RISK FACTORS AND CRITERIA OF FIRE AND EXPLOSION HAZARD AT FERROALLOYS GRINDING*

AE .M ARCHENKO

E.O. Paton Electric Welding Institute of the NAS of Ukraine
11 Kazimir Malevich Str., 03150, Kyiv, Ukraine. E-mail: office@paton.kiev.ua

Considered are the main indices, characterizing the fire and explosion hazard of products of grinding of ferroallys, applied in electrode technology. The effect of grinder type on behaviour of ferroalloy powders is noted, and comparative evaluation of industrial installations used in electrode production, is given. A conclusion is made about the need for regular certification of each specific technology of ferroalloys grinding. 11 Ref., 4 Tables, 3 Figures.

K e y w o r d s : welding production, fire and explosion hazard, electrode technology, ferroalloys grinding, manufacturing quality, technology certification

General information about explosion hazard of metallic powders. Grinding, screening and transportation of grinding products is accompanied by the formation of explosive aerosol suspensions and combustible deposits. Their inflammation and explosions inside the grinding and mixing equipment, in the pneumatic conveyor and aspiration systems, fans and bag filters repeatedly resulted in destructions, injuries and death of personnel. The inflammations and explosions were caused by thermal sources, as well as by local fires, provoked by warming up from a mechanical effect or by sparking of triboelectric nature.

In the process of explosion development, as a rule, dust participates, swirled from the surface of the equipment and building structures, as well as inside the ventilation systems.

Pieces of material in the initial stage of grinding are destroyed under the combined action of crushing and impact, and at the stage of fine grinding, under the impact combined with abrasion. The total energy of grinding E_{gr} is spent for elastic and plastic deformation of grains $a_{def}\Delta V$, for heating Q, as well as for destruction of particles with the formation of a new surface $s\Delta S$:

$$E_{gr} = a_{def}\Delta V + s\Delta S + Q,$$

where a_{def} is the energy of elastic and plastic deformation per a unit of volume of a solid body; s is the specific surface energy; ΔV is the deformed part of the volume of the material being grinded; ΔS is the increment of the material surface as a result of the grinding process.

The surface increment during a coarse grinding is negligible and the energy consumption for destruction is considered to be proportional to the volume of the body being destroyed. During fine grinding, the consumption of energy for the growth of a newly formed surface prevails. The ratio of the components of power consumption for grinding depends on the type of milling equipment, as well as on the mill set.

The potential fire and explosion hazard of the process of ferroalloy grinding depends on its physical

Table 1 Values of temperature of beginning of the exothermic reaction $T_{s.e}$ of powders of ferroalloys fraction of 0–40 μm [1]

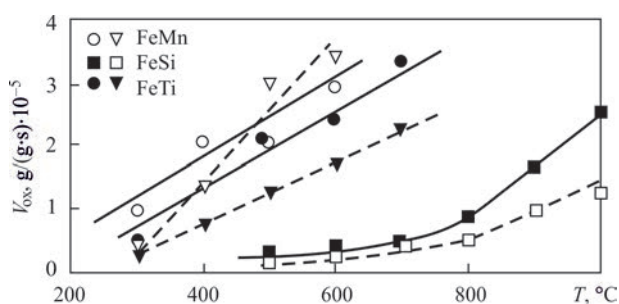| Ferroalloy	Grinding method	$T_{s.e}$, °C
Ferromanganese	Grinding	200
	Vibration milling	140
Ferrotitanium	Grinding	220
	Vibration milling	180
Ferrosilicium	Grinding	450
	Vibration milling	450

Figure 1 Effect of temperature on oxidation rate in the air environment of particles of ferroalloys with a size of 0–40 μm, sieved from powders produced by vibrating milling (solid curve) and grinding (dashed) [1]

---

*Retrospective review on the materials published in small editions and sources of non-welding profile.
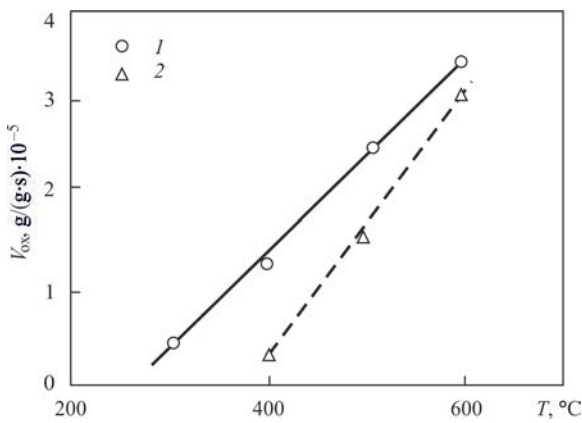
Figure 2 Effect of temperature on oxidation rate of ferromanganese particles of the size of 0–50 μm (*1*) and 0–100 μm (*2*) sieved from powders produced by grinding in the PALLA mill [1]

and chemical properties, as well as on the type and modes of operation of the grinding equipment.

