

# HIGH PERFORMANCE METAL-MATRIX COMPOSITE COATINGS

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**Abstract:** *The effect of the initial structure of the fillers on the structure formation of the dissolution-and-diffusion type interfaces in macroheterogeneous composite coatings with a metal binder has been investigated. It has been shown that by combining phases in the filler structure, which differ in resistance to molten binder during infiltration, it is possible to attain an increased resistance of composite coatings to dry friction, abrasive, gas abrasive, and corrosion wear. The compositions of composite coatings to strengthen the surface of the parts of machine-building industry have been recommended.*

**Keywords:** COMPOSITES, INFILTRATION, BINDER, FILLER, INTERFACES, PERFORMANCE CHARACTERISTICS

## 1. Introduction

Macroheterogeneous composites produced by a furnace infiltration find the wide application as coatings to protect and restore the quick-worn parts of the machine-building and metallurgical equipment. The widest use has found a coating, whose composition consists of the W–C (relit) eutectic alloy or related alloys (WC–6Co, WC–8Co, etc.) as a filler and MNMts 20–20 manganese melkhor (Cu–20Ni–20Mg alloy) as a metal binder. This composite material was designed for facing charging equipment of blast furnaces of metallurgical plants, which work under the conditions of gas-abrasive wear. The use of the coating made it possible to solve the problem of this type parts durability increasing their operating life by a factor of 3–15.

To expand the applications of this class of composite coatings, further studies were conducted in two main directions. The first direction was associated with the use of a more wear-resistant than manganese melkhor binder. The operating characteristics of composite coatings were increased by a factor of 1.5–2 in the case of the infiltration by iron-based binders. However, the main disadvantage of these coatings is the intensive interaction of tungsten carbide with molten iron alloys in the course of the infiltration at a sufficiently high melting temperature of the latter. With the aim to reduce the filler dissolution rate on the average by 15–20%, it was proposed to use filler particles of a spherical form produced by thermocentrifugal atomization of a rotating bar. The result attained was related to a decrease of the area of spherical granules that contact with a molten binder, but no attention was paid to changes in the granules structure with increase of their cooling rate up to  $10^3$ – $10^4$  K/s.

The second direction covers studies conducted with the aim to replace the expensive filler based on tungsten carbides by a cheaper high-melting alloy and maintain basic operational characteristics of composite coatings. For example, alloys containing carbides of chromium, titanium, boron, etc. are proposed. Nitrides of titanium, aluminum, zirconium, etc. are also promising fillers of composite coatings. Borides of metals occupy a special place among filler alloys designed for reinforcing metal binders. Borides have a higher hardness and lower brittleness as compared with those of corresponding carbides and nitrides. The best known is the filler of composition 80 wt. %  $TiB_2$  and 20 wt. %  $CrB_2$ . As a binder of composite coatings reinforced by (Ti,Cr) $B_2$  filler, the manganese melkhor with additions of Mo, Si, and other components that inhibit the boron diffusion into the metal binder is used.

In many publications on the development of the novel composite coatings, a special attention is given to the investigation of the processes of wetting and contact interaction at the interfaces between the hard filler and molten binder during the infiltration. Such an approach is justified, since the structure and properties of these boundaries in the long run are responsible for the performance of composite coatings. However, it should be noted that inadequate attention is given to the prognosis of the contact interaction kinetics with regard to the initial structure of the fillers, though one may efficiently control these processes, e.g., by combining phases of

different stabilities in the filler structure. Therefore, in this study we investigated the effect of the filler phases having crystalline, microcrystalline, and quasicrystalline structures on the formation of the interfaces in composite coatings designed for operation under the conditions of the dry friction, abrasive, gas-abrasive, and corrosion wears.

## 2. Experimental Procedure

Samples of composite coatings were prepared in three stages: i) preparation of the filler; ii) preparation of the binder; iii) production of composite coating by a furnace infiltration. The fillers were prepared from W–C, Fe–B–C, Cr–Ti–C, Al–Co–Cu, Al–Ni–Co alloys by mechanical crushing ( $v_{cool} = 10$ – $20$  K/s) or thermocentrifugal atomization of a rotating bar ( $v_{cool} = 10^3$ – $10^4$  K/s). In the first case the filler particles were of irregular shape, in the second case they were spherical. The particle sizes varied from 0.2 to 2.5 mm. Alloys on an iron, copper, or aluminum base were used as binders. The furnace infiltration was performed for 15–60 min at a temperature, which exceeded the binder melting point by 50–100 K. The filler content of a finished composite coating was 50–70 vol %.

The structure of the alloys and composite coatings was studied by quantitative metallographic and X-ray analyses as well as X-ray energy dispersive spectrometry and scanning electron microscopy using standard procedures. The corrosion resistance of composite coatings was assessed by the gravimetric method in HCl aqueous solution at room temperature for 4 hours. The corrosion rates were measured every hour. The resistance of composite coatings to abrasive wear was studied on an NKM plant and to gas-abrasive wear on an OB876 device. The tribological characteristics were defined by the shaft–plug scheme at the dry friction on the grade 45 steel at a sliding rate of 20 m/s and load of 4 MPa.

## 3. Results and Discussion

The composite coatings studied may be divided into three groups:

- coatings based on iron alloys reinforced by crystalline and microcrystalline tungsten carbides or crystalline chromium–titanium carbides;
- coatings based on copper alloys reinforced by crystalline and microcrystalline iron borides;
- coatings based on copper or aluminum alloys reinforced by quasicrystalline Al–Co–Cu or Al–Co–Ni fillers.

During the infiltration, the formation of the filler–binder interfaces in the above composite coatings occurs by the solution-and-diffusion mechanism. This allows one to control the properties by varying the contact interaction intensity at the interfaces, which is regulated by the choice of the filler and binder compositions. The Fe–3.5B–0.2C binder (in wt. %) is for the infiltration of the filler particles made of W–C eutectic alloy ( $v_{cool} = 10$ – $20$  K/s). The choice is justified by the boron positive effect on technological

characteristics of iron binders like relatively low melting temperature, fluidity, oxidation resistance, etc. Before the infiltration, this alloy has a hypoeutectic structure consisting of primary crystals of boron-doped ferrite and Fe-Fe<sub>3</sub>(B,C) eutectics. The contact interaction of the molten Fe-B-C binder with the W-C filler during the infiltration is accompanied by dominating dissolution of W<sub>2</sub>C carbide. The second WC carbide is dissolved to a much lower degree and is observed from the filler side as inclusions into a solid ring of the Fe<sub>3</sub>W<sub>3</sub>C phase (Fig. 1a).

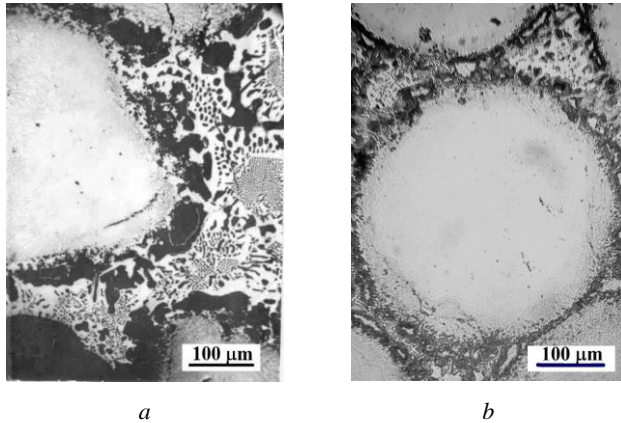


Fig. 1 Microstructure of composite material with the Fe-B-C binder reinforced by the W-C filler cooled at a rate of 10 (a) and  $10^3-10^4$  (b) K/s.

On the side of the hardened binder in the tungsten doped Fe-Fe<sub>3</sub>(B,C) eutectics, there are numerous inclusions of the Fe<sub>3</sub>W<sub>3</sub>C phase as well. A change of the binder structure near the interface is caused by the enrichment of the melt, whose composition corresponds to the composition of the Fe-Fe<sub>2</sub>(B,C) initial eutectics, with tungsten and carbon from the dissolving filler. For the same reason during the consequent recrystallization forms the Fe<sub>3</sub>W<sub>3</sub>C phase in the contact interaction zone between the filler and binder. This phase is responsible for the impairment of corrosion, abrasive, and gas abrasive wear resistances of composite coatings.

In the structure of composite coatings reinforced by rapidly cooled spherical granules of the W-C filler ( $v_{cool} = 10^3-10^4$  K/s), the width of contact interaction zones at the interfaces decreases by a factor of 10-15 (Fig. 1b) and is 15-20 μm. This points to a decrease of the dissolution rate of the filler eutectic phases in the molten iron binder during the infiltration. The result obtained may be attributed to an increase of the uniformity of the W<sub>2</sub>C-WC fine-differentiated eutectic structure of the filler and difficulty of the penetration of the Fe-B-C molten binder deep into the filler along the interfaces of eutectic phases and boundaries of eutectic colonies during wetting. Because of this, the Fe<sub>3</sub>W<sub>3</sub>C phase is virtually absent in the structure of the contact interaction zones. Thanks to this, the composite coatings of the above composition exhibit higher wear resistance in abrasive and gas abrasive media (Table 1).

Table 1: Compositions and properties of abrasive and gas-abrasive resistant composite coatings. \*Note: A composite material with the MNMts 20-20 binder and W-C ( $v_{cool} = 10^3-10^4$  K/s) filler was used as the reference.

Binder	Filler		Coefficient of relative abrasive wear resistance [units]	Coefficient of relative gas-abrasive wear resistance [units] at T [K]	
	Alloy	$v_{cool}$ [K/s]		293	673
Fe-B-C	W-C	$10-10^2$	$1.29 \pm 0.07$	$1.24 \pm 0.09$	$1.32 \pm 0.05$
Fe-B-C	W-C	$10^3-10^4$	$1.54 \pm 0.08$	$1.41 \pm 0.08$	$1.56 \pm 0.03$
Fe-B-C	Cr-Ti-C	$10-10^2$	$1.58 \pm 0.09$	$1.30 \pm 0.07$	$1.39 \pm 0.05$
MNMts 20-20	Fe-B-C	$10-10^2$	$0.83 \pm 0.06$	$0.71 \pm 0.07$	$0.80 \pm 0.04$
MNMts 20-20	Fe-B-C	$10^3-10^4$	$0.68 \pm 0.05$	$0.88 \pm 0.05$	$1.17 \pm 0.04$

Besides, these coatings are characterized by stability in acid medium (Table 2). This is due to the fact that in corrosion tests the interfaces between the filler and hardened binder are destroyed first. Therefore, the corrosion rate decreases with decreasing rate of the

filler dissolution. Owing to the operation characteristics inherent in these composites, they may be efficiently used as protective coatings on the parts of equipment for power and chemical industries.

Table 2: Compositions and properties of antifriction and corrosion-resistant composite coatings.

