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Wetting and interfacial interaction in TiCrC–Ni system

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Wetting and interfacial interaction between the titanium-chromium carbide and molten nickel were investigated by sessile drop technique in vacuum environment at a temperature of 1500°C. Molten nickel shows excellent wetting of TiCrC, forming the contact angle $\theta = 8°$. The interfacial interaction in the TiCrC–Ni system involves the dissolution and infiltration of the ceramic substrate along grain boundaries with Ni to a depth of 400–600 μm. The diffusion of Ti, Cr, and C from the ceramic substrate into molten nickel leads to a change in the chemical composition of the drop. Upon cooling, the recrystallization of titanium and chromium carbides occurs with the formation of new phases TiC_x–Cr, Cr_3C_2–Ti and Cr_7C_3–Ni–Ti in the drop and the interaction zone. Thus, the TiCrC ceramics can be successfully used to develop the cermets in combination with Ni as a matrix or binder. However, in the manufacture of composite materials TiCrC–Ni, it is necessary to take into account the interaction between TiCrC and Ni with a subsequent change in their chemical composition.

Keywords: titanium-chromium carbide, cermet, nickel, wetting, contact angle, interaction zone.

Змочування і міжфазна взаємодія у системі TiCrCiNi. *А.П.Уманський, А.Е.Терентьєв, М.С.Стороженко, Г.А.Баглюк, В.Б.Муратов, А.А.Васильєв, В.Е.Шелудько*

Досліджено контактну взаємодію між нікелем і гарячепресованою керамікою зі складного карбіду титану-хрому TiCrC у вакуумі при температурі 1500°C. Вивчено кінетику процесу та визначено крайові кути змочування у цій системі. Виявлено, що рідкий нікель добре змочує TiCrC з утворенням контактного кута $\theta = 8$ град. При цьому контактна взаємодія здійснюється шляхом розчинення і просочення нікелем кераміки за межами зерен на глибину 400–600 мкм. Виникають процеси дифузії Ti, Cr і C з підкладки у краплю, що призводить до зміни її хімічного складу. При охолодженні у краплі і перехідній зоні відбувається рекристалізація карбідів титану та хрому з утворенням нових фаз TiC_x–Cr, Cr_3C_2–Ti і Cr_7C_3–Ni–Ti. Таким чином, за критерієм контактного кута змочування кераміка TiCrC може успішно використовуватися для створення керметів у поєднанні з Ni в якості матричного сполучного компонента. Однак необхідно враховувати факт можливої взаємодії компонентів з наступною зміною їх хімічного складу.

Исследовано контактное взаимодействие между никелем и горячепрессованною керамикой из сложного карбида титана-хрома TiCrC в вакууме при температуре 1500°C. Изучена кинетика процесса и определены краевые углы смачивания в этой системе. Выявлено, что жидкий никель хорошо смачивает TiCrC с образованием контактного угла $\theta = 8$ град., при этом контактное взаимодействие осуществляется путем растворения и пропитки никелем керамики по границам зерен на глубину 400–600 мкм. Возникают процессы диффузии Ti, Cr и C из подложки в каплю, что приводит к изменению ее химического состава. При охлаждении в капле и переходной зоне происходит рекристаллизация карбидов титана и хрома с образованием новых фаз TiC_x–Cr, Cr_3C_2–Ti и Cr_7C_3–Ni–Ti. Таким образом, по критерию контактного угла смачивания керамика TiCrC может успешно использоваться для создания керметов в сочетании с Ni в качестве матричного связующего компонента. Однако необходимо учитывать факт возможного взаимодействия компонентов с последующим изменением их химического состава.

1. Introduction

Metal-ceramic composites are widely used as construction elements or protective coatings in many industrial fields such as airspace, nuclear power, engineering, printing, etc. As a rule, in such composites, the ceramic phases include carbides, nitrides, borides, oxides, and carbonitrides of tungsten, titanium, chromium, molybdenum; while nickel, iron, cobalt, copper, aluminum, other metals and alloys are used as metallic phases [1–12]. The combination of ceramic and metal components leads to significantly improved performance: high hardness and strength, fracture toughness, fatigue life, wear and corrosion resistance. Furthermore, by the proper selection of components and manufacturing processes, it is possible to design metal-ceramic composites with properties that meet specific requirements [1, 7, 13–16].

