REDUCTION OF WO_3 TO WC NANO PARTICLES BY REFLUX REACTION

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WC is an important material mostly used for cutting tool application. Reduction of WO_3 to WC is being done by several techniques. The existing chemical processes involved in its reduction are long and energy consuming. In this work efforts have been made to reduce WO_3 to WC by reflux reaction technique. The composite obtained after reflux reaction has been analyzed to see the feasibility of the conversion of WO_3 to WC. The preliminary study exhibited the feasibility of conversion of WO_3 to WC. The technique seems to be promising one and cost effective for low temperature synthesis of ultrafine WC particles. The synthesized powders were characterized using X-ray diffraction, scanning electron microscope, energy dispersive X-rays, and transmission electron microscopy for phase identification and micro structural analysis.

Keywords: *tungsten carbide; transmission electron microscopy; nanoparticles.*

Cemented Tungsten carbide (WC) is an important material for cutting tool industry [1–3]. The particle size of WC has remarkable effect on the hardness and other mechanical properties of material. As the size is reduced, a large fraction of atoms may lie at the grain boundaries which may contribute to the enhancement in material toughness. Substances of small grain size are known to have a strong influence on the mechanical properties of materials [4–6]. Nanocrystalline cemented carbide with ultrafine grain has become one of the hottest research areas of the present time [7]. Spray conversion [8–12], mechanical ball milling [13–21], chemical vapor phase reaction synthesis [22–30] and plasma processing technique [31–32] are the basic techniques used to synthesize nano-WC/WC–Co composite [8]. The shortcomings of all these techniques are that they involve high temperature synthesis process. The present work is an effort to synthesize ultrafine WC particles by chemical vapor phase reflux reaction. The method is simple and efficient to obtain nanopowders of mixed oxides or metal composite. Basically this process consists of vaporizing and condensation of a carbon source through refluxing action which allows the reaction to proceed where carbon engulf the precursor WO_3 powder to convert it into the nanosized WC. The idea behind this work is to find the feasibility of WC nanopowder synthesis at lower temperature where synthesis can be made easy.

Experimental. ***Chemicals*.** The powders of tungsten oxide (WO_3) and magnesium (Mg) were used as initial ingredients. The average particle size and purity of both ingredients were 20 μm, 99.9%, and 178 μm, 98% respectively. Magnesium powder was selected as a reducing agent. Apart from this, glycerol (99.9%) was used as a carbon source in the present study. All the chemicals were used in as received condition without further purification.

***Methodology*.** Experiments were performed in a round bottom flask (1000 ml) fitted with chilled water cooled condenser which allows the liquid to condense during

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experiment. WO_3 (3 g), magnesium turning (3 g) and glycerol (100 ml) were used as initial ingredients in all the reactions. The flask containing these ingredients is heated at 300°C for 96 h (S_1). Cold water was circulated with the help of small submersible pump through the condenser to extract the heat out of the condenser which allows the liquid to condense back in the round bottom flask. A guard tube was also applied at the top of the condenser having fused calcium chloride flakes covered with cotton from both sides to absorb moisture and also to facilitate plugging of the loss of volatile material if any through the condenser. Slow heating was done to start the reaction. As the reaction proceeded the color of the liquid started changing and finally converted to dark brown. At this stage the reaction was stopped. The thick liquid was then filtered. In another set of experiment the reaction time was increased to 168 h (S_2) to see the possibility of any change in the reaction product. The powder was then further treated with HCl (1:3) to remove unreacted Mg and other soluble phases from the product. The acid treated samples were washed with distilled water first followed by ethanol to eliminate the water absorbed in the powders. The dried powders were characterized to investigate the formation of WC phase in the synthesized mass.

Characterization. Both samples were studied by X-ray diffraction (XRD) using a Rigaku (model Geiger flex) X-ray diffractometer using CuK_α radiation ($\lambda = 1.54A^\circ$). During the experiment the scanning speed and diffraction angle were 5°/min and 20° to 80° respectively. Microstructural examinations of samples were done under transmission electron microscope (TEM) (model Hitachi (H-7500)) and Scanning electron microscope (SEM) (model Quanta 200 FEG, FEI, Netherland)). For TEM study the synthesized powders were suspended in alcohol. One drop of the suspension was dropped on SiO_2 coated copper grid and alcohol was allowed to evaporate.

