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Formation of High Temperature Compounds in W-C-B System by Reactive Spark Plasma Sintering

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The formation of high temperature composites in W-C-B system from fine-grained powders in dependence on the ratio of components by using reactive spark plasma sintering was studied. The mixture of W_2C and C nanoparticles was used as tungsten and carbon precursors. The W_2C and carbon mixture with different ratio of components was prepared by reduction of WO_3 in presence of CH_4 in nitrogen inductively coupled plasma. The specific surface area of the mixture was in the range of 36 – 42 m^2/g in dependence on the content of carbon. The W_2C and carbon particles were mixed mechanically with amorphous boron and densified using the spark plasma sintering technique at 1500 – 1700 °C and pressure of 30 MPa for 4 minutes. The sintered bodies contained WB_2 and B_4C phases. The ratio of phase depends on the content of the components in the raw mixture.

Keywords: amorphous boron, tungsten carbide nanoparticles, reactive spark plasma sintering, tungsten diboride, boron carbide composites.

1. INTRODUCTION

Several tungsten boride phases (W_2B, WB, WB_2, W_2B_5, WB_4) and their composites (TiB_2-WB_2, WC-WB-W_2B_5, (Ti, W, Cr)B_2 due to high melting point, hardness, electronic conductivity, chemical inertness are promising candidates for the industrial application as corrosion-resistant, abrasive, electrode materials [1 – 5] or new alloy tools [6].

Tungsten borides are usually produced by solid state reaction between tungsten and amorphous boron powders [1] or by self-propagating high-temperature synthesis (SHS) [2].

The formation of tungsten borides phases in solid state reactions occurs at high temperature (800 – 1550 °C) in vacuum or argon atmosphere for 2 h. The SHS is simple, energy efficient and low cost process but it includes additional milling of the product obtained. However, the application of the tungsten boride powders prepared is limited due to poor sinterability. One of the trends for solving this problem is reactive spark plasma sintering of raw powders [3, 4, 7] and application of sintering additives with a low melting point such as nickel or cobalt borides [3]. This approach allows obtaining dense WC-WB-W_2B composites with the grain size in the range of 20 – 25 µm at 1700 – 1800 °C [4] or tungsten boride layer on W discs with thickness in the range of 35 – 112 µm in the temperature range of 1000 – 1400 °C with holding time of 30 min [7].

The further improvement of formation and densification of tungsten borides will be connected with application of nanosized raw powders. Regarding pyrophoric characteristics of nanosized tungsten, it is necessary to replace it with more stable compounds.

The aim of the present work was formation of tungsten boride based composites during reactive plasma sintering of mixture of amorphous boron with W_2C-C nanoparticles produced by the thermal plasma technique.

2. EXPERIMENTAL

The W_2C-C nanoparticles with different carbon content were prepared by evaporation and reduction of coarse grained commercially available WO_3 (purity 99.8 %) powder in a radio-frequency discharge nitrogen plasma in the presence of methane. The experimental apparatus consisted of radio-frequency oscillator (5.28 MHz) with maximum plate power of 100 kW, water cooled cylindrical stainless steel reactor and bag filter for collection of nanoparticles as well as gas and powders supply systems. The flow rate of the plasma forming gas - nitrogen was 8.0 m^3/h and feed rate of WO_3 was in the range of 1.2 – 1.6 kg/h. The raw powder was introduced into the plasma flame through 8 tubes by carrier gas – nitrogen. The reducing gas – methane was injected into the reactor in the vapour region of WO_3 at a distance of 20 – 30 mm below the introduction plane of oxide [8]. The chemical composition of the nanoparticles prepared was determined as ratio between flow rate of WO_3 and methane.

The prepared WC_2-C nanoparticles with several content of carbon with the average particle size in the range of 10 – 15 nm were mechanically mixed with amorphous boron (98.7 %). The chemical composition of the prepared mixtures is shown in the Table 1. XRD patterns of mixtures showed only presence of W_2C.

The prepared mixtures were pressed into graphite dies with diameter of 30 mm. The dies were placed into SPS apparatus (SPS-825.CE, SPS Syntex Inc.).

