The synthesis of TiO_2 Nanoparticles Powder by Milling and Coprecipitation Mixed Method

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Abstract: Ilmenite type Fe_2O_3 waste (which is processed from natural iron sand) was processed into TiO_2 nanoparticles powder carried out by leaching with HCl and then using high-energy milling (HEM) for 50 hours. The characteristics of the powder such as particle size, size distribution and phases were analyzed using various techniques such as XRD, SEM, EDS and particle size analyzer. Synthesis and characterization of ilmenite type iron sand have been successfully made into TiO_2 by milling and coprecipitation mixed method. The purity level of TiO_2 was obtained by 85.01%. The particle size of TiO_2 was approximately 500 nm.

Keywords: high energy milling; milling coprecipitation method; titanium dioxide.

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I. INTRODUCTION

The main products of iron sand processing could be magnetite (Fe_3O_4/FeO.Fe_2O_3) hematite (Fe_2O_3) and ilmenite ($FeTiO_3$/FeO.TiO_2) [1]. Ilmenite type Fe_2O_3 waste (which is processed from natural iron sand) was processed into TiO_2 nanoparticles as one of the pigment raw materials, cosmetics, photocatalytic and if doped on barium hexaferite material it could increase its absorption to electromagnetic waves (radar) [2]. The ability of absorbing electromagnetic waves would increase if the particle size was in Nano order [3–6].

Some researchers used milling coprecipitation method to obtain great particle size and purity of TiO_2 nanoparticles. If the raw material was milled to 325 mesh then leached with HCl or H_2SO_4, the purity of TiO_2 was obtained 90% [7]. While roasting at 400°C with NaOH and double leaching TiO_2 purity obtained 49.2 wt%, using KOH the purity was 54.5 wt%. After 2 hours of roasting at 1000°C and double leaching with water and organic acids, purity of TiO_2 obtained 84 wt% [8]. After leaching and calcining the milled and annealed mixture of $FeTiO_3$/C under the optimal conditions, the TiO_2 nanoparticles with a size of 10-200 nm and purity >98.0% were obtained [9]. Other methods were used by researchers such as by using thermal plasma synthesis in a non-transferred arc thermal plasma reactor [10], electrochemical method [11], gel-sol method [12] can obtain 20-25 nm particle size.

In this paper, only processing ilmenite iron sand will be processed into TiO_2 nanoparticles powder carried out by leaching with HCl and then using high-energy milling (HEM) for 50 hours.

II. MATERIALS AND METHODS

The initial raw material of ilmenite type Fe_2O_3 waste comes from Cianjur iron sand. The initial preparation for the raw material begins with the process of milling iron sand for 10 hours. Milling iron sand powder is sieved using a 325 mesh sieving machine, so a homogeneous powder of up to 325 mesh pass size is obtained and continued with a magnetic separation process that obtained the dominant ilmenite phase as a source of TiO_2 and reduced the impurity phase in raw materials such as iron (Fe), silicon (Si), aluminum (Al), and magnesium (Mg).

In this leaching process, a technical HCl solution was used with a concentration of 32%. The acquisition of TiO_2 by leaching HCl begins by mixing the sand powder with strong magnetic separation with hydrochloric acid in a beaker glass. Then the resulting TiO_2 deposits are washed, dried and milled using high-energy milling (HEM) for 50 hours. The characteristics of the powder such as particle size, size distribution and phases were analyzed using various techniques such as XRD (X-ray diffractometer), SEM (scanning electron microscope), and EDS (energy dispersive spectroscopy). The XRD equipment used by the Pan Analytical brand to determine the phases formed. X-ray anode uses is CuK_α (λ = 1.5406 Å) with a step size of 0.02. Quantitative analysis was performed using the general structure analysis system (GSAS) software [13]. Surface morphology uses SEM tools and elementary analysis using EDS tools from JEOL JED 350 brand.

III. RESULT AND DISCUSSION

In the leaching process, exothermic events occur because the reaction between iron sand and hydrochloric acid pro-

(a) Sample A (b) Sample B (c) Sample C

FIG. 1: Physical changes according to the precipitates formed. (a) Dark gray precipitate, (b) light gray precipitate, (c) beige precipitate.

