

STUDY ON THE CARBOTHERMAL REDUCTION OF COATED WITH HYDROCARBONS POWDERED WO_3 IN THE TEMPERATURE INTERVAL 20-1000°C

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Abstract

The carbothermal reduction of both WO_3 powder coated with hydrocarbons and graphite - WO_3 powder mixture were studied by thermogravimetric analysis in the temperature range 20-1000°C and different heating rates. The phase composition of the obtained residue of the experiments with coated WO_3 powder is determined by X-ray structural analysis. The kinetics of the carbothermal reduction of tungsten trioxide depends on the manner of introducing the carbon. It goes on more intensively in the case of coating WO_3 powder rather than blending it with graphite, independently of the heating rate. The formation of WC by carbothermal reduction of carbon coated WO_3 clearly proceeds through reduction to W, followed by carburization into WC. The WO_3 reduction completes at 1000°C after 30 min independent of the heating rate.

Keywords: *thermogravimetry, reduction, tungsten oxide, hydrocarbons coating, tungsten carbide*

INTRODUCTION

Tungsten carbide is material possessing high chemical stability, corrosion resistance, high hardness and wear resistance up to high temperatures, which has led to its broad application in the production of dies and metalworking tools, wear resistant machine parts, electrical resistances, etc. [1-7]. Powdered tungsten carbide (WC) is the raw material for these applications and the creation of methods for the production of powders with homogenous composition and grain size is the task, finding new better decisions.

The production of WC passes through two stages. First the oxide is reduced to high pure tungsten in a hydrogen environment and then the obtained tungsten is mixed with carbon and heated to 1400–1600°C to turn into carbide [3].

Different alternatives for the reduction of WO_3 for the production of WC are described in the literature. Graphite, carbon black or different gases are used as reducing agents, for example: carbon oxide [8], hydrogen [9], hydrogen and methane in different ratios [10, 11], methane [12], hydrogen and methane as a reducing agent and ethylene and ethane for the carbide formation [13]. These methods, along with their advantages, have one basic disadvantage – a highly explosive environment and difficulty in maintaining the stoichiometric carbon – tungsten ratio.

Kodambaka was the first to propose a method for obtaining WC from a precursor – coated with carbon WO_3 [14]. Later this method was developed by Swift G. A. and R. Koc [15]. The coating is carried by thermal pyrolysis of a gas (propylene) at temperature of

550°C. In spite of the undoubted advantages of the method, the problem with the highly explosive environment, when coating the powder, still remains.

A new method for obtaining carbides, which uses precursor -coated with a carbon-hydrogen containing substance (CHCS) metal oxide, overcomes the listed disadvantages. Carbon-hydrogen containing substance (CHCS) is obtained by pyrolysis of polyvinyl chloride (PVC) [16]. Chlorine containing compounds are emitted during the pyrolysis, which necessitates looking for alternate decisions. Our previous investigations prove that the polyvinyl alcohol – PVA successfully replaces PVC for obtaining CHCS without chlorine release [17-19]. To develop the technology for the production of tungsten carbide we have to be familiar with the carbothermal reduction of the coated with hydrocarbons powder of WO_3 , which is the object of the present study.

EXPERIMENTAL PROCEDURE

The interaction of the carbon with WO_3 at the temperatures of carbide formation can be described by the reactions:



The weight of the sample consequently is reduced with the release of the carbon oxides, which can provide information on the process course rate. The experiments were carried out with a thermogravimetric system SETARAM MBT 10-8, measuring weight change of the sample as function of time during heating with different speeds up to 1000°C in a suitable environment. The basic components of the thermogravimetric system are electro magnetic balance and a furnace supplied with a vacuum and gas media set. Some of the more important characteristics of the electro magnetic balance are: a) maximal useful load 10 g; b) range of automatic measure ± 20 mg; c) relative sensitivity $4 \cdot 10^{-8}$ g. The operational temperature range of the electric resistance furnace is from 20 to 1000°C. The temperature rate is set by thermal regulator SETARAM PT-3000, supplied with a programmer providing different heating speeds. The temperature is measured by thermocouple Pt-PtRh10 connected to a cold junction compensator.

