PECULIARITIES OF THE INTERACTION OF A HIGHLY CARBONIZED FERROCHROME WITH IRON DURING SINTERING OF 65% Fe-35% FH800 COMPOSITE

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Abstract: *The influence of temperature of sintering on structure formation, phase composition, microhardness of components of powder composite 65 % wt. Fe – 35 % wt. FH800 were investigated. It has been established that the increase in the temperature of sintering from 1050 ℃ to 1250 ℃ leads to some increase in volumetric shrinkage, density and decrease in porosity of samples of material which was made from coarse-grained source powders of industrial production components. It was found that the sintering of green compacts in the range of 1000-1300 ℃ causes significant changes in the chemical and phase composition of the carbide component of the composite, which are described by a series of phase transformations:* $M_7C_3 \rightarrow M_3C$ *(1000-1150 ℃)* $\rightarrow M_7C_3$ *(1200 ℃)* $\rightarrow M_3C$ *(1250-1300 ℃)*
Keywords: *powder materials, composite, sintering, FH800, microhardness.*

Powder metal matrix materials of the class of carbide steels «iron-high carbon ferrochrome FH800» are promising wear-corrosion-resistant composites that can be successfully used for the manufacture of products operated under conditions of simultaneous action of friction forces, abrasive wear and corrosion-active media [1].

The complex of properties of such materials is determined not only by the composition and the ratio of the initial components, but also to a large extent by the additional formation at the sintering and interaction of the solid and metal components of the new phases. Obviously, such interaction inevitably leads to a redistribution of elements of the charge components between the solid and metal phases of the composite. Depending on the sintering temperature, the iron as a result of the interaction with the carbide component of the ferrochromium can form double chromosome carbides of different chemical compositions. Since the main solid component of the high-carbon ferrochrome FH800 is a complex carbide of $(Cr, Fe)_7C_3$ type so such an interaction reduces to its dissolution in the iron matrix of the composite. Information on the mechanism of dissolution $(Cr, Fe)\ _7C_3$ in iron and iron carbon alloys is very limited, and about sintering is practically absent. It was established [2,3] that with the increase in the temperature of the iron-carbon (2.9-3.3% C) melt, the dissolution rate of medium carbon ferrochrome (65% Cr, 3% C) increases from 0.41 at 1570 K to 7.152 kg/m^2*s at 1720 K. The solubility parameter at temperatures close to soliduet of ferrochrome (1570 K) approaches the magnitude of the diffusion coefficient of chromium in an iron-carbon melt, indicating that the diffusion mechanism is close to that of the dissolution.

The authors of the works [4,5] investigated the possibility of application for the creation of a powder-bearing material on the basis of iron carbonate ferrochromium FH650. It is established that the mechanism of dissolution of ferrochrome is similar to the mechanism of dissolution of orthorhombic chromium Cr_3C_2 carbide, but the dissolution process begins at slightly lower temperatures (~ 1000 ℃) and in the interval 1000-1100 ℃ proceeds faster than Cr_3C_2.

It was found out that for the hot stamping method of wear-resistant structural material with carbide inclusions in an iron matrix it is expedient to use a powder of ferrochrome which contains both shallow fractions (less than 50 microns) and fractions of a size of about 200 microns [4].

The purpose of the work is to study the influence of the sintering temperature on the formation of the structure, phase composition and microhardness of the carbide and metal components of the powder composite 65% by weight. Fe - 35% by weight. FH800.