Binder	Filler		Friction coefficient	Wear intensity [ $\mu\text{m}/\text{km}$ ]	Corrosion rate in 1 N-HCl, [ $\text{g}/\text{m}^2\cdot\text{h}$ ]
	Alloy	$v_{cool}$ [K/s]			
Fe-B-C	W-C	$10^3-10^4$	0.29	21.2	$0.18 \pm 0.02$
L62	Al-Co-Cu	$10-10^2$	0.04	3.0	$0.79 \pm 0.01$
L62	Al-Co-Ni	$10-10^2$	0.09	7.9	$0.89 \pm 0.03$
MNMts 20-20	Fe-B-C	$10-10^2$	0.32	27.5	$0.22 \pm 0.02$

The composite coating with the Fe-B-C binder reinforced by the Cr-20Ti-10C (wt. %) filler is also characterized by a high stability in abrasive and gas abrasive media (Table 1). Before the infiltration this filler has a two phase structure of (Cr,Ti)<sub>3</sub>C<sub>2</sub> primary crystals and (Cr,Ti)<sub>7</sub>C<sub>3</sub> peritectic phase. During the infiltration, due to the contact interaction of filler particles with the Fe-B-C molten binder, the (Cr,Ti)<sub>7</sub>C<sub>3</sub> phase dissolution mainly occurs. The binder basically penetrates deep into the filler along the grain boundaries of peritectic phase. This may be explained by the fact that during the filler fabrication these regions are last to crystallize and are enriched with low-melting components. The rapid dissolution of the (Cr,Ti)<sub>7</sub>C<sub>3</sub> phase may also be promoted by the transformation of this carbide to the (Cr,Ti)<sub>23</sub>C<sub>6</sub> carbide due to the loss of carbon in the contact with the molten binder. The second (Cr,Ti)<sub>3</sub>C<sub>2</sub> phase of the filler does not virtually dissolve and therefore, is present at the interfaces in the form of dark inclusions into eutectic structure of the hardened Fe-B-C binder (Fig. 2).

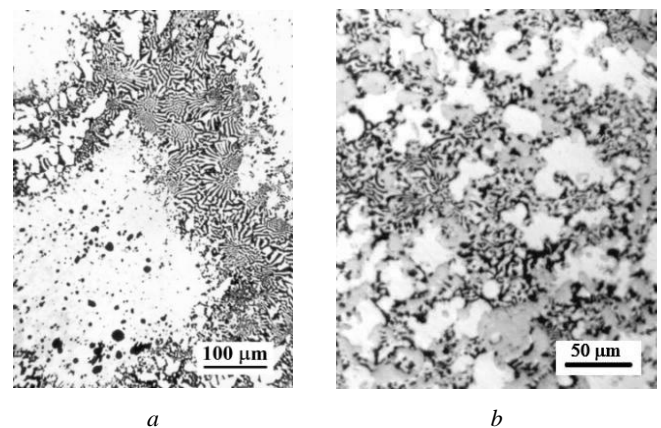
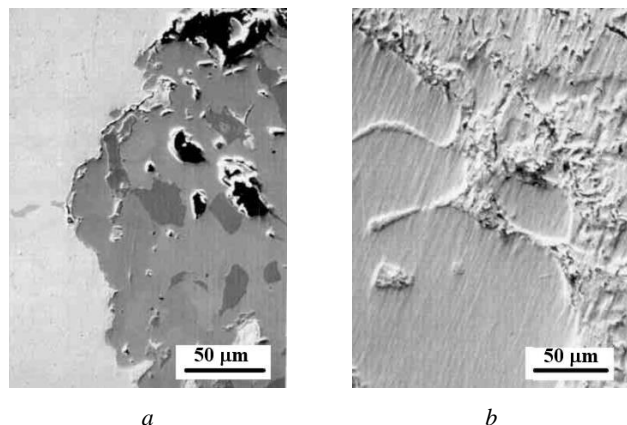


Fig. 2 Microstructure of composite coatings with the Fe-B-C binder reinforced by the Cr-Ti-C filler (a) and zones of contact interaction between the filler and binder (b).

The width of contact interaction zones attains 250 μm. Since the increase of the dissolution rate of crystalline phases of the Cr-Ti-C filler does not bring about the undesirable phases in the structure of interfaces, their formation ensures a strong adhesion of the filler and binder. Because of this, under the conditions of abrasive and gas abrasive wear, a high stability of the composite material with the iron binder reinforced by Cr-Ti-C filler is attained. This material is of a considerable promise for strengthening and restoration of parts of metallurgical and mining equipment. The revealed features of dissolution of eutectic and peritectic fillers in iron binders are observed in the case of the infiltration by copper binder as well.

