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Original article

Development of Interparticle Bonding during Sintering of Metal Powders with the Addition of Carbon

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Abstract
Introduction. Publications on sintered metal powder parts consider interparticle bonding in hot-deformed materials and features of low-alloy structural steels, as well as the use of carbon-containing materials. The authors of the presented article have previously investigated sintering in relation to structural changes in the material, described changes in physical and mechanical properties, reduction of oxides, recrystallization, etc. This paper shows the relationship of mechanical properties of powder steels with the parameters of intracrystalline bonding. The kinetics of its development during sintering is demonstrated for the first time. The study objective is to find out how sintering affects the interparticle bonding and structure of powder alloys with iron and carbon. The task is to study the technological modes of sintering samples from alloyed and pure iron powder to achieve the best mechanical characteristics.
Materials and Methods. The powders of the Höganäs company were sintered at a temperature of 900-1150 ºC for 0.5–2.5 hours. The protective gas medium (dissociated ammonia) made it possible to prevent oxidative and other sintering reactions. For static cold pressing, a hydraulic press 2PG-125 with a maximum force of 1250 kN was used.
Results. For the first time, the presence of intracrystalline bonding mechanisms with different intensity during sintering has been experimentally established. The dependences of the increment of the relative area of the contact surface on the duration of the isothermal exposure were constructed. With an increase in the sintering temperature to 1150 ºC and a holding time of more than 80 minutes, the contact surface area gradually increased. It was shown that the samples from the powder grades under consideration formed an intracrystalline bonding on the entire contact surface at 1150 ºC. Therefore, this technology can be recommended for practical use. The addition of graphite to the charge slows down the growth of the contact surface. At the same time, the molds from pure powder ABC100.30 and from Distaloy HP-1 powder showed differences. In the first case, with the addition of graphite to the charge, the contact surface developed more intensively than in the second one. The obtained results were recorded in the photo and visualized in the form of graphs.
Discussion and Conclusion. According to the results of mechanical tests, it is possible to estimate the proportion of the contact section of the molding with intracrystalline bonding. Its feature is the structural correspondence of the interparticle surface of the splice and the intergrain boundary. The value of this boundary is determined by comparing the relative area of the contact section with the intracrystalline bonding and the relative area of the contact surface. The possibilities of improving the quality of bonding of powder steels by increasing the temperature and time of their exposure during sintering are determined.

Keywords: metal powders, interparticle bonding, hot-deformed powder materials, intracrystalline bonding, interparticle surface, grain boundary

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Научная статья

Развитие межчастичного сращивания при спекании металлических порошков с добавлением углерода

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Аннотация

Введение. В публикациях о спеченных деталях из металлических порошков рассматриваются межчастичное сращивание в горячедеформированных материалах и особенности низколегированных конструкционных сталей, а также применение углеродосодержащих материалов. Авторы представленной статьи ранее исследовали спекание во взаимосвязи со структурными изменениями материала, описывали изменение физических и механических свойств, восстановление оксидов, рекристаллизацию и т. д. В данной работе показана связь механических свойств порошковых сталей с параметрами внутрикристаллитного сращивания. Кинетика его развития во время спекания демонстрируется впервые. Цель исследования — выяснить, как спекание влияет на межчастичное сращивание и структуру порошковых сплавов с железом и углеродом. Задача — изучить технологические режимы спекания образцов из легированного и чистого железного порошка для достижения наилучших механических характеристик.

Материалы и методы. Порошки фирмы «Хёганес» (Höganäs) спекали при температуре 900–1150 °С в течение 0,5–2,5 часов. Защитная газовая среда (диссоциированный аммиак) позволяла предотвратить окислительные и другие реакции спекания. Для статического холодного прессования задействовали гидравлический пресс 2ПГ-125 с максимальным усилием 1250 кН.

