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Mineralogical Characterizations of Langkawi Ilmenite Ore for Carbothermal Reduction

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ABSTRACT

The mineralogical characterizations of Langkawi's ilmenite were investigated using XRD, XRF and SEM/EDS for morphological analysis. The minerals mainly consist of the phases of $FeTiO_3$, Fe_3O_4 and TiO_2 by Rietveld refinement, which indicated that the ore contains 35.85% of TiO_2 and 26.52% of Fe_3O_4. The amount of the elements calculated from the quantitative and XRF analysis are reliable and in acceptable ranges. The morphology of the ore shows that the ore is formed mainly in sub-rounded grains with titanium and iron as the main elements. The ore is categorized as a low-grade ore, but it can be upgraded for TiO_2 production using carbothermal reduction reactions, where the results of XRD, XRF, SEM showed an extractable amount of TiO_2 more than 32wt%.

Keywords: Ilmenite Ore, Titanium Dioxide, Chemical Composition, Phase and Structure analysis

1. INTRODUCTION

Pantai Pasir Hitam is a black sand beach located in Langkawi Island in Kedah. The name of the beach comes from the color of its sand. The sand is black in color due to the high content of black minerals. Rutile, hematite, ilmenite, monazite, and magnetite are the minerals associated with Langkawi black sand [1]. These minerals were formed by the erosion and weathering of nearby granite in mount Raya. Titanium naturally exists in form of rocks or sands as in ilmenite ore ($FeTiO_3$) or even rutile, anatase, and brookite, where they all have the same formula (TiO_2) with different crystalline structure [2]. High grade ores such as rutile are comparatively rare [3]. The available deposits are formed in association with large amounts of oxides such magnetite (Fe_3O_4) or hematite (Fe_2O_3), vastly in beach sand deposits due to natural processes like erosion and concentration. More than half of the world's titanium mineral production is generated from placer deposits of ilmenite and rutile, which is accountable for almost 50% of worldwide whitening pigment productions. Shoreline placer deposits provide ilmenite of higher TiO_2 content compared to magnetic deposits, which provide ilmenite with up to 40% of TiO_2 content [4]. Langkawi black sand consists of quartz and black minerals [5].

Rutile consists of TiO_2 (90% - 98%) with a small amount of iron oxide, while commercial ilmenite contains 40% - 60% titanium oxide with oxides of iron as the main impurities. Fe_2O_3 and

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secondary TiO_2 in the ilmenite ore are formed due to geological weathering and leaching of ilmenite. Ilmenite ore also contains oxides of Si, Al, Ca, Mg, Mn, Cr, and other possible impurities. Oxides concentration of ilmenite depends on the minerals forming conditions. Normally, rutile is used directly for titanium production [6]. However, ilmenite ores must be upgraded into synthetic rutile or TiO_2-rich slags for further processing to produce titanium products. Historically, natural rutile is used for high Ti concentrations, but it has been exhausted due to high demand [7].

Generally, TiO_2 recovery methods involve thermal treatments, chemical extractions, or a combination of these two methods. Sulfate and chloride are the two main hydrometallurgy extraction processes used to produce titanium dioxide. Both methods have their own requirements. The widely known sulfate process use ilmenite as raw material, which is disadvantageous due to large volume of waste. On the other hand, chloride process utilizes rutile as feedstocks, which is more convenient due to economic and environmental concerns [8]. Besides rutile, reduced or nitrided ilmenite can also be used in chloride process [9][10].

Almost 60% of TiO_2 production is produced by chloride process, which make Ti-rich slags or synthetic rutile are needed now more than ever. The limitations of chloride process are the high chlorination temperature and recycling of ferric chloride [11]. Ilmenite might requires a combination of both methods, due to high content of impurities such as quartz, Mg and Mn oxides [12]. Thermal treatments such as carbothermal reduction can upgrade ilmenite to synthetic rutile, reduced ilmenite, nitrided ilmenite or a Ti-rich slag, which lead to progressive removal of Fe with other impurities remaining [13]–[15]. High temperature carbothermal reduction methods increase TiO_2 concentration of the ilmenite ore by upgrading low-grade menials to above 80% of TiO_2 or converting it to carburized or nitrided ilmenite [2], [16]–[18]. Then, remaining impurities and Fe are removed by leaching process [18][19]. This makes ilmenite more efficient resource for TiO_2 production. In some cases, the ilmenite of the black sands is concentrated beforehand by magnetic separation. Mineral characterizations are significant to identify the minerals before any extraction process. But there are no records of Langkawi ilmenite ore characterization, except some studies on Langkawi black sand identification [1][19]. Thus, the aim of this study is to characterize Langkawi ilmenite ore, for TiO_2 extraction by carbothermal reduction reactions. In this study, the qualitative and quantitative approach of characterizations will be used to analyze Langkawi ilmenite ore. Scanning electron microscope (SEM/EDS) and X-ray diffraction (XRD) are used to identify unknown mineral concentrations.