The formation of compounds and their sintering was conducted in the temperature range of 600 – 1800 °C in a

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vacuum and pressure of 30 MPa. The heating rate was 100 °C/min and holding time at sintering temperature was 2 or 4 min. After sintering the samples were polished to remove graphite from surface.

Table 1. Chemical composition of the mixtures used

Samples	Chemical composition, wt.%			
	W	C	B	O
W1	78.30	2.30	18.10	1.30
W2	70.50	4.26	24.10	1.14
W3	68.80	4.78	25.20	1.22
W4	64.70	5.72	28.32	1.26
W5	52.50	8.57	37.70	1.23

The phase composition of the bulk materials was determined by X-ray diffraction (XRD) analysis (8Advanced, Bruker AXS). The crystallite size was calculated from broadening diffraction maxima of WB_2 using software Eva12. The content of component was controlled by X-ray photoelectron spectroscopy (XPS, Pioneer, Bruker AXS). Density of the samples was determined by using the Archimede's method.

3. RESULTS AND DISCUSSION

Accordingly to the spark plasma sintering (SPS) curves (Fig. 1) the shrinkage of the powders included at least 3 stages.

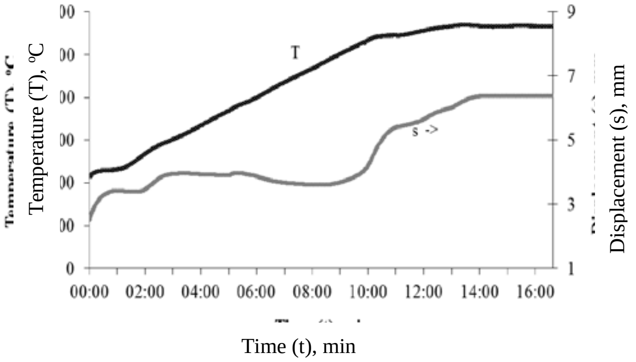

Fig. 1. Temperature and punch displacement curves of the sintering W_2C-C/B mixture by using SPS process

The first stage of the shrinkage started at the temperature range of 600 – 750 °C due to the densification of the samples and extraction of absorbed gases because XRD patterns of the samples pressed at 600 °C were similar to that of the raw powders and their showed only broad diffraction maxima of W_2C (Fig. 2).

The next stage of the shrinkage in the temperature range of 950 – 1200 °C showed small decrease of the shrinkage and was connected with partial decomposition of W_2C phase and formation of tungsten borides – WB and WB_2. The remarkable densification of the samples was observed at the temperature in the range of 1450 – 1600 °C when the final products – WB_2 and B_4C were formed and sintered.

Obviously, the formation of the final phases and their sintering will be promoted by additional heat of exothermic reactions. The final relative density in the range of 97.0 – 98.1 % was reached at 1700 °C – 1800 °C during 4 min depending on the composition (Table 2).

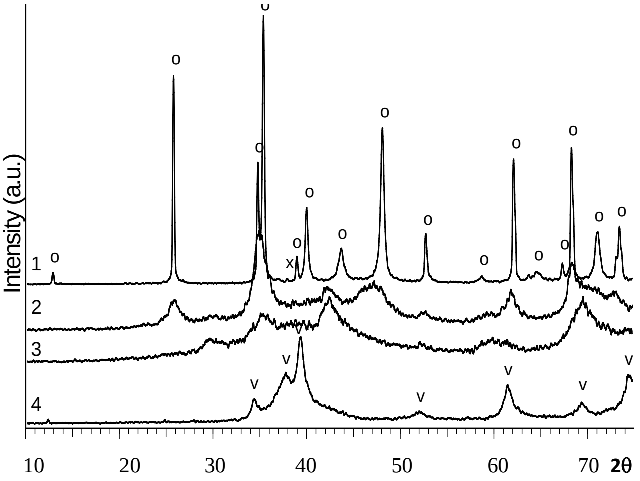

Fig. 2. XRD patterns of the SPS samples calcinated at: 1 – 1600 °C; 2 – 1200 °C; 3 – 1000 °C; 4 – 600 °C; o – B_2W; x – B_4C; v – W_2C

Table 2. Relative density of W3 and W4 samples via SPS temperature, holding time 4 min

Sintering temperature, °C	Relative density, %	
	sample W3	sample W4
1500	82.0	83.0
1600	89.0	91.0
1700	97.0	98.0
1800	97.6	98.1

The dense bulk materials sintered at 1800 °C with C content above 4.78 wt.% contained only crystalline WB_2 and B_4C (Fig. 3); XRD patterns of the mixtures with C content below 4.26 wt.% showed only diffraction maxima of WB_2 because the low content of the formed B_4C.