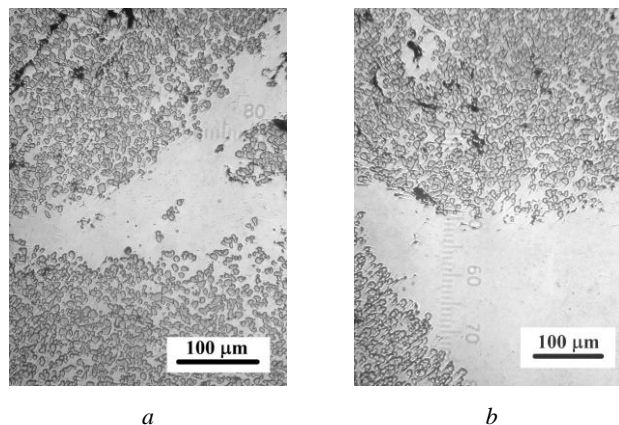
Of interest are composite coatings based on MNMts 20-20 manganese melkhor reinforced by iron borides. In the structure of fillers of compositions 9.0-12.0 B, 0.01-0.17 C, the rest being Fe (all wt. %) there are primary crystals of Fe(B,C) iron monoboride and crystals of Fe<sub>2</sub>(B,C) iron hemiboride. The latter are formed both by the peritectic reaction and crystallize directly from the liquid because the stoichiometric composition of this phase is close to the composition of the peritectic point (Fig. 3a).



**Fig. 3** Microstructure of composite coatings with the MNMts 20–20 binder reinforced by Fe–B–C filler cooled at a rate of 10 (a) and  $10^3$ – $10^4$  (b) K/s.

However, as the cooling rate increases up to  $10^3$ – $10^4$  K/s in producing the boride filler by thermocentrifugal atomization, it acquires a microcrystalline structure. Depending on the granules diameter, the size of  $\text{Fe}_2(\text{B,C})$  crystals ranges from 1.0 to 4.5  $\mu\text{m}$ . In addition, the Fe– $\text{Fe}_2(\text{B,C})$  metastable eutectics appears along the  $\text{Fe}_2(\text{B,C})$  phase boundaries. As a result, in infiltration the molten binder penetrates along the  $\text{Fe}_2(\text{B,C})$  grain boundaries over the whole volume of granules of the rapidly cooled filler (Fig. 3b) and the so called “through” infiltration is observed. Therefore, despite the retardation of the dissolution of Fe(B,C) and  $\text{Fe}_2(\text{B,C})$  microcrystalline phases in molten melkhior by a factor of 5–7 as compared with crystalline phases, the strong adhesion of the filler with a hardened binder is attained. As a result, the gas abrasive wear resistance of composite coatings reinforced by microcrystalline filler increases (see Table 2). There are no traces of chipping the filler under the impacts of abrasive that are usually observed on the worn surface of other composite coatings. At the same time coatings reinforced by boride crystalline filler are characterized by a higher resistance to abrasive wear thanks to the optimal combination of the filler hardness and plasticity. In addition, the reliable adhesion with the binder is assured due to more intensive dissolution of crystalline phases during the infiltration. After the binder solidification, the contact interaction zones up to 50  $\mu\text{m}$  in width form at the interfaces, which contain no brittle phases. Thus, the wear resistance of composite coatings reinforced by iron borides in abrasive and gas abrasive media increases with increasing rate of the fillers dissolution in the molten melkhior. This is brought about by the presence of metastable or crystalline phases in the filler’s structure. The set of operation characteristics of these composite coatings makes it possible to increase the service lives of various parts of metallurgical equipment.

