A CRITICAL REVIEW ON THE QUALITY OF TITANIA SLAG PRODUCTION THROUGH REDUCTION OF NON-ROASTED ILMENITE USING HYDROGEN

Tshedza NETSHIENDEULU, Michel Kalenga WA KALENGA

University of Johannesburg, Johannesburg, Republic of South Africa, tshedzanet21@gmail.com, michelk@uj.ac.za

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Abstract

The quality of titania slag has been largely investigated using coke. However, the environmental threats caused by carbon emissions has opened a platform to investigate the use of other reductants and their impacts on the slag quality. The aim of this investigation is to correlate the impact of hydrogen used as reductant in the pre-reduction of ilmenite on the quality of the titania slag. Reduction is a pyro-metallurgical process where metal is extracted from its ore by heating and melting it at elevated temperatures in a furnace with the addition of fluxes and reductants. In this research paper hydrogen was used as reductant during prereduction of ilmenite. Argon was concomitantly blown in with hydrogen to dilute the explosive effect of hydrogen at high temperatures. A thermogravimetric analyser (TGA) was used to perform experiments at 800, 900 and 1000 ℃. The aim of using hydrogen was to assumably increase the rate of reactions. The good quality titania slag in the pre-reduced sample must contain high iron, low Ti_2O_3, high TiO_2 and high mass loss. The optimal concentration of hydrogen was investigated firstly through prediction using Fact sage and confirmed secondly through TGA test. The fact sage predictions and TGA tests aligned well with one another. The optimal conditions for the prereduced ilmenite, were found to be 50:50 for the Ar:H_2 ratio at 1000℃ for 180 minutes.

Keywords: Metallurgy, steel, properties, applications, testing methods

1. INTRODUCTION

Naturally, ilmenite occurs as a black titanium oxide mineral with a sub metallic to metallic lustre [1]. This mineral is abundantly found in igneous and sedimentary rocks [2]. Ilmenite is also used in small amounts to generate synthetic rutile, a type of titanium dioxide utilized to make white, extremely reflective pigments. Titanium dioxide is most used as a whiting powder, extremely reflective used as pigments. These pigments give paint, paper, adhesives, polymers, toothpaste, and even food a bright white hue [3]. In the past years, the reduction of ilmenite has always been conducted using carbon. However, the use of carbon required a pre-reduction step called roasting. The purpose of roasting ilmenite was mainly to done to facilitate the separation of titanium dioxide from the ore and for the generation of valuable by-products such as titanium dioxide. The chloride route involves the carbo-chlorination of ilmenite with chlorine gas to form tetrachloride which gets oxidised to form titania oxide [4]. The current industrial practice for titania-slag production is through carbothermic reduction of ilmenite. Not only that the process is environmental unfriendly because of the release of harmful gases [5,6] but also costly. Although pyrometallurgical processes are faster than hydrometallurgical practice, it is important to comprehend reaction mechanisms during reduction [7]. In the past recent years, research has a focus on finding solutions to combat global warming and decrease energy consumption in different pyrometallurgical processes [7]. Hydrogen metallurgy has shown great prospects in replacing the traditional carbothermic reduction [8]. Hydrogen is a suitable reductant for this process because it has been reported that hydrogen has a lower bond energy than carbon at high temperatures [2]. This means that the hydrogen-hydrogen bonds will be easier to break up compared to the carbon- carbon bonds.

$FeO.TiO_2 + H_2 = Fe + TiO_2 + H_2O$ (1)

$2TiO_2 + H_2 = Ti_2O_3 + H_2O$ (2)

It has been reported that the mechanism that takes place into steps for the reactions above (1,2) with the first step being the diffusion of hydrogen through the porous layer of unreacted titanium dioxide followed by the reaction between hydrogen with ilmenite leading to iron and titanium dioxide [4,9]. The rate of reaction is generally attributed to concentrations of reactants and products over time [10] and the intrinsic chemical reaction and the diffusion of gaseous species through the product layer [7]. Moreover, it was reported that the partial reduction of titanium with hydrogen at temperatures ranging from 876- 1014℃ was possible [9]. To determine that mass loss during ilmenite reduction using hydrogen, the following equation (3) was proposed [11]:

$$w = \frac{m_0 - m_t}{m_{cal}} \times 100\% \quad (3)$$

where:

m_o - the mass of the initial sample (kg)

m_t - the the mass of sample after reduction time t (kg)

m_{cal}- the mass loss obtained by theoretical calculation (kg)

In this study, the sample was reduced in a rotary kiln furnace with temperatures ranging from 600 – 1000 ℃, with a mixture of H_2/CO and results critically interpreted.

