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Cr-20Ti-10C particulate metal matrix composites

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Metal matrix composites containing Cr-20Ti-10C reinforcement fabricated by infiltrating at 1200 °C to 1280 °C for 30 to 60 min have been investigated. Peculiarities of the formation of the interfaces between Cr-20Ti-10C solid alloy and Fe-3.5B Fe-3.5B-20Cr, Fe-3.5B-5Ti, Fe-3.5B-10Cu, Cu, Cu-20Ni-20Mn liquid alloys (wt. pct) have been determined. Copper only weakly wets Cr-20Ti-10C that does not form any new phases when reacts with liquid copper. The wettability can be improved by adding 20 pct Ni and 20 pct Mn to copper. The wetting of Cr-20Ti-10C by iron-base melts is much better. Fe-3.5B alloy exhibits the smallest contact angle. When raising the infiltrating temperature and prolonging the infiltrating period, wetting properties of Cr-20Ti-10C improve. Difference in wetting behavior of the carbide has been explained using substance configuration model by G.V. Samsonov.

Keywords: solid alloy, melt, interface, wettability, contact angle, electronic structure.

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I. Introduction

The mechanical properties of chromium and titanium carbides have been regarded with great interest because these alloys have tremendous potential for applications as reinforcement particles of metal matrix composites fabricated by infiltrating. Among such alloys, special attention has been given to Cr-20Ti-10C alloy because of its attractive properties of high oxidation resistance, high melting point, and high strength at high temperatures.

The particle/matrix interface is probably the most critical region in metal matrix composites because the mechanical properties are largely limited by the efficiency of the particle/matrix bond. Besides, since infiltrating is carried out at high temperatures, there is a distinct possibility that exposure to molten matrix at high temperatures may severely degrade the particles and/or result in extensive particle/matrix chemical reaction. Thus, an understanding and strict control of the course of interfacial reactions occurring between the particulate and matrix during infiltrating are essential to obtaining good mechanical properties of the composites.

Therefore, the aim of this work has been to study the development of the interfacial zones in copper-base and iron-base matrix composites reinforced with the Cr-20Ti-10C particulate and to investigate how the interface responds to variations of temperature and holding time during infiltration.

II. Experimental procedure

The metal matrix composites were fabricated by infiltrating of Cr-20Ti-10C particulate by copper- and iron-base alloys at 1200 °C to 1280 °C for 30 to 60 min. The used particulate had irregular shape and was about 0.5 to 2.0 mm in size. Optical and scanning electron microscopy was employed to investigate the specimens.

The processes occurring at the carbide/matrix interfaces of the composite materials were studied using *superincumbent drop* method [1]. The experimental investigations proceeded by measuring and calculating a so-called wetting or contact angle. Here a "drop" of the metal being investigated was placed on the Cr-20Ti-10C substrate. Then they both were heated simultaneously in a vertical tube furnace with a tungsten heater that was placed in the vacuum chamber. The working pressure did not exceed 6.65 Pa. A relative temperature resolution was better than 1 °C, the absolute accuracy was about ± 3 °C. After melting metal and reaching certain temperature, the liquid drop was held on the substrate during preset period of time (a holding time, τ) and cooled at the rate not exceeding 4 to 6 K/min. The shape of the drop was studied and the contact angle (θ) was measured by drawing a tangent to the drop/gas interface and calculated using the following formula:

$$\text{tg } \theta/2 = h/a,$$

where: h – drop height, mm; a – maximum drop radius, mm.

The value of the contact angle gave an indication of

the strength of the surface bonding between the liquid metal and the substrate. The interfacial zone was investigated by metallographic, X-ray, and electron probe microanalyses.

III. Results

The Cr-Ti-C carbide exhibits two-phase structure consisting of dark primary crystals of $(Ti_{0.5}Cr_{0.5})_3C$ and light crystals of $(Cr_{0.95}Ti_{0.05})_7C_3$ (Fig. 1). The results of the determination of structural, physical and mechanical characteristics of the carbide are shown in Table 1.

