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Vapour Phase Synthesis and Characterization of TiN Nanoparticles

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The special features of nano-structured nitrides, especially those of transition metals, have been motivating the search for new synthesis methods. This paper is primarily focused on the characterisation of nanoscale titanium nitride (TiN) synthesised from homogeneous phase method, based on the reaction between ammonia and titanium chloride vapour as reactants. The experimental apparatus is briefly described, and thermodynamic analysis of the reactional system is presented to support the feasibility of obtaining nanoparticles of titanium nitride. The experimental results showed that the reaction parameters, temperature and space time, have an important effect on powder particle size. The produced powder was characterised by X-ray diffraction and transmission electron microscopy, which revealed, respectively, the presence of oxidized titanium nitride particle size, distribution and morphology. The TEM observed particle size was smaller than 50 nm. It was also observed the formation of ammonium chloride (NH_4Cl) as co-product of the nitridation reaction. During the handling of the TiN powder, TiO_2 was formed due to its reaction with the air moisture.

1. Introduction

In recent years, TiN has been widely used in various chemistry and engineering applications since it can behave as a typical ceramic coating on metal substrates thereby improving surface properties such as corrosion and wear resistance (Mosbah, 2006). Other applications of TiN are also recognized in the production of electrodes and decorative materials (watches, bracelets, etc.), in the aerospace industry (turbines and jet engines) and in some medical devices (orthopaedic and dental prostheses and heart valves) due to its good biocompatibility with the human body (Kola, 1996).
Ceramic powder, in general, has been studied for many years and description of methods dedicated to TiN synthesis, in particular, can be found in different works reported in the specialized literature. Di Lello (2001) studied the process for obtaining aluminium nitride powder from the reaction between ammonia (NH_3) and aluminium chloride ($AlCl_3$), both in the vapour phase, using nitrogen (N_2) as AlN carrier gas. Elger (1989) studied the production of high purity titanium nitride powder with a narrow range of particle sizes, from the reaction of titanium tetrachloride with nitrogen (N_2) or ammonia (NH_3) in the presence of magnesium (Mg). Huang (2007) developed a method to synthesize nano-crystalline titanium nitride through a reaction between TiO_2 and $NaNH_2$. The X-rays diffraction analysis showed the product as cubic TiN phase with lattice parameter of 4.242 Å. Yang (2003) also produced titanium nitride particles of about 8 nm in size by the method of synthesis of nitriding-reduction, using the reaction of titanium tetrachloride ($TiCl_4$) with ammonium chloride (NH_4Cl) and metallic sodium (Na). Dekker (1994) studied the reaction of $TiCl_4$ with magnesium in a nitrogen atmosphere for the production of TiN. The same authors also studied the formation of TiN powder, using titanium tetrachloride, ammonia and hydrogen at temperatures ranging from 900 K to 1173 K (Dekker, 1999). Based on these reports, it seems that titanium nitride can be formed from different chemical reactions

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and stoichiometries. The purpose of this work is to study the synthesis of TiN, based on the reaction between ammonia (NH_3) and titanium tetrachloride ($TiCl_4$) in the vapour phase, and the effects of temperature and space time on the size, morphology, crystal structure and compositional features of TiN nanoparticles produced.

2. Thermodynamics Considerations

Ammonia is a common nitrogen source for production of titanium nitride powders. The equilibrium composition for ammonia decomposition is shown in Figure 1 (a). It can be seen in this thermodynamic simulation that ammonia starts to dissociate into nitrogen and hydrogen gases at low temperatures and the equilibrium is achieved around 450°C. According to the experimental kinetics data by Holzrichter and Wagner (1981), the decomposition of ammonia is not fast enough to allow the equilibrium to be achieved, particularly considering de residence time used to carry out these experiments. This fact ensures that ammonia does not significantly decompose, thereby reducing the formation of nitrogen, non-reactive specie in the experimental conditions used. Therefore, no ammonia decomposition is considered in the thermodynamic simulation for the nitridation reactions of titanium nitride formation. Figure 1 (b) shows the equilibrium composition for nitridation reactions as a function of temperature, using excess of ammonia and argon as $TiCl_4$ carrier gas. According to the equilibrium composition diagram, under atmospheric pressure, complete conversion is possible to be reached at around 750°C. It can also be seen that, under these conditions, NH_4Cl will be formed at low temperatures. Based on these findings, the experimental studies were carried out in temperatures starting at 800°C, as described below.

