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Effect of (Ti:B) atomic ratio on mechanical properties of TiB_2–Fe composites "in situ" fabricated via Self-propagating High-temperature Synthesis

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ABSTRACT

The TiB_2-based Fe–matrix cermets with titanium addition (literarily different Ti:B ratio) were fabricated from elemental powders "in situ" using the Self-propagating High-temperature Synthesis method (SHS) under high pressure. The effect of Ti:B ratio on microstructure and phase composition with particular focus on matrix phase were analyzed using X-ray diffraction (XRD) and Wavelength Dispersive Spectroscopy (WDS) for composites with intended 25 vol.% and 35 vol.% of Fe. Moreover, for composites with 35 vol.% of Fe bending strength and compressive strength were investigated. The compressive strength reached maximum value in material with Ti:B atomic ratio of 0.49, which possessed the highest TiB_2 content and matrix phase consisting of Fe and Fe_2B. However, modulus of rupture (MOR) test indicated that composite with titanium excess (Ti:B atomic ratio of 0.525) was characterized by the highest bending strength, due to successful elimination of Fe_2B intermetallics.

1. Introduction

Due to extraordinary microhardness (34.0 GPa), outstanding tribological properties [1–4], low density (4.52 g/cm^3), and good thermal and electrical conductivity [5–9] (60 W/m^{-1} K^{-1}) [10], the TiB_2 is considered as a ceramic phase reinforcing advanced cermets [6,11]. The Young's modulus (E) of 529 GPa [3] and transverse rupture strength of even 1500 MPa [4] can be reached for nearly monolithic TiB_2 material. Therefore, TiB_2-rich Fe matrix cermets with high volume fraction of TiB_2 are potentially good candidates for machine parts for aerospace, automotive, military, defense, and marine, characterized by high wear resistance as well as for nuclear industry [12–14]. A large damping capacity [15] and predictable fracture mode are desirable for materials used in constructions where unwanted vibrations are induced during operation under irregular loading.

Particular attention is being paid to Al [15–18], Cu or Fe as a toughening binder [2,6,8,11,19–21], because cermets can be obtained in these systems. In order to fully utilize the high refractoriness of TiB_2 (melting point of 3225 °C), Fe is a better candidate for a metallic matrix. Also high E (190–210 GPa) [22] and higher hardness of Fe, indicate that better mechanical performance (i.e. damping capacity or high specific modulus) should be expected.

The application of SHS combined with high pressure, revealed to be a useful method for "in situ" fabrication of TiB_2-based Cu–matrix highly densified cermets [20]. Therefore, the TiB_2-based cermets for those investigations were prepared using SHS under a high pseudo-isostatic pressure, which is one of the most progressive and energy saving methods to obtain TiB_2 and TiB_2-reinforced materials [2,23–25]. Such method was also used to fabricate the composites used in the previous study [12,20,25], especially that the Ti excess can be easily controlled by using the mixtures of elemental (Ti, B, Fe) powders.

However, the production of TiB_2–Fe cermets is a challenge, since the field of crystallization for pseudo-binary TiB_2–Fe system is narrow, as indicated in the isothermal section of the Fe–B–Ti ternary system [26]. So far, several researchers [22,24], including the present authors [25], reported the formation Fe_2B boride in the matrix while the intended matrix phase was elemental Fe (=not so easy to understand). Different hypothetical explanations of the unexpected Fe_2B phase were discussed in the recently published papers. For instance, when metallurgical ingredients such as ferroboron or ferrotitanium are used [11,24], impurities originated from those components, especially C; they are considered as those affecting

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the formation of Fe_2B precipitates in Fe or steel matrix TiB_2-based cermets [1,22]. The other authors suggested that it might be caused by not sufficiently fine (coarse) Ti or Fe powders [24]. However, most likely the crystallization of Fe_2B in Fe is caused by Ti dissolving in Fe. Those effects subsequently lead to Ti-deficiency, or excess B which reacts with Fe [1,22,25].

The application of structural components in engineering requires both strength and good fracture toughness to avoid catastrophic failure. Since Fe-based compounds and intermetallics are in general brittle, both Fe_2B [13,27] and Fe_2Ti [9,28], should affect the mechanical properties, especially flexural strength and compression or tensile strength. However, the effect of Fe_2B and Fe_2Ti on the mechanical properties of TiB_2–Fe cermet is not fully understood with well-controlled microstructures.

Therefore, the aim of this work was to investigate the effect of Ti excess (literally various Ti:B ratio) on the phase composition for those in situ fabricated composites. In order to eliminate the effect of impurities those cermets were fabricated using high purity elemental powders. Similar attempts to modify the matrix phase were emphasized by Azkona et al. [4] for Ni-containing TiB_2-based composites, as well as reported recently by Zhang and coworkers [15] for Al–matrix cermets.