Upon solidification all composites contain 50 to

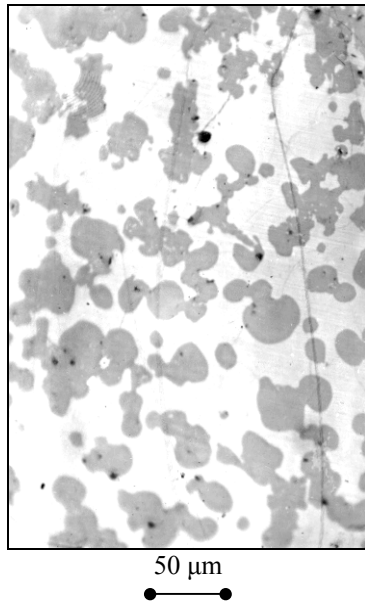


Fig. 1. Microstructure of Cr-Ti-C, x 200

60 vol. pct of Cr-20Ti-10C particles embedded in the matrix. Copper matrix composites, regardless of the infiltrating temperature, display the worst overall structure plagued with massive porosity. Polished

lowering temperature to 1050 °C gives rise to significant porosity.

The structure of iron-base matrix composites displays the formation of interfacial zones which vary in thickness from 50 μm to 250 μm. The interfacial zones produced as a result of contact interaction consist of $(Cr,Ti)_7C_3$ and $(Ti,Cr)_3C$ embedded in $\alpha-Fe_3(C,B)$ eutectic alloyed with Cr and Ti (Fig. 2). The microhardness of the eutectics is 8.5 GPa. The composition of the interfacial zones between the carbide and Fe-3.5B melt alloyed with 20 pct Cr or 5 pct Ti does not change. But, globular copper inclusions appear additionally when 10 pct Cu is added to Fe-3.5 alloy. Table 2 shows a

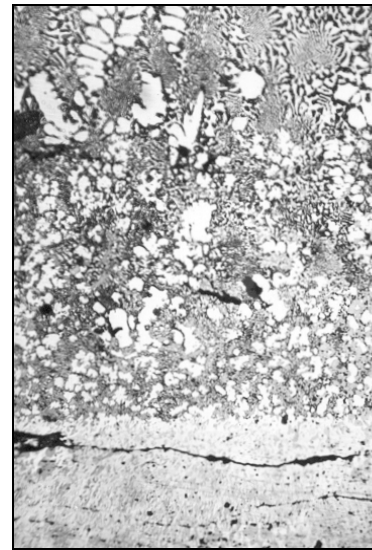


Fig. 2. Microstructure of the interface between Cr-20Ti-10C and Fe-3.5B matrix, x 200.

summary of the micro X-ray analysis and the identified phases. At higher infiltrating temperatures and longer holding times the formation of $(Cr,Ti)_7C_3$ can be accelerated. The thickness of the interfacial zones

Table 1

The properties of the Cr-20Ti-10C carbide

Characteristics	Phase		Cr-Ti-C
	$(Cr,Ti)_7C_3$	$(Ti,Cr)_3C$	
Microhardness, GPa	19.5±0.5	25.1±0.6	-
Microbrittleness, units	4.4±0.3	1.28±0.2	-
Brittle microstrength, GPa	1.95±0.3	5.94±0.1	-
Specific weight, g/cu cm	-	-	5.33±0.24
Apparent weight, g/cu cm	-	-	12.01±0.5

metallographic sections of the samples show no evidence of any visual change at the particulate/matrix interfaces.

The interfacial zones are not clearly seen around the particulate in Cu-20Ni-20Mn matrix as well. Although, the Ti content in the matrix near the interfaces is observed to be slightly higher than that away from the interface. A moderate amount of porosity is also seen in the matrix of these composites infiltrated at 1150 °C, but

changes, as illustrated in Fig. 3.

The above observations are in good agreement with the results of the determination of wettability of the chromium and titanium carbide by copper-base and iron-base alloys using *superincumbent drop* method (Fig. 4). Copper only weakly wets the Cr-20Ti-10C alloy at 1200 °C to 1300 °C, and only at 1350 °C a contact angle equals to 46° (Fig. 4,b). Alloying copper with Ni and Mn

decreases a contact angle by 29° at 1250 °C, although adhesion of the drop to the substrate occurs only at the temperatures exceeding a melting temperature of the drop by 60 °C to 80 °C.

