

Investigation on Phase Evaluation of Ilmenite Ore by Carbothermal Reduction and Carboiodination Reaction

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ABSTRACT

This article presented the thermochemical calculation and experimental investigation on the phase evaluation of ilmenite ore (FeTiO_3) via carbothermal reduction and carboiodination reaction for titanium production using graphite as a reducing agent. The carbothermal reduction and carboiodination reactions were performed in two different furnaces. The carbothermal reduction was evaluated at a temperature of 1550°C with inert argon gas utilizing a horizontal tube furnace. The carboiodination reactions were evaluated in temperatures ranging from 900°C , 950°C , and 1000°C using a vertical tube furnace with mixed iodine gas with argon gas. XRF and XRD were used for analyzing the chemical compositions and the phase evolutions of raw ilmenite ore and the reduced samples, respectively. The findings showed that the Perak ilmenite ore predominantly has a greater concentration of TiO_2 (71.27wt%), Fe_2O_3 (18.85wt%), and some other oxides like aluminum oxide and quartz. In addition, XRD revealed that the ilmenite phase was converted into rutile (TiO_2) titanium oxide (Ti_3O_5 , Ti_2O_3), titanium carbide (TiC), and iron (Fe) phases, after the carbothermal reduction process. However, after the carboiodination reaction, the ilmenite and rutile phases remained at temperatures 900°C , 950°C , and 1000°C . The HSC Chemistry software was used in the determination of the thermochemical calculation and the possible reactions during the reaction which play an important role in shortening the reduction process. The results revealed the carboiodination process is a promising process that can reduce energy consumption and shorten the titanium production processes, and it needs more studies.

Keywords: Phase evaluation, Carbothermal reduction, Carboiodination reaction, XRD, HSC Chemistry software

1. INTRODUCTION

Titanium is spread in most regions of the world and the earth's crust contains about 0.44%. Titanium is a metal characterized with high strength, lightweight, and high corrosion resistance. Due to their remarkable mechanical qualities with a low density, titanium and its alloys are highly prized elements in technology and industry [1]. Whereas titanium alloys are utilized extensively in the automotive, biomedical, metallurgical, and aerospace industries. Moreover, the widespread consumption of titanium dioxide is increasing rapidly, which is used in the industries of pigmentation, paper goods, and plastics. As a result, titanium minerals have increased in value [1, 2]. Although titanium is the tenth most common element in the lithosphere, it is not easily accessible in its elemental form. However, titanium can be found in its ores due to its powerful connection to oxygen. Rocks and sands like ilmenite ore (FeTiO_3), brookite, rutile, and anatase are examples of natural materials that contain titanium [3]. Typically, it can be found as oxides like

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anatase (>95% TiO₂), rutile (95% TiO₂), and ilmenite (40-80% TiO₂) [4]. The principal source of titanium is ilmenite ore, which is composed primarily of rutile (TiO₂) and ilmenite (FeTiO₃). Ilmenite ore is a mineral that contains iron, titanium, and other minor elements. It is a commercially significant mineral, primarily because it is utilized to make titanium oxide pigments [5]. For instance, 94% of the world's titanium resources come from ilmenite, 4% from rutile, and the remaining 6% from minerals like leucosene [2], [6]. Therefore, processing low-grade titanium ores like ilmenite has received a lot of interest. Typically, only 5% of the ilmenite that is mined is utilized to make titanium metal; the remainder is utilized to make titanium dioxide and synthetic rutile [2, 6-7]. As a result, ilmenite is gradually increasingly becoming more common as a replacement for natural rutile due to its easy accessibility [8].

Ilmenite processing faces various challenges due to the different factors involved in its extraction. Addressing these challenges in the processing of ilmenite is crucial to ensure the efficient extraction of titanium and the production of high-quality titanium dioxide and other products derived from ilmenite. Ongoing research and technological advancements aim to overcome these challenges and optimize the processing of ilmenite for various applications. Ilmenite reduction is an important stage in the ilmenite ore processing to the extraction of titanium or rutile pigment. One of the most important techniques for processing ilmenite ore is carbothermal reduction, which pursues reducing the oxides into titanium dioxide and metallic iron, which is subsequently separated from iron using mechanical or chemical means [9]. This method involves the reduction of ilmenite with carbonaceous materials at high temperatures, which induces various phase transformations. Thus, utilizing the carbothermal reduction method, it is possible to extract titanium carbide, titanium carbonitride or titanium nitride, synthetic rutile, and titanium oxycarbonitride [10]. The reduction of ilmenite by carbothermal reduction is affected by temperature, the composition of the ore, reduction times, and reductant agents. Temperature, the composition of the ore, and the reductant agents are the critical parameters in the carbothermal reduction of ilmenite by carbon [11–13]. Furthermore, the reduction atmospheres have a considerable impact on the temperatures that are used during the reduction process [14].

Carbothermal reduction is an effective technique for extracting metals from ores and metal oxides when paired with carbon sources. Carbon is the favored reducing agent because of its abundance and inexpensive cost [15]. Variable sources of carbon, such as graphite, activated carbon, coke, and carbon black demonstrate varied reduction actions throughout carbothermal reduction processes [16]. The carbothermal reduction has several distinct advantages, including high yield and economic and environmental friendliness.

The carbothermal reduction consists of two different processes that are used to reduce the ilmenite ore which are direct and indirect reduction [17]. Direct carbothermal reduction involves the reduction of ilmenite ore when reacting with a carbon source as a reducing agent to produce titanium dioxide, iron, and carbon monoxide. The reaction happens at temperatures ranging from 850°C to 1000°C. While indirect reduction involves the reduction of ilmenite ore when reacting with carbon monoxide to produce titanium dioxide, iron, and carbon dioxide. The reaction happens at temperatures of 1000°C [18].

Another ilmenite reduction method involves reducing ilmenite with carbon and iodine. This leads to the reaction of carbon with oxygen present in ilmenite to form carbon monoxide, while iodine reacts with titanium to form titanium tetraiodide (TiI₄). This method is called carboiodination. This method is suggested by Schlender and Adam (2017) [19]. It is a method that introduced the use of iodine instead of chlorine in the carbohalogens reaction. This method is cost-effective and has low energy requirements to produce titanium [19]. The carboiodination reaction method to produce titanium offers several advantages over traditional methods. The reaction can occur at lower temperatures. This results in reduced energy consumption, making the process more energy-efficient and environmentally friendly. Also, the use of iodine

promotes the formation of high-purity titanium compounds [20]. Where iodine can be separated from the reaction products more easily, which helps in purifying the final product, improving its quality, and obtaining purer titanium compounds. The production of titanium by carboiodination eliminates the need for several stages of purification, which shortens production time and reduces costs [19]. Figure 1 introduces the comparison between common titanium production process steps and carboiodination concept.