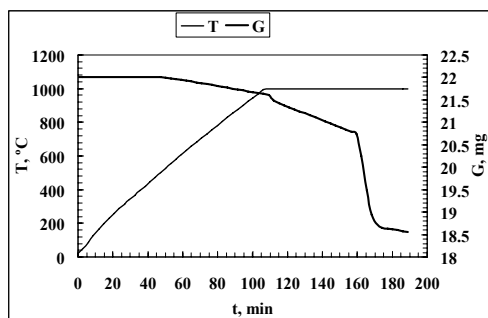
The experimental procedure is as follows: a) powdered WO_3 is coated with hydrocarbons in a manner described in [16] and the coated powder is heated additionally at 600°C; b) a mixture of powdered WO_3 and graphite is prepared separately; c) a sample with 20-25 mg (mixture or coated powder) is placed in the crucible of the balance; d) the system is closed, vacuumated and then filled with argon; e) the range of measurement is selected and the balance is adjusted to zero; f) the temperature rate is set and the system is started. The change of the mass of the sample in the crucible is recorded continuously as a function of temperature from 20 to 1000°C.

The phase composition of the obtained residue of the TGA experiments with coated powder is determined by X-ray structural analysis, carried out with an X-ray device for structural investigations Philips Micro 111 with copper radiation and a graphite monochromator. Relative volume content and unit cell parameters for each of the identified phases were evaluated after the whole pattern least-squares fit to the experimental data, performed by the Powder Cell program [20]. Diffraction line profiles were approximated by the pseudo-Voigt function. Published values for the atomic coordinates were used in calculating the starting model diffraction spectra.

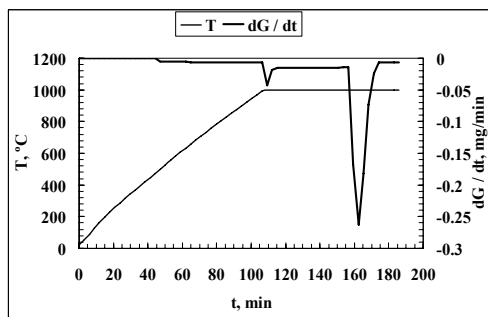
RESULTS AND DISCUSSION

Thermogravimetric analysis of mixtures of powdered WO_3 and graphite and CHCS coated WO_3 powder at two heating rates, $9.2^\circ\text{C}/\text{min}$ and $5.65^\circ\text{C}/\text{min}$, were carried out. One more experiment with a speed of $3.6^\circ\text{C}/\text{min}$ with the coated powder was carried out.

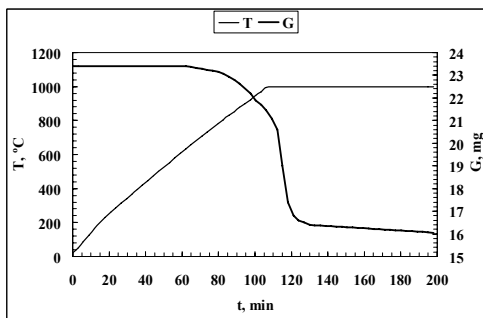
The thermogravimetric curves received at $9.2^\circ\text{C}/\text{min}$ heating speed can conditionally be divided into four sections: first – lack of weight loss – to $\sim 520^\circ\text{C}$; second – (and forth) – weight loss with constant speed during heating from ~ 520 to 1000°C (and holding at 1000°C respectively); third – intensive weight loss during isothermal holding at 1000°C , passing into the fourth sector – weight loss with constant speed at the same isothermal conditions, Figs.1,2.



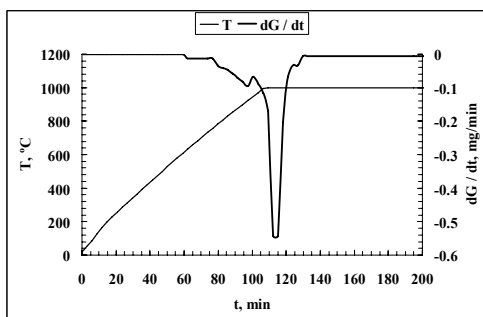
a



b



a



b

Fig.1. Change of the weight with time (a) and speed of weight change (b) of mixture WO_3 + graphite during heating with speed $9.2^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

Fig.2. Change of the weight with time (a) and speed of weight change (b) of precursor – coated with hydrocarbons WO_3 during heating with speed $9.2^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

During heating the mixture of WO_3 and graphite with $9.2^\circ\text{C}/\text{min}$ speed, the processes of intensive weight loss starts at ~ 50 min after reaching 1000°C , Fig.1a, b. The intensive weight loss for the coated powder is observed even during the process of heating – at temperature $\sim 950^\circ\text{C}$ (Fig.2a, b). The lower temperature of the beginning of the process for the coated powder is due to the better contact between the carbon donor and the WO_3 particle and the higher activity of the released during the hydrocarbons pyrolysis atomic (nascent) hydrogen.

