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Microstructure and elemental analysis of iron-based powder composite materials

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Abstract. This paper studies the kinetics of structure formation of an iron-bronze composite containing solid lubricants. Depending on the compacting pressure and sintering temperature, binary and complex phases are detected in the iron-bronze structure. The presence of solid lubricants in the composition of the composite material significantly reduces interaction of the liquid (bronze) and solid (iron) phases during sintering. Talc and graphite, which are heat–resistant at a sintering temperature of 850 – 1150 °C, were used as solid lubricants. The presence of talc, located on the surface of compressed particles of iron, copper, tin and graphite, significantly reduces the effect of their interaction. At the same time, the micro-talc particles envelop them, and its thermal stability retains this state up to high temperatures (approximately 900 °C). It was established that there is no perlite in the microstructure of iron-bronze sintered at a temperature of 850 °C. This can be explained by the talc adsorbing ability on the surface of iron particles which prevents diffusion of carbon into the iron crystal lattice. An increase in the sintering temperature up to 1000 °C leads to the formation of perlite in the iron-bronze structure, while the amount of perlite predominates over ferrite. This indicates the partial burnout of talc from the surface of iron particles and the opening of diffusion paths to carbon. At a sintering temperature of 1150 °C, perlite and a grid of light inclusions are formed in the microstructure of the iron-bronze samples. According to the results of electron microprobe analysis, the light inclusions are solid solutions of variable compositions such as Fe–Cu–Sn, Cu–Fe–Sn, Cu–Sn–Fe. In order to confirm these assumptions, a phase *X*-ray diffraction analysis was performed. Diffraction patterns of these samples are represented by reflections of iron and copper crystals. The absence of diffraction effects (characteristic of tin crystals) is conditioned by tin solubility in the copper lattice. This is due to the low melting point of tin (232 °C) and its ionic radius, which allows isomorphically replacing of copper and iron ions with tin ions (their difference is less than 15 %).

Keywords: iron-bronze, heat treatment, structure, phase, powder composition, liquid, sintering, non-metallic phases, perlite, solid particles

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Микроструктура и элементный анализ порошковых композиционных материалов на основе железа

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Аннотация. Изучена кинетика структурообразования композиционного материала типа железо-бронза, содержащего твердые смазочные материалы. В зависимости от давления прессования и температуры спекания в структуре железо-бронзы обнаруживаются бинарные и сложные фазы. Наличие твердых смазочных веществ в составе композиционного материала значительно снижает взаимодействие жидкой (бронза) и твердой (железо) фаз при спекании. В качестве твердых смазок используются тальк и графит, которые являются термостойкими при температуре спекания 850 – 1150 °С. Присутствие талька, который располагается на поверхности спрессованных частиц железа, меди, олова и графита, значительно снижает эффект их взаимодействия: микрочастицы талька обволакивают их, а за счет термической стойкости сохраняется такое состояние до высоких температур (примерно 900 °С). Показано, что в микроструктуре железо-бронзы, спеченной при температуре 850 °С, перлит отсутствует. Это объясняется адсорбирующей способностью талька на поверхности частиц железа, что препятствует диффузии углерода в его кристаллическую решетку. Повышение температуры спекания до 1000 °С приводит к образованию в структуре железо-бронзы перлита, при этом количество перлита преобладает над количеством феррита. Это свидетельствует о частичном выгорании талька с поверхности частиц железа и об открытии путей диффузии углероду. При температуре спекания 1150 °С в микроструктуре образцов железо-бронзы образуется перлит и сетка светлых включений. По результатам микрорентгеноспектрального анализа светлые включения являются твердыми растворами переменных составов типа Fe–Cu–Sn, Cu–Fe–Sn, Cu–Sn–Fe. Для подтверждения этих предположений был проведен фазовый рентгеноструктурный анализ. Дифрактограммы

образцов представлены рефлексами кристаллов железа и меди. Отсутствие дифракционных эффектов, характерных для кристаллов олова, связано с его растворимостью в решетке меди. Это объясняется низкой температурой плавления олова (232 °С) и его ионным радиусом, который позволяет изоморфно замещать ионы меди и железа ионами олова (их разность составляет менее 15 %).

