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Effect of sintering temperature on the microstructure and properties of dense(TiO_2) ceramics

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اللهم لك الفضل والمنّة والحمد على الفضل والنعمة، لقد وفقني الله تعالى لأن أقوم بالبحث والدراسة في مجال

Effect of sintering temperature on the microstructure and properties of dense(Tio2) ceramics

بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

“بلَ ْ هُوَ آيَاتٌ بيّنَاتٌ فِّي صُدُورِ الَّذِّينَ أُوتوُا الْعِّلْمَ” ﴿٤٩ العنكبوت﴾

صدق الله العلي العظيم

Supervisor Certification

I certify that this thesis entitled "Preparation of Ceramic oxides from Natural Sources " had been carried out under my supervision at the University of Babylon/ College of Material's Engineering/ Department of ceramic and buildings materials as a Part of Requirements Achieve graduate Degree in Materials Engineering / Department of Ceramic and Building Materials Engineering.

Signature: Assist.Prof. Dr. Israa khahtan Sabree

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Properties and applications	Properties and applications	

Abstract

In the process of producing of TiO2 ceramics, there are important parameters that can influence the ceramic properties of TiO2, namely the sintering temperature. The sintering temperature can have an effect on the level of density and strength of TiO2 ceramics and changes in the TiO2 crystal structure. TheTiO2 ceramics are said to have crystal structures at low temperatures and crystal structures at high temperatures. The application of TiO2 ceramics is very broad, and is very dependent on the crystal structure. The purpose of this paper is to investigate the effect of sintering temperatures on density, porosity, hardness, compressive strength and crystal structure of TiO2.

Titanium dioxide powder has been compacted to form green samples which sintered with variation of temperature of 800 ^{o}C, and 1000 ^{o}C. The characterization of sintered samples includes measurement of density, porosity, hardness, compressive strength and XRD. The results show that the sintered 800 ^{o} C sample has the smallest density of 2.66 g/cu.cm and the largest porosity 40.5 % and hardness 38.8 Hv. For the sintered 1000o C sample has greatest density 3.4 g/cu.cm and smallest porosity of 30.4% and hardness 3.48 Hv.

Chapter one

1-1 Introduction

Titanium dioxide (TiO_2) has good chemical stability and Is widely used in aerospace, aerospace and marine applications. Titanium dioxide [titanium(IV) oxide or titania] has a molecular formula TiO2 with 79.87 as molecular weight. TiO2, a non-toxic material, chemically stable, biocompatible and strong oxidizing agent (with large surface area) has very high photocatalytic activity. It is an inexpensive material with high dielectric constant and low production cost. people's needs for TiO2 In medical, sports and clothing are also increasing. There are three crystal forms of TiO2, namely: Rutile, Anatase, and Brookite. Among them, the plate titanium type is very unstable in nature, so it Is rare in nature. At present, rutile and anatase are the main research objects and applications. Among the three crystal forms, rutile Is a thermodynamically stable phase, while anatase Is a metastable phase, and the phase transition of anatase to rutile (A→R phase transition) Is an Irreversible phase transition process .

Both the rutile and anatase types belong to the cubic system. The unit cell parameters are: anatase type a=3.7852Å, c=9.5139Å; rutile type a=4.58Å, c=2.95Å. Under normal conditions, the temperature at whichh pure anatase titanium dioxide Is converted to rutile titanium dioxide is 610 to 915°C . In order to completely convert anatase titanium dioxide Into rutile titanium dioxide, the calcination temperature Is preferably higher than 1000°C . In the process of grain growth, the order of occurrence of different crystal faces Is different, and the activity of each crystal face Is different. Some researchers have studied the titanium dioxide dominated by anatase (001) crystal plane , a lot of research has been done by scholars at home and abroad on the phase transition of titanium dioxide.

Sintering of nanostructured TiO2 ceramics has been paid on dielectric properties of nanostructured bulk TiO2 ceramics .It is well known that the properties of electroceramics are affected by their microstructural features (such as grain size, porosity, secondary phases) and defect structure (such as point and electronic defects). So Phase transition and microstructural development of sintered samples were important to study the resultant properties and applications.