The X-ray graph of the coated with hydrocarbons WO_3 , after heating with speed $9.2^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min, shows the presence of diffraction peaks of W and WC, (Fig.3). X-ray and TGA analysis show that significant reduction of the oxide presence has occurred. In the case of the coated powder the process starts at 950°C and it is completed after 30 min.

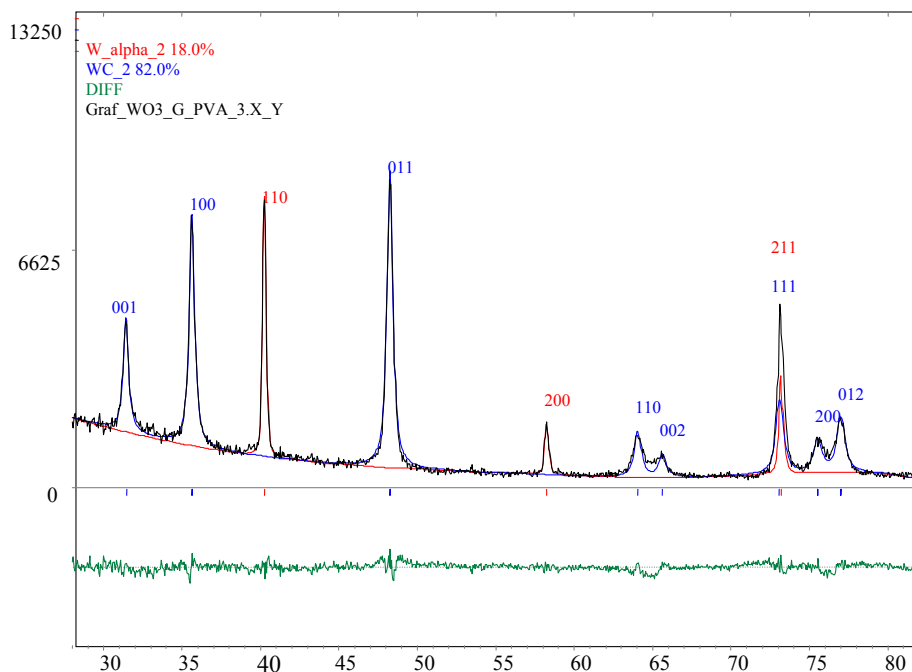
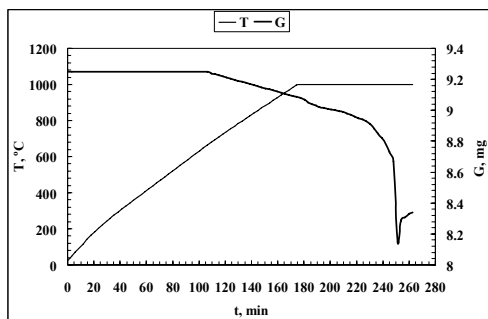
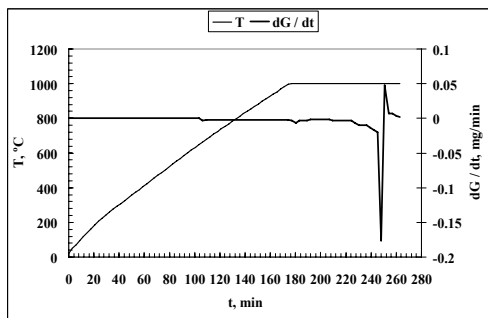


Fig.3. X-ray graph of the coated with hydrocarbons WO_3 after heating with speed $9.2^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

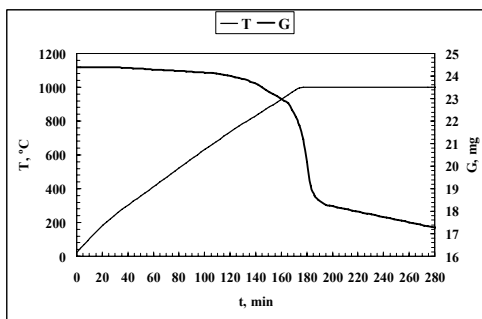
The thermogravimetric curves, obtained at a heating rate of $5.65^\circ\text{C}/\text{min}$ have the same character as those at rate $9.2^\circ\text{C}/\text{min}$, Figs.4, 5.