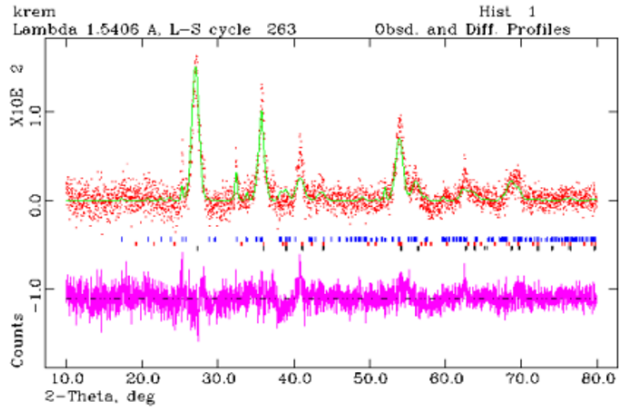


FIG. 2: Results of XRD pattern refinement of sample C with GSAS software.

duces heat to form a slurry. From the leaching process, three layers of sludge were obtained according to their specific gravity. The 3 layers of color formed on slurry which undergo a precipitation process were dark gray precipitate, light gray precipitate, and beige precipitate, respectively, shown in Fig. 1.

The lowest are dark gray (sample A), the middle are light gray (sample B), and the top are beige (sample C). The lowest are thought to still contain a lot of iron and are increasingly decreasing. So sample C is thought to have the largest titanium content.

Due to its light mass, TiO_2 is slightly soluble. The beige precipitate, which is slightly soluble, was characterized using XRD. The result of the XRD pattern of the sample in the form of powder already referred to with the Generalized Structure Analysis System (GSAS) software shown in Fig. 2.

The results of the qualitative analysis of sample C using the GSAS program showed that the sample consisting of a dominant phase was titanium dioxide with hexagonal crystal symmetry (space group P 42/ m n m) and two impurity phases. Qualitative and quantitative analysis refers to Open Database Crystallography with card numbers (COD: 180909), (COD: 1011033), and (COD: 180909) for the TiO_2, $FeTiO_3$, and Fe_2SiO_4 phases, respectively.

TABLE I: Analysis result using XRD and GSAS.

Phase	TiO_2	$FeTiO_3$	Fe_2SiO_4
Wt %	85.01	4.35	10.64

The full results of XRD characterization and structural parameter of refinement result can be seen in Table I and Table II, respectively.

Fig. 2 shows that the results of refinement of X-ray diffraction patterns have excellent fitting quality according to fit criteria (Rwp) and goodness of fit (χ^2) [13]. Rwp is the weight ratio of the difference between observation patterns and XRD calculations (ideal Rwp value $<$10%). Whereas χ^2 (chi-squared) is the ratio of XRD patterns observed that is proportional to expectations.

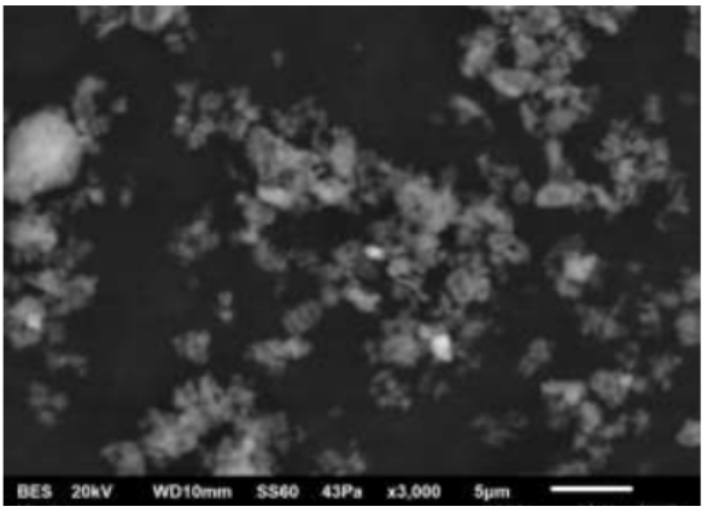
In Fig. 1, Table I and Table II show that based on the results of refinement of X-ray diffraction patterns of sample C, where sample C has three phases. The results of this refinement are also supported by observations of particle surface morphology for the two single phases using SEM as shown in Fig. 3. The result of elementary analysis uses SEM-EDS as shown in Fig. 3.

