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Mechano-chemical Synthesis of Stoichiometric Titanium Nitride Powder for Cutting Tool Applications

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Abstract

Non-oxide titanium nitride (TiN) powder for cutting tool applications was pyrometallurgically synthesized via the carbo-nitridation reduction process by direct reduction of low-grade ilmenite in a nitrogen-controlled atmosphere. Mechanical activation, through which particle size reduction in the as-mixed samples was achieved, yielded the desired results. In order to monitor the reaction kinetics and observe the rate of weight loss of the reacting species, thermal analysis was conducted on the as-mixed samples. The reduction product, which contains iron (Fe) and titanium nitride (TiN), was leached in a hydrochloric acid solution. The as-leached powder (pure TiN) obtained after the acid treatment was characterized using XRD and FESEM. The results of the XRD and FESEM analyses show that the synthesized powder after the acid treatment contains a stoichiometric TiN of 4.249Å lattice parameter. No significant presence of other impurities was observed in the EDX result except a negligible trace of carbon, which can be advantageous in cutting tools for tribological purposes. The overall result shows that the synthesised TiN powder compares favourably with the known commercially available TiN powders.

Keywords: Mechano-chemical, Stoichiometry, Carbo-nitridation; Acid treatment; TiN powder; Cutting tools.

1. Introduction

Non-oxide ceramic materials have lately gained wider applications in engineering fields due to their exceptional wear resistance, high thermal stability and excellent hot hardness. They are widely employed as advanced coatings and structural components in machine tools operations, and this of course has stood them out as choice materials where other engineering materials are given less attention [1, 2]. Titanium nitride with a sodium chloride structure is a choice non-oxide ceramic material known for its unique properties [3]. These properties include but not limited to; excellent corrosion and oxidation resistance, high melting temperature, high modulus of elasticity, excellent wear resistance, and most importantly, excellent electrical and thermal conductivity [4-6]. Because of the aforementioned excellent properties, titanium nitride has been singled out for cutting tool applications in addition to its excellent wear resistant in tool coating [7, 8]. Other areas of applications for titanium nitride are optoelectronic materials used in the production of light-emitting diodes [9], semiconducting lasers [10], high-refractory ceramics [11], super-hard cutting tools, aircraft parts, solar cells, and electro-catalysis [12, 13]. Due to these unique and excellent properties that endear titanium nitride to many industrial applications, it is of utmost interest to develop more economical routes for the production of titanium nitride powder, most especially from ilmenite, low-grade titanium ores.

In the last three decades, many attempts have been made to synthesise titanium nitride from different forms and types of titanium ores. Among these production routes are; nitrogen atmosphere-controlled direct nitridation of titanium metal [14], titanium powder compaction in liquid nitrogen [15], high temperature self-propagating synthesis [16], solid state reduction of titanium ore [17], carbo-nitrothermic reduction of low grade titanium ores in nitrogen controlled atmosphere [18-20]. From the aforementioned techniques, the commonly employed routes for the production of titanium nitride are carbo-nitrothermic reductions of titanium dioxide with carbon containing materials in the presence of nitrogen [21]. However, titanium dioxide, a highly sought-after titanium mineral has been reported to be fast consumed globally [22], hence, the use of low grade ores, e.g. ilmenite, has become a thing of interest [23, 24]. The production of titanium nitride from ilmenite presents less competition in sourcing for rutile (TiO_2), a very scarce titanium mineral, and at the same time eliminating the necessity required in producing titanium dioxide from low grade titanium ore before usage in the production of non-oxide ceramic materials such as TiN, TiC and/or TiCN [25]. It is on this note that ilmenite becomes a global commodity and one of the highly sought-after raw materials for non-oxide ceramic composite production [26, 27]. Coincidentally, South Africa, a leading producer of ilmenite in the world, has been reported to possess the capacity to produce about 37% of the world titanium production [28]. South Africa processes ilmenite to high purity pig iron for steel production, and titanium dioxide and titania slag for TiO_2 pigments used in paints, paper and plastics [29, 30]. Hence, a logical conclusion of this would be to extent the processing of the ilmenite to final stage of producing stoichiometric ceramic composite such as TiN, while reducing the needs to first produce TiO_2 from ilmenite before the subsequent production of the ceramic composites from it [21, 31].