Currenly, the WC–Co and WC–Ni composites remain in widespread commercial use as wear-resistant materials and coatings; however, the catastrophic oxidation of tungsten carbide at high temperature (> 600°C), as well as the lack of cobalt and tungsten prompts the search for suitable alternatives [17–19].

Titanium-chromium carbide with high melting temperature, high thermal and electrical conductivity, excellent thermal shock resistance, high hardness and chemical inertness is a promising material to develop metal-ceramic composites [20, 21]. Several attempts have been made to produce and investigate the TiCrC-based metal-ceramic materials and protective coatings [20–24]. In particular, under fretting conditions, the TiCrC–FeCr plasma-sprayed coatings demonstrate a high level of wear resistance comparable to WC–Co coatings [20]. The addition of TiCrC particles into the NiCrBSiC alloy results in an improvement of wear-resistance of plasma-sprayed coatings under dry sliding conditions [22]. The author of [23] determined that the TiCrC-based cermet coating has erosion resistance, comparable to that of the tungsten carbide cermet coating, but with a much higher thermal shock resistance. In [24], the nickel additions were found to substantially decrease the oxidation rate of the TiCrC-based composites and shift the thermal effects toward much higher temperatures. Thus, the TiCrC–Ni system is appealing to design wear-resistant composite materials and protective coatings for the operation at high temperatures.

It should be noted that nearly all production processes of metal-ceramic materials and coatings, such as liquid-infiltration techniques, powder metallurgical techniques, hot pressing, self-propagating high-temperature synthesis or reactive synthesis, thermal spraying, physical-vapour deposition, are associated with interfacial phenomena between liquid metal and solid ceramic components [25–28]. The interfacial bonding between the ceramic reinforcements and the metal matrices is an important factor that affects the mechanical and tribological properties of the composites. That is why, the development of TiCrC-based composite materials with nickel binder requires the investigation of high-temperature wetting and interfacial interaction in the TiCrC–Ni system.

Although the wetting behavior of TiC in contact with metal alloys have been investigated rather extensively [29–35], the experimental data on the wettability of TiCrC are very limited [36]. The aim of this study is to study the interfacial interaction of titanium-chromium carbide in contact with molten nickel at 1500°C to develop metal-ceramic materials.

2. Experimental

The experiments were carried out using the TiCrC plates as solid ceramic specimens. Commercially pure TiCrC powder (9–10 μm), produced by self-propagating high-temperature synthesis (LTD "Composite Systems", Ukraine) [12], was applied to obtain ceramic specimens ($\varnothing = 9$ mm, $h = 2$ mm) by hot pressing. For improvement of wetting processes, the specimen surfaces were polished.

The electrolytic nickel powder (GOST9722-79) was placed in alundum crucibles and melted at 1600°C in an argon environment. Pieces of 0.5–1 g were cut from the obtained ingot and used in the wetting tests. Before the sessile drop test,

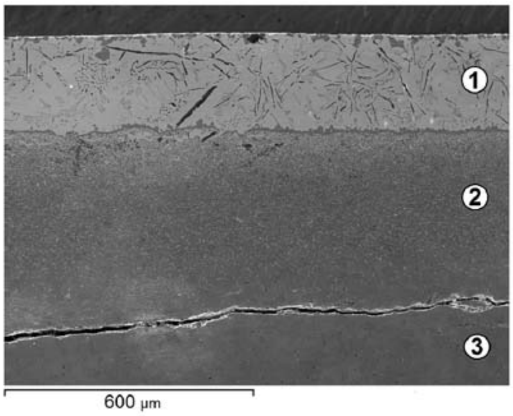

Fig. 1. Microstructure of the contact interaction zone between TiCrC and Ni: 1 — Ni drop; 2 — interaction zone; 3 — TiCrC substrate.

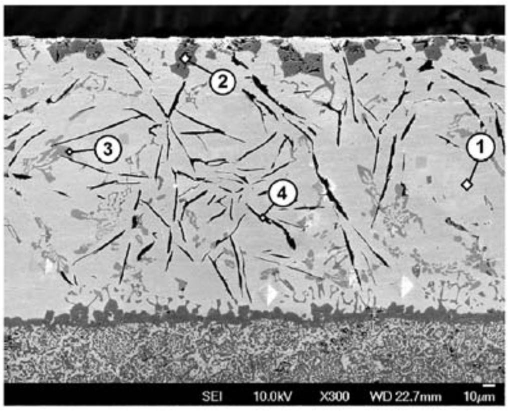

Fig. 2. The microstructure of the drop on the surface of TiCrC substrate.

the ceramic and alloy specimens were cleaned with alcohol.

The wetting was evaluated by contact angle measurements using the sessile drop technique at 1550°C under a vacuum of about $1.33 \cdot 10^{-3}$Pa. The specimens were maintained at 1550°C for 10 min after the constant angle was set and then cooled inside the vacuum chamber to avoid oxidation. After the wetting tests, the metal-ceramic couples were crosssectioned and polished.

The metal-ceramic interface structure and chemical composition were studied using a JEOL JAMP 9500 microscope, equipped with a SEM-EDS (energy dispersive spectrometry) unit.

3. Results and discussion

The test shows that wetting of TiCrC by molten Ni is very good. The melt forms an initial contact angle of 43 degrees, which then decreases to a final contact angle of 8 degrees in 1 min. The microstructure of the contact interaction zone is heterophase both from the drop side and the substrate side (TiCrC) (Fig. 1). Inside the drop, the metallic phase consists of a solid solution of chromium, titanium, and carbon in nickel (Fig. 2, Table 1: spectrum 1) with inclusions of various chemical compositions. Large (up to 30 µm) dark grains formed on the surface of the drop upon its cooling, which was identified by SEM as chromium-doped tita-

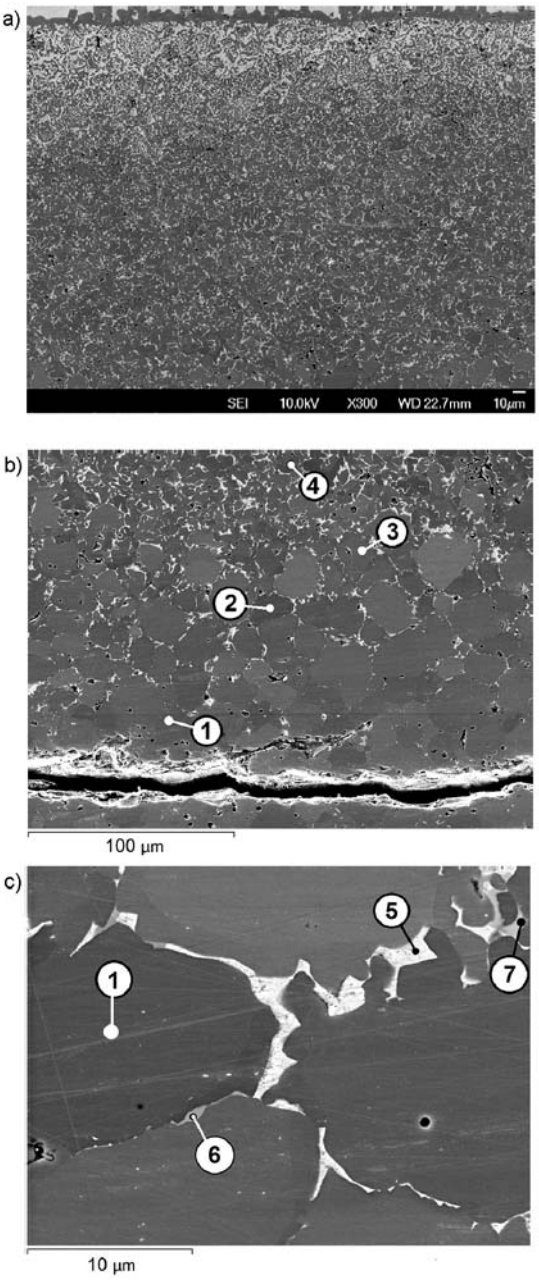

Fig. 3. The microstructure of interaction zone in the TiCrC–Ni system: a — general view; b, c — views from the lower boundary, near the crack.

Table 1. Chemical and phase compositions of the drop formed on the surface of TiCrC substrate

Spectrum	Chemical composition, at. %								Phase composition
	C	Ni	Ti	Cr	Fe	O	P	S	
1	4.38	81.92	1.91	9.87	0.57	0.50	0.52	0.33	Ni-Cr-Ti-C
2	43.43	0.27	51.52	4.78	–	–	–	–	TiC–Cr
3	36.46	0.79	0.57	61.18	0.30	0.43	0.20	0.08	Cr_3C_2
4	97.78	0.20	0.06	0.03	0.18	1.58	–	0.17	C

Table 2. Chemical and phase compositions of the interaction zone in the TiCrC–Ni system

Spectrum	Chemical composition, at. %					Phase composition
	C	P	Ti	Cr	Ni	
1	43.13	0.00	42.92	13.57	0.37	TiCrC
2	42.49	0.03	43.42	14.06	0.00	TiCrC
3	42.49	0.10	43.12	14.18	0.11	TiCrC
4	43.41	0.19	49.24	6.94	0.22	TiC–Cr
5	5.14	0.84	3.51	11.37	79.14	Ni–Cr–Ti–C
6	36.76	0.09	11.32	51.04	0.79	Cr_3C_2–Ti
7	26.07	0.00	5.37	56.66	11.90	Cr_7C_3–Ni–Ti

Table 3. Chemical and phase composition of the boundary interaction zone in the TiCrC–Ni system

Spectrum	Chemical compositions, at. %					Phase composition
	C	P	Ti	Cr	Ni	
1	5.04	1.07	2.48	11.23	80.18	Ni–Cr–Ti–C
2	42.41	0.18	54.99	1.76	0.65	TiC_x
3	35.31	0.00	2.42	61.56	0.71	Cr_3C_2
4	42.92	0.00	51.97	4.88	0.22	TiC_x–Cr
5	35.33	0.00	0.74	62.92	1.01	Cr_3C_2
6	6.07	0.60	1.67	9.58	82.08	Ni–Cr–Ti–C

nium carbide. (Fig. 2, Table 1: spectrum 2). Smaller light-grey inclusions are formed by the chromium carbide Cr_3C_2 (Fig. 2, Table 1: spectrum 3). The third phase, represented by the needle-like black inclusions, consists of free carbon (Fig. 2, Table 1: spectrum 4).

The inclusions of carbides and free carbon in the initial nickel indicate a chemical interaction in the TiCrC–Ni system. It can be assumed that in the process of high-temperature wetting, the substrate of double chromium-titanium carbide dissolves, followed by diffusion of Ti, Cr, and C into the drop zone (Fig. 3, Table 2). Upon cooling, the solubility of the elements in nickel decreases, which leads to the crystallization of particles of titanium and chromium carbides in the drop zone.

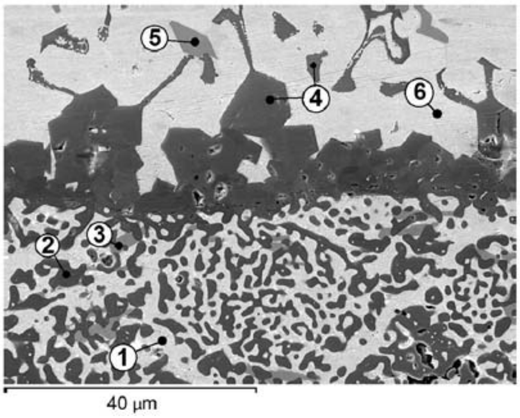

Fig. 4. The microstructure of the interaction zone on the drop interface (×1000).