Fe-3.5 liquid alloy exhibits the smallest contact angles that decrease with increasing holding time and temperature. Alloying Fe-3.5B with Cr and Ti, the components of the substrate, increases the melting

which contributes to the rapid dissolving of the phase. The high-melting-temperature ternary $(Ti,Cr)_3C$ phase retains unchanged during all the processes of contact interaction, and, therefore, it is present in the form of dark inclusions in the eutectic structure. The dissolving of the ternary phase is hampered not only by relatively high melting temperature of the phase, but also by an increase in the melting temperature of the surrounding

Table 2

Alloy No.	Matrix	Interface	
		Structural composition	Phase composition
1	Cu	-	-
2	Cu-20Ni-20Mn	solid solution of Ni,Mn,Ti in Cu	solid solution of Ni,Mn,Ti in Cu
3	Fe-3.5B	$(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$, α -Fe ₃ (C,B) eutectic alloyed with Cr and Ti	solid solution of Ti,Cr in α , $(Fe,Cr)_3(C,B)$, $(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$
4	Fe-3.5B-10Cu	$(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$, Cu, α -Fe ₃ (C,B) eutectic alloyed with Cr, Ti	Cu, solid solution of Ti, Cr in α , $(Fe,Cr)_3(C,B)$, $(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$
5	Fe-3.5B-20Cr	$(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$, α -Fe ₃ (C,B) eutectic alloyed with Cr and Ti	solid solution of Ti,Cr in α , $(Fe,Cr)_3(C,B)$, $(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$
6	Fe-3.5B-5Ti	$(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$, α -Fe ₃ (C,B) eutectic alloyed with Cr and Ti	solid solution of Ti,Cr in α , $(Fe,Cr,Ti)_3(C,B)$, $(Cr,Ti)_7C_3$, $(Ti,Cr)_3C$

temperature of the drop and, correspondingly, contact angles. With up to 10 pct Cu added to the Fe-3.5B alloys,

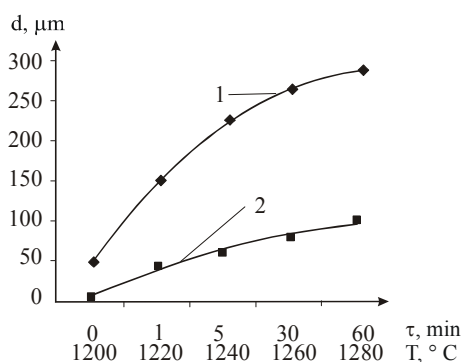


Fig. 3. Thickness (d) of the interfacial zone between Cr-Ti-C and Fe-3.5B as a function of: 1 – temperature (T), 2 – holding time (τ).

contact angles also decrease with the increase in a holding time. The results are compiled in Figure 4.

IV. Discussion

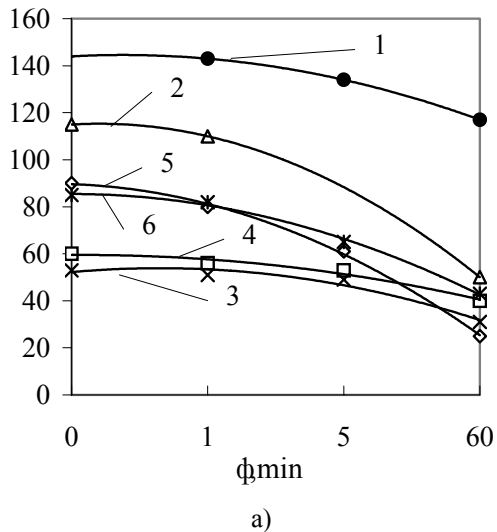
As compared to copper-base alloys, the adhesion of iron-base alloys to the carbide substrate occurs upon metal melting, interfacial zones forming. The origin of the formation of these interfaces is probably related to the partial dissolution of the low-melting-temperature phase identified as Cr_7C_3 alloyed with titanium from the particulate into molten matrix. Due to a loss of carbon Cr_7C_3 carbide decomposes to the lower $Cr_{23}C_6$ carbide,

eutectic alloyed with diffusing titanium. The stability of the $(Ti,Cr)_3C$ phase during the contact interaction processes confirm the results of determination of microhardness, microbrittleness, and brittle microstrength of the ternary phase present in the eutectic structure of interfacial zone and the ternary phase of the original cast Cr-20Ti-10C carbide.

The suggested mechanism seems to explain the increase in the thickness of the interfacial zone by the intensification of the diffusion of carbon from the particulate into the matrix. These processes give rise to forming regions of Cr-20Ti-10C carbide depleted with carbon that are relatively remote from the interface, and, that is why, to lowering the melting temperature of the Cr_7C_3 carbide alloyed with titanium and its transforming to the lower $Cr_{23}C_6$ carbide, on the one hand, and to lowering the melting temperature of the Fe-B eutectic enriched in carbon, on the other hand. There is enough time for the heat needed to melt the Cr_7C_3 carbide alloyed with titanium to transfer deep into the particulate, which creates additional preconditions for developing contact interaction processes and widening interfacial zones. This assumption evidences that the said mechanism of contact interaction retains at the stage when the interaction proceeds through the liquid phase and that there is a continuous contact of liquid (and solid) iron matrix with the particles.

