(54) Title: TREATMENT OF MINERALS FOR EXTRACTION OF ZIRCONIUM

(57) Abstract

A mixture of alumina (Al₂O₃) and zircon (ZrSiO₄) was subjected to mechanical milling. The presence of alumina was found to greatly enhance the disordering of zircon. Acid leaching of the milled oxide mixtures resulted in complete dissolution of the zirconium, along with a proportion of alumina and only traces of silica. Zirconium leaching was not possible with zircon milled alone. Quantitative results of the leaching process are given.
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TREATMENT OF MINERALS FOR EXTRACTION OF ZIRCONIUM

Technical Field

The present invention relates to the treatment of minerals, and particularly for the treatment of zircon mineral (ZrSiO₄) for the extraction of zirconium. More particularly, the present invention relates to the cold milling of particulate zircon mineral to form nanostructured products, from which the silica (SiO₂) and various minerals can be separated by a leaching process.

Background of the Invention

The mechanochemical treatment of inorganic solids is very much an open subject. It has almost limitless potential application to many processes in materials science and in the industrial fields of metallurgy and ceramic materials technology. Of these, minerals extraction is an extremely interesting target for practical application of mechanically activated chemical processing. As a result of the smaller particle sizes, higher surface areas and surface energies produced by mechanical processing, many structural transformations or chemical reactions can occur which are energetically unfavourable under ambient conditions of temperature and pressure. It was recently demonstrated that transformation and chemical reduction for complex oxide compounds occurs during mechanical milling.

Zirconium is an important material in the nuclear industry, where it is used as cladding for fuel rods. While this accounts for more than 90% of Zr metal consumption, the metal also finds many other chemical and industrial uses. The mineral zircon (ZrSiO₄) would seem to hold great potential as a source of zirconium. However, its highly refractory nature makes separation a costly process. The traditional methods that are used to decompose zircon are either thermal or chemical. The thermal route involves dissociation using a plasma torch followed by rapid cooling, which causes zirconia and silica to crystallise individually. Zircon can be decomposed chemically but only by the use of aggressive reagents and elevated temperatures the two major process routes employed being alkali fusion and carbochlorination. Both thermal and chemical routes are economically expensive with high energy inputs. Therefore, a process which renders zircon readily soluble, and thereby allows simple chemical recovery of the Zr, should
have vast benefits to the associated industries. In this application, the inventors provide results of the mechanical milling of zircon with alumina.

Ball milling of ores, with and without additives, to facilitate the comminution process (the reduction of particle size) is not new. The early potential of ball milling for the reduction and extraction of ores, however, has generally not been fulfilled, and interest in such ore processing technology has waned. The development of a new form of high energy ball mill at The Australian National University, and the success that has been achieved in mechanical alloying work with that ball mill (see, for example, the specifications of International Patent Application Nos. PCT/AU91/00248, PCT/AU92/00073 and PCT/AU94/00057, have stimulated new interest in the cold milling of ores. That new ball mill, which is described in the specification of International Patent Application No. PCT/AU90/00471 (WIPO Publication No. WO91/04810), enables controlled energy milling of a charge to be effected. The present inventors have now discovered that under certain milling conditions, minerals containing silica, such as zircon, can be reduced while being converted into a nanostructural form, and that silica and other minerals can be removed from this product (for example, using hydrochloric acid).

The basic requirements of the cold milling process are: (i) that high energy milling is carried out at room temperature for a sufficient time period (up to 300 hours) to produce a powder having nanostructural form, and (ii) that the milling is effected in the presence of suitable additives to the ball mill charge.

**Summary of the Invention**

The present invention seeks to provide a method of treating minerals containing silica, such as zircon mineral, to convert such minerals into a form where the silica content and the various other minerals can be removed by a simple leaching process.

The present invention seeks to provide a method of treating minerals containing silica, utilising a cold milling process.

