SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE TiN POWDER BY REACTIVE MILLING

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Abstract.

TiN powder was obtained by reaction milling of a titanium powder in air. The Ti powder was milled in an attrition mill or a Spex 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 12 h in the Spex mill. It took 96 h in the attrition mill to complete the reaction. The XRD results indicate that a cubic TiN-like phase crystalline structure was produced in the two mills, with a lattice parameter of 4.38 Å and 4.23 Å, respectively. The morphology of the obtained powders was nodular, with particle size within the nanometric size range.

Introduction.

The reactive milling is a process where chemical reactions are activated by the mechanical energy of the milling and downsizing of particles takes place [1]. 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 [2].

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 and also in a Spex 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 in Spex.

Reactive milling to obtain TiN in a Spex mill. A Spex mill was used equipped with a stainless steel container in which 5g Ti powders were loaded in each test in air atmosphere, using 6 stainless steel small balls of 5 mm diameter as milling elements. In order to avoid that the milled powder stuck in the walls of the containers, first the necessary amount of control agent was determined, making millings with different methanol content, varying from 0 to 0,7 milliliter, in intervals of 0,1 milliliter. Once the optimal amount of methanol was determined, millings were made for different time intervals of 3, 6, 9 and 12h at 400 r.p.m. In all cases, the containers atmosphere was refreshed every 3 hs. Each milling process was followed by X-rays characterization of powders based on the milling time. [3].

Reactive milling to obtain TiN in a atricionador 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.

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. Figure 1 shows the XRD patterns of milled powders in the attricionator for 0, 24, 48, 72 and 96 h. 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 flat, 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 96h milling .

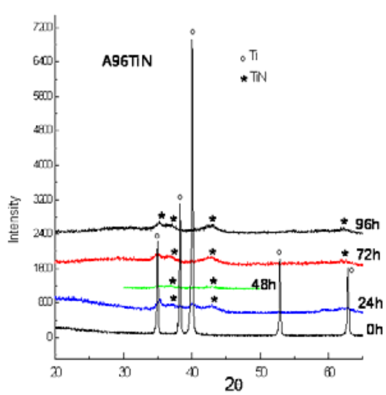


Figure 1. X-rays diffraction patterns of Titanium powders milled in the attricionator for 0, 24, 48, 72 and 96 h.

XRD patterns of Titanium powders obtained in the Spex by different milling times are shown in Figure 2. Table 1 summarizes the phases identified for every time of milling. After 3 h milling, the Titanium phase continues to appear but the peaks are wider and of smaller intensity than in the original powder, which indicates that the size of Titanium particles diminishes and lose chrystallinity, of similar way to which happens in the attricionator. After 6h milling, wide TiN peaks appear, that are better defined by increasing milling time. Well defined peaks of TiN appear in powders milled for 9 and 12 h. XRD patterns of powders milled for 9 and 12h have two very small peaks that were identified as of Fe. In Table 2 the content of milled Fe powders is reported. Very likely, this element is introduced in the powders as a product of the wearing down of the containers and of the milling elements.

Previous results demonstrate clearly that the formation of TiN in the Spex is much faster than in the attricionator, because the milling is more intense. However, this process has the disadvantages that only small amount of powders can be processed, in addition to which the contamination with Fe is much greater.

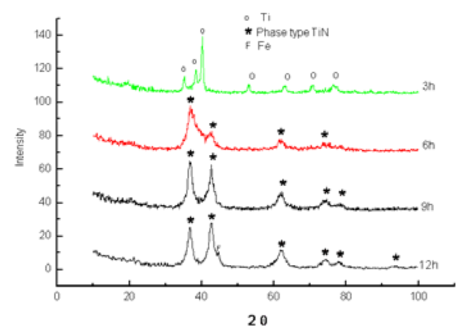


Figure 2. – XRD patterns of Titanium powders milled in the Spex for 3, 6, 9 and 12 h.

Table 2. Identified phases and Iron content of milled powders in the Spex.

Time of milling	Identified phase.	Content of Fe (% weight)
3 h	Ti	0.61
6 h	Ti, TiN	5.62
9 h	Ti, TiN, Fe	----
12 h	TiN, Fe	5.8

Lattice parameters of milled powders for 96 h in the attricionator and 12 h in the Spex were determined by the method of least square. The graph used for the powders milled in the Spex is shown in Figure 3. The powder of TiN obtained by milling in the Spex during 12 h has a lattice parameter of 4,234 Å. The lattice parameter of the powders milled in the attritionator during 96 h was of 4,38 Å. Both values are different from the lattice parameter of pure TiN, which is of 4,242 Å [3].