2. METHODOLOGY

2.1 MATERIAL AND EQUIPMENT

- Ilmenite ($FeO.TiO_2$) – the selected sample or host ore of titanium used for the purpose of this project.
- Reductant – hydrogen is used as a reductant
- Diluent – Argon was used to dilute hydrogen: this is to avoid explosions in the furnace
- Alumina crucible
- X-Ray Fluorescence
- Pulveriser: This is a mechanical device used to reduce size of material.
- Thermogravimetric analyser (TGA): used for recovering iron and separating it from slag.
- Dessicator: cools down crucible with product in an inert environment.
- Tongs: Assist in the handling of heated materials.
- Microbalance: Used to record any changes in mass.

2.2 EXPERIMENTAL PROCEDURE

I. Sample preparation

The as received Ilmenite was pulverised to obtain a homogenized sample. Approximately 60g of the pulverized sample was taken for characterization using different analytical techniques and the rest of the sample was pre-reduced.

II. Characterization

The 60g of pulverized raw material was characterized using mainly XRF

III. Prereduction: a Fact Sage prediction was conducted using different temperatures to determine the temperature where possible reduction of ilmenite and the TiO_2 concentration. This is followed by experiments

IV. Comparison of products

The head sample and product samples were compared to ascertain the composition changes that have presumably occurred.

3. RESULTS AND DISCUSSION

FactSage prediction of the reduction of ilmenite in presence of hydrogen

The predictions using FactSage are presented in **Figure 1** considering a constant amount of hydrogen using 200g of ilmenite in the temperature range of 600 and 1200 °C.

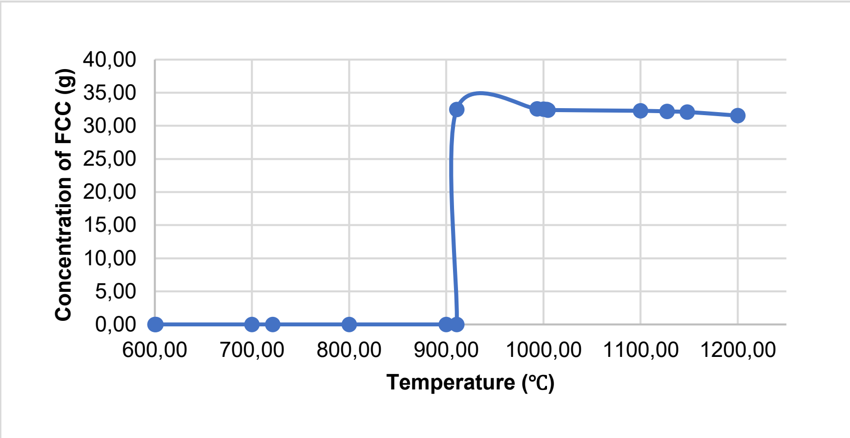

Figure 1 Relationship between temperature and the concentration of FCC

From **Figure 1** it can be observed a sharp increase at 910,75°C corresponding to the beginning of the formation of the FCC begins while the highest concentration is obtained Between 900 and 1000°C whereas a slight decline is depicted above 1000 °C. The reason of the first peak at 910,75 °fC, signifies that Ilmenite starts being reduced at 900 °C. Therefore, iron will start getting reduced almost immediately because of it lower reducing temperature which is below that of ilmenite accounting to the formation of the FCC phase. The slight drop in the concentration of hydrogen after 1000℃ is due to the melting point of ilmenite which begins at 1050 °C. Additionally, this drop is an indication that the iron in the sample has been completely reduced.

Figure 2 below shows the correlation between TiO_2 concentration against temperature. It is observed that the concentration of Titanium dioxide increased from 600- 700 ℃ by 10g. After the first peak which is at 700 ℃ the concentration of TiO_2 remained constant, till it reached a decline at the temperature of 990℃.

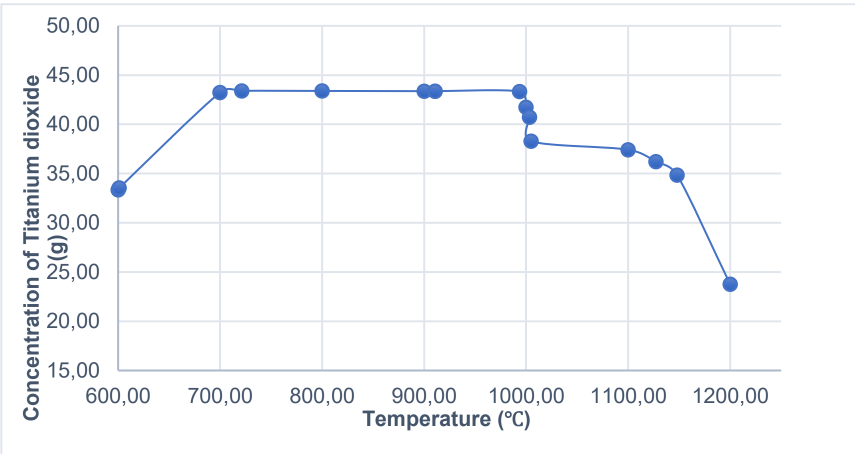

Figure 2 Correlation between TiO_2 and temperature

A huge drop in the concentration of TiO_2 occurred between the temperature range of 1100-1200 °C. The first increase in the concentration of TiO_2 indicates the increase in the reduction of ilmenite. The decrease in concentration of TiO_2 from 1100-1200 °C is an indication of successful reduction with TiO_2 reporting to the slag phase from 1100°C.

Table 1 provides the XRF results of the head sample. It transpired that the ore is acidic since the basicity is less than unity.

Table 1 XRF results of the ilmenite head sample and different tests

XRF results for head sample											
	Compound	**FeO**	**TiO_2**	**SiO_2**	**MnO**	**Al_2O_3**	**Cr_2O_3**	**MgO**	**CaO**	**ZrO_2**	**Nb_2O5**
Mass (%)	**Head sample**	52,23	41,47	2,49	1,18	0,93	0,60	0,28	0,16	0,12	0,10
	Test 1	54,52	41,03	1,61	1,49	0,46	0,22	0,11	0,12	0,12	0,11
	Test 2	54,62	40,91	1,69	1,52	0,43	0,20	0,13	0,10	0,14	0,09
	Test 3	56,70	39,82	1,03	1,45	0,26	0,14	0,06	0,09	0,13	0,12
	Test 4	55,99	40,08	1,36	1,37	0,38	0,23	0,08	0,09	0,15	0,12
	Test 5	61,31	34,86	1,83	0,73	0,53	0,14	0,15	0,09	0,12	0,08

From **Table 1**, the FeO content increased. This is presumably due to the reduction for FeO and the mass loss is the H_2O that is released during reduction although Fe is kept as FeO in the XRF results generated.

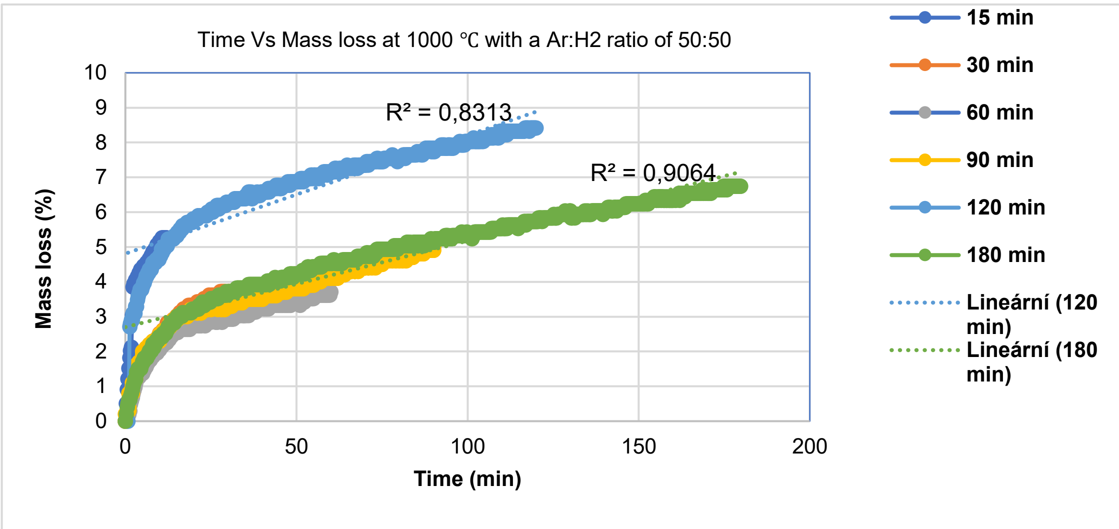

Figure 3 Correlation between Time and Mass loss (%) at 1000 °C with a Ar:H_2 ratio of 50:50

From **Figures 3** shows the correlation between time and mass loss percentage for a Ar:H_2 ratio of 50:50. It transpired that up to around 25 minutes the increase was sharp and linear increase thereafter.