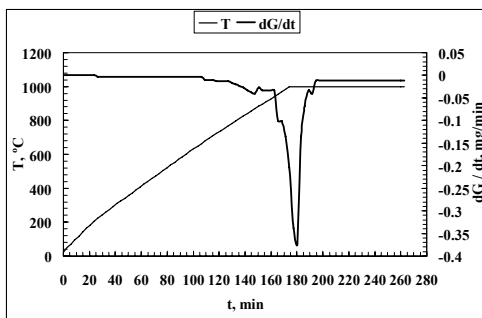
a



b



a



b

Fig.4. Change of the weight with time (a) and speed of weight change (b) of mixture WO_3 + graphite during heating with speed $5.65^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

Fig.5. Change of the weight with time (a) and speed of weight change (b) of precursor – coated with hydrocarbons WO_3 during heating with speed $5.65^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

There is an incubation period of about 60 min after reaching the temperature of 1000°C for the mixture of WO_3 and graphite, and then an intensive weight loss process takes place, Fig.4b. The temperature of the beginning of intensive discharge for the CHCS coated powder is expectedly lower $\sim 940^\circ\text{C}$, i.e. the beginning of intensive reduction is at a lower temperature and at the same time it is completed within 30 min, Fig.5. The X-ray graph of the residue shows the presence of diffraction peaks of W and WC, Fig.6.

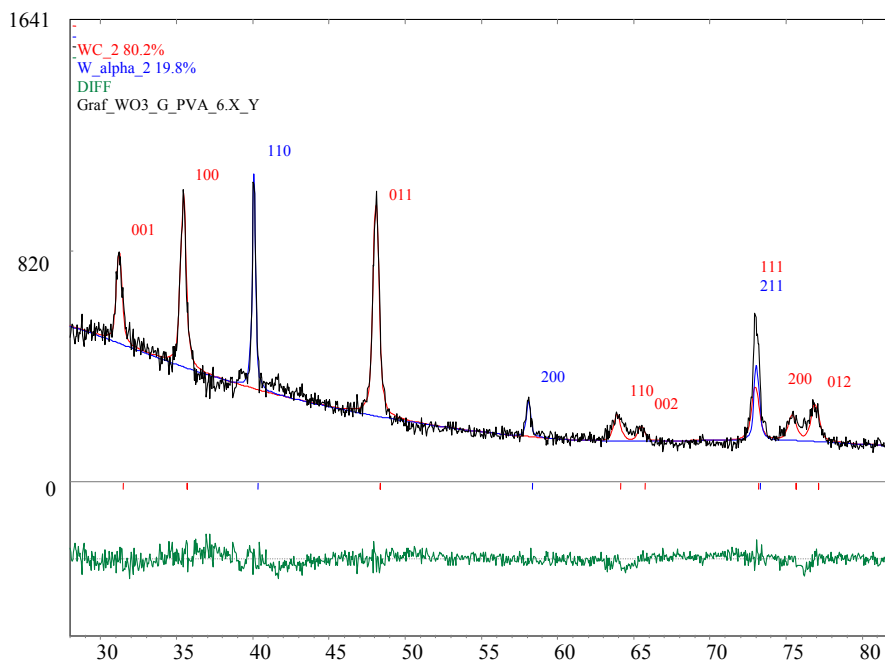


Fig.6. X-ray graph of the coated with hydrocarbons WO_3 after heating with speed $5.65^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

The thermogravimetric curve of the coated powder, obtained at a heating rate of $3.6^\circ\text{C}/\text{min}$, does not principally differ from those obtained at higher heating rates, and expectedly the temperature of the intensive discharge is reduced, $\sim 930^\circ\text{C}$, Fig.7.

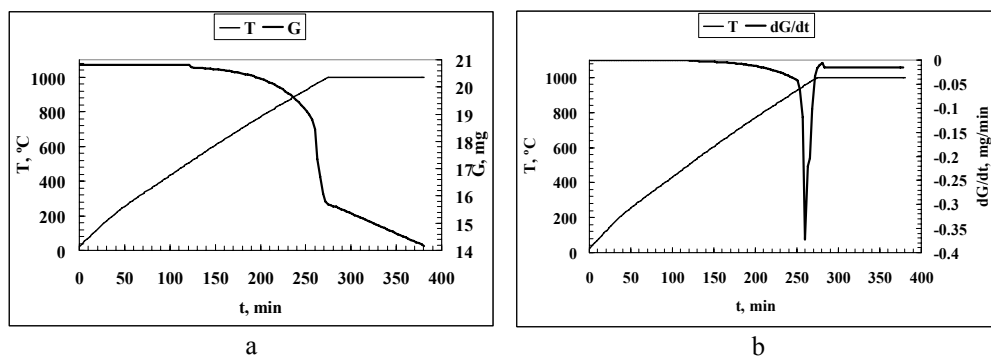


Fig.7. Change of the weight with time (a) and speed of weight change (b) of precursor – coated with hydrocarbons WO_3 during heating with speed $3.6^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

In this case the X-ray graph of the residue also shows a presence only of diffraction peaks of W and WC, Fig.8.