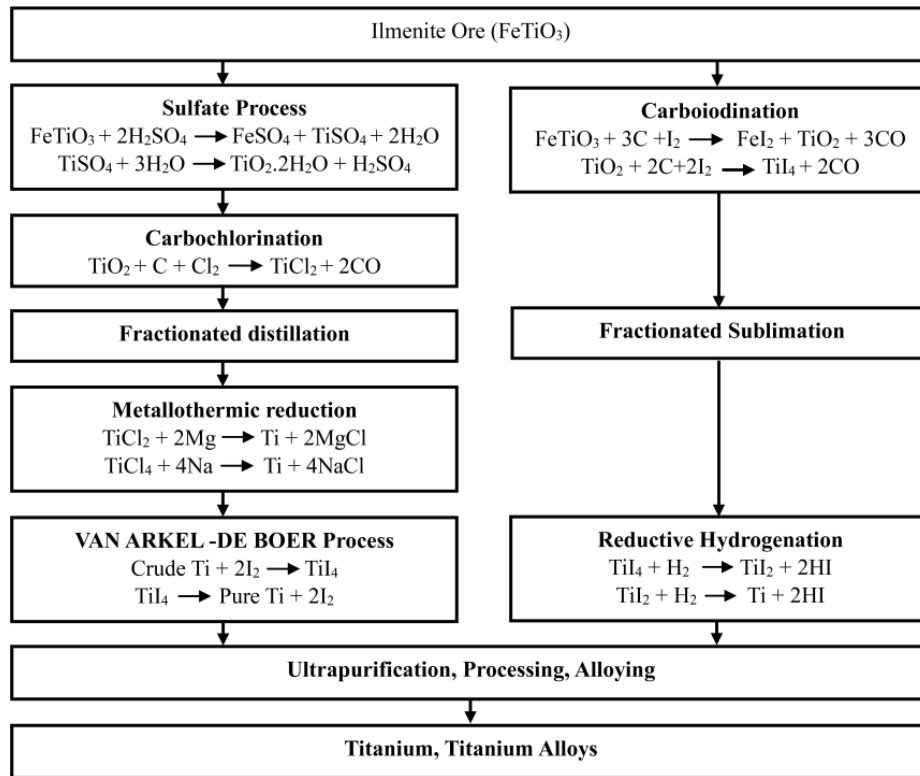


Figure 1. Comparison of the common titanium production process steps and suggested carboiodination concept [19].

During the several past years, many researchers investigated the phase evolutions of titanium resources ore during carbothermal reduction. Tripathy *et al.* (2012) studied the Indian ilmenite ore during the carbothermal reduction in the temperature range of 1000°C – 1200°C for one hour using graphite and coke as reduction agents. They claimed that at higher temperatures of reduction, lower titanium oxides were formed, and ilmenite vanished [15]. Yunos *et al.* (2020) investigated the Langkawi ilmenite ore phase utilizing carbothermal reduction at various reaction durations. They discovered that when the reduction duration was rising from 2 to 4 hours, the phase for FeTiO₃ changed to produce TiO₂, Fe, Fe₃C, FeO, and TiC [17]. He *et al.* (2021) investigated the phase development of titanium oxycarbide (TiC_xO_y). The study revealed that the ilmenite may be completely reduced to TiC_xO_y and Fe with a carbon concentration of (Ti: C, 1: 3-1: 4) at 1550°C and a reduction conducting time of 2 hours [12]. Mohammed *et al.* (2022) investigated the phase changes that resulted from the reaction of the Langkawi ilmenite ore with palm char during the carbothermal reduction at temperatures between 1200°C and 1400°C. The study demonstrated that at the highest reduction temperature of 1400°C, the ilmenite ore phase was transformed into iron titania, titanium carbide, titanium dioxide, and iron [18].

Even though a lot of studies have been done on the phase evaluation of carbothermal reduction, a study on the phase evaluation carboiodination reaction of ilmenite to transferer into titanium and titanium dioxide has not been reported yet. This research aimed to investigate the phase evaluation of Perak ilmenite ore during carbothermal reduction at 1550°C for one hour and carboiodination reaction at temperatures 900°C, 950°C, and 1000 °C for 30 minutes. This investigation was performed by combining the phases evaluations of reduction outputs and thermodynamic calculation analysis.

2. METHODOLOGY

2.1 Sample Preparation

In this study, ilmenite, graphite, and sublime iodine were used as materials in the experiments. Perak ilmenite ore was supplied by Ooi Cheng Huat Company Pvt. Ltd, Perak, Malaysia. The magnetic separating technique is used to separate nonmagnetic elements such as quartz from heavier materials utilizing a spiral separator [21, 22]. Before being used as the main raw material in the laboratory analysis, the separated ilmenite was dried. In addition, the materials were ground down to a fine powder size of around 63 μm with the assistance of a planetary ball mill. The ball planetary mill was turned on for four hours and was set its speed at 400 revolutions per minute. Furthermore, the sieving pan was utilized to sieve the powder into 63 μm . The pure powder of graphite was utilized as a reduction agent. After the samples had all been ground into powder, The quantities of graphite and Perak ilmenite ore were estimated utilizing a molar ratio of 3:1 calculated according to the ratio of total reducible oxygen to total carbon. The graphite and ilmenite ore were combined in a glass bottle utilizing a roll mill machine. The mixing sample was compressed under 15 MPa in a closed die mold with a 10 mm diameter to create cylindrical pellets with a mass of approximately 1.3g.

2.2 Thermochemical Calculation

The thermochemical calculation was performed in HSC chemistry software to calculate the Gibbs free energy (DG°) using simulation studies. The simulation studies were performed to comprehend the phase evolution of the carbothermal reduction of ilmenite and the reaction's mechanism to understand whether the reaction is spontaneous or not. Also, the stability composition diagrams are useful for estimating the prevailing phases in a system, but they assume that all phases are pure substances and do not account for mixture phases. In addition, the assumptions are often based on the available thermodynamic and kinetic data for the involved compounds and reactions which may include assuming the ideal behavior of components or neglecting certain kinetic effects. Therefore, the accuracy of simulation results can be affected by the assumptions made about the system being studied, such as the phase reactions during thermochemical calculations, the assumptions made about the data structure, and the complexity of the model. While the experimental studies conduct actual chemical experiments and measure various parameters such as temperature, time, pressure, concentration, and reaction rates. Therefore, the experimental studies reflect the real-world scenario being studied and are more accurate.

2.3 Carbothermal Reduction and Carboiodination Reaction

The carbothermal reduction process of a mixing sample of Perak ilmenite ore with graphite was executed utilizing a horizontal tube furnace. Both ends of the furnace's tubes were closed. The process was conducted at temperatures of 1550°C for one hour with 0.1 L/min of argon gas flow. The carboiodination reaction of a mixing sample of Perak ilmenite ore with graphite was executed utilizing a vertical tube furnace. The reaction was performed at temperatures 900°C, 950°C, and 1000°C for 30 minutes. The iodine solution was heated up, and then, the I₂ (gas) was mixed with

an argon gas flow rate of 0.1 L/min and passed through the furnace. The stoichiometric molar ratio of ilmenite, graphite, and iodine gas was (1:3:2).

