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The effect of carbon and nickel additions on the precursor synthesis of Cr_3C_2-Ni nanopowder

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ABSTRACT

Decreasing crystal size to nanoscale is a proven method to enhance material properties. In this study, nanosize Cr_3C_2 and Cr_3C_2-Ni were synthetized and the reaction sequence was studied. Aqueous precursors using only water-soluble raw materials with varying carbon contents and a nickel addition were spray-dried. Glycine was used as a carbon source and chromium acetate hydroxide as a chromium source in the precursor solutions. Nickel nitrate hexahydrate was introduced as a nickel source to yield a metallic binder into the carbide nanopowder.

Resulting powders were heat-treating to identify an applicable precursor composition producing the targeted Cr_3C_2 phase with crystal size of tens of nanometers. Thermal synthesis tests of the precursor powders to yield Cr_3C_2 took place at a temperature between 900 and 1300 °C under an Argon atmosphere. The synthesis of nanosize Cr_3C_2-Ni powder was successful at 1000 °C in 30 min, in a case of the best precursor. In order to produce the carbide phase with no residual oxide traces, relative carbon load has to be 48 wt%, while the stoichiometric amount of carbon in Cr_3C_2 is 13 wt%. When also introducing the nickel source into the precursor, an even higher carbon load was required. The carbon surplus needed to enable the Cr_3C_2 synthesis attributes to the non-homogeneity of the precursor composition.

The chemical synthesis starting from water-soluble raw materials is a promising way of preparing nanosize Cr_3C_2-Ni with the targeted phase configuration.

1. Introduction

Chromium carbides are well-known and widely used for wear protection purposes. There are three forms of chromium carbides, namely Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$, with different atomic ratios of carbon to chromium. Among these carbides, Cr_3C_2 has a good set of properties of high strength, excellent coverage resistance, low density and good chemical stability. Nanosize Cr_3C_2 in a metallic matrix (i.e. binder) has shown promising results in gaining improved hardness [1–3], friction properties [2,4,5] and wear resistance [2,4,6,7]. 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.

The traditional method of producing Cr_3C_2-Ni or Cr_3C_2-NiCr powders involves the preparation of Cr_3C_2 and Ni (or NiCr) separately by agglomeration and sintering, followed by blending the two constituents using spray-drying [5]. The conventional method yields micron and sub-micron Cr_3C_2-powders, nanosize carbide production being limited. He et al. prepared a nanostructured Cr_3C_2–25(Ni20Cr) powder from a pre-alloyed Cr_3C_2 ceramic and a NiCr solid solution by using mechanical ball milling [3]. Manufacturing nanocarbides by ball milling is slow and a risk of contamination is notable [8]. Also, health and safety issues of nanoscale particles during mechanical manufacturing processes have increased concerns [9].

Nanosize Cr_3C_2 has also been produced from chromium oxide by utilizing gas phase synthesis and microwave heating methods [10–12]. According to the theories presented, the phase transformation sequence during the heat treatment is $Cr_2O_3 \rightarrow CrO \rightarrow Cr_7C_3 \rightarrow Cr_2C \rightarrow Cr_3C_2$ [11] or $Cr_2O_3 \rightarrow CrO \rightarrow Cr_3C_{2-x}$ ($0 \leq x \leq 0.5$) $\rightarrow Cr_3C_2$ [12]. Another theory for Cr_3C_2 formation from Cr_2O_3 has been published by Majahan et al. when they used a chemical-reduction route in the presence of Mg in an autoclave at 700 °C: $Cr_2O_3 \rightarrow Cr \rightarrow Cr_{23}C_6 \rightarrow Cr_7C_3 \rightarrow Cr_3C_2$ [13]. The synthesized powder was a mixture of Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$, and Cr_2O_3 phases with a carbon layer on the particles. When the amount of

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carbon source (acetone) was increased, a complete reduction and carburization of Cr_2O_3 took place, resulting in only Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$ phases. The size of the particles was reported to be about 30–50 nm. Lai has shown decarburization of Cr_3C_2 to Cr_7C_3 and finally to $Cr_{23}C_6$ during exposure to high temperature [14]. Producing chromium carbides by reduction of chromium oxide with a gas phase synthesis is a faster method compared to the mechanical milling but also includes nanopowder processing with potential health issues.