Ferroalloys differ in their grinding capability, therefore, the powders of various ferroalloys produced using the same grinder differ in dispersity, as well as fire and explosion hazard. The same can be said about the powders of the same ferroalloy, produced using different grinders.

The fire and explosion hazard of the technology of ferroalloys grinding is evaluated according to the procedure, which provides a laboratory and production stage [1].

At the laboratory stage, the chemical composition, dispersion, kinetic indicators of powder oxidation, state of particles surface, as well as the characteristics of flammability and explosiveness, first of all of the most active dust fractions evolved from them, are determined.

At the production stage, the powders of ferroalloys for electrode coatings, produced under industrial conditions in different grinding installations, are tested. The flammability and explosiveness of powders, their dust fractions (smaller than 50 μm), the samples of

which are taken from the aspirated gas (air) of the aspiration systems and from the dust deposits on building structures and technological equipment, are also investigated.

To characterize the fire and explosion hazard of grinding products, the following indicators are used [2–5].

Kinetic parameters of powder oxidation in the pre-inflammation period of heating: the temperature of the start of exothermic process $T_{s.e}$ and the oxidation rate V_{ox}.

Self-inflammation temperature is the lowest ambient temperature at which self-inflammation of sample is observed in the layer and in suspended state ($T_{s.ig}$, $T_{s.inf}$, °C). This indicator is found by introducing a certain mass of a substance into a vessel, heated to a stepwise rising temperature, and determining its minimum value at which self-inflammation occurs.

Lower flammability concentration limit (LFCL, g/m^3) and flame spreading (LCLS g/m^3) is the minimum content of a combustible substance in a homogeneous mixture with an oxidizing environment, at which the inflammation and spreading of the resulting flame through the mixture at any distance from the inflammation source is possible.

Maximum safe oxygen concentration in a gas environment, at which the inflammation of a substance and the flame spreading occur (MSOC, %).

Inflammation temperature of aerosol is the minimum temperature of an external source (usually a heated surface) at which the aerosol is inflamed (T_{inf}, °C).

During testing, aerosol of a certain concentration is brought into contact with a heated surface. For each concentration, the minimum inflammation temperature is determined, and then as the inflammation

Table 2 Indicators of pyrophornity and explosibility of powders of ferroalloys, used in the technology of electrode production [7]

Material	Powder in layer			Aerosol				
	Fraction share −005 %	$T_{s.ig}$, °C	T_{ig}, °C	T_{inf}, °C	LFCL, g/m^3	P_{max}, MPa	V_{max}, MPa/s	MSOC, vol.%
Ferromanganese FMn-92	12.5[1]	–	–	–	260	0.15	3.0	12.3
	100.0[2]	–	550	–	76	0.32	5.0	7.8
	100.0[3]	–	–	–	74	0.38	20.0	–
Ferrosilicon Fs = 45	17.0[1]	It is not inflamed by thermal (up to 1100 °C)						
	100.0[2]	and pyrotechnical source of ignition (burning temperature is 2500 °C)						
Ferrotitanium Ft =30	14.5[1]	–	–	–	430	0.10	0.9	15.8
	95.0[2]	400	530	370	90	0.37	8.0	10.0
	100.0[3]	–	–	–	82	0.36	12.0	12.0
Manganese metal, d_{av} = 44 μm		240	450	–	130	0.33	3.0	–
Silicom metal, d_{av} = 74 μm		790	700	55	100	5.80	8.4	11.0

temperature, the lowest of these values is accepted at different concentrations.

The maximum explosion pressure is P_{max}, MPa, which represents the highest excessive pressure, occurring during the so-called deflagration, i.e. homogeneous, combustion of the dust-air mixture in a closed vessel at an initial atmospheric pressure of the mixture of 101.3 kPa. To determine P_{max}, the dust-air mixture of the preset composition is ignited in the volume of a reaction vessel and an excessive pressure is recorded, which is developing when the combustible mixture ignites. Changing the concentration of fuel in the mixture, the maximum value is chosen from the obtained results.

Rate of explosion pressure increment V_{max}, MPa·s^{-1} is the derivative of the explosion pressure over time in the ascending region of the dependence of the explosion pressure of the combustible mixture on time. The principle of method of its evaluation is the experimental determination of maximum explosion pressure of a combustible mixture in a closed vessel, construction of a diagram of change in the explosion pressure over time and calculation of average and maximum speed using known formulas [3].

When categorizing the production grinding installations, the requirements of PUE7 are also taken into account [6].

Comparison of the kinetic parameters of the ferroalloy oxidation. Ferromanganese FMn 92, ferrotitanium FTi 30 and ferrosilicon FSi 45, which are used as deