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Wetting and interfacial behavior of Fe-based self-fluxing alloy-refractory compound systems

In this study the wettability and interfacial behaviour of the TiC–FeNiCrBSiC and TiB₂–FeNiCrBSiC systems were investigated. The wetting experiments were performed by the sessile drop method at 1150 °C under a vacuum. The contact angles of TiC and TiB₂ wetting by melted Fe-based self-fluxing alloy were 51° and 36°, respectively. Thermodynamic calculations were carried out to understand the metal-ceramic interaction mechanism in the TiC–FeNiCrBSiC and TiB₂–FeNiCrBSiC systems. The structure of the interface region in the TiB₂–FeNiCrBSiC system was characterized by the optical microscopy and SEM-EDS analysis. The formation of Fe, Ni, Cr and Mo complex borides was revealed within the interface region of the TiB₂–FeNiCrBSiC system.

Keywords: self-fluxing alloy, refractory compound, contact angle, titanium diboride, titanium carbide.

INTRODUCTION

Modern high-performance machinery and mechanisms operate at high speeds, loads, and temperatures. In order to provide the reliable operation of engineering components the protective coatings should be applied to prevent the intensive wear and corrosion of functional surfaces Ni- or Fe-based self-fluxing alloys (NiCrBSiC or FeNiCrBSiC) are widely used in the surface engineering to provide wear resistance of various components, whose surfaces are subjected to severe tribological conditions. These alloys usually contain some amount of alloying elements such as boron, silicon, chromium and carbon. B and Si are added into alloy to form with nickel or iron eutectic with low melting point (950–1080 °C) and provide self-fluxing ability of material. The hardness and wear resistance of self-fluxing coatings is achieved by the formation of hard phases such as nickel and chromium borides, chromium carbides [1].

However, the wear resistance of NiCrBSiC or FeNiCrBSiC coatings can be significantly improved by adding refractory carbides and borides. Several attempts have been made to enhance tribological properties of self-fluxing alloys by introducing the TiC, CrB₂, TiB₂ reinforcements [2]. In our previous work the NiCrBSiC–TiB₂ thermal-sprayed coatings were investigated [3–5]. It was shown that the addition of titanium diboride particles into a nickel-based self-fluxing alloy leads to a significant improvement of the wear resistance of the plasma-sprayed coatings.

Fe-based self-fluxing alloys are promising candidates for matrices of composite materials for coatings spraying. The wetting behavior of molten alloys in contact

with ceramic substrates is of key importance in the fabrication of metal-ceramic composites.

To choose the reinforcing additives for FeNiCrBSiC-based composite materials the wetting and interfacial reactions of TiB₂ and TiC with Fe-based self-fluxing alloy have been investigated in the present study.

MATERIALS AND METHODS

In this study the commercially available powder of FeNiCrBSiC self-fluxing alloy (Ni – 37 wt %, Cr – 14 wt %, Si – 2.5 wt %, C – 1.4 wt %, B – 2.2 wt %, Mo < 1 wt %, Fe – base) was chosen for the development of the composite material. This alloy is classified as the eutectic one; its base is a readily available and inexpensive component, i.e., iron, making it promising for the fabrication of wear-resistant composite powder materials. The FeNiCrBSiC powder was melted in alumina crucibles at 1150–1200 °C under vacuum conditions ($p = 10^{-4}$ Pa). Small pieces of the solidified FeNiCrBSiC alloy were used for wetting tests.

Hot-pressed TiB₂ and TiC plates (14×14×2 mm) were applied as the substrates for the tests. Apparent porosity of the TiB₂ and TiC specimens was 2.5 %.

Wetting studies were carried out by means of the sessile drop technique in a special furnace. The sessile drop tests were performed at temperature $T = 1150$ °C under vacuum conditions ($2 \cdot 10^{-3}$ Pa). Just before sessile drop test the ceramic plate and alloy piece were cleaned with alcohol. After the test, the metal-ceramic couples were cooled inside the vacuum chamber until the temperature dropped to 20 °C.

The microstructural and energy dispersive spectroscopy (EDS) analysis of cross-sectioned metal-ceramic couples were performed using scanning electron microscopes (SEM) JEOL-9500FS and REM-106L.