However, the conventional method of processing ilmenite often requires high temperature during the reduction synthesis, and most often above 1300 °C [7]. As such, there is always a need to catalyse the reduction rate of the ilmenite either by pre-treatment e.g. mechanical activation, pre-oxidation or addition of reduction additives [32-34]. High temperature activation of mechanically activated mixture of carbon and ilmenite to synthesise TiO_2 and Fe, backed by acid treatment, has proved to be the most economically viable route for synthesising high-quality titanium nitride powder that can meet the requirements of the engineering industry [35]. Among the noticeable advantages of mechanical activation is that it exposes more

surface area of the as-milled sample [36], thereby playing a keynote role in doubling the impact of the reduction process and increasing the rate at which the synthesised powder dissolves during the subsequent reduction stage and acid treatment, respectively [37]. Consequently, reduction time and temperature can be reduced significantly, and the acid treatment operation thereafter can be conducted at lower temperature range [38].

In an attempt to establish what has been achieved in the last three decades, our literature review showed that despite the significant research that has been done in trying to valorise South African ilmenite, limited research was seen reported on the production of stoichiometric TiN powder from the South African ilmenite [39]. Hence, this study aims to synthesise pure titanium nitride powder from ilmenite via a direct reduction process that can be used for different types of cutting tool production for drilling, cutting, and machining applications.

2. Experimental

2.1. Materials

Concentrate of ilmenite with mean particle size of about 180 μm was obtained from Richards Bay Minerals, South Africa and graphite (TIMCAL TIMREX $\text{\textcircled{R}}$ KS6) of about 99.9% purity was obtained from Imerys Graphite & Carbon, Switzerland. **Fig. 1 (a)** and **(b)** shows the morphology and X-ray diffraction peaks the ilmenite concentrate, respectively. The result of the elemental analysis of the ilmenite concentrate as conducted by XRF is as presented in **Table 1**. This result was presented in the form of their stable oxides. Hydrochloric acid, in analytical form from Merck KGaA, 64271 Darmstadt, Germany, was used during the preparation of the acid solution for the acid treatment stage.

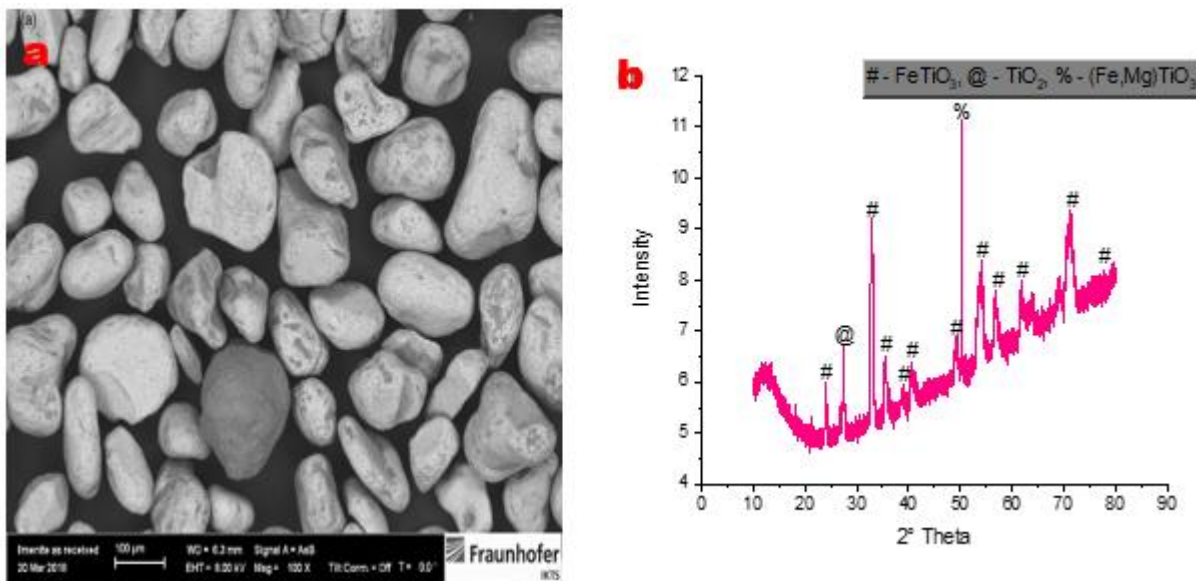


Fig. 1 (a) FESEM micrograph; (b) X-ray diffraction peaks of Richards Bay Minerals.

Table 1 Chemical analysis of Richards Bay Minerals (weight fraction,%)

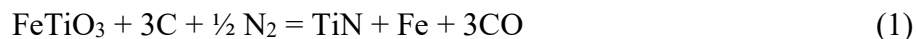
TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	MgO	MnO	ZrO ₂	Cr ₂ O ₃	Nb ₂ O ₅	CaO	ZnO	P ₂ O ₅
45.06	48.06	1.72	2.94	0.55	0.95	0.13	0.22	0.09	0.13	0.03	0.07

The chemical composition from the XRF shows that the ilmenite concentrate contains significant amounts of oxide impurities of Al, Mg, Si, etc.

