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Journal of Solid State Chemistry 179 (2006) 2939–2943
JOURNAL OF SOLID STATE CHEMISTRY
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The directional crystallization of W–B–C–*d*-transition metal alloys

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Received 20 September 2005; received in revised form 26 April 2006; accepted 25 May 2006
Available online 2 June 2006

Abstract

Crystallization from the melt during arc melting and directional solidification during induction zone melting of pseudo-alloys tungsten carbide (WC)–MeB_2 (*Me*—Ti, Zr, Cr) and a number of alloys of the W–B–C system ($WB_{0.12}C_{0.74}$; $WB_{0.25}C_{0.75}$; $WB_{0.34}C_{0.32}$; $WB_{0.49}C_{0.76}$; $WB_{0.59}C_{0.76}$; $WB_{0.89}C_{0.75}$; $(WC)_{0.9}B_{0.1}$) has been studied. It was shown that the alloys WC—80 mass%–ZrB_2—20 mass% and WC—72 mass%–WB—28 mass% are the closest ones to eutectic compositions. Investigation of the microstructure of eutectic alloys in the WC–WB system by thin foil method has revealed that both matrix and reinforcing phases are single crystalline.

Hardness tests by indentation of the eutectic structure area ($P = 10.3$ N) do not result in radial crack formation, which is evidence of the essential plasticity of the obtained composite material. It is established that new ceramic–ceramic eutectic composite materials based on WC with transition metal diborides and with a boride phase of tungsten may be created. Such materials can be successfully applied in contemporary high-temperature techniques.

Keywords: Carbide; Boride; Eutectic; Directionally crystallization; Microstructure; Hardness

1. Introduction

Carbide phases, tungsten carbide WC and W_2C, and complex systems based on them are of special interest among *d*-transition metal carbides. Although WC has a slightly higher toughness in comparison with other refractory compounds, the possibility to moderate its hardness and to somewhat reduce its brittleness (especially in the cast state) presents a challenging and rather important task.

The goal of this work is to elucidate the possibilities of improving the resistance of molten tungsten carbides to brittle fracture by creating composite materials on their base with additions of some non-oxygen refractory compounds, particularly metal borides. This will allow decreasing the content of expensive tungsten and making the resulting materials more cost effective.

The methodology of the work lies in studying the possibility of reinforcing the re-melted matrix of the WC (which usually consists of a mixture of two carbide phases WC and W_2C) by means of eutectic structure formation during the crystallization process. The eutectic structure is characterized by uniformly distributed reinforcing elements, such as threadlike or platelike structural elements that are formed from another, sufficiently plastic and strong phase incorporated into the matrix phase.

It was previously shown by the authors of the present work that, for example, under conditions of co-crystallization of eutectic mixtures of some boride phases, particularly $Me^{I}B_6$ (Me^{I} = rare earth metal) and $Me^{II}B_2$ (Me^{II} = transition metal), the transition metal boride phase (MeB_2) crystallizes in platelike or, more often, in threadlike shape due to its specific hexagonal crystal structure. Such a structure results in improved strength and diminished brittleness of the obtained composite materials [1,2].

There is practically no information on constitutional diagrams of pseudo-binary systems WC-transition metal diboride. According to [3,4], ternary phases are absent in the W–B–C system, and boron is not soluble in WC.

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doi:10.1016/j.jssc.2006.05.021

2. Experiment

Pseudo-alloys WC–MeB_2 (Me = Ti, Zr, Cr) and a number of alloys in the W–B–C system ($WB_{0.12}C_{0.74}$; $WB_{0.25}C_{0.75}$; $WB_{0.34}C_{0.32}$; $WB_{0.49}C_{0.76}$; $WB_{0.59}C_{0.76}$; $WB_{0.89}C_{0.75}$; $(WC)_{0.9}B_{0.1}$) were studied.

Samples were prepared by crystallization of pre-sintered rods prepared from mixtures of corresponding phases by means of arc melting or directional crystallization in vertical crucibles using inductive zone melting in a modern setup "Crystal 111".

Transmission (PEM U) and scanning (Stereoscan S4-10) electron microscopy, XRD phase analyses (HZG-4A), micro- and macrodurometery (PMT-3), measurement of pycnometric density and Young's modulus (ultrasonic method) were used to characterize materials. Density (ρ), microstructure, morphology of phase components, phase component distribution, real structure (method of thin foils), structure of fractured surfaces, phase composition, microhardness ($P = 1.9$ N) (H_μ), hardness ($P = 10.3$ N) (H_v), fracture toughness (K_{1c}) and Young's modulus were studied.