Results and discussion. The possible reactions which may occur can be written as:

$$2WO_3 + 2C_3H_8O_3 + 2Mg \rightarrow 2WC + C + 6MgO + 3CO_2 + 8H_2 , \quad (1)$$

$$2WO_3 + 2C_3H_8O_3 + 2Mg \rightarrow W_2C + 2MgO + 5CO_2 + 8H_2 \quad (2)$$

The XRD pattern of the as synthesized sample *S*(1) showed the presence of $MgWO_4$ and MgO phases along with WC and WO_3 phases (Fig. 1*a*). After acid treatment the sample (S_1) exhibited WC and unreacted WO_3 phases. However, the XRD peaks of WC became broader after acid treatment (Fig. 1*b*), particularly the WO_3 phase.

This might be attributed to the fact that WO_3 powder also gets broken to fine size during reflux reaction. In addition to this, the peaks of WC and WO_3 are shifted to the lower angle as compared to standard WC (ICDD card No.25-1047), $MgWO_4$ (ICDD card No.27-0789), and WO_3 (ICDD card No.83-0949) peaks which clearly indicates that the disordering is increasing in this sample. The disordering might be due to high aspect ratio of WC nanoparticles as compared to the crystalline counterparts of WC [33]. X-ray diffractogram of the sample (S_2) in which the reaction time is longer as compared to (S_1) is given in Fig. 1*c*, *d*.

The detailed XRD analysis shows that with the increase in reaction time from 96 to 168 h peak intensities of WC increases which shows that the volume fraction of WC phase has increased. The particle size calculated from the peak broadening also shows that the size of particle has also reduced. In both cases, the lattice parameter was calculated using Bragg's law. The calculated lattice constant for WC phase in the sample S_1, a = 2.910 Å, c = 2.834 Å were very close to the reported value of hexagonal WC (a = = 2.906 Å, c = 2.837 Å, (ICDD card No.25-1047). Similarly for sample S_2, the lattice parameters for WC phase a = 2.986 Å, c = 2.839 Å are also in close approximation of the standard value reported for it. In order to investigate a possibility of the preferred orientation, a comparison of the peak intensity with standard specimen was done using Harris analysis [34] to obtain the texture coefficient using the relationship given below:

$$P(h_i k_i l_i) = \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \left[\frac{1}{n} \sum_{i=1}^{n} \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right]^{-1},$$

where $P(hkl)$ is the texture coefficient of the plane specified by Miller Indices (hkl), $I(hkl)$ and $I_0(hkl)$ are the specimen and standard intensities respectively for a given peak and n is the number of diffraction peaks. With increase in the reaction time the texture coefficient of plane (100) increased from 1.03 to 1.43 (see Table). This shows that the microstructure is strongly textured in plane (100). The increase in reaction time hinders the growth of plane (001) and (101).

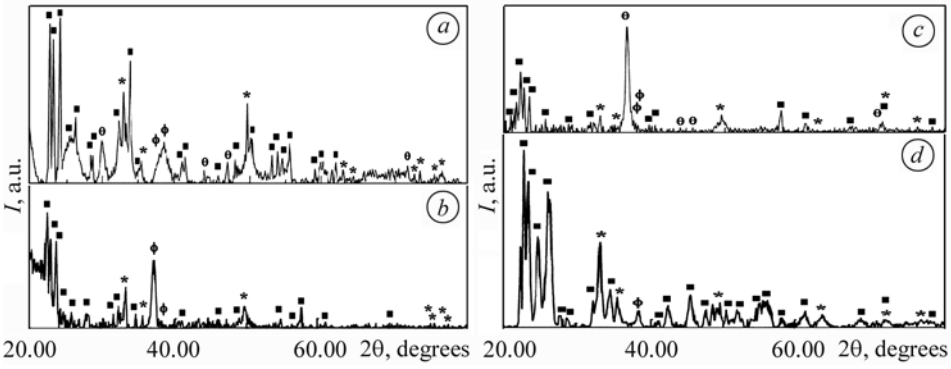

Fig. 1. XRD pattern of S_1 (a, b) and S_2 (c, d): ✶ – WC; ϕ – $MgWO_4$; θ – MgO; ■ – WO_3.

Scanning electron microscopy. SEM micrograph of sample S_1 is shown in Fig. 2*a–d* which was synthesized during reflux reaction of 96 h.

