A NEW PRECURSOR FOR SYNTHESIS OF REFRACTORY METAL CARBIDES

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Abstract

This paper deals with the possibility of using a new precursor for carbide production. The new precursor was coated with hydrocarbon refractory metals or their oxides. Synthesis was carried out in an atmosphere of argon (W and B) or nitrogen (Ti). X-ray diffraction data showed that synthesis of Ta, B, and Ti-B carbides was practically completely finished during 120 min at lower temperature in comparison with the conventional synthesis. Uniform distribution of carbon and the close contact between reactants was achieved with the coated precursor.

Keywords: carbide, hydrocarbon-coated powder, refractory metals, synthesis

INTRODUCTION

Carbides typically have advantage of high values for melting temperature, strength, wear resistance and a low thermal expansion coefficient. Tungsten carbide has high hardness, high melting temperature, high fracture toughness, high thermal conductivity, and a low thermal expansion coefficient. It is therefore used for many applications. WC, as a hard metal, is used in cutting tools; saw blade tips, drills, and many other high wear applications [1–3]. Tungsten carbide is also used in the manufacture of high temperature furnace crucibles and other components. Additional applications include the use of WC in catalysis industries and aerospace coatings [4-6].

Titanium carbide is a ceramic material with many applications in key high technologies, from mechanical to chemical and microelectronics because of its high melting point, high hardness, high electrical conductivity, high chemical and thermal stability, high wear resistance, and high solubility for other carbides. Titanium carbide is used in coated steel press tools, grinding wheels, wear-resistant coatings, high-temperature heat exchangers, magnetic recording heads, turbine engine seals, and bulletproof vests. Titanium carbide is also utilized in the production of SiC-TiC, Si_3N_4-TiC, and Al_2O_3-TiC and ZrO_2-Ti(C, N) composites [7, 8].

Boron carbide, due to its high hardness, chemical inertia, good technological and neutron-absorbing characteristics, has an important application in aeronautics, defense and nuclear industries [2, 9-10]. Particularly important are its low specific weight and high hardness, the latter even surpassing diamond and boron nitride at temperatures over 1100ºC [11].

For all these applications, the synthesis of carbide powders with a homogeneous chemical composition, fine particle size, narrow particle size distribution, and loose agglomeration are of great importance.

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The powders can be produced by the direct synthesis of relevant elements, or by the reduction of their oxides. The main shortcoming of direct synthesis is that it requires very high temperatures from 1700 to 2100ºC.

The carbide production from metal oxides generally proceeds as a two-step process. At first, the oxide is reduced to a high purity metal in a hydrogen atmosphere. Then the metal is mixed with carbon and the reaction of these elements is running at the temperatures of 1400–2000ºC to produce the carbide [2]. This process requires both high temperature and a long time to be completed, so carbide produced by this method generally has large particles and agglomeration, thus it requires milling. Additionally, the use of carbon black introduces impurities into the product. A new method for production of carbides by the reduction of oxides of high-melting point metals using gaseous hydrocarbons has been established in recent years as the most promising method due to lower temperatures required for the process, and as a consequence, low energy consumption [12-14].

As an illustration of the advantages of this method could be US Patent No. 5.417.952 describing the process of synthesis based on the carbothermic reduction of a new precursor. The precursor is obtained from titanium oxide (TiO_2) and gaseous hydrocarbon (C_3H_6) and it provides high contact area between reactants. The TiC powders are synthesized at 1550ºC for 4 h in a flowing argon atmosphere and then 6 hours H_2 treatment at 1200ºC, and 1 hour of dry ball milling using WC balls. The synthesis of WC powder is completed above 1400ºC by using a similar precursor - carbon coated WO_3 [14].

The main shortcomings of all mentioned methods - a dangerous reaction atmosphere and comparatively high temperature - remain even if carbon coated oxide is used as precursor.

The main aim of this work is to investigate the potential of a new precursor – coated with hydrocarbon refractory metals or their oxides for the synthesis of refractory metal carbides.

EXPERIMENTAL PROCEDURE

The technique for coating metals or ceramics [15-17] was developed in IMS BAS and SRI BAS Sofia and successfully applied to PM applications [18, 19].

The main steps of the coating process are:

1. decomposition of polyvinyl chloride (PVC) powder in the atmosphere of pure Ar or N_2 during 30 min at temperatures of 390-400ºC. A black shining substance is obtained; an analysis showed only the presence of C and H and the generalized formula CnHn could represent it;
2. milling and dissolving of the CnHn powder in toluene (C_7H_8);
3. filtration of the solution for elimination of the insoluble particles;
4. mixing of metallic powder (B, Ti, Ta or W) with a filtrated solution of a known concentration of CnHn dependent on the stoichiometric concentration of C in carbide;
5. evaporation of the solvent under conditions of continuous stirring of the mixture.

