FORMATION OF ZIRCONIUM NITRIDE VIA MECHANOCHEMICAL DECOMPOSITION OF ZIRCON

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Over the last few years mechanochemistry has become well established as a new method of advanced materials preparation. Mechanochemistry can often provide a pathway for processes such as gas-solid chemical reactions, which would normally be considered unfavourable or impossible at room temperature. Recently we have demonstrated a mechanochemically activated process for extraction of zirconia from the mineral zircon ($ZrSiO4$) [1,2].

Formation of metal nitrides usually requires the use of expensive starting materials and processing, such as pure metals, high temperatures and plasma nitriding equipment. As a continuation of our zircon studies, in this paper we report some results of the Mechanochemical reduction of zircon, and for the first time subsequent reaction with nitrogen to form zirconium nitride (ZrN). This process can be described by the equation:

$$3ZrSiO_4 + 8Al + 1.5N_2 = 4Al_2O_3 + 3ZrN + 3Si$$

Milling was carried out in three steps: 1) low speed grinding of $Al+ZrSiO_4$ in vacuum, 2) high speed milling to effect the reduction, and 3) continued milling after the addition of nitrogen. Powders produced were examined by X-ray diffraction. The first step showed no reaction occurred during low speed grinding. The second step proved to be a slow reaction without the "ignition" often seen in other mechanochemical reduction works [3]. The final step was also gradual, and did not always go to full nitridation over the duration of the experiment, giving a product of composition $ZrN_{0.6}$ to $ZrN_{1.0}$. This is quite acceptable as transition metal nitrides are often non-stoichiometric [4].

These results show that the formation of a useful hard material such as ZrN can be formed from a raw mineral by two stage mechanochemical processing. Further investigations are currently being undertaken to eliminate Fe contamination and produce pure ceramic oxide-nitride composites.

1 T. Puclin, W. A. Kaczmarek and B.W. Ninham, *Mater. Chem. Phys.* 40 (1995) 105.
2 International PCT Patent Application, The Australian National University.
3 L.L. Wang, Z.A. Munir, and Y.M. Maximov, Review. "Thermite reactions: their utilization in the synthesis and processing of materials" *J. Mat. Sci.* 28 (1993) 3693.
4 "Ullmann's Encyclopedia of Industrial Chemistry", (VCH Verlagsgesellschaft, Weinheim) vol. A17 pp352-4.