Obtaining ZrN, ZrO, ZrC powder in a nitrogen atmosphere by means of a Ball Mill.

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Abstract. Properties such as thermal insulation, excellent structural and chemical stability, resistance to high temperatures make the zirconium compounds, their oxides and nitrides are of great interest to the scientific community. In the present work, the production of ZrN, ZrO and ZrC from a highly energetic ball mill is experimentally studied. The synthesized powders were characterized by X-Ray Photoelectron Spectroscopy and Scanning Electron Microscopy. The spectra performed demonstrate the ZrN, ZrO and ZrC formation, in addition the images obtained by SEM show a considerable increase in the size of the particles, since initially they were at 100 nm and were obtained in the order of 250 nm.

1. Introduction

Zirconium compounds, their oxides and nitrides are of great interest in different fields of application [1], due to their properties such as thermal insulation, excellent structural and chemical stability, as well as their good resistance results in aggressive operations, since they allow to work at high temperatures as turbines for the aerospace industry. Currently the zirconium focuses its attention on the manufacture of electronic devices as sensors [2]. The milling process has gained importance due to the large number of products that can be obtained in certain environmental conditions, also because the processing time is much shorter than other systems [3]. One of the objectives of grinding is to reduce the size of the particles [4], by means of a mechanical alloy. This process has been established for several years and considered one of the best methods to produce high quality mineral powder [5], which can produce homogeneous nanoparticles [6]. This technique involves the repeated fragmentation of dust particles in a highly energetic ball mill; in the first stage, the material suffers a deformation due to the flattening of the particles, then due to this flattening they tend to stick together and the size of the particles increases [7]. As milling progresses, parts of this adhered material are separated from the grinding balls by forming particles of different sizes due to continuous circular motion. The centrifugal force caused by this rotation acts on the grinding load (balls and material), causing them to roll on the inner walls of the container rising and throwing through the vessel at high speeds.

In the present work, the production of ZrN, ZrO and ZrC from the repeated fragmentation of zirconium powder in a nitrogen atmosphere by means of a ball mill is experimentally studied. Three types of tests were carried out for grinding times of 1, 3 and 5 hours. The synthesized material was characterized by X-Ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) where it was possible to demonstrate the presence of the components as well as the growth of the particles of the mentioned material and
leaving the study open in order to improve the conditions that allow reducing the size of the particles to these components.

2. **Set up**

Three types of milling were carried out in times of one hour (S1), three hours (S2) and five hours (S3), the conditions can be observed in table 1. The milling was carried out with rest intervals of 2 min, where the direction of the rotation was changed in each interval; a speed of 400 rpm was used. The ratio in each case was 1:10 of the weight of the balls per material. The mill used Retsch brand PM 200, with a 50 ml container, which was introduced nitrogen gas.

The high resolution spectra of XPS were obtained in an XPS / ISS / UPS-A Centeno SPECS. For the measurements, a monochromatized Al Kα X-ray source (FOCUS 500) operated at 200 W was used. The energy of the hemispheric analyzer was set at 100 eV for the general spectra and at 30 eV for high resolution spectra. The regions analyzed for the samples were: C1s, O1s, N1s and Zr3d. To perform the XPS analysis, the samples were placed on copper conductive tape, since the samples were in powder. The spectra were deconvoluted with casaXPS program, Lorentzian and Gaussian functions were used and the 284.6 energy (C1s) as calibrating. An Electronic Scanning Microscope - SEM brand TESCAN model MIRA 3 FEG-SEM was used to obtain 100,000X images at a field distance of 2.08 μm. Before entering the sample to the SEM it was necessary to coat it with Au.

| Sample | weight Zr (g) | Time of grinding | Diameter of the balls | Number of balls |
|--------|---------------|-----------------|----------------------|----------------|
| S1     | 2.06          | 1 h             | 3 mm                 | 224            |
| S2     | 2.01          | 3 h             |                      |                |
| S3     | 2.04          | 5 h             |                      |                |