Objects and research methods

As the starting components for the production of samples of composite 65 wt. % Fe - 35 wt.% FH800 was used iron powder (manufactured by the State Enterprise "Powder Metallurgy Plant" (Brovary, Ukraine)), PCG 3.260.28 and a powder of high carbon (8% C) ferrochromium FH800 which was obtained by grinding lump ferroalloys to a particle size of 100-200 μm. The powder mixtures were prepared in a laboratory drum mixer (2 h) and wet milling in a ball mill for 70 h. Experimental samples were pressed on a hydraulic press at a pressure of 800 MPa. Sintering was carried out in a vacuum electric furnace at a dilution of $1.33 \cdot 10^{-2}$ Pa in the temperature range 1000-13000 °C with a step of 500 °C at an isothermal expiration of 30 minutes. Density and porosity of samples were determined by the calculation and hydrostatic method in accordance with ISO 27.38.2009. The microstructure and phase composition of sintered specimens were investigated in an optical (Olympuis LX-70) scanning (TESCAN VEGA) electron microscope, an X-ray diffraction analysis on a DRON-3 diffractometer. Local microscopic analysis was performed on the MS-46 microprobe. The microhardness of structural components was determined on the device PMT-3 for a load of 0.49 N. The mechanical properties were investigated using the INST RON 8802 machine.

Results and discussion

Investigation of the influence of the temperature of sintering on volumetric shrinkage, porosity, density and microhardness of the structural components of the composite 65%Fe - 35% FH800 (by wt.) showed (table 1) that the increase in the sintering temperature from 1000 to 1300 ℃ leads to some increase in shrinkage, density and decrease in porosity of samples. It should be noted that the sintering at a temperature of 1000 ℃ instead of shrinkage led to an increase in the volume of samples (negative shrinkage). This may be due to the Frenkel effect of the I genus, which manifests itself in the difference in the coefficients of heterodiffusion of chromium and iron in the composite. Also, an increase in the volume of samples results in a decrease in the diffusion mobility of γ-Fe atoms compared to the mobility of α-Fe atoms at temperatures slightly higher than $\alpha \rightarrow \gamma$ (910 ℃).

Table 1 *– Influence of sintering temperature on physical and technological properties of samples of composite 65% Fe - 35% FH800*

T, °C	Material Properties				
	ΔV/V, %	Porosity,%	γ, g/cm^3	H,μ, GPa	
				Matrix	Carbide
20	-	21,50	5,86	1,19	13,47
1000	+11	21,15	5,89	1,37	11,6
1050	0	20,74	5,92	1,39	10,43
1100	0	21,01	5,90	2,06	7,34
1150	1,25	20,60	5,93	1,24	12,26
1200	1,30	20,45	5,94	5,67	9,88
1250	5,10	17,80	6,14	4,98	10,39
1300	4,8	19,50	5,98	4,97	12,90

As can be seen from Table 1, sintering (even at temperatures of 1250 and 1300 ℃), does not provide for obtaining specimens of material with minimum porosity and maximum density. This is due to the coarse-grained powders of the initial components of the mixture. It was discovered that the increase in the temperature of sintering up to 13000 °C leads to the partial melting and distortion of the shape of the samples, therefore, to obtain virtually unpolluted material, it is necessary to use more dispersed iron powders and high carbon ferrochromium. The effectiveness of this approach has been demonstrated by us earlier in the works [6,7].

The study of microstructure of 65% Fe - 35% FH800 composites shows that small particles of high-carbon ferrochrome, already in the formation stage, are located on the boundaries between particles of iron powder, forming a kind of discrete shell around them (Fig.1).

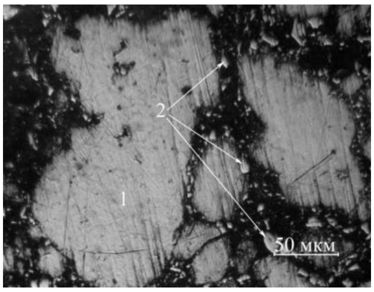


Fig.1 *The fragment of the microstructure and the local X-ray microanalysis points are indicated by the arrows) pressing of the 65% Fe-35% FH800 composite*

The X-ray microanalysis of the pressing components showed that, as expected, the middle of particles of iron powder contains (% at.): 99.48 Fe, 0.44 Cr, 0.07 C (t.1), and the basis of small particles of FH800 is chromium-iron carbide (57.28 Cr, 12.62 Fe and 30.09 C), corresponding to the formula M_7C_3. Sintering of green compacts, except that affecting the volume shrinkage, porosity, density and microhardness leads to significant changes in the chemical and phase composition of the carbide and, to a lesser extent, the metal composite component (Table 2).