2.2. Procedures

2.2.1. Grain size refinement

To achieve the mechanical activation, the TIMREX graphite and ilmenite concentrate were measured and mixed in a 1:3 molar ratio of ilmenite to graphite, **Eq. (1)**. The samples were thoroughly mixed using ethanol and milled in a planetary ball mill (PM100, Retsch, Germany) for 120 min. A 250 mL milling pot and 10 mm diameter balls, both made of hardened steel, were used during the mechanical activation.



The resulting homogeneous mixtures after the mechanical activation was dried in a laboratory drying cabinet, Thermo Electron LED GmbH, Germany, at 120 °C as a consolidation stage on the initial evaporation in a rotary evaporator, CVC 3000, Germany, to ensure that the used ethanol and some other moisture contents therein were completely removed.

2.2.2. Carbo-nitridation reduction

In an isothermal reduction process, the dried sample containing ilmenite and carbon was reduced in a high-temperature laboratory furnace, Thermal Tech., USA. In each set of the experiments, seven graphite crucibles containing 20g each of the dried samples were put in the furnace. To ensure an inert atmosphere, the furnace was purged with Ar gas, which was later switched to nitrogen in the remaining part of the reduction process. The furnace was heated up to 1275 °C at a 5 °C/min heating rate and held for 30 min before it was cooled to the ambient temperature at a 5 °C/min cooling rate. The resulting product hereby termed as-reduced samples, which are the remaining powders inside each crucible, were measured and the differences between their initial weights and final weights were used to compute the degree of reduction, **Eq. (2)** [40, 41].

$$\% \text{ weight loss} = \frac{w_o - w_t}{w_o} \times 100\% \quad (2)$$

The initial weight of the as-milled samples is w_o while the final weight of the as-reduced samples is w_t .

2.2.3. Acid treatment

The as-reduced samples, which contain Fe-TiN powder, were leached for about 4 h at 90 °C in a hydrochloric acid solution. This was done to remove the metallic Fe and other minor impurities which might have dissolved in the iron phase. The leaching experiment was carried out on an electromagnetic stirrer operated at a rotational speed of 400 rpm. The ratio of Fe-TiN powder to 10% HCl acid solution was kept at 1g:10 ml. The resulting pregnant solution therefrom was filtered, and the residue was washed several times with distilled water before being dried in a

laboratory drying cabinet at 120 °C for 60 min. Thereafter, the final powder was characterised using an X-ray diffractometer (XRD, Brucker D8 Advance, Germany) with Cu-K α radiation (λ = 1.54060 Å) operated on a scan rate of 0.01 (°)/s in 2 Theta (°). Its morphology and microstructure were characterised using field emission scanning electron microscope (FESEM: ZEISS Gemini Nvision 40, Germany) equipped with an energy dispersive spectrometer (EDS) for point analysis.

2.2.4. Thermal analysis

In establishing further the reduction behaviour of South African ilmenite, thermal analysis was carried out on the as-milled samples using a laboratory thermal analyser, STA 449 F1, Netzsch-Geraetebau GmbH, Germany. After establishing an inert atmosphere, the as-milled powder of 54.63 mg was put in an alumina crucible and reacted in the thermal analyzer at a heating rate of 10 °C/min under a continuous flow of nitrogen gas at a gas flow rate of 83 mL/min. The purity of the used Ar and nitrogen gases was 99.999%. The thermal analyzer was wrapped from 20 °C to 1300 °C, and the occurring reaction kinetics were recorded. As soon as the target temperature was reached, the process was reversed, and the furnace was cooled to 20 °C at a heat removing rate of 10 °C/min.

3. Results and discussion

3.1. Effect of particle size reduction on the ilmenite precursor

In order to examine the effect of mechanical activation on particle size reduction, particle size analysis (PSA) was carried out on the as-milled samples. **Fig. 2 (a)** shows the graph of the particle size distribution of the as-received ilmenite and the mean particle size obtained after milling for 120 min. It was observed that the mean particle size of the as-mixed samples (mostly dictated by the d_{50} of the ilmenite) has been reduced from 180 μm to 4.73 μm . The XRD patterns of the as-milled samples shown in **Fig. 2 (b)**, affirms that a significant fraction of the as-received ilmenite contains TiO_2 (rutile), and still remains as TiO_2 after milling for 120 min. Hence, the only crystalline phases after the mechanical activation were FeTiO_3 and TiO_2 , which suggests that no chemical reaction had taken place during the mechanical activation. However, the peaks of these phases became more broadened after milling for 120 min, which suggests that particle size reduction has occurred. The peaks of the non-crystalline phases, which were believed to be impurities, were not detected by the Bruker X-ray diffractometer. Although this may also be attributed to the damages caused to the crystal lattice of these oxides during the extended milling, which later resulted in decreased crystallinity and increased lattice strain [42].