3. **Results**

In figure 1, C1s spectral line to different times of the milling is observe. S1 sample is find 284.6 eV, 283.47 eV, 284.6 eV ± 0.3 eV and 287.06 eV ± 0.3 eV binding energies, in the S2 sample 284.6 eV, 285.86 eV ± 0.3 eV and 288.55 eV ± 0.3 eV binding energies and S3 sample 282.82 eV, 284.6 eV ± 0.3 eV and 287.85 eV ± 0.3 eV binding energies. In the literature is observe that energies under 283 eV are characteristic to a carbide [8], in our case it could be assigned to ZrC, the which is present in S1 and S3 samples. In these figure is observe 284.6 eV binding energy too, to calibrated the spectrum, and energies upper to 284.6 eV were assigned to CNx and CO components [9, 10].

![Figure 1. C1s spectral line](image-url)
In figure 2 is observe change the O1s spectral line to different times of the milling. The carbides metallic (ZrO and ZrO$_2$ components) appear in energies under to 531.00 eV [11, 12], in our samples 528.21 ± 0.3 eV, 529.8 ± 0.3 eV for S1 sample, 529.54 ± 0.3 eV, 530.73 ± 0.3 eV for S2 sample and 530.61 ± 0.3 eV, 531.03 ± 0.3 eV for S3 sample; the oxycarbide only was found in S1 and S2 samples (531.25 ± 0.3 eV and 531.88 ± 0.3 eV) [13] besides that oxynitrades appear in S3 sample in energies to 532.7 ± 0.3 eV [8].

![O1s spectral line](image1)

Figure 2. O1s spectral line

In figure 3 is observe N1s spectral line to different times of the milling. 395.49 ± 0.3 eV (S1 sample), 395.81 ± 0.3 eV and 397.73 ± 0.3 eV (S2 sample) and 395.33 ± 0.3 eV (S3 sample) binding energies correspond to nitrogen hybridizations with transition metals, and 398.99 ± 0.3 eV (S1 sample) and 398.77 ± 0.3 eV (S3 sample) are energies that correspond to oxy/carbide nitrides [14-16].

![N1s spectral line](image2)

Figure 3. N1s spectral line.

In figure 4 is observe Zr3d spectral line to different times of the milling. To every sample is found ZrO$_2$ ( 181.52 ± 0.3 eV S1 sample, 183.2 ± 0.3 eV S2 sample and 181.45 ± 0.3 eV, 182.47 ± 0.3 eV S3 sample) [17]. 180.32 ± 0.3 eV (S1 sample) and 180.55 ± 0.3 eV (S2 sample) are assigned to ZrC [18] and 180.77 ± 0.3 eV (S2 sample) is assigned to ZrN [19]. In milling energies at 3 hours was possible has ZrN components, beside with ZrO; in next works will intend increase the amount ZrN, to obtain a 100% ZrN powder.

In Figure 5, SEM images at 500 nm are observed, for a) Zirconium powder, b) S1, c) S2 and d) S3. For the dust of Zr particles of radios between 113 nm and 130 nm are observed, which leads us to conclude that effectively have nanoparticles to start the process. In S1 an increase in size between 229 nm and 265 nm is observed, this increase is due to the absorption of nitrogen, carbon and oxygen. For S2 the size of the particles is maintained. Finally in the grinding of five hours there is a considerable increase in the size of the particles since they are around 260 nm and 389 nm, in this case there is a coalescence of the nanoparticles.
4. CONCLUSIONS
The components ZrN, ZrO and ZrC were obtained through the grinding process. The morphological results show a considerable growth in the size of the particles, with respect to the zirconium used initially, which leads to rethink experiments with changes of variables over time of 3 hours, to obtain nanoparticles of zirconium nitride. The evolution of the zirconium nitride phase to the oxynitride takes place regardless of the grinding time under a nitrogen gas atmosphere and remains as a research subject in future work.
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5. References

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