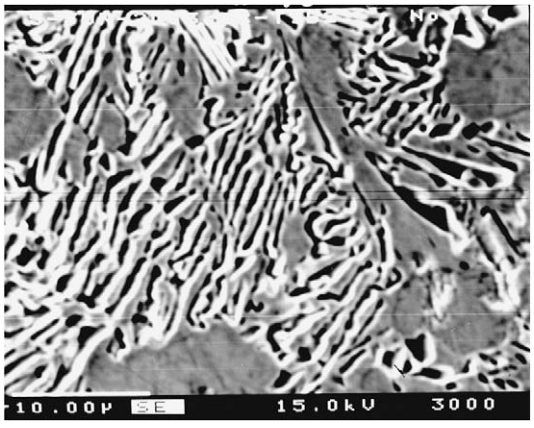

Fig. 1. Microstructure of the composite material WC—5 mass% TiB_2.

3. Result and discussion

3.1. Systems WC–MeB_2

Samples with a TiB_2 content of 5, 15 and 25 mass% were investigated. The existence of eutectic interaction in these systems was confirmed (Fig. 1).

Results of XRD phase analyses of composite materials prepared by the arc-melting method in the WC–TiB_2 system are presented in Table 1. As was to be expected, with the increase of the TiB_2 content the content of a-WC is diminished. Also, trace amounts of WB and W_2B phases were detected in the material, which confirms the interaction between tungsten and boron.

The character of component interaction in the WC–ZrB_2 system was studied on the samples obtained both by directional crystallization (20 mass% ZrB_2), and by arc melting (10, 20, and 30 mass% ZrB_2).

Composite material with 20 mass% of diboride phase obtained by direction crystallization presents the major interest. Investigation of the microstructure of a quenched drop of this composition suggested a possible presence of eutectic interaction: the diboride phase is uniformly distributed in the WC matrix (Fig. 2a). The existence of the eutectic structure with fibrous morphology is confirmed by the results of fracture study (Fig. 2b).

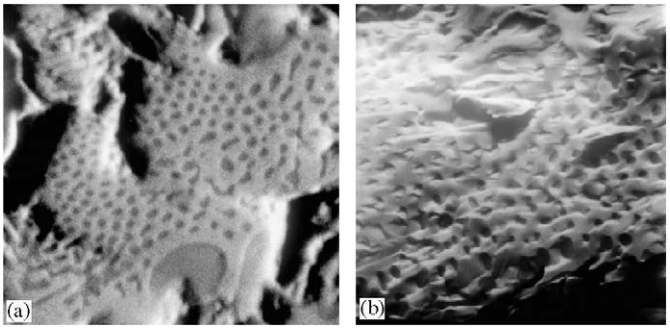

Fig. 2. Microstructure of a quenched drop (a) and the structure of a fracture surface (b) of the WC—20 mass% ZrB_2 sample.

Table 1
Characteristics of tungsten carbide based composite materials with addition of transition metal diborides produced by arc melting

#	System	Diboride phase content (at%)	Results of XRD analysis
1	WC–TiB_2	13.0	α-WC, β-WC, α-W_2C, TiB_2-traces
2		33.0	β-WC, α-W_2C, TiB_2, traces of phases W_2B, WB appeared
3		41.3	B-WC, α-W_2C, TiB_2, WB
4	WC–ZrB_2	14.60	WC, W_2C-small, ZrB_2-traces
5		30.35	WC-less, W_2C-bigger, ZrB_2-bigger
6		42.60	WC-less, W_2C-bigger, ZrB_2-bigger
7		63.44	W_2C, ZrB_2
8	WC–CrB_2	12.2	α-W_2C, α-WC, CrB_2-traces
9		31.9	α-W_2C, β-WC, CrB_2-traces
10		40.0	α-W_2C, β-WC, CrB_2

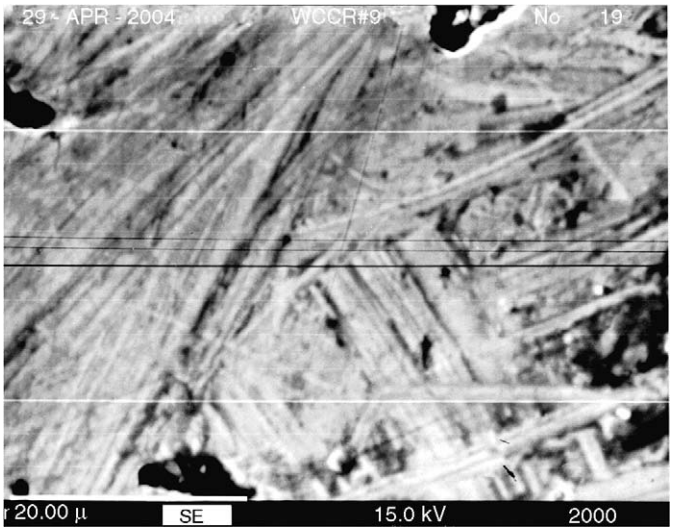

Fig. 3. Microstructure of the composite material WC—20 mass% CrB_2.

