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A study of formation of nanometric W by room temperature mechanosynthesis

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Abstract

Nanometric particles of elemental tungsten can be produced by solid state room temperature reduction of tungsten (VI) oxide with magnesium metal. The reaction is driven by high-energy ball milling powder mixtures of WO₃ and Mg and involves a thermite route that allows for very short reaction times (as small as 8 min) under the proper milling conditions. The evolution of the reaction was followed as a function of time by X-ray diffraction, showing a gradual decrease in crystallite size of the reactant WO₃, with formation of intermediate reaction products, until a near-instantaneous reaction takes place leaving only MgO and elemental W as final products. MgO was removed by leaching in diluted HCl and high purity tungsten (purity >99%) was obtained with a typical molar yield of 84%. The W powders are formed of impact welded aggregates of small particles of homogeneous dimension of about 70–100 nm, the typical crystallite size is 19 nm.

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1. Introduction

Tungsten is used in four main different applications [1-3]: as tungsten carbide, as an alloy additive, as essentially pure tungsten, and as tungsten chemicals. Tungsten carbide is probably the most common hard material in use today for cutting tools and other high strength applications because of its high hardness at high temperatures. This application accounts for about 65% of tungsten usage, mostly in the form of cemented carbides. For carbide formation the tungsten is blended with carbon and heated at high temperatures (about 1600 °C) in a hydrogen atmosphere. Scientific literature reports also the formation of WC by reaction between W and C during extended ball milling [4–6]. About 16% of tungsten usage is as an alloy additive: tungsten is added to steels and forms a dispersed tungsten carbide phase that imparts a finer-grain structure and increases the high temperature hardness. The finergrain size improves toughness and produces a more durable cutting edge. Metallic tungsten accounts for 16% of tungsten consumption; tungsten is often used because of

its high melting point and low vapor pressure. The best known use is for lamp filaments. Tungsten is also used as an electron emitter because it can be used at very high temperatures; it also improves arc stability and gives longer life to welding electrodes; metallic tungsten is also used in many other applications (furnace elements, heat shields, etc.). Nonmetallurgical uses include brilliant organic tungsten dyes and pigments that can be used in a variety of materials. Tungstates are used as phosphors in fluorescent lights, cathode-ray tubes, and X-ray screens, while tungsten compounds are used as catalysts in petroleum refining.

The most widely used process for producing tungsten is based on a long route from either ore wolframite (FeWO₄) or from scheelite (CaWO₄) [2,3]. Wolframite is dissolved in acid and the tungsten separated from impurities by lime precipitation as CaWO₄. Scheelite is then dissolved in acid and precipitated using ammonia to form ammonium tungstate which is subsequently calcined to form WO₃. The trioxide is thermally reduced with hydrogen to form metallic tungsten.

Mechanosynthesis has been shown to be very effective for preparation of many metals with high melting points and ceramic materials [4–11]. In the case of elemental

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tungsten, another route to form the metal is by reaction of scheelite with metallic magnesium during extended ball milling in a tumbling mill for 100 h in an inert atmosphere [4]: the final products are tungsten, CaO and MgO; the oxides can be easily removed by leaching in acid, leaving a fine powder composed of 99% pure tungsten metal.

Another interesting route for producing elemental tungsten is based on a mechanochemical synthesis using magnesium and tungsten trioxide as starting materials [12]. The reaction takes place during a room temperature, high energy milling process lasting only 60 s, to form metallic tungsten and magnesium oxide; subsequent leaching by dilute nitric acid of the unwanted oxide leaves elemental tungsten. That process is substantially a combustive reaction that takes place once the ignition temperature is reached during ball impacts: the conditions reported in literature allow for no control of the reaction, and an abrupt increase in temperature occurs; moreover, the final powders are polydisperse and of irregular shape, because the reaction takes place almost instantaneously, preventing homogeneous mixing and pulverization of the reactants, an important condition in order to get a homogeneous and finely dispersed powder product. In this work, we show how the mechanochemical route already reported in literature could be improved thanks to a very fast process based on the thermite reaction of Mg with tungsten trioxide with different milling conditions: the reaction pathway has been studied in order to be able to control the process in view of a possible scaling-up for commercial use. A higher ball-topowder weight ratio was employed in order to obtain very fine pulverization and very large contact surfaces of reagents, with longer (of the order of minutes) reaction times and with a more gradual release of the heat of reaction. The final product is thus a more finely dispersed powder, of regular, rounded shape, and fairly homogeneous nanometric (70-100 nm) dimensions, with crystallite size of the order of a few tens of nanometers (typical crystal size: 19 nm); all the reported properties are of great importance in view of possible use of these powders in powder metallurgy technology.