Chapter two

2-1 Introduction

Nowadays, nano-structured materials are an important area of research owing to their several unique characteristic features. Among all the transition metal oxides, TiO_2 nano-structures are the most attractive materials in modern science and technology. TiO_2 has been widely used commercially in doughnuts,

cosmetics, pigments, catalysts, sunscreens,solar cells,water splitting etc. TiO_2 is being used in plastics, paints, varnishes, papers, medicines, inks, medications, toothpaste, food products, and industries.In 1972 first of all, Fujishima and Honda reported photo-assisted water splitting under UV light on a TiO_2 photo anode as a semiconductor.The diverse claims can be separated into “environmental” and “energy” groups, several of which depend on the TiO_2 properties itself as well as on the changes of the TiO_2 material host (e.g. with organic and inorganic dyes). In previous years, the research activity expansion has been observed in nanotechnology and nanoscience. On the modification, preparation and properties of nano-materials, a signifcant amount of research, reports and reviews have been published recently to know and pr´ecis the progress in this field. TiO_2 nanostructures in various forms, among the unique characteristics of nanomaterials, are gaining broader applications due to their sizerelated characteristics. For nanometer scale TiO_2 the energy band structure becomes discrete due to its surface, photochemical and photo physical properties. Consequently, several works have focused on nano crystalline TiO_2 syntheses with a high surface area. As a photocatalyst,TiO_2 nanostructures have drawn much attention and are projected to show a signifcant role in serving to resolve several pollution and environmental problems. Thus, using TiO_2 for H_2 production and photo-assisted water splitting devices offers a way for hygienic and low price production of hydrogen by solar energy.

recent investigation and the development efforts, which tack energy and environmental challenges in consideration. Besides, the crystal structure, optical, electrical/electronic and adsorption, surface area, porosity properties of TiO_2 nanostructure are discussed. The procedures of preparations, fabrications (nanoparticles, nanorods, nanowires, and nanotubes), the conditions of syntheses and accountability for regulation of titanate nanostructures morphology are also discussed.

2-2 Properties of TiO_2 nanostructures

2-2 1 Crystal structure of TiO_2

TiO_2 crystal exists in three common polymorphs in nature i.e. brookite, anatase, rutile,and some few common structures of TiO_2 II i.e. columbite, TiO_2 III: baddeleyite,TiO_2 (R) (ramsdellite), TiO_2 (B) (monoclinic) and TiO_2 (H) (hollandite).

Rutile is the most thermodynamically constant among the different polymorphs structures. From 400 to 1200 C, it's critical temperature can vary which depends on the grain impurities and size. The optical and electrical properties and crystal structural of rutile, brookite and anatase are given in Table 1. These are discussed in the following paragraphs.

Rutile

In a tetragonal structure, with 6 atoms per unit cell (Fig. 1), rutile is the most stable having TiO_6 octahedron showing a slight orthorhombic distortion. Rutile phase is stable while at these conditions TiO_2 converts thermodynamically into auspicious phase. For unit sizes > 14 nm, rutile phase becomes more stable than anatase.Predominantly, the crystals of natural rutile exhibit (110) surface.This surface is the most stable stoichiometric rutile surface.In the unit cell of rutile, 4 oxygen atoms form a partial octahedron about Ti while 2 titanium atoms (at [0, 0, 0] and $\frac{1}{2}$; $\frac{1}{2}$; $\frac{1}{2}$) positions, separately are available. Distinctly, octahedron is linked to 10 near octahedra, out of which 2 parts an edge and eight share a bend with it. The octahedral edge shared are aligned along [001] direction as shows in Fig. 1.

Anatase

TiO_6 octahedron distortion is significantly large for anatase phase while TiO_2 has a tetragonal structure, hence, the symmetry of anatase is lower than orthorhombic (Fig. 1). The energy change between these 2 phases is minor closely (2 to 10 kJ mol^{1}).[71] At 0 K, the rutile phase is not more thermodynamically constant than anatase. The unit cells of anatase

