OBTAINING AND CHARACTERIZATION OF TiN POWDER BY REACTIVE MILLING

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Abstract.

TiN powder was obtained by reactive milling of a titanium powder in air. The Ti powder was milled in an attrition mill. Characterization of the powders was carried out by means of chemical analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The reaction took place in 96 h in the attrition mill. The XRD results indicate that a cubic TiN-like phase crystalline structure was produced in attrition mill, with a lattice parameter of 4.38Å. The morphology of the obtained powders was nodular, with particle size within the nanometric size range.

Introduction.

TiN is a covalent ceramic that has high hardness, high melting temperature, good electrical conductivity at high temperatures, good resistance to acids and bases, and good thermal stability[1]. On the basis of its excellent properties, TiN has been used as covering of cutting tools, like covering of Cu electrodes to resist corrosion in semiconductor processes and as abrasive materials [2].

Due to the fast present technological growth, it has been required not only to obtain advances in substance synthesis with new properties, but also in the generation of new methods to produce them. The use of high temperatures to process diverse ceramic compounds has some disadvantages nowadays. The main one is from the economic viewpoint and environment preservation, since consumption of great amounts of electrical energy and fuel is required, also generating polluting gas emanation that deteriorates the atmosphere. It is for that reason that it is attractive to experiment with new processing techniques alternative to the conventional methods, such as mechanical alloying [3], including its variants of mechanical transformation and reactive milling. By mecano-synthesis, diverse materials can be obtained under nominal conditions of room temperature [4].

The reactive milling is a process where chemical reactions are activated by the mechanical energy of the milling and downsizing of particles takes place [5]. For that reason it is called mechanical synthesis. The method has been strongly indicated as a potential method for the production of new materials, particularly advanced ceramic under controlable conditions [6].

Because titanium is a very reactive element, it can easily form compounds with oxygen, carbon and nitrogen. The objective of the present study has been to study the formation of TiN by the method of reactive milling, starting from elementary Titanium powders milled in air atmosphere. The method used involves a mechanical activation of the reactions of elementary titanium with nitrogen of the environment, by means of the milling of powders. In order to study the effect of the milling intensity, Titanium powders were milled in an attricionator mill.

Experimental Procedure.

Material used. Materials used for the production of the new phase of TiN were Titanium powders with a nominal purity of 99,99 % (Aldrich), and reactive degree methanol that was used as control agent.

Reactive milling to obtain TiN in a attricionator mill.- Another lot of Titanium powders was milled in an Process Union attricionator mill in a 3,25 l stainless steel container, using 50g of powders of Ti and 7 milliliter of methanol control agent in each test. As milling element 3 kg of stainless steel balls of 3 mm diameter were used. This mill is not hermetic, so that air atmosphere is renewed constantly during the milling. The times of milling were 24, 48, 72 and 96 h, at 400 r.p.m. Before extracting powders of the milling container, it is let cooling down for 2hs. In all cases a small sample (~ 0,1 g) was taken from powders every 24 h. The milling process was followed by X-rays characterization of powders based on the milling time [7].

Characterization of powders.- The evolution of phases of milled powders. was followed by X- ray diffraction (XRD) using a Siemens D 500 diffractometer with k-α radiation of Cu and collimator of 1 mm, doing a scanning from 10 to 100º in 2θ at 2°θ/min with increments of 0.03° 2θ. The lattice parameter of TiN powders was determined by the method of least square. The particle size was measured in a Malvern Zetasizer IV equipment.

Results.

Effect of the milling time.- The time of milling to obtain a new phase depends on the type of mill that is used, of the agent of milling and the speed or intensity of the milling. Figure1 shows the XRD patterns of milled powders in the attricionator for 0, 24, 48, 72 and 96h. After 24h milling, Titanium diffraction peaks are broadened and their intensity is considerably reduced, which indicates that particle size diminishes and powders tend to lose chrystallinity. This pattern also shows a very wide and poor defined peak of TiN. After 48h milling, the pattern is lat, which possibly indicates that the Titanium powders amorphize after this milling time. After 72h milling, Titanium signals disappear completely and wide and low intensity TiN peaks appear. This process continues up to 96 h milling .