The process could thus be extended to tungsten minerals like scheelite and thus could find potential commercial applications, having lower costs and requiring relatively simple equipment in comparison with the industrial processes now in use.

2. Materials and methods

Tungsten (VI) oxide WO_3 (purity >99%, particles size about 20 microns) was provided by Aldrich. Commercial Mg (purity >99.5%, particles size between 350 and 125 microns) was bought from Pometon S.p.A. (Italy). The synthesis of elemental tungsten was performed in a vibratory ball mill (Spex 8000 mixer-mill) using carbon steel balls (diameter: about 8 mm) according to the reaction:

$$WO_3 + 3Mg \rightarrow W + 3 MgO$$

Milling was performed with a ball-to-powder weight ratio of 24:1. The vial used for milling was sealed in a glovebox under a pure argon atmosphere; Mg was employed in excess (about 10% w/w more than stoichiometric amount) in order to account for surface oxidation of the metal and to residual oxygen that could be adsorbed onto reactant surfaces and onto vial walls. Milling was performed at room temperature and different reaction times were investigated ranging from a few minutes up to several hours.

Milled products were then leached using 2.0 M HCl under magnetic stirring for 2 h (solid content of the dispersion: 1% w/w) in order to remove MgO, Fe released by the vial and milling balls, and unreacted Mg. The residual solid was then centrifuged and washed first with 2.0 M HCl and then several times with distilled water in order to remove traces of acid. Powders were finally dried at 120 °C in air.

Scanning electron micrographs of the products were obtained through a JEOL 5600 instrument.

XRD patterns were collected on milled products and leached products using an INEL diffractometer equipped with a CPS-120 position-sensitive detector and a germanium monochromator using Co K α (λ =0.1789 nm) radiation. The mean crystallite size was calculated from the method described elsewhere [9,13] using the full width at half maximum (FWHM) of the X-ray peaks corrected for instrumental broadening and taking into account strain effects.

3. Results and discussion

Milling of tungsten (VI) oxide and magnesium has been investigated at different reaction times in order to understand the mechanism of the reaction. In Fig. 1 the XRD diffraction data for milled powders at different milling times are reported: it is evident that reaction is nearinstantaneous and takes place after only 8 min of milling. This trend is quite similar to that found for reaction of boron oxide and magnesium [14-15]. Further milling of the mixture results in a widening of W(0) diffraction peaks (see Fig. 2). After a few hours milling, W-Fe compounds begin to form (Fe is present as a pollutant due to ball and vial wall consumption during prolonged milling), thus decreasing the overall final yield of metallic tungsten (Fig. 2). Interesting information on the reaction path can be obtained by analysis of XRD data at different milling times before reaction has taken place. The crystal sizes of elemental Mg and W(VI) oxide against milling time are reported in Fig. 3. It is clear that the crystal size of Mg is quite large, between about 40 and 65 nm, in comparison with W(VI) oxide. The starting powders show a gradual decrease in crystal size for Mg down to about 40 nm after 4 min milling, then crystal size increases again: this could



Fig. 1. XRD traces of mixture Mg+WO₃ at different milling times (milling conditions: 0.87 g powders, balls-to-powders ratio 24:1, 8 balls) and powder products after leaching (elemental W). (\bigcirc) Mg; (+) WO₃; (*) W; (\times) MgO; (#) W₂₀O₅₈.

be due to local melting of Mg metal because of temperature increase with local reactions between Mg and WO₃ after a few minutes milling (melting point for Mg is about 922 K, thus this temperature can be easily reached locally). On the other side, the crystal size of W(VI) oxide gradually decreases down to about 14 nm, when the reaction takes place in a near-instantaneous way, between the seventh and the eighth minute of milling, when the amount of excess surface energy is such that reaction can be self-propagating. After 7 min milling, a diffraction peak due to an intermediate reaction product is present that can be attributed to W₂₀O₅₈, thus showing that the reduction of W(VI) oxide is a very fast but multi-step reaction. Moreover, diffraction peaks of elemental tungsten are present in



Fig. 2. XRD traces of mixture $Mg+WO_3$ (milling conditions: 0.87 g powders, balls-to-powders ratio 24:1, 8 balls) after completion of the reaction at different milling times (3 h and 40 min); and powder products after leaching (purified powders after 3 h milling, and after 40 min milling). (*) W; (\times) MgO; (§) Iron–tungsten compounds.