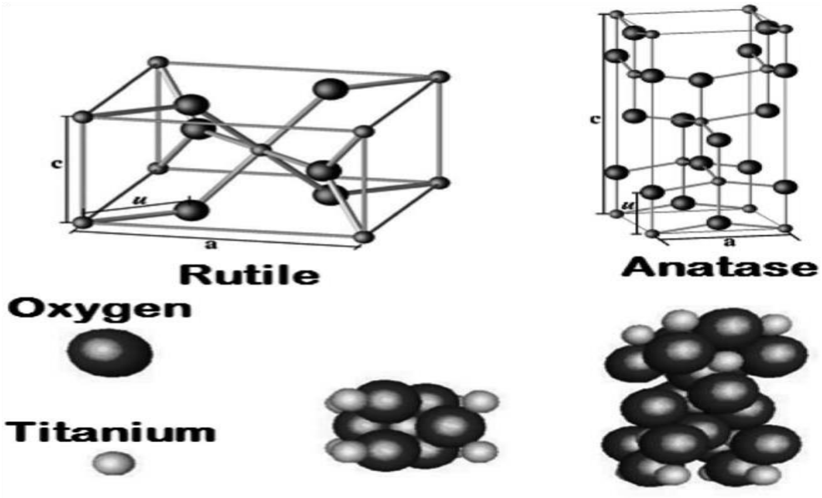
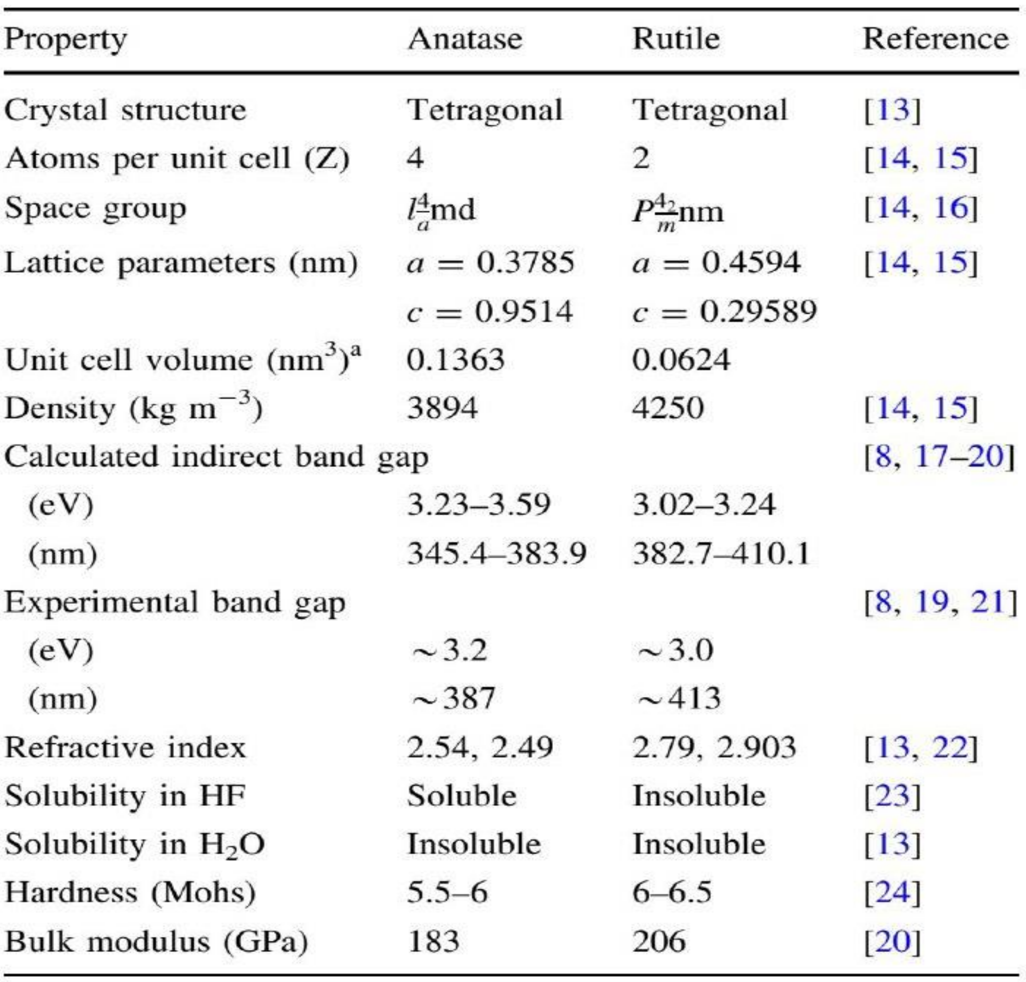


Fig. 1 Crystal structures of the rutile and anatase phases of TiO_2. Small spheres represent Ti atoms, large spheres represent oxygen atoms.