Ключевые слова: железо-бронза, термическая обработка, структура, фаза, порошковая композиция, жидкость, спекание, неметаллические фазы, перлит, твердые частицы

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Introduction

Studies [1 – 3] investigate the kinetics of structure formation during sintering of composite material containing 3.0 % Cu, 1.5 % Sn, remainder: iron. It was established that at a temperature above 232 °C, due to melting of tin, a liquid phase is formed in the system. However, due to existence of oxide layers on fine iron and copper particles, they are not wetted by tin [4; 5]. With an increase in the sintering temperature to 850 °C, there occurs active recovery of all particles of solid phase and their dissolution in liquid phase [6 – 9].

The studies demonstrate that the interaction of the liquid phase with iron particles at the sintering temperature of 850 °C in 1 h, and the subsequent cooling lead to the formation of a fine grain multiphase heterogeneous structure. *X*-ray studies demonstrated that the structure of the sintered samples contains binary chemical phases (Cu_3Sn, CuSn, $FeSn_2$, Fe_3Sn_2, FeSn), as well as the phases of complex composition.

Experimental

The chemical composition of mixtures of the considered iron bronze composite materials containing solid lubricants are summarized in Table 1. The mixtures also contain solid lubricants (graphite and talcum in combination with copper and iron).

The components were mixed in a *Y*-type mixer in 1 h. The charges were compacted using a Mannesmann hydraulic press under pressure of 400, 700 and 1000 MPa. Sintering was carried out in a Koyo Lindberq conveyer furnace at temperatures of 850, 1000 and 1150 °C in an environment of endothermal gas.

The microstructures of the experimental samples were analyzed using a Neofot-21 metallographic microscope, and elemental analysis at certain points using a Camsan *X*-ray spectral microanalyzer.

Results and discussion

The metallographic analysis of all samples considered demonstrates that their structure at 850 °C nearly does not contain perlite (Fig. 1). This, first of all, is related to the fact that talcum is adsorbed on the surface of metal particles with high adhesion, preventing carbon diffusion across iron surface [10; 11]. In addition, it was established that a sintering temperature of 850 °C is insufficient in the thermodynamic conditions considered herein for carbon diffusion [8; 12; 13].

Talcum and graphite at 850 °C are characterized by thermal stability and screen the surface of copper and iron particles, thus maintaining them separately. Presumably, due to the same reason iron and copper particles are not wetted by the tin liquid phase.

With an increase in the sintering temperature to 1000 °C, the perlite structure in the alloy with the composition *A* dominates over the ferrite structure with solid lubricants, and single highlighted bright inclusions are visible (Fig. 2).

An increase in the sintering temperature to 1150 °C leads to formation of cementite in the alloy with the composition *A* in the form of grid around the pores and along the particle boundaries.

In the structure of these samples single highlighted bright inclusions are not detected, while particles of solid lubricants are hardly noticeable (Fig. 3).

Table 1

Chemical composition of the charge

Таблица 1. **Химический состав шихты**

Alloy	Content of powder in the charge, %					
	Copper	Tin	Graphite	Talcum	Zinc stearate	Iron
A	9.0	1.0	2.0	3.5	–	remainder
B	9.0	1.0	2.5	3.5	0.5	remainder
C	18.0	2.0	1.5	2.0	–	remainder

