Development of Technologies for Obtaining Metal Powders (Iron) from Production Waste and Studying Their Properties

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The article discusses the modern methods of fabrication of iron powders, carries out their classification, analyses the analytical data about powders made from various types of raw materials. The kinetic regularities of the reduction of iron oxides are analysed from the point of view of the adsorption–autocatalytic theory. The structure and mechanical properties of iron powders are considered. The morphology, structure, phase and elemental compositions of the mill scale of the Uzbek Metallurgical Plant are analysed. Technology for the recovery of scale is developed, including the following stages: drying at 250–340°C, grinding in a ball mill for 2 hours, magnetic separation, sieving through a 40-mesh sieve, mixing the charge, recovery for 2 hours in H_2 at the temperatures: 650–700°C (I zone), 950–1000°C (II zone).

У статті розглядаються сучасні методи виготовлення залізних порошків, проводиться їх класифікація, аналізуються аналітичні дані про порошки, виготовлені з різних видів сировини. Кінетичні закономірності відновлення оксидів Феруму аналізуються з точки зору адсорбційно-автокаталітичної теорії. Розглянуто структуру та механічні властивості порошків заліза. Проаналізовано морфологію, структуру, фазовий і елементний склади вторинної жужелиці Узбецького металурґійного заводу. Розроблено технологію відновлення жужелиці, що включає наступні етапи: сушка при 250–340°C, шліфування в кульовому млині протягом 2 годин, магнетне збагачення (відокремлення), просіювання через 40-коміркове сито, змішування шихти, відновлення протягом 2 годин у H_2 за температур у 650–700°C (I зона) і 950–1000°C (II зона).

Key words: iron powder, kinetics, reduction, iron oxide, adsorption, structure, mechanical properties.

Ключові слова: залізний порошок, кінетика, виділення металу з руди, оксид Феруму, адсорбція, структура, механічні властивості.

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1. INTRODUCTION

The most important task of the economic and social development of the Republic of Uzbekistan is the acceleration of scientific and technological progress in all branches of industrial production through the use of new materials, progressive technologies, and processes that ensure the predominant output of products with a decrease in material consumption per unit of consumer properties of machinery and equipment.

Powder metallurgy, which is one of the promising technologies of metallurgical and machine-building production, is of great importance in solving the problems posed, the methods of which make it possible not only to create materials with new quality and strength characteristics, but also to introduce waste-free or low-waste technologies for the production of powder metal materials and products of various appointments based on them.

If in the manufacture of parts by traditional methods (casting, forging, stamping followed by mechanical processing) the metal utilization factor is 0.4−0.6, then powder metallurgy allows increasing it to 0.95−0.97 [1, 2].

Powder metallurgy processes, as a rule, proceed at temperatures lower than in large metallurgy (0.7−0.8 from the melting point), thereby providing energy savings. The energy consumption of powder metallurgy is 29 MJ/kg and is significantly lower than the energy consumption of foundry (34−38 MJ/kg), cold stamping (41 MJ/kg), hot stamping (46−49 MJ/kg), cutting (66−82 MJ/kg) [4, 5].

Powder metallurgy has one more advantage—environmental one, because it is not associated with the release of harmful products that pollute the environment.

A feature of powder metallurgy—the possibility of creating compact materials from mixtures of powders, bypassing the stages of melting and casting, opens up broad prospects for the development of new powder metal materials with a variety of properties inherent both in components of a metallic and non-metallic nature, and arising from the interaction of heterogeneous nanodispersed systems.

Using the methods of powder metallurgy, it is possible to obtain composite products from so-called 'pseudo-alloys', the components of which either sharply differ in melting temperature, or do not fuse at all (tungsten−copper, tungsten−silver, copper−molybdenum, *etc*.), but are widely used in electrical and radio engineering, electronics.

Powder metallurgy methods have created a large group of new

composite materials, which include dispersion-hardened, antifriction and frictional, cermets, fibre-reinforced materials, *etc*. Structurally, this group of materials is a plastic metal matrix that cements the inclusions of the hardening phase.

The development of fundamental and theoretical foundations and new technologies created the prerequisites for expanding the range and scope of powder products. If 20−25 years ago the bulk of powder products was represented by parts of friction units (antifriction and frictional), now more than 60% of manufactured parts are structural, operating under conditions of complex stress and shock exposure, elevated temperatures, corrosive environments, *etc*., when high strength, density, impact strength, special properties are required from parts [6, 7].

2. THE RELEVANCE OF THE PROBLEM

At present, powder metallurgy is a rapidly developing industry, including the production of powders, metals, and alloys with particles of different dispersion, granules, threads, and other shapes; production of various machine parts and devices, tools, and special-purpose items; development and creation of metallic powder materials and non-metallic substrates; strengthening and restoration of machine parts and devices, as well as imparting increased mechanical or special physicochemical properties to the surface of products by methods of coating with powder composite materials.

In this regard, new promising processes for obtaining powder products are being introduced into practice, as well as new types of high-performance equipment; great attention is paid to scientific developments in the field of powder metallurgy and materials based on them [8].

Among the technological methods for the production of structural products, the method of cold pressing in closed moulds with subsequent sintering has the greatest application [9, 10].

The advantage of obtaining parts in this way is, first of all, high productivity and the possibility of their mass production without using or with the use of minor mechanical processing, which reduces waste and metal losses by 10−15 times in the manufacture of even products with complex shapes [11, 12].

This technology retains inexhaustible possibilities for the creation of new materials based on iron powders with the additional use of alloying and heat treatment methods [13, 14].

In recent years, hot pressing technology has been rapidly developing, which consists of the simultaneous pressing and sintering of powders, which makes it possible to obtain a dense product with a certain level of mechanical properties. With hot pressing, it is pos-

sible to significantly reduce the temperature process and thereby slow down the recrystallization process that ultimately leads to the formation of a fine-grained structure and an increase in mechanical properties in the low-temperature region [15, 16].

In contrast to conventional sintering, the methods of hot moulding of blanks and products are carried out on equipment that is more complex, require special preparation of the tooling, and are inferior to it in performance. However, the effect in terms of strength properties and wear resistance is fully justified from both the technical and economic points of view. Methods of hot working with pressure are especially effective in the manufacture of large products, using difficult to sinter or substandard powders when it is necessary to obtain high density and strength of products, which are unattainable under the conditions of conventional sintering.