Table 1 Properties of anatase and rutile



Property	Anatase	Rutile	Reference
Crystal structure	Tetragonal	Tetragonal	[13]
Atoms per unit cell (Z)	4	2	[14, 15]
Space group	$I\frac{4}{a}md$	$P\frac{4_2}{m}nm$	[14, 16]
Lattice parameters (nm)	$a = 0.3785$	$a = 0.4594$	[14, 15]
	$c = 0.9514$	$c = 0.29589$	
Unit cell volume (nm^3)^a	0.1363	0.0624	
Density (kg m^{-3})	3894	4250	[14, 15]
Calculated indirect band gap			[8, 17–20]
(eV)	3.23–3.59	3.02–3.24	
(nm)	345.4–383.9	382.7–410.1	
Experimental band gap			[8, 19, 21]
(eV)	~3.2	~3.0	
(nm)	~387	~413	
Refractive index	2.54, 2.49	2.79, 2.903	[13, 22]
Solubility in HF	Soluble	Insoluble	[23]
Solubility in H_2O	Insoluble	Insoluble	[13]
Hardness (Mohs)	5.5–6	6–6.5	[24]
Bulk modulus (GPa)	183	206	[20]

2-3 Titania applications

The primary application of titanium dioxide is as a white pigment In paints, food colouring, cosmetics, toothpastes, polymers, and other Instances in which white colouration Is desired . The reason for this Is the high refractive Indices of rutile and anatase, which result In high reflectivity from the surfaces. Consequently, titanias of small particle size and correspondingly high surface areas are used owing to the resultant opacifying power and brightness. However, paints utilise polymeric binders to fix the pigment and, when In contact with titania, the polymer may oxidise when exposed to sunlight. This effect Is known as chalking and, In addition to the direct degrading effect of ultraviolet (UV) radiation, is accelerated by the photocatalytic activity of $TiO2$, whichh also is enhanced by the high surface area of this material .The potential for the application of the photocatalytic effect In $TiO2$ has attracted considerable interest over the last three decades. Titania photocatalysts are known to be applicable in a range of Important technological areas:

- Energy

Electrolysis of water to generate hydrogen . Dye-sensitised solar cells (DSSCs)

- Environment

Air purification

Water treatment

- Built Environment

Self-cleaning coatings Non-spotting glass

- Biomedicine

Self-sterilising coatings

Photocatalytic effect

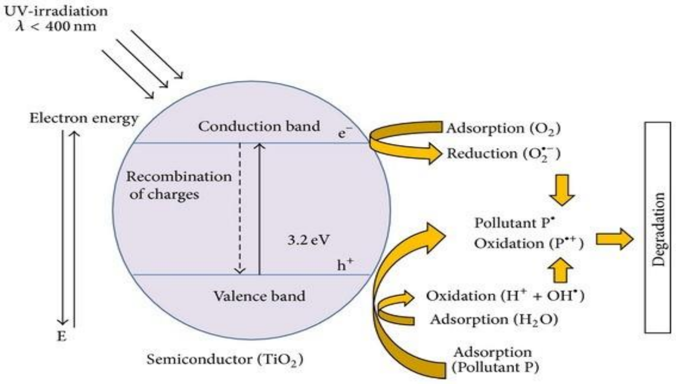
Photocatalysed reactions for applications such as those mentioned above are facilitated through the presence of adsorbedradicals(fromairor water)on theTiO2 surface. These radicals, whichh are atomic species with a free unpaired electron, are formed upon reaction of an adsorbed molecule (such as O2 or H2O) with a photo-generated charge carrier (from an electron–hole pair or exciton) when TiO2 is exposed to radiation exceeding its band gap;
This radiation normally Is in the UV wavelength region (290–380 nm). These electron–hole pairs are formed when an electron Is elevated from the valence to the conducting band, leaving behind an electron hole, .
The electrons In the conduction band facilitate reduction of electron acceptors and the holes facilitate oxidation of electron donors . Examples of the photo-generation of radicals in atmospheric and aqueous environments are given In the following reactions. Since the numbers of atoms per unit cell Is halved upon going from rutile to anatase, the lattice parameters and unit cell volumes must be viewed accordingly
The photoactivity of anatase and rutile have been high surface area, the same property that contributes to Its examined and Interpreted by Sclafani and Herrmann] optical properties. A high surface area leads to a higher with reference to the densities of surface-adsorbed species. Density of localised states, whichh involve electrons with