The heating rate and cooling rate profiles for carbothermal reduction and carboiodination reactions were determined as shown in Figure 2. In carbothermal reduction, the heating rate in the horizontal tube furnace was 10°C /min for 155 minutes. It started at room temperature to reach the maximum temperature (1550°C). and then, the samples were directly injected for 60 minutes as shown in Figure 2a. After that, the cooling stage started with a cooling rate of 10°C /min for 155 minutes to reach room temperature. The cooling rate value depends on the defined value for the heating rate for the furnaces. Slow heating and cooling rates were executed to prevent breaking the reaction tube and the heating rods due to thermal stress. Thus, the sample during the carbothermal process did not react during heating/cooling. These conditions were confirmed by previous literature and thermochemical calculations [17, 18]. While, in the carboiodination reaction, the heating rate in the vertical tube furnace was 20°C /min for 45 minutes which was started from room temperature to reach the selected temperature (900°C). The carboiodination reaction was performed at a temperature of 900°C for 30 minutes of reaction based on the literature review [19] and from thermochemical calculations. The selection of 30 minutes reaction time was due to low temperature when compared to the carbothermal reduction where the process was required for better reduction performance. After that, the cooling stage was started at 900°C with a cooling rate of 20°C /min for 45 minutes to reach room temperature as shown in Figure 2b. Also, the heating and cooling rate profiles for the carboiodination reaction were utilized at reaction temperatures of 950°C and 1000°C.

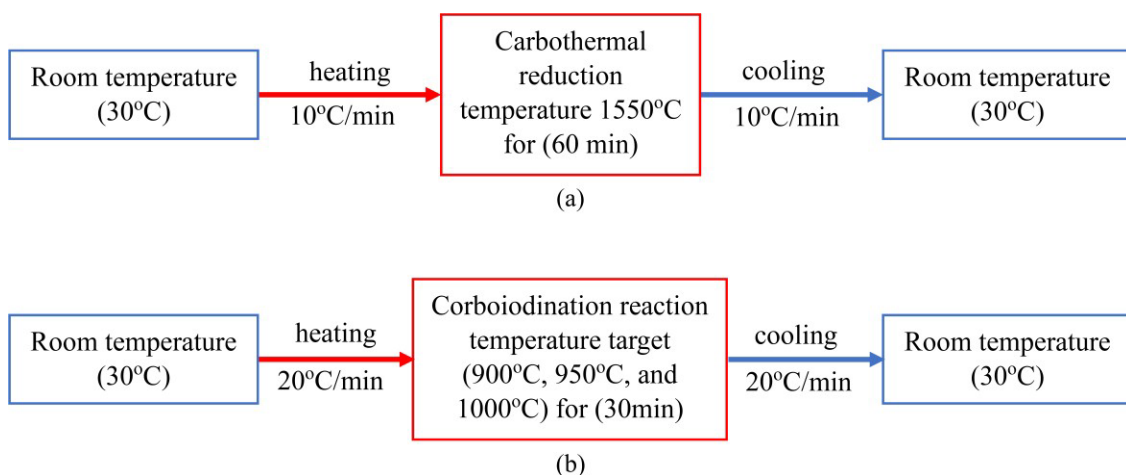


Figure 2. Heating rate temperature profile for a) carbothermal reduction and b) carboiodination reaction.

2.4 Chemical Composition and Phase Evaluation Analysis

The chemical composition of Perak ilmenite ore was examined utilizing “Energy Dispersive X-ray Fluorescence (EDXRF)” technology from ThermoFisher. The ultimate analysis of graphite was performed by the CHNS/O elemental analyzer. Also, X-ray diffractometry (XRD) was utilized to characterize and phase evaluate the ilmenite ore before and after the execution of carbothermal reduction and carbonation reaction. Utilizing the Bruker D2 Phaser diffractometer's XRD model with CuK α radiation. Irradiation was placed through a cathode tube. The scanning range 2θ was performed from 10° to 90°. The step size was 0.02° and a step rate of 0.1 s/step. In order to evaluate the phases that occurred in the samples, the XRD pattern examination was assessed utilizing the “X'pert High Score Plus software” and then compared to the “Inorganic Crystal Structure Database (ICSD)” [23]. The peak position in the XRD patterns represents information

about the symmetry of the material and crystal structure. Table 1 shows the ICDD-Sets which were used for phase analysis of ilmenite compounds by X-ray powder diffraction in this study.

Table 1 ICDD-Sets used for X-ray powder diffraction phase analysis

Formula	Name	No. of ICSD
FeTiO ₃	Ilmenite	01-075-1208, 01-089-2811, 01-075-1204
TiO ₂	Rutile	01-088-1173, 01-076-0319, 01-077-0440, 01-089-4920
TiO ₂	Anatase	01-089-4203
Ti ₂ O ₃	Titanium oxide	01-071-1047
Ti ₃ O ₅	Titanium oxide	01-082-1138
TiC	Titanium carbide	03-065-0971
Fe	Iron	00-050-1275
Fe ₂ O ₃	Iron oxide (Hematite)	01-089-7047
C	Carbon (Graphite)	01-075-2078
SiO ₂	Silicon Oxide	01-087-0703

3. RESULTS AND DISCUSSION

3.1 Raw Material Characteristics

The Perak ilmenite ore chemical composition was analyzed, and the results are shown in Table 2. According to a mineralogical examination, the Perak ilmenite ore consisted of 71.27 wt% TiO₂, 2.723 wt% SiO₂, and 18.854 wt% Fe₂O₃. Also, additional oxides such as MgO, Al₂O₃, CaO, K₂O, and SO₃ were present in the composition in less proportions. The chemical composition analysis revealed that the Perak ilmenite ore is classified as medium-grade ore [18].

Table 2 Chemical composition of Perak's ilmenite ore

Compound	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	MgO	P ₂ O ₅	K ₂ O	CaO	SO ₃
(Wt.%)	71.27	18.854	3.00	2.723	0.64	0.1326	0.117	0.097	.03221

The carbon percentage in the graphite reductant was examined utilizing a "CHONS elemental analyzer (Vario MACRO — Elementar)" based on the ASTM standard (D5373-93). The CHONS elemental analyzer revealed that carbon accounts for 91.2 wt% of graphite, while Oxygen accounts for 5.4%, sulfur accounts for 0.5%, and hydrogen accounts for 0.2%. Table 3 displays the graphite composition analysis results.