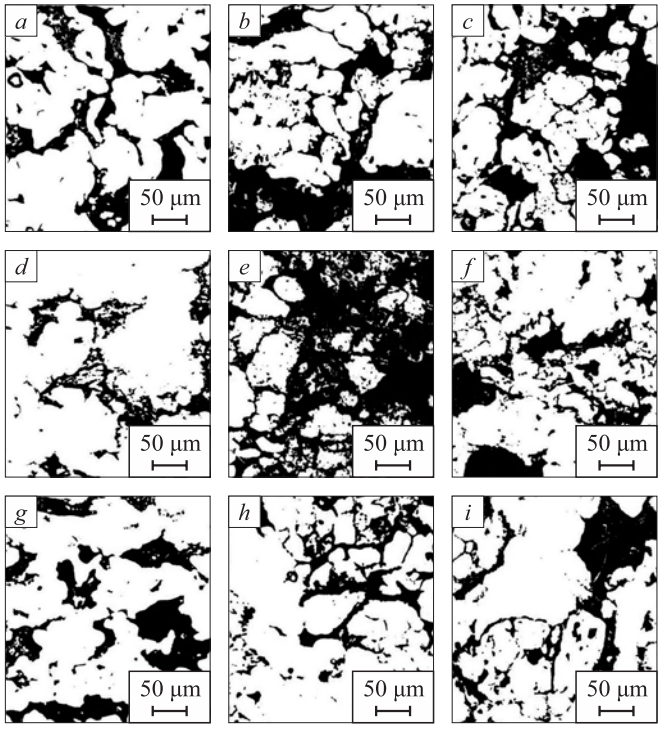

Fig. 1. Microstructure of sintered iron-bronze at a temperature of 850 °C:
a, *b*, *c* – composition *A*; *d*, *e*, *f* – composition *B*;
g, *h*, *i* – composition *C*;
pressing pressure 400 (*a*, *d*, *g*), 700 (*b*, *e*, *h*), 1000 (*c*, *f*, *i*) MPa

Рис. 1. Микроструктура спеченной при 850 °С железо-бронзы:
a, *b*, *c* – состав *A*; *d*, *e*, *f* – состав *B*; *g*, *h*, *i* – состав *C*;
давление прессования 400 (*a*, *d*, *g*), 700 (*b*, *e*, *h*), 1000 (*c*, *f*, *i*) МПа

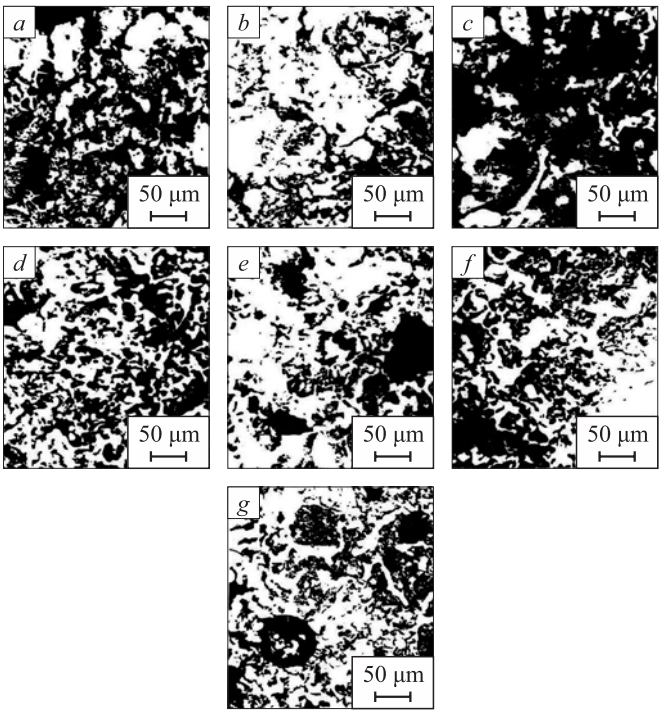

Fig. 2. Microstructure of sintered iron-bronze powder at a temperature of 1000 °C:
a, *b*, *c* – composition *A*; *d*, *e*, *f* – composition *B*; *g*, *h*, *i* – composition *C*

Рис. 2. Микроструктура спеченного при температуре 1000 °С порошка железо-бронзы:
a, *b*, *c* – состав *A*; *d*, *e*, *f* – состав *B*; *g*, *h*, *i* – состав *C*

The microstructure of the alloy with the composition *B* is comprised of fine particles of bright inclusions and cementite in a high amount. In some places these particles surrounding the perlite matrix, form a continuous lattice. The matrix of alloys is comprised of fine perlite, which is characteristic of the cuprous compositions on the basis of iron [8; 14 – 16].

In order to study the chemical composition of the particles in a Camsan *X*-ray spectral microanalyzer, the microstructure was analyzed at certain selected points of the alloys with the compositions *B* and *C* (Fig. 4). The chemical compositions (Table 2) at different points sharply differ from each other. For instance, the alloy with the compositing *B* is comprised of Fe – Cu – Sn solid solution at high concentrations of copper in points *1*, *2* and *6* (97.88, 98.76 and 94.38 % (hereinafter wt. %)). The amount of elements on certain particles is summarized in Table 2.