2-4 Mechanism of TiO2 as Photocatalysis

Photo-catalysis is the composing of photochemistry and catalysis with both light and a catalyst being desired to onset or precipitate a chemical conversion . The photo-catalytic process starts with the absorption of electromagnetic radiation, Which excites an electron from the valence band to the conduction band, leaving a hole in the valence band. (Fig. 2) Is a schematic representation of this process. In this process UV light Irradiation is used by photon energy equal to or greater than TIO2 band gap energy ($h\nu \geq 3.20$ eV at $\lambda \leq 380$ nm); electron-hole pairs (The charge carrier) are generated . The negatively charged electron moves from the valance band (VB) to the conduction band (CB) leaving behind the positively charged hole. Then, the electron and hole take part In reduction oxidation reactions with species that are adsorbed on the surface of TiO2, such as water, hydroxide

(OH-) ions, organic compounds or oxygen. The valence band hole (h+) is highly oxidizing while the conduction band electron (e-) is highly reducing . The charge carrier h+ oxidizes H2O or OH- ion to the hydroxyl radical (OH•) that is a highly potent, non-selective oxidant. It easily attacks pollutants adsorbed at the surface of titanium dioxide or in aqueous solution degrading them to H2O and CO2 . On the conduction band (CB) the electron reduces adsorbed oxygen (O2) species to superoxide (O2•), then undergoes a series of reactions to give the OH• radical. The reaction of these radicals with organic substance, environmental pollutants or harmful microorganisms results In the decomposition of the latter .

In a case where the above discussed processes do not occur, recombination of the charge carriers results and energy Is released in the form of heat. This causes great reduction in TiO2 photocatalysis efficiency . Electron-hole recombination is reaction competing with hole-donor and electron-acceptor electron-transfer reactions. Recombination can occur either in the semiconductor bulk or at the surface resulting in the release of heat (or light) and is detrimental for the photocatalytic activity as the redox properties of the semiconductor are quenched .



.Fig. 2. Principal photo-catalytic process in the TiO2 particles

The photocatalysis performances are affected by several parameters such as mass/concentration, light Intensity, wavelength, pH, and temperature, the nature of a photocatalyst, Particle Size, Surface area, the adsorption nature and concentration of the substrate . There are many fields of applications for TiO2 nanoparticles due to perfect properties included air purification, water purification, decontamination, antibacterial, tooth paste, UV protection, photocatalysis, sensing and paint application, (Fig. 3) shows many TiO2 applications

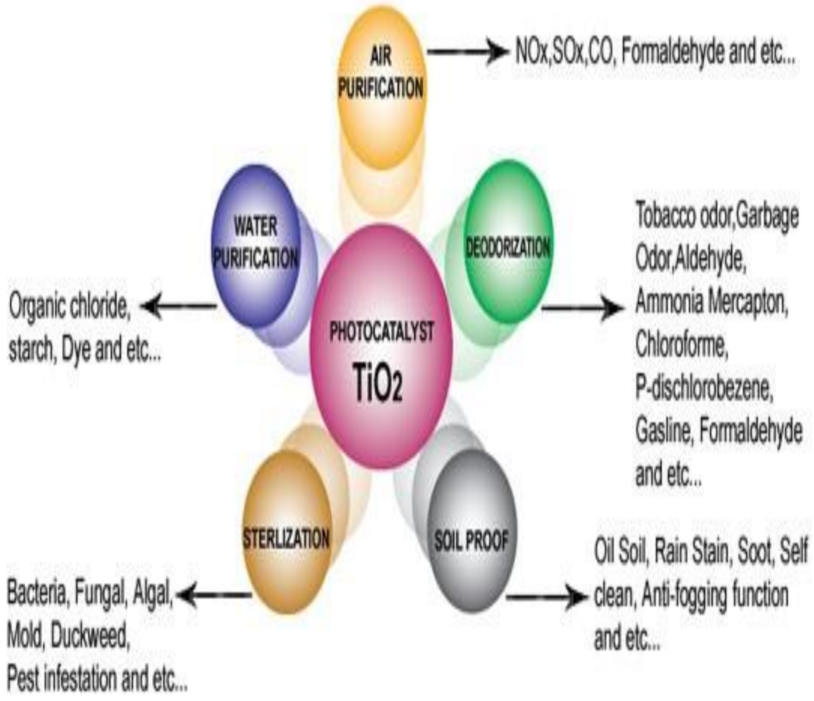


Fig. 3. Applications fields of TiO2 NPs

2-5 Effects of sintering temperature on the microstructure and dielectric properties of titanium dioxide ceramics

TiO2 has been widely studied with respect to synthesis of nanosized powders , thin film fabrication , and sintering of nanostructured TiO2 ceramics , little attention has been paid on dielectric properties of nanostructured bulk TiO2 ceramics. It is well known that the properties of electroceramics are affected by their microstructural features (such as grain size, porosity, secondary phases) and defect structure (such as point and electronic defects). the effect of sintering conditions on the microstructural development and dielectric properties of TiO2 ceramics for potential application is very impartment.