In one broad form, the present invention provides a method of treatment of silica
containing minerals to facilitate the removal of silica and various minerals. The method
comprising high energy milling of the silica containing mineral in particulate form in
the presence of a suitable additive for a period sufficient to form a nanostructural
product.

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Preferably, said silica containing mineral is zircon (ZrSiO₄).

Also preferably, said additive is a chemical activator.

10

Most preferably, said chemical activator is alumina (Al₂O₃).

In a preferred embodiment said nanostructural product is zirconia (ZrO₂).

Preferably, the high energy milling is effected in a ball mill of the type described
PCT/AU90/00471.

Preferably the method includes the additional step of leaching the nanostructural
product of the milling to remove at least a major proportion of the zirconia (ZrO₂)
therein.

20

Preferably, said leaching is effected using acid, such as hydrochloric acid.

**Brief Description of the Drawings**

25 The present invention will become more fully understood from the following
detailed description of a preferred but non-limiting embodiment thereof, described in
connection with the accompanying drawings, wherein:

Fig. 1 is a schematic diagram of ball mill used in experiments, the mill being
shown with magnets in a high energy grinding and impacting configuration:

30

Fig. 2 shows XRD patterns of dry milled zircon: a) premilled material b) 170 h.
c) 340 h, and d) 500 h;
Fig. 3 shows XRD patterns of dry milled zircon with alumina a) premilled material b) 170 h. and c) 340 h;

Fig. 4 shows EDXRA spectra of milled zircon with alumina: a) 170 h, and b) 340 h;

Fig. 5 shows EDXRA spectra of milled zircon with alumina after leaching: a) milled 170 h and b) milled 340 h; and

Fig. 6 shows EDXRA spectra of solids obtained from filtrates after drying: a) sample milled 170 h, and b) milled 340 h.

**Detailed Description of preferred Embodiments**

A preferred but non-limiting embodiment of the invention will be hereinafter described in relation to an actual experimental procedure, describing the results and conclusions drawn therefrom. It should be noted that this embodiment is provided for the process of understanding the invention, but, the invention should not be considered to be limited to the described embodiment.

**EXPERIMENTAL PROCEDURE**

The milling process was conducted in a vertical stainless steel AISI lini-Ball mill operating in high energy mode at room temperature under vacuum (-100 Pa). See Fig.1 for a schematic diagram of the milling process. Four ferromagnetic balls (α-Fe with Cr hardened surface) with a weight of ~70 g each were used. By application of a strong external magnetic field during milling the effective ball mass was increased to ~5 kg. Use of the magnets, designed to control the ball movement, has been described in earlier literature.

The mill was charged with 4.36g of zircon (Westralian Sands Ltd, premilled to 0.5-1.0 mm) and 3.64g of alumina (α-alumina, 1.0Rm. Leco Corp), i.e. a 3:2 molar ratio of Al₂O₃:ZrSiO₄. This composition was shown by Di Rupo et al to be optimal for "reaction sintering". The air was then removed from the mill. Milling was carried out at a rotation speed of ~160 rpm. and samples taken at 170 and 340 hours. A control
sample, containing 8g of zircon, was also milled.

Leaching of milled materials was carried out as follows: Concentrated HCl (36%) was added to 0.2-0.3g of sample (accurately weighed) in a ratio of 50ml acid per gram of sample, and allowed to leach at room temperature for a) 1 day with dilution to 3 times initial volume using deionized water and leaching for a further 3 days, or b) 4 days with no dilution. Both methods produced identical results. Samples were agitated several times per day. The leached solutions were then filtered through pre-weighed 0.2 μm Nucleopore polycarbonate filters (after a dilution for method b), dried at 105°C for 24 hours, and the solids weighed. The filtrates were made up to 100ml with water for chemical analysis.

