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Preparation and characterization of TiN powder by reactive milling in air

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TiN powder was obtained by the reactive milling of a titanium powder in an air atmosphere, utilizing 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 over a period of 96 hours in the attrition mill. The XRD results indicate that a cubic TiN-like phase crystalline structure was produced in the mill, with a lattice parameter of 4.38 Å. The morphology of the obtained powders was nodular, having particle sizes within the nanometric size range.

Key word: Attrition, Mill, Powders, Milling, TiN.

Introduction

TiN is a covalent ceramic that possesses superior hardness, a 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 a coating for cutting tools, for the coating of Cu electrodes to resist corrosion in semiconductor processes, and as an abrasive material [2].

Due to the rapid pace of technological growth these days, it has been necessary not only to obtain advances in substance synthesis with new properties, but also to generate new methods by which to produce them. At present, the use of high temperatures to process diverse ceramic compounds has some disadvantages. The main drawbacks stem from the economic and environmental-preservation standpoints, since the consumption of great amounts of electrical energy and fuel is required. This is not only costly, but also generates polluting gas emanations that deteriorate the atmosphere. It is for these reasons that it is attractive to experiment with new processing techniques, alternative to those of 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 at room temperature [4].

Reactive milling is a process whereby chemical reactions are activated by the mechanical energy of the milling and a downsizing of particles takes place [5]. For that reason it is called mechanical synthesis. This method has been strongly suggested as a potential for the production of new materials, particularly advanced ceramics under controllable 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 an air atmosphere. The method used involves a mechanical activation of the reactions of elementary titanium with the 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 attrition mill.

Experimental Procedure

Material used

The 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 a control agent.

Reactive milling to obtain TiN in an attrition mill

One batch of titanium powders was milled in a Process Union attrition mill in a 3.25 l stainless steel container, using 50 g of Ti powder and 7 millilitres of a methanol control agent in each test. As a milling element, 3 kg of stainless steel balls 3 mm in diameter were used. The mill was not hermetic, so the air atmosphere was renewed constantly during the milling. The milling times were 24, 48, 72, and 96 hours at 400 rpm. Before extracting the powders from the milling container, they were allowed to cool down for 2 hours. In all cases, a small sample (~0.1 g) was taken from the powders every 24 hours. The milling process was followed by an X-ray characterization of the powders based on the milling time.

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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 a collimator of 1 mm, scanning from 10 to 100 degrees in 2θ at 2 degrees/minute, with 2θ increments of 0.03 degrees. The lattice parameter of the TiN powders obtained was determined by the method of least squares. The particle size was measured in a Malvern Zetasizer IV.

Results

Effect of the milling time

The milling time to obtain a new phase depends on the type of mill used, the milling agent, and the speed or intensity of the milling. Fig. 1 shows the XRD patterns of powders milled in the attrition mill for 0, 24, 48, 72, and 96 hours. After 24-hours of milling, titanium diffraction peaks are broadened and their intensity is considerably reduced, which indicates that the particle size has diminished and the powders tend to lose their crystillinity. This pattern also shows a very wide and poorly-defined peak of TiN. After 48 hours of milling, the pattern is flat, which possibly indicates that the titanium powders amorphize after this milling time. After 72 hours of milling, titanium signals disappear completely, and wide and low-intensity TiN peaks appear. This process continues up to the 96 hour of milling. The lattice parameters of powders milled for 96 hours in the attrition mill, were determined by the method of least squares.

Morphology and particle size of the milled powders

In Fig. 2, the morphology of the powders obtained is shown before and after the 96-hour process of reactive milling. The TiN powders have an irregular morphology, with a particle size greater than 20 mm (Fig. 2(a)). Powders milled for 96 hours in the attrition mill are shown in Fig, 2(b). This powder is formed by particles having a spherical tendency and sizes of less than 1 μm in diameter.

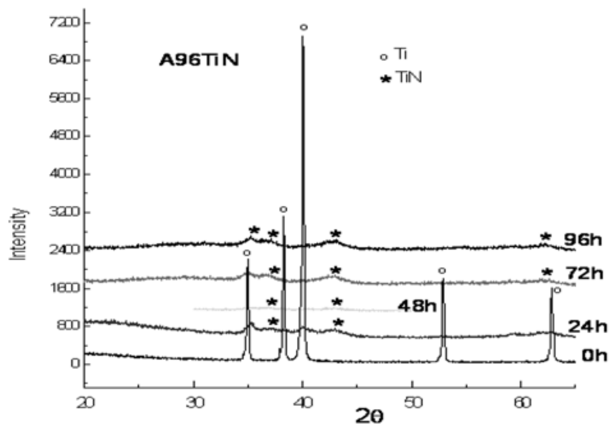

Fig. 1. X-ray diffraction patterns of titanium powders milled in the attrition mill for 0, 24, 48, 72, and 96 hours.

