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Synthesis of nano-WC from water soluble raw materials: Effects of tungsten source and synthesis atmosphere on chemical and phase structure evolution

Ulla Kanerva *, Juha Lagerbom, Marjaana Karhu, Anna Kronlöf, Tarja Laitinen, Erja Turunen

VTT Technical Research Centre of Finland, Sinitaival 6, P.O. Box 1300, FI33101 Tampere, Finland

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ABSTRACT

The chemical synthesis of WC from water-soluble precursors was studied. Ammonium paratungstate APT, ammonium metatungstate AMT as tungsten source and glycine as a carbon source were dissolved in water and spray-dried, and thermal synthesis in Ar and Ar-4 vol-% 4H_2 atmospheres was performed. In order to understand the effects of the tungsten source and atmosphere on the synthesis steps, and chemical and phase structure, thermogravimetry (TGA) with Differential Scanning Calorimetry (DSC) and mass spectrometry was used together with X-ray diffractometry and chemical analysis. The eventual goal is to produce pure WC phase without lower carbides and on the other hand without extra unreacted carbon. Due to the better solubility and subsequently more homogeneous nucleation of WC, AMT was found to be a more suitable precursor. Using AMT and glycine, 10–100 nm sized WC was synthesised at 1300 °C in both atmospheres. However, extra carbon was present in the product. New insights were gained into the reaction sequences.

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1. Introduction

Thermal sprayed cemented carbides such as WC–Co(Cr) and Cr_3C_2–NiCr coatings are well known and widely used for wear protection purposes. Nanocarbides in cermets have shown promising results in gaining the hardness [1], wear performance in abrasion, cavitation [2] or slurry type of wear conditions [3,4]. Even friction properties have been reported to be improved by the use of nanocarbides [5]. The driving force for reducing the carbide grain size comes from the fact that, as the carbide size becomes smaller, the binder mean free path is reduced, resulting in higher resistance to deformation and material loss. Many researchers [6–9] have pursued such a hypothesis so as to improve the wear performance of HVOF WC–Co by reducing the WC grain size to the nanoscale.

The conventional method for producing conventional micro-sized WC is solid state synthesis. At first, WO_3 is reduced to metallic W, which is then mixed together with carbon, and finally the mixture is heat treated at 1400–2000 °C in a hydrogen atmosphere. However, due to the long duration time and high temperature of the solid state reaction process, the manufacturing of nano-sized carbides is limited. A number of techniques are presented in the literature for producing nano-sized tungsten carbide powder such as, for example, mechanical alloying (MA) [10,11], plasma methods [12,13], chemical vapour condensation processing (CVC) [14] and solid state reaction method [15]. However, firstly a lack of economical and commercial nano-carbide manufacturing methods, and secondly inhibition of carbide grain size growth, are still major obstacles in benefitting nanotechnology in tungsten carbide applications [16]. Novel precursor synthesis methods have been developed with water-soluble raw materials and simple heat treatment steps [17,18]. In consolidation the research focus has been to study the effect of grain growth inhibitors and process development [19,20].

Novel precursor synthesis methods include water-soluble raw materials and the reduction of tungsten oxide followed by carburization. Water-soluble tungsten source materials are typically ammonium paratungstate (APT) or ammonium metatungstate (AMT), and the carbon source is an organic compound or carbonising gas. In synthesis, at first the tungstate has been reported to form an oxide, WO_3, which further reduces to lower oxides and finally to metallic W by CO/CO_2, H_2 or carbon. Metallic W is then reacted with a carbon bearing gas or carbon (carburization) [17,18,21]. Carbon can also be added by mechanical milling to oxide mixture produced by drying a water solution of salts [22].

However, the literature does not describe in detail how to control the exact amount of carbon in these novel precursor methods. During solid carbon reduction, both CO and CO_2 may form, and the ratio is difficult to control accurately. Carbon control is a crucial issue, suppressing the sub-stoichiometric carbide (W_2C) formation, but also avoiding weakening the effect of extra free carbon in the structure. Carburization temperature is another issue in controlling the grain growth of fine carbides. The finer the carbide size, the lower the synthesis temperature

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* Corresponding author.

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must be. On the other hand, in thermal spraying, decarburization occurs due to extremely high temperatures. Decarburization becomes more severe with the decrease of carbide particle size because of the large surface area. The decarburization not only reduces the wear-resistant phase but also leads to the formation of a brittle Co–W–C ternary binder phase [23]. Therefore, a slight surplus of carbon is preferred over stoichiometry or deficiency so as to compensate the decarburization. Carburization with CO/CO_2 tends to result in WC without any free carbon. With solid carbon source content of carbon in precursor is easy to control and vary.

The objective of the work was to test the preparation of WC from water-soluble materials in a spray dryer and to follow the reaction sequences, starting from the raw materials throughout the WC synthesis steps from 20 to 1300 °C. Furthermore, the objective was to compare the reaction sequences of two precursors made with solutions with differing solubilities. The reaction steps of the WC synthesis starting from the precursor particles to the final WC product were monitored by calorimetry. Step by step, the chemical composition of the formed gases, crystal structure, morphology as well as the carbon and oxygen contents of the WC product was analysed. The study of reaction sequences and evolved gas analysis represents novel knowledge in this field, enabling a deeper understanding of phenomena and further developing high quality nano-sized WC powders with the essential carbon control. The research hypothesis of the present study is that this novel manufacturing route with water-soluble raw materials is a potential way to prepare pure nano-structural WC with the correct phase structure, but the effect of raw materials and atmosphere on reaction sequences needs deep understanding so as to ensure the correct chemical composition.