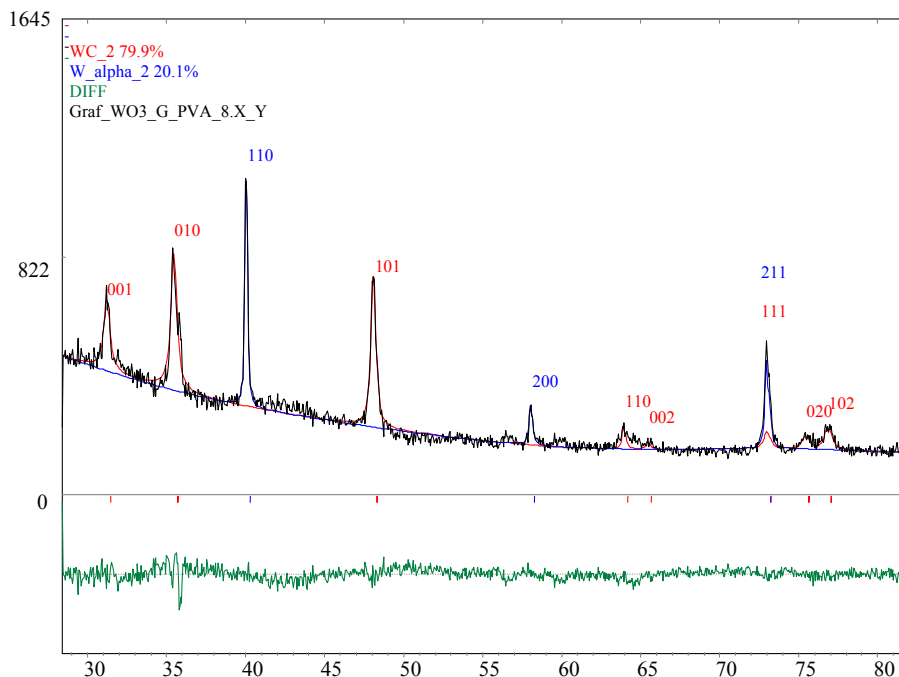


Fig.8. X-ray graph of the coated with hydrocarbons WO_3 after heating with speed $3.6^\circ\text{C}/\text{min}$ to 1000°C and holding for 80 min.

The carbothermal reduction of WO_3 is described by the reaction:



Thermodynamically the reaction is possible at temperatures above 600°C and it is assumed that it goes on with formation of intermediate oxides such as: WO_2 , W_5O_{14} , $\text{W}_{18}\text{O}_{40}$, $\text{W}_{20}\text{O}_{58}$ and $\text{W}_{24}\text{O}_{68}$ [21]. In this study the WO_3 reduction is carried out completely at 1000°C after 30 min and we do not observe WO_3 or any other inferior tungsten oxide in the X-ray diffraction patterns.

From Figures 1-6 one can see that the kinetics of the carbothermal reduction depend on the manner of introducing the carbon in the powder mixture. The reduction of WO_3 in experiments with coated powder goes on more intensively than in those of mixtures with graphite, independently of the heating rate.

A qualitative assessment of the phases in samples, treated at different heating rates, is made on the basis of the comparison of their integral intensities. The results are presented in Table 1.

Tab.1. Relative volume content and unit cell parameters for W and WC, obtained in the residue of TGA experiments.

Fig.6			Fig.8		
[%]	Lattice [Å]		[%]	Lattice [Å]	
	a	c		a	c
19.79	3.1612	-	20.13	3.1637	-
80.21	2.9017	2.8390	79.81	2.9005	2.8406

It is observed on the X-ray diffraction patterns that the relationship between WC and W phases is not dependent on the heating rate. The quantity of WC is ~ 80% and that of W ~ 20% on the three X-ray graphs. This is proof that the process is completed with one and the same ratio between the final products, independently of the heating rate.

CONCLUSION

- Combining the use of TGA and X-ray diffraction analysis, the formation of WC by carbothermal reduction of carbon coated WO₃ clearly proceeds through reduction to W followed by carburization into WC. The WO₃ reduction completes at 1000°C after 30 min independently of the heating rate.
- The thermogravimetric data show that the reduction of WO₃, coated with hydrocarbons, goes on more intensively than the one of mixtures with graphite, independently of the heating rate.
- The X-ray structural analysis shows the presence of diffraction maximums of W and WC only, the inferior oxides observed by other authors, are not registered. The data of the quantitative X-ray analysis shows that the ratio W/WC is almost equal after holding for 30 min at 1000°C, independently of the heating rate.

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