By varying the amount of phases in the filler’s structure which differ in stability under effect of molten metal binder, one may also ensure the formation of defect-free interfaces in macroheterogeneous composite coatings reinforced by quasicrystalline fillers. Quasicrystalline phases that have unique physical, mechanical, and operation properties are characterized by a low surface tension. This impedes the wetting of these phases by infiltrating metals. Therefore, the basic methods to obtain composite coatings reinforced by quasicrystals are extrusion, cold and hot pressing, static and dynamic compacting of mechanically activated powders, directed crystallization, etc. Though it is possible to achieve the adhesion at the interfaces of composite coatings by choosing the optimal amount of crystalline and quasicrystalline phases in the filler structure. Our studies have shown that the promising quasicrystalline fillers for composite coatings are Al–Co–Cu and Al–Co–Ni alloys in combination with binders on a copper or aluminum base. The decagonal quasicrystalline D-phase stable up to 1000°C forms in the above alloys. In the case that the content of this phase is no less than 80–85% of the filler volume, it remains in the structures of composite coatings after the thermal cycle of infiltration (Fig. 4).



**Fig. 4** Microstructure of composite coatings with the L62 brass binder reinforced by the Al–Co–Cu (a) and Al–Co–Ni (b) fillers.

In the contact with the molten binders the filler crystalline phases like  $\text{Al}_4(\text{Co,Cu})_3$ ,  $\text{Al}(\text{Co,Cu})$ ,  $\text{Al}_3(\text{Co,Cu})_2$ ,  $\text{Al}_9(\text{Co,Ni})_2$ ,  $\text{Al}_5(\text{Co,Ni})_2$  dissolve to a higher degree than the quasicrystalline D-phase. The strong adhesion of the filler and copper-based binder is also achieved due to the “through” infiltration (Fig. 4).

The tests of composite coatings reinforced by quasicrystalline fillers show a decrease of the friction coefficient and wear intensity (see Table 2). Besides, these coatings are characterized by a high resistance to acid media. This result correlates with the above conclusion that to achieve corrosion stability, one should decrease the dissolution rate of phases of a filler in a molten binder. These composite coatings may be used to strengthen parts of the automobile transport and rocket-and-space equipment.

#### 4. Conclusions

The character of the contact interaction processes occurring at the interfaces between the filler and the molten binder during the infiltration of macroheterogeneous composites of the dissolution-and-diffusion type may be predicted by considering the initial structure of fillers. In wetting hard fillers of eutectic type, one of the eutectic phases has been dissolved in the molten binder at a higher rate, with binder penetrating deep into the filler along the interfaces and eutectic grain boundaries. Peritectic filler has been dissolved mainly where grain boundaries of peritectic phase are located. The dissolution rate of the phases of the filler in a molten binder during the infiltration of the composites depends on their structure and decreases in the following order: crystalline→microcrystalline→quasicrystalline phases. The intensity of interfacial reactions may also be controlled by combining phases of various stabilities in the structure of the filler. This approach makes it possible to predict performance characteristics and enhance their level due to strict control of interfacial reactions during infiltration.

The lower friction coefficients and wear intensity at dry friction have been shown by composites reinforced by the fillers containing in the structure no less than 80–85 vol. % of stable quasicrystalline phase. The resistance to abrasive and gas abrasive wear has been ensured by the presence of crystalline phases in the filler structure provided that an increase of their dissolution rate in the molten binder during the infiltration does not give rise to brittle phases formation in the contact interaction zones at the interfaces between the filler and the binder. To attain high stability of composite coatings in acid media, the fillers should contain microcrystalline or quasicrystalline phases.

So, developed metal-matrix macroheterogeneous composite coatings obtained by furnace infiltration feature high performance characteristics. Technology of furnace infiltration allows fabricating one-layer or multilayer composite coatings for various applications. Layers of the composites may differ in the filler or the matrix compositions or structure type. They can be utilized for excellent abrasive or corrosive resistance.