Analysis of Physical Properties and Phase Transformation in TiO_2 due to Sintering Temperature Variation

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Abstract. Titanium oxide has a fairly high thermal stability, and the ability to be used repeatedly without losing its catalytic activity. It has formed using the sintering method with variation of sintering temperature. The pellet of Titanium Dioxide was pulverized using the HEM for 1 hour and continued with compacting to form a pellet with the Carver Press with 8 tons of force. Then the pellets are sintered using a furnace with temperature variations of 850°C,1000°C,1150°C and 1250°C. The characterization are density, porosity, XRD and hardness. The results showed that the 850°C sample had the smallest density with a value of 2.23 $gr/cm3$ and had the largest porosity around 14% and the smallest hardness value of 228 HV and indicated an anatase phase. The results of phase analysis with XRD indicate that phase changes occur from the anatase to the rutile phase while the temperature increases.

Keywords: Titanium dioxide, sintering, milling, density, porosity.

1 Introduction

Ceramic materials have characteristics that allow them to be used in a variety of applications. This is because ceramics have more advantages than metal as industrial materials, including non-corrosive, light, hard, strong, and stable at high temperatures [1]. The ceramics used as reference in the research are Titanium Dioxide, also known as titanium (IV) oxide or titania, which has various uses and can be found in many products, from paints to food to cosmetics [2]. Titanium oxide is known to be non-toxic (non-toxic), has a fairly high thermal stability, and the ability to be used repeatedly without losing its catalytic activity [3]. There have been many studies on the microstructure, physical properties of Titanium Dioxide with several methods including the sol-gel method, acid solution and others. However, research on testing the physical properties of Titanium Dioxide using High Energy Milling and the sintering process itself is still rarely carried out. Meanwhile, the physical properties of a material can be used to determine good ceramic quality [4]. Therefore, this research was conducted to make ceramics with raw materials Titanium Dioxide using High Energy Milling to obtain a powder with the same size and more homogeneous so that during the pellet formation or compaction process, the sample will be denser and complete combustionoccurs during the sintering process. During the sintering process, the temperature used is quite high ranging

SICBAS 2023, November 03, Palembang, Indonesia

DOI 10.4108/eai.3-11-2023.2347937

from 850°C to 1250°C. The temperature range used was also investigated not more than the melting point of titanium itself which is around 1800°C [5], so that the TiO_2 material does not change its physical, mechanical or chemical properties. Characterization using Titanium Dioxide material has the potential to know the physical properties contained in this material which include density, the number of voids (porosity) and the level of hardness. Where density, porosity andhardness can express the density of the TiO_2. material2 itself to find out whether the TiO_2 material will be easier to porous or not.

Further characterization using X-Ray Diffraction to identify crystal size, crystal structure. And XRD will display a description of the specific peaks and to determine the phase contained in TiO_2. ceramics. Regarding characterization X-Ray Diffraction. It is expected that there will be a phase change formed from the anatase phase to rutile due to the increase in the sintering temperature variation. So that the crystal structure can be analyzed along with what changes occur in the presence of different phases. Based on the description above, this study discusses the manufacture and characterization of Titanium Dioxide ceramics using High Energy Milling at various sintering temperatures of 850°C, 1000°C, 1150°C and 1250°C with the hope of being used as a reference in learning and getting better ceramic materials as needed.

2 Research methodology

Pure TiO_2 ceramic powder was used as raw material and the sample was milled by using the High Energy Milling for 1 hour and the mass ratio between the ball of milling and powder is 1:10. The sample is then separated from the ball mill by using a filter then weight the mass of powder. The fine powder was added a celluna binder (3 % of wt) , then compacted with the force of 8 tons to form of a pellet. The pellet of TiO_2 was sintered with a temperature variation of 850°C, 1000°C, 1150°C and 1250°C to find the characterization of its density, porosity, hardness and the phase changes if it's occur. The density was calculated using the equation [6]:

$$\rho = \frac{m}{V} \tag{1}$$

Where:

ρ = bulk density (gr/cm^3)
m = mass of sample (gr)
v = volume of sample (cm^3)

The measurement of porosity was conducted according Archimedes and calculated using equation [7]:

$$\varphi = \frac{m_W - m_O}{m_W - m_S} \times 100\% \tag{2}$$

Where:

φ = porosity (%)
m_W = mass of sample after soaking in the distilled water for 48 hours (g)

m_0 = mass of dried sample (g)

m_S = mass of sample hanging in water (g)

Then the sample that has been calculated for density and p orosity was tested for phase transformation by using XRD and analysis of XRD patterns were done by using match software. Then the hardness ofthe sample was measured by using Durometer with load 1000g. Average values of hardness were calculated from three times repetition for each samples.

