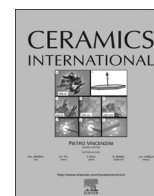




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# Acrylamide route for the co-synthesis of tungsten carbide–cobalt nanopowders with additives

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## ABSTRACT

In this work, cemented tungsten carbide nano-particles were prepared by a chemical method called acrylamide gel. In this process, first, a xerogel containing tungsten and cobalt oxide particles was synthesized. Then, it was carburized by a hydrogen reduction heating process.

Acrylamide and N, N-methylene-bis-acrylamide monomers were used as an in-situ carbon. Ammonium meta tungstate  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ , and cobalt nitrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  salts were used as the precursor.

Both reduction and carburization reactions were carried out simultaneously and the formation of the intermediate phases of  $\text{W}_2\text{C}$ ,  $\text{Co}_3\text{W}_3\text{C}$ , and  $\text{Co}_6\text{W}_6\text{C}$  led to decrease in the activation barrier.

Transactions of reduction and carburization processes were studied by X-ray diffraction analysis at various temperatures. Accordingly, tungsten carbide phase formation was completed at 1100 °C. The formation of W–C and V–C bonds was verified by Raman spectroscopy. SEM images showed the average nano particle size of 50 nm.

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## 1. Introduction

Bulk cemented tungsten carbide is widely used in demanding industrial applications such as cutting tools, mining and oil drilling, blasting, transportation, forestry tools, spray nozzles, sealing grout pumps, etc [1]. High hardness, high toughness, and wear resistance are always desirable for these applications. Furthermore, Nano-crystalline grain structure using nano-sized WC-Co powders promise dramatic improvement of these properties [2].

Currently, there are many methods which are used to carburize tungsten oxide ( $\text{WO}_3$ ) powder for the preparation of cemented tungsten carbide nanoparticles, such as, carbothermal hydrogen reduction [3], chemical vapor condensation by methane gas [4], self-propagating high-temperature synthesis (SHS or combustion synthesis) [5,6]. The most important disadvantage of these methods was the particle agglomeration during carbonization in high temperatures. Earlier attempts to use in-situ carbon sources took place in former [6]. It is well known that additional carbon remaining in the products causes the suppression of grain growth inhibition and high concentration of tungsten dissolved in the binder [7]. To avoid the presence of excess carbon in compounds,

in some procedures, organic compounds are used as carbon sources [8,9]. Here we try to use acrylamide gel as a source of carbon as well as network steric stabilizer for nano particles.

Acrylamide gel is a new method to the synthesis of Tungsten carbide–Cobalt powders. It has the advantages such as molecular-level combination that leads a homogeneous composition, not requiring advanced apparatus, inexpensive salts and organic materials as precursors compared with metal alcoxides, and good controlling of particle size by the polymeric net [9–11]. We could also add vanadium carbide (VC) to WC–Co powders as a grain growth inhibitor by this simple method. Therefore, homogeneity of the additive is given by this method that has more effect on grain growth suppression. In fact, in the hydrogel method, polymeric net plays a spatial precision stabilization role in nanoscale dimensions and is an in-situ carbon source for carburization. This polymeric gel is formed by co-polymerization of acrylamide (as monomer) and N,N-methylene-bis-acrylamide (as cross linker). Polymerization reaction initiates by the addition of ammonium persulphate through the production of free radicals and reaction with inactive monomers. The resulting gel is porous and size of its pores depends on polymerization conditions. The main difference between this method and sol-gel is in the use of an external agent as gully maker [9–11].

The purpose of the present work is to obtain both WC and cobalt metal nanopowders simultaneously using polymeric

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monomers as a carbon source.

## 2. Experimental procedure

The procedure used to prepare WC-Co with VC additive nanocomposite particles can be divided into 3 subsequent stages: solution, gelation, and calcination. First acrylamide (AM) ( $C_2H_3CoNH_2$ , Merck, Germany) and N,N'-methylene-bis-acrylamide (MBAM) ( $CH_2CH_3CONH$ ) $CH_2$ , Merck, Germany) monomers were easily dissolved in the mixture of aqueous solutions of ammonium meta-tungstate (AMT) ( $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ , Sigma-Aldrich), cobalt nitrate ( $Co(NO_3)_2 \cdot 6H_2O$ , Merck, Germany), and ammonium meta-vanadate ( $NH_4VO_3$ , Merck, Germany). The concentration of monomers solution was 1.2 M. Then, the resulting solution was stirred completely for 45 min and gradually heated in a water bath at 75 °C to obtain a transparent pink sol. When the temperature reached about 75 °C, 2 mL of 0.2 M ammonium persulphate aqueous solution ( $(NH_4)_2S_2O_8$ (APS), 10 wt%, Merck, Germany) was added to the mixture as the initiator. An orange semi-transparent gel was rapidly produced. The gel was dried at 100 °C for 24 h to yield a xerogel. At the next stage, the obtained xerogel was grinded to form a homogenous powder. The powders were calcined at 900 and 1000 °C under a hydrogen atmosphere for 1 h. To analyze the thermal decomposition and reduction process, a thermogravimetric (TG)/differential thermal analysis (DTA) experiment was carried out in hydrogen gas. The flow rate for each gas was 50 mL/min, the heating rate was 10 °C/min, and the temperature was varied from room temperature to 1100 °C.