EXPERIMENTAL RESULTS AND DISCUSSION

The FeNiCrBSiC alloy wets TiB₂ and TiC substrates as shown in Fig. 1. The initial contact angle of TiC wetting by the FeNiCrBSiC alloy is 117° and then the contact angle changes slowly until the final value $\theta = 51^\circ$ is reached (see Fig. 1, curve 1). The FeNiCrBSiC alloy wets TiB₂ substrate, forming the final contact angle of 36° in 15 min from the melting point (see Fig. 1, curve 2).

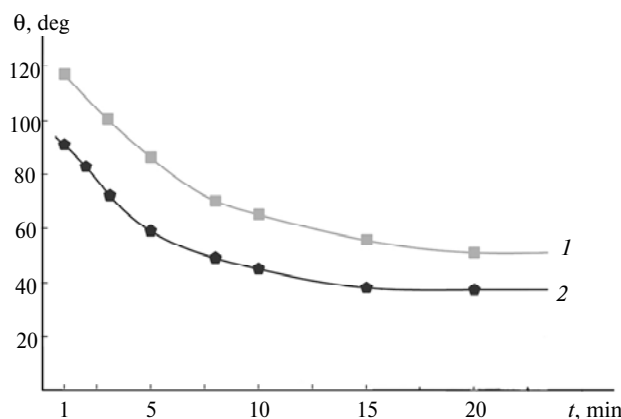


Fig. 1. Wetting kinetics in the refractory compound–FeNiCrBSiC systems: 1 – TiC; 2 – TiB₂.

To understand the interaction mechanism in the TiC–FeNiCrBSiC and TiB₂–FeNiCrBSiC systems, the reaction thermodynamics have been calculated [6, 7].

The calculations of the changes in the reaction enthalpy ΔH°_{298} make possible to compare the feasibility and favorability of these reactions and to detect the expected stable phases and their compositions at the metal/ceramic interface. Reactions at the ceramic/metal interface cause the formation of new phases, which can influence both the wetting in system and performance of composite materials. The reactions that can occur in the TiB₂/FeNiCrBSiC system between the substrate and alloy components are as follows:

TiB₂-FeNiCrBSiC system:



Thermodynamic studies have shown that the reactions (1), (2), (9) and (10) have negative values of enthalpy changes and are considered as thermodynamically feasible.

TiC-FeNiCrBSiC system:





The thermodynamic studies have shown that reactions (23), (24), (9) and (29) are thermodynamically feasible due to the negative values of enthalpy reaction changes.

Thus, some chemical reactions can occur both in the TiB_2 -FeNiCrBSiC and TiC-FeNiCrBSiC systems. The Cr_3B_3 , Ni_3B and Ni_4B_3 phases are the main reaction products at the interface in the TiB_2 -NiCrBSiC system. It should be noted, that the same phases are found to be formed in the FeNiCrBSiC alloy [1]. That is why the formation of Cr_3B_3 , Ni_3B and Ni_4B_3 should not lead to the deterioration of composite materials properties. Indeed, the formation of Ti_2B_5 and SiC compounds are more likely to precipitate at the metal/ceramic interface in the TiC-FeNiCrBSiC system. It is reasonable to assume that the formation of such new compounds affects the wetting behaviour of the TiC-FeNiCrBSiC system increasing the contact angle. Therefore, the titanium carbide is worse wetted by the FeNiCrBSiC alloy as compared with TiB_2 . Furthermore, the formation of such compounds in the TiC-FeNiCrBSiC system can cause the embitterment of composite materials. Taking into account the wetting behavior and thermodynamic calculations, TiB_2 was chosen as more attractive reinforcing additive for a Fe-based self-fluxing alloy.

The structure of the cross-sectioned, the TiB_2 -FeNiCrBSiC couple has been studied by the SEM microanalysis after complete the sessile drop test. Three main areas were revealed in the TiB_2 -FeNiCrBSiC system: the solidified drop (Spectrum 1), the interaction region (Spectrum 2, 3), and the ceramic substrate (Spectrum 4) (Fig. 2).

The heterogeneous structure of a solidified drop presents an eutectic that consists of (FeNi)Si-based matrix (Fig. 3, a, point 4, the table) and grains of Cr, Fe, Ni and Mo carboborides (see Fig. 3, a, point 1–3, the table).

The formation of 70 μm -thick interaction region was detected at the alloy-ceramic interface. The interaction region comprises two zones: on the FeNiCrBSiC drop side and TiB_2 side. The interaction zone on the drop side is 40 μm thick and characterized by the (FeNi)Si matrix and the diffusion redistribution of elements (see Fig. 2, Spectrum 2). Obviously, the ceramic substrate dissolution into melted

alloy and penetration of the melted alloy into the solid take place. Boron diffuses from the TiB₂ substrate into the drop region resulting in the formation of large complex Cr, Fe, and Mo boride grains of up to 10–30 μm in size (see Fig. 3, *b*, point 2).