The sintering temperature can have an effect on the level of density and strength of TiO2 ceramics and changes in the TiO2 crystal structure. TheTiO2 ceramics are said to have crystal structures at low temperatures and crystal structures at high temperatures. The application of TiO2 ceramics is very broad, and is very dependent on the crystal structure. Therefore, recent research has focused on improving the mechanical properties of sintered TiO2 . Nowadays, little attention has been paid on dielectric properties of nano structured TiO2 ceramics. It is well known that the properties of electro ceramics are affected by their microstructural features (such as grain size, porosity, secondary phases) and defect structure (such as point and electronic defects)

Chapter three
Experimental Work

3-1 Raw Materials :

1. Powder of Titanium dioxide (TiO2)(China).supplied from laboratory of ceramic materials

2.The Binder material: Binder are substances that improve the mechanical strength of ceramic bodies, so they can pass through production steps. In many cases, binder addition to bodies are essential (without them some production processes would be impossible). The binder material used in this research is Polyvinyl alcohol (PVA).

3-2 Samples Preparation Method: -

1-The TiO2 powder was taken to the x-ray device to characterize their component and impurity.

2- .To produce the pressing samples, powders were mixed with PVA as a binder and put the mixture in a mold of a diameter (20mm) as shown in figure (2) than using hydrolytic press in load reach about (1Mpa) and remain under this load for time reach (2min) in order to distribution of load for all sample.

3- After that samples were dried in the oven at temperature about (100°c) for (24hr).

4- The samples were sintered in furnace at temperature about (800 and 1000°c) for period reach to (2hr).

Fig (1) mold shape

3-3 The laboratory Tests: -

3-3-1 Particle size analysis

The particle size for both used powders were characterized using Better size 2000 Laser particle size analyzer

3-3-2 Hardness Test

Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration. However, the term hardness may also refer to resistance of bending, scratching, abrasion or cutting. Vickers Micro hardness was measured according to ASTM standard C1327-90(1990), The type of device used for testing hardness in this research is Vickers hardness device as shown in figure (3) (HVS-1000 CHINA). Because of the bioglass is brittle ceramic material, the applied force is about 1.96N and used time reach to 15sec. hardness (Hv.) was calculated using equation:

$Hv=1.854(p/d2)$ ------------ (1).

Fig (2) Hardness device

3-3-3 The Compression Test

It is used to determine the behavior of materials under crushing loads. Compression strength for samples were tested using universal testing machine shown in figure (4), the cross head speed was 0.5 mm/min, the test was made according to ASTM standard C-773

Fig (3) compressive device

3-3-4-Porosity test:

Apparent porosity for the samples were tested according to ASTM (373-88) using Archimedes method according to the following procedure:

1 -Drying the test specimens to constant mass by heating in an oven at 100°c, followed by cooling in a desiccator then measure the dry mass D**.**

2-Immersing the specimens in a pan of distilled water and boiling them for 5h, tacking care that the specimens are covered with water at all time. Using setter pins or some similar device to separate the specimens from the bottom and sides of the pan and from each other. After 5h boiling, allowing the specimens to soak for an additional 24hrs.

3-After impregnation of the test specimen in water, then the suspended mass (S), was determined to the nearest 0.01g, while suspended in water.

4-After determination of the suspended mass, each specimen was blotted lightly with a moistened cotton cloth to remove all excess water from the surface. The saturated mass (M), was determine to the nearest 0.01g after rolling the specimen lightly on the wet cloth.

The apparent porosity, P, expresses as a percent as:

$P = \{(M - D)/V\} * 100$

Where $V = M - S$

Chapter Three

Results and Discussion

3-1 Porosity and Density Results

the variation of porosity and density for samples with sintering temperature were measured. The porosity are relatively high for standard sample as well as for composite sample the reason of that may belong to use low pressing load during sample production process.