These processes resulted in the fact of all metal particles being coated with a layer of CnHn thus obtaining a precursor – coated with hydrocarbon metal or oxide powder, Fig.1.

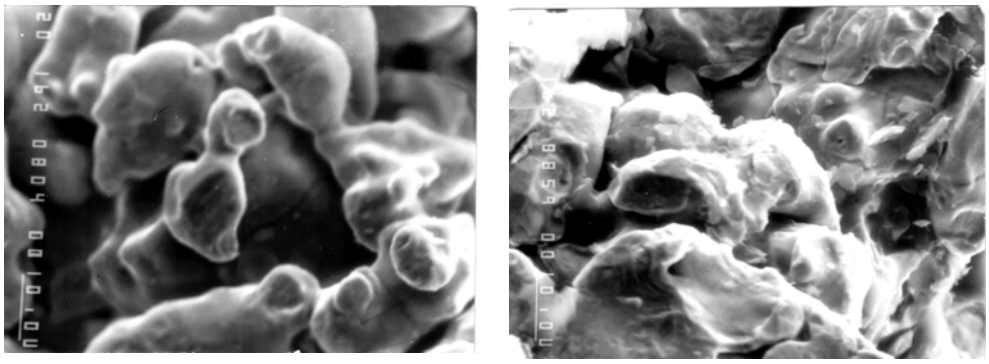

Fig.1. SEM image of: a) original metal powder, b) metal powder coated by hydrocarbon.

Samples were prepared by pressing hydrocarbon-coated powders at 600 MPa. Synthesis of carbides was carried out in the atmosphere of argon (W, Ta, B) or nitrogen (Ti) at the temperatures of 1280-1300ºC during 120 min, then furnace cooled. Hydrocarbon was completely dissociated during synthesis process up to 1100ºC and its active vapour products catalyzed by the hot metal surfaces to produce finely divided nascent carbon. This carbon was well distributed, resulting in a higher specific surface, and a close contact between reactants was achieved, which allows the best possibility for carbonization to occur.

The X-ray study was applied only for a review on phase transformation during synthesis of the initial materials. The measurements were carried out at an ambient temperature on XRD diffraction system Philips X'Pert Pro equipped with a Cu cathode with a positional sensitive detector (X'Celerator) in Bragg-Brentano para-focusing geometry.

The specimens were measured at operational voltage 40 kV and current 50 mA. The X-ray diffraction (XRD) data were taken from the wide 2 Theta range from 10 (20) to 80(90) degrees. To achieve a good quality of the XRD spectra, step size was set to 0.015 degrees.

XRD patterns were analysed by the X`Pert HighScore software. For stripping Kα2 line the Ladell and Rachinger method was used and compared.

RESULTS AND DISCUSSION

It is well known that carbide of refractory metals cannot be sintered at 1300ºC without a metal binder. All examined samples showed that the carbonization occurred simultaneously with a partial sintering of the precursor.

System Ti-C-N

The X-ray diffraction analysis carried out showed that the phases TiC0.3N0.7, TiC and traces of TiO were observed in the samples produced from hydrocarbon coated Ti powder, Fig.2.

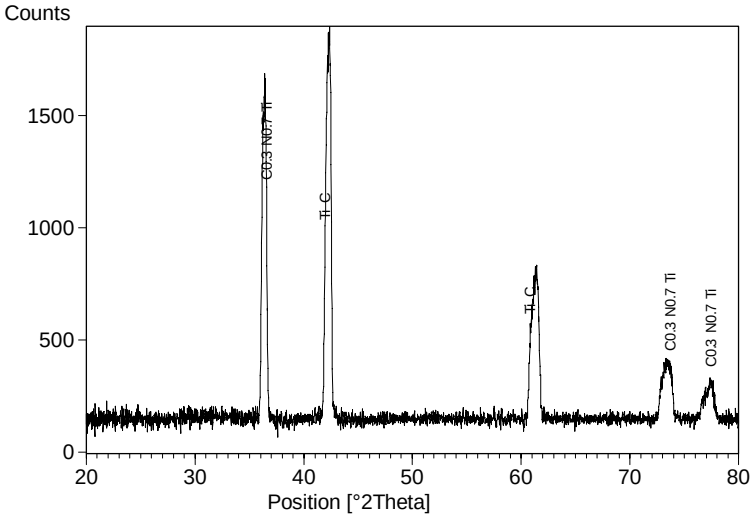

Fig.2. X-ray plot of Ti coated with hydrocarbon and sintered at 1300ºC in nitrogen.