Copper is the predominant element in points *3* and *4*. At the boundaries of these points, Fe – Cu – Sn solid solutions are located with a higher (34.22 %) copper content. The amount of non-metal inclusions is very low [17; 18], indicating destruction of the talcum structure at a heating temperature of 1500 °C and complete disappearance of free graphite [19 – 21].

Table 2

Chemical composition of the iron-bronze in micro-volume

Таблица 2. **Химический состав железо-бронзы в микрообъеме**

Alloy	Number of analysis points	Content of elements, wt. %			
		Fe	Cu	Sn	Nonmetal inclusions
P = 700 MPa; *T* = 1150 °C					
B	*1*	97.883	1.640	0.358	0.119
	2	98.460	1.242	0.225	0.073
	3	3.150	92.033	4.804	–
	4	3.807	89.964	6.120	0.106
	5	63.644	34.227	2.133	–
	6	94.380	4.050	1.065	0.008
P = 700 MPa; *T* = 1000 °C					
C	*1*	74.467	20.619	1.895	0.024
	2	13.289	80.392	5.806	0.066
	3	52.619	42.013	3.692	1.679
	4	69.052	27.818	2.200	0.936
	5	74.371	23.697	1.937	–
	6	69.535	28.184	2.160	0.126

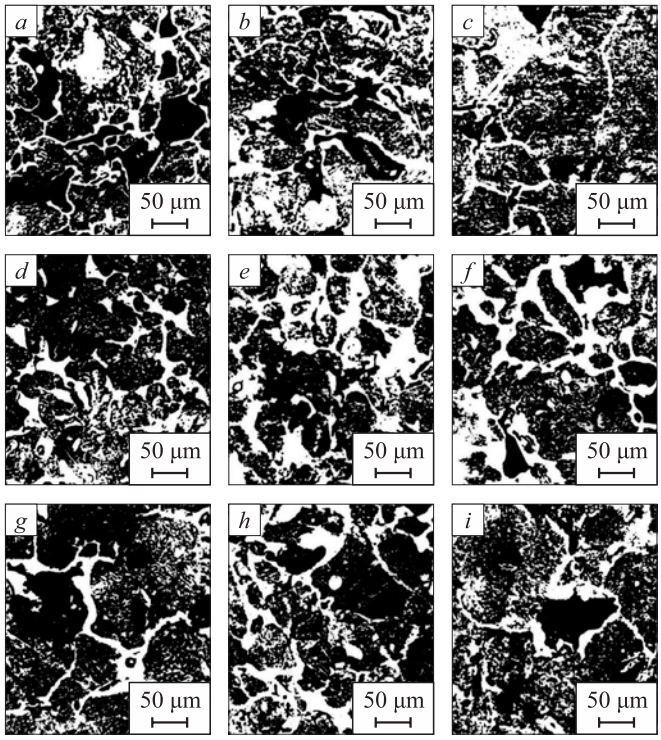

Fig. 3. Microstructure of a sintered iron-bronze composite at a temperature of 1150 °C:
a, *b*, *c* – composition *A*; *d*, *e*, *f*, *g*, *h*, *i* – composition *B*;
a, *b*, *c*, *e*, *g*, *i* – core; *d*, *f*, *h* – surface;
pressing pressure 400 (*a*, *d*, *g*), 700 (*b*, *e*, *h*), 1000 (*c*, *f*, *i*) MPa

Рис. 3. Микроструктура композита на основе железо-бронзы, спеченного при температуре 1150 °C:
a, *b*, *c* – состав *A*; *d*, *e*, *f*, *g*, *h*, *i* – состав *B*;
a, *b*, *c*, *e*, *g*, *i* – сердцевина; *d*, *f*, *h* – поверхность;
давление прессования 400 (*a*, *d*, *g*), 700 (*b*, *e*, *h*), 1000 (*c*, *f*, *i*) МПа