Density and porosity are two material properties that influence each other, where if the porosity of a material is high, the density of the material will be lower but if the material has lower porosity it vice versa. Figure 1 and Figure 2 shows that the changes in density values is inversely proportional to the values of porosity. According Figure 1, the highest density value is achieved 3.46 g/cm3 at a sintering temperature of 1000°C with lower porosity value 30.4%.

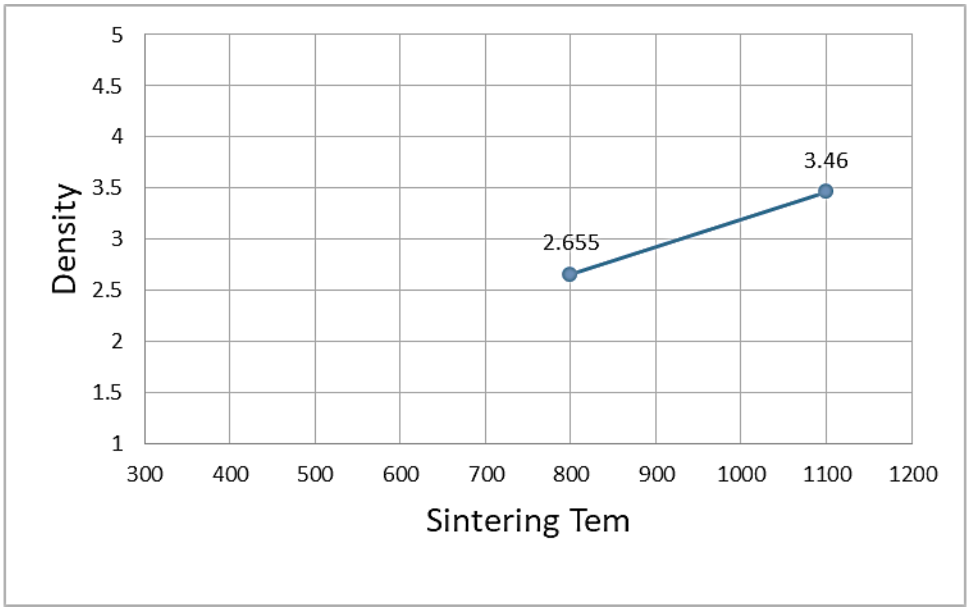


Fig (4) Variation the density with sintering temperature

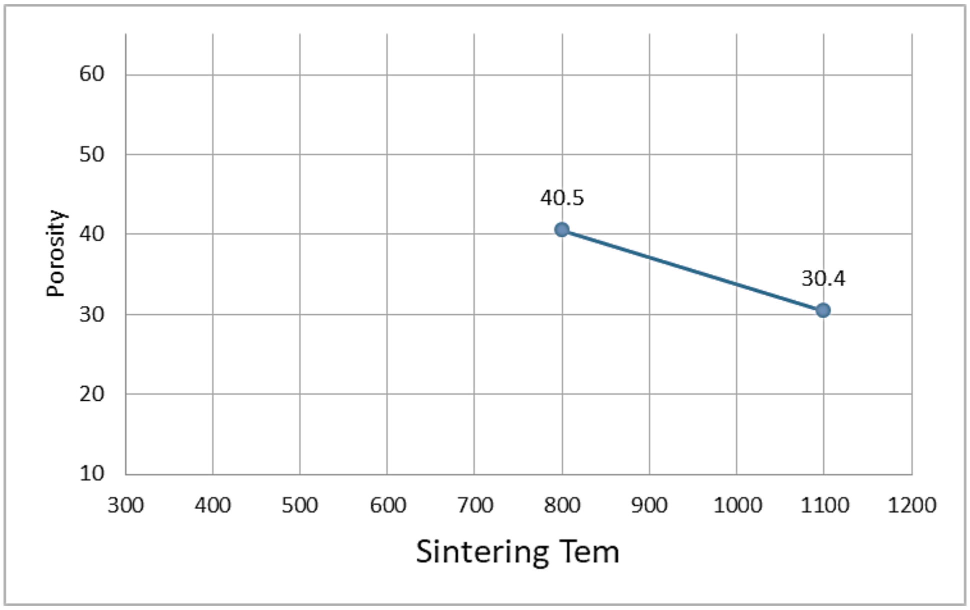


Fig (4) Variation the Porosity with sintering temperature

3-2 Mechanical Properties

3-2-1 Hardness

Figure (3) explain that the hardness increase with increasing sintering temperature. That give an indicator for improving the mechanical properties.