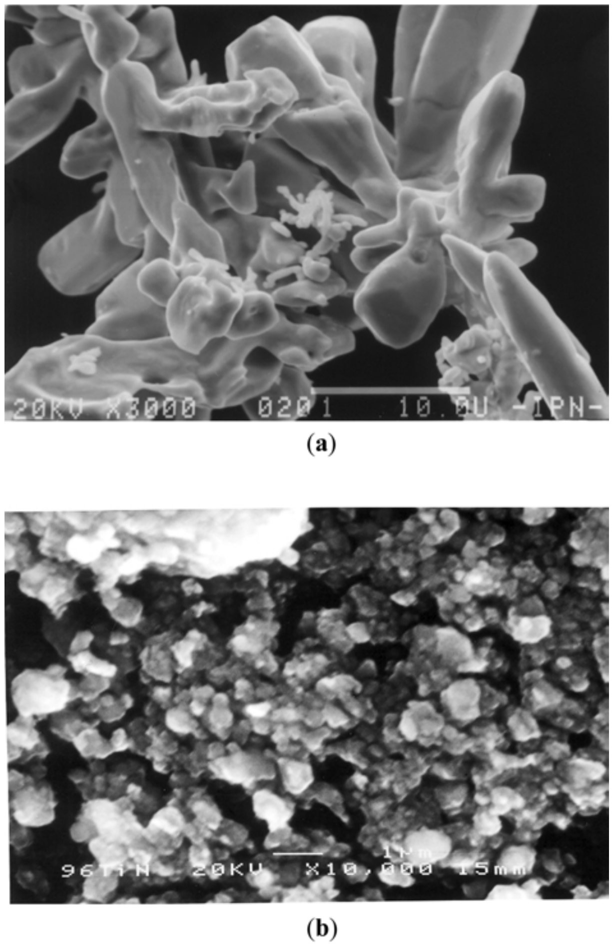

Fig. 2. SEM micrographs of (a) a powder of original Ti and (b) a powder milled in the attrition mill for 96 hours.

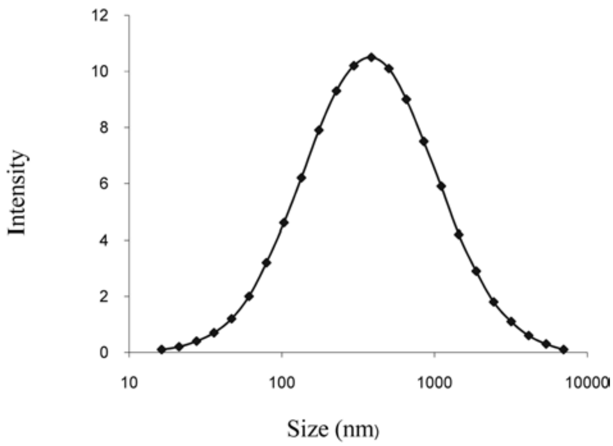

Fig. 3. Particle size distribution of the powder milled for 96 hours.

The size distributions of the TiN powders obtained by milling in the attrition mill for 96 hours appear in Fig. 3. These powders show a Gaussian particle size distribution. The powder milled in the attrition mill reaches an average size of around 500 nm, but has a very wide size distribution ranging from 20 nm up to 5,000 nm (5 μm).

Discussion of results

The formation of the TiN phase by reactive milling depends on several factors, including the type of mill, the atmosphere of milling, the ball-to-Ti powder load-ratio, the milling temperature, and ball size. In this study, the main difference studied was the type of mill.

XRD results indicate (in a general manner) that in both mills, upon the reaction between the powders and the nitrogen of the air, there appears a phase identified as TiN-type, with a cubic structure. The powders milled in the attrition mill for 96 hours have a lattice parameter of 4.38 Å, which would correspond to a Ti (N, O, C) compound. This value is different from the lattice parameter of pure TiN, which is 4.242 Å.

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

The previous discussion shows the advantages of the reactive milling being carried out in an attrition mill- although the disadvantages of this method must be taken into account, *i.e*. a greater contamination with iron, and the fact that only a certain amount of powder can be milled at one time.

Conclusions

Spherical-shaped particle powders with a TiN-type phase can be synthesized very easily from elementary powders of Ti by means of reactive milling, using an attrition mill, in an air atmosphere. In the attrition mill, 96 hours of milling gives a type Ti (N, O, C) compound, with a lattice parameter of 4.38 Å and an average particle size of 500 nm. This powder builds into clusters due to its small particle size.

Acknowledgments

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