3 Result and discussion

3.1 Density and porosity analysis

The samples in the form of pellets that have been sintered are then measured to determine the density and porosity values. This test is carried out to see the density of a sample.

The method used in the density test is to use the ratio between the mass to the volume of Titanium Dioxide as in equation (2.1) while the porosity uses the Archimedes method, as in equation (2.2). The sample used for characterization was initially 2.5 grams of each sample before being compacted. The resultsof the density and porosity measurements can be seen in table 1.

Table 1. Results of measurements of density and porosity of TiO2

Temperature (°C)	$\boldsymbol{\rho}$ $(\boldsymbol{gr/cm^3})$	$\boldsymbol{\varphi}$ **(%)**
850	2,23	14
1000	2,35	16
1150	2,36	15
1250	2,37	5

Based on Table 1, it can be seen the effect of the sintering temperature on the density of the material, where there is an increase in the density value from a low temperature to a higher temperature. However, it is different proportional to the porosity value. Where there is a changes in the value of porosity as the sintering temperature increases and decline at the end temperature. The graph of changes in the density and porosity values of Titanium Dioxide is shown in Figure 1.

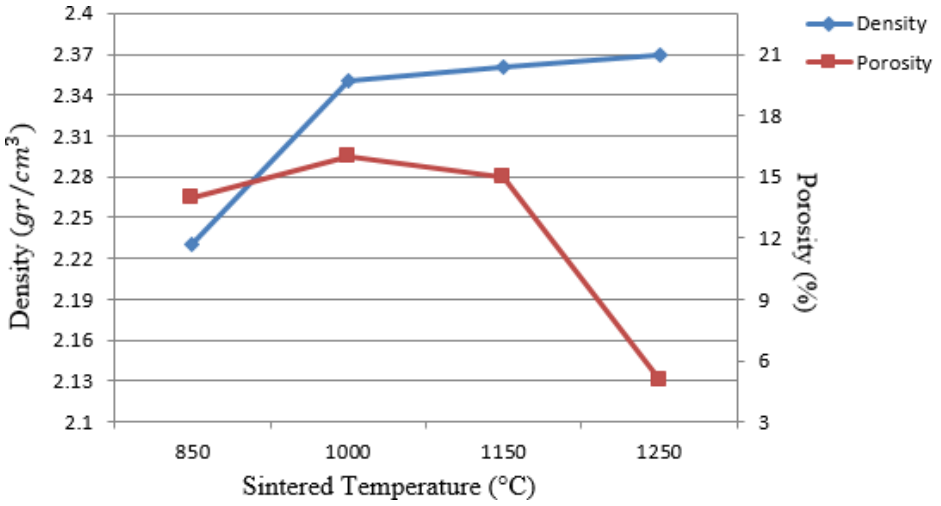

Fig 1. Graph of density and porosity of sintered TiO2

Figure 1 shows that the increase in sintering temperature is directly proportional to the density value and inversely proportional to the porosity. This triggers densification, where the grains on the ceramic are getting closer and the impurities in the TiO2 start. From the results of this study, it was found that the largest density value was at a temperature of 1250°C of 2.37 gr/cm3 while the theoretical density is 3.95 gr/cm3 before being treated [8]. Meanwhile, the porosity value is at a temperature of 1250°C at 5%. This value includes the size of the porosity value which is small compared to the porosity at the lower temperature. This porosity value is not much different from the research literature on the porosity of Titanium Dioxide due to the sintering temperature at 1250°C using the extrusion method. 3.5% [9]. Although at high temperatures small porosity is obtained, the other porosity values are still classified in a fairly high percentage, which means that there are still many pores in the pellet sample. The increase in the density value which is not too significant is caused, among others, by the mass of the sample itself. However, there was a decrease in mass after sintering. This is because the sample experienced shrinkage after the sintering process. Shrinkage is related tothe densification process that occurs and causes a decrease in volume and mass.