Thus, sintering at 1000ºC leads to the conversion of the output carbide M_7C_3 into a cementite carbide type M_3C, which is stored to a temperature of sintering 1150ºC. With the subsequent increase in the sintering temperature to 1200°C, the M_3C carbide is initially converted into an intermediate carbide M_7C_3, after which the latter at a sintering temperature of 1250, 1300 ºC is transformed into a double carbide of M_3C_2 type with a maximum carbon content and a minimum content of chromium and iron.

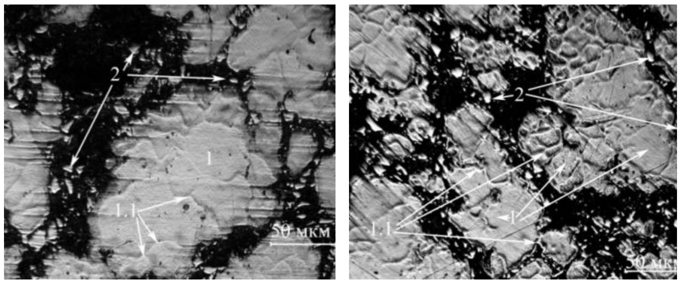
Thus, the thermally activated process of carbide transformations in the system of 65% Fe-35% FH800 occurs by diffusion of chromium and carbon atoms from the M_7C_3 carbide in iron and the counter flow of iron atoms from the matrix in the FH800.

Summing up the above we can imagine the mechanism of carbide transformations of the studied system in the form of a chain M_7C_3 → M_3C (1000-1150 ºC) → M_7C_3 (1200 ºC) → M_3C_2 (1250-1300ºC). The chemical and phase composition of the metal component with an increase in the temperature of sintering in the range of 1000-1300 ºC practically does not change. Only a slight increase in Cr and C content (up to 0.87-0.94% to 2.11%, respectively) can be noted after sintering at 1250-1300 °C.

A detailed analysis of the microstructures and the chemical composition of the sintered samples of the composite shows that at the temperatures of sintering of 1000-1050 ºC in separate large particles of iron the boundaries of grains on which diffusion concentration is concentrated (% at.) to 3.5% of chromium and about 1.14% carbon (Fig. 2 b, c). The increase in the temperature of sintering to 1100-1150ºC causes the appearance of paraffin particles of the iron powder of chromium austenite edges (Fig. 2 g, d), which contains (% at.) to 1.11 Cr and about 2.27 C. The structure also stores a carbide phase in the form of M_3C (56.15 Cr -18.77 Fe-25.09 C). Burning at 1200-1250 ºC leads to the appearance in the core particles of iron carbon, which amounts to 1.23(% at.) at 1200ºC and increases to 2.11% at 1250ºC. It should also be noted that light, smooth outer zones of iron particles contain (10,1-11,63% at.) Chromium and about 0,15-0,55(% at.) carbon at 1200ºC, the M3C carbide is transformed into a carbide of the type M_7C_3 (Fig. 2 is, g). In the middle of individual particles of iron powder at 1250ºC, the amount of carbon reaches 8.38% at. And transitional eutectic zones based on iron are formed containing 3.28(% at.) Cr and 12.79 (% at.) C (t.5). The carbide phase of M_7C_3 undergoes transformation to M_3C_2. Samples of the material which were sintered at 1300 ºC consist mainly of two phases: metal, which in the form of light zones is formed in the form of particles of an iron powder and is an alloy of the type of chromium steel X15 (84,1% of Fe Fe - 15,11% of mass Cr – 0, 78% by weight C) and carbide, which is isolated on the boundaries of iron grains in the form of a complex carbide M_3C_2. There is also the formation of separate eutectic zones based on iron containing (% at.) - 4.19 Cr and 4.98 C (Fig. 2).