Large losses of metal occur from corrosion and wear of structures and machine parts. In this regard, a new direction of powder metallurgy is acquiring great importance in increasing wear resistance and corrosion resistance by applying powder materials to the surface of products [17, 18].

Various methods of applying layers (surfacing, plasma spraying, electrophoresis, vapour deposition, detonation spraying, *etc*.), as practice shows, due to the small thickness of the coating, cannot always be effectively used to protect the working surfaces of equipment parts, tools and technological equipment operating in hydroabrasive and aggressive environments, at high pressures and elevated temperatures. Therefore, there is a need for a broad development of work on the creation and implementation of technologies for applying layers of more than 2 mm to ensure reliably a long service life of equipment units.

In this respect, powder metallurgy methods are promising (centrifugal, sintering, pressing with subsequent sintering, electrical contact sintering, hot pressing, *etc*.), which make it possible to obtain layers with high physical, mechanical and operational properties, and a given structure.

Among these methods, preference should be given to the hot pressing method, since the application of pressure accelerates the compaction process and the formation of strong contacts of the powder coating with the substrate.

However, to solve the problem of strengthening the working surfaces of machine parts and mechanisms by applying layers by hot pressing, it is necessary to study the physical and mechanical properties of powder layers on a compact basis, to identify the mechanisms of compaction and formation of a joint depending on the parameters of hot pressing (temperature, pressure, isothermal holding).

Thus, based on the analysis of literature data, it can be concluded that the development of new technological solutions for the processing of iron powders obtained from production of waste is possible only after a wide range of studies of their morphology, structure, physicochemical and technological properties, since, ultimately, they determine the conditions for forming and sintering, as well as the mechanical and operational characteristics of materials based on iron powders.

To develop technology for producing layers from powder materials, it is necessary to study the kinetics of changes in the density of the layer and the strength of its connection with the substrate, depending on the type of starting materials and the main parameters of hot pressing: temperature, pressure, isothermal holding.

3. RESEARCH METHODS

Metallographic, x-ray phase, and electron-microscopy analyses; test for mechanical properties.

4. STUDY RESULTS

Methods for Obtaining Metal Powder Materials. To obtain iron powders, a wide variety of methods are used that is explained not only by the need for powders for various purposes but also by the search for technologies, which would ensure the production of the cheap and high-quality powders [19, 20]. The classification of methods for producing iron powders is shown in Fig. 1.

In terms of composition, all iron powders can be classified into two groups: low-carbon (iron powders proper) and alloyed iron powders [21−23].

The first group should include iron powders containing permanent, hidden, and accidental impurities. Permanent impurities include sulphur, phosphorus, manganese, and silicon, which are present in any steel, scale, or ore that can be the starting material for producing iron powder. The content of these elements in powders is usually in the range, wt.%: sulphur 0.01−0.04, phosphorus 0.01−0.05, manganese 0.3−0.7, silicon 0.2−0.4.

Latent impurities (oxygen, hydrogen, nitrogen) present in the feedstock for the production of iron powder in various quantities, ranging from fractions of a percent in steels, and ending in percent in scale and ores and remaining in small amounts in iron powders.

Accidental impurities are entering the starting materials for the production of iron powders from steels, ores, scrap, and scrap metal.
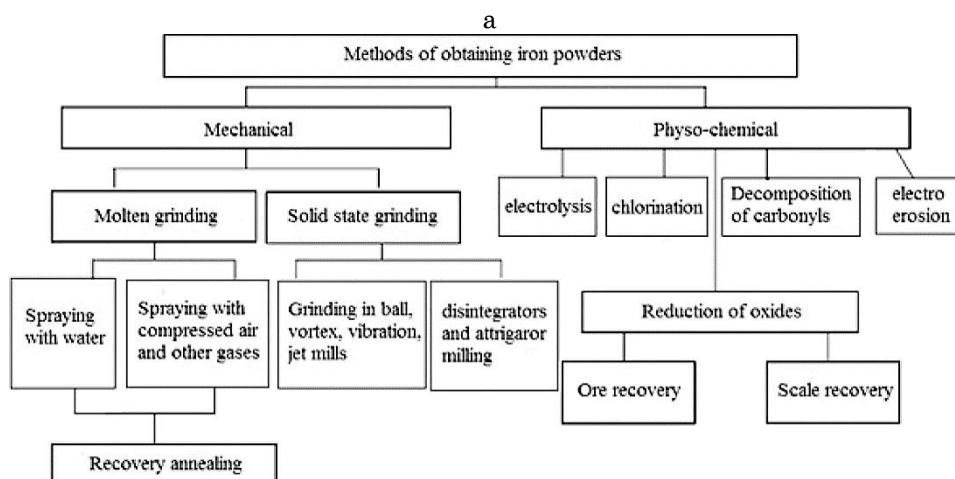
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Methods of obtaining iron powders

Mechanical

Physo-chemical

Molten grinding

Solid state grinding

electrolysis

chlorination

Decomposition of carbonyls

electro erosion

Spraying with water

Spraying with compressed air and other gases

Grinding in ball, vortex, vibration, jet mills

disintegrators and attrigaror milling

Reduction of oxides

Ore recovery

Scale recovery

Recovery annealing

Fig. 1. Classification of methods for producing iron powders.

The presence of the listed impurities is an inevitable consequence of the technological process of producing iron powder from carbon steels, scales, and ores.

The second group should include iron powders containing alloying elements in quantities exceeding impurity and introduced into the powder particles by one of the following methods:

1. alloyed iron powders obtained by grinding or spraying alloy steels, as well as their waste, followed by reduction annealing of raw materials.

2. alloyed iron powders obtained by surface alloying of powder particles.

3. naturally alloyed iron powders obtained by reduction of naturally alloyed ores, pulverized raw materials, or mill scale of alloyed steels, or from shavings formed during the mechanical processing of these steels.

Powders of this group obtained by various methods have the following composition, mass.%: iron 98.0–99.0, oxygen 0.02–1.0, carbon 0.005–0.12, silicon 0.006–0.64, phosphorus 0.001–0.5, manganese 0.002–0.03, and sulphur 0.005–0.003.

For comparison, we note that the average content of impurity elements in iron powders and cast steels (hot-rolled, carbon engineering) is approximately the same, except for the manganese content, which in steels is brought to 0.9 mass.%.