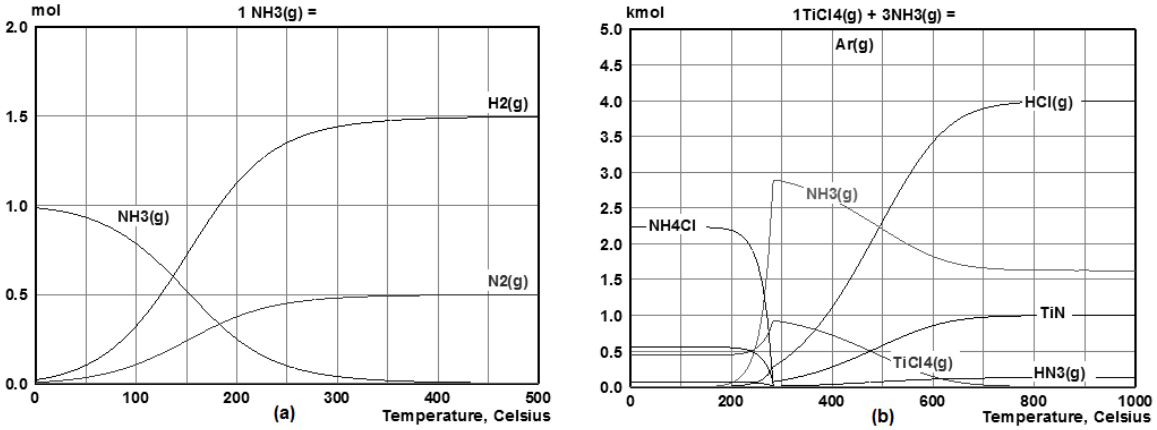

Figure 1 - Equilibrium composition diagram (a) for ammonia decomposition and (b) for the reactional system $TiCl_4/3NH_3$ as a function of temperature.

3. Experimental Studies

Titanium nitride powder was produced by reacting $TiCl_4$ and NH_3 in the vapour phase using the experimental apparatus shown in Figure 2. This apparatus consists of three main parts: vaporization system, tubular reactor and powder collector system. The vaporizer consists of a glass vessel (500 mL) electrically heated. The $TiCl_4$ vaporized at a temperature of approximately 80°C was carried by an argon flow rate to the central region of the reactor. The reactor consists of a quartz tube heated by an electric furnace. The temperature reaction was monitored and controlled by a type K thermocouple connected to a digital temperature controller.

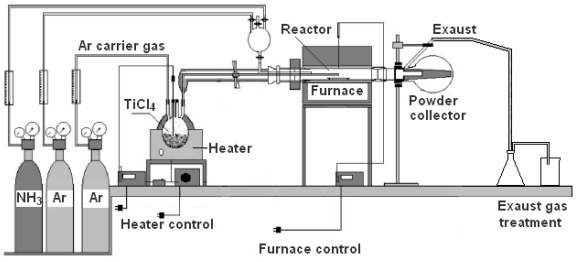

Figure 2 - Schematic drawing of the equipment used for the synthesis of TiN from the vapour phase.

The powder produced by the reaction between $TiCl_4$ and NH_3 was collected in the powder collector system. It was also observed the formation of ammonium chloride (NH_4Cl), a by-product of the process. Therefore,

further thermal treatment was necessary to eliminate the ammonium chloride. This process was performed by heating the filter collected powder at temperatures about 300°C, under an argon atmosphere. The hydrochloric acid (HCl) formed during the synthesis was neutralized by a basic solution of sodium bicarbonate ($NaHCO_3$).

The synthesized titanium nitride powders were collected and characterized aiming the identification of size, morphology, crystalline nature and composition of the nanoparticles in the produced powder. X-ray diffraction (XRD) using a Siemens - D5000, scanning electron microscopy (SEM) using a Zeiss 960 instrument equipped with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) using a JEOL 2010 instrument operated under 200 kV accelerating voltage and also equipped with an EDS detector were used.

4. Results and discussion

4.1. Effect of temperature on the average crystallite size

An objective of this study was to analyse the influence of temperature on the synthesized TiN crystallite size. Experiments were carried out at different temperatures, however maintaining constant the reactants proportions and the space time (σ). The results are shown in Figure 3. It can clearly be seen in this figure that average crystallites sizes using the Powder Cell 2.4 program, decreases with temperature increasing during synthesis reaction.