The structural analysis of samples was performed by X-ray powder diffraction (XRD) using a Philips diffractometer with CoKα radiation. XRD patterns were identified using the PDF CD-ROM Retrieval/Display System V2.13a 1987-1992 (International Centre for Diffraction Data). Solid state elemental analysis was carried out using the Rutherford backscattering technique (RBS); liquid state analysis for Fe, Si, and Al using Flame Atomic Absorption Spectrometry (varian Spectra AA-30). Qualitative elemental analysis was carried out using Energy-Dispersive S-ray Analysis (EDXA) on a Jeol 6400 scanning electron microscope. Gravimetric analysis of solutions for Zr was carried out using mandelic acid precipitation.

RESULTS

The milling of zircon with alumina appears to result in a rapid disordering of both initially crystalline materials under the conditions examined. The X-ray diffraction (XRD) patterns of milled zircon (as a control) is shown in Fig. 2. The milled zircon shows significant line broadening and decrease in peak intensities when compared with the premilled material. The other main development is formation of a broad peak centred around 2θ = 34°±2° with full width at half height Δ2θ = 15°±2°, which indicates the existence of a partially disordered phase. The process of formation of the disordered phase is milling time dependent and for the 340 h and 500 h milled samples is clearly visible. This disordering, which increases with time to approximately 85% at 340 h and nearly 100% after 500 h, is in good agreement with recently reported work.
The milled complex oxide mixture (Fig. 3) undergoes a rapid loss of the crystalline zircon phase, showing only a minimal (200) reflection after 170 h. which is barely detectable after 340 h. The alumina disorders more slowly, but this process also is almost complete by 340 hours. This would seem to indicate that the disordering process of zircon is enhanced by the presence of the alumina, possibly due to the lower hardness of zircon in comparison to alumina (7.5 and 9 Mohs respectively).

The hard abrasive nature of these oxides results in significant iron contamination from the mill construction materials - about 8.9wt% for milled zircon (340 h) and 18.4wt% for the zirconalumina mixture (340 h). The compositions of the milled materials (as given by RBS) are shown below in Table 1. These results agree well with values calculated theoretically from the starting composition, when allowance for Fe contamination is made. Note that Hafnium is always present as a contaminant of zirconium due to the highly similar chemical nature of the two, and is included in the values for Zr. Slight differences between theoretical and measured values of composition are due to the inherent inaccuracy of the RBS method when analysing for lighter elements such as oxygen.

Table 1. Composition of milled material as oxides (and iron) before leaching (as given by RBS)

<table>
<thead>
<tr>
<th>Chemical composition (RBS)</th>
<th>Zircon milled for 340 h</th>
<th>Zircon/Alumina milled for 170h</th>
<th>Zircon/Alumina milled for 340 h</th>
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<tr>
<td>Al₂O₃ wt%</td>
<td>0</td>
<td>41.3</td>
<td>39.4</td>
</tr>
<tr>
<td>Fe wt%</td>
<td>8.9</td>
<td>14.6</td>
<td>18.4</td>
</tr>
<tr>
<td>SiO₂ wt%</td>
<td>29.7</td>
<td>14.2</td>
<td>13.6</td>
</tr>
<tr>
<td>ZrO₂ wt%</td>
<td>61.4</td>
<td>29.9</td>
<td>28.6</td>
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Milled Al₂O₃/ZrSiO₄ powders examined by EDXA showed significant amounts of Al, Si, Zr, Fe, and traces of Cr (a component of the steel from the mill and balls), as expected (Fig. 4).
Leached Materials

In order to determine if there were significant differences between zircon milled with alumina and zircon milled alone, both powders were examined in the leaching experiment. Zircon milled for 500 h (rather than 340 h) was used for leaching, as this sample had a higher degree of disorder and should therefore show any effect of milling more strongly. Leaching experiments on both powders show significant differences which are described below.