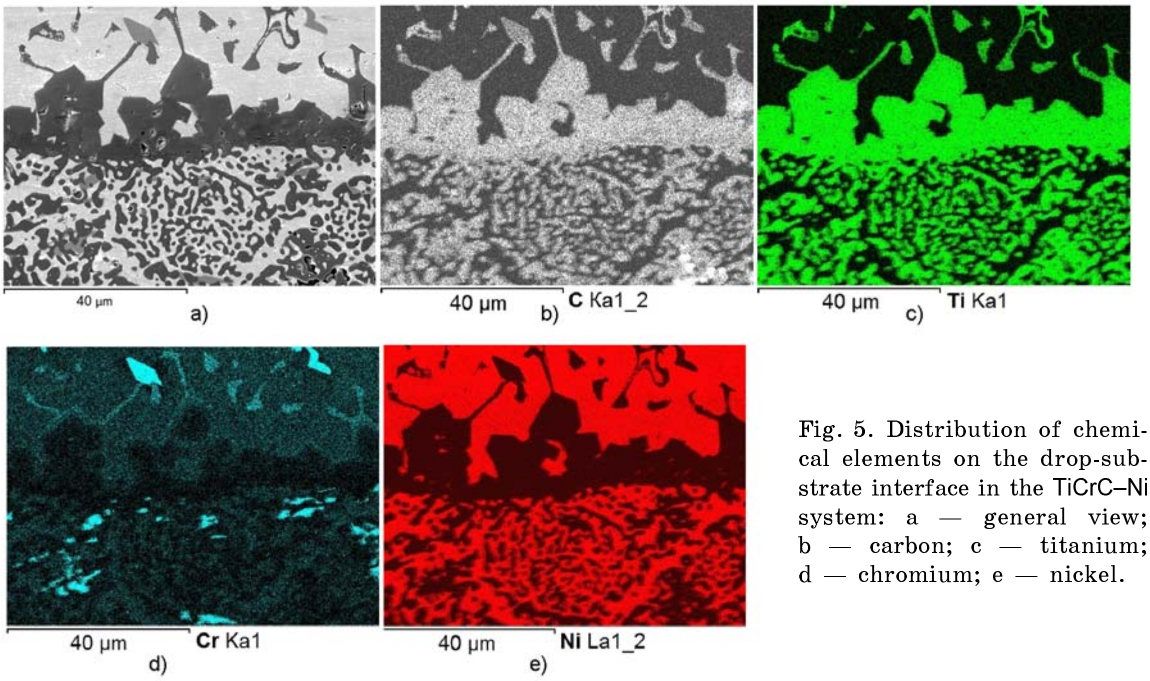

Fig. 5. Distribution of chemical elements on the drop-substrate interface in the TiCrC–Ni system: a — general view; b — carbon; c — titanium; d — chromium; e — nickel.

Microstructure and phase composition analyses of the contact interaction zone show that the dissolution of the ceramic substrate occurs along grain boundaries of double chromium-titanium carbide. SEM reveals the formation of a saturated solution Ni–Cr–Ti–C at TiCrC grain boundaries (Fig. 3c, Table 2: spectrum 5). The amount of dissolved TiCrC grains decreases with distance from the drop interface (Fig. 3a, b).

When the Ni–Cr–Ti–C solution cools down, crystallization and formation of chromium car bide phases doped with titanium and nickel Cr_3C_2–Ti and Cr_7C_3–Ni–Ti also occur in the space between the grains (Fig. 3c, Table 2: spectra 6, 7).

The presence of chromium carbide grains is also observed in the drop border zone: light gray grains are present both in the substrate and in the drop (Fig. 4, Table 3: spectra 3, 5). Dark-colored grains of titanium carbide, doped with a small amount of chromium, were found also along the drop-substrate interface (Figs. 2 and 4, Table 3, spectrum 4). It indicates that titanium carbide recrystallization took place upon cooling in the drop zone near the substrate surface.

The maps of elements distribution within the interface region also confirm the dissolution and infiltration of TiCrC substrate with nickel and the diffusion of titanium, chromium, and carbon into the drop (Fig. 5).

4. Conclusions

The results of this work allow us to draw the following conclusions:

— molten nickel excellently wets the titanium-chromium carbide ceramics (TiCrC) with wetting angle $\theta = 8$ deg;

— the TiCrC–Ni system has an active interaction between phases by dissolution and infiltration of the ceramic substrate with Ni and simultaneous diffusion of Ti, Cr, and C into the drop;

— titanium is an interphase-active element in the TiCrC–Ni system;

— the TiCrC–Ni system can be successfully used to develop metal-ceramic composites.

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