Available online at www.sciencedirect.com
ScienceDirect
Journal of Solid State Chemistry 179 (2006) 2939–2943
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

The directional crystallization of W–B–C–*d*-transition metal alloys

Yuriy Paderno, Varvara Paderno*, Alfred Liashchenko, Volodymyr Filipov, Alina Evdokimova, Anna Martynenko

Frantsevich Institute for Problems of Materials Science of NASU, 3 Krzhyzhanovsky Street, 03142 Kiev, Ukraine

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.

*Corresponding author. Fax: 380 44 444 31 21.
E-mail address: paderno@ipms.kiev.ua (V. Paderno).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
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.

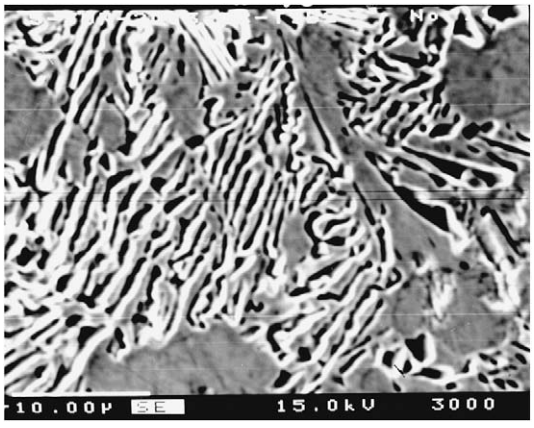

Fig. 1. Microstructure of the composite material WC—5 mass% TiB_2.

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).

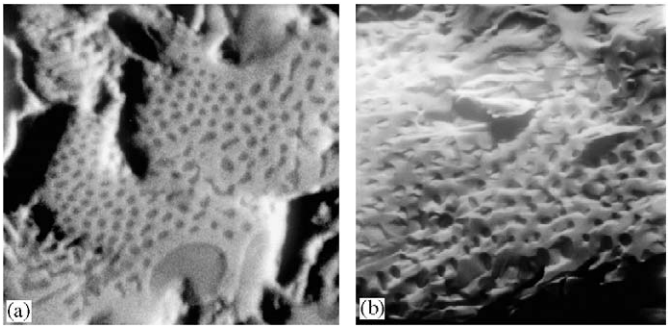

Fig. 2. Microstructure of a quenched drop (a) and the structure of a fracture surface (b) of the WC—20 mass% ZrB_2 sample.

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