Production of Iron Powders by the Reduction Method. A comparison of methods for the production of the iron powder allows us to conclude that the oxide reduction process is the most promising method for the production of cheap universal-purpose powder. Giv-

en the high productivity of the recovery process, the use of cheap raw materials and high-quality reductants, ensuring the completeness of recovery, correct engineering design, and full automation of technological cycles, it can be argued that the recovery process is the most profitable from a technical and economic point of view for obtaining cheap iron powders [24, 25].
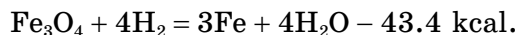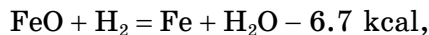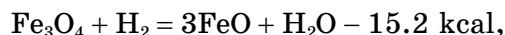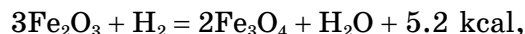
The development of the industrial production of iron powders by the reduction method was preceded by the development of the theoretical foundations of this process.

The kinetics of the reduction of iron oxides were studied, the equilibrium constants of the ongoing reactions were determined, and kinetic equations were derived, taking into account the influence of factors such as the rate of diffusion and chemical reactions on the process rate [26, 27].

The existing methods for the reduction of iron oxides are classified according to the reductant used, the type of charge and the method of feeding it into the reduction zone, the pressure of the reducing gases, and the process temperature.

The reduction can be both an independent technological process for obtaining iron powders (the raw material is scale, ore), and the final part of the technological process in the production of powders by crushing steel melts with water or compressed air, in which iron particles are oxidized.

The process of reduction of iron oxides with hydrogen can be described by the following chemical reactions:

$$3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O + 5.2 \text{ kcal,}$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O - 15.2 \text{ kcal,}$$

$$FeO + H_2 = Fe + H_2O - 6.7 \text{ kcal,}$$

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O - 43.4 \text{ kcal.}$$

According to the adsorption–autocatalytic theory, the reduction process consists of the adsorption of a reducing gas on the oxide surface, the destruction of the oxide crystal lattice, the formation of intermediate oxide phases, and, at the last stage, the metal phase, desorption of gaseous reaction products from the surface of particles [28].

The detachment of oxygen atoms from oxides during their reduction is thermodynamically easier than dissociation because, in the course of the reaction, the energy of binding of oxygen with a reducing agent is released. As a result, either the activation energy of the reaction decreases, and the process is accelerated at a given temperature, or the reaction becomes possible at lower temperatures.

The acceleration of the chemical interaction of oxides with a reducing agent is also stimulated because the boundary between the oxide and the metal reduced from it in most cases is a catalyst for the process, as a result of which, it becomes autocatalytic one. For this reason, the dependence of the free energy of the formation of oxides on temperature makes it possible to estimate the relative thermodynamic strength of these oxides upon reduction [29].

General Principles for the Recovery of Mill Scale. One of the urgent problems of ferrous metallurgy is the use of secondary raw materials and production wastes in the national economy, which are not used in the smelting of high-quality metal in open-hearth and electric arc furnaces.

Such production wastes include scale, which is formed during the rolling of boiling carbon steels, containing 70−75% iron in the form of oxides. In the rolling shops of metallurgical plants, tens of thousands of tons of scale are accumulated, the chemical composition of which depends on the operation of the rolling technological process, at which it was formed. The purest scale is formed during the cooling of rolled products in cold spans; it is not clogged with oxides difficult to recover, does not require magnetic separation, and is cheap and enough clean raw material source for obtaining iron powders.

Usually, mill scale is heavily contaminated with mechanical impurities, unstable in particle size distribution and bulk density, which greatly complicates its use. Therefore, the scale is first subjected to screening to separate large mechanical inclusions (14 mm^3) from it, then dried at a temperature of 350−500°C. In this case, the scale is freed from oils and other combustible impurities [30]. A dried scale with a moisture content of no more than 0.5% is subjected to magnetic separation to remove non-metallic inclusions, mainly, silica. Then, the scale is milled in mills to a particle size of < 1.0 mm.

For the reduction of scale with hydrogen, continuous muffle or tube furnaces with external heating are used. The dross is placed in trays or boats that move continuously through the hot zone of the oven. Hydrogen is supplied from the side of the refrigerator and the counter-flow principle ensures the most complete recovery. The time required for complete-scale recovery depends on its type, particle size, layer thickness, temperature, pressure, and humidity of hydrogen, and other factors.

According to one of the options [31], the reduction is carried out in a tubular two-zone furnace at 650−700°C (I zone) and 700−800°C (II zone).

In another embodiment [32], the reduction is carried out in a continuously operating conveyor furnace at 980°C. The recovery

time is of about 5 hours, and furnace productivity is 90 kg/h. There is a known method of reducing iron oxides by converted natural gas at 1100−1150°C [33].

It is proposed to make briquettes from scale and carry out reduction with natural gas conversion products at 900−950°C (stage 1). Then, the obtained sponge iron (the degree of recovery is 90−96%) is ground and additional reduction is carried out in hydrogen at 950−1000°C (stage 2) [34].

The work [35] presents the results of experimental studies of the reduction of iron oxides with wet hydrogen at normal pressure and isothermal conditions in the range 390−500°C. As a result of experiments, it was found that the rate of reduction in the kinetic region of reaction at normal pressure linearly depends on the concentration of water vapour in the gas mixture at their low content, which can be explained by a simple blocking of the active surface of the solid phase by water molecules.

Complete reduction of fine fractions of iron oxides with moist hydrogen is practically impossible due to the adsorption of water vapour on their surface. Therefore, the reduction of iron oxides is advisable to be carried out at moderate temperatures with completely dried hydrogen in installations operating on the counter-flow principle.

Experiments have shown that under these conditions, fine oxide particles with a large specific surface area also have a high reduction rate at low temperatures.

At the same time, an increase in the specific surface area of particles by several times does not entail the same increase in the reduction rate, which indicates a large influence of the internal porosity of oxides on the reduction process.

Besides, an increase in the reduction temperature to 600−800°C leads to a sharp decrease in the rate of the process due to recrystallization of the metal powder, and the time required for the complete reduction of fine oxides (< 0.05 mm) with hydrogen is longer than the time required for the recovery of larger particles of 0.3−0.4 mm.

Study of the Morphology, Structure, Phase and Elemental Compositions of Mill Scale of the Uzbek Metallurgical Plant. Considering that steel at the plant is smelted from scrap metal, one should expect the presence of a wide range of impurity elements in various concentrations. Therefore, comparative studies of the morphology and chemical composition of mill scale and iron oxide grade pure for analysis (P.F.A.) were presented.