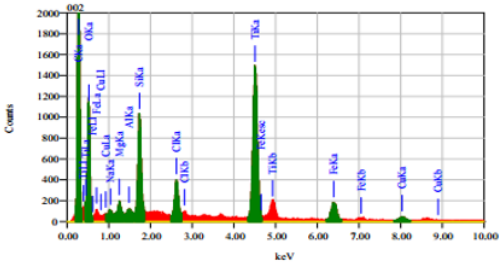
Fig. 3 shows that the particle morphology of sample C has excellent particle homogeneity and is almost uniform across the entire sample surface with polygonal particle shapes and particle sizes ranging from 500 nm. This means that the dominant phase is found in the sample. Based on the XRD analysis of the phase is the TiO_2 phase of 85.01%.

According to the results of the elementary analysis, it was shown that in sample C it has Ti elements that are in accordance with the XRD refinement results. The assumption of the reaction formed in sample C is as follows:

TABLE II: Structural parameter of refinement result.

Phase	Parameter
TiO_2 Rutile phase	Crystal structure: Tetragonal
	(space group) : P 42/m n m
	Lattice parameters: a = b = 4.5937$\mathring{A}$, c = 2.9581$\mathring{A}$, $\alpha = \beta = \gamma = 90°$
$FeTiO_3$ phase	Crystal structure: Rhombohedral
	(space group) : R -3
	Lattice parameters: a = b = c = 5.5200$\mathring{A}$, $\alpha = \beta = \gamma = 54.830°$
Fe_2SiO_4 phase	Crystal structure: Orthorombic
	(space group) : P b n m
	Lattice parameters: a = 4.7390$\mathring{A}$, b = 9.8990$\mathring{A}$, c = 5.9790$\mathring{A}$, $\alpha = \beta = \gamma = 90°$





ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.1657

Element	(keV)	Mass%	Error%	Atom%
C K	0.277	46.35	0.03	60.56
O K	0.525	31.87	0.21	31.26
Na K*	1.041	0.33	0.07	0.23
Mg K	1.253	0.52	0.05	0.33
Al K*	1.486	0.15	0.04	0.09
Si K	1.739	3.35	0.04	1.87
Cl K	2.621	1.43	0.04	0.63
Ti K	4.508	12.16	0.07	3.98
Fe K	6.398	2.78	0.13	0.78
Cu K*	8.040	1.05	0.28	0.26
Total		100.00		100.00

FIG. 3: Result of SEM-EDS analysis of Sample C.

$$\text{ilmenite type of iron sand} \rightarrow FeTiO_3 + Fe_2O_3 + Fe_{2.18}Ti_{0.42}O_3 + SiO_2 \quad (1)$$

$$FeTiO_3 + Fe_2O_3 + Fe_{2.18}Ti_{0.42}O_3 + SiO_2 + HCl \rightarrow FeTiO_3 + Fe_2SiO_4 + TiO_2 \quad (2)$$

Synthesis and characterization of ilmenite type iron sand have been successfully made into TiO_2 by milling coprecipitation method. The purity level of TiO_2 was obtained 85.01%. The particle size of TiO_2 was approximately 500 nm. morphology has good particle homogeneity and is almost uniform across the entire sample surface with polygonal particle shapes and particle sizes approximately 500 nm.

IV. SUMMARY

The synthesis of TiO_2 nanoparticles powder by milling and co-precipitation mixed method has been successfully carried out. The results of refinement of the X-ray diffraction pattern of the best-synthesized sample showed that the sample had a dominant phase, namely the TiO_2 phase of 85.01%. Particle

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