The presence of TiC0.3N0.7 phase proved the possibility of synthesis in nitrogen atmosphere of both carbides and carbonitrides by using the new precursor or solely carbides in argon atmosphere. The samples were examined by optical metallography as well. The microstructure was comprised of the pores and TiC and TiC0.3N0.7 grains with approximately the same size, Fig.3.

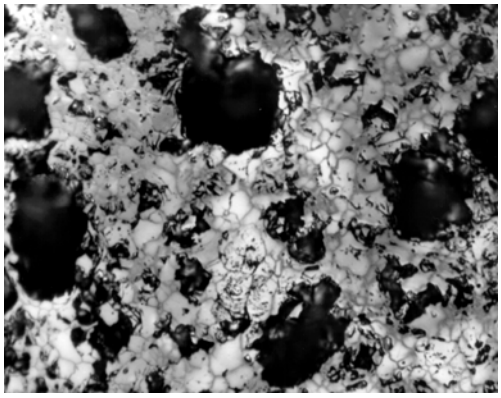

Fig.3. Microstructure of Ti coated with hydrocarbon and sintered at 1300ºC in nitrogen.

System B-C

The synthesis of carbide from hydrocarbon coated B powder resulted in the formation of phase B_4C. Traces of unreacted B were observed as well, Fig.4.

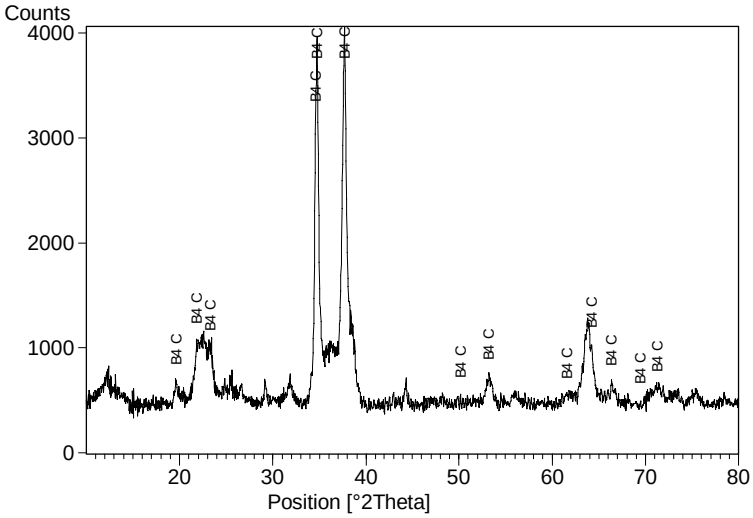

Fig.4. X-ray plot of B coated with hydrocarbon and sintered at 1300ºC in argon.

System B-Ti-C

A mix of coated Ti and B powders has been used as a precursor for synthesis. The phases TiB_2, TiC and B_4C were observed, Fig.5.

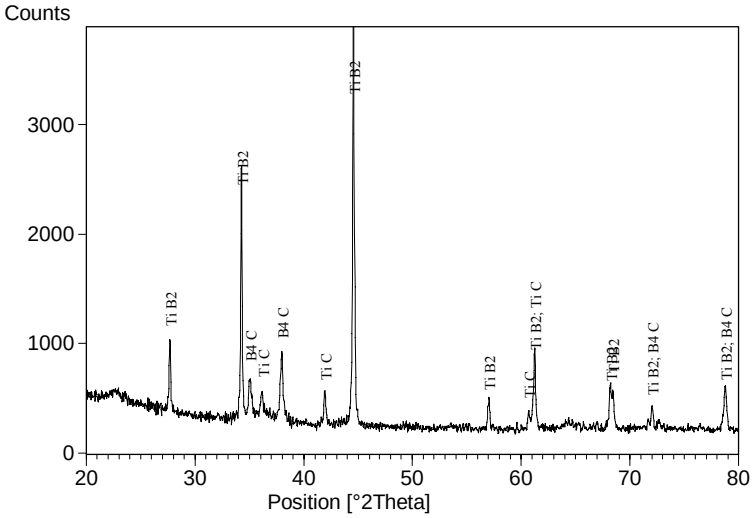

Fig.5. X-ray plot of mix B and Ti coated with hydrocarbon and sintered at 1300ºC in argon.