It has been shown that iron oxide particles have a generally spherical shape, which is typical for α-Fe_2O_3 [16]. The scale understudy is granules of various sizes (up to 10 mm) of arbitrary shape
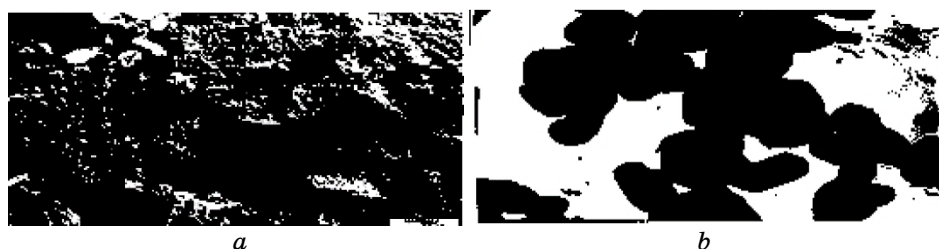
Fig. 2. Microstructure of the initial scale (*a*, ×150) and electron-microscopy structure of milled scale (*b*, ×17.500).
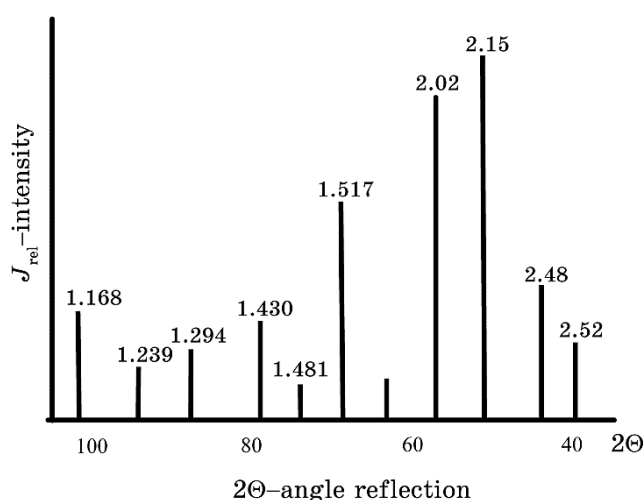

Fig. 3. Section of the x-ray diffraction pattern of mill scale.

with a porous structure (Fig. 2) [16].

As can be seen from the x-ray diffraction pattern (Fig. 3), the scale contains wüstite (FeO) [0.248, 0.215, 0.151, 0.129, 0.123 nm^3], magnetite (Fe_3O_4) [0.248, 0.148 nm^3], and there are traces of hematite (α-Fe_2O_3) [0.252, 0.148, 0.110 nm^3] (Fig. 3).

A comparison of the chemical composition of the scale of the Uzmetkombinat with the results of the analysis of the scale of the Orsk-Khalilovsk metallurgical plant (Table 1) indicates a significant difference in their chemical composition.

The scale of Uzmetkombinat is a powder of low-alloy steels.

Before the investigation, the scale was dried at 300–400°C, grinding in a ball mill at a ratio of the mass of raw materials and steel balls of 1:1 for 1.3 and 6 hours.

After grinding, magnetic separation of the powder was carried out on a belt transport shown in Fig. 4.

TABLE 1. The average chemical composition of the scale of JPA 'Uzmetkombinat' and Orsk-Khalilovskiy metallurgical plant.

Elements	Fe total	Si	Al	Ca	Mg	Ba	Sr	$x \cdot 10^{-3}$				
								Mn	Ti	S	Nb	Ga
Scale of Uzmetkombinat content, wt.%	72.0–5.0	1.5	1.0	80	60	20	70	300	10	80	4	0.4

Elements	Cr	Ag	Cu	Pb	Zb	Ni	Co	$x \cdot 10^{-3}$				
								Mo	Sn	Ge	La	Zr
Scale of Uzmetkombinat content, wt.%	30	20	400	6	8	100	10	10	3	10	10	5

Elements	Fe total	Si	Al	Ca	Mg	Ba	Sr	$x \cdot 10^{-3}$				
								Mn	Ti	S	Nb	Ga
Scale of Orsk-Khalilovsky Metallurgical Combine content, wt.%	96.01	0.85	—	20	—	—	—	67	—	0.7	—	20

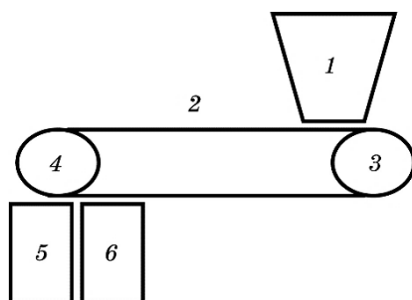| Elements	Cr	Ag	Cu	Pb	Zb	Ni	Co	$x \cdot 10^{-3}$				
								Mo	Sn	Ge	La	Zr
Scale of Orsk-Khalilovsky Metallurgical Combine content, wt.%	25	—	—	—	—	25	—	—	—	—	—	—

Fig. 4. Installation of magnetic separation.
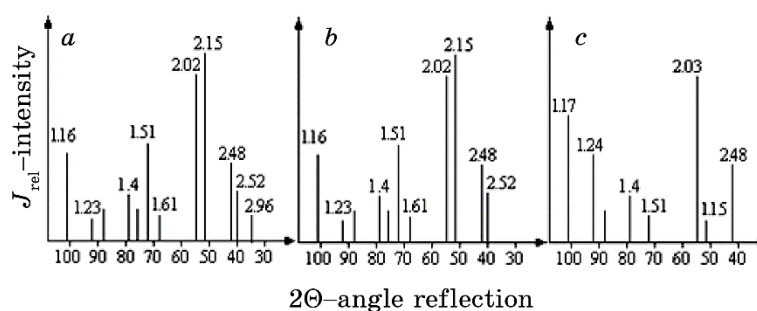

2Θ–angle reflection

Fig. 5. X-ray diffraction pattern of reduced iron powder at different temperatures: *a*—600°C; *b*—700°C; *c*—800°C.