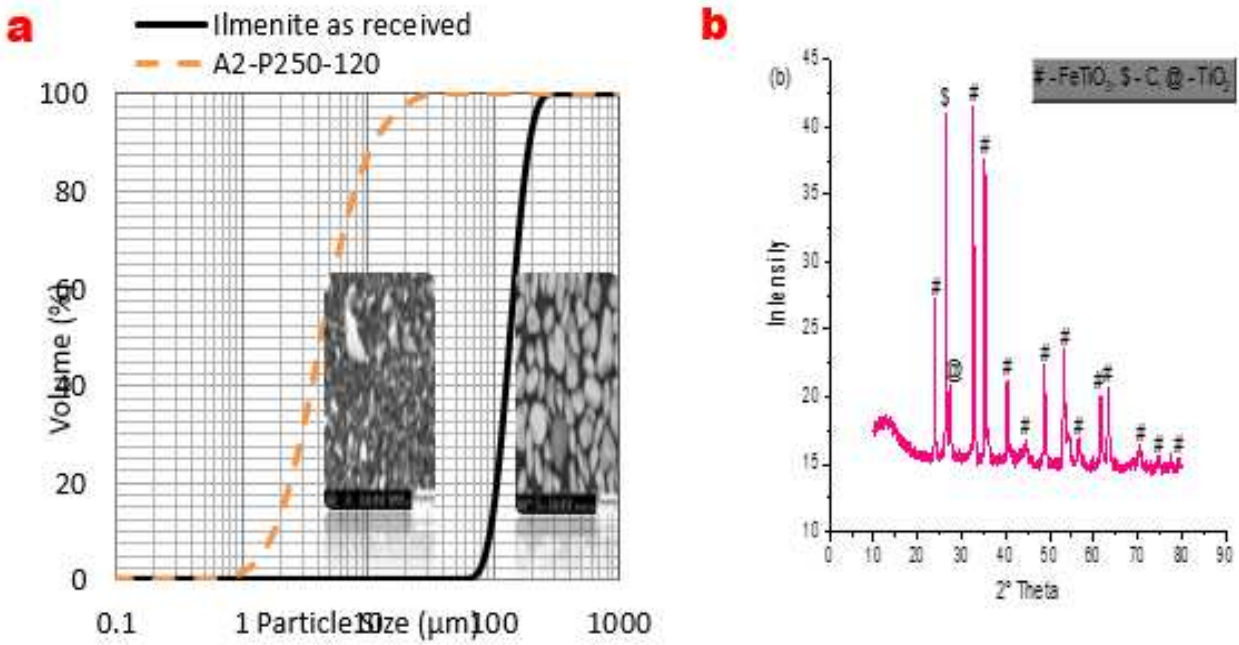


Fig. 2 (a) Particle size distribution graph (b) X-ray diffraction patterns of as-milled samples, respectively.

3.2. Reduction synthesis and the effects of reaction temperature on the as-milled samples

The XRD patterns of the as-reduced samples after carbo-nitridation reduction is shown in **Fig. 3**. It was observed that the main phases present after the reduction process were cubic TiN, metallic Fe, gamma Fe (i.e. Fe₃C) and negligible traces of carbon. Although TiN might have started forming below the experimented temperature of 1275 °C, however, the full cubic structure of TiN with a 4.249 Å lattice parameter was only observed at this temperature. This confirms that the ilmenite (FeTiO₃) as the precursor together with the fraction of TiO₂ present in it have totally reduced to metallic iron and cubic TiN phases. The strong peak intensity of these phases was an indication of the completeness of the reduction reaction at 1275 °C. However, oxides of Mg and Mn got reduced and separated in the gaseous state during the reduction process [43].