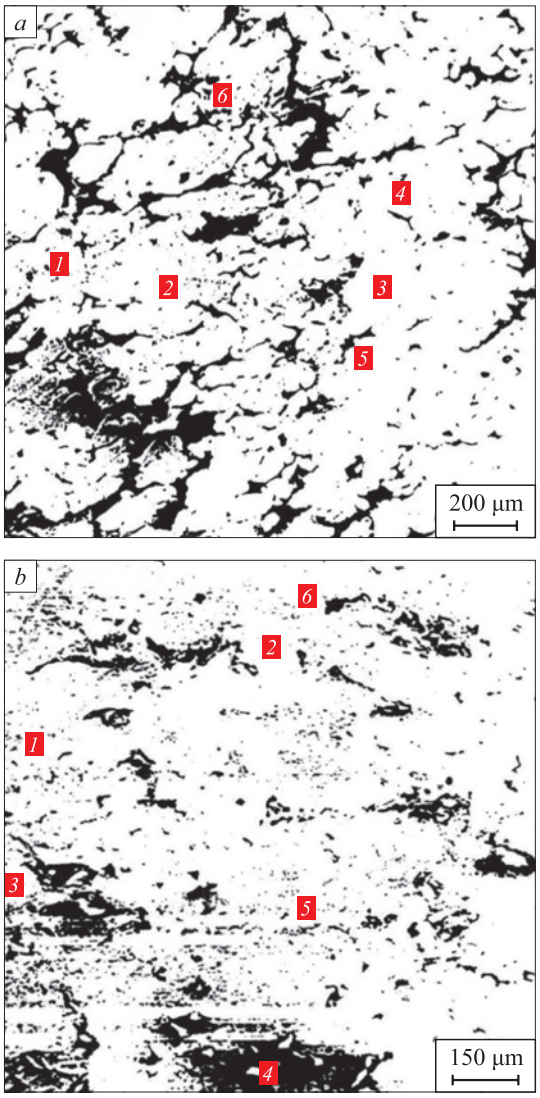

Fig. 4. Location of the points determining chemical composition of the iron-bronze powder:
a – sample *4*; *b* – sample *8*

Рис. 4. Расположение точек, определяющих химический состав порошка железо-бронзы:
a – проба *4*; *b* – проба *8*

It was established that in the points of the alloy with the composition *C* analyzed herein, there exist Fe–Cu–Sn solutions on the basis of iron and copper. However, due to high content of copper and tin in the alloy the chemical composition at the points significantly differs from the respective points of the alloy with the composition *B*. This shows that they are rich in copper and tin. In points *3* and *4*, a significant amount of non-metal inclusions (graphite and talcum) was detected, confirming the thermal stability of talcum at 1000 °C.

The presence of talcum located along the pores and between the particles significantly reduces interaction between the liquid and solid phase.

As a consequence of the sintering of iron, copper, and tin, a new composite structure of iron–bronze type is formed. The misconstrue of these compositions is comprised of solid solutions of variable Fe–Cu–Sn composition on the basis of iron. This indicates heterogeneity of structure of the sintered composite.

In order to confirm this, a phase *X*-ray structure analysis of iron bronze composite powdered material was performed. Diffractometric curves were plotted using a DRON-2.0 facility in filtered iron beams. The reflections specific for iron and copper are mainly revealed in the diffraction patterns (Fig. 5) of the samples considered.

For example, in the reflections of crystals reflected from crystallographic planes (110), (200), (211), (220), the wavelength is 0.2024 nm. In the reflections of crystals reflected from crystallographic planes (111), (200), (220), (311), (222), the wavelength is 0.2083; 0.1803; 0.1272; 0.1086 and 0.1040 nm.

The absence of diffraction effects characteristic of tin and zinc is related, on the one hand, to their solubility in iron and copper lattices. This is due to the low melting points of tin (232 °C) and zinc (420 °C), on the other hand, with their ionic radii, allowing the copper and iron