Результаты исследования. Впервые экспериментально установлено наличие разных по интенсивности механизмов внутрикристаллитного сращивания при спекании. Построены зависимости приращения относительной площади контактной поверхности от длительности изотермической выдержки. С ростом температуры спекания до 1150 ºС и времени выдержки более 80 мин площадь контактной поверхности постепенно увеличивается. Показано, что у образцов из рассматриваемых марок порошка при 1150 ºС формируется внутрикристаллитное сращивание на всей контактной поверхности. Следовательно, данную технологию можно рекомендовать для практического использования. Добавление в шихту графита замедляет рост контактной поверхности. При этом формовки из чистого порошка ABC100.30 и из порошка Distaloy HP-1 демонстрируют различия. В первом случае с добавлением в шихту графита контактная поверхность развивается интенсивнее, чем во втором. Полученные результаты зафиксированы на фото и визуализированы в виде графиков.

Обсуждение и заключение. По результатам механических испытаний можно оценить долю контактного сечения формовки с внутрикристаллитным сращиванием. Его признак — структурное соответствие межчастичной поверхности сращивания и межзеренной границы. Значение этой границы определяется при сопоставлении относительной площади контактного сечения с внутрикристаллитным сращиванием и относительной площадью контактной поверхности. Определены возможности повышения качества сращивания порошковых сталей за счет увеличения температуры и времени их выдержки при спекании

Ключевые слова: металлические порошки, межчастичное сращивание, порошковые горячедеформированные материалы, внутрикристаллитное сращивание, межчастичная поверхность, межзеренная граница

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Introduction. Sintered parts from traditional and new compositions are widely used in industry. The latter include partially alloyed powders, nanopowders. The emergence of new initial structural materials requires additional study of the processes of formation of consolidated materials at all technological stages.

Since the beginning of the 21st century, there has been a growing interest of scientists in this topic [1–7]. For example, interparticle bonding during the formation of hot-deformed powder materials has been studied. The features of low-alloy structural steels in such processes were described. Deformation and compaction of powder materials were considered. In, the authors identified patterns of mechanical properties depending on the heat treatment modes, which also affect the quality of interparticle contacts of powder materials. Works [8–10] focus on the study of carbon-containing materials for the manufacture of powder parts from hard alloys. In addition, sintering process is simulated under various modes.

In the early works of the authors of the presented article, sintering process was investigated depending on the structural changes of the material. The removal of residual stresses after pressing, changes in physical and mechanical properties, reduction of oxides, recrystallization, etc. are described. Let us note that sintering of powder steels is a complex and not fully studied process. This work continues the study of interparticle interactions of powder steels. The relationship between their mechanical properties and the quality of intracrystalline bonding is revealed. The authors demonstrated for the first time the kinetics of the development of intracrystalline bonding for the studied materials during sintering. Various modes of sintering of samples are analyzed; the proportions of the contact section of the molding with intracrystalline bonding of powder materials are estimated.

The work objective is to find out how sintering affects interparticle bonding and structure of powder alloys with iron and carbon. The task is to study the technological modes of sintering samples from alloyed and pure iron powder to achieve maximum mechanical characteristics that ensure the formation of high-quality interparticle bonding.

Materials and Methods. During sintering, the formation of the contact surface of the powder material is considered from the standpoint of its initial state, which changes during exposure at high temperature. That is, we are talking about a sequential increment of the contact surface.

For static cold pressing, 2PG-125 hydraulic press with a maximum force of 1250 kN was used. Sintering was carried out at a temperature of 900-1150 °C for 0.5–2.5 hours. To prevent oxidative and other sintering reactions, a protective gas medium (dissociated ammonia) was provided.

Iron powders of the Swedish company Höganäs [1–3] were used in the work (Table 1).

Table 1

Types and characteristics of the powders used by the Swedish company Höganäs

Powder type	Method of production
ABC100.30	Spraying of iron melt
Distaloy HP-1	Double diffusion alloying of Astaloy 85Mo powder:1.5% Mo+4%Ni,2%Cu

Data on the total chemical composition are presented in Table 2.

Table 2

Chemical composition of the powders studied

Powder type	Content of elements, mass. %								
	C	O	Mo	Ni	Cu	Mn	Si	S	P
ABC100.30	0.001	0.04	–	–	–	0.06	0.007	0.01	0.004
Distaloy HP-1	0.01	0.08	1.5	4	2	0.08	0.005	0.03	0.003

In the processes under consideration, sintering is both a final and an intermediate operation [1–4]. In the first case, the consolidation of the material ends at this stage. The sintering process, in addition to structural changes in the material, contributes to:

– removal of residual stresses after pressing;
– changes in the physical and mechanical properties of the material;
– reduction of oxides;
– recrystallization, etc.