2. MATERIAL AND METHODS

2.1 Materials

The ilmenite ore used in this study was collected from Pantai Pasir Hitam, Langkawi Island in Kedah State, Malaysia. The ore was cleaned then dried at 100 °C in an oven for 24 hours. Magnetic separation process used to remove non-magnetic minerals such as quartz. Finally, the ore was ground and sieved into 63 μm size for characterization samples preparation.

2.2 Methods

X-ray diffractometry (XRD) is used to investigate the mineralogical phases for the representative sample of the ilmenite ore. This is performed using XRD model of Bruker D2 Phaser diffractometer with Cu Kα1 radiation and scanning rate of 1 s/step. The scanning range was 10° to 90° for 2Θ. XRD data is studied using X'Pert HighScore Plus - v3.0e (3.0.5) software for phase and Rietveld quantification analyses [20]. Rietveld refinement method is used for quantitative analysis of Langkawi ilmenite ore. Acquired X-ray spectra is analyzed by MAUD XRD Refinement Software. The initial raw data files of the phases are obtained from Crystallography Open Database, where it is compared to the standard International Centre for Diffraction Data (ICDD) database [21].

The ilmenite ore morphology is studied using scanning electron microscope (SEM) - Jeol JSM-6460LA [22]. EDS analyzer is used to investigate the elemental distribution in the ilmenite ore. The sample is mounted on carbon tape on the sample holder. Then it is coated with thin platinum layer in a vacuum evaporator for about 15 min before running the SEM analysis at 20kV and SEI signal.

The chemical composition of the Langkawi ilmenite ore sample was analyzed using Energy Dispersive X-ray Fluorescence (EDXRF) manufactured by ThermoFisher.

3. RESULTS AND DISCUSSION

3.1 Phases Analysis

The phase purity and crystallinity of Langkawi ilmenite ore were examined by XRD. Based on the XRD patterns shown in Figure 1, the ore have six main phases, which are Rutile TiO_2 (35.85%), Magnetite Fe_3O_4 (26.52%), Silicon Dioxide SiO_2 (16.46%), Ilmenite $FeTiO_3$ (11.76%), Aluminum oxide Al_2O_3 (5.83%) and Armalcolite $MgTi_2O_5$ (3.57%). $FeTiO_3$, TiO_2, and Fe_3O_4 are the main phases that were found in previous study conducted by N. Begum et al [1] and S. Rezan et al [23], where psuedorutile and ilmenite are the main phases of the ilmenite concentrates.

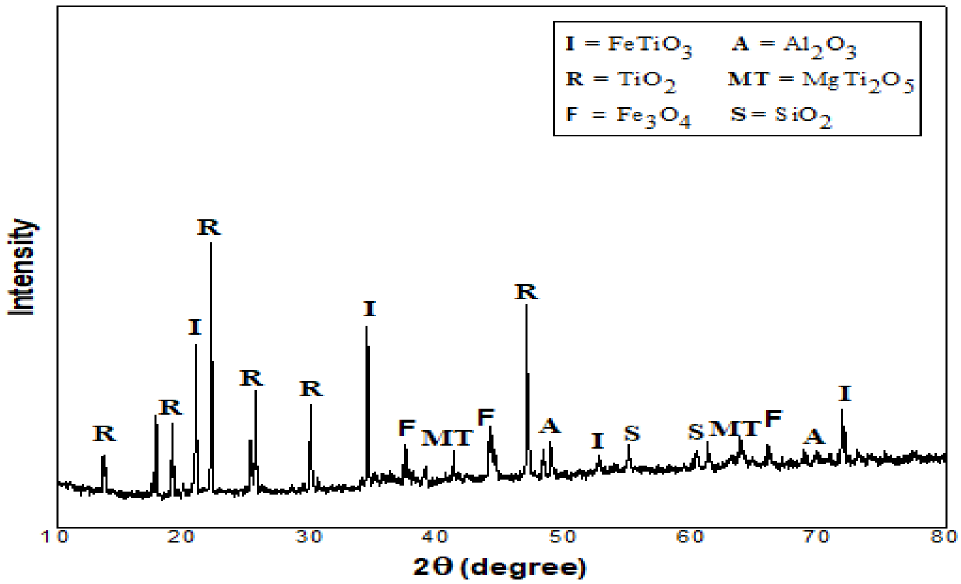

Figure 1. X-ray diffraction pattern of Langkawi ilmenite

This shows that TiO_2 has the highest concentration in Langkawi ilmenite mineral, which is quite similar to amounts shown by XRF analysis in Table 1. It shows that TiO_2 and Fe_3O_4 make most of Langkawi ilmenite ore accumulating of almost 60% of the mineral weight. These results are consistent with previous research using Langkawi's ilmenite ore for carbothermal reduction process [24]. The rest compositions are made of impurities and traces such as SiO_2 and MgO. The main peaks of $FeTiO_3$ (ilmenite) (ICDD# 01-080-1213), TiO_2 (Rutile) (ICDD# 01-072-7119) and Fe_3O_4 (magnetite) (ICDD# 01-079-0416) are obviously observed in the XRD patterns. The amount of second phases is associated to Al_2O_3 (ICDD# 01-074-4582), SiO_2 (cristobalite alpha) (ICDD# 01-077-8626) and $MgTi_2O_5$ (armalcolite) (ICDD# 01-076-2373). The crystal structure of the Langkawi ilmenite is orthorhombic with space group cmcm with lattice parameters a=3.7498 Å, b=9.8057 Å and c=10.0675 Å. The values precisely meet with standard data (ICDD# 01-080-1213).

Table 1 Oxide compounds of Langkawi ilmenite ore using XRF analysis

Compound	TiO_2	Fe_3O_4	SiO_2	Al_2O_3	MgO	CaO	Na_2O	Others
Concentrations (%)	32.33	26.54	21.42	15.88	1.39	0.46	0.45	1.53

3.2 Morphological Observation

SEM analyses of Langkawi ilmenite ore morphology are as shown in Figure 2. The figure shows SEM image of the ilmenite ore up to 100x magnification. It shows that the ilmenite mineral textures are large grains with smooth surface in the range of 50 – 63 µm, mainly having sub rounded shapes as shown in (spot 1), (spot 2) and (spot 3). There are some other shapes present as well, like flat and semi-rhombohedra morphology (spot 2). Titanium, iron and aluminum alongside with some traces of Mg and Mn and other elements are subsist in the ore as shown in ore's spectrum taken by EDS analysis of (spot 1), (spot 2) and (spot 3). These shiny grains like the one in (spot 2) shows high content amounts of metallic elements of Ti and Fe with w% of 31.38% and 28.89% respectively. The other elements will be separated or removed during the carbothermal reduction or processes such as leaching.

