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Nanostructured tungsten carbide synthesis by carbothermic reduction of scheelite: A comprehensive study

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ABSTRACT

Mixtures of scheelite and graphite or carbon black, with different $CaWO_4$:C weight ratios, have been mechanically milled for 24 h. One mixture was mechanically milled for 8 h to assess the role of a shorter milling time. The resulting powders have been studied by thermal analysis, isothermal annealing at different temperatures (1100–1400 °C), X-ray diffraction (XRD) and scanning electron microscopy (SEM) to determine the effect of temperature and content of carbon on microstructure and phase purity of tungsten carbide formed by carbothermic reduction of scheelite ($CaWO_4 + 4\,C \rightarrow CaO + WC + 3\,CO$). The experimentally observed reduction reaction sequence showed the formation of the intermediate phases Ca_3WO_6, W and W_2C. A thermodynamic analysis proved that tricalcium tungstate (Ca_3WO_6) is a stable phase that forms independently of the partial pressure of CO, and that – under inert gas flow – the reaction can take place at temperatures as low as 700 °C. However, the onset of the reaction was affected by the carbon content and heating rate, and therefore kinetics effects determine the temperature at which the reaction occurs.

All powders subjected to 1 h isothermal annealing exhibited micrometer-sized CaO particles and submicrometer-sized WC aggregates consisting of crystallites with an average size ranging between 40 and 90 nm, depending on carbon content and annealing temperature.

A shorter milling time did cause a small increase of residual W_2C in the powder after heat treatment.

A slight stoichiometric excess of carbon black was sufficient to ensure complete reduction of scheelite and formation of high phase purity WC, with very small amounts of W_2C. After leaching with diluted HCl, the obtained powder is suitable for manufacturing ultra fine grained cemented carbides tools and wear parts.

1. Introduction

Raw materials are of utmost importance for both developing and developed countries because they are essential to maintaining and improving quality of life. Securing reliable and unhindered access to certain raw materials is a growing concern within the European Union (EU) and across the globe. Materials are considered 'critical' when there is a high demand from industry combined with a risk to their supply. According to a recent report published on May 2014 by the European Commission (EC), tungsten is still included in the EU list of critical raw materials (CRMs) [1]. Actually, twenty raw materials were identified as critical by the EC, being tungsten the material with the largest economic importance [1].

Tungsten is a very special metal, with unique properties (very high melting point, very high density, large hardness, chemical and thermal stability, just to mention a few). By 1930, the demand of tungsten and its alloys and compounds experienced a steady growth due to increasing industrialization in the world. Before and around 1920, tungsten was only important as a steel alloying element and as a filament in incandescent lamps. However, since 1930, cemented carbides (also called hardmetals) attained a greater share in tungsten consumption. The main component of hardmetals is tungsten carbide (WC), one of the hardest materials. Cemented carbides are hard but "flexible" materials. In fact, their properties can be tuned and adjusted by changing composition and microstructure, e.g. by varying the amount and grain size of WC, the content of the binder phase (Co or Ni), and/or by adding other carbides (such as TiC and/or TaC). Consequently, cemented carbides are in reality a very wide range of materials with different properties, and are used mainly for cutting tools, abrasives, dies, or molds. The ability to adjust the properties of a tool, or of a wear part, to fit a specific application represents an important advantage over high speed steel, and explains the replacement of the latter in many industrial productions. Therefore, it's not surprising to discover that more than 60% of the world's consumption of tungsten is in the form of tungsten carbide [2,3] and, therefore, cemented carbides are the main driving factor behind tungsten demand. In addition, hard metal with ultrafine grain size (≤200 nm) is attracting a growing interest in the world tungsten carbide market, and nanocrystalline (<100 nm) WC–Co materials are the subject of interest of research programs owing to the expectations

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that the mechanical behavior of the sintered part may improve significantly when grain sizes reduce to nanometer scale [3,4].

Several factors have resulted in the EU categorising tungsten as a CRM. Actually, China accounts for 85 % of world tungsten mine production. Other producers are Austria, Bolivia, Canada, Peru, Portugal, Russia, Thailand and other countries in Africa.

Chinese domestic demand has increased rapidly in the past years. This increase in Chinese demand, combined with increased controls by the Chinese Government on domestic tungsten industry and tungsten exports, has strongly contributed to a rising tungsten price [3]. Moreover, world consumption of primary tungsten is forecasted to grow by ~3–5 % annually over period 2014–2018 [5]. These facts should explain the concerns over security of supply of tungsten to western processors and industry end-users.

Metallurgy of tungsten usually starts from wolframite, (Fe, Mn)WO_4, and scheelite, $CaWO_4$. The production of WC from tungsten ores currently requires the prior production of tungsten metal. The preferred routes include concentration by mineral processing techniques followed by chemical dissolution. About 70 % of world tungsten reserves are in the form of scheelite mineral. Scheelite has a tetragonal crystal structure and is normally found in quartz veins and in contact with skarn ores of complex mineralogical composition. From an ore, scheelite is typically concentrated via a flotation process [6]. Then, processing of scheelite concentrate starts with its digestion in acid followed by base treatment to obtain Na_2WO_4 solution under hydrothermal conditions. After several solution treatment and purification steps, the intermediate product is pure ammonium paratungstate (APT). Tungsten is then obtained from APT by conversion to tungstic oxide (at 300–800 °C) followed by reduction with hydrogen (600–1100 °C). Finally, WC is prepared from elemental tungsten and carbon black at temperatures as high as 1300–1700 °C under high vacuum or highly purified reducing atmosphere [2,7]. The high cost of WC production is attributed to:

a) the rising price of the raw material,
b) a number of complex hydrometallurgy steps and several high-temperature processes.