On the other hand, the samples that have undergone the sintering process become denser because the particle structure of the material unites and forms a unified mass. When the sintering temperatureis higher, the grains contained in the sample are denser and denser, resulting in smaller pores due to grain growth in the sintering process. In contrast to density, the porosity value obtained tends to fluctuate, where at a temperature of 1000°C the porosity value increases. Meanwhile, at 850°C and 1150°C to 1250°C the porosity decreased. This can indicate that at a temperature of 1000°C there may be gas trapped during the compaction process which causes empty space in the sample. So that at the time of sintering the trapped oxygen gas has not had time to come out. Then when the porosity characterization was carried out, when the sample was immersed in a fluid for 48 hours, the fluid entered the sample causing the saturated mass to be greater than the mass before immersion. Meanwhile, from 1150°C to 1250°C, the porosity decreased by a difference of 10%.

As for the porosity test, the sample was hung in the air to get the value and a sample immersed in a fluid suspended in air to obtain the value of each sample is treated differently, where the time tohang the sample varies. different. However, this does not affect the mass of the sample when it ishung. Because it hangs for a long time or a short time, the mass recorded on the balance remains the same. Unlike the case with the sintering process which causes compaction of the powder so that it affects the difference in mass and volume of each sample. When compared to when the mass of the sample is suspended in water, it is smaller than the mass of the sample when suspended in air. This is because the buoyancy force is greater than gravity so the object will be lighter in the water. Other factors that can affect the difference in density and porosity values include time milling which is used only 1 hour so that the titanium powder granules are not completely homogeneous which results in many cavities in the sample when compaction is carried out. In addition, the sintering temperature used is different. So the ceramics have not yet fully matured.

3.2 Hardness analysis

The sintered pellet samples were then measured to determine the hardness value of the material usinga Shore A Durometer. The results of the hardness test can be seen in table 2 .

Table 2. Results of measurements of Hardness Vickers of TiO2

Temperature (°C)	Hardness Vickers (HV)
850	228
1000	241
1150	276
1250	309

Based on Table 2, it can be seen that the effect of sintering temperature to test hardness where the higher the sintering temperature, the greater the hardness value and vice versa. The graph of thechange in the hardness value of Titanium Dioxide is shown in Figure 2 which shows that as the sintering temperature increases, the hardness of the ceramic material increases. This shows that the increase in sintering temperature is directly proportional to the hardness value of the material. This canbe seen from the graph which tends to be linear. At a sintering temperature of 1250°C, it has the highest hardness value than the other temperatures. The increase in hardness values is also related to density and porosity. This shows that at high temperatures, the combustion process occurs well which results in greater material density with good density and a low percentage of porosity. That is, with low porosity, the cavities in the sample are also decreasing, so that compaction and shrinkage occur which causes the sample to be denser and firmer.