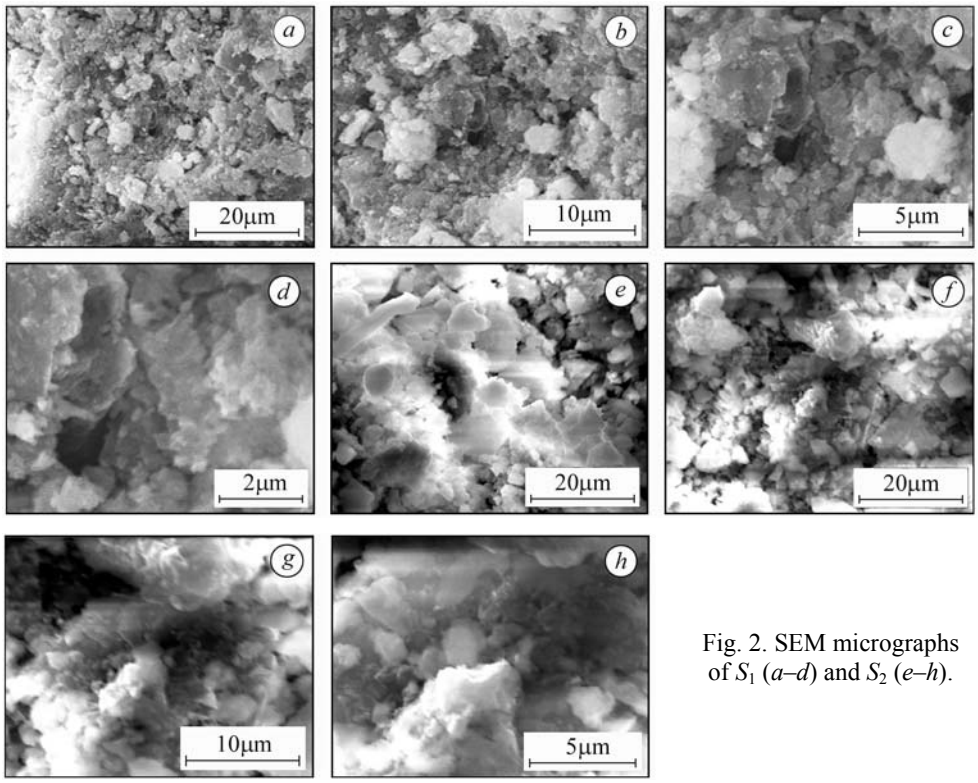

Fig. 2. SEM micrographs of S_1 ($a–d$) and S_2 ($e–h$).

The structural feature shows the agglomerated nanoparticle. The powders present demonstrate the mixed morphology features. At some places powders of faceted mor-

phology can be seen. These powders belong to WC phase in the system. Fig. 2*e–h* shows SEM micrograph of sample S_2, synthesized during reflux reaction of 168 h.

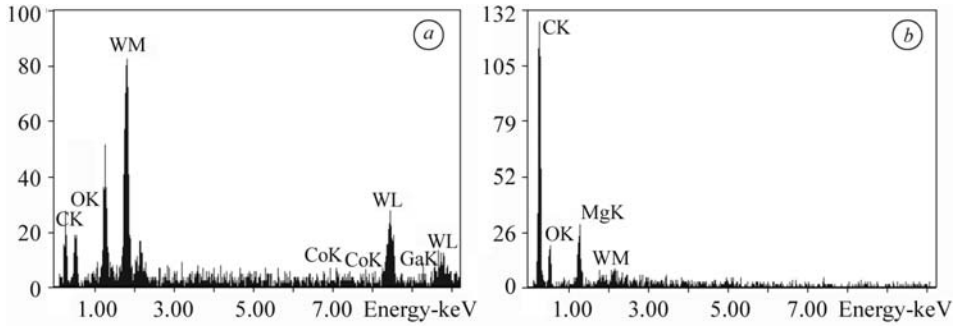

Fig. 3. EDX of S_1 (*a*) and S_2 (*b*).

Here also fine size powders can be seen. The structural features are similar but the variation in shape of the synthesized powders can be seen.

EDAX results. The EDAX analysis of sample S_1 and sample S_2 is shown in Fig. 3 respectively. It shows the presence of carbon, oxygen and tungsten as major constituents which further confirmed the formation of the carbide phase.

Transmission electron microscopy results. TEM of the synthesized particles was done to know the particle size of the synthesized powders. From the selected area diffraction pattern the lattice constant of different phases can be determined. Fig. 4*a*, *b* shows the TEM micrograph of the synthesized powder taken from different areas. Looking at the features of micrograph it can be said that there are different types of phases which vary from spherical to elliptical, cylindrical to rectangular. In these micrographs a particle having a faceted feature is of WC powder.