Table 3 Ultimate evaluation of graphite

Composition	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen
(Wt.%)	91.2535	0.2090	0.0000	0.5379	5.4102

The XRD analysis for Perak ilmenite ore was performed, and the result revealed that the ilmenite (FeTiO₃) and rutile (TiO₂) are the primary phase composition in the ilmenite ore; in addition, a minor amount of anatase (TiO₂), hematite (Fe₂O₃) and SiO₂ are also present. Figure 3 displays the outcome XRD for Perak ilmenite ore.

The XRD outcome demonstrated that the substance ilmenite (FeTiO_3) was detected at angles $2\theta = 23.8^\circ, 32.5^\circ, 35.2^\circ, 40.2^\circ, 48.7^\circ, 53^\circ, 56.2^\circ, 61.5^\circ, 63.2^\circ,$ and 87° based on (ICSD 01-075-1208), while rutile TiO_2 was detected at angles $2\theta = 27.7^\circ, 36.3^\circ, 39.6^\circ,$ and 69.8° based on (ICSD 01-088-1173). The Anatase (TiO_2) compound existed at angles $2\theta = 25^\circ$ based on (ICSD 01-089-4203). Hematite (Fe_2O_3) was detected at angles $2\theta = 41^\circ$ and 73° based on (ICSD 01-089-7047). Silicon dioxide was seen also in the peaks at angles $2\theta = 26^\circ$ and 54° based on (ICSD 01-087-0703). The Silicon dioxide may result from the quartz granules of the ore when the magnetic separating procedure. These findings are consistent with a study by Ahmadi *et al.*, (2017), which investigated the availability of Malaysian ilmenite ore for commercial production. where the results discovered that the largest quantities of minerals contain rutile, pseudorutile, and ilmenite, along with several other oxides such as quartz. Also, similar findings were found in Kalimantan ilmenite [24]. Additionally, the composition of the minerals of the natural ilmenite ore from Bama exhibits a similar pattern, with ilmenite as the main phase and rutile as a minor component [8]. The different discovery was XRD analysis for Langkawi ilmenite ore, where it showed the largest peaks in the phase analysis of raw ilmenite ore were at angles of 21° and 45° with compound FeTiO_3 . While the other compounds TiO_2 existed at 55.9° , Fe_2TiO_4 presented at angles of 29.6° and 55° , and Fe_2O_3 and pseudorutile were present at 26.6° [17].

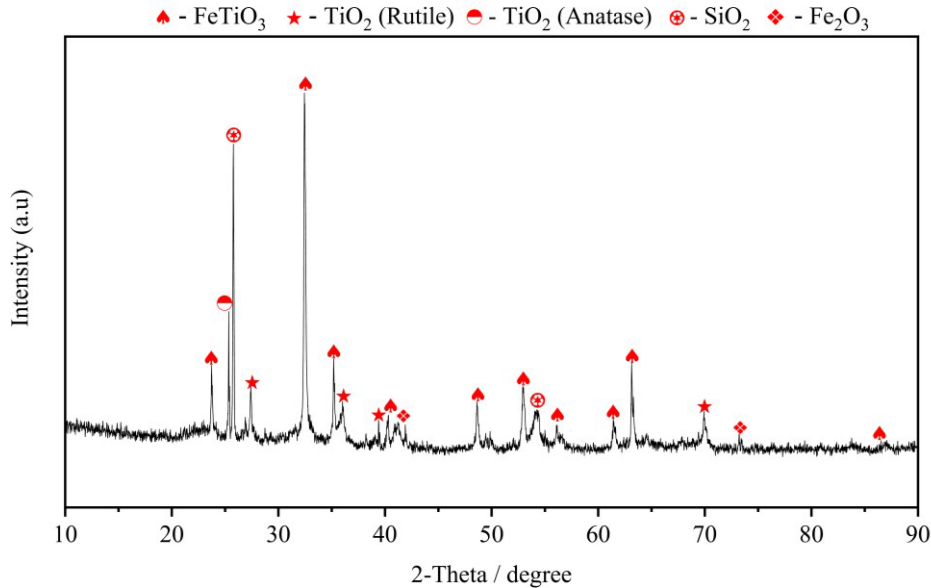


Figure 3. XRD patterns of ilmenite ore raw material.

3.2 Thermodynamics Calculation for Reduction Mechanism

Based on the phase of the carbothermal reduction outputs, several possible chemical reactions between graphite and ilmenite were shown in Equations (1)– (9). In the scenario of solid carbon (C) used as a reducing agent, the potential carbothermal reduction reactions can be expressed as Equations (1)- (8). In the scenario of solid carbon monoxide (CO) utilized as a reductant, the carbothermal reduction reactions can be represented as Equations (9).





To comprehend the phase evolution of carbothermal reduction of ilmenite, the mechanism of the reaction was examined by taking into account the effect of temperature and the Gibbs free energy (ΔG°). The ΔG° for each chemical reaction indicates whether the reaction is spontaneous or not. A spontaneous reaction is indicated by a negative ΔG° , whereas a non-spontaneous reaction is indicated by a positive ΔG° . The HSC Chemistry software was utilized to perform the examination and understand the procedure. Figure 4 depicts the correlation between ΔG° and temperature (0–1550 °C) for the reactions (1)– (9).

The equilibrium compositions diagram of the $\text{FeTiO}_3\text{-C}$ reaction during different temperatures is shown in Figure 5. The diagram shows that multiple products (Fe , TiO_2 , Ti_2O_3 , Ti_3O_5 , and TiC) were generated depending on the stoichiometric inputs of FeTiO_3 and C . This diagram was created using HSC Chemistry software based on thermodynamic data to show the thermodynamic calculation of the reaction of ilmenite with carbon. The stability of the responses under a given condition can be determined through the thermodynamic calculation output diagram by calculating Gibbs's free energy.

From the diagram in Figure 5, it is noted that rutile (TiO_2) is the main product of the carbothermal reduction process and is relatively stable. It remains stable over a wide range of temperatures and its reduction is more favorable at higher temperatures. In addition, iron (Fe) is produced as a product of the carbothermal reduction of ilmenite. Its composition becomes more favorable with increasing temperature. Titanium oxides (Ti_2O_3 and Ti_3O_5) are intermediate phases that can form during the carbothermal reduction of ilmenite, but their stability is limited compared to rutile (TiO_2). They tend to be formed in smaller amounts and may be present in transient stages during reduction. Titanium carbide (TiC) was formed when carbon reacted directly with rutile or with intermediate titanium oxides at high temperatures and under carbon-rich conditions, as it is stable at high temperatures.