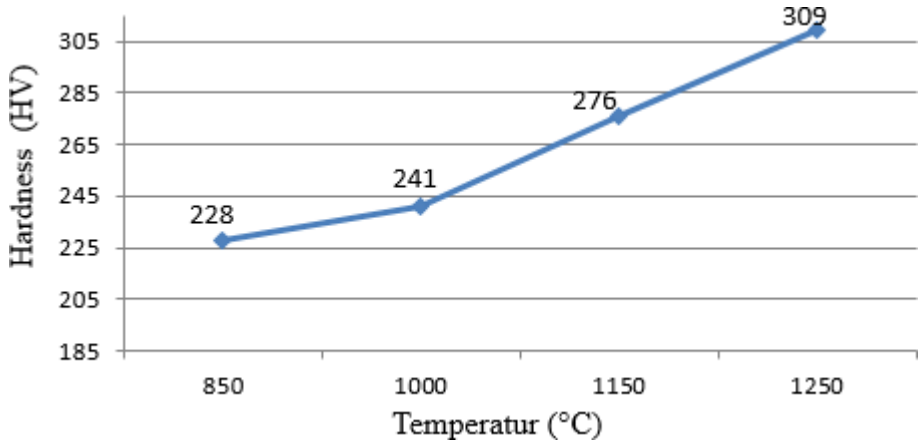

Fig 2. Graph of Sintering Temperature Variation on Hardness Test Hardness

3.3 XRD analysis

In this research, the crystal structure and phase test of Titanium Dioxide ceramic material has been successfully carried out using X-ray Diffraction (XRD) analysis. This XRD analysis uses an X-ray of 40 kV, 30 mA and a CuKa wavelength of 1.541862. To find out the size of the crystal, the type of crystal and the phase of the material, we can use the match application which will bring up specific peaks along with their Miller index. As for the working system, the sample that wants to know the crystal structure and phase analysis will be shot with X-rays at a range angle 10°-90°. X-rays that hit the sample will be diffracted by the atoms that make up the sample and will produce a certain diffraction pattern. Following are the results of the X-ray diffraction test on Titanium Dioxide samples at various sintering temperatures. For this reason, the phase change in Titanium Dioxide can be seen in table 3.

Table 3. Effect of sintering temperature on phase change of Titanium Dioxide

Temperature (°C)	Phase	FWHM (deg)	2θ	Crystal Size (Å)
850	Anatase	0,348	25.26	244
1000	Rutil	0,324	27.40	263
1150	Rutil	0,322	27,40	265
1250	Rutil	0,317	27,41	270

3.3.1 Anatase phase

Through Table 3, we can see that during the XRD process, there was phase changes occurred. Whereasat lower temperature such as 850°C has the anatase phase. While the others are rutile dominantly. it can be seen that the phase formed is an anatase phase with a tetragonal crystal type. Where from figure 3, there are 12 diffraction peaks with almost the

same pattern with the highest peak at an angle of 25° and the crystal size is not much different. The highest peak at 850°C is at an angle 25.264° with a crystal size of 244. The results of this XRD have similarities to several previous studies, including at a sintering temperature of 850°C, an anatase phase with tetragonal crystal types and peaks was produced at an angle of 25° [10].