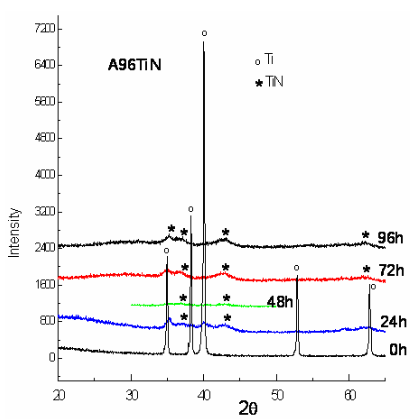
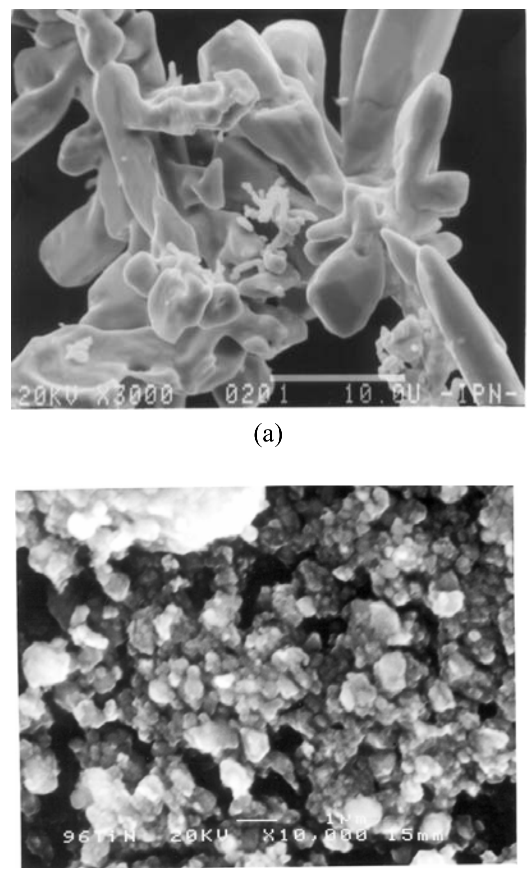


Figure1. X-rays diffraction patterns of Titanium powders milled in the attricionator for 0, 24, 48, 72 and 96 h.

Lattice parameters of milled powders for 96h in the attricionator, were determined by the method of least square.

Morphology and particle size of milled powders. In Figure 2 athe morphology of powders appears before and after the process of 96h reactive milling. The powders of TiN has an irregular morphology with sizes higher than 20 μm (Figure 2a). Milled powders for 96h in the attricionato is shown in Figure 2b. This powder is formed by particles with spherical tendency of less than 1μm of diameter, that form clusters.

The distributions of sizes of powders of TiN obtained by milling in the attricionator for 96h appear on Figure3. Powders show a Gaussian particle size distribution. Powders milled in the attricionator reaches an average size of around 500 nm, but it has a very wide size distribution from 20 nm up to 5,000. nm (5 μm).



(a)

(b)

Figure 2. Micrograph of: (a) powders of original Ti and (b) powders milled in the attricionator by 96 h.

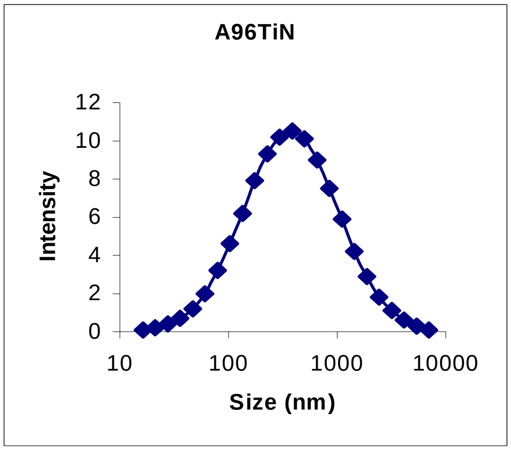


Figure 3. Distribution of size of milled powders. (a) Milled powders in attricionator by 96 h.

Discussion of results.

The formation of the TiN phase by reactive milling depends on several factors, such as: Type of mill, atmosphere of milling, balls load to Ti powder lod ratio, milling temperature and balls size In this work, the main difference studied was the type of mill.

XRD results indicate, of general way, that in both mills the reaction between powders and the nitrogen of the air is carried out, appearing a phase identified as TiN type, of cubical structure. The powders milled in the attricionator during 96h has a lattice parameter 4,38Å that would correspond to a Ti(C, N,O)compound. The value is different from the lattice parameter of pure TiN, which is of 4,242Å.

The morphology of powders obtained is nodular, with a particle size of the nanometric order as considered by the analysis made by scanning electron microscopy and from the distribution size measurement of particle of powders.

The previous discussion shows the advantages to make the reactive milling in a mill attricionator type, although the disadvantages of this method must be taken into account, i.e. a greater contamination with iron, and that only a amount of powders can be milled.

Conclusions.

Spherical powders with a TiN type phase can be synthesized very easily by reactive milling from elementary powders of Ti, using an attricionator mill, in an air atmosphere. In the attricionator, in 96 h milling obtains a type Ti(C, O, N) compound is obtained, with a lattice parameter of 4,38Å and an average particle size of 500 nm.. This powder build clusters due to its small size.

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