The important stage of contact interaction and formation of adhesion bonding is the stage of chemical interaction at which the processes of electron interaction play a dominant part. Therefore, the discussion of electronic structure of the components involved in the processes proceeding at the interfaces is essential at this

point. As follows from the substance configuration model suggested by G.V. Samsonov [2], the adhesion processes are directed at the formation of stable configurations between the atoms of a contacting couple. Since a statistical weight of atomic stable configurations, d^0 , d^5 , d^{10} , (SWASC) predetermines the properties controlled by energy of interfacial bonding in the lattice,



bond and makes the sp^3 -configuration more stable.

When the chromium and titanium carbide is wetted by molten metals, the system uses all the resources to increase a SWASC of the sp^3 -configurations, which is connected with the reconstruction of all types of bonds between metal and carbon atoms that are peculiar to the carbides. In this case, apart from stabilization of the sp^3 -

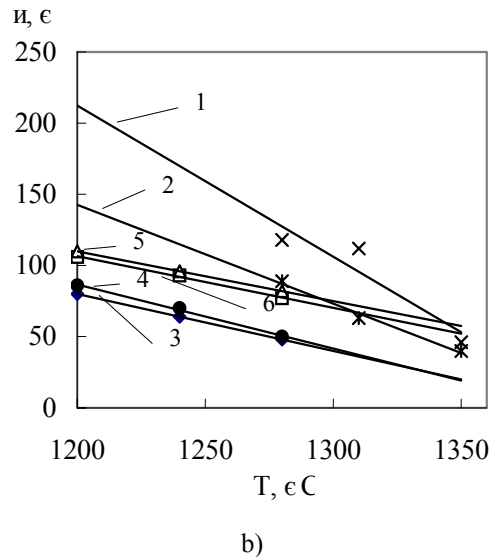


Fig. 4. Influence of holding time, τ , at $T = 1250$ °C (a) and temperature, T , at $\tau = 1$ min (b) on contact angles between Cr-Ti-C and: 1-Cu; 2-Cu-Ni-Mn; 3-Fe-3.5B; 4-Fe-3.5-10Cu; 5-Fe-3.5B-20Cr; 6-Fe-3.5B-5Ti.

the obtained experimental results can be explained with SWASC of the components participating in the interfacial processes taken into account.

Chromium and titanium carbides feature the highest statistical weight of the sp^3 -configurations formed by carbon atoms in the carbides. Due to the Cr-C interaction some number of the valence d-electrons are excited to the sp-states participating in the formation of covalent bonds with carbon configurations. Besides, the donor-acceptor Cr-C interaction inducing a partial electron transfer from metal to carbon characterizes the ionic component of the said bond. And the partial collectivization of the metal electrons determines the metal component of the bond. Because directed covalent bond formed by the sp^3 -configurations is the strongest one, the strength of the bond in chromium carbides depends, mainly, on the SWASC of the sp^3 -configurations, but the stability of the d^5 -configurations in a SWASC of the d^5 -configurations defining a contribution of the Cr-C covalent bonds plays 'second fiddle'.

When chromium carbide is alloyed with titanium whose electrons are slightly bonded in the d-subshell and capable of exciting to participate in the Ti-C covalent bond and to become collectivized, the donor capacity of metal atoms compared with that of the M-C bond increases and the contribution of the shielded M-M interaction decreases. As a result, a SWASC of the d^5 -configurations of the metal component decreases and a SWASC of the sp^3 -configurations of carbon sublattice increases, and, simultaneously, a portion of covalent constituent in the M-C bond increases. This eases the excitation of electrons for the participation in the M-C

configurations by collectivized electrons and ionic component of donor-acceptor nature, it is necessary to form covalent bonds at the expense of the increase in a SWASC of the sp^3 -configurations of carbon and the decrease in a SWASC of the d^5 -configurations of metal.

Copper features 100-pct SWASC of the d^{10} -configurations; nickel is similar to copper (95-pct SWASC). The d-subsystem of manganese is described by an average $d^{5.4}$ -configuration, i.e., alongside 60-pct SWASC of the d^5 -configurations, there is a significant number of the intermediate-spectrum configurations in the metal, which corresponds to a relatively low energetic stability of the valence subshell of this element. Because copper and nickel feature strong tendency toward increasing a SWASC of the d^{10} -configurations, any rearrangement of electrons in such system will lead to energetically disadvantageous destruction of the stable configurations in one of the components. Therefore, poor wetting of Cr-20Ti-10C by copper and copper-nickel alloys is observed. Alloying with Mn that has some number of excess electrons improves wetting significantly, but overheating of the melt is needed to form bonds across the interface.

