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Effects of fabrication method on initial powder characteristics and liquid phase sintering behaviour of tungsten

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ABSTRACT

Direct electrochemical production of tungsten involves removal of oxygen in solid state from an important tungsten compound, calcium tungstate, in molten salts. A detailed experimental study was performed to characterize the liquid phase sintering behaviour of the tungsten powder (W^E), which was produced by the direct electrochemical reduction technique. All of the tungsten heavy alloy (WHA) compositions covered in this study, contained four parts nickel, one part cobalt and over 90 wt% tungsten. The pellets were sintered at 1500 and 1550 °C under continuous flow of an equimolar hydrogen-argon gas mixture. A commercially available tungsten powder (W^C) was also used to prepare the same tungsten heavy alloy compositions as those prepared by the electrochemically produced tungsten powder to act as a control group. Scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and hardness measurements were employed for characterization. The analyses provided that; the tungsten powder as obtained from the direct electrochemical reduction process contained some unreduced $CaWO_4$ particles and they limited the grain growth and mass transport in the liquid phase. Although calculated relative densities were a bit lower than desired, the tungsten heavy alloys produced by the electrochemical reduction technique was promising for use when average grain size, dissolved tungsten contents and general/matrix hardness values are considered.

1. Introduction

The interest in tungsten powder production by an alternative method has increased considerably in the past few years due to strategical importance and high price of this metal [1–7]. Process drawbacks, such as too many steps to obtain tungsten oxides, low driving force for reduction of oxides, continuous heat requirement and difficulty of handling H_2 gas stimulate the investigations. A novel method for tungsten production using electrochemical reduction of $CaWO_4$ in a eutectic NaCl-$CaCl_2$ electrolyte was reported in 2010 [4]. According to the process [4–7], when an appropriate potential difference, which will not enable continuous electrolysis of molten salts compromising the electrolyte, is applied between the $CaWO_4$ cathode and the graphite anode, oxygen atoms in $CaWO_4$ dissolve into the electrolyte as oxygen ions and move to the anode where they form CO and/or CO_2. Metallic tungsten powder could be obtained after removing calcium containing by-products in dilute HCl solutions. The process promises significant energy savings and a relatively simple production procedure. Although scheelite ($CaWO_4$) is the most abundant form of tungsten deposits, it is rarely employed in conventional route due to difficulties in leaching of this mineral [8]. However, in the method mentioned above [4], scheelite mineral or pure calcium tungstate obtained by purification of scheelite can be used. When the mineral is directly reduced in the process, the product powder will be more appropriate to use in iron and steel industry. The powder will likely include iron, manganese, etc. impurities because these metals will also be produced by electrochemical reduction of their minerals that are usually found in scheelite deposits.

Initial particle characteristics such as particle size, shape, distribution and purity are the key parameters which determine the thermodynamic and kinetic procedure for the sintering process. The electrochemical reduction method [4] forms a tungsten powder which demonstrates different characteristics when compared to the commercial one. The properties such as a bunch of grape structure and nanoscale particle size are the distinct characteristics of the powder [4].

Tungsten and tungsten alloys are widely used in many specific industrial and ordnance applications due to possessing remarkable properties such as high density, high strength at high temperatures,

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good corrosion and wear resistance. However, high melting point and brittle nature of W limit its fabrication methods. They are mostly processed by powder metallurgy (PM) routes.

One of the ways to obtain desired mechanical properties is to infiltrate compacted tungsten powders by mostly copper containing liquids [9]. The infiltrated species with higher ductility causes a significant improvement on some mechanical properties such as wear resistance. Another method is to surround tungsten particles by a matrix phase which holds tungsten particles together and also improves toughness by undergoing deformation [10, 11]. The products obtained by the former and latter methods are named as tungsten-based metal matrix composites (MMCs) and tungsten heavy alloys (WHAs), respectively.

Desired strength and physical characteristics such as conductivity and magnetic permeability determine the compositions of the WHAs. They generally contain Ni and other suitable transition metals like Cu, Fe and Co [11–16]. In addition, trace amounts of some high density and refractory metals are added to control the grain size of W which is one of the most important concerns in liquid phase sintering treatment [17–19].

Although, the above-mentioned method [4–7] promises a potential to become an alternative to the current tungsten production technique, sintering behaviour of this powder has not yet been characterized. Selected WHA compositions were prepared using electrochemically produced (W^E) and commercially available (W^C) tungsten powders in this study. Both groups were sintered using different W contents, sintering temperatures and durations to address the sintering behaviour of W^E powder and its differences from a commercial powder. From this point on, the WHAs will be named as W^EHAs or W^CHAs depending on the tungsten powder used in the preparation.