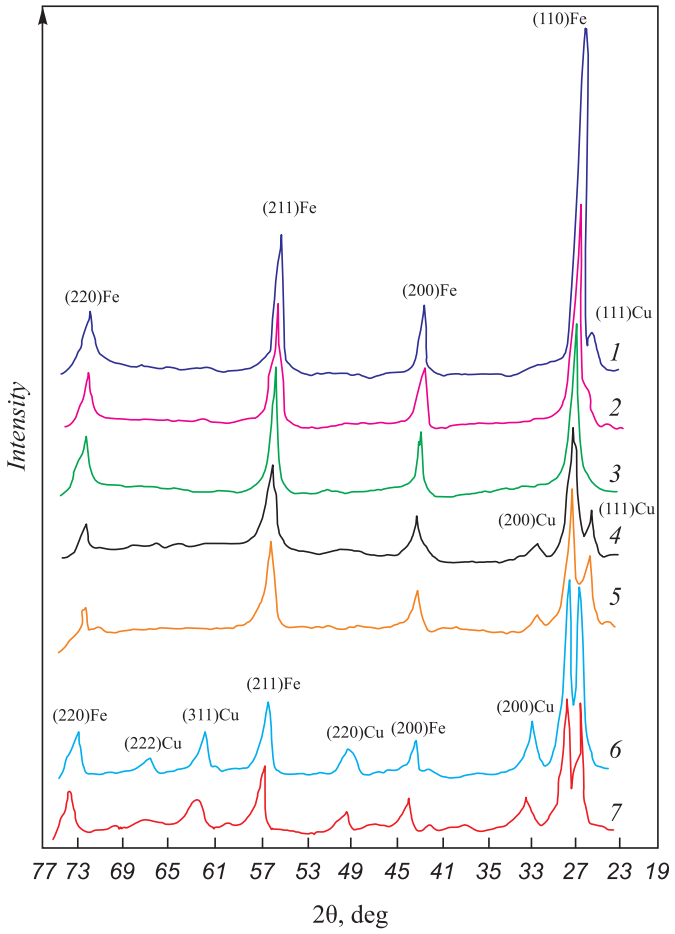

Fig. 5. Diffractometric curves of the iron-bronze samples at sintering temperature of 800 (*1*), 1000 (*2*, *5*), 1150 (*3*, *6*), 850 (*4*, *7*) °C and compacting pressure of 700 (*1 – 3*), 1000 (*4*, *5*, *7*), 400 (*6*) MPa: *1 – 3* – composition *A*; *4 – 6* – composition *B*; *7* – composition *C*

Рис. 5. Дифрактометрические кривые железо-бронзовых образцов при температуре спекания 800 (*1*), 1000 (*2*, *5*), 1150 (*3*, *6*), 850 (*4*, *7*) °С и давлении прессования 700 (*1 – 3*), 1000 (*4*, *5*, *7*), 400 (*6*) МПа:
1 – 3 – состав *A*; *4 – 6* – состав *B*; *7* – состав *C*

ions to be substituted isomorphically with tin and zinc ions (their difference is less than 15 %).

The stability of copper and iron lattices differs slightly from that of pure copper and iron:

$$a = d(nkl)\sqrt{h^2 + k^2 + l^2},$$

where *d*, *n*, *k*, *l*, *h* are the coefficients.

A comparison of the diffraction effects of iron and copper demonstrates that the sample of composition *A* at 800 °C contains a minor amount of copper. Therefore, the diffraction pattern is presented mainly by iron.

Sample *3* with an increase in the sintering temperature to 1000 °C contains only traces of copper. This confirms the aforementioned statement that copper particles at 800 °C are isolated by the tin liquid phase. Copper at this temperature is unsolved in iron.

In points *4* and *5* of the alloy with the composition *B*, sintered at 850 and 1000 °C, the amount of copper or Cu – Sn is nearly by twice higher than in the alloy with the composition A. The highest amount of copper and Cu – Sn was detected in point 6 of the alloy with the composition *C*, sintered at 1150 °C.

Conclusions

The microstructure of sintered iron with solid lubricants is multiphase. The compositions of complex phases were determined using *X*-ray studies and spot microanalysis. It was established that these are iron based Fe – Cu, Sn–C solid solutions of type and copper based Cu – Fe – Sn–C solid solutions. It was determined that the content of these solid solutions significantly decreases with an increase in the sintering temperature from 850 to 1000 °C. Nevertheless, the higher the graphite content and the sintering temperature, the higher the chance of the formation of free cementite in the structure. This is despite the existence of heat resistance in the composition.

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