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HEAT-RESISTANCE OF FE-C-CU BORONIZING POWDER METALLUGICAL CONSTRUCTIONAL MATERIALS

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ABSTRACT

One of the methods of saving raw materials is related to the introduction of chemical-thermal treatment methods into practice. These methods make it possible to change the phase composition on the surface of the details, which leads to a significant improvement in their surface properties while retaining a coarse core. At the same time, however, the behaviorof the formed diffusion layers in working under extreme conditions has not been sufficiently studied. Boride coatings are known to have high hardness and good wear resistance under normal operating conditions, but at present, their resistance to high operating temperatures is not well studied. In the presented study with the methods of the X-ray analysis is traceable behavior of boride coatings formed on powder-metallurgical samples of the Fe-C-Cu system with a density of 6,60g/cm3 after isothermal containment for 60min. at temperatures ranging from 700 to 1150°C. The results of X-ray analysis are presented in the form of diagrams in which the interference maxima of phases and their intensity are schematically shown.

INTRODUCTION

The process of high temperature oxidation of metals can be represented by the chemical interaction of the metal with an oxidizing gas medium at high temperature when no wet layer is present on the surface of the metal. High temperature oxidation of metals is a particular case of chemical corrosion, under which it is understood the undesirably practical destruction of metals resulting from their self-interacting interaction with the surrounding environment through the mechanisms of chemical heterogeneous reactions. Chemical corrosion of metals is observed in various dry gases - oxygen, air, combustion products, water vapors, halides, sulfur, etc., as well as non-electrically conductive liquids - oil, fuel oil, resins. As a result, oxidation of metals should be understood as chemical corrosion in environments found in a certain aggregate state - in the form of gas, this kind of corrosion is called gas corrosion. The ability of metals to withstand high temperature oxidation - corrosion at high temperatures, is called heat resistance or oxidation resistance. [12]

It follows that the terms high temperature oxidation and heat resistance of metals are characterized by the same phenomenon.

In accordance with the introduced terms, oxidation is characterized as a process of chemical interaction of metals at high temperatures with oxygen, carbon dioxide, sulfur, iodine, chlorine or gaseous substances. The product of this reaction is the corresponding chemical compounds - oxides, sulphides, halides and others. [1,7,15] Due to the oxidation of metals and the formation of new compounds on their surface, the mass, size and shape of the manufactured parts and aggregates change. This can lead to a significant reduction in the duration of their operation.

Among the possible processes for high temperature oxidation of metals, their oxidation with oxygen is especially important. Oxidation of metals is the most common type of corrosion in gas media at high temperatures.

This type of corrosion is one of the greatest hazards to the workability of metal parts in machines and aggregates operated at high temperatures. The spread of this type of corrosion in machine building is a great concern for the researchers.

In the chemical sense, the oxidation of powder metallurgical materials takes place in reaction 1. [4,8,10,13]

$$xMe + y/2O_2 \rightarrow MexOy \quad (1)$$

where: Me - the metal interacting with oxygen;
x and y - stoichiometric coefficients.

If the oxidised metal is iron, the final product is magnettite - 2. [4,7]

$$3Fe + 2O_2 \rightarrow Fe_2O_3 \quad (2)$$

Based on the fact that chemical corrosion is a self-generated process, it is necessary to determine the conditions under which it will proceed. In practice, it follows from equation 1 that in the most general case the reaction can proceed as from left to right - oxidation of the metal as well as in the opposite direction - dissociation of the oxide, and may be in dynamic equilibrium -

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simultaneous oxidation of metal and dissociation of the oxide, but the amount of metal, oxygen and oxide over time remain unchanged.

EXPOSITION

The aim of the study is to establish the resistance of boride diffusion layers formed on iron powder metallurgical materials from the Fe-C-Cu system. The iron matrix is based on iron powders NC 100.24 obtained by the reduction method. The copper powders used are obtained by electrolysis of aqueous solutions [2] and the carbon is in the form of UF4 standard graphite powders where the carbon concentration is in the range of 96 ÷ 97%. After mixing, the powders are compressed with a force of 400 MPa, and after sintering at 1150°C - for 3, hours in a dissociated ammonia medium their density is 6.60 g/cm^3. [11,14]

Saturation with boron was carried out in a semi-permeable saturation medium, Equation 3, [9,10] at 900°C for 3h. The phase composition of the formed diffusion coating is Fe_2B and FeB, and the diffusion layer thickness is 80÷100μm.

$$(80\div84)\%Na_2B_4O_7+(11\div15)\%SiC+$$

$$+\ (2\div5)\%K_2Cr_2O_7 \qquad (3)$$

In order to establish the resistance of the formed boride diffusion layers at high operating temperatures, the samples were reheated in air at 500÷1150°C. For the low temperature range - up to 900^{o}C specimens are tested at every 100oC and in the high temperature - 900÷1150^{o}C, every 50^{o}C. The retention time at each test temperature is 60min. After reheating, the samples are chilled in air.