Determining the technological parameters of sintering presses are: temperature regime, sintering duration, parameters of pretreatment of material particles by pressure, etc.

In the second case, the subsequent thermomechanical action plays an essential role in the structure formation of the material, and sintering is considered as a preparatory stage, the main purpose of which is the homogenization of the metal base.

With the development of the basic provisions of works [1, 2, 5], the essence of the intensity and efficiency of sintering was clarified. These indicators allow us to judge the change in size, the development of the structure and properties of sintered materials. According to works [5–8], a method for determining the relative area of the contact surface of a porous body has been created.

Results. When sintering charges from ABC.100.30 and Distaloy HP–1 powders, the dependences of the development of the contact surface on the initial density, temperature and sintering time were obtained (Fig. 1, 2). At the same time, they we guided by the material described in [5].

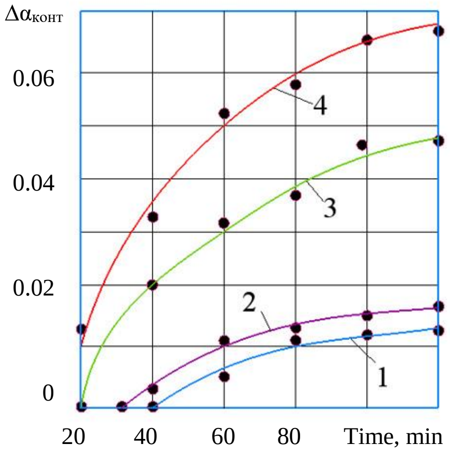


Fig. 1. Dependence of the increment of the contact surface relative area on the duration of isothermal exposure during sintering of the molding from ABC100.30 +0.5%C powder for different initial densities and temperatures: 1 — 950 °C,7.35 g/cm^3; 2 — 1150 °C, 7.35 g/cm^3; 3 — 950 °C, 6.9 g/cm^3; 4 — 1150 °C, 6.9 g/cm^3

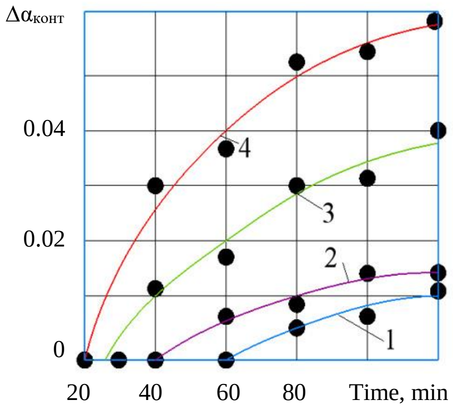


Fig. 2. Dependence of the increment of the relative contact surface area on the duration of isothermal exposure during sintering of the powder molding Distaloy HP–1+0.5%C for different initial densities and temperatures: 1 — 950 °C, 7.4 g/cm^3; 2 — 1150 °C, 7.4 g/cm^3; 3 — 950 °C, 6.6 g/cm^3; 4 — 1150 °C, 6.6 g/cm^3

With increasing temperature and sintering time, the contact surface area monotonically increased, the intensity faded as the sintering duration increased.

In molds made of ABC100.30 pure powder with the addition of graphite to the charge, the contact surface developed more intensively compared to molds made of Distaloy HP-1 powder. This could be explained. The fact was that smaller particles of copper, nickel and molybdenum were baked to the surface of the iron particles of Distaloy HP-1 powder. They formed solid solutions in Fe_{γ}, which complicated the course of diffusion processes (compared to pure metal). As a result, the growth of the contact surface slowed down.

The intensity of the contact surface formation depended on the initial relative density. An increase in this indicator slowed down the process, since the approach of the material structure to a non-porous state reduced the driving force of consolidation.

The addition of graphite to the charge slowed down the growth of the contact surface. This was due to a decrease in the self-diffusion coefficient of iron atoms, especially at the initial stage of sintering in contact areas with high carbon content.