Recently, solution chemical synthesis methods for the fabrication of nanosize carbide powders have received increased attention, including precursor preparation and thermochemical conversion processes such as reduction and carburization [15–17]. In the synthesis of chromium carbide, it has to be taken into account that chromium has a very high affinity to react with oxygen. For this reason, there is a competition between the formation of chromium oxide and chromium carbide during the synthesis [18]. Preiss et al. have prepared "fine grain" Cr_3C_2 powder from an aqueous solution of tartaric acid ($C_4H_6O_6$) and chromium trioxide (CrO_3) by heat treatment at 1000 °C in argon [19]. Zhao *et al.* have used a solution-derived precursor method to synthesize Cr_3C_2 nanopowder with an average crystallite size of 27 nm from ammonium dichromate ($(NH_4)_2Cr_2O_7$) and nanosize carbon black powder [20]. In another study, Zhao has synthesized a V_8C_7–Cr_3C_2 nanocomposite powder from ammonium vanadate (NH_4VO_3), ammonium dichromate ($(NH_4)_2Cr_2O_7$) and glucose ($C_6H_{12}O_6$, carbon source) [21]. The raw materials were dissolved in water, after which the solution was dried at 200 °C, followed by thermal treatment of the precursor at 900–1100 °C in vacuum. Average crystallite sizes of the V_8C_7–Cr_3C_2 nanopowders synthesized at 900, 1000 and 1100 °C were 31.5, 43.2 and 89.4 nm, respectively. Carbon content of the carbides was 14.9 wt%, being close to the stoichiometric value of 13 wt% for Cr_3C_2. Advantages of the carbide preparation via aqueous routes using water-soluble raw materials were identified as high homogeneity of reactants [19–21], easy variability of the precursor elemental composition to ensure the carbide formation [19–21], no need for risky organic solvents [19] and inexpensive raw materials with respect to chromium oxides used in the conventional methods [20].

Despite the fact that studies of wet-chemical synthesis of Cr_3C_2 have been reported in the literature, the influence of carbon and nickel load on the carbide reaction with water soluble raw materials is not fully understood. That is, mainly synthesis of chromium carbide with no metallic binder has been investigated [19–21]. Luo et al. synthesized a Cr_3C_2-NiCr powder from an aqueous solution of chromium chloride ($CrCl_3$), glucose ($C_6H_{12}O_6$) and nickel chloride ($NiCl_3$) by spray-drying and heat treatment at 1300 °C in an argon atmosphere [22]. Xiao et al. converted chemically synthesized NiCr into Cr_3C_2–20%Ni by a heat treatment at 880 °C under methane [23]. In the both studies, only a fixed amount of nickel and carbon sources was tested and no conclusion about how the relative amount of carbon with respect to chromium and nickel affects the carbide formation can be drawn.

In this work, preparation of Cr_3C_2 and Cr_3C_2-Ni nanopowders from water-soluble materials using spray-drying and a simple heat treatment step is being introduced. Relative precursor carbon load with respect to chromium was varied to analyse the efficiency of carbide formation. Carbide synthesis as a function of reaction temperature was also surveyed to study the carburization efficiency at different temperatures to reach the Cr_3C_2 phase. Finally, a water-soluble nickel source was added into the precursor solution to show formation of a nickel matrix as a result of the thermal treatment.

Thermal decomposition, differential scanning calorimetry and evolving gas analyses of the precursors were utilized to understand the phenomena taking place during the heat treatment sequence. Crystal structure and morphology, as well as the carbon and oxygen contents, of the final products were characterized to realize the applicability of the method to produce nanosize carbide. It was shown that the chemical synthesis route introduced here is a potential way of preparing nanosize Cr_3C_2 and Cr_3C_2-Ni from water-soluble raw materials. That is, this article demonstrates a simple, safe and cost-effective way of preparing chromium carbide nanopowders, with no need for energy demanding gas phase carburization.