The scale powder is loaded in portions into the receiving hopper (1), from which it is poured out by gravity in a layer of 0.5−1.0 cm onto a conveyor belt (2) made of thin vacuum rubber. The conveyor belt is driven by two rollers (3) and (4), one of which (4) is a permanent magnet. The rolls are driven by an electric motor with a drive. The powder, moving along the conveyor, reaches the opposite end, and its non-magnetic fraction is dumped down into the hopper (5), and the magnetic fraction, as the effect of the magnetic field weakened, is dumped into the hopper (6). Together with the particles of the magnetic fraction, 0.05−0.1 mass.% of non-magnetic particles are entrained by mechanical adhesion, but their concentration does not significantly affect the quality of the final product.

The average chemical composition of the scale is given in the Table 1.

After magnetic separation, the powder is poured into steel and graphite boats in weights of 0.5, 1.0, 1.5 kg. In this case, the height of the powder layer was of 10−30 mm.

The reduction was carried out in a stream of hydrogen in a single-zone industrial furnace at 600, 700, and 800°C for 1 hour.
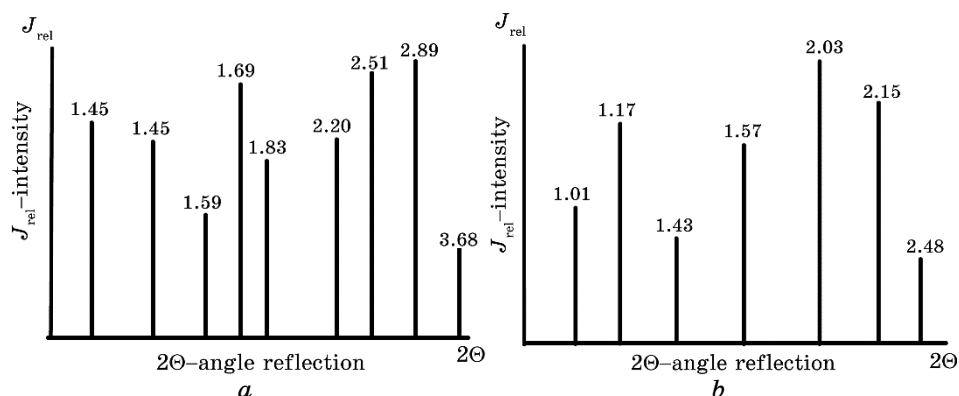
Fig. 6. X-ray diffraction pattern of initial iron oxide (*a*) and reduced iron at 800°C (*b*) for 1 hour.

The reduction of scale at 600°C leads to the formation of α-Fe ($\cong 40\%$), FeO ($\cong 38\%$), [0.248, 0.153 nm^3] FeO* ($\cong 11\%$), Fe$_3$O$_4$ [0.297, 0.161 nm^3] ($\cong 11\%$). The total iron content in the samples is $\cong 80$ wt.% (Fig. 5, *a*). The reduction of scale at 700°C forms the system α-Fe ($\cong 55\%$), Fe$_2$O$_3$ [0.250, 0.116 nm^3], FeO [0.151, 0.123 nm^3] ($\cong 23\%$), FeO* ($\cong 15\%$), Fe$_3$O$_4$ [0.161 nm^3] ($\cong 7\%$). The total iron content in the samples is $\cong 87$ wt.% (Fig. 5, *b*). The reduction of scale at 800°C leads to the formation of the α-Fe ($\cong 70\%$), FeO [0.151, 0.124 nm^3] ($\cong 30\%$), FeO* ($\cong 30\%$). The total iron content in the samples is $\cong 94$ wt.% (Fig. 5, *c*).

The FeO* phase present in all samples contains 48.5% Fe and corresponds to the formula Fe$_{0.35}$O and corresponds to the preparation obtained by the decomposition of FeC$_2$O$_4$ at 800°C (ASTM, 6-0711) [37]. FeO* in terms of *d*(*hkl*) values differs from FeO present in the initial scale and is, apparently, a solid solution FeO–Fe$_3$O$_4$ [0.368, 0.251, 0.220, 0.183, 0.163, 0.153 nm^3] (based on FeO), which is usually written as Fe$_x$O ($x > 0$). To compare the results obtained, we also analysed samples of iron oxide (P.F.A.) reduced at 800°C (Fig. 6, *a*).

However, due to the high chemical activity of the obtained ultra-granular iron powders, the presented diffractogram (Fig. 6, *b*) determines the phase composition of the already oxidized product. It includes α-Fe, FeO [0.248, 0.215 nm^3] and Fe$_3$O$_4$.

The spectral analysis of the samples obtained by reducing the scale at 700°C is presented in Table 2.

A comparison of the results obtained with the results of the analysis of the content of impurities in the initial scale (Table 1) shows that its reduction at 700°C leads to an increase in the concentration of practically all the elements present. However, in reality, this is

TABLE 2. Average chemical composition (wt.%) of the iron powder obtained by reduction of scale at 700°C.

Element	Si	Al	Ca	Mg	Ba	Sr	Mn	Ti	Cr	Ag	Pb
Mass.%	2.0	2.0	0.06	0.2	0.02	0.02	0.50	0.03	0.08	0.0001	0.006
Element	Zb	Ni	Co	Mo	Sn	Nb	La	Zr	Ga	Cu	other
Mass.%	0.008	0.20	0.01	0.01	0.003	0.007	0.007	0.004	0.0004	0.15	—
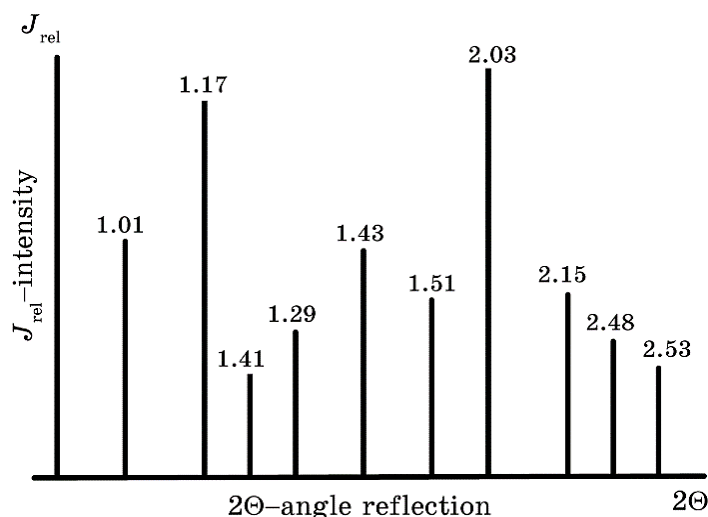
Fig. 7. X-ray diffraction pattern of iron samples obtained by reducing scale in two stages: *1*—650°C (1 hour); *2*—800°C (1 hour).

due to the analysis methodology, which does not take into account the reduction in the volume of dross after its recovery. Nevertheless, it can be argued that under the selected reduction conditions, no significant refining of the product occurs [38].