2. Materials and methods

Raw materials for the precursor were ammonium paratungstate ($(NH_4)_{10}W_{12}O_{41}$ 5 H_2O), APT, and ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$ 3H_2O), AMT, as tungsten source, and glycine ($C_2H_5NO_2$) (molecular weight 75.07) as carbon source. Table 1 presents raw materials and precursor formulas. Estimation of theoretical raw material portions was made based on chemical calculations. Assumptions in the calculations were: 1) Ammonium ion and water were assumed to evaporate as such, without any reactions with other ions resulting in WO_3, 2) to form WC, the addition of carbon as glycine was needed to reduce WO_3 to W, and 3) the reduction was assumed to occur entirely to form CO instead of CO_2. According to calculations C / (C + W) relation should be 20,7% in NS4 and NS7, respectively. In our experimental precursor the relation was in NS4 28% and in NS7 27% to ensure pure WC formation and have a surplus rather than a deficiency of carbon to study its behaviour during synthesis. In stoichiometric WC compound C / (C + W) relation is 6.13%. The exact use of carbon in the reduction of the tungstate was not known beforehand; the worst case of pure CO formation was assumed instead to be the formation of CO_2.

Precursors were dissolved in distilled water by using a magnetic mixer with a heating unit. In the case of NS4, the first water was warmed up to 80 °C and then glycine was added and mixed until the solution was clear. Next, APT was added to the solution and mixed until dissolution was complete. APT was not fully soluble without glycine, but AMT dissolves fully. In the case of NS7, AMT and glycine were mixed with 80 °C water in separate vessels and combined after dissolution. Mixing was continued for 1 h after combining. Both precursors were dried with a laboratory scale spray dryer Buchi B-290. The spray dryer was used in order to ensure the homogeneity of the mixture and thus avoid separation of the raw materials during water evaporation. In spray-dried powders, the distance between the W-source and C-source can be at a maximum the diameter of the dried particle.

Heat treatments of the dried product were carried out under inert an Argon (Ar) gas atmosphere and under a reductive 4% Hydrogen in Argon (Ar-4%vol-% H_2) gas atmosphere at 1300 °C so as to evaluate the effects of the heat-treatment atmosphere. Small-scale samples were heat-treated in a TG/DSC unit with a heating rate of 10 °C/min in the temperature range between 30 °C and 1300 °C without any holding time. Larger batches (5 g) for the carbon content measurements of precursors were handled in an inert gas tube furnace. In furnace trials, the heating rate was 3.3 °C/min to 400 °C, at which the holding time was 120 min. Because of the bigger batch sizes in the furnace compared to TGA (thermogravimetric analysis), the holding time was used to ensure sufficient time for released gas components to evaporate. Then the temperature was increased to 1300 °C with the same heating rate. The holding time at 1300 °C was 30 min.

The thermal decomposition of the starting materials (glycine, APT, AMT) and precursors (NS4, NS7) was studied by measuring the weight loss as a function of temperature using thermogravimetric analysis (TGA, Netzch STA 449 F1 Jupiter) giving a simultaneous Differential Scanning Calorimetry (DSC) signal. The accuracy of the temperature measurement is 0.1% and the device has been calibrated against the non-substances. Qualitative mass spectrometer (QMS, Netzch QMS 403 D *Aëolos*) coupled directly to TGA device exhaust was used for evolved gas analysis. Morphology and particle size of the final product were analysed with an UltraPLUS Thermal Field Emission Scanning Electron microscope (Carl Zeiss Microscopy GmbH). Qualitative phase analyses were done by using an X-ray diffractometer (XRD, Empyrean, PANalytical B.V., ALMELO, Netherlands) with Cu-Kα radiation source, and analysed using HighScore Plus software. Carbon and oxygen contents of measurements were analysed with LECO CS-230 with an infrared detector.

To conclude, the reactions steps of the WC synthesis starting from the precursor particles to the final WC product were monitored by calorimetry and analysed step by step for the chemical composition of the gases formed, crystal structure, morphology as well as carbon and oxygen contents of the WC product. Table 2 summarizes the heat treatments carried out and characterisations of raw materials and precursors.

3. Results

TGA-measurements with a DSC-signal and directly coupled mass spectrometer gave information about thermal decomposition and the evaporating gases of starting materials and precursors during heating and synthesis. Fig. 1 presents DSC-signals (Fig. 1a) and TG-curves (Fig. 1b) as the functions of temperature of the raw materials glycine,

Table 1
Raw material and precursor compositions w-%.

Precursor	Raw materials					
	W-source			C-source		
	Chemical	Purity (%)	Amount w-%	Chemical	Purity (%)	Amount w-%
NS4	Ammonium paratungstate $(NH_4)_{10}W_{12}O_{41}\cdot 5\ H_2O$	99.98	54	Glycine $C_2H_5NO_2$		46
NS7	Ammonium metatungstate $(NH_4)_6H_2W_{12}O_{40}\cdot 3\ H_2O$	99.995	54.4	Glycine $C_2H_5NO_2$		45.6

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