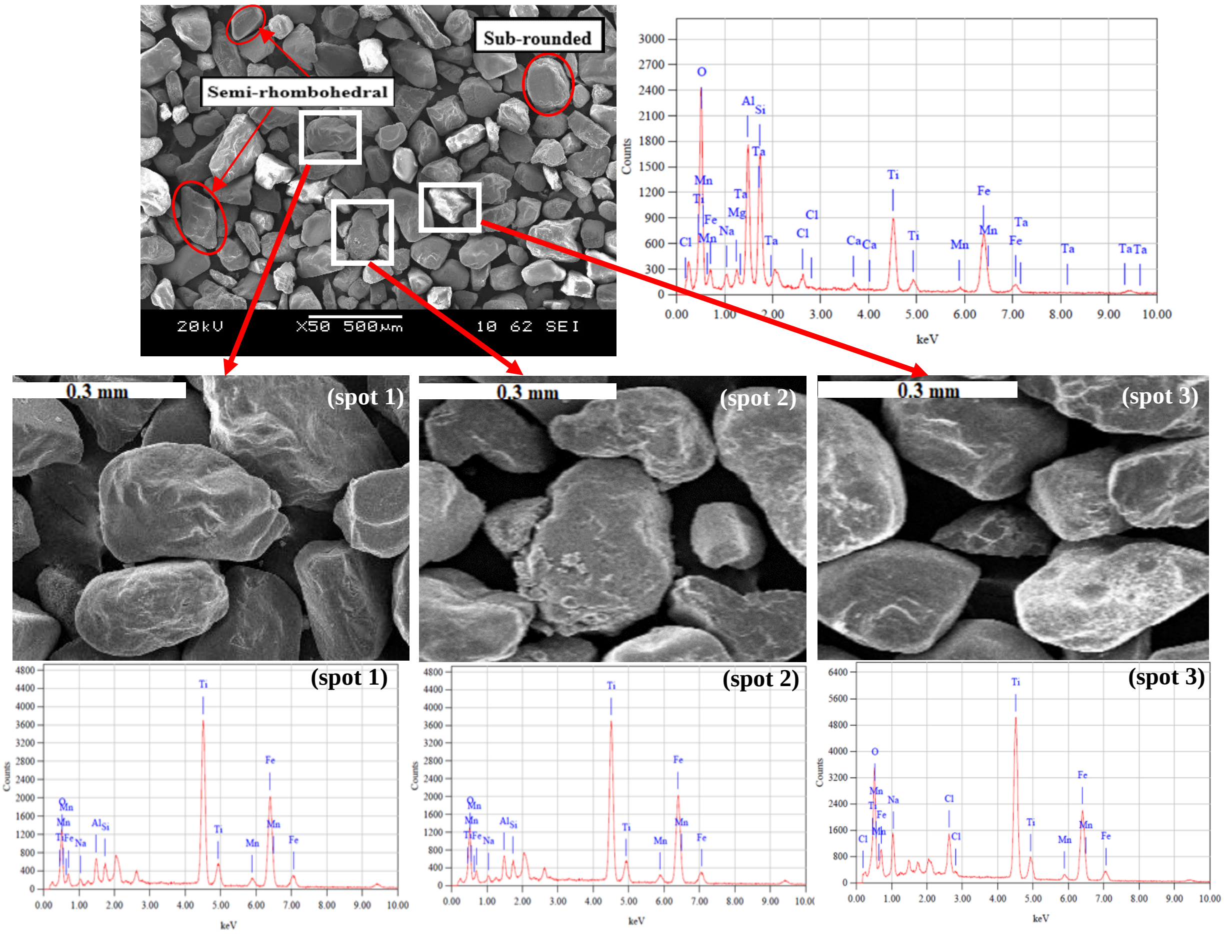

Figure 2. SEM/EDS images of Langkawi ilmenite ore and SEM/EDS analysis of specific rutile particle (spot 1), sub-rounded particle (spot 2) and semi-rhombohedral particle (spot 3)

3.3 Chemical Characterizations

The elemental composition of the Langkawi ilmenite ore is presented in Table 1. It shows that Ti, Al, Si, and Fe are the main constituent elements of the ilmenite ore. In order to confirm the formation of $FeTiO_3$ compositions, EDS analysis was performed. During the EDS measurement, different areas were focused and the corresponding peaks are shown in Figure2. High titanium and iron formations can be seen in the ilmenite ore composition in the EDS spectrums. Spectrum 1 shows EDS analysis of interlocking mineral of Ti, Fe, O, and Mn are 35.38wt%, 31.89wt%, 28.98wt%, and 2.08wt% respectively. While spectrum 3, shows 34.45wt% of Ti with small trace of some elements as shown in Table 2. Details of the EDS spectra of Langkawi ilmenite ore values measured in atomic and weight % are listed in Table 2.

Table 2 EDS spectra values

Element	Spectrum 1		Spectrum 2		Spectrum 3	
	w%	At%	w%	At%	w%	At%
O	28.98	54.94	26.88	50.88	16.21	37.11
Ti	35.38	22.34	31.38	19.84	34.45	26.29
Fe	31.89	18.17	28.89	15.67	41.51	27.52
Si	-	-	-	-	1.53	1.99
Al	-	-	-	-	4.30	5.23
Mn	2.08	1.65	-	-	2.00	1.86
Mg	1.67	2.63	-	-	-	-

These representative images of Langkawi ilmenite ore detect ilmenite and iron grains as major elements components in the ore. This results match with the XRD data, which show that more than 50% of the ore compositions are TiO_2 and Fe_3O_4. This shows that ilmenite and magnetite are the main valuable minerals in Langkawi ilmenite ore.

4. CONCLUSION

The overall results show that the Langkawi ore has high TiO_2 and Fe_2O_3 composition. Ilmenite, rutile and hematite were the main detected elements in XRD. The quantitative analysis by Rietveld refinement shows that the amount of available titanium and iron oxides within the ore were found to be about 35.85% and 26.52% respectively. These magnitudes are similar to results obtained by XRF. The ore is also associated with small amount of MgO phase presented in the mineral as trace and impurities. Smooth surface of sub-rounded large particles is clearly observed according to SEM images which indicates high degree of water erosion near the sea. Thus, Langkawi ore can be classified as low-grade mineral ore. Beneficiation processes to upgrade Langkawi ilmenite ore into Ti rich synthetic rutile might be required through magnetic and non-magnetic separation. Generally, these results show that the ilmenite ore from Langkawi beach has valuable mineralogical compositions. The ore contains some amounts of minerals such as Al and Fe which can be separated by-products via further treatment. These outcomes can be used in low-grade processing routes of Langkawi ilmenite ore with potential economical result for TiO_2 production.

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