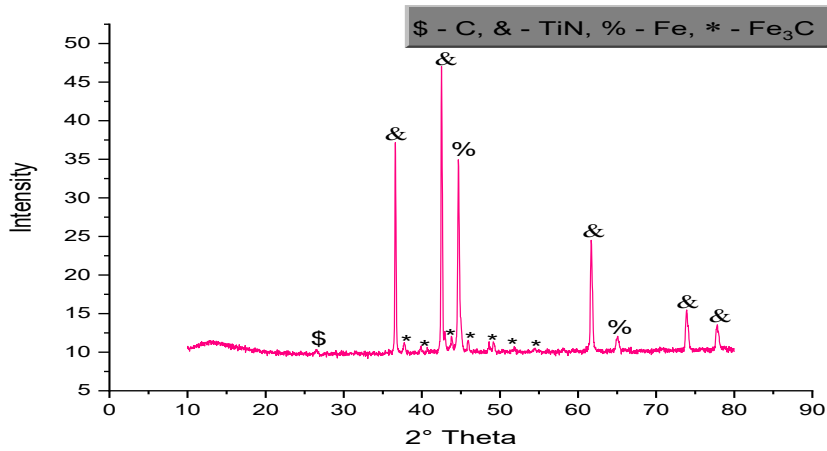


Fig. 3 X-ray diffraction patterns of as-reduced samples

The results of the microstructural analysis of the as-reduced samples are presented in **Fig. 4**. It was observed that the TiN phases were embedded in the Fe matrix phases with a clear demarcation in between. The grey region (labelled as 2) and the bright region (labelled as 1) in the morphologies of the as-reduced samples were analysed to be TiN and Fe phases, respectively. Due to the insignificant traces of carbon in the reduced samples, its presence could not be detected by the field emission scanning electron microscope (FESEM). However, energy dispersive spectrometry (EDS), as shown in **Fig. 4 (c and d)** was able to detect the presence of carbon in the samples. Impurities such as Mn, Al, and Si, which could not be totally reduced and separated during the gaseous state, were trapped, dissolved in the iron phase, and subsequently removed by acid treatment during the powder purification stage [44].

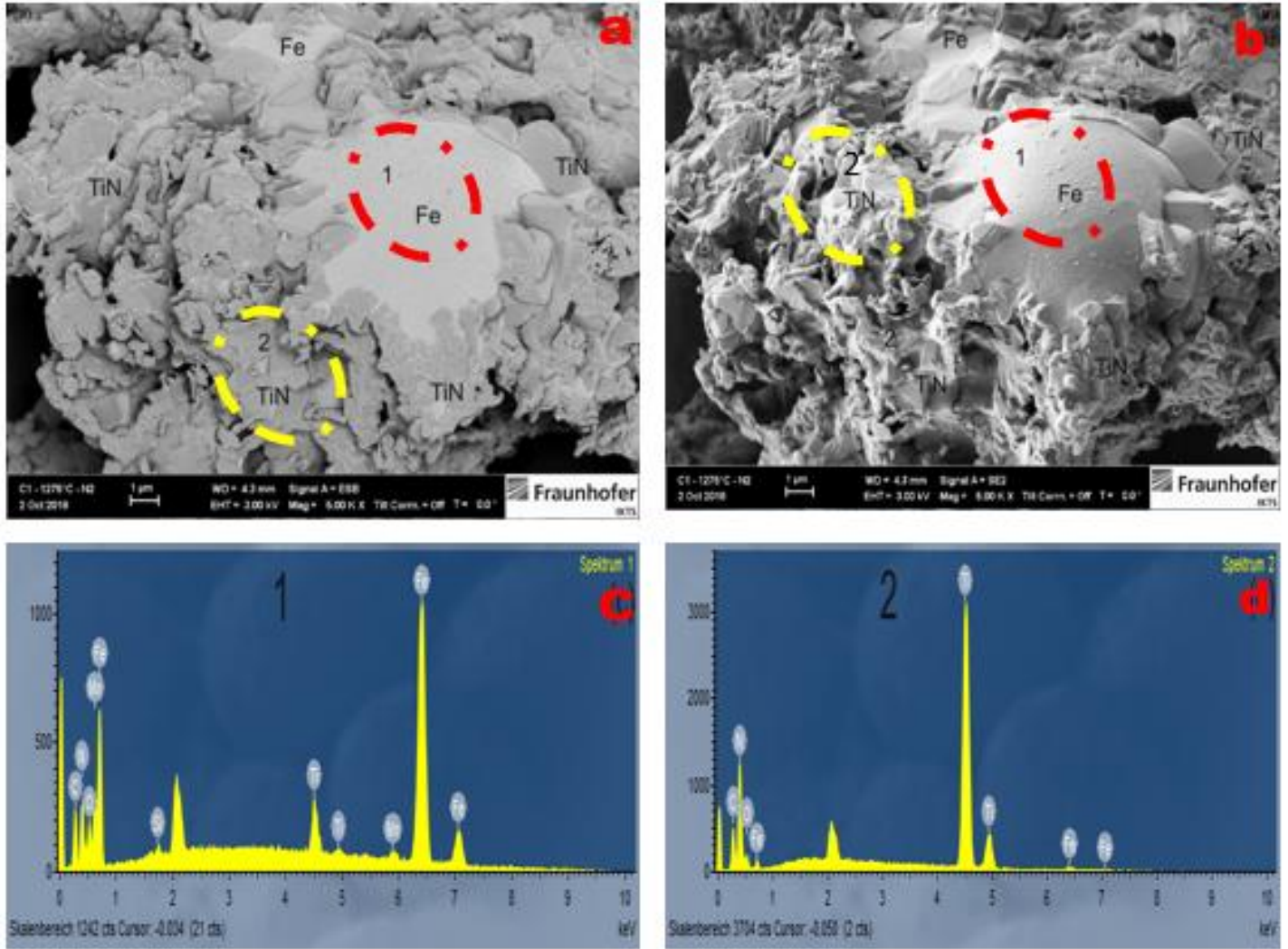


Fig. 4 FESEM micrographs (a) and (b) and EDX images of the as-reduced samples (c) and (d)