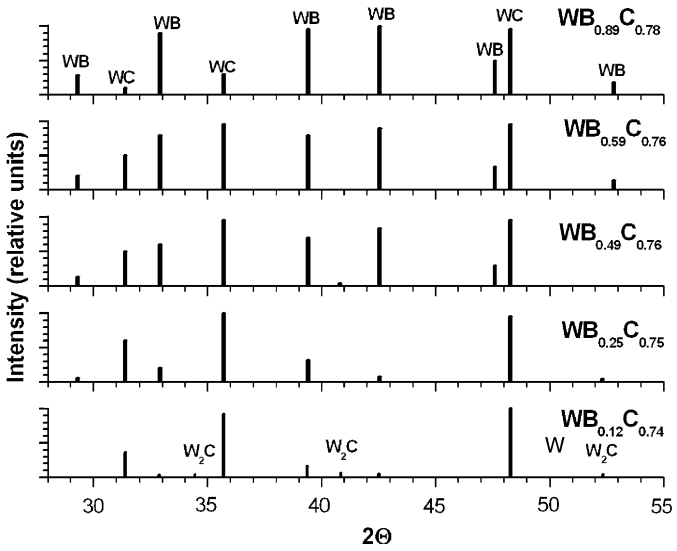

Fig. 4. XRD patterns obtained from the alloys of the W–B–C system.

Compositions of the composite materials obtained by arc melting and determined by XRD are presented in Table 1. According to these results, with the increase of the diboride phase content, the content of WC phase is diminished, and the W_2C and ZrB_2 content increases.

In the WC–CrB_2 system samples with 5, 15, and 20 mass% of diboride phase were investigated. The possibility of eutectic interaction resulting in lamellar structure formation was established (Fig. 3). An increase of the diboride phase content results in a reduction of the *a*-WC phase content, formation of the *b*-WC phase, and an increase of the *a*-W_2C and CrB_2 phase content.

3.2. Composite materials in the ternary W–C–B system

The following alloys in the W–B–C system were investigated: $WB_{0.12}C_{0.74}$; $WB_{0.25}C_{0.75}$; $WB_{0.34}C_{0.32}$; $WB_{0.49}C_{0.76}$; $WB_{0.59}C_{0.76}$; $WC_{0.89}C_{0.78}$ and $(WC)_{0.9}B_{0.1}$.

XRD patterns obtained from the compounds investigated are presented in Fig. 4.

The presence of insignificant trace W_2C phase was detected by XRD. Probably it was formed as a result of WC decomposition ($WC \rightarrow W_2C + C$) during melting.

Real structure investigations of the obtained materials by thin foil method showed that both matrix and reinforcing phases are present in single-crystal form. The WC matrix phase has hexagonal symmetry, and the W_2B reinforcing phase has cubic symmetry (Fig. 5a and b).

Electron microscopy of the microstructure of the obtained composite materials showed that the pseudo-alloy of the composition $WB_{0.49}C_{0.76}$ (that corresponds to 28 ± 2 mass% WB content) has a practically uniform eutectic structure (Fig. 6a). $WB_{0.12}C_{0.74}$, $WB_{0.25}C_{0.75}$, $WB_{0.34}C_{0.32}$ were shown to be hypoeutectic, an excess of the WC-based phase was observed (Fig. 6b–d).

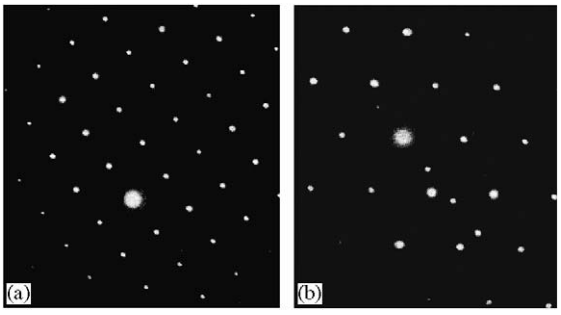

Fig. 5. Electron-diffraction patterns obtained from the matrix (a) and reinforcing (b) phases in pseudo-alloy $WB_{0.34}C_{0.32}$.

