temperatures on the Young's modulus of the samples.

energy of the sample increased to 4.0575 J when the niobium content was increased to 2% (F1) at the same sintering temperature. Furthermore, increasing the amount of niobium oxide of the sample to 4% (F2), the absorbed energy of the sample is observed to reduced to 2.8648 J. Further reduction is observed in the absorbed energy of the sample to 0.9631 J when the niobium oxide content was increased to 6% (F3). Moreover, slight increment is observed in the absorbed energy of the sample to 1.1623 J when the amount of niobium oxide content of the sample was increased to 8% (F4) at the same sintering temperature of 1200°C. Any more increase in the niobium oxide content to 10% (F5) leads to the absorbed energy being reduced to its minimum of 0.3349 J.

However, at the sintering temperature of 1300 °C the absorbed energy of the sample F is observed to be increase from 1.2921 J at 1200 °C to 4.1753 J. Increasing the niobium oxide content to 2% (F1) at 1300 °C, it was observed that the absorbed energy of the sample sharply reduced to 0.9567 J. Further increase in the niobium oxide content to 4% (F2) it is observed that the absorbed energy of the sample increased to 1.2604 J. Further reduction in the absorbed energy of the sample to 0.7104 J is recorded when the amount of niobium oxide content was increased to 6% (F3) at the same temperature. Moreover, increasing the niobium oxide content to 8% (F4), it is observed that the absorbed energy of the sample increased to 2.2875 J. Any

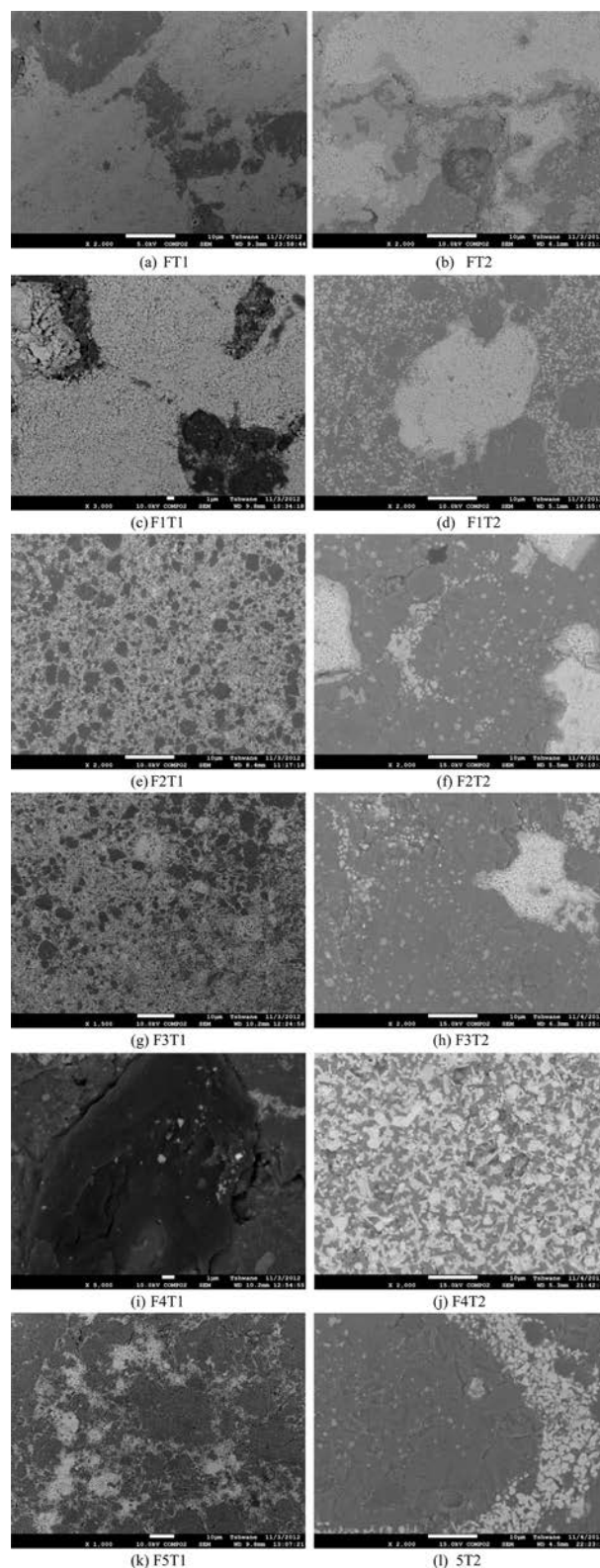


Fig. 8. SEM images of the sintered ceramic composites samples. (a) FT1, (b) FT2, (c) F1T1, (d) F1T2, (e) F2T1, (f) F2T2, (g) F3T1, (h) F3T2, (i) F4T1, (j) F4T2, (k) F5T1 and (l) F5T2.

further increase in the niobium oxide content to 10% (F5) leads to the absorbed energy being reduced to 0.3944 J.

Young's modulus of elasticity (YME)

Fig. 7 and Table 4 show the effect of sintering temperature and niobium oxide additives on the Young's modulus of elasticity (YME) of the samples. From the figure, it is observed that at 1200°C, the YME of the sample F was 55208 N/mm², increasing the amount of niobium oxide content to 2% (F1), it

observed that the YME of the sample increased to 71096 N/mm², any further increase in the niobium oxide content leads to progressive reduction in the value of the YME for the various sample. However, increasing the sintering temperature of the sample to 1300°C the YME of the sample F is observed to increase from its value at 1200°C to 64994 N/mm². Further increase in the amount of the niobium oxide content could be broadly sum to lead to reduction in the YME values of the various samples.

Conclusions

At 1200°C the presence of niobium oxide in the samples favours the decomposition of zircon to silica phases and zirconia. The combined effects of increased sintering temperature to 1300°C and addition of niobium oxide favour the formation of more sillimanite in preference to mullite. At 1200°C niobium oxide additive inhibits the mullitization process in preference for the formation of aluminum niobate and iron (II) niobate. Niobium oxide inhibits the formation of mullite in preference to the formation of aluminum niobate and sillimanite. It also favours decomposition of zircon to the silica phases and zirconia. It could be broadly summarized that increase in the niobium oxide content lead to increased bulk density at 1300°C. The sample with optimum physico-mechanical properties is considered to be sample FT2 with 10% ZrO₂, 0% Nb₂O₅, 90% clay and sintered at 1300°C held at the sintering temperature for 60 minutes.

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