The result of the thermal analysis of the as-milled sample under a continuous heating rate of 10 °C per minute is shown in **Fig. 5**. The thermal analysis was conducted in a nitrogen-controlled atmosphere. From the obtained differential thermal analysis curve, minor weight losses due to the removal of moisture and volatile matters started at a low temperature of 282.5 °C, and this continued until the temperature reached 875 °C, although no sign phase transition was observed. Thereafter, a large and very sharp endothermic peak was recorded at exactly 980.5 °C, and this continued until 986.1 °C. This phase transition signifies the reduction of ilmenite (FeTiO_3) to metallic Fe and TiO_2 [30]. Above this temperature range, the solid-solid reaction between FeTiO_3 and carbon particles changed to a solid-gas reaction, which is more favourable at higher temperatures above 1000 °C [18]. At this stage, there was significant mass loss, which corresponds to the formation of new phases, i.e. Fe and TiO_2 . Above 1158.1 °C, there was another pronounced endothermic peak that signified the formation of cubic TiN from the *magneli* ($\text{Ti}_n\text{O}_{2n-1}$), which were the reduction products of TiO_2 between 986.1 °C and 1158.1 °C. Although the formed TiN at 1158.1 °C was not a stoichiometric cubic phase since TiN has a wide

range of stoichiometry, including TiN_{1-n} and $0 < n < 0.61$ [7]. However, our detailed analysis revealed that, as the temperature increased up to 1275 °C, the observed TiN was found to be stoichiometric with a lattice parameter of 4.249 Å. A Further increase in temperature above 1275 °C showed no signs of new phase formation.

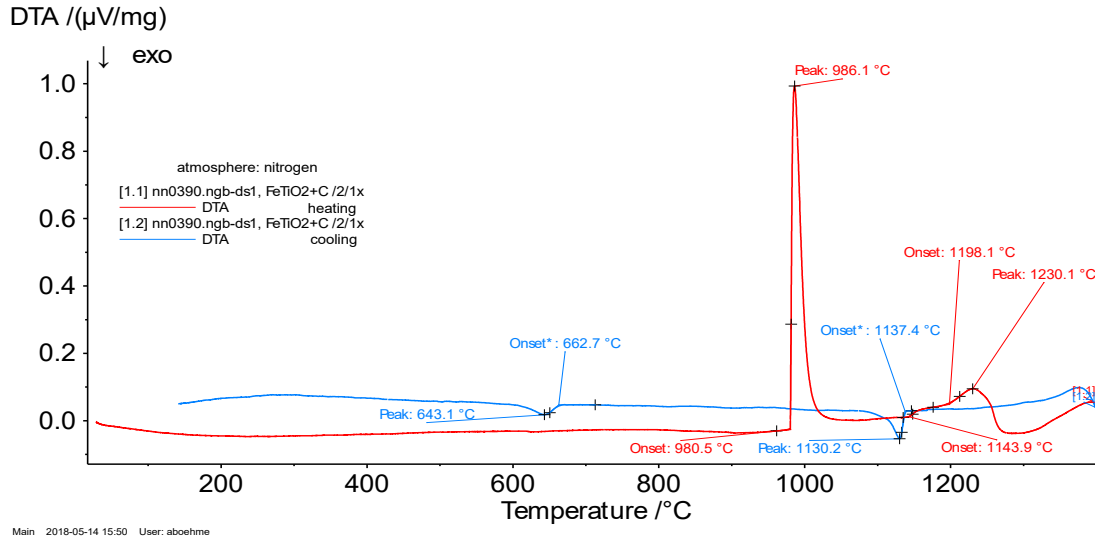


Fig. 5 DTA curve of the as-milled samples after thermal treatment

3.3. Effect of acid treatment on the as-reduced samples

The result of the X-ray diffraction analysis of the powder obtained after the acid treatment is presented in **Fig. 6**. It was observed that the diffraction patterns of the leached powder only have the peaks of cubic TiN. The peaks of Fe and Fe₃C were no longer detected after the acid treatment. This confirms the ability of the HCl acid solution to remove the metal iron and most of the impurities dissolved in it as shown in **Eq. (5)**.