Resistance of the boride layers at high temperatures is determined by X-ray analysis. It was carried out with the aid of X-ray diffractometer "Dron-2.0" in unfiltered Kα radiation from a ferric anode with wavelength λ = 1.93728Å and characteristics of the generator U=24kV and I=14mA.

The interval of the X-ray frames taken at angle 2Θ is 40 ÷ 120 ° and the scanning is at each degree.

Determining the sequence of values for dhkl / n and phase determination uses reference data in X-rays decoding. The experimental results obtained from the X-ray calculations are shown in Table 1.

It presents the measured angles of the interference peaks formed on the X-rays and the calculated interplanar distances by the equation of Wulf-Breg-4. [5,6] The latter are compared with reference data [3,6] of the respective phase to which the maximum and its intensity belong.

$$2d_{HKL} . \sin\theta_{HKL} = \lambda \qquad (4)$$

The graphical interpretation of the obtained experimental results is presented in the form of stroke diagrams - fig.1 ÷ 4.

From Fig. it can be seen that on the captured X-ray of the boiled specimens, after interpolation at 700 ° C for 20, 40 and 60 minutes, interference peaks were recorded only on the high-boride phase - FeB. .It can be seen that the retention time of 20 to 60min. practically does not affect the intensity of the maxima.

Similarly, the results of the captured X-rays of samples held for 60 minutes at 800 ° C, with the exception that the strongest line 8 of Table 1, the low boride phase - Fe2B Fig.2 . This indicates that during continuous retention at this temperature, the integrity of the high phase phase coating - FeB - is destroyed.

At isothermal retention temperatures of 900 to 1000°C, most of the interfering phases of the high phase phase disappear and in their place the maximum of the low phase phase Fe2B - Fig.3.

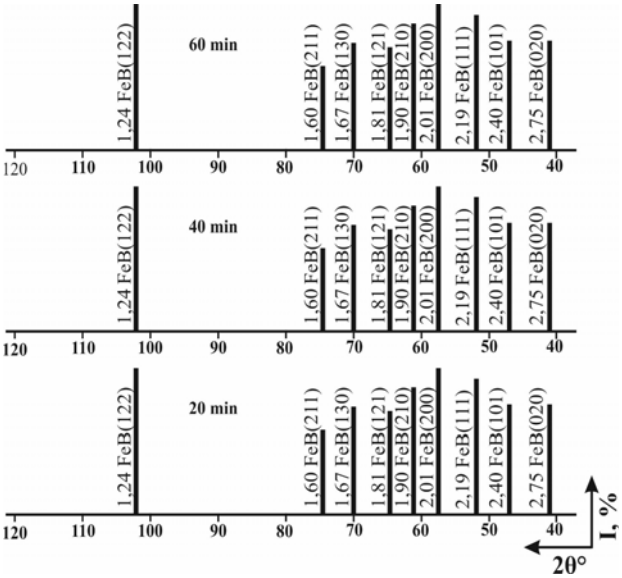

Fig.1. Schematic X-ray of boronizing samples after isothermal hold at 700°C for 20÷60min

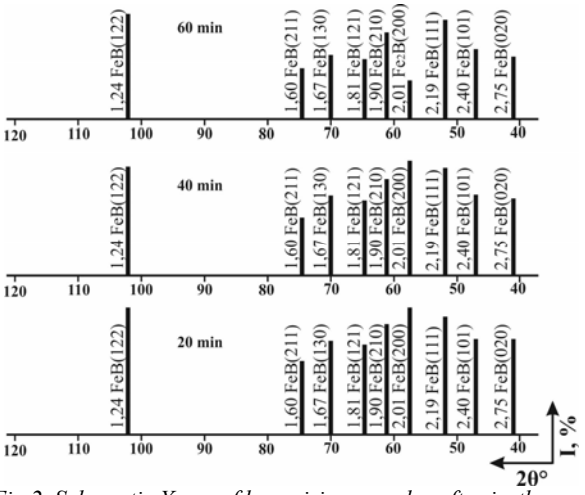

Fig.2. Schematic X-ray of boronizing samples after isothermal hold at 800°C for 20÷60min