The investigation of some physical characteristics of the obtained composites (Table 2) combined with XRD results confirmed the validity of the above-mentioned constitutional diagram of the quasi-binary WC–WB system.

Analysis of the indentation imprints made on the different phases that were formed in the samples produced in the W–B–C system shows that on the WC phase area the imprint is larger in size and the number of radial cracks is much higher compared with the imprint made on the eutectic structure area. This made it impossible to accurately determine the values of fracture toughness (K_{1c}) by the indentation method; it can, however, be considered as evidence of the essential plasticity of the obtained composite material (Fig. 7a).

It should be mentioned that indentation tests under the same load performed on any commercial material based on sintered WC results in catastrophic rupture of the imprint area (Fig. 7b).

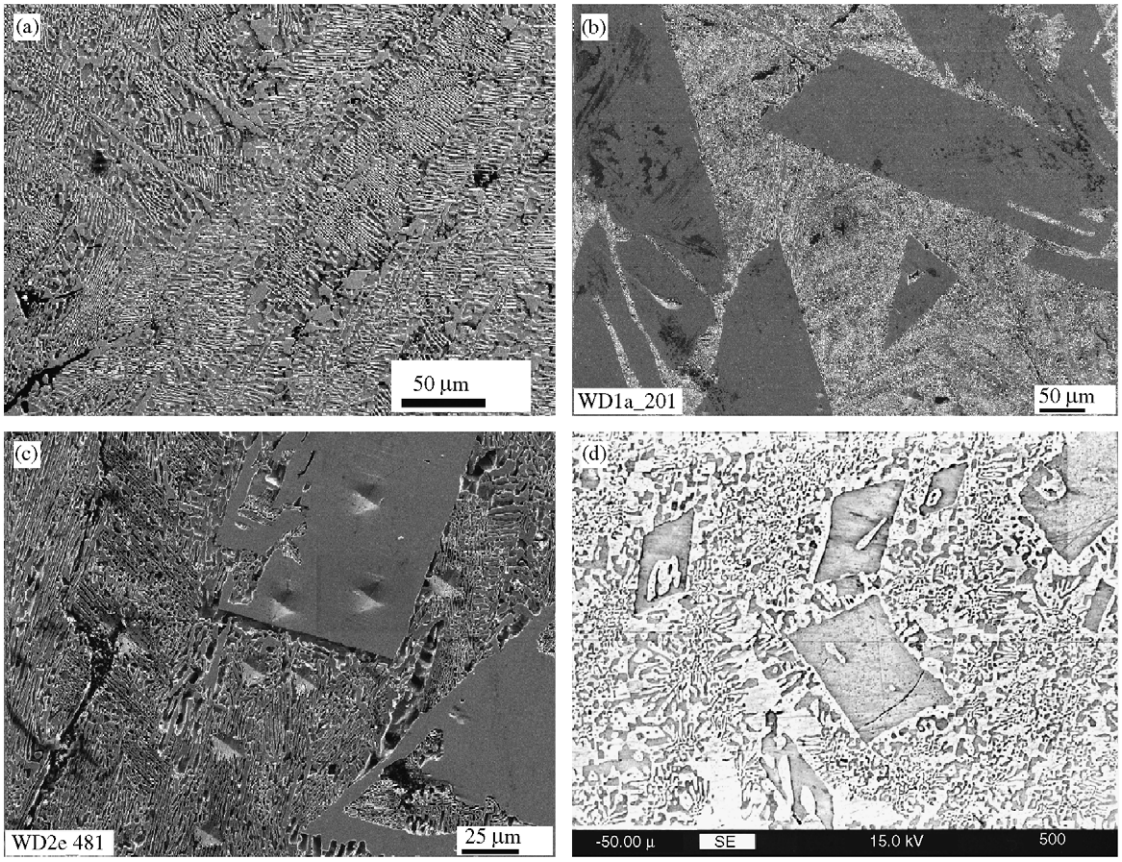

Fig. 6. Electron-microscopic patterns of the W–B–C system pseudo-alloy microstructure: (a) $WB_{0.49}C_{0.76}$; (b) $WB_{0.12}C_{0.74}$; (c) $WB_{0.25}C_{0.75}$ and (d) $WB_{0.34}C_{0.32}$.

Table 2
Composition and some characteristics of pseudo-alloys produced in the W–B–C system

#	Composition	Phase composition	Density, (hydrostatic method) ρ (g/sm^3)	Elastic modulus, E (GPa)	Hardness (GPa) $P = 10.3$ N		Microhardness (GPa), $P = 1.9$ N	
					Phase WC	Eutectic	Phase WC	Eutectic
1	$WB_{0.12}C_{0.74}$	WC, WB_{small}, W_2B_{traces}	15.2	490	12.0	30±2	23.0	27.4
2	$WB_{0.25}C_{0.75}$	WC, WB, W_2B_{traces}	14.7	320	12.0	30±2	23.5	28.0
3	$WB_{0.34}C_{0.32}$	WC, WB	13.3	—	12.0	30±2	—	—
4	$WB_{0.49}C_{0.76}$	WC, WB	14.1	250	—	30±2	—	30.5
5	$WB_{0.59}C_{0.76}$	WC, WB	13.9	280	—	30±2	—	29.8
6	$WB_{0.89}C_{0.78}$	WC, WB	12.4	180	—	—	—	28.5
7	$(WC)_{0.9}B_{0.1}$	WC	15.6	—	12.0	—	—	—
8	WC + 2% C	WC	15.7	650	12.0	—	13.5	—

K_{1c} values measured for the samples produced in the WC–TiB_2 system were 7–10 MN m$^{1/2}$, 5–7 MN m$^{1/2}$ in the WC–ZrB_2 system and 3–5 MN m$^{1/2}$ in the WC–CrB_2 system, respectively.

The microhardness of alloys in the WC–TiB_2 system (26–30 GPa) is somewhat higher than for the pure WC (18–24 GPa); the higher the TiB_2 content, the higher is the hardness of the composite material. The microhardness of the WC–ZrB_2 (20–22 GPa) and WC–CrB_2 (16–19 GPa) alloys is very close to that of WC. The hardness (H_v) for WC–TiB_2 and WC–ZrB_2 alloys is about 19 GPa, for WC–CrB_2 about 15 GPa.

The results of studying the mechanical properties together with microstructural investigations lead to the following conclusions.

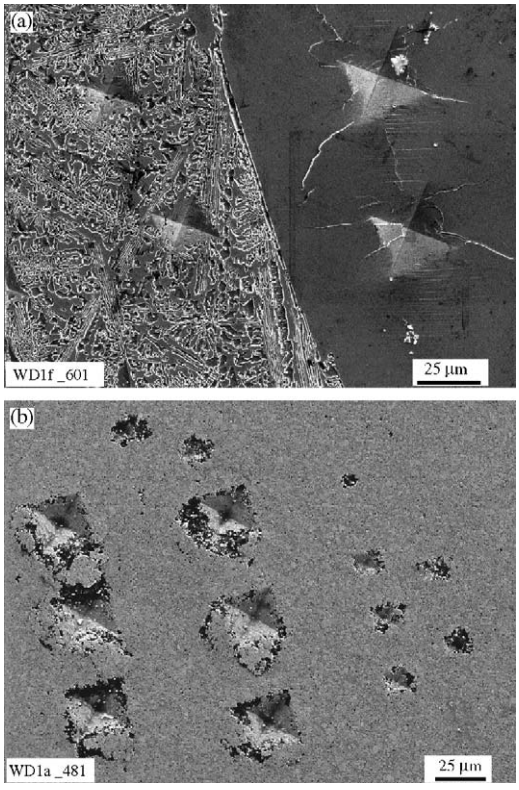

Fig. 7. Indentation marks obtained on different structural elements of $WB_{0.12}C_{0.74}$, pseudo-alloy produced by direction crystallization (a) and on sintered tungsten carbide (b).

4. Conclusions

1. It is established that new ceramic–ceramic eutectic composite materials with an excellent combination of properties can be produced on the basis of WC with the addition of transition metal diborides, and on the basis of tungsten boride phases. These materials can be successfully applied in contemporary techniques.
2. It was determined that the alloys WC—80 mass%–ZrB_2—20 mass% and WC—72 mass%–WB—28 mass% are the closest ones to eutectic compositions.
3. An examination of the real structure of the eutectic alloy in the WC–WB system by the thin foil method showed that both matrix and reinforcing phases are present in single-crystal form.
4. A marked increase in hardness (both H_v and H_μ) was observed at the point of transition from alloys with an excess of WC grains to those with a eutectic structure (WC–WB pseudo-alloy).
5. Indentation of the eutectic structure area ($P = 10.3$ N) does not result in radial crack formation, which is evidence of the essential plasticity of the obtained composite material.

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