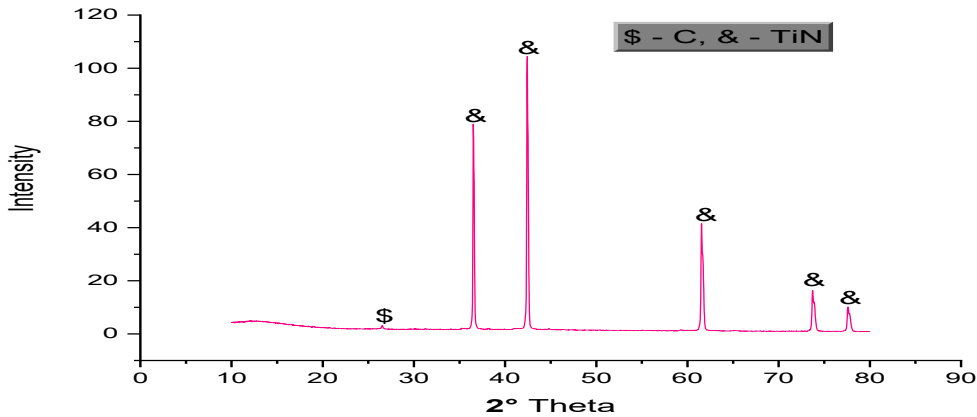
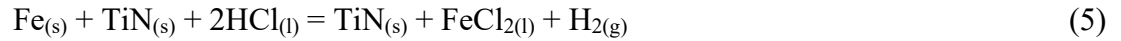


Fig. 6 X-ray diffraction peaks of the leached powder

Fig. 7 shows the morphology and the EDX results of the leached powders. **Fig. 7 (a and b)** clearly revealed that the Fe matrix and the dissolved impurities in it have been totally leached out, and the only detectable phase after the acid treatment is the grey portion, i.e. TiN. This shows that the remaining powder after the acid treatment is pure TiN. Although traces of carbon were still present in the leached powder, which were detected by EDX, **Fig. 7 (c)**. However, the presence of this little trace of free carbon, which is the excess carbon from the reduction process, may be beneficial as a tribological property for the cutting tools when they are produced from the synthesised TiN powders [44]. As a result of this, no attempt was made to remove this leftover carbon from the leached powder because it was seen as being beneficial for cutting tool application.