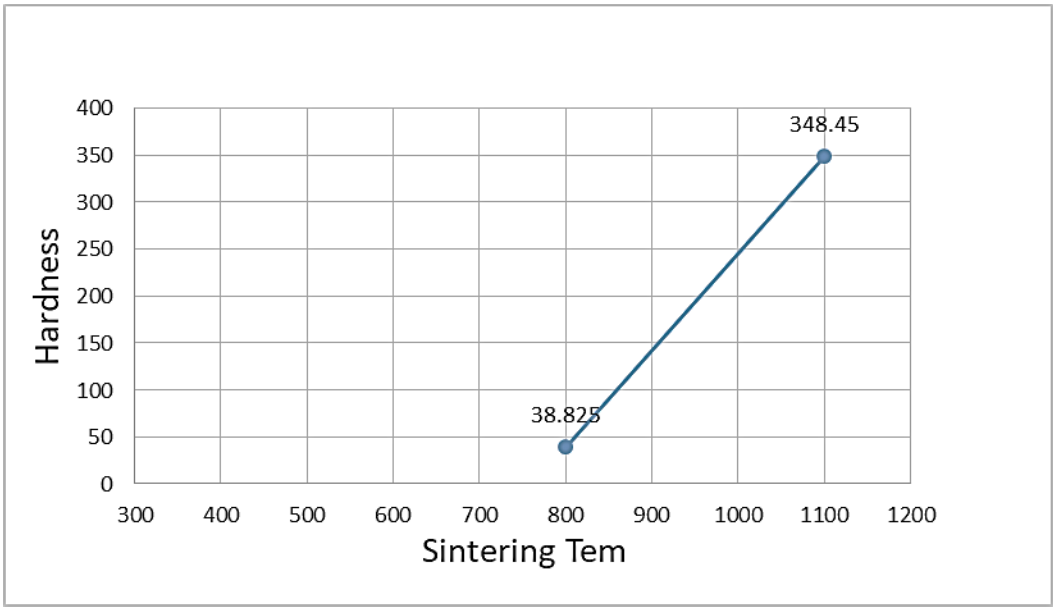


Fig (3) Variation the Hardness with sintering temperature

3-2-2 Compression test

Figure (4) showed increasing of compressive strength with increasing sintering temperature.. It can be observed that there is a significant improving in the mechanical properties due to a reduction in porosity and phase transformation.

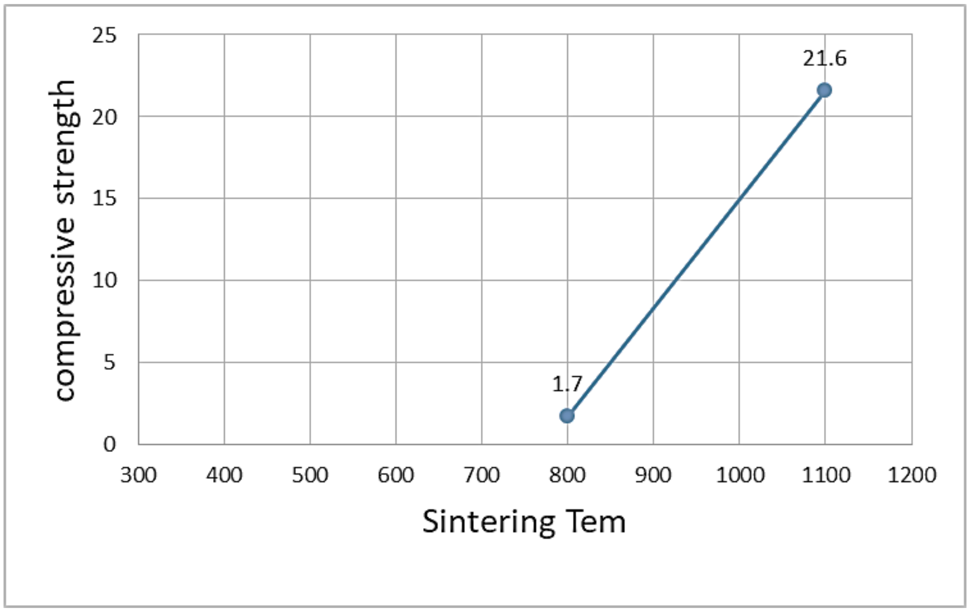


Fig (4) Variation the compressive strength with sintering temperature