Table 2 *- Influence of sintering temperature on chemical and phase composition of metal and carbide components of composite 65% Fe - 35% FH800*

T, ^{0}C	Content of elements in phases, % at., (% wt.)							
	Metal			Carbide				
	Fe	Cr	C	Cr	Fe	C	C_c/ C_s	carbide type
20	99,4 (99,5)	0,45 (0,41)	0,07 (0,015)	57,2 (79,6)	12,6 (17,4)	30,5 (8,9)	0,43	M_7C_3
1000	99,0 (99,32)	0,66 (0,61)	0,27 (0,05)	58,39 (70,83)	17,1 (22,3)	24,4 (6,8)	0,32	M_3C
1050	99,1(99,4)	0,59 (0,55)	0,22 (0,047)	56,60 (68,10)	19,5 (25,2)	23,8 (6,6)	0,31	M_3C
1100	98,9 (99,3)	0,64 (6,6)	0,36 (0,07)	56,07 (68,27)	18,8 (24,6)	25,0 (7,0)	0,33	M_3C
1150	99,1 (99,2)	0,78 (0,72)	0,06 (0,01)	56,1 (68,3)	18,7 (24,5)	25,1 (7,0)	0,33	M_3C
1200	99,2 (99,2)	0,55 (0,51)	1,24 (0,27)	53,09 (67,68)	17,21 (23,57)	29,6 (8,7)	0,42	M_7C_3
1250	96,9 (98,6)	0,94 (6,89)	2,11 (0,46)	44,68 (63,44)	15,3 (23,4)	39,9 (13,1)	0,66	M_3C_2
1300	98,7 (99,0)	0,87 (0,82)	0,39 (0,08)	45,06 (64,24)	14,7 (22,5)	40,2 (13,2)	0,66	M_3C_2



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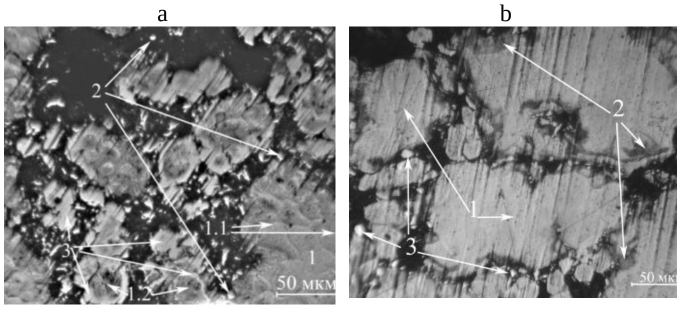

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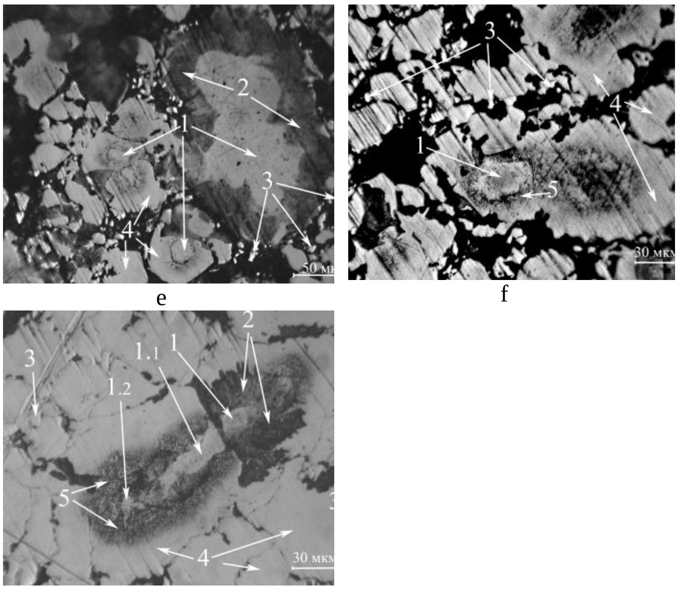

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Fig.2 *Fragments of microstructures and places of the local X-ray microanalysis points of 65% Fe composite - 35% of FH800, sintered at temperatures 1000-1300ºC*

Since it is known that mechanoactivation of powder mixtures leads to more intensive interaction of components, the effect of wet grinding in a ball mill for 70 hours on structural formation, the composition of the metal and carbide phases and the mechanical properties of 65% Fe - 35% FH800 composite were investigated. It was found that sintering of a fine-grained mixture at 1250 °C for 30 min. provides the formation of a practically unpolluted structure of samples of the material (Fig. 3) with high physical and mechanical properties (Table 3).