The interfacial processes look different when iron-base alloys wet the chromium and titanium carbide. Iron has a low statistical weight of the intermediate-spectrum configurations, with amount of the collectivized sp-electrons insignificant. Iron atoms can give away some number of their valence electrons with the preferential formation of the stable d^5 -configurations, which ensures an increase in statistical weight of the most stable sp^3 -configurations in the system. This assumption explains

the better wettability of the Cr-20Ti-10C alloy by iron-base melts. Adding of chromium and titanium to the Fe-B alloy leads to the reduction in the amount of localized valence iron electrons and the increase of a SWASC of the d^5 -configurations, which is connected with the fact that Cr and Ti have either the high SWASC of the d^5 -configurations or the strong possibility of their formation at the expense of their own electrons due to $s \rightarrow d$ transitions as well as at the expense of iron electrons. Hence, when iron atoms are replaced with chromium and titanium atoms, the fewer amounts of valence electrons participate in the electron exchange. Correspondingly, contact angles at the interfaces between the Cr-20Ti-10C alloy and Fe-3.5B-20Cr or Fe-3.5B-5Ti melts increase.

Copper and iron differ in SWASC by about 50 pct. Therefore, copper does not mix with iron even in the liquid state. As a result, at the interface between Fe-3.5B-10Cu melt and the carbide appear globular copper inclusions. Correspondingly, copper added to the Fe-3.5B alloy does not practically influence the contact angles.

V. Conclusions

In summary, it can be concluded that copper only weakly wets Cr-20Ti-10C that does not form any new phases when reacting with liquid copper. The wettability can be improved by adding 20 pct Mn to copper.

The wetting of the Cr-20Ti-10C alloy by iron-base melts is much better and is accompanied by the processes of chemical interaction over the whole range of investigated temperatures. The Cr-20Ti-10C alloy reacts with Fe-3.5B molten alloy, forming mixtures of $(Cr,Ti)_7C_3$ and $(Ti,Cr)_3C$ embedded in $\alpha\text{-Fe}_3(C,B)$ eutectic alloyed with Cr and Ti. The reduction of the intensity of the processes of chemical interaction can be achieved by alloying Fe-3.5B melt with 20 pct Cr and 5 pct Ti.

When raising the infiltrating temperature and prolonging the infiltrating period, wetting properties of the Cr-20Ti-10C carbide improve. Difference in wetting behavior of the carbide appears to stem from the electronic structure of the constituents.

Since the Cr-20Ti-10C reinforcement and copper-base matrix are mutually nonreactive and insoluble during infiltrating, it results in poor bonding across the interface. The iron-base matrix and the reinforcement are soluble at the infiltrating temperature but are reasonably nonreactive below the melting temperature of the matrix. Eutectic Fe-3.5B alloy can be successfully used as a metal matrix in the composite materials reinforced with the chromium and titanium-carbide. This material exhibits strong adhesion at the particulate/matrix interfaces.

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I. Спиридонова, О. Сухова

Композиційні матеріали з металевою матрицею, зміцнені частками Cr-20Ti-10C

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В роботі досліджені композиційні матеріали з металевою матрицею та наповнювачами Cr-20Ti-10C, які одержували просоченням при температурах 1200 °C-1280 °C на протязі 30-60 хв. Були визначені особливості формування міжфазних границь розподілу між твердим сплавом Cr-20Ti-10C та рідкими сплавами Fe-3,5B; Fe-3,5B-20Cr; Fe-3,5B-5Ti; Fe-3,5B-10Cu; Cu; Cu-20Ni-20Mn (мас. %). Мідь погано змочує сплав Cr-20Ti-10C, не утворюючи нових фаз в зоні взаємодії. Змочування міддю поліпшується при її легуванні 20% Ni та 20% Mn. Змочування сплаву Cr-20Ti-10C розплавами на базі заліза значно краще. Найменший контактний кут утворює сплав Fe-3,5B. При збільшенні температури і тривалості просочення змочування сплаву Cr-20Ti-10C рідкими металами покращується. Отримані результати пояснені за допомогою конфігураційної моделі речовин Г.В. Самсонова.