The phase composition, microstructure and the properties of SHS products fabricated under pseudo-hot-isostatic pressure conditions (SHS-p-HIP) in a ternary Ti–B–Fe system were characterized. The optimum composition is discussed, considering the relative density, microstructure and hardness. Moreover, mechanical properties for composites with various Ti excess were evaluated quantitatively using bending and compression tests for composites with various phase compositions of the matrix.

2. Experimental procedure

2.1. Samples preparation

The experiments were carried out with TiB_2–Fe–Ti composites, where a 25 or 35 volume fraction of Fe and various amounts of Ti excess were applied. Commercial powders of titanium (45 μm, purity – 99.4%), amorphous boron (0.8 μm, purity – 96%), and iron (1–9 μm, purity – 99.9%) were used to obtain an initial compact. The chemical compositions of the "green samples" mixtures used for SHS are shown in Table 1, so the intended phase composition of investigated composites is indicated on the ternary phase diagram (Fig. 1).

The "green compacts" made of elemental powders were wrapped in graphite foil and then were hermetically closed in steels can. The SHS-p-HIP process was carried out in vacuum furnace (10 Pa) situated on universal pressing machine. The SHS reaction was initiated by heating element coiling steel can. The onset of the synthesis was recognized due to the thermocouple attached to the bottom part of the can. After the sudden temperature rise was noticed the pressure was increased form the initial one (20–30 MPa) to the final one (150 MPa) and held for 5 min. Samples were synthesized and densified due to highly exothermic effect associated with TiB_2 synthesis from elemental powders, no additional heating source was used, except for reaction initiation. The samples were cooled down with furnace. The experimental procedure applied in order to prepare composites with various Ti additions was described previously [20,25].

2.2. Investigation of the sintered samples

The sintered samples were cross-sectioned and polished with diamond dispersive, finally with the grain size of 1 μm. The X-ray diffraction (XRD) analysis combined with Rietveld method was used to determine the phase compositions quantitatively. A scanning electron microscope (SEM) with electron probe microanalyser (EPMA) was applied to observe the microstructure of samples, at the same time a WDS analyzer was used to map the distribution of elements. Transmission electron microscope (TEM) was also employed to confirm phases in the material containing Fe_2B precipitates, based on diffraction patterns. The hardness and microhardness of samples were measured with a Vickers hardness tester under three different loads of 1, 10, or 30 kg, respectively. The effect of TiB_2 on the toughness was evaluated by a MOR test, by the 4-point bending technique using rectangular samples $2.5 \times 5.0 \times 25.0$ mm with outer span lengths of 21.0 mm, and crosshead speed of 0.2 mm/min, based on the formula described in ASTM: C1161 – 02c standard. Testing forces were applied by means of the mechanical testing machine Instron 5584 with a load capacity of 100 kN. The same machine was used for a compression test, where compressive strength was determined using bulk samples $5\ mm \times 5\ mm \times 10\ mm$ in size. Those samples were placed between high strength steel bases and sprayed with h-BN solution lubricant. Both compressive strength and engineering strain were calculated using the ASTM: C1424 – 99 US technical standard.

3. Results and discussion

3.1. Microstructure

The composites investigated in this study contained 25 or 35 vol.% of Fe, because the previous research [25] indicated that this amount of Fe was optimal in order to achieve high relative density for "in situ" fabricated composites. In each scanning electron image (SEI) the light gray phase corresponds to the Fe-based matrix, while TiB_2 appears as rectangular or hexagonal dark grains which is related to hexagonal structure (P6/mmm, space group 191) of TiB_2. The entirely black small spots correspond to pores. There are also some inclusions in the matrix, but their composition will be discussed with XRD and WDS results. The microstructure of investigated composites observed using SEM (Figs. 2 and 3) confirmed a good homogeneity and an essentially low porosity.

No significant effect of Ti addition on the TiB_2 grain size in the microstructure was observed. However, the volume fraction of the matrix phase increases at the same time, especially for samples with 35 vol.% of Fe and a more essential Ti addition (Fig. 3).

As the volume fraction of matrix phase increased, some inhomogeneity demonstrated by wider areas rich in the matrix phase become more common for such "in situ" fabricated composites.

Table 1
Compositions of the starting mixtures.

	Samples assignation	Ti (at.%)	B (at.%)	Fe (at.%)	Ti:B at. ratio	Ti excess (at.%)
1.	TiB_2–25 vol.%Fe	26.55	54.21	19.25	0.490	Deficiency
2.	TiB_2–25 vol.%Fe–3 vol.%Ti	26.97	53.89	19.14	0.501	0.60
3.	TiB_2–25 vol.%Fe–6 vol.%Ti	27.40	53.58	19.02	0.511	1.18
4.	TiB_2–35 vol.%Fe	23.72	48.44	27.84	0.490	Deficiency
5.	TiB_2–35 vol.%Fe–6 vol.%Ti	25.02	47.61	27.37	0.525	1.73
6.	TiB_2–35 vol.%Fe–12 vol.%Ti	26.44	46.71	26.85	0.566	3.63