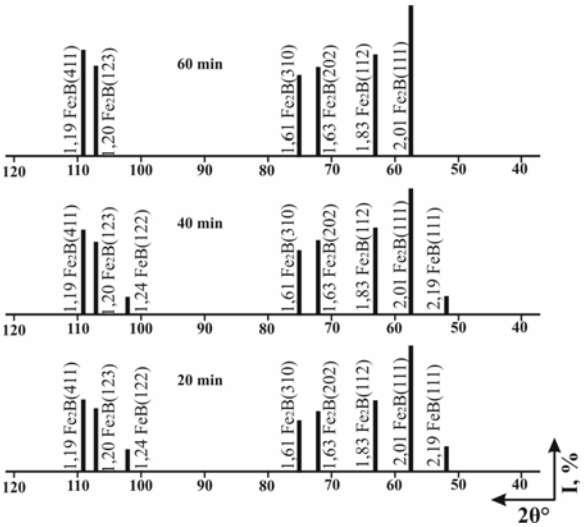

Fig.3. Schematic X-ray of boronizing samples after isothermal hold at 900°C for 20÷60min

Table № 1. Experimental data

№	Experimental data				Table data			
	2Θ	**Θ**	**sinΘ**	**d_{HKL}**	**d_{HKL}**	**фаза**	**HKL**	**I,%**
1	41º 14/	21º 37/	0,3522	**2,748**	2,750	**FeB**	020	**0,85**
2	42º 12/	21º 06/	0,3601	**2,691**	2,690	**Fe_2O_3**	112	**1,00**
3	45º 24/	22º 42/	0,3859	**2,511**	2,510	**Fe_2O_3**	101	**0,75**
4	47º 36/	23º 48/	0,4036	**2,403**	2,400	**FeB**	101	**0,85**
5	50º 16/	25º 08/	0,4246	**2,278**	2,280	**FeB**	120	**0,85**
6	52º 28/	26º 14/	0,4426	**2,193**	2,190	**FeB**	111	**1,00**
7	57º 36/	28º 48/	0,4816	**2,012**	2,010	**FeB**	200	**1,00**
8	57º 36/	28º 48/	0,4819	**2,010**	2,010	**Fe_2B**	111	**1,00**
9	57º 36/	28º 48/	0,4819	**2,010**	2,010	**Fe_α**	110	**1,00**
10	61º 16/	30º 38/	0,5099	**1,903**	1,900	**FeB**	210	**1,00**
11	63º 14/	31º 57/	0,5293	**1,825**	1,83	**Fe_2B**	112	**0,55**
12	63º 32/	31º 46/	0,5263	**1,840**	1,840	**Fe_2O_3**	202	**0,63**
13	64º 46/	32º 23/	0,5352	**1,814**	1,810	**FeB**	121	**0,85**
14	70º 54/	35º 27/	0,5800	**1,674**	1,670	**FeB**	130	**0,85**
15	72º 56/	36º 28/	0,5943	**1,632**	1,630	**Fe_2O_3**	123	**0,63**
16	72º 56/	36º 28/	0,5943	**1,630**	1,630	**Fe_2B**	112	**0,55**
17	74º 34/	37º 17/	0,6054	**1,601**	1,600	**FeB**	211	**0,85**
18	75º 16/	37º 58/	0,6016	**1,603**	1,600	**Fe_2B**	310	**0,55**
19	81º 22/	40º 41/	0,6523	**1,483**	1,485	**Fe_2O_3**	103	**0,50**
20	85º 20/	42º 40/	0,6774	**1,435**	1,430	**Fe_α**	200	**0,15**
21	102º 50/	51º 25/	0,7818	**1,239**	1,240	**FeB**	112	**1,00**
22	107º 24/	53º 42/	0,8058	**1,202**	1,202	**Fe_2B**	123	**0,85**
23	109º 24/	54º 42/	0,8161	**1,187**	1,187	**Fe_2B**	411	**0,70**
24	113º 10/	56º 35/	0,8343	**1,166**	1,166	**Fe_α**	211	**0,38**

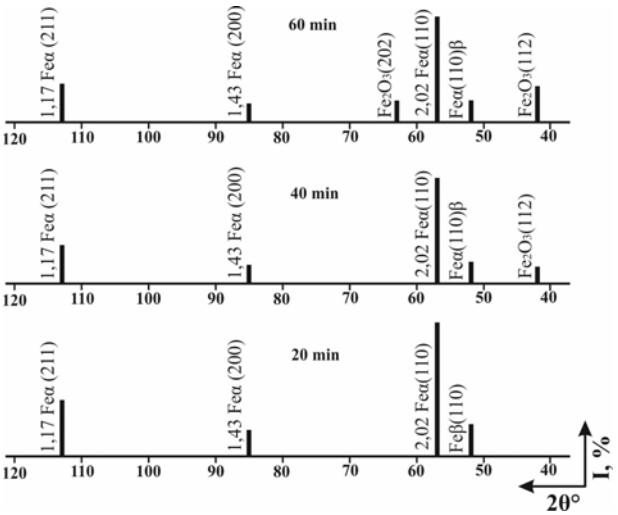

Fig.4. Schematic X-ray of boronizing samples after isothermal hold at 1150°C for 20÷60min

From the figure it can be seen that within a short retention time of 20 to 40 minutes, remnants of the strongest line 6 of Table 1 are observed. This shows that at this temperature it is possible to encounter high boride phases in the thick layer of Fe_2B.