As can be seen in Fig. 2, the results of electron-microscopy studies of the reduction products of scale, milled to different degrees of fineness (10–500 μm), showed that finer iron powders are obtained from more dispersed scale, the pyrophoricity of which increases with a decrease in the reduction temperature that is manifested in terms of the thickness of the oxide film on the surface of particles.

Under the accepted experimental conditions, the lower layers of the scale powder are not completely restored due to insufficient recovery time (600 and 700°C) or the difficulty of hydrogen penetration due to the formation of a dense surface crust by sintered iron particles (at 800°C).

Based on the data obtained, it was concluded that the reduction process must be carried out in two stages at 600–700°C and 800°C. It is necessary to add a baking powder to the scale composition— soot or iron powder.

Based on these prerequisites, a series of experiments were carried out to restore scale, ground in a ball mill for 1 hour, in a two-phase furnace at temperatures: I zone—650°C; II zone—800°C.

For the study, steel and graphite boats were used, and the scale powder was mixed with 5% graphite or 5–10% iron powder. The charge was poured both into clean boats and onto a thin layer of iron powder.

The results obtained allowed us to conclude that under the selected reduction conditions, soot practically does not contribute to the reduction process and remains in the charge in a free state.

The best option is to recover the charge, which consists of a mixture of scale (90%) and iron (10%) powders. However, the iron powder sticks to the steel boat. Therefore, in terms of technology, preference should be given to graphite boats. The results of x-ray phase analysis of the product obtained by reducing a mixture of scale (90%) and iron (10%) in graphite boats in two stages (1 hour– 650°C, 1 hour–800°C) showed that the resulting powder is 98% from α-Fe [0.253, 0.248, 0.215, 0.129 nm^3] (Fig. 7).

However, during storage, there is the slow oxidation of iron powder, [0.244, 0.212, 0.150, 0.128 nm^3]; therefore, experiments proved the need to increase the temperature of the II stage of reduction to 950–1000°C (Fig. 8).

Technological Scheme of Obtaining Iron Powders by Reducing Scale. Preparation of raw materials. If the scale is taken from perennial dumps located in an open area, then it is preliminarily subjected to screening and flotation with running water to remove pieces of silica and alumina. The scale in the spans of rolling mills is not subjected to such an operation.

The scale is dried at 250–340°C to remove moisture, oil, *etc*. Milling of scale is carried out in a ball mill at a ratio of the mass of raw materials and steel balls 1:1 for 2 hours.

After grinding, the powder is magnetically separated on a belt conveyor equipped with an electromagnetic system to remove particles of impurities. The yield of the non-magnetic fraction is 3–10%, depending on the scale contamination.

The powders are sieved through a 40-mesh sieve to remove coarse fractions, which are resent for grinding. The amount of the coarse fraction usually does not exceed 3–5%.

Batch Preparation. To accelerate the reduction process and facilitate the circulation of hydrogen, 8–10 wt.% iron powder is added to the scale powder. The batch is mixed in a mixer or ball mill for 1
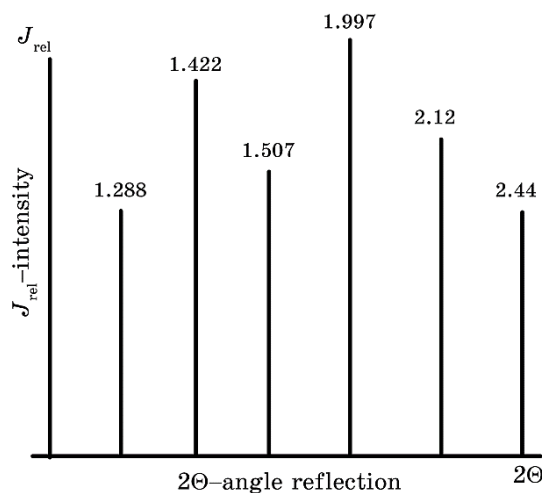
Fig. 8. X-ray diffraction pattern of iron samples obtained by reducing scale in two stages: *1*—650°C (1 h); *2*—1000°C (1 h).

Fig. 9. The microstructure of an iron sponge was obtained by reducing the mill scale, ×1000. *1*—α-Fe.

hour.

Scale Recovery. The charge is poured into standard graphite boats with a layer thickness of 25–30 mm, which are placed in the muffles of an industrial furnace consisting of two zones, and a refrigerator, and are continuously advanced using a pusher.

The temperature of zone I of the furnace is 650–700°C, zone II is 950–1000°C. Hydrogen is supplied from the side of the refrigerator and the counter-flow principle ensures the most complete recovery. The residence time of boats with a charge in each temperature zone is 1 hour, *i.e.*, the restoration process is carried out in 2 hours.

Grinding of the Sponge Iron. The resulting iron sponge (Fig. 9) is subjected to grinding in a ball mill for 2 hours.