Let us see how the carbon content affected the strength of sintered alloys under different sintering modes (Fig. 3, 4).

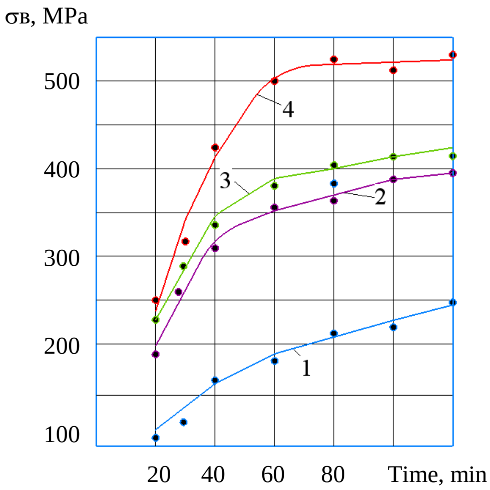


Fig. 3. Dependence of the strength limit of the sintered molding from ABC100.30+0.5% C powder on the time of isothermal exposure and the initial density: 1 — 6.9 g/cm^3, 950 °C; 2 — 6.9 g/cm^3, 1150 °C; 3 — 7.35 g/cm^3, 950 °C; 4 — 7.35 g/cm^3, 1150 °C

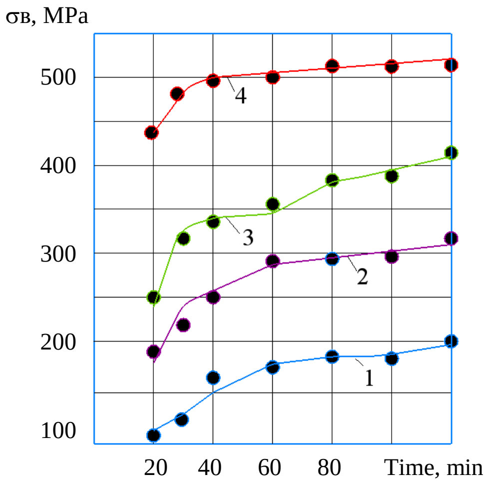
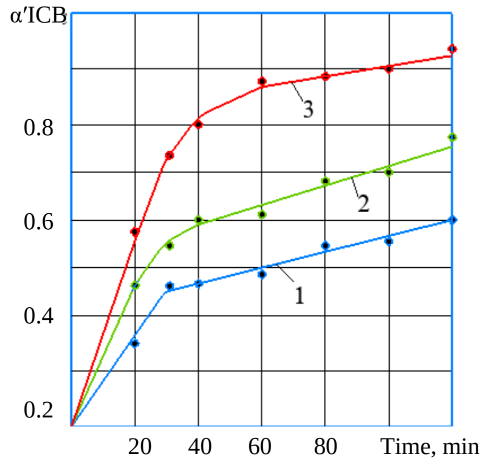


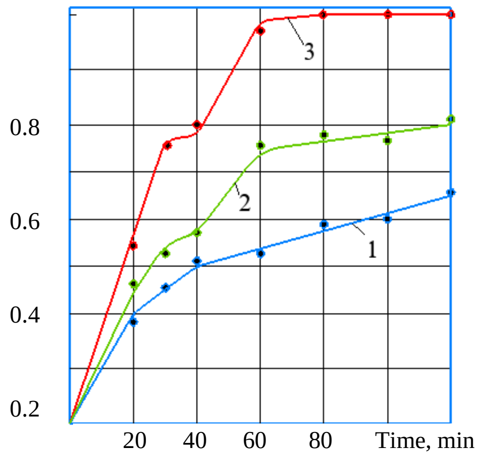
Fig. 4. Dependence of the strength limit of sintered molding from Distaloy HP–1+0.5%C powder on the time of isothermal exposure and initial density: 1 — 6.9 g/cm^3, 950 °C; 2 — 6.9 g/cm^3, 1150 °C; 3 — 7.35 g/cm^3, 950 °C; 4 — 7.35 g/cm^3, 1150 °C

The ultimate strength of the material based on ABC100.30 powder with a carbon content of 0.5 % was 610 MPa, the ultimate strength of the material based on Distaloy HP—1 powder with a carbon content of 0.5 % was 508 MPa.