The technology currently employed to produce WC powders descends from the technology of tungsten metal production and, therefore, involves energy and environmental costs to synthesize high purity powders of the metal. In fact, toxic and hazardous chemicals are required in the complex processing and purification sequences involved in the production of pure APT [6]. Moreover, several energy-intensive, high temperature steps are needed to calcinate APT, to reduce WO_3 to W, and to convert W into WC.

The creation of a supply source of WC for hardmetal manufacturing industries is becoming a serious issue, which could be addressed by finding enriched ore (e.g. enriched scheelite) in the international market in such quantities as to meet the production needs of small and medium-sized enterprises (SMEs) that produce hard metal components, tools and wear parts. In addition, processes which could allow producing WC powders by reducing the use of chemicals and the amount of industrial waste, as well as by decreasing the number of high-temperature processing steps and their temperatures, are particularly appealing from an environmental point of view. For both these reasons, there is a renewed interest in the carbothermal reduction of tungstates and, in particular, of scheelite [8,9].

Terry and Azubike [10,11] studied the reduction–carburization (with graphite and coal) of chemically prepared $CaWO_4$. The scheelite/graphite, or scheelite/coal, weight ratio they employed ($CaWO_4$:C = 75:25) was such that the mixture contained twice the stoichiometric quantity of carbon required by reaction:

$$CaWO_{4(s)} + 4C_{(s)} \rightarrow CaO_{(s)} + WC_{(s)} + 3CO_{(g)}. \tag{1}$$

They used rather coarse powders of $CaWO_4$ and graphite (or coal), with a grain size of several tens of μm, and could not attain complete conversion to WC and CO even after 20 h at 1200 °C. XRD data showed the formation of Ca_3WO_6 and W as intermediate phases and suggested that carbon diffusion is the rate determining step for WC formation. As a consequence, Terry and Azubike proposed that the reduction sequence follows the path:

$$3CaWO_{4(s)} + 6C_{(s)} \rightarrow Ca_3WO_{6(s)} + 2W_{(s)} + 6CO_{(g)} \tag{2}$$

$$Ca_3WO_{6(s)} + 3C_{(s)} \rightarrow 3CaO_{(s)} + W_{(s)} + 3CO_{(g)}, \tag{3}$$

and, finally, the tungsten metal is carburized to WC via W_2C.

Few years later, Johnson and Nguyen [12] studied the same carbothermal reduction of $CaWO_4$ with carbon black at 1227 °C, also under an atmosphere of CO. They too used a mixture of $CaWO_4$ and carbon black powder with a 75:25 weight ratio. Their findings confirmed that the first step of the reduction process is a solid-state reaction with carbon leading to Ca_3WO_6 as an intermediate product, and that the presence of CO in the gas atmosphere did not help the overall reaction kinetics.

Welham [13,14] studied the carbothermal reduction of a stoichiometric mixture of graphite and scheelite (i.e. $CaWO_4$:C = 85.7:14.3 weight ratio). He found that extensive milling allowed reducing the temperature of reaction by 300 °C. Actually, TGA-DTA (20 °C/min) data showed that, when the mixture was subjected to a preliminary 40 h ball milling, *i*) the weight loss due to CO formation (see reaction 1) occurred in the range 800–1100 °C and *ii*) the overall mass loss took place in two distinct steps (also evidenced by two endothermic overlapping peaks). However, Welham proposed that the reduction sequence follows a path slightly different than that proposed in refs. 10–12, being W_2C formed, instead of W, as an intermediate reduction product:

$$3CaWO_{4(s)} + 7C_{(s)} \rightarrow Ca_3WO_{6(s)} + W_2C_{(s)} + 6CO_{(g)} \tag{4}$$

$$2Ca_3WO_{6(s)} + 7C_{(s)} \rightarrow 6CaO_{(s)} + W_2C_{(s)} + 6CO_{(g)} \tag{5}$$

The positive role of high-energy milling has been reported also for the carbothermal reduction of natural wolframite [15,16].

More recently, Singh and Pandey [17] reported the synthesis of nanocrystalline WC by carbothermal reduction of scheelite ore ball-milled up to 100 h with activated charcoal. However, these authors employed a very large excess of carbon. In fact, the mixture they employed ($CaWO_4$:C = 1:2 weight ratio) contained twelve times the stoichiometric quantity of carbon required by reaction (1). Following the carbothermal reduction (4 h at 1025 °C), CaO was removed by leaching with diluted hydrochloric acid; the resulting powder showed only WC X-ray diffraction (XRD) peaks. Activated charcoal does not show well-defined XRD peaks and, consequently, a large excess of carbon, probably surpassing the weight of WC, could have remained after acid leaching.

In this paper we report a systematic study of the carbothermal reduction of ball-milled $CaWO_4$. For the first time, we performed a thermodynamic study of the process and studied in detail the effect of carbon phases (microcrystalline graphite and carbon black), $CaWO_4$:C weight ratio and temperature on the reduction-carburization of pure scheelite. The aim of the present study is to understand whether or not different processing parameters, namely temperature and $CaWO_4$:C weight ratio, can influence the reaction kinetics and the grain size of WC. Finally, along with traditional thermogravimetric analyses, suitable TGA-DSC experiments were performed by interrupting the heating cycle at specific points on DSC traces. The XRD analyses of the "quenched" powders allowed to confirm that Ca_3WO_6 forms prior to CaO (according to thermodynamics predictions), and that W and W_2C are metastable intermediates. Moreover, we show that the amount of carbon affects both the onset of the reduction reaction and the size of WC particles.