Addition of concentrated HCl to the milled zircon resulted in a slight fizzing reaction, after which the solid appeared quite inert. Upon adding HCl to the Al₂O₃/ZrSiO₄ milled mixture there was a more vigorous reaction and evolution of gas due to the contaminating iron reacting with the acid. This resulted in the solution rapidly becoming yellow, although the solid material remained black. A slower reaction with gradual bubble formation persisted for several hours after. Over a period of 4 days, the black solid became grey, then finally a dirty white. The zircon sample over the same period remained black. The percentage of solids recovered by filtration are given below in Table 2, along with values for material found in solution.

Table 2. Composition of filtrates and mass of solids remaining after leaching, as percentage of starting material (as oxides, and iron)

<table>
<thead>
<tr>
<th>Dissolved material</th>
<th>Milled zircon 340 h</th>
<th>Milled zircon/alumina 170h</th>
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<td></td>
<td>500 h milled sample</td>
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<tr>
<td>Al₂O₃ wt%</td>
<td>-</td>
<td>11.7</td>
<td>16.0</td>
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<tr>
<td>Fe wt%</td>
<td>-</td>
<td>12.2</td>
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<tr>
<td>SiO₂ wt%</td>
<td>-</td>
<td>1.05</td>
<td>0.5</td>
</tr>
<tr>
<td>ZrO₂ wt%</td>
<td>-</td>
<td>25.2</td>
<td>26.9</td>
</tr>
<tr>
<td>Solids remaining</td>
<td>% wt</td>
<td>93.3*</td>
<td>48.63</td>
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Note that a control solution (acid only) which went through the same leaching and filtration process contained no detectable amounts of Al or Fe, but did contain SiO₂ in an amount equal to the lowest detected in a sample, equivalent to around 0.1 wt% of the starting material.

Samples of leached powders and solids obtained from solutions after drying were also examined using EDXA. After leaching, peaks from Al and Si were still strongly present in the spectrum of the recovered powder, along with low intensity peaks indicating a trace of Zr. No contamination by Fe was detected, (cf. Figs.5a and 5b) in good agreement with the data presented in Table 2. Solid residues obtained by evaporating the filtrates showed Al, Zr, Cl and Fe as expected (Fig.6). From the elements present in the solid residue and its extremely hygroscopic nature it is assumed that the zirconium is present in the form of zirconyl chloride, ZrOCl₂ 8H₂O. Some contamination by Si was detected in the EDXA spectra.

Slight differences between the recovered and calculated amounts of zirconium can easily be accounted for by handline losses due to the small amounts of samples used (<200 mg), and by the error inherent in the RBS method, which was used to determine the starting compositions. As an example, the Fe content calculated by AAS (assuming complete dissolution of the Fe, as was shown above) is around 2wt% lower than that given by RBS. Thus, an error of about +2wt% would seem reasonable for all of the data presented.

From the above results for zircon/alumina milled powders, it can be inferred that the leaching process

i) removes little or no SiO₂,

ii) removes a significant proportion of the Al₂O₃, and,

iii) removes almost all of the zirconium.

The zircon milled alone, showing little mass loss upon leaching and having an Fe content close to this mass loss, was not examined further. Preliminary experiments with heat treatment show that the process of Zr dissolution can be greatly accelerated (<1
hour): this process is to be quantitatively examined in later studies.

Similar experiments using 10M NaOH as a leaching solution were also conducted. These showed minimal extraction of solids (3% dissolved for 500 h milled zircon, 9% dissolved for milled zircon/alumina mixture) and were not pursued further.

Finally, experiments with other materials milled with zircon have also been conducted and the products tested with acid, without any extraction Milling with sodium chloride, for example, does not result in disordering - presumably the softness of this material serves to protect the zircon rather than aid in its disordering. Milling with aluminium metal did produce a partly disordered material, which contained significant amounts of alumina (indicating reduction of the zircon had occurred), but again in acid did not show any leaching effect.