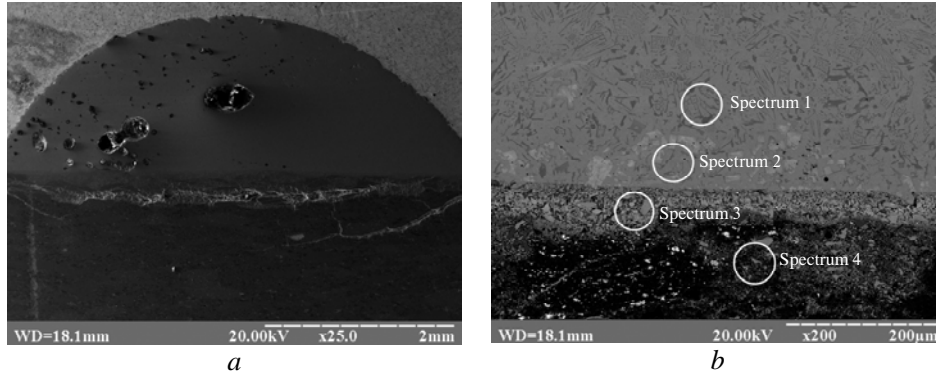


Fig. 2. Structure of the TiB₂-FeNiCrBSiC couple showing: general view of the TiB₂-FeNiCrBSiC sample (*a*), interface region (*b*).

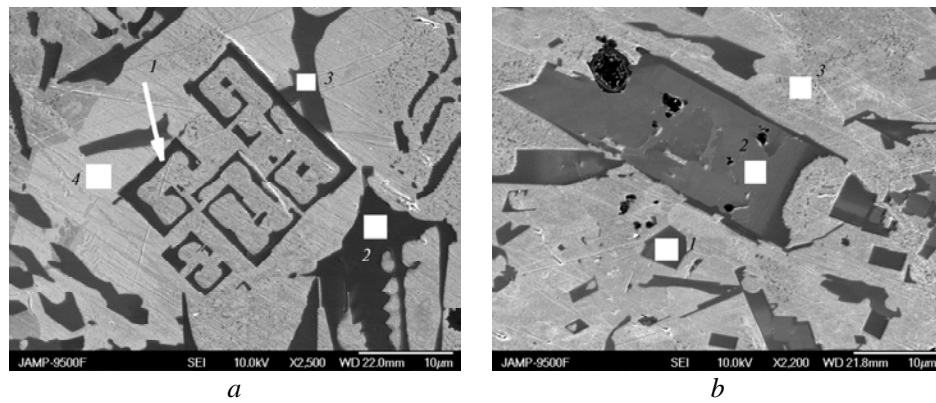


Fig. 3. Structure of a drop (*a*) and the interaction region on the drop side (*b*) in the TiB₂-FeNiCrBSiC system.

Chemical composition of the interaction products in the TiB₂-FeNiCrBSiC system

Structure	Point	Element, wt %							
		B	C	Si	Ti	Cr	Fe	Ni	Mo
Drop (Fig. 3, <i>a</i>)	1	4.64	1.41	0.15	–	45.06	23.68	9.38	15.68
	2	7.10	1.41	0.07	–	44.13	25.13	8.68	13.16
	3	5.12	0.24	–	–	11.88	56.75	24.79	0.36
	4	–	0.23	7.12	–	1.48	20.81	70.26	–
Interaction zone on the drop side (Fig. 3, <i>b</i>)	1	8.00	–	–	–	44.73	21.63	6.17	19.35
	2	7.47	–	–	–	31.45	14.54	4.49	40.66
	3	–	–	3.74	–	4.29	37.00	54.97	–

(Contd.)

Interaction zone on the substrate side (Fig. 4)	1	0.34	6.89	0.62	61.82	2.58	2.27	3.44	12.83
	2	–	15.60	0.75	52.12	3.66	3.28	6.27	14.24
	3	6.60	1.48	2.41	0.85	26.46	26.52	22.33	12.06
	4	1.28	1.65	–	1.46	34.97	12.93	5.09	42.00

The thickness of the interaction zone on the TiB_2 side reaches 30 μm . The heterogeneous structure of this zone includes grains of Fe, Ni, Cr and Mo complex borides (Fig. 4, point 3, 4), whose composition varies across the interface region. Moreover, the grains of titanium carbide were found to form in the interaction region (Fig. 5), that can be explained by the carbon diffusion from the drop zone into the metal-ceramic interface during high-temperature test. It is also confirmed by the fact that the solidified drop contact area has lower C content (up to 0.4 wt %) as compared with the initial one in the FeNiCrBSiC alloy (1.4 wt %).