After grinding, the powder is sieved through a 60-mesh sieve. Coarse fractions of the powder are returned to the initial cycle for
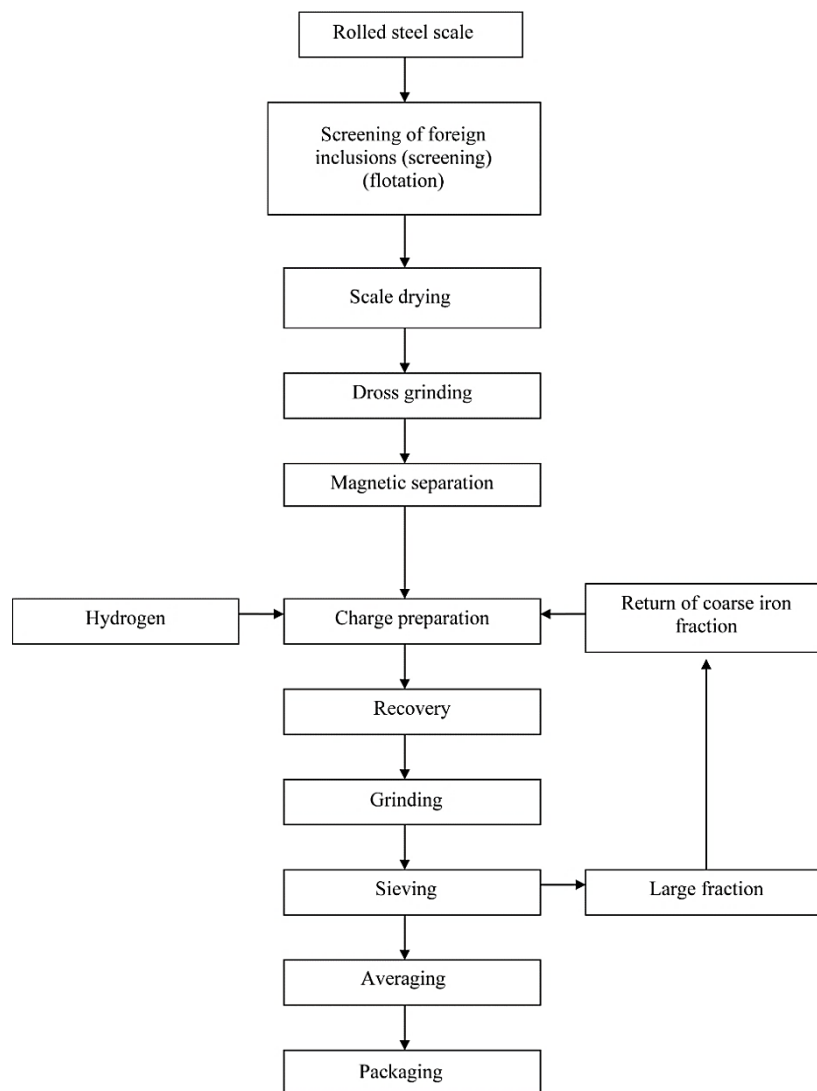
Fig. 10. Technological scheme for obtaining iron powders from the scale of the Uzmetkombinat.

batching the scale.

The technological scheme for obtaining iron powders from the scale of the APO Uzmetkombinat is shown in Fig. 10.

Composition and properties of iron powders. The iron powder obtained by this technology is α-Fe and has the chemical composition shown in Table 3. The results of studying the technological properties of iron powders are presented in Table 4.

TABLE 3. Iron powder chemical composition.

Element	Fe	Si	Al	Mg	Mn	Ba	Ti	Cr
Content, mass.%	98.9	0.3	0.1	0.01	0.2	0.009	0.001	0.05
Element	Zr	S	C	O_2	Ca	Ni	Co	other
Content, mass.%	0.001	0.03	0.05	0.2	0.008	0.1	0.04	0.15

TABLE 4. Technological properties of iron powders.

Particle size, mm	0.16−0.20	0.10−0.16	0.063−0.10	0.05−0.063	not less than 0.05
Grading, %	1.5	10−30	20−35	20−30	15−30
Bulk density, g/sm³	2.2−3.0				
Fluidity, s/50 g	40				
Compressibility at $P = 700$ MPa, g/sm³	6.5−7.0				

5. CONCLUSION

The modern methods of obtaining iron powders are considered, their classification is carried out, and analytical data of powders made from various types of raw materials are given.

The kinetic regularities of the reduction of iron oxides are analysed from the point of view of the adsorption−autocatalytic theory. The principles of reduction of mill scale with hydrogen are generalized, the influence of external factors on the reduction process is considered.

The structure and mechanical properties of iron powders are considered.

As concluded, regardless of the production method and raw materials, iron powders have different properties with the same chemical composition.

The morphology, structure, phase and elemental compositions of the mill scale of the Uzbek Metallurgical Combine are analysed. It is concluded that it is a powder of low alloy steels.

The dependence of the change in the phase composition of iron on the temperature and time of scale reduction is investigated. As a result, an optimal mode of obtaining iron powder was developed, the characteristics of which meet the GOST 9849-86 requirements.

The scale recovery technology has been developed, which includes the following stages: drying at 250−340°C, grinding in a ball mill for 2 hours, magnetic separation, sieving through a 40-mesh sieve, mixing the charge, recovery for 2 hours in H_2 at a temperature: I zone—650−700°C, II zone—950−1000°C.

REFERENCES

1. E. T. Denisenko, O. P. Kulik, and T. V. Yeremina, *Poroshkovaya Metallurgiya*, No. 4: 4 (1983) (in Russian).
2. S. S. Kiparisov and G. D. Libenson, *Poroshkovaya Metallurgiya* [Powder Metallurgy] (Moscow: Metallurgiya: 1980) (in Russian).
3. *Poroshkovaya Metallurgiya. Spechennyye Kompozitsionnyye Materialy* [Powder Metallurgy. Sintered Composite Materials] (Ed. V. Shatt) (Moscow: Metallurgiya: 1983) (Russian translation).
4. I. M. Fedorchenko and I. N. Frantsevich, *Poroshkovaya Metallurgiya. Materialy, Tekhnologiya, Svoistva, Oblasti Primeneniya: Spravochnik* [Powder Metallurgy. Materials, Technology, Properties, Applications: Handbook] (Kiev: Naukova Dumka: 1985) (in Russian).
5. F. Eizenkolb, *Uspekhi Poroshkovoi Metallurgii* [Advances in Powder Metallurgy] (Moscow: Metallurgiya: 1989) (Russian translation).
6. D. M. Karpinos, L. I. Tuchinskiy, and L. R. Vishnyakov, *Novyye Kompozitsionnyye Materialy* [New Composite Materials] (Kiev: Vishcha Shkola: 1977) (in Russian).
7. J. N. Dzneladze, R. P. Shchegoleva, L. G. Golubeva, E. M. Rabinovich, and B. A. Borok, *Poroshkovaya Metallurgiya Staley i Splavov* [Powder Metallurgy of Steels and Alloys] (Moscow: Metallurgiya: 1978) (in Russian).
8. V. V. Skorokhod, *Poroshkovaya Metallurgiya*, No. 10: 20 (1985) (in Russian).
9. P. G. Kurilov and V. M. Ribaulin, *Proizvodstva Konstruktsionnykh Izdeliy iz Poroshkov na Osnove Zheleza* [Manufacture of Structural Products from Iron-Based Powders] (Moscow: Metallurgiya: 1972) (in Russian).
10. *Novyye Protsessy i Materialy Poroshkovoy Metallurgii* [Technology of Metal Powders] (Ed. L. H. Yaverbaum) (Moscow: Metallurgiya: 1983) (Russian translation).
11. V. E. Perelman, *Formovanie Poroshkovykh Materialov* [Powder Materials' Forming] (Moscow: Metallurgiya: 1979) (in Russian).
12. V. B. Akimenko, V. Ya. Bulanov, V. E. Rukin et al., *Zheleznyye Poroshki* [Iron Powders] (Moscow: Nauka: 1982) (in Russian).
13. V. N. Antsiferov and V. V. Akimenko, *Spechennyye Legirovannyye Stali* [Sintered Alloyed Steels] (Moscow: Metallurgiya: 1988) (in Russian).
14. S. S. Yermakov and N. F. Vyaznikov, *Poroshkovyye Stali i Izdeliya* [Powder Steels and Products] (Leningrad: Mashinostroenie: 1990) (in Russian).
15. M. S. Kovalchenko, *Teoreticheskie Osnovy Goryachey Obrabotki Poristykh Materialov Davleniem* [Theoretical Foundations of Hot Pressure Treatment of Porous Materials] (Kiev: Naukova dumka: 1980) (in Russian).
16. V. A. Ivensen, *Kinetika Uplotneniya Metallicheskikh Poroshkov pri Spekanii* [Kinetics of Metal Powder Compaction during Sintering] (Moscow: Metallurgiya: 1971) (in Russian).
17. M. N. Fokin and Yu. V. Yemelyanov, *Zashchitnyye Pokritiya v Khimicheskoy Promyshlennosti* [Protective Coatings in the Chemical Industry] (Moscow: Khimiya: 1981) (in Russian).
18. N. N. Dorozhkin, T. M. Abramovich, and V. I. Zhornik, *Poluchenie Pokrytiy Metodom Pripekaniya* [Production of Coatings by Baking Method] (Minsk: Nauka i Tekhnika: 1980) (in Russian).
19. V. Yu. Bulanov and V. F. Ukhov, *Poluchenie Zheleznykh Poroshkov iz Prirodno-*