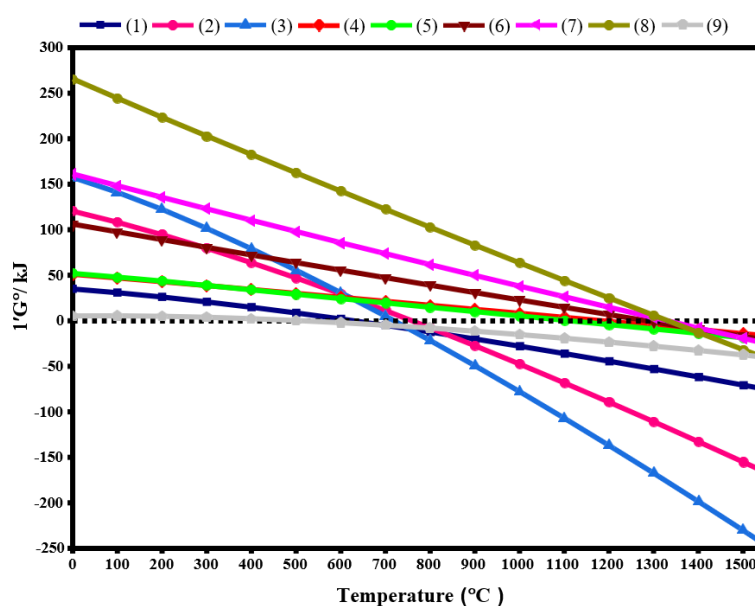


Figure 4. The relationship between ΔG° and temperature for all possible carbothermal reduction.

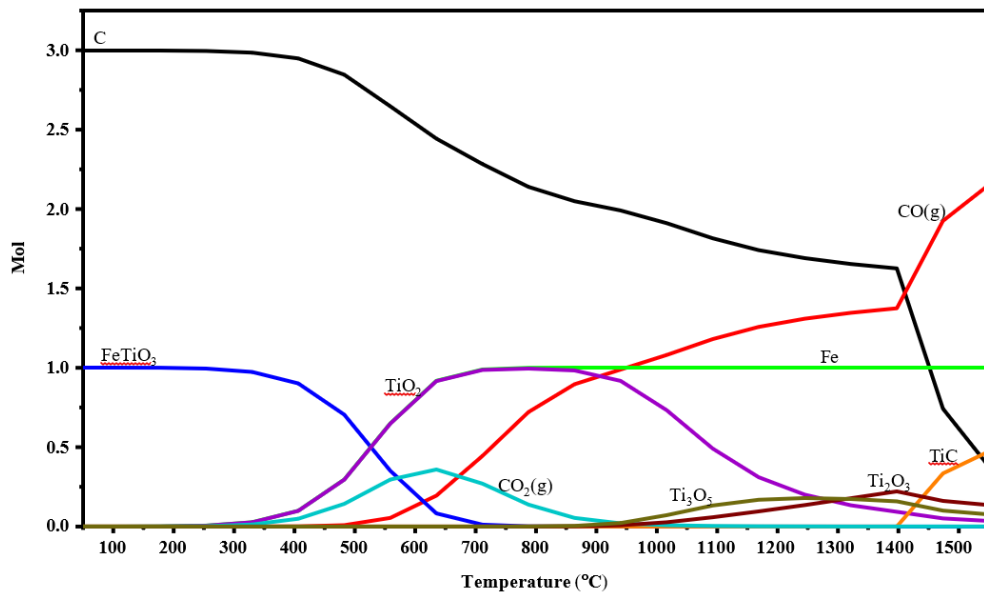


Figure 5. The equilibrium compositions diagram of the ilmenite (FeTiO₃) -graphite(C) system with Temperatures.

Based on the carboiodination concept, several possible chemical reactions between carbon, iodine, and ilmenite were shown in Equations (10)– (20).



Figure 6 depicts the correlation between DG° and temperature (0-1000°C) for the carboiodination reactions (10)– (20). It is noted that all reactions are spontaneous and can be carried out at a temperature between 200°C and 1000°C. The equilibrium compositions diagram of the FeTiO₃-C-I₂ reaction during different temperatures is shown in Figure 7.

The diagram shows that multiple products (TiI₄, TiI₂, TiO₂, Ti₂O₃, Ti₃O₅, TiC, Fe, and FeI₂) were generated depending on the stoichiometric inputs of FeTiO₃, C, and I₂. From the diagram in Figure 7, it is noted that rutile (TiO₂) and FeI₂ are the main products of the carboiodination reaction and can be obtained at a temperature of up to 400°C and are relatively stable. The TiO₂ remains stable over a wide range of temperatures. With increasing temperatures, it reduces to form Titanium tetraiodide (TiI₄).

This indicates that the carboiodination process is a promising process that can reduce energy consumption and shorten the titanium production processes. Also, titanium oxides (TiO , Ti_2O_3 , and Ti_3O_5), Fe, and TiC can form during the carboiodination reaction at high temperatures.

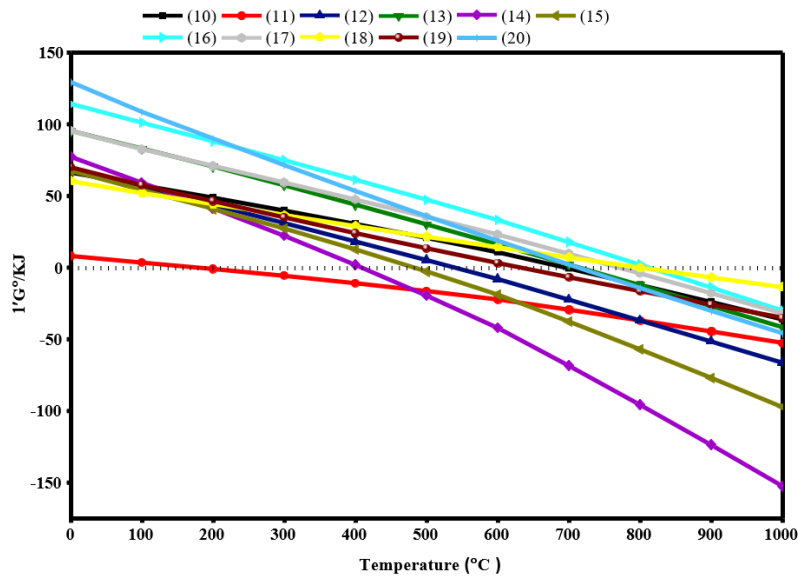


Figure 6. The relationship between DG° and temperature for all possible carboiodination reactions.

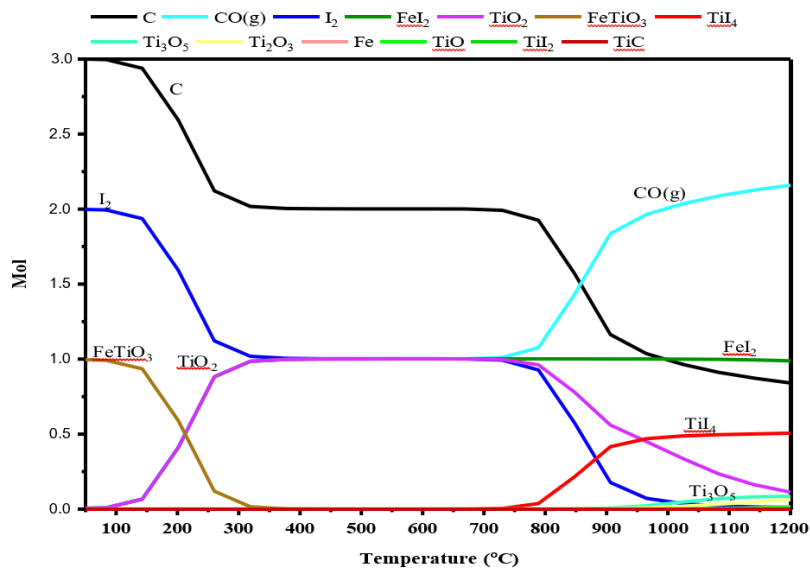


Figure 7. The equilibrium compositions diagram of the $(\text{FeTiO}_3 - \text{C} - \text{I}_2)$ reaction system with Temperatures.

3.3 Carbothermal Reduction and Carboiodination Phase Evaluation

In carbothermal reduction, one experiment with a target temperature of 1550°C for one hour was carried out. The XRD analysis of the Perak ilmenite ore after carbothermal reduction was conducted and it is shown in Figure 8. The XRD results illustrated that at a reduction temperature of 1550°C , the ilmenite phase from Perak ilmenite ore was converted into the rutile (TiO_2), titanium oxide (Ti_3O_5 , Ti_2O_3), titanium carbide (TiC), and iron (Fe) phases. The TiO_2 was presented at an angle $2\theta = 27^\circ, 36^\circ, 39^\circ, 44^\circ$ and 62° based on (ICSD 01-076-0319). Where the

TiO₂ phase is considered the main phase for the direct reduction of FeTiO₃ with carbon as an Equation (1) or indirect reduction of FeTiO₃ with CO as an Equation (9). The Ti₂O₃ was detected at an angle 2θ = 23° and 32° based on (ICSD 01-071-1047). Also, Ti₃O₅ was detected at an angle 2θ = 26°, 55°, 57°, 69°, and 83° based on (ICSD 01-082-1138). The formation of Ti₂O₃ and Ti₃O₅ phases is due to the direct reduction of FeTiO₃ and TiO₂ with an abundance of carbon as the Equations (2,3,4,5). TiC existed at an angle 2θ = 35°, 42°, and 72° based on (ICSD 03-065-0971). The detection of the TiC phase via a carbothermal reduction demonstrated that the FeTiO₃ was more thoroughly reduced. The appearance of the TiC phase is a result of the reaction of titanium oxides with carbon in the solid state as in Equations (6, 7, and 8).

In addition, Fe (iron) was discovered at an angle 2θ = 49° based on (ICSD 00-050-1275). The Fe phase is formed from CO gas produced by the (C + CO₂ = 2CO) reaction, which rises continuously until a significant amount of gas is produced. Then Fe₂O₃ reduces into FeO, and finally to Fe [25]. These changes are projected to happen in two steps, with the first involving a faster reduction of ferric to ferrous iron and the second involving a slower reduction of ferrous iron to metallic iron [26]. The findings demonstrated that at a temperature of 1550°C, graphite was as efficient as an agent of reduction. This is due to the transformation of ilmenite to lesser oxides was occurred at shorter time intervals and sufficient reduction temperature. Whereas graphite is a highly effective reducing agent for reducing ilmenite ore at temperatures of 1100°C degrees and for longer reduction times [15].

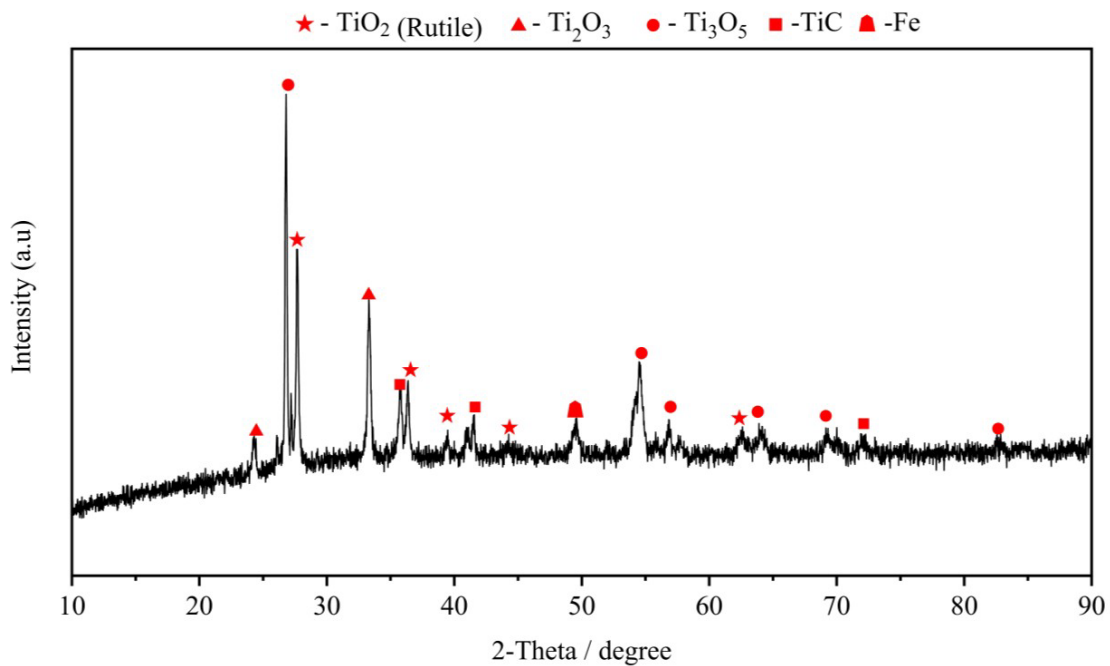


Figure 8. XRD patterns of carbothermal reduction at temperature 1550°C.