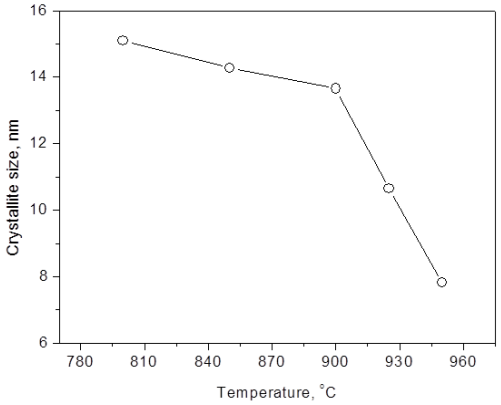

Figure 3 - Effect of temperature on the average crystallite size.

The mentioned decrease in crystallite size with increasing temperature can be explained by the greater expansion in the gas mixture inside the reactor leading to an increase in velocity and consequently a decrease in the particles growth. It should also be attributed to the increase in reaction rate and the number of TiN nuclei, with a consequent increase in the rate of homogeneous nucleation (higher number of critical nucleus) thereby generating smaller particles.

4.2. Effects of space time on the average crystallite size

The study of the space time effect on the crystallite size was performed, keeping constant the gaseous reactants proportion, at 900°C. The results indicate a monotonic increase in crystalline size with the space time, as shown on Figure 4.

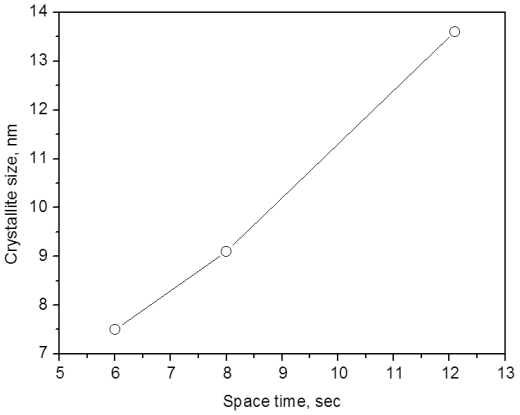

Figure 4 - Effect of space time on the average crystallite size.

As expected, the increase in space time is responsible for an increase in the average crystallite size, which can be attributed to a greater residence time of TiN stable nuclei inside the reactor, resulting in further growth of crystallites.

4.3. Characterization of the titanium nitride collected powders

The powder samples analysed were produced at a temperature of 1173 K with argon carrier gas and ammonia flow rate of 0.54 L/min and 0.57 L/min, respectively.

4.3.1. Analysis by Diffraction X-Ray - Without heat treatment

Figure 5 shows the diffractogram of powders synthesised collected from filter paper.

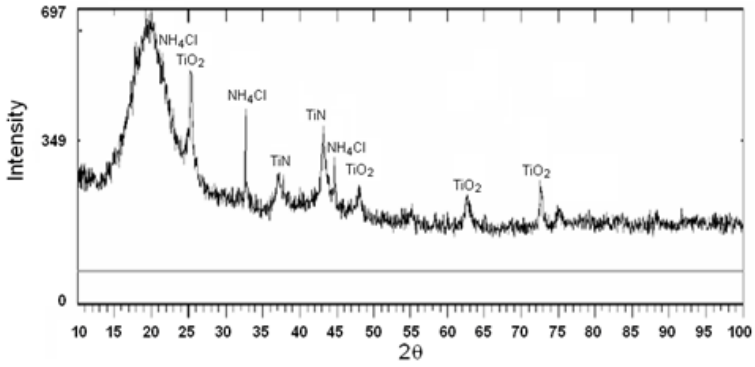

Figure 5 - X-ray spectrum of powder deposited on the filter paper.

The diffractogram shows the presence of TiN, NH_4Cl and TiO_2. The occurrence of NH_4Cl was expected thermodynamically as a by-product of the nitridation reaction. It can be observed the intense peaks of NH_4Cl suggesting high content of this material in the sample collected due to the lower temperature. The presence of TiO_2 is explained by the reaction of TiN powder, very reactive due to its high specific surface area, with oxygen and moisture in the air during the handling of the samples during the characterization procedures).