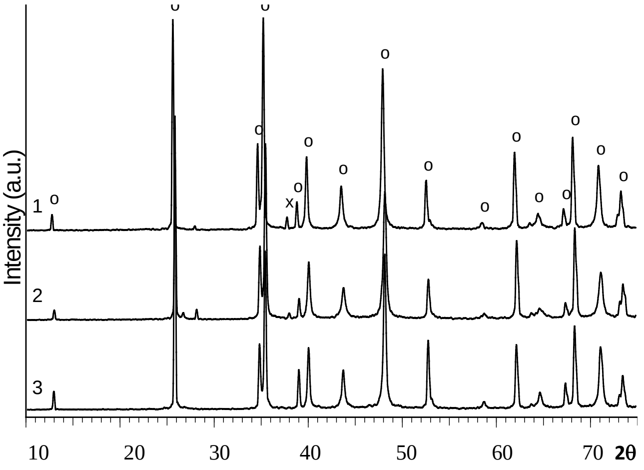

Fig. 3. XRD patterns of sintered materials in dependence on sample chemical composition: 1 – sample W5; 2 – sample W3; 3 – sample W1; o – B_2W; x – B_4C

According to data [8], sintering of W_2C-C nanoparticles with content of carbon about 6 wt.% at 1500 °C resulted in formation of a single WC-phase material. However, the analysis of the phase composition of sintered B-W_2C-C mixture suggests that reaction of boron with tungsten is preferable with respect to formation WC from W_2C-C nanoparticles. The presence of W_2B-phase together with WB_2-phase at sintering temperature up to 1200 °C confirmed that carbon in W_2C was replaced gradually by boron and remaining its amount reacted with carbon forming B_4C. This is contradictory with data [4] where preferable reaction $W_2B + C = WB + WC$ was observed.

The calculated crystallite size of WB_2-phase is in the range of 45 – 76 nm depending on the content of tungsten boride and sintering temperature (Fig. 4).

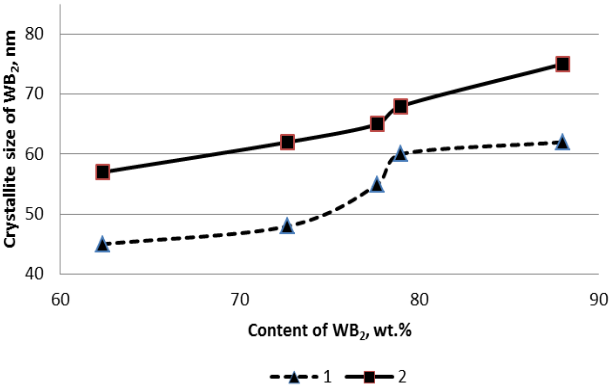

Fig. 4. Crystallite size of WB_2 in dependence on content of WB_2 in W-C-B powders sintered at 1 – 700 °C and 2 – 800 °C

Increase of the crystallite size of WB_2-phase with the content of boride indicated that presence of B_4C hindered growth of boride crystallites at both sintering temperatures. On the other hand, sintering temperature of 1800 °C had a little influence on the density of the samples but it promoted crystallite growth.

The obtained results showed that reactive spark plasma sintering of the W_2C/C nanoparticles with amorphous boron will be succesfully applied for preparation dense WB_2-B_4C composite materials at 1700 – 1800 °C with fine-grained microstructure. The ratio of WB_2 and B_4C is determined by the content of tungsten, carbon and boron in the raw powders.

4. CONCLUSIONS

The reactive spark plasma sintering of the mixture of W_2C/C nanoparticles with amorphous boron allows manufacture dense WB_2-B_4C composite materials with fine-grained microstructure at 1700 – 1800 °C during 4 minutes.

The formation of B_4C inhibits the crystallite growth of WB_2 during the sintering process.

Acknowledgments

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