Legirovannogo Syr'ya [Production of Iron Powders from Natural Alloyed Raw Materials] (Moscow: Nauka: 1978) (in Russian).

20. I. D. Rodomyselskiy, *Poroshkovaya Metallurgiya*, No. 2: 32 (1979) (in Russian).
21. E. Ya. Popichenko and A. G. Bolshechenko, *Poroshkovaya Metallurgiya*, No. 2: 81 (1978) (in Russian).
22. A. M. Polyak and E. K. Sivaeva, *Izvestiya VUZov. Chernaya Metallurgiya*, **7**: 142 (1986) (in Russian).
23. Yu. S. Karabasov, *Fiziko-Khimiya Vosstanovleniya Zheleza iz Oksidov* [Chemistry of Iron Reduction from Oxides] (Moscow: Metallurgiya: 1986) (in Russian).
24. M. Peterdlik, V. Rubesh, I. D. Rodomyselskiy et al., *Poroshkovaya Metallurgiya*, No. **7**: 6 (1971) (in Russian).
25. V. V. Skorokhod, Yu. M. Solonin, and I. V. Uvarova, *Kineticheskie, Diffuzionnyye i Reologicheskie Protsessy v Tekhnologii Poroshkovykh Materialov* [Kinetic, Diffusion and Rheological Processes in Powder Technology] (Kiev: Naukova Dumka: 1990) (in Russian).
26. I. N. Frantsevich and V. I. Trefilov, *Poroshkovaya Metallurgiya v SSSR: Istoriya, Sovremennoye Sostoyanie, Perspektivy* [Powder Metallurgy in the USSR: History, Current State, Prospects] (Moscow: Nauka: 1986) (in Russian).
27. P. N. Ostrik, S. A. Artemenko, A. N. Popov et al., *Poroshkovaya Metallurgiya*, No. 12: 1 (1969) (in Russian).
28. R. A. Andrievskiy, *Poroshkovoye Materialovedenie* [Powder Materials Science] (Moscow: Nauka: 1991) (in Russian).
29. N. Z. Pozdnyak, *Apparaty i Tekhnologicheskoe Oborudovanie Poroshkovoi Metallurgii. Konstruktsionnyye Materialy i Oborudovanie* [Apparatuses and Technological Equipment of Powder Metallurgy. Structural Materials and Equipment] (Kiev: IPM AN UkrSSR: 1976), p. 124 (in Russian).
30. V. Gretchenko, A. F. Chumakov, and N. A. Roslavtsev, *Poroshkovaya Metallurgiya*, No. 2: 101 (1992) (in Russian).
31. G. M. Zhidomirov, A. G. Pelmennikov, N. K. Zhanpeisov, and A. G. Grebenyuk, *Kinetika i Kataliz*, **28**, No. 1: 86 (1987) (in Russian).
32. G. M. Zhidomirov and I. D. Mikheykin, *Itogi Nauki i Tekhniki. Ser. Stroenie Molekul i Khimicheskaya Svyaz* [Results of Science and Technology. Ser. Molecular Structure and Chemical Bond] (Moscow: VINITI: 1984), vol. **9** (in Russian).
33. *Sovremennyye Problemy Poroshkovoy Metallurgii* [Modern Problems of Powder Metallurgy] (Kiev: Naukova Dumka: 1970), p. 21 (in Russian).
34. H. Remy, *Kurs Neorganicheskoy Khimii* [Treatise on Inorganic Chemistry] (Moscow: Mir: 1971) (Russian translation).
35. Kh. M. Mamarakhimov and Sh. M. Shakirov, *Kompozitsionnyye Materiali*, **2**: 55 (2007) (in Russian).
36. R. U. Kalamazov, Kh. M. Mamarakhimov, Sh. M. Shakirov, and F. R. Turaev, *Vestnik. Tashkent GTU*, **3**: 94 (2004) (in Russian).
37. H. Youssef and M. Eudier, *Production and Properties of a New Porous Bearing. Friction and Antifriction Materials* (NewYork–London: Plenum Press: 1970), p. 291.
38. Kh. M. Mamarakhimov, *Vestnik. Tashkent GTU*, **4**: 56 (2007) (in Russian).
39. Kh. M. Mamarakhimov, *Tekhnika i Tekhnologiya*, **5**: 66 (2007) (in Russian).
40. C. Herring, *J. Appl. Phys.*, **2**, No. 5: 437 (1970).
41. Kh. M. Mamarakhimov and A. K. Dzhuraev, *Vestnik. Tashkent GTU*, **2**: 66 (2009) (in Russian).