4.3.2. Analysis by Diffraction X-Ray - with Heat treatment

Figure 6 is shown a spectrum of X-ray powder deposited on filter paper, after heat treatment at temperature about 550 K under inert atmosphere of argon (Ar) to remove the ammonium chloride (NH_4Cl).

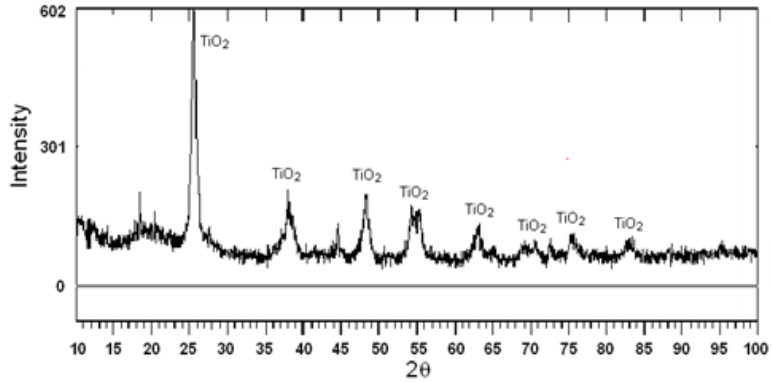

Figure 6 – Spectrum of X-ray powder deposited on the filter paper treated.

The heat treatment totally removed the by-product ammonium chloride. It can also be observed that the TiN was totally transformed in TiO_2 due to handling and the longer time of exposition in the air.

4.3.3. Characterization of synthesized powder by scanning electron microscopy (SEM)

In order to evaluate the overall morphology and composition of particles aggregates, representative samples were characterized by scanning electron microscopy (SEM). Imaging with conventional secondary electrons detector could not resolve individual particles. However, qualitative analyses of the elements were made by energy dispersive X-ray spectroscopy (EDS). For this purpose the electron prove was positioned onto sample regions exhibiting different contrast. All analysed samples correspond to particles synthesized in the following reaction conditions: Ar flow rate carrier gas of 0.54 L/min, NH_3 flow rate of 0.57 L/min and reaction temperature of 900^{o}C. Figure 7 (a) shows a SEM image of particles aggregates and the region 1 and 2 where EDS spectra were acquired. Figure 7 (b) shows the EDS spectra for regions 1 and 2.

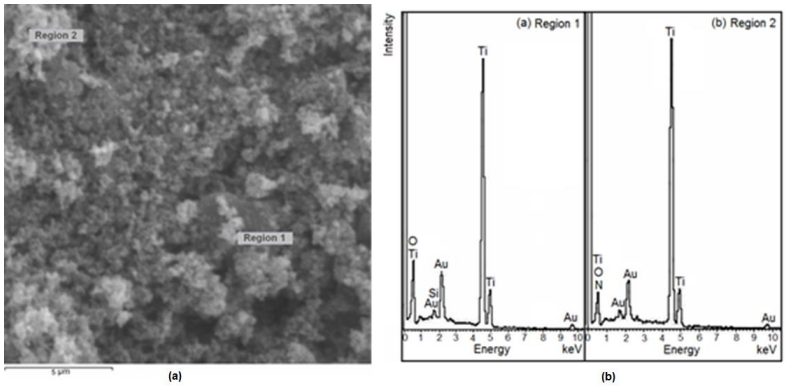

Figure 7 – (a) SEM image of collected TiN powder and (b) EDS spectra for regions 1 and 2.

It is observed that the EDS spectrum 1 confirms the elements titanium and oxygen in the composition of the particles due to TiN oxidation during handling, and in spectrum 2 the confirmation of titanium, oxygen and nitrogen, suggests the production of titanium nitride (TiN) during the synthesis processes. The Au peak is due to the fine gold layer deposited on the sample surface to avoid electron charging effect.

4.3.4. Characterization of synthesized powder by Transmission Electron Microscopy (TEM)

All TEM studies were performed on samples of TiN powders obtained under the same reaction conditions described above. A JEOL 2010 instrument under 200 kV accelerating voltage was used. The microscope was operated in conventional diffraction contrast and phase contrast modes, allowing resolving crystal atomic planes. A suspension of particles in isopropyl alcohol was produced by ultrasonic agitation and a drop of this suspension was placed on a conventional TEM grid covered with a lacy film.