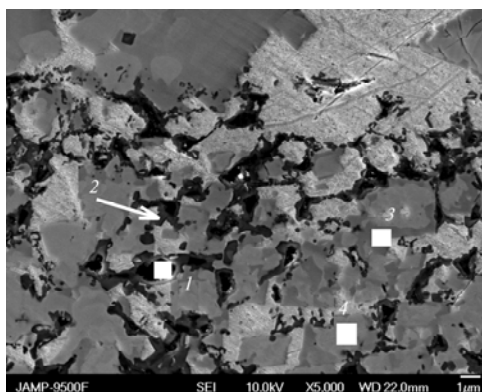


Fig. 4. Structure of the interaction region on the substrate side in the TiB_2 -FeNiCrBSiC system.

So, the results obtained indicate that the interaction region is formed at the metal-ceramic boundary due to some chemical reactions and diffusion of TiB_2 and FeNiCrBSiC elements. The structure of the interaction region consists of the (FeNi)Si-based matrix and inclusions of Fe, Ni, Cr and Mo complex borides.

CONCLUSIONS

The wettability of TiB_2 and TiC substrates by the FeNiCrBSiC self-fluxing alloy was investigated by means of a sessile drop technique. The FeNiCrBSiC alloy demonstrates good wetting with TiB_2 and CrB_2 substrates forming a final contact angles of 36° and 0, respectively. The contact angle of TiC wetting by FeNiCrBSiC alloy is 51° .

Thermodynamic calculations revealed that some chemical reactions can occur both in the TiB_2 -FeNiCrBSiC and TiC-FeNiCrBSiC systems. The obtained results suggest that the interaction in the TiB_2 -FeNiCrBSiC system during composite materials sintering promotes the formation of additional hard boride and carbide phases. The investigation of interaction region in the TiB_2 -FeNiCrBSiC system confirms the formation of heterogeneous structure composed by a (FeNi)Si-based matrix and complex Cr, Fe, Ni and Mo carboborides.

