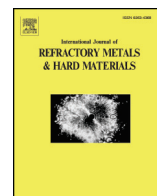




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Optimizing the synthesis of ultrafine tungsten carbide powders by effective combinations of carbon sources and atmospheres

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ABSTRACT

Nanostructured WC powders can provide technologically attractive properties due to the fine microstructures obtained after sintering. Either W or WO_3 powders are used for the industrial production of WC. In both cases, the contact area between carbon and tungsten precursors has a critical influence on the reaction temperatures, which in turn affects grain growth and agglomeration of particles. Different methods have been studied to increase the reaction rates by enhancing the contact between reactants: carbon coating of tungsten powder, solid-gas reactions of tungsten powders with atmospheres containing CH_4 , or mechanical activation followed by thermal activation of tungsten and carbon precursors.

In this work WC-powders were obtained by mechanical activation of tungsten and carbon precursors followed by thermal activation of these mixes at temperatures up to 1100 °C. A systematic study has been carried out combining two dissimilar carbon sources (graphite and carbon black), with different atmosphere compositions (Ar, Ar-50H₂, Ar-10CO) and studying the evolution of phases at different stages of the synthesis. The results show how the efficiency of the interaction between carbon sources and atmospheres affects the completion of the synthesis. The synthesis of WC from WO_3 in H₂ containing atmospheres is enhanced when using carbon black sources, however in CO containing atmospheres the most effective interaction is with graphite.

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1. Introduction

Conventional production of WC powders consists on heating a mix of tungsten and carbon powders in H₂ atmosphere at temperatures ranging between 1300 and 1700 °C. Direct carburization of WO_3 powder is an alternative method for producing high quality submicron and ultrafine WC powders in industrial scale, which considers oxide reduction in nitrogen atmosphere at 1350 °C followed by carburization in hydrogen at 1650 °C. Due to the decomposition of the oxides in small nuclei during the reduction stage – which will be after transformed into WC – fine WC particles are achieved at the end of the process. H₂ has been traditionally excluded in the reduction stage in order to avoid formation of volatile $WO_2(OH)_2$ that promotes tungsten crystal growth by chemical vapor transport [1].

In both processes, since the reactants involved are in the solid state, the extent of the reactions is limited to the contact area between tungsten and carbon. Increasing the contact between reactants accelerates the reaction rates and reduces the reaction temperatures avoiding

grain growth and limiting the agglomeration caused by local sintering of particles at high temperatures.

The use of carbon-coated W or WO_3 precursors provided single phase submicron WC powders at temperatures below 1100 °C [2–4]. Synthesis of submicron WC powders at temperatures around 850 °C is possible if using reactants in gaseous state [5]. Mechanical activation of $WO_3 + C$ mixes before thermal processing in inert atmospheres provides major enhancement in solid-state reaction rate, yielding single phase WC powders with grain sizes below 200 nm at reaction temperatures around 1200 °C [6,7]. Additions of CO to the initial mix modify the reduction-carburization sequence and decrease to 900 °C the temperature needed for complete carburization [8,9].

Besides the production method, it can be expected that the characteristics of the carbon source used in the synthesis will also affect the rate of the reaction. For instance, in graphitic structures particles must be located at the edges of the carbon basal planes in order to react, and therefore graphite with lower particle sizes should have a higher reactivity [10–12]. Also, the specific surface area of carbonaceous materials controls the gasification rate, which means that carbons with a higher specific surface area (such as carbon black) might have enhanced reactivity with the atmosphere.

The aim of the work presented here is to describe how the efficiency of different carbon sources (graphite or carbon black), and their

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interactions with the atmosphere can affect the synthesis of mechanically activated mixes of precursors. The reactions involved in reduction and carburization processes occurring during the synthesis of WC are governed by complex interactions between the material to be processed, the carbon source used, and the active gases present in the atmosphere (H_2 , H_2O , CO , CO_2) and since all these phenomena take place simultaneously and the equilibrium of the reactions are interlinked, the different interactions cannot be influenced independently.

2. Materials and experimental procedure

Powders of metallic W ($d_{90} \sim 4.8 \mu m$) and WO_3 ($d_{90} > 20 \mu m$) from Wolfram Bergbau und Hütten AG, Austria were used as tungsten precursors. Two different carbon sources: graphite KS4 ($d_{90} \sim 3.8 \mu m$, BET $25.9 m^2/g$) and carbon black E250G (BET $67 m^2/g$) from Imerys Graphite and Carbon, Switzerland, were considered in the study. The raw materials were loaded in air in a planetary mill Pulverisette 5 (Fritsch GmbH, Germany) and mixed by ball milling using bowls and balls made of tungsten carbide. The diameter of the balls was 10 mm, and the ball to powder weight ratio was 10:1. The raw materials were mixed for 2 h with a rotation speed of 300 revolutions per minute (rpm).

The effect of the atmosphere on the carburization process was evaluated on mixes containing metallic tungsten powder and carbon with a composition set equal to the stoichiometry of the reaction in Eq. (1).



In order to analyze the efficiency of a combined processes of reduction followed by carburization, a parallel study was carried out in mixes containing WO_3 as precursor. In this latter case, the stoichiometry of the mix was different depending on the targeted atmosphere (see Table 1). Thermal activation was performed inside a Netzsch DIL402C dilatometer in order to ensure an excellent control of the process atmosphere and thermal profile. The temperatures used for thermal activation in each atmosphere are indicated in Table 1. The heating rate used was $10^\circ C/min$, and the cooling rate was approximately $50^\circ C/min$.

Thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed in a simultaneous thermal analyzer Netzsch STA-449F1 Jupiter on the as-received WO_3 powder as well as on $WO_3 + C$ mixes with stoichiometry 4/1 (Mix A). Mixes were heated up to $1300^\circ C$ with $10^\circ C/min$ heating rate and then held at that temperature for 10 min. Dynamic atmosphere of either Ar, Ar-10 vol.% CO or Ar-50 vol.% H_2 was used for these experiments, using a gas flow of 100 ml/min.

After thermal activation, powders were analyzed by X-ray diffraction (XRD) in a Bruker D8 Advance X-ray diffraction instrument, using $CrK\alpha$ radiation ($\lambda = 2.2897 \text{ \AA}$). The diffraction peaks were matched with the International Center of Diffraction Data (ICDD) powder diffraction files (PDF-4) [13].

The size and morphology of the synthesized powders was observed using high resolution scanning electron microscopy (HR SEM) with a LEO Gemini 1550 (Carl Zeiss – LEO electron microscopy, GmbH, Germany).

Table 1
Characteristics of the thermal activation processes: stoichiometry of the mix, temperature, time and atmosphere.

Precursors	Mix stoichiometry	Thermal activation
W powder	Graphite KS4 or carbon	1 mol C/1 mol W
WO_3 powder	Mix A	700, 900, 1100 $^\circ C$ - 30 min Ar, Ar-50H ₂ , Ar-10CO
	Mix B	900, 1000, 1100 $^\circ C$ - 30 min Ar, Ar-CO
	2 mol C/1 mol WO_3	700, 900, 1100 $^\circ C$ - 30 min Ar-50H ₂

3. Theoretical considerations

Depending on the agent assessing the reduction of WO_3 , different reduction/carburization reactions are possible (Table 2). The theoretical mass losses associated to the reduction to metallic W or transitions between oxides are presented in Table 3, considering H_2 , C or combination of $2C/2H_2$ (Eq. (4)). The calculations in Table 3 consider as initial reactants either tungsten oxide WO_3 (without any carbon) or $WO_3 + C$ mixes with different stoichiometry.

4. Results

4.1. Reduction of WO_3 powder by reactive atmospheres

The reduction of WO_3 powder was studied by analyzing the evolution of the sample mass during the thermal cycle.

Thermogravimetry curves for the reduction of WO_3 (without carbon additions) in either Ar-50H₂ or Ar-10CO atmospheres are shown in Fig. 1. Reduction of WO_3 with H_2 starts at approximately $515^\circ C$ and is completed at $1210^\circ C$. The mass loss associated to this transition – 20.73% – is in excellent agreement with the theoretical mass loss needed for the complete transformation of WO_3 into metallic W (20.7% – Table 3). In Ar-10CO the reduction starts at $838^\circ C$ and is not completed during the thermal cycle considered in this study. The mass loss registered in this case – 2.27% – is only slightly higher than the theoretical mass loss for the transformation of WO_3 into the lower oxide $WO_{2.72}$ – (1.9%, see Table 3).

XRD patterns from the WO_3 powders reduced in different atmospheres (Fig. 2) confirm the transformations predicted through thermogravimetry curves. In case of reduction in Ar-50H₂ the final product after treatment at $1300^\circ C$ is metallic tungsten, while after reduction in Ar-10CO the XRD pattern of the powder corresponds precisely to the oxide $W_{18}O_{49}$ ($WO_{2.72}$).

4.2. Reduction in $WO_3 + C$ mixes

Fig. 3 presents the thermogravimetry curve for $WO_3 + C$ mixes treated in different atmospheres. Experiments in Ar are used for identifying the individual effect of carbon as reducing agent without additional reducing agents in the atmosphere. Experiments in Ar- H_2 and Ar-CO provide information about the combined effect of H_2 -C or CO-C in the reduction process.

In Ar-50H₂, the total mass loss registered at the end of the experiment (17.34%) corresponds exactly to the theoretical mass loss for the complete reduction of the oxide only by H_2 (Table 3: $WO_3 \rightarrow W$ Mix A/ H_2 – 17.2%). However, the temperature needed for the complete reduction of the oxides is considerably lower in $WO_3 + C$ mixes ($1050^\circ C$) than in pure WO_3 powder ($\sim 1210^\circ C$).

Thermal analysis on $WO_3 + C$ mixes in Ar and Ar-10CO atmospheres renders identical TG and DTA curves. Reduction of oxides in Ar and Ar-10CO starts at approximately $980^\circ C$ and finishes at $1100^\circ C$, with a similar mass loss (29.88% in Ar and 29% in Ar-CO) that corresponds to the theoretical mass loss for the transformation $WO_3 \rightarrow W$ for the case of

Table 2
Possible reduction/carburization mechanisms.

Reducing agent	Global reduction-carburization reaction	Stoichiometry (mol $WO_3/mol C$)
H_2	$WO_3 + 3H_2 + C = WC + 3H_2O$	Eq. (2) 1/1
C	$WO_3 + 4C = WC + 3CO$	Eq. (3) 1/4
C and H_2	$WO_3 + 2H_2 + 2C = WC + CO + 2H_2O$	Eq. (4) 1/2
	$WO_3 + H_2 + 3C = WC + 2CO + H_2O$	Eq. (5) 1/3
CO	$WO_3 + 5CO = WC + 4CO_2$	Eq. (6) –
C and CO	$WO_3 + CO + 2C = WC + 2CO_2$	Eq. (7) 1/2
C and CO	$WO_3 + 3CO + C = WC + 3CO_2$	Eq. (8) 1/1

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