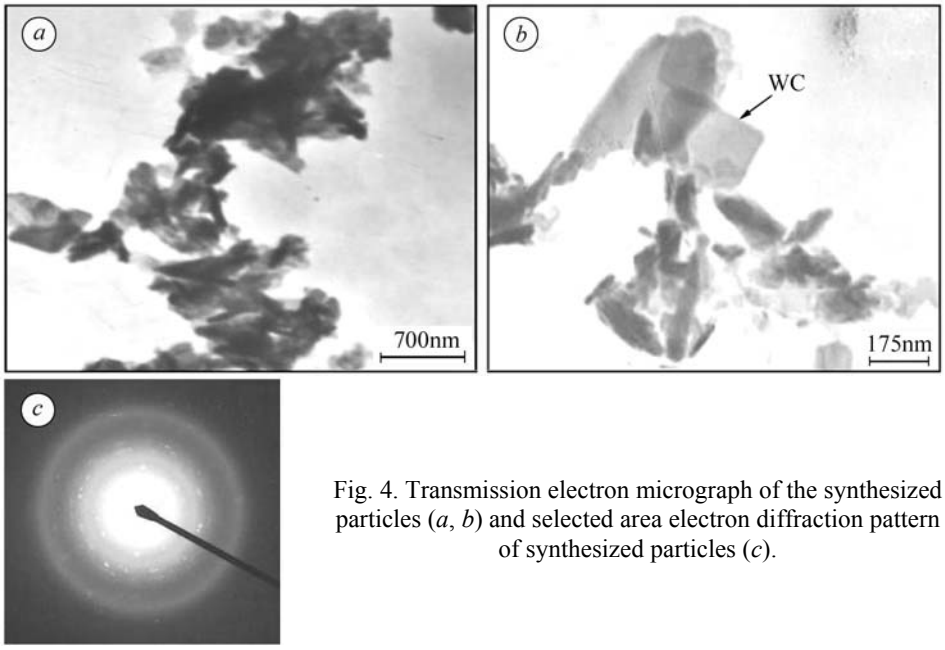

Fig. 4. Transmission electron micrograph of the synthesized particles (*a*, *b*) and selected area electron diffraction pattern of synthesized particles (*c*).

The overall structure gives a complex type of phenomena from which it can be concluded that reduction of WO_3 with glycerol is feasible but condition has to be optimized. It is essential to optimize the role of reducing element magnesium and also the condition required for reduction by using different reducing agents.

Selected area electron diffraction (SAED) taken for faceted powders is also shown in Fig. 4*c* which confirmed the presence of [101] and [110] planes of WC. The X-ray analysis, TEM studies and SAED pattern indicate that the particles which are synthesized are within the nanosized range.

Different phases, structure, particle size and texture coefficients corresponding to different planes

Sample label	Phases	Crystal structure	Particle size (XRD), nm	ICDD CARD No.	Planes	Texture coefficient
S_1	WC	Hexagonal	160	25-1047	100	1.03
					101	0.81
					001	0.74
	WO_3	Triclinic	330	83-0949	002	0.72
					020	1.14
					200	0.75
S_2	WC	Hexagonal	98	25-1047	100	1.43
					101	0.84
					001	0.68
	WO_3	Triclinic	270	83-0949	002	0.72
					020	1.01
					200	0.87

CONCLUSION

It is possible to convert WO_3 to WC nanoparticles using the reflux action technique. The reaction time plays a vital role in the synthesis of nanosized WC particles. If the reaction time is increased the particle size decreases. A detailed study to optimize the reaction parameters to get maximum yield is required.

РЕЗЮМЕ. Металокерамічні ванадієві (WC) матеріали використовують для виготовлення різальних інструментів. Перетворюють WO_3 в WC за допомогою різних методик. Хімічні процеси, задіяні у такій редукції, досить тривалі та енергоємні. Проаналізовано композити, отримані після реакції зворотного струму з метою виявлення можливості перетворення WO_3 у WC. Ця методика перспективна і економна для низькотемпературного синтезу ультрадрібних частинок WC. Синтезовані порошки досліджено методами рентгенівського дифракційного аналізу, сканівної електронної мікроскопії, та енергорозсіювального рентгенівського аналізу, трансемісійної електронної мікроскопії.

РЕЗЮМЕ. Металлокерамические ванадиевые (WC) материалы используют для изготовления режущих инструментов. Превращение WO_3 в WC проводят с помощью разных методик. Химические процессы, которые принимают участие в такой редукции, достаточно продолжительные и энергоемкие. Проанализированы композиты, полученные после реакции обратного тока с целью выявления возможности превращения WO_3 в WC. Данная методика является перспективной и экономной для низкотемпературного синтеза ультрамелких частиц WC. Синтезированные порошки исследовали методами рентгеновского дифракционного анализа, сканирующей электронной микроскопии, энергорассеивающего рентгеновского анализа, трансэмиссионной электронной микроскопии.

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