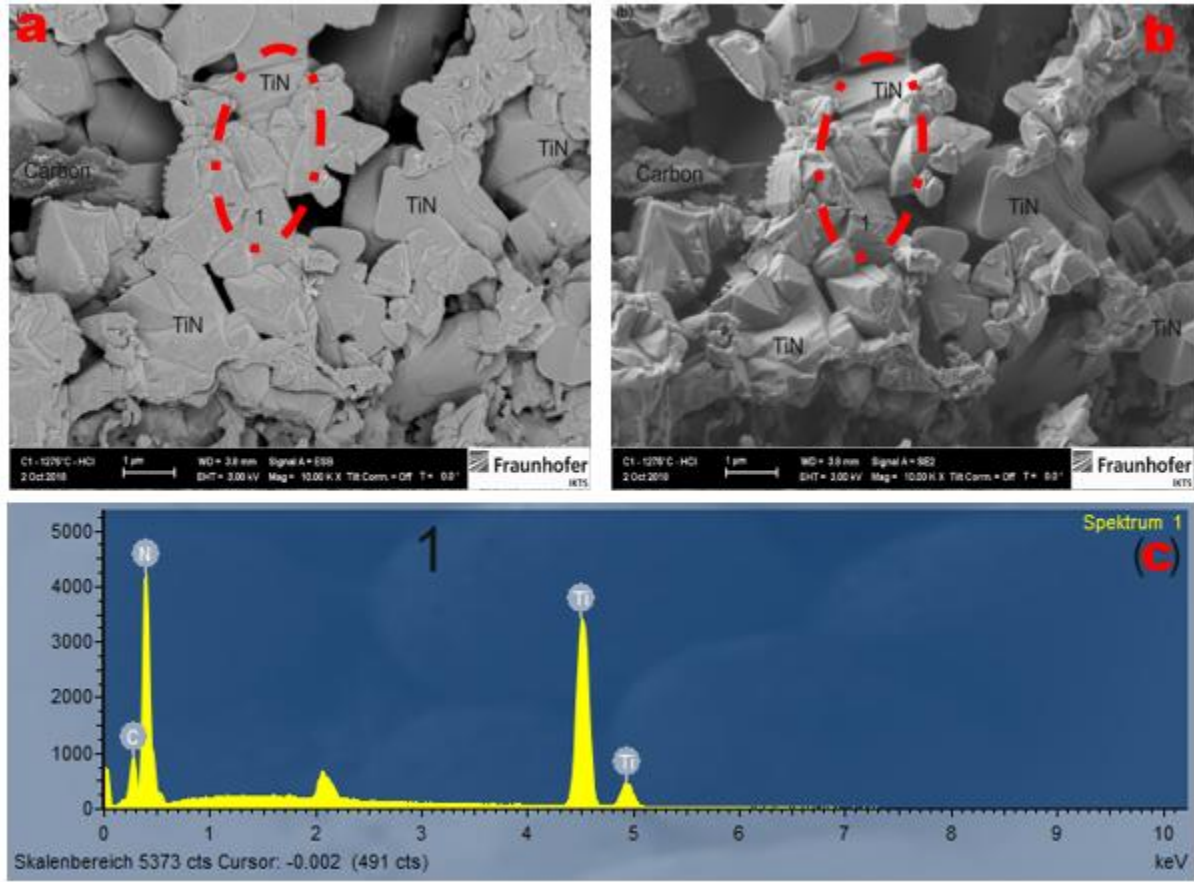


Fig. 7 FESEM micrographs (a) and (b) and EDX image of the leached powder (c)

To further confirm the compatibility of the leached TiN powder as synthesized in the study, its XRD patterns were compared with XRD peaks of commercially available TiN, **Fig. 8**. The result shows that the synthesised TiN powder measures up with its counterpart in the market.

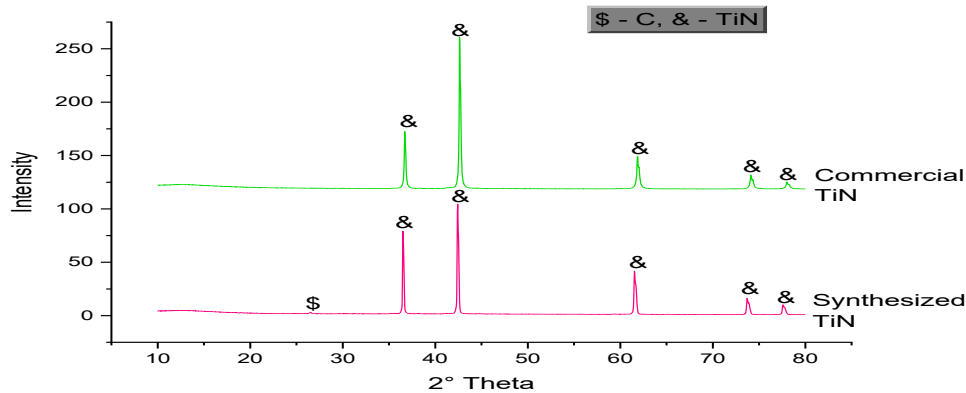


Fig. 8 The diffraction peaks of the synthesised TiN powder and the commercially available TiN powder.

4. Conclusion

This study aimed to synthesise stoichiometric titanium nitride powder from ilmenite, a low grade titanium ore, via single-stage reduction process for different types of cutting tool applications such as drilling, cutting, and machining operations. To ensure improved structural and surface properties of the as-mixed ilmenite-graphite sample are achieved, mechanical activation (BPR of 10:1, 120 min and 250 rpm) via planetary ball milling was conducted and this yielded a reduced particle size of the as-mixed sample for the subsequent high temperature reduction stage, and increased specific surface area of the as-reduced sample for the leaching treatment. On the basis of the obtained results, the following conclusions are hereby drawn:

- ❖ That the mechanical activation of the precursors milled for 120 min led to the broadening of the peaks of ilmenite, TiO_2 , and graphite, which reaffirmed that they were the only detectable phases in the as-received samples.
- ❖ That the carbo-nitridation reduction of the as-milled samples at 1275 °C for 30 min resulted in the synthesis of metallic Fe and cubic stoichiometric TiN.
- ❖ That the pure TiN powder obtained after the acid treatment was cubic and stoichiometric TiN, and not any form of sub-stoichiometric or *magneli* phases of TiN.

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writing-original draft preparation: T. Mojisola, MM. Ramakokovhu, LH. Paijan and KA. Bello; writing-review and editing: T. Mojisola, MM. Ramakokovhu and LH. Paiajn; supervision: PA. Olubambi, S. Ebad, WR. Matizamhuka and KA. Bello.

Declarations:

Conflicts of Interest: All the authors have declared that they have no competing interests, either financially or personally, which may influence the study hereby reported in the manuscript. Consequent upon that, the authors have all agreed to the manuscript's submission for this publication.

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Data Availability Statement: The data used in this study will be made available on a special demand through the lead author.

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