System Ta–C

The process of carbonization of Ta to TaC was essentially completed at 1300ºC. Traces of impurities can be seen in the X-ray plot, Fig.6. These impurities were unidentifiable in term of initial chemical composition of raw material.

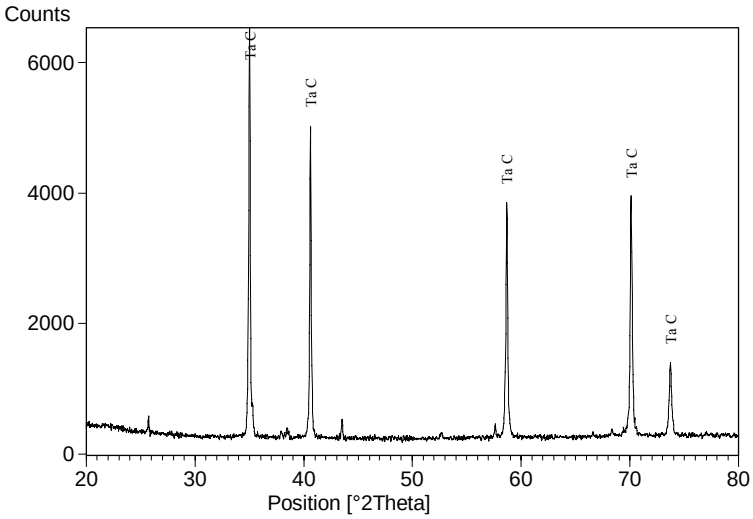

Fig.6. X-ray plot of Ta coated with hydrocarbon and sintered at 1300ºC in argon.

System W–C

The phases W_2C, WC and W were observed in the samples produced from hydrocarbon coated W powder, Fig.7.

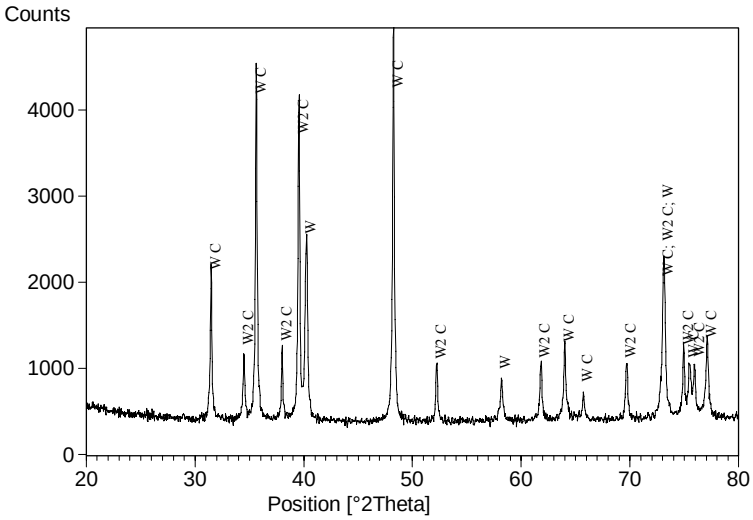

Fig.7. X-ray plot of W coated with hydrocarbon and sintered at 1300ºC in argon.

The remaining elemental W in the sample was probably due to carbon insufficiency. Swift and Koc [14] have supposed that temperatures higher than 1400ºC would be required to complete the carbonization of W into WC.

The obtained results could be explained by the peculiarity of solid state diffusion. As it is known the solid-state diffusion controls refractory metal carbide formation at 1300ºC. The promoting effect of hydrocarbon used as carbon donor is due to two causes. On the one hand, during thermal treatment of coated powder hydrocarbons decompose to more active nascent carbon and hydrogen. They penetrate more quickly into metal lattice and possess higher chemical activity. On the other hand, the hydrocarbon decomposition process results in a layer of carbon on each Ti particle as well. By this way there is realized an intimate contact between the C-donor and metal particles. Both - increased contact area and more active nascent carbon - accelerate titanium – carbon solid-state diffusion and enable carbide formation at lower a temperature in comparison with those of other methods.

CONCLUSION

- The experiments carried out have proved the possibility to obtaining refractory metal carbides by using a new precursor - coated by hydrocarbon metallic powders.
- Due to the intimate contact metal/hydrocarbon and the uniform distribution of carbon on the metal surface, the synthesis was realized at temperatures (1280-1300ºC) lower than the conventional ones (1400 – 2100ºC).
- The process of carbonization of Ta, B, and Ti-B mix coated powders was practically completed during a synthesis time of 120 min.

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