According to the results of mechanical tests and the value of the tensile strength of the reference samples, the relative area of the contact cross section with intracrystalline bonding (α′ICB) was determined depending on the initial density and sintering modes of molds made of ABC.100.30+0.5%C (Fig. 5) and DistaloyHP–1+0.5%C (Fig. 6) powders.



a)



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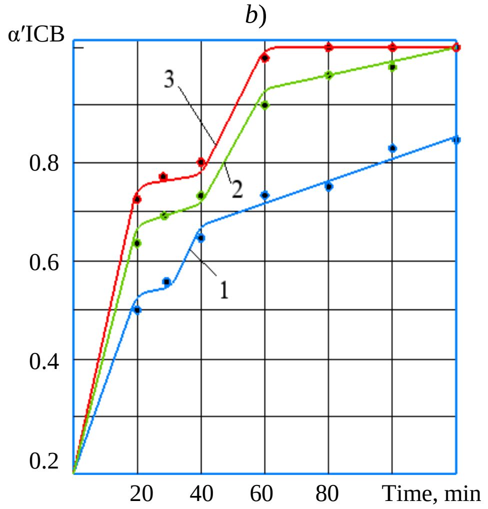

c)

Fig. 5. Kinetics of the development of intracrystalline bonding on the contact surface, depending on the sintering modes and the initial density (ABC.100.30+0.5%C): *a* — 6.9 g/cm^3; *b* — 7.2 g/cm^3; *c* — 7.35 g/cm^3. 1 — 950 °C; 2 — 1050 °C; 3 — 1150 °C

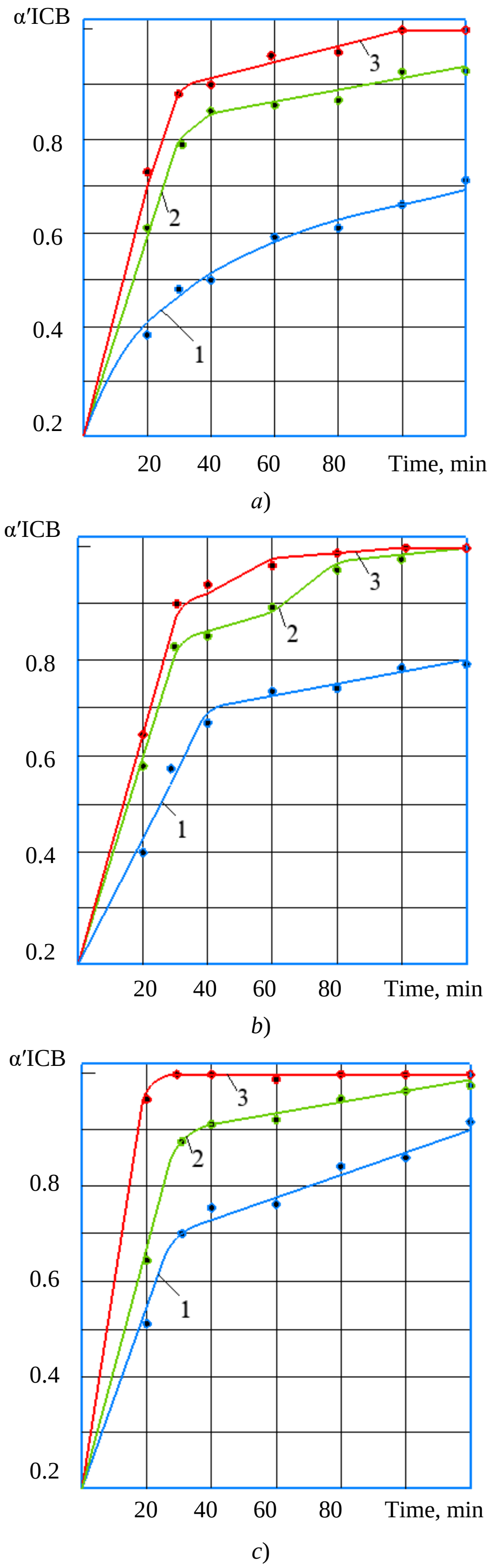

Fig. 6. Kinetics of the development of intracrystalline bonding on the contact surface depending on the sintering modes and the initial density (DistaloyHP–1+0.5%C): *a* — 6.6 g/cm^3; *b* — 7 g/cm^3; *c* — 7.4 g/cm^3.
1 — 950 °C; 2 — 1050 °C; 3 — 1150 °C