In carboiodination reaction, three experiments with target temperatures of 900 °C, 950 °C, and 1000 °C were carried out. Figure 9 (a) to (c) presented the XRD analysis patterns for reducing the ilmenite Ore (FeTiO₃) with graphite and solution iodine using carboiodination reaction at a temperature of 900°C, 950°C and 1000°C, respectively. The carboiodination reaction was performed with iodine solution during argon gas flow utilizing a Vertical Tube Furnace. The carboiodination reactions were executed for 30 minutes. The XRD results illustrated that at a carboiodination reaction at temperatures 900, 950, and 1000°C, the ilmenite, rutile, and carbon phases were detected. In carboiodination at 900°C, the XRD outcome in Figure 9a demonstrated that the FeTiO₃ was detected at angles 2θ = 24°, 33°, 36°, 40°, 48°, 53°, 61°, and 63° based on (ICSD 01-089-2811), TiO₂ at angle 2θ = 27°, 36°, 54°, 56°, 69° and 70° based on (ICSD 01-077-0440),

and carbon at angles $2\theta = 27^\circ$ based on (ICSD 01-075-2078). While in carboiodination at 950°C , XRD patterns in Figure 9b revealed that the FeTiO_3 was shown at angles $2\theta = 24^\circ, 33^\circ, 35^\circ, 40^\circ, 49^\circ, 53^\circ, 62^\circ,$ and 63° based on (ICSD 01-075-1204), TiO_2 at angle $2\theta = 27, 36, 54, 57,$ and 70 (ICSD 01-089-4920), carbon at angles $2\theta = 27^\circ$ based on (ICSD 01-075-2078). However, the XRD results for carboiodination at 1000°C as shown in Figure 9c confirmed that the FeTiO_3 was noticed at angles $2\theta = 24^\circ, 33^\circ, 35^\circ, 40^\circ, 49^\circ, 53^\circ, 62^\circ,$ and 63° based on (ICSD 01-089-2811), TiO_2 at angle $2\theta = 27, 36, 54, 57,$ and 70 (ICSD 01-089-4920), carbon at angles $2\theta = 27^\circ$ based on (ICSD 01-075-2078).

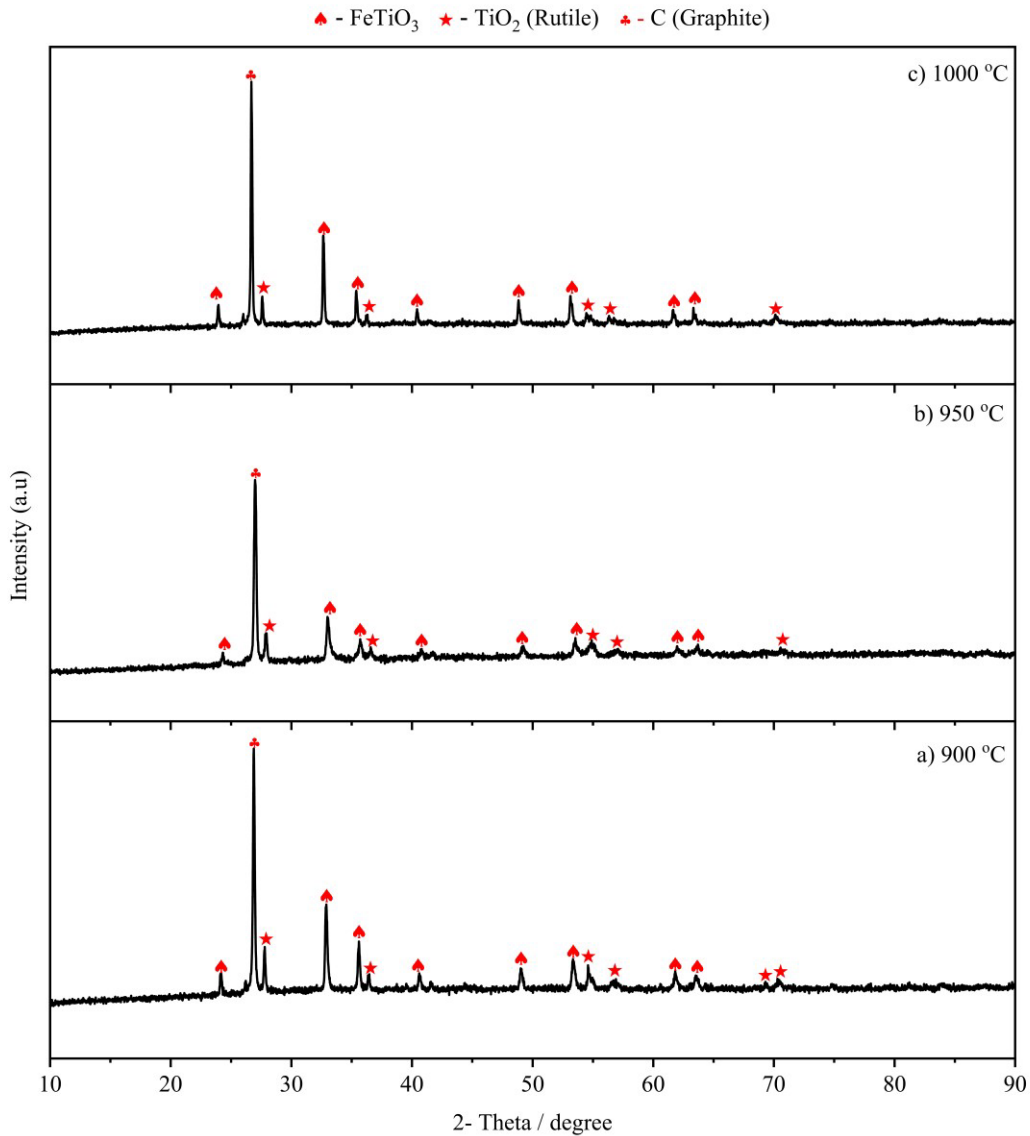


Figure 9. XRD patterns of carboiodination reaction at (a) 900°C , (b) 950°C , and (c) 1000°C .

The ferro-pseudobrookite or pseudobrookite forms from the reaction of phases Fe_2O_3 with TiO_2 or FeTiO_3 phase with TiO_2 which existed in FeTiO_3 ore, however, these phases did not occur in the carboiodination reaction. This phase did not form due to the halogenation elements (Iodine) very easily reacting with elemental elements like Fe and Ti to form FeI_2 and TiI_4 [19]. In addition, carbon reacted with oxygen to form carbon monoxide as the Equations (11,18, and 21).



The XRD patterns demonstrated that the phases of rutile (TiO_2), ilmenite (FeTiO_3), and graphite (C) still existed, and the phases did not change with the temperature variations due to the reaction was not completed while graphite with crystalline structure was not able to reduce completely at low reduction temperature ($< 1100\text{ }^\circ\text{C}$) [8], and further investigation of this process will be focused on the effect of temperature, iodine gas flow rate and the reaction time.

Table 4. Shows the ilmenite phases after carbothermal reduction and carboiodination reactions. It can be noticed that the ilmenite phases after carbothermal reduction are consistent with the carbothermal thermochemical calculation expected. However, the resulting phases after the carboiodination reactions are not consistent with carboiodination thermochemical calculation by HSC chemistry software. This indicates that the reduction of ilmenite by carboiodination reaction to produce pure titanium needs further research and development.