CONCLUSIONS

This procedure began as an attempt to produce a dispersion of crystalline zirconia (ZrO₂) in mullite (3Al₂O₃·2SiO₂) from zircon and alumina using mechanochemical processing. This would produce free ZrO₂ by acid leaching. This mullite-formation reaction is quite well known as a process called reaction sintering, which is usually carried out at temperatures of around 1600°C. In the course of this research it was hoped that the structural disorder produced by mechanical milling would induce a room temperature reaction, or significantly reduce the temperature required to undergo the mullite formation reaction. Acid leaching of the powders produced by milling showed that the zircon reactivated had been significantly altered, as is detailed below.

The ball milling of zircon mineral with alumina results in a disordered mixture which is highly amenable to leaching with hydrochloric acid in order to remove the zirconium. Zircon milled alone in similar conditions also results in a disordered phase. However the material so produced is still extremely inert to acid. The milling process also introduces a significant contamination of iron from the ball mill (much higher than is usually observed in mechanical milling) due to the hard abrasive nature of the oxides used: however the iron can be completely removed by the HCl leaching process.
After the leaching process, all of the zirconium was found to be in solution (within experimental accuracy). This is the most significant result of this work. In contrast, all of the silica remained in the solid, which raises interesting questions about the nature of the milled material. While significant amounts of the alumina were also found to have dissolved, most remained in the solid phase. The zirconium obtained from solution after drying appears to be present as the compound ZrOCl₂·8H₂O.

The milling and leaching process will be understood by persons skilled in the art to have significant potential as a low energy, low cost method for extracting zirconium from zircon.

It should be understood that the invention has been broadly hereinbefore described with reference to a particular embodiment and an actual experimental procedure. Numerous variations and modifications will become understood to persons skilled in the art. All such variations and modifications should be considered to fall within the spirit and scope of the invention as hereinbefore broadly described.
THE CLAIMS

1. A method of treatment of silica containing minerals to facilitate the removal of silica and various minerals, the method comprising high energy milling of the silica containing mineral in particulate form in the presence of a suitable additive for a period sufficient to form a nanostructural product.

2. The method as claimed in claim 1, wherein said silica containing mineral is zircon (ZrSiO₄).

3. The method as claimed in claims 1 or 2, wherein said additive is a chemical activator.

4. The method as claimed in claim 3, wherein said chemical activator is alumina (Al₂O₃).

5. The method as claimed in any one of claims 1 to 4, wherein said nanostructural product is zirconia (ZrO₂).

6. The method as claimed in any one of claims 1 to 5, in which the high energy milling is effected in a ball mill of the type described and claimed in the specification of International Patent Application No. PCT/AU90/00471.

7. The method as claimed in any one of claims 1 to 6, including the method includes the additional step of leaching the nanostructural product of the milling to remove at least a major proportion of the zirconia (ZrO₂) therein.

8. The method of claim 7, in which said leaching is effected using acid, such as hydrochloric acid.

9. A method of treatment of silica containing material, substantially as herein described.
10. A method of treatment of minerals for extraction of zirconium, substantially as herein described.
FIG. 1

STAINLESS-STEEL CELL

MAGNETIC STEEL BALLS

NdFeB-MAGNETS

VERTICAL PLANE AB

A

B
FIG. 3

(a) ZIRCON
+ ALUMINA
x IRON

(b)

(c)

INTENSITY (a.u.)

2θ

10°  30°  50°  70°  90°  110°

SUBSTITUTE SHEET (RULE 26)
FIG. 4(a)

FIG. 4(b)

SUBSTITUTE SHEET (RULE 26)
FIG. 6(a)

FIG. 6(b)
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

Int Cl: C22B 1/00 3/00 3/08 3/10 34/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC C22B 1/00 3/00 3/08 3/10 34/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JAPI: crush; grind; mill.
WPAT: crush; grind; mill

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>FR 2469462 A1 (RHONE-POULENC INDUSTRIES) 22 May 1981 see example 1, page 5 line 36 - page 6 line 35</td>
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Date of the actual completion of the international search
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8 January 1996

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