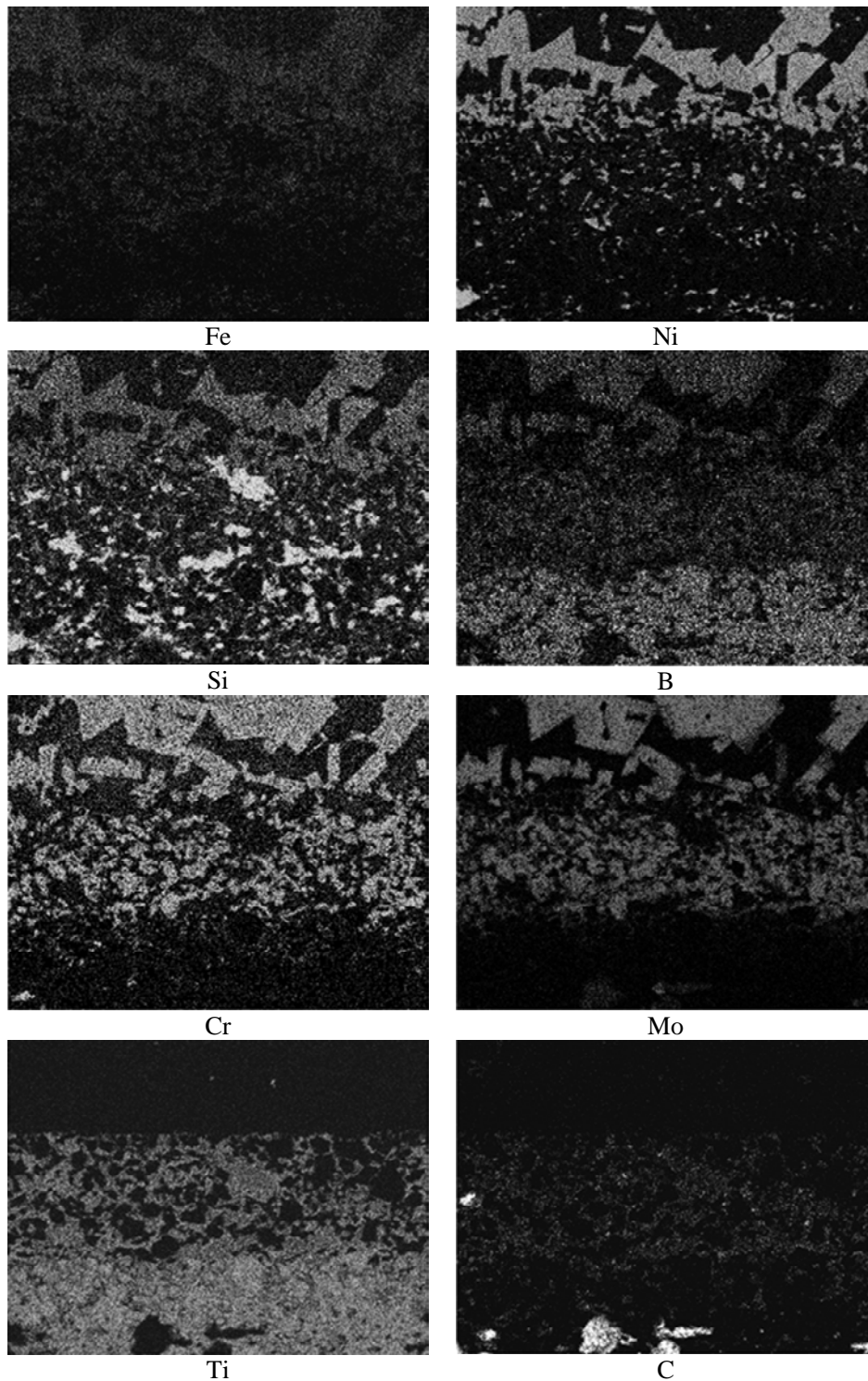


Fig. 5. Chemical elements distribution within the interface region between the drop and ceramic substrate in the TiB_2 -FeNiCrBSiC system.

So, the addition of TiB_2 particles into FeNiCrBSiC alloy as well as formation of new complex carbide and boride phases should improve the wear-performance of

TiB₂-FeNiCrBSiC composite materials and coatings. Furthermore, in our previous studies, the positive effect of TiB₂ additives into a Ni-based self-fluxing alloy on the structure and operating performance has been shown [3, 8]. Thus, TiB₂ is a promising candidate for reinforcing additives for Fe-based self-fluxing alloy in order to develop composite powder material for the wear-resistant coatings.

Досліджено змочування та контактну взаємодію в системах TiC-FeNiCrBSiC і TiB₂-FeNiCrBSiC. Кінетику змочування вивчено методом "лежачої краплі" в вакуумі при температурі 1150 °С. Кут змочування TiC і TiB₂ самофлюсівним сплавом на основі заліза становили 51° і 36° відповідно. Для виявлення особливостей контактної взаємодії на межі металевий сплав-кераміка проведено термодинамічні розрахунки систем TiC-FeNiCrBSiC і TiB₂-FeNiCrBSiC. Методами оптичної та скануючої електронної мікроскопії вивчено структуру зони взаємодії в системі TiB₂-FeNiCrBSiC. Виявлено формування складних боридів Fe, Ni, Cr і Mo в зоні взаємодії системи TiB₂-FeNiCrBSiC.

Ключові слова: самофлюсівний сплав, тугоплавка сполука, кут змочування, контактна взаємодія, диборид титану.

Исследовали смачивание и контактное взаимодействие в системах TiC-FeNiCrBSiC и TiB₂-FeNiCrBSiC. Кинетику смачивания изучали методом "лежащей капли" в вакууме при температуре 1150 °С. Углы смачивания TiC и TiB₂ самофлюсующимся сплавом на основе никеля составляли 51° и 36° соответственно. Для выявления особенностей контактного взаимодействия на границе металлический сплав-керамика были проведены термодинамические расчеты систем TiC-FeNiCrBSiC и TiB₂-FeNiCrBSiC. Методами оптической и электронной микроскопии изучали структуру зоны взаимодействия в системе TiB₂-FeNiCrBSiC. Установлено формирование сложных боридов Fe, Ni, Cr и Mo в зоне взаимодействия системы TiB₂-FeNiCrBSiC.

Ключевые слова: самофлюсующийся сплав, тугоплавкое соединение, угол смачивания, контактное взаимодействие, борид титана.

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