Figure 4 depicts the correlation between temperature and mass loss for a constant time of 180 minutes. It transpired that the mass loss increased with the temperature increase for the time of retention of the sample in the furnace. However, two stages are identified. The first stage of reduction up to 20 minutes was rapid with exponential increase. The increase in mass loss became linear afterward with similarity in the trend for all three temperatures. **Figure 5** shows the correlation between mass loss percentage and Ar:H_2 ratio namely 50:50, 60:40 and 80:20 at 1000 °C for 180 minutes. It was observed that the highest mass loss was obtained at 50:50 ratio followed by 60:40 with 80:20 having the lowest mass loss. It was, however observed same trends for the ratios.

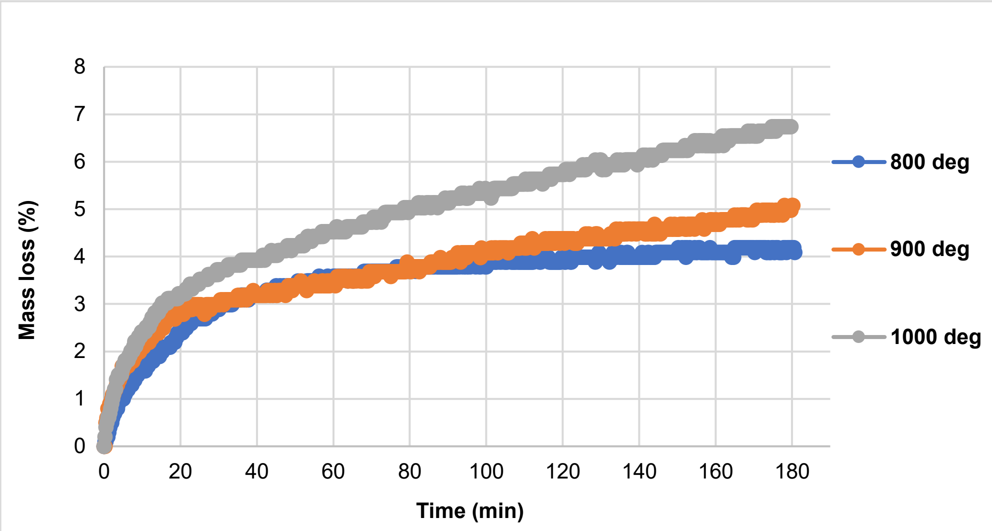

Figure 4 Correlation between Temperature and Mass loss (%)

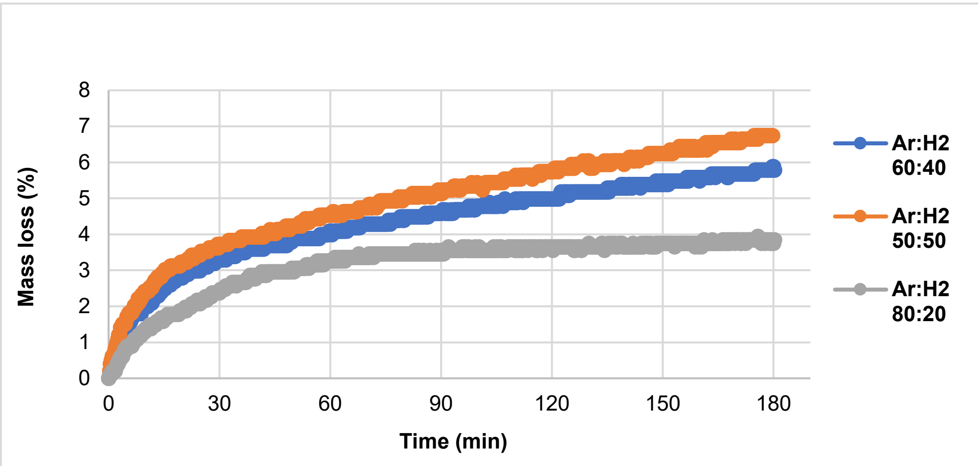

Figure 5 Correlation between Mass loss (%) and Ar:H_2 ratio at 1000 °C

4. CONCLUSION

The reduction of ilmenite using hydrogen as reductant has been tested for few years. A critical review was undertaken in this project. Thermodynamic predictions using Fact Sage aligned well with results obtained experimentally using a TGA. Results obtained have shown that from different temperatures used optimum results were obtained at 1000°C. Secondly, different Ar:H_2 ratios were experimentally tested. 50:50, 60:40 and 80:20 Ar:H_2 ratios were used at the optimum temperature. The optimum yield was obtained at 50:50 Ar:H_2 ratio. Finally, time was varied up to 180 minutes. It was observed that the mass loss increased in two stages. The first stage was a rapid stage with exponential increase followed by a linear stage. The second stage can be named slow reduction stage. Conclusively, the results obtained alludes to the hypothesis that it is possible to reduce ilmenite with hydrogen.

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