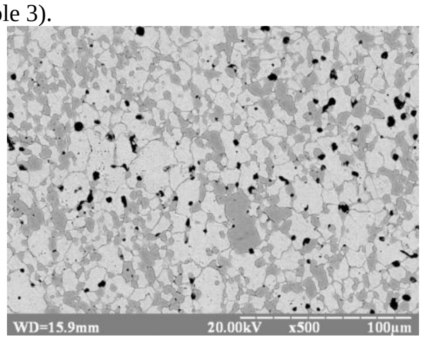

Fig. 3 *Microstructure of composite of finely divided mixture 65% Fe - 35% FH800 sintered at 1250ºC and carbon for 30 minutes*

As can be seen from Fig. 3, the microstructure of the composite is heterogeneous and consists of 3 phases, light gray, dark gray and black.

Microrentgenospectral analysis showed that the light-absorbing phase contains, (% at.) 59.83 Cr - 25.10 C - 15.06 Fe and is a chrome-plated carbide of type M_3C. Dark soil consists of 81.22 (% at.) Fe – 18 (% at.) Cr – 0.77 (% at.) C, which, in terms of (% wt.) corresponds to chromium steel 17X17, and black represents pores.

The X-ray and phase analysis of the 1250ºC sintered thin-layer composite composite showed that the X-ray spectrum fixes the most intense line belonging to a complex carbide of type M_7C_3 with a hexagonal lattice. Also observed in a small number of chromium carbide lines Cr_7C_3 and Cr_3C_2, and austenitic phase γ-Fe with an elemental cell parameter of 03607 nm. thus, mechanical activation of a powder mixture of 65% Fe - 35% of FH800 and sintering at 1250 °C (30 min.) Ensures the production of chromium steel 17X17- (Cr, Fe)$_3$C composite close to the equivalent composition. The study of properties confirmed that the use of finely divided powders is provided by the rare-phase sintering at 1250ºC to obtain practically non-porous composite specimens with high mechanical characteristics (Table 3).

Table 3 *- Properties of specimens of composites of finely divided mixtures of 65% Fe - 35% of FH800 sintered at 1250 ºC (τ = 30 min.)*

ΔV/V, %	f,%	γ, g/cm^3	HRA	δ, MPa	Microhardness, GPa	
					Matrix	Carbide
35.9	1.5	7.44	74.5	1760-1900	5.32	12.5

Conclusions

1. The influence of temperature of sintering on structure formation, phase composition, microhardness of components of powder composite 65 % wt. Fe – 35 % wt. FH800 were investigated. It has been established that the increase in the temperature of sintering from 1050 ºC to 1250 ºC leads to some increase in volumetric shrinkage, density and decrease in porosity of samples of material which was made from coarse-grained source powders of industrial production components.

2. It was found that the sintering of green compacts in the range of 1000-1300 ºC causes significant changes in the chemical and phase composition of the carbide component of the composite, which are described by a series of phase transformations: $M_7C_3 \rightarrow M_3C$ (1000-1150 ºC) $\rightarrow M_7C_3$ (1200 ºC) $\rightarrow M_3C$ (1250-1300 ºC)

3. The mechanical activation of the initial powdered charge by wet milling in a ball mill provides the method of liquid phase sintering at 1250ºC of practically unpolluted composite type of chromium steel 17X17 - (Cr, Fe)$_3$C equivalent (close range 50:50) composition with a density of 7.44 g/cm3 with a hardness of 74.5 HRA and a bending strength of 1760-1900 MPa.

4. The use of a fine powder (<50 microns) of high-carbon ferrochrome FH800 as a powder mixture can be used to obtain a chromium-plated steel of type 17X17 and a chromium-molybdenum carbide of the type M_3C through the sintering of liquid fossils at 1250°C.

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