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Synthesis of nanocrystalline tungsten and tungsten carbide powders in a single step via thermal plasma technique

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ABSTRACT

The capability of thermal plasma technique to produce nanocrystalline tungsten powder from tungsten oxide and tungsten carbide powder form a mixture of tungsten oxide and carbon in a single step process was investigated. The amount of tungsten and tungsten carbide powders formed strongly depended on the hydrogen flow and power. Due to short exposure time of tungsten oxide and carbon to plasma, complete reduction or carburization was not achieved. The crystallite size of the reduced W and the resulting W_2C was under 70 nm. The free carbon, total carbon and surface area of the powders decreased with increase in hydrogen flow rate and power. The results from the study highlight the challenges involved in obtaining successful reduction and carburization of the tungsten oxide in a one step process. Near complete carburization was achieved after heating the plasma treated powders at significantly lower temperature of 1000 °C for 1 h in hydrogen atmosphere. The results from the study introduce a potential two-step process to economically manufacture nano size tungsten carbide powder.

1. Introduction

Nanocrystalline grain size cemented tungsten carbide has significant potential to exhibit superior properties of hardness and toughness resulting in improved performance and life of cutting tools [1–6]. The ability to economically manufacture nanocrystalline size tungsten and tungsten carbide powder is critical to obtain cemented tungsten carbide products with nano grain size structure.

The traditional process for manufacturing tungsten and tungsten carbide powders is very complex involving several critical steps. The tungsten powder is produced in multiple steps by reducing tungsten oxide in hydrogen atmosphere. The tungsten powder is further mixed with carbon and heated to temperatures above 1600 °C for carburization and formation of tungsten carbide [7,8].

Over the past few decades, several processes like wire explosion [9], ball milling [10,11], chemical vapor synthesis [12], plasma synthesis [5,6] etc. were developed to synthesize nano size tungsten powder. However, the developed processes are expensive involving several manufacturing steps and demonstrate poor control of the particle size and distribution of obtained nano tungsten powders. The requirement of high carburization temperature results in formation of coarser tungsten carbide grains even if the starting tungsten powder is nano size.

Zaytsev et al. [13] recently reported successful fabrication of nano size tungsten carbide powders via a self-propagating high-temperature synthesis (SHS) method starting from a mixture of tungsten oxide, magnesium and carbon. The process developed by Zaystev et al. however requires additional chemical leaching and refining steps to obtain nano size WC powders after SHS.

Kanerva et al. [14] synthesized nano WC powders starting from water soluble precursors (ammonium paratungstate (APT)/ammonium metatungstate (AMT) and glycine). The developed process requires spray drying the starting powders prior to heat treatment to obtain nano size WC. Some other techniques like ball milling [15,16] and wire explosion [17] were recently explored for synthesis of nano size tungsten carbide powder. However the developed processes are very expensive and have low probability for commercially manufacturing large quantities of nano size tungsten carbide powders with consistent quality.

Research studies have been lately reported utilizing thermal plasma technology to manufacture nano size metal and ceramics powders [18–21]. The plasma technology is widely used in the industry for densification and spheroidization of the powders and has a high commercialization probability for synthesis of nano size metal and ceramics powders. Manufacturing nanocrystalline size powders via thermal plasma technology has unique advantage as the powders can be obtained in a single step starting from oxides. Zhang et al. [6] have successfully utilized thermal plasma technology to synthesize nano size tungsten powder starting from ammonium paratungstate.

In the present study, the feasibility of thermal plasma technique to produce nanocrystalline size tungsten powder from tungsten oxide and tungsten carbide powder from a mixture of tungsten oxide and carbon in a single step process was investigated.The effect of power and hydrogen flow on the tungsten oxide reduction and subsequent carburization was studied. The results from the study will assist in better understanding the various phenomena occurring during tungsten oxide reduction and carburization of tungsten in thermal plasma

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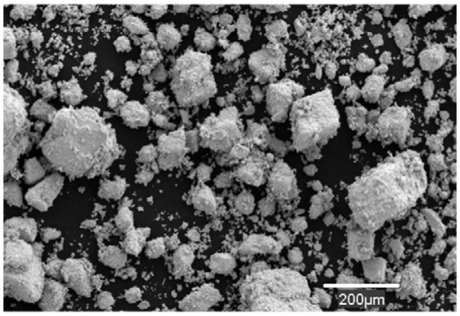

Fig. 1. SEM micrograph of the tungsten oxide.

environment and aid in developing an inexpensive process for manufacturing nano size tungsten and tungsten carbide powders. Due to negligible practical applications of unreduced and partially carburized tungsten powders, the ability of post heat treatment process at lower temperatures in combination with thermal plasma technique was also investigated to achieve complete carburization of the tungsten.