Fig. 3. The crystal sizes of elemental Mg (\Box) and WO $_{3}$ (\bigcirc) against milling time.

the XRD spectra of milled powders even after only 4 min milling: this shows that a very small amount of W(VI) oxide begins to react with Mg as soon as a critical value of excess surface energy is reached: actually, this could be due to a statistical distribution of structural defects and to the extended network of intergranular boundaries (crystal size) for the powder and could take place even after a very short milling time, much shorter than the average one, as shown by experimental data. The free energy of the reaction between W(VI) oxide and Mg is highly negative, and the reaction is also strongly exothermic; moreover, the very high adiabatic temperature for the reaction (about 3710 K), calculated according to the procedure reported elsewhere [16] accounts for a thermite reaction: thus, once a critical crystal size for W(VI) oxide is reached, reaction can be self-propagating, with Mg reducing the mechanically activated W(VI) oxide (the kinetics of this reaction is clearly favored by increasing the surface energy of W(VI) oxide and favoring the intimate contact by reactants during ball milling). A typical molar yield of 84% for metallic W has been obtained: the crystal size of W(0) after 8 min milling has been found to be 19 nm; in this case, the crystal size after leaching with acid did not show any significant increase. Thus, no substantial dissolution of W(0) had taken place (massive metallic tungsten is slowly attacked by concentrated mineral acids only at high temperatures). The crystal size for W(0) after prolonged milling showed a significant decrease after 3 h milling (9 nm) but not after 40 min milling (19 nm, the same result obtained after 8 min milling). Leaching with acid of powders after 3 h milling resulted in an increase of crystal size for elemental W; no substantial changes were found in the other case (40 min milling). This means that prolonged milling for 3 h favored the formation of a large fraction of small crystallites of W(0), as confirmed by the small average crystal size; these crystallites are more reactive and more easily leachable even employing a diluted mineral acid like HCl.

SEM micrographs (Fig. 4) for elemental W powders



Fig. 4. SEM micrographs at different magnifications of elemental tungsten powder after leaching.

after purification (the powders have shown a W content higher than 99%, as shown by XRD analysis and by microanalysis; a quantitative determination of the residual Mg content with a volumetric titration method with EDTA solution confirmed the other analytical data) clearly show the presence of a submicrometer size population, with a very large amount of particles below 200 nm, although particles tend to aggregate. At higher magnification, powders look like aggregates of very small particles with dimensions lower than 100 nm.

Submicrometer particles have been obtained thanks to the very fine pulverization of powders during high energy ball milling: the presence of MgO as co-product has acted as a dispersant for the metallic W, avoiding agglomeration of W (this kind of problem is often met in high energy milling).

A simple leaching with acid can remove the unwanted MgO leaving pure W as a finely dispersed powder.

The route that has been described here is very important because elemental W powder can be obtained on a submicrometer scale with a one-step process followed by leaching with acid: the traditional industrial process involves a technology that requires higher costs. A further milling of powders after completion of the redox reaction for producing W can favor the production of finer powders. On the other side, it also favors formation of unwanted compounds (e.g. iron-tungsten compounds, as it has been shown previously) thus decreasing the final yield of elemental W, with pollution of the product with compounds that in some cases cannot be easily removed with a simple leaching with acid: for this reason, no investigations were performed with long milling times.

4. Conclusions

A new method for obtaining metallic tungsten by reduction of tungsten (VI) oxide with magnesium thanks to mechanosynthesis has been shown to be accomplished with high yields and short reaction times (as low as 8 min). The level of pollution from grinding media, in the limit of the investigation techniques that have been employed, does not seem to be significant, and no other reaction products seem to be present in appreciable amounts, thanks to the very large contact surface between reactants and the selfpropagating nature of the reaction that allows for very short reaction time. This new process for producing elemental tungsten could thus be very interesting in view of industrial applications. In fact, the final product is a nanostructured powder (crystallite size less than 20 nm) formed by nanometric particles with regular rounded shape that are relatively monodispersed in the 70–100 nm range.

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