Table 4 Comparison among ilmenite ore, carbothermal, and carboiodination phases

Ilmenite ore phase	Carbothermal phase at 1550°C	Carboiodination phase		
		900°C	950°C	1000°C
FeTiO_3	TiO_2 (Rutile)	FeTiO_3	FeTiO_3	FeTiO_3
TiO_2 (Rutile)	Ti_2O_3	TiO_2 (Rutile)	TiO_2 (Rutile)	TiO_2 (Rutile)
SiO_2	Ti_3O_5	Graphite	Graphite	Graphite
TiO_2 (Anatase)	TiC			
Fe_2O_3	Fe			

4. CONCLUSIONS

According to the XRD investigation, the results revealed that the primary phase composition for Perak ilmenite consisted of the ilmenite (FeTiO_3), rutile (TiO_2), and a minor amount of anatase (TiO_2), hematite (Fe_2O_3), and SiO_2 . Thermochemical calculation by HSC chemistry can be utilized to predict the possible reactions during the reaction which plays an important role in shortening the reduction process. The thermochemical calculation showed the carboiodination reaction is a promising process to produce titanium that can reduce energy consumption and shorten the processes. The carbothermal reduction of Ilmenite (FeTiO_3) was completely reduced to TiO_2 , Ti_3O_5 , Ti_2O_3 , TiC, and Fe phases at a temperature of 1550°C with a reduction time of one hour. The ilmenite phases after carbothermal reduction are consistent with the expected carbothermal thermochemical calculations. The phases after carboiodination reaction experiments are not consistent with carboiodination thermochemical calculation. It was evident the difference was due to the reaction conditions. Whereas, the thermochemical calculations are based on a static and closed system, while the laboratory experiments were conducted in an open and non-static system. The difference between carboiodination reaction experiments results and carboiodination thermochemical calculations indicated that the reduction of ilmenite by carboiodination reaction to produce pure titanium needs further research and development.

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REFERENCES

- [1] Platadis, E., Kaldre, I., Blumbergs, E., Goldšteins, L. & Serga, V., *Sci. Reports*, vol. 9, issue 1 (2019) pp. 1–13.
- [2] Perks, C. & Mudd, G., *Mineral Econ.*, vol. 34, issue 3 (2021) pp. 345–370.
- [3] Sharifah, A. S. S., Saidin, H. S. N., Baharun, Rezan S. A., & Hashim, H., *Adv. Mat. Research, Trans Tech Publ*, vol. 858, (2014) pp. 265–271.
- [4] Nguyen, T. H., & Lee, M. S., *Min. Pro. and Ext. Metall. Rev.*, vol. 40, issue 4 (2019) pp. 231–247.
- [5] El Khalloufi, M., Drevelle, O., & Soucy, G., *Minerals*, vol. 11, issue 12 (2021) pp. 1425–1445.
- [6] Perks, C. & Mudd, G., *Int. Geology Rev.*, vol. 64, issue 7(2022) pp. 987–1008.
- [7] Zhang, W., Zhu, Z., & Cheng, C. Y., *Hydrometallurgy*, vol. 108, issue 3–4 (2011) pp. 177–188.
- [8] Wang, Y., Yuan, Z., Guo, Z., Tan, Q., Li, Z., & Jiang, W., *Trans. of Nonferrous Metals Soc. of China*, vol. 18, issue 4, (2008) pp. 962–968.
- [9] Kostova, N. G. *et al.*, *Bulg. Chem. Commun*, vol. 47, (2015) pp. 317–322.
- [10] Ahmadi, E., Fauzi, A., Hussin, H., Baharun, N., Ariffin, K. S., & Rezan, S. A., *Int. J. of Min., Metall., and Mat.*, vol. 24, (2017) pp. 444–454.
- [11] Dewan, M., Zhang, G., & Ostrovski, O., *XXV International Mineral Processing Congress 2010, IMPC 2010*, vol. 2, issue 5 (2010) pp. 1521–1532.
- [12] He, C. *et al.*, *Minerals*, vol. 11, issue 2 (2021) pp. 104–120.
- [13] Ponomar, V. P., Brik, O. B., Cherevko, Y. I., & Ovsienko, V. V., *Che. Eng. Res. and Design*, vol. 148, (2019) pp. 393–402.
- [14] Dewan, M. A. R., Zhang, G., & Ostrovski, O., *Metall. and Mat. Trans. B: Pro. Met. and Mat. Proc. Sc.*, vol. 40, issue 1 (2009) pp. 62–69.
- [15] Tripathy, M., Ranganathan, S., & Mehrotra, S. P., *Trans. of the Ins. of Mining and Metall., Section C: Mineral Processing and Extractive Metallurgy*, vol. 121, issue 3 (2012) pp. 147–155.
- [16] Yunos, N. F. M., Ismail, A. N., Munusamy, S. R. R., Idris, M. A., & Sahajwalla, V., *J. of Sustainable Metall.*, vol. 7, issue 2 (2021) pp. 412–426.
- [17] Yunos, N. F. M., Chong, A. I., Mohamed, J. H., & Idris, M. A., *Mat. Sc. Forum*, vol. 1010, (2020) pp. 391–396.
- [18] Mohammed, A. I., Yunos, N. F. M., Idris, M. A., Najmi, N. H., Jamal, Z. A. Z., & Nomura, T., *Chem. Eng. Research and Design*, vol. 178, (2022) pp. 583–589.
- [19] Schlender, P. & Adam, A. E. W., *Ind. and Eng. Chemistry Research*, vol. 56, issue 23 (2017) pp. 6572–6578.
- [20] Chen, X., Hua, W., Liu, Y., & Min, F., *Trans. of Nonferrous Metals Soc. of China*, vol. 19, issue 5 (2009) pp. 1348–1352.
- [21] Khuzaima, N., Ahmad, K. R., Ahmad Zaidi, N. H., Hashim, M. K. R., & Rezan, S. A., *Solid State Phenomena*, vol. 280, (2018) pp. 440–447.
- [22] Mohammed, A. I., Yunos, N. F. M., Idris, M. A., Jamal, Z. A. Z., Hayazi, N. F., & Nomura, T., *Int. J. of Nanoelectronics and Mat.*, vol. 15, issue 1 (2022) pp. 1–8.
- [23] Hellenbrandt, M., *Crystallography Rev.*, vol. 10, issue 1 (2004) pp. 17–22.
- [24] S. Wahyuningsih, P. P. Sari, & A. H. Ramelan, “Recovery TiO₂ by leaching process of carbothermic reduced Kalimantan ilmenite,” in *AIP Conference Proceedings*, AIP Publishing LLC, (2018) pp. 20028.
- [25] Najmi, N. H., Yunos, N. F. M., Othman, N. K., & Idris, M. A., *J. of Mat. Res. and Tech.*, vol. 8, issue 2 (2019) pp. 1720–1728.
- [26] Bhalla, A., Kucukkargoz, C. S., & Eric, R. H., *J. of the South. African Ins. of Mining and Metall.*, vol. 117, issue 5 (2017) pp. 415–421.