2. Materials and experimental methods

Initial morphology and supplier information and particles size of the powders used in this study are given in Fig. 1 and Table 1, respectively.

The W^E powder was subjected to a pre-sintering treatment to

Table 1
General characteristics of the elemental powders.

Element	Particle size range (μm)	Bulk density (g/cm^3)	Source
W^C	1–5	4	Alfa Aesar 10400
W^E	< 1	1.5^B–2.8^A	Recived [20][a]
Ni	3–7	1.9–2.3	William Rowland Vale 123
Co	1.6	0.89	Alfa Aesar 10455

[a] Produced according to [20], B-before CET, A-after CET.

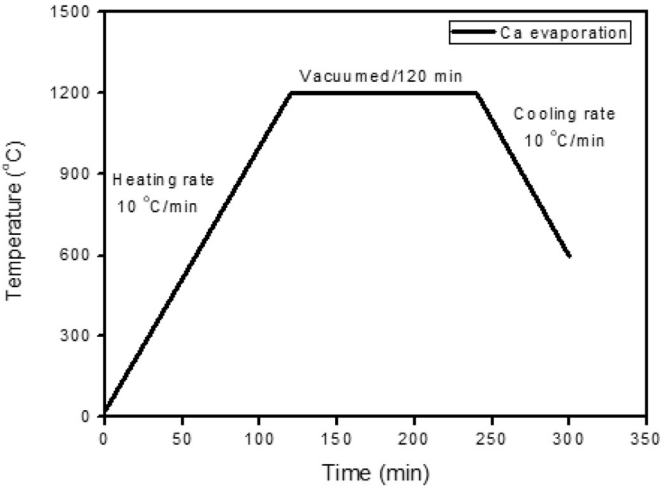

Fig. 2. Schematic representation of the calcium evaporation treatment (CET) procedure.

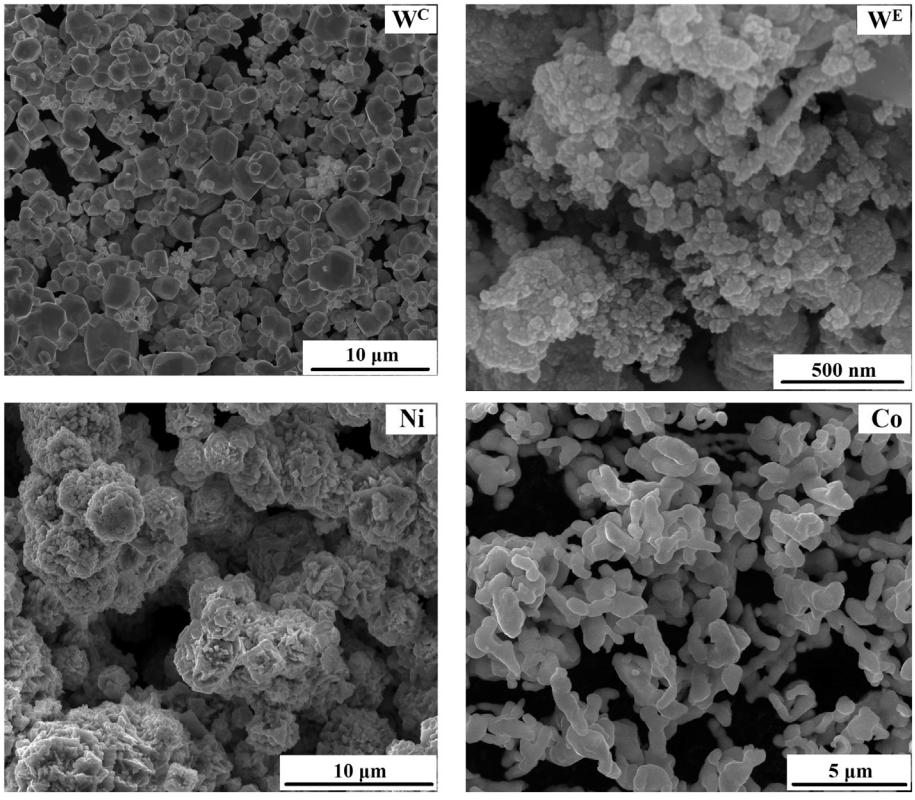

Fig. 1. Morphologies of the initial powders.