Table 1
Relative compositions of the aqueous precursors.

Precursor	Relative composition (wt %)			Relative initial precursor carbon content (wt%)	Initial precursor carbon load (wt%)
	Cr-A	glycine	Ni-N	C/(Cr + C)	C
CrC − 1	80	20	0	23.3	6.3
CrC − 2	70	30	0	36.2	10.0
CrC − 3	60	40	0	48.3	13.8
CrCNi − 1	60	20	20	23.3	4.5
CrCNi − 2	50	30	20	36.2	7.2
CrCNi − 3	40	40	20	48.3	9.9
CrCNi − 4	30	50	20	60.2	14.1

*Cr-A = chromium acetate hydroxide, Ni-N = nickel nitrate hexahydrate. Initial carbon contents are calculated taken glycine as the only carbon source.

2. Materials and methods

In this study, three Cr_3C_2 and four Cr_3C_2-Ni aqueous precursors with different carbon contents were prepared, spray-dried, heat-treated and analysed. The precursor raw materials were chromium acetate hydroxide, $(CH_3CO_2)_7Cr_3(OH)_2$ (Cr-A), as a chromium source, glycine, NH_2-CH_2-COOH, as a carbon source and nickel nitrate hexahydrate, $Ni(NO_3)_2{\cdot}6H_2O$, as a nickel source. In this formulation, glycine is considered as the only carbon source for carbide formation. All the substances were purchased from Sigma-Aldrich and used as received. Table 1 presents relative ratios and formulas of the aqueous precursor combinations investigated, as well as the relative initial carbon loads of the precursors. Precursors CrC-1, CrC-2, and CrC-3 contain only chromium acetate hydroxide and glycine to produce chromium carbide. Precursors CrCNi-1, CrCNi-2, CrCNi-3 and CrCNi-4 also include nickel nitrate hexahydrate to introduce nickel as a binder material into the end-products.

Precursor solutions were prepared by dissolving the raw materials in separate vessels in 70 °C distilled water, followed by combining the solutions, using a magnetic stirrer. Precursors were dried with a laboratory scale spray-dryer Buchi B-290 (input and output temperatures of 200 °C and 110 °C, respectively). The spray-dryer was used to ensure homogeneity of the mixtures and to avoid separation or segregation of the raw materials during the water evaporation. Raw materials were analysed as received. All the heat treatments were performed in a high temperature tube furnace having an inert argon atmosphere with temperature ranging from 900 to 1300°C. The spray-dried precursors were carburized using the following heating sequence; 1) 100 °C/h to 400 °C; 2) 120 min holding time at 400 °C to ensure sufficient time for released gas components to evaporate; 3) 200 °C/h to the carburization temperature of 900–1300 °C; 4) 30 min holding time at the respective carburization temperature; 5) controlled cooling of 300 °C/h to 50 °C prior to sample removal from the furnace. The heating sequence is illustrated in Scheme 1. Spray dried precursors were carburized as free powders with no compression prior to the thermal treatment.

Thermal decomposition of the precursors was studied using a thermogravimetric analysis (TGA) equipped with a differential scanning calorimetry (DSC) function (Netzch STA 449 F1 Jupiter). For TGA/DSC experiments, samples of about 10 mg were analysed with a heating rate of 10 °C/min from 50 to 1300 °C with no holding times. A qualitative mass spectrometer (QMS, Netzch QMS 403 D Aëolos) coupled directly to the TGA exhaust enabled the evolved gas analysis during the heat treatment sequences. Qualitative phase analyses were carried out by an X-ray diffractometer (XRD, Empyrean, PANalytical B.V.) with Cu-Kα radiation source, and analysed using the HighScore Plus software.

The final products were characterized with a field emission