The presented dependences indicate that the introduction of graphite into the charge intensified the processes of formation of intracrystalline bonding in comparison with materials from a carbon-free charge. The results of the research coincided with the data of works [9–11].

During sintering at heating and isothermal exposure, the surface layers of iron and graphite particles continuously interacted through their contact areas (including the gas phase) [12–15]. Let us note that carbon was an active reducing agent of iron oxides, therefore, at temperatures above 500–600 °C, reduction reactions occurred at the places of contact of iron particles with graphite. This contributed to the formation of juvenile contact with subsequent particle fusion. Favorable conditions were created for the formation of a carbon-containing gas medium due to reactions between graphite and iron particles. The reduction processes were intensified due to a significant increase in the kinetics of chemical reactions at the metal — gas interface. The growth was fixed relative to the diffusion coefficients in the contact areas of iron particles with graphite and over the entire surface of the particles. Surfaces in contact with the furnace atmosphere were also taken into account. At the same time, carbon diffused into iron particles through the formed metal contacts on the surface of the particles. Before the transformation of $\alpha \rightarrow \gamma$, the formation of a phase in the contact points of cementite was most likely. This phase had a more significant carbon diffusion coefficient at the temperatures under consideration. This was due to the insignificant dissolution of carbon in α-iron and slow diffusion in ferrite.

If the contact surface of the iron powder material developed more intensively than that of the doped powder material, then it was the latter that should be preferred when forming intracrystalline bonding.

Intracrystalline bonding is formed in two stages:

– isothermal aging of the molding in the austenitic region;

– cooling with the decomposition of austenite into a ferrite-cementite mixture.

The role of the second stage consisted in the predominant development of the interparticle bonding surface as a region of facilitated nucleation of ferrite grains and cementite plates that ensured the migration of the boundary through the surface of the physical separation of particles. This was confirmed by the results of microstructural analysis. Fig. 7–10 shows the microstructures of the material with different levels of interparticle bonding.

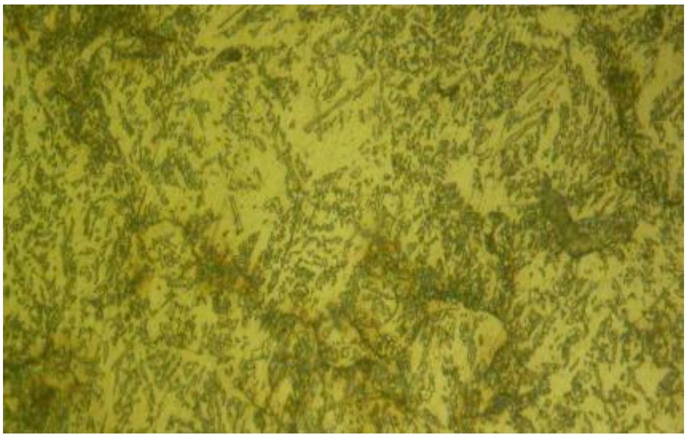

Fig. 7. Microstructure of the sample from ABC100.30+0.5%C powder after sintering at 1050 °C for 40 minutes, ×200