On the X-ray of samples isothermally retained at temperatures above 1100°C, initially only interference peaks of Armco iron were recorded. After longer retention, however, at 40min, corrosion processes occur, as a result of which the traces of the strongest line of the bi-ferric trioxide - line №2 of Table №1 - fig.4. With prolonged retention at temperatures of 1100÷1150oC, the oxidation processes at the boundaries of the ferrous beads are activated, as a result of which on the X-rays the traces of the second most powerful line of Fe2O3 - №3 of Table №1 appear.

The data from the X-ray analysis showed that the boride coatings formed from the triple Fe-C-Cu system have high resistance at operating temperatures up to 900°C.

With increasing isothermal retention temperature above 950°C on the surface of the samples there is a deoxidation and formation of a thin layer of iron oxides at the boundaries of the iron beads.

This gives us reason to assert that the formed boride coatings on the samples we are studying are suitable for operation in regimes up to 900÷950°C, which completely coincides with the findings of the boronizing samples of solid materials [15,16]

CONCLUSIONS

From the obtained experimental results it can be concluded that the formed biphasic boride coatings on powdered metallurgical specimens with a density of 6,60 g/cm^3 of the triple Fe-C-Cu system are resistant to atmospheric conditions to temperatures in the range of 900÷950°C. At working temperatures higher than 950°C there is a deboridization of the working surfaces and the course of oxidation processes accompanied by the formation of oxides of the type Fe_2O_3.

REFERENCE

[1] Buchkov D. et al., Thermochemical treatment, Tehnika, Sofia, 1998

[2] May I., L. Schetky, Cooper in iron and steel, John Wiley and sons. Toronto, 1988, p.307, ISBN 0-471-05913-7 .

[3] Mirkin L., X-ray analysis - reference Metallurgy, Moscow, 1976.

[4] Mitev I., Modern Industrial Technology - part III, (Progressive methods of mechanical shaping), EX-PRESS, Gabrovo, 20016, ISBN 978-954-490-511-8

[5] Mitev I., Crystallography, EX-PRESS, Gabrovo, 2012, ISBN 978-954-490-3610-7

[6] Mitev I., Structural analysis, EX-PRESS, Gabrovo, 2013, ISBN 978-954-490-363-3

[7] Mitev I., Powder Metallurgy – part I (Receive powder metallurgy materials and products, University Press „V. Aprilov", Gabrovo, 2004, ISBN 954-4683-233-2.

[8] Mitev I., Powder Metallurgy – part II (Powder Metallurgical Products with Sructural and Instrumental Purpose, University Press „V. Aprilov", Gabrovo, 2004, ISBN 954-4683-234-0.

[9] Mitev I., K. Popov, Applicability of Liquid Areas for Saturation During Boronizing of Construction Powdered Materials of Fe-C-Cu System, International Journal of Emerging Technologies in Computational and Applied Sciences (IJETCAS), ISSUE 6, vol.4, 2013, p.341÷345, ISSN (online) 2279-0055, ISSN (print) 2279-0047.

[10] Mitev I., K. Popov, Thermochemical treatment of dust permeable construction materials, Manufacturing and Machine, v.ol.17 2012, p.74 ÷ 77, ISSN 1312-8612.

[11] Mitev I., R.Maimarev, Sintering the Binary Powder Materials in the Presence of a Liquid Phase, Manufacturing and Machinep, vol,17, 2012, p.70÷73, ISSN 1312-8612.

[12] Nikitin B., Calculation of Heat Resistance of Metals, Metallurgy, Moscow, 1996.

[13] Randal M., Powder Metallurgy of Iron and Steel, Wiley, Michigam, 2007, p.496, ISBN 047-1157392.

[14] Todorov R. and other, Materials and Equipment for Powder Metallurgical Construction Products, Publishing BAS, Sofia, 1988.

[15] Voroshnin L. and others. Thermochemical processing of reinforced ceramic materials. Minsk, Science and Technology, 1987, p.272

[16] Voroshnin L., Boronizing of industrial steels and cast iron, Belorus, Minsk, 1991.