Figure 8 (a) corresponds to a pattern of diffraction rings well defined, indicating that this is a polycrystalline material, as many small crystals are diffracting at the same time. Figure 8 (b) is a bright field electron micrograph, where one can see that a fine dispersion of particles with spherical morphology and particle size smaller than 50 nm in average. Figure 8 (c) corresponds to a micrograph obtained under centred dark-field illumination. The objective lens aperture has selected a limited number of diffracted beams of the most prominent ring, thereby allowing resolving individual nanoparticles with higher contrast as compared with the corresponding bright field image.

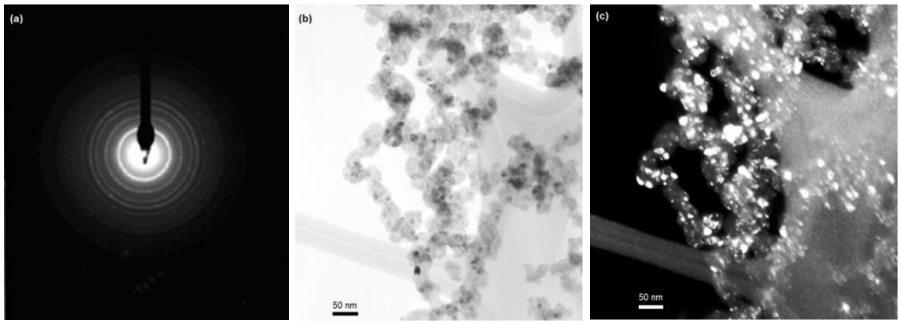

Figure 8 - (a) diffraction pattern. (b) bright field image. (c) dark field image focused on a sample of TiN synthesized 1173K.

Figure 9 shows a high resolution image obtained under phase contrast illumination.

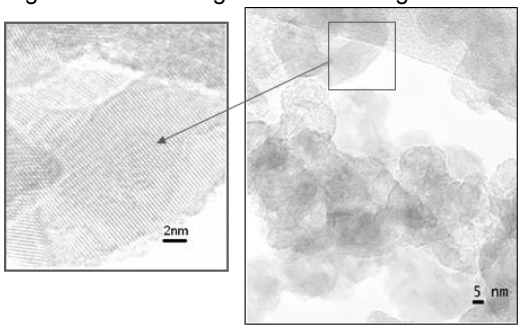

Figure 9 – HRTEM image obtained under phase contrast illumination atomic planes are resolved

In this micrograph a limited number of nanoparticles are conveniently oriented respect the incident electron beam so that atomic planes are projected. Continuous fringes along the entire particle length indicate that individual particles are single crystals.

5. Conclusions

The synthesis of TiN nanoparticles from a reaction between titanium tetrachloride ($TiCl_4$) and ammonia (NH_3), both in the vapour phase, was produced in a home-made experimental set-up. The results of the study of the effect of temperature and space time on the average size of crystallites showed a highly significant correlation. With increasing temperature from 800 to 950˚C the average size of crystallites decreases from 15 to 8 nm and space time from 6 to 12 seconds leads to an increase in the average size of crystallites from 7.5 to 13.5 nm. Analysis of the diffraction of X-ray powder produced showed the presence of titanium nitride (TiN), but also that of anatase (TiO_2) and ammonium chloride (NH_4Cl). The presence of TiO_2 is explained by the reaction of TiN, very reactive due to its high specific surface, with oxygen and moisture from the air during the handling of samples. The presence of ammonium chloride (NH_4Cl) was expected, because he is a by-product of the reaction between $TiCl_4$ and NH_3. The analysis of the product powder by X-ray diffraction and transmission electron microscopy (TEM) revealed quite clearly its crystalline character. In High resolution TEM mode, individual nanoparticles can be identified as single crystals. The measured particle size was 13 nm. Qualitative analyses of the elements were conducted by energy dispersive spectroscopy (EDS) attached to both the SEM and the TEM instruments consistently confirming the presence of titanium, oxygen and also nitrogen. The observations of produced powder by TEM have shown, in general, individual nanoparticles with spheroidal morphology. However, some particles show a faceted shape suggesting a tendency of reaching a more stable thermo dynamical configuration.

Acknowledgements

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