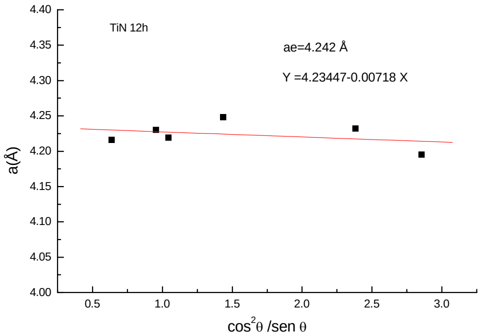
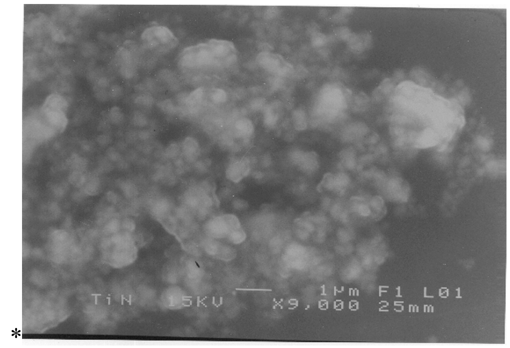


Figure 3. Illustration of the method of square minimums to determine the reticular parameter of the TiN obtained by milling of 12 h in the Spex.



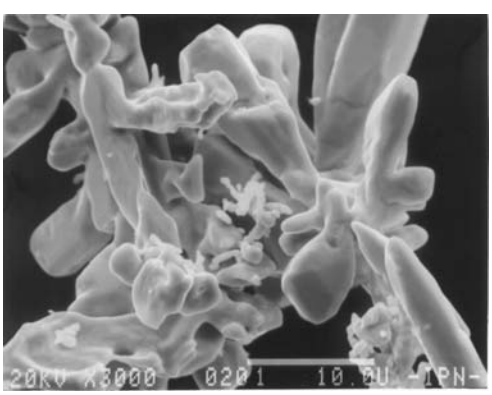
(b)

Figure 4. Micrograph of: (a) powders of original Ti and (b) powders milled in the Spex by 9 h.

Morphology and particle size of milled powders.

In Figure 4 the morphology of powders appears before and after the process of 9h reactive milling of in the Spex. The powders of TiN has an irregular morphology with sizes higher than 20 μm (Figure 4á). Milled powders for 9h in the Spex is shown in Figure 4b. 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 96 h and in the Spex by 12 h appear on Figure 5. Both 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). On the other hand, the powder milled in the Spex is much finer, of about 178 nm, and has a much narrower size distribution that goes from 45 nm to 515 nm.



(a)

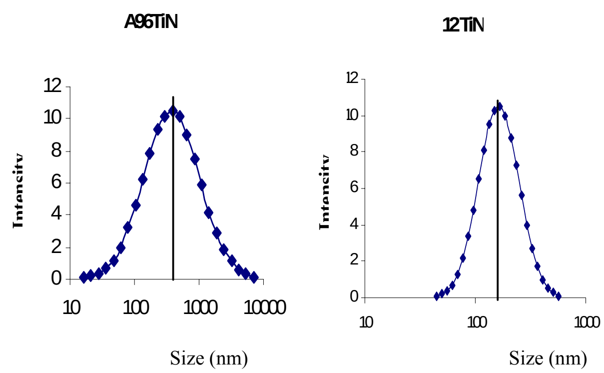


Figure 5. Distribution of sise of milled powders. (a)mMilled powders in attricionator by 96 h, (b) Milled powders in Spex by 12 h.

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 96 h has a lattice parameter 4,38 Å that would correspond to a Ti(C type, N)compound. The powders milled for 9 h in the Spex has a lattice parameter of 4,23 Å, so that it would be a compound of Ti(O, N) type. The greater speed of formation at the Spex is because this mill is a more powerful one than the attricionator.

The morphology of powders obtained is nodular, with a particle size of the nanométrico order as considered by the analysis made by scanning electron microscopy and from the distribution size measurement of particle of powders. This difference also could be explained by the fact that milling in the Spex is much more intense.

The previous discussion shows the advantages to make the reactive milling in a mill Spex type, although the disadvantages of this method must be taken into account, i.e. a greater contamination with iron, and that only a limited 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 a attricionator mill or a Spex, in an air atmosphere. The formation of TiN is much faster in the Spex than in the attricionator. In the attricionator, in 96h milling obtains a type Ti(C, N) compound is obtained, with a lattice parameter of 4,38 Å and an average particle size of 500 nm. In the Spex, in 9h milling a Ti(O type, N) powder is obtained with a lattice parameter of 4,242 Å, and an average particle size of 178 nm. This powder build clusters due to its small size.

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