The structure of the powder was examined at room temperature by X-ray diffraction (XRD) with Cu-K $\alpha$  radiation (AXS-D8, Holland). The morphology and particle size of the powder were examined using FE-SEM (F4160, Hitachi, Japan). The formations of V-C and W-C bonds were proved by Raman Spectroscopy (second harmonic of Nd:Yag laser with  $\lambda=532$  nm).

## 3. Results and discussion

Fig. 1(a) shows the Raman Spectroscopy surveys for V-C and W-C bonds formation in the prepared powder. As it can be seen the W-C bond position is at 337  $cm^{-1}$ . Raman shift of W=C bond is also indicated at 937  $cm^{-1}$ . According to Fig. 1(a) as a reference, D peak of W-C bond is at 1340  $cm^{-1}$  and moreover D peak of V-C

bond is at 1360  $cm^{-1}$  [12]. The asymmetric Raman shift at 1353  $cm^{-1}$  is assigned to the combination of D peaks of V-C and W-C bonds in Fig. 1(b). The unsymmetrical shift at 1581  $cm^{-1}$  is also referred to the blend of G peaks of W-C and V-C bonds. Decomposition of these peaks is difficult due to their proximity. These results show that the reduction process is done completely because there was no oxide compounds shift.

Also, X-ray diffraction pattern was used to characterization of the phase transformation of the WC-10% Co nanocomposite powder during the reduction processing at 900 and 1100 °C (Fig. 2). It exhibits characterizing peaks of tungsten carbide, the intermediate phases and Cobalt at 900 °C. It seems that WC phase is a dominant phase. By increasing temperature to 1100 °C, the peaks of intermediate phases are eliminated and only WC and Co phase remains with a small amount of  $W_2C$  phase. The average crystalline size is estimated from the Scherrer equation. This value is 32 nm at 1100 °C.

Based on diffraction thermal analysis in Fig. 3, the first peak is related to the water evaporation at 100 °C. The weight loss in rang of 250–750 °C accompanied by the release of heat that is Due to exit of structural water and organic compounds from the system. The drastic change of thermal curve at 280 °C is the shift of process type from endothermic to exothermic. It seems that in addition of the crystallization of amorphous phases, ignition has taken place. This claim has been proven in the thermogravimetric analysis diagram (Fig. 3a). It shows the maximum weight change at 280 °C. Oxygen for combustion provided of organic compounds and mineral salts sources.

The decomposition of organic phases starts in the range of 250–300 °C. Despite the removal of some of the organic compounds in the process of restoration, the carbon content is enough to carburizing of the powder. It seems that in this stage, stack of active carbon remains in the adjacency of tungsten and cobalt ions through the pores of xerogel. It makes the carburizing at higher temperatures. In the range of 450–550 °C a relatively wide exothermic peak can be seen that is due to reduction of Cobalt Oxide. At 750 °C with exit of remaining organic compounds from the system, an endothermic peak is observed in the graph. This process can also be found from the weight changes in TG diagram. In the DTA diagram, a relatively wide exothermic peak is observed in the temperature range of 900–1100 °C that shows the carburization and reduction of products. In practice, due to two simultaneous reduction and carburization process, showing a known distance between them is difficult.

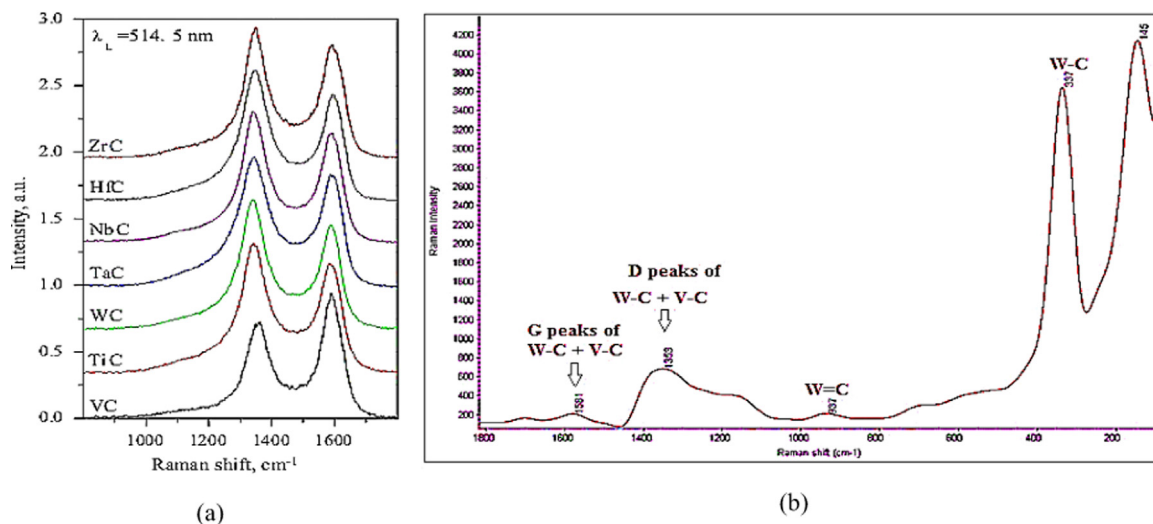


Fig. 1. (a) Reference Raman spectra for some carbides [12] (b) Raman spectrum of sample sintered at 1000 °C.

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