1.1. Experiment

The tungsten oxide mixture (21.5% WO_2 and 78.5% $W_{18}O_{49}$) in as-received condition showed good flowability and was used as the starting powder to verify the feasibility of plasma technology to manufacture nano size tungsten powders. W oxide (21.5% WO_2 and 78.5% $W_{18}O_{49}$) was mixed with 15 wt. % carbon. The starting powders should exhibit good flowability characteristics for reduction and carburization via thermal plasma technique. The oxide powder exhibited good flowability characteristics and was chosen for the study. However other compositions of the tungsten oxide mixes might also show good flowability which was not investigated in the present study. The present study was focused on understanding the capability of thermal plasma technique to reduce and carburize tungsten oxide in one step process. The effect of various compositions of starting tungsten oxide powders in successful reduction and carburization in one step process via plasma technique is a good subject for future studies.

An APMI gun using Metco (Type 7MC-II) plasma flame spray control unit was used for carrying out the reduction and carburization experiments. OFHC copper was used as anode and the cathode was made from 2 wt. % thoriated tungsten. The reduction experiments were carried out at hydrogen flow rates of 0.06, 0.14 and 0.28 m^3/h and at power levels of 34 ± 2 kW and 50 ± 3 kW. The reduction and carburization experiments were carried out at hydrogen flow rates of 0.06, 0.14 and 0.28 m^3/h and at power levels of 36 ± 3 and 63 ± 4 kW. A feed rate of 11 g/min was used for the experiments. Argon gas at flow rate of 0.26 m^3/h was used as the cover gas.

A secondary heat treatment was carried out on the plasma reduced powders to complete the carburization of the powders. Typically

Table 1
XRD analysis of the powder obtained from plasma reduction of the tungsten oxide.

Hydrogen flow rate (m^3/h)	Power (kW)	W (%)	$W_{18}O_{49}$ (%)	WO_2 (%)	W (nm)	WO_2 (nm)	$W_{18}O_{49}$ (nm)
0.06	34	25.5	60	14.5	96.2	83.7	60.8
0.14	34	26	57	17	78.3	70.1	74.8
0.28	34	30.5	53	16.5	86.4	93.8	>100.0
0.06	50	24	62.5	13.5	>100.0	>100.0	>100.0
0.14	50	27	56	17	85.4	92.5	39.5
0.28	50	34.5	51	14.5	83.1	71.7	>100.0

Table 2
Variation of surface area of the plasma reduced powder with power and hydrogen flow rate.

Hydrogen flow rate (m^3/h)	Power (kW)	Surface area (m^2/g)
0.06	34	3.92
0.14	34	2.5
0.28	34	2.61
0.06	50	2.84
0.14	50	2.73
0.28	50	2.54

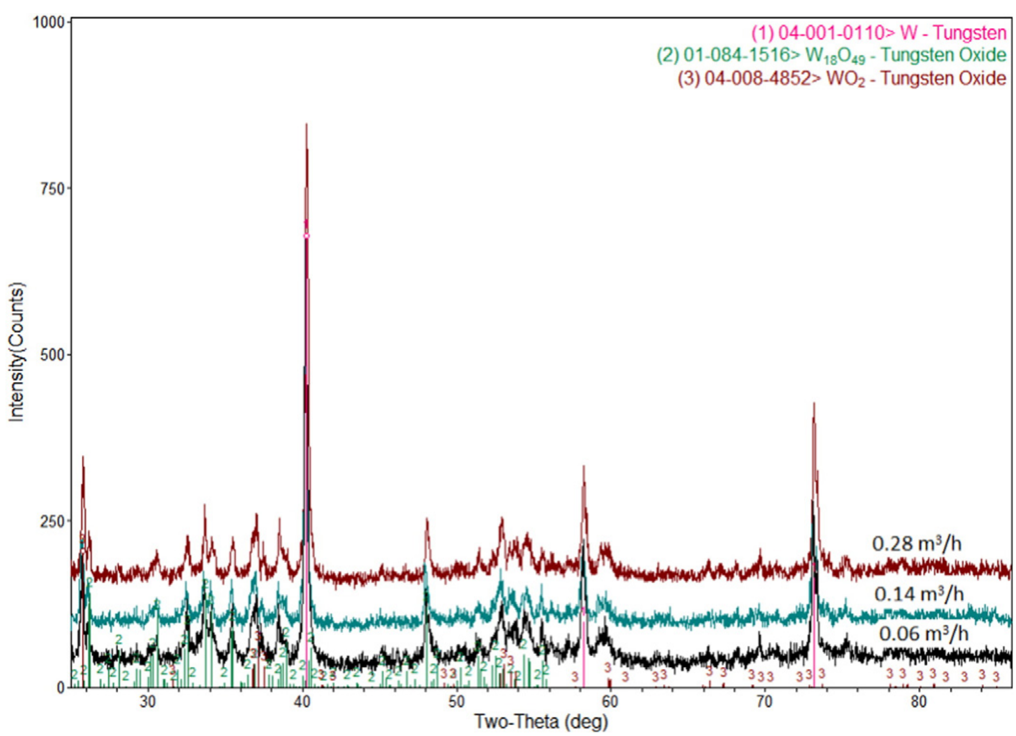

Fig. 2. XRD plots of the tungsten oxide powder at different hydrogen flow rates after plasma reduction at 50 kW.