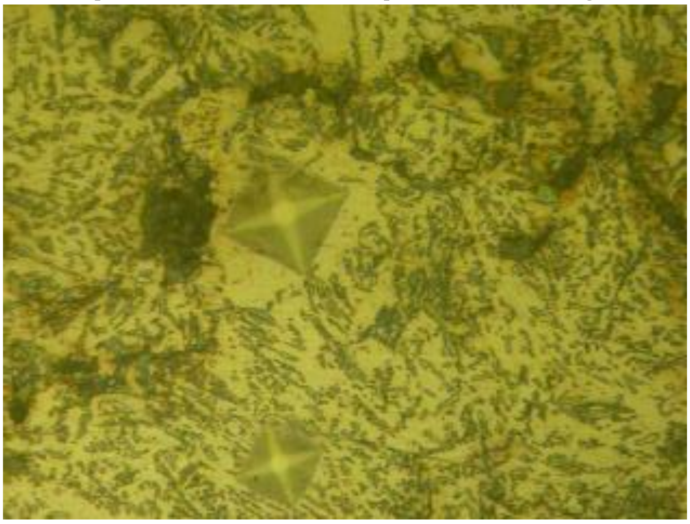

Fig. 8. Microstructure of the sample from Distaloy HP–1+0.5%C powder after sintering at 1050 °C for 20 minutes, ×200

The presented microstructures are characteristic of a low level of bonding, since the boundary of the powder particles is clearly visible.

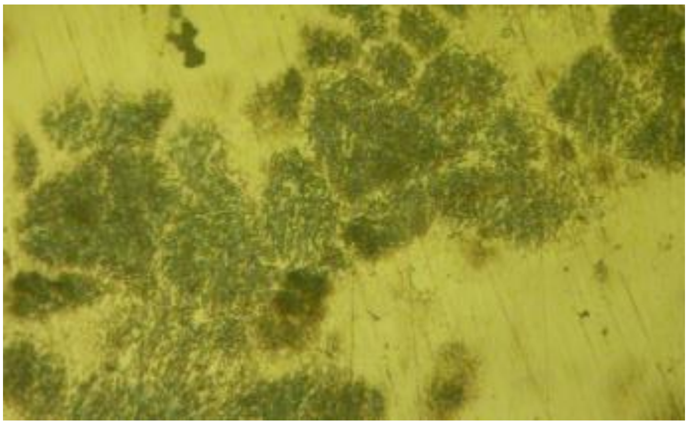

Fig. 9. Microstructure of the sample from ABC100.30+0.5%C powder after sintering at 1150 °C for 40 minutes, ×500

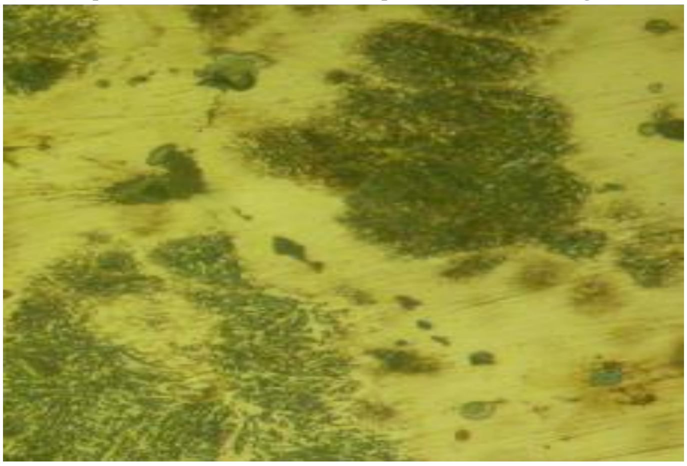

Fig. 10. Microstructure of the sample from Distaloy HP–1+0.5%C powder after sintering at 1150 °C for 40 minutes, ×500

Nonmetallic inclusions identify the former boundary of the physical separation of particles through which ferrite grains germinate. That is, the former particle interface is located inside the grain, and this is a sign of intracrystalline bonding [16].

Discussion and Conclusion. The results of the work allow us to assert that during sintering, the mechanisms of formation of intracrystalline bonding are different in intensity [5, 9, 16]. At first, the bonding is fast, then its speed decreases. Compressions with the lowest values of the initial density are characterized by the longest duration of the process of accelerated development of intracrystalline bonding, which is observed at the first stage. Moreover, with an increase in the sintering temperature, the intensity of this stage increases. The formation of intracrystalline bonding on the entire contact surface is observed in molds obtained under sintering conditions at a temperature of 1150 °C. The peculiarity of molds made of DistaloyHP–1 and ABC100.30 powders has been experimentally established. Under sintering conditions, intracrystalline bonding occurs within 60 and 80 minutes, respectively.

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