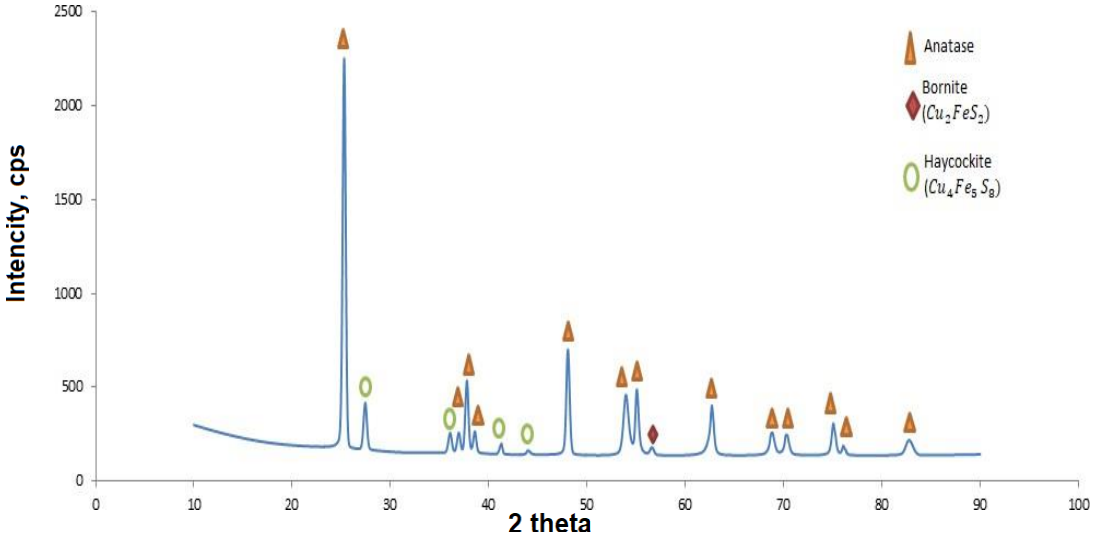

Fig 3. Graph of XRD TiO2 sintered at 850°C

3.3.2 Rutile phase

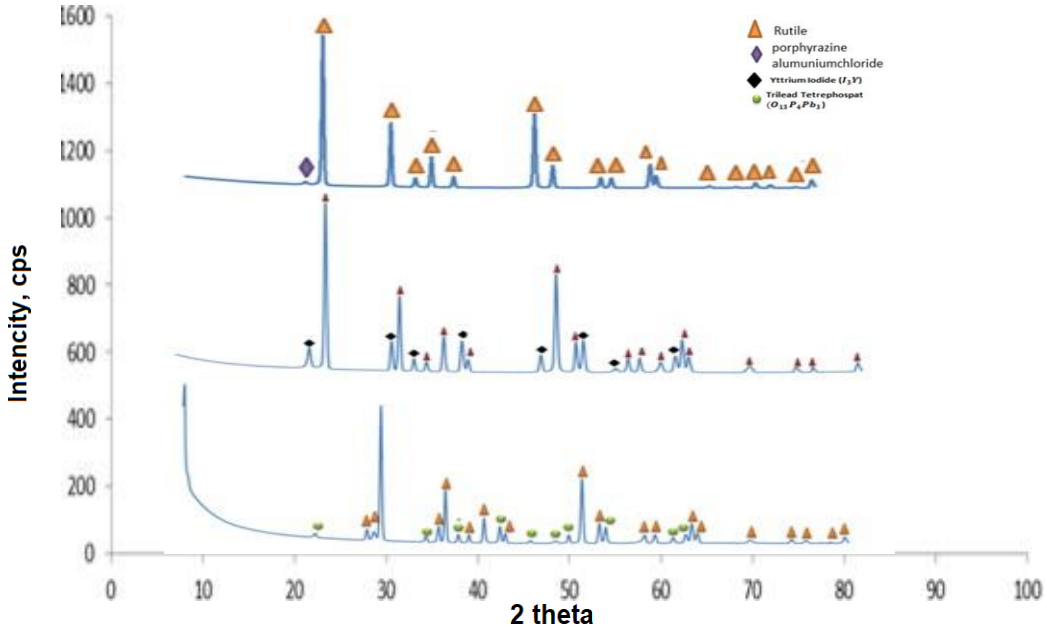

Fig 4. XRD Graph at temperatures 1000°C, 1150°C and 1250°C

Based on Figure 4, it is known that there is a phase change to rutile with a tetragonal crystal type. Inaddition, at temperatures from 1000°C to 1250°C, the resulting phase is the rutile phase. Thus, this is the same as the research that synthesized Titanium Dioxide using the sol-gel method at room temperature, that the rutile phase was formed from the heating process and the transformation of the anatase to rutile phase became complete when it reached a higher heating temperature [11].

The other phases that appear during characterization include the phase Bornite, Phorphyrazine Alumuniumchloride, Yttrium Iodide, etc. which can be caused by the impurity of the Titanium Dioxidematerial itself. In Titanium Dioxide other compositions cause the powderis not 100% pure made of Titanium Dioxide. The three graphs in Figure 4 have almost the same diffraction pattern with different number of diffraction peaks. At a sintering temperature of 1150°C it has a rutile phase and has 24 diffraction peaks. Where the diffraction peak produced at this temperature is more than at a sintering temperature of 1000°C. The sintering process causes crystal growth. This can be known by looking at the crystal size of each of the highest peaks. At a temperature of 1250°C the crystal size in the rutile phase was larger than at 1150°C and 1000°C. This is also related to the data on the width of the half-peak diffraction (FWHM), whereas the FWHM value decreases, the crystal size increases. So that with the increase in sintering temperature, the width of the diffraction peak is getting smaller and the crystal size is also increasing.

4 Conclusion

With the increase in sintering temperature, the density value increases and the hardness value increases. As for the porosity fluctuations that occur, at a temperature of 1000°C the porosity value increases. Meanwhile, at 850°C and 1150°C to 1250°C the porosity decreased. As the sintering temperature increases, a phase change occurs from anatase at a temperature of 850°C to rutile at a temperature of 1000°C to 1250°C. As for the crystal structure of anatase and rutile, it is known that the crystal types are tetragonal. The higher the sintering temperature, the width of the half-peak diffraction (FWHM) will be narrower and smaller while the crystal size will be larger.

Acknowledgements

This research was supported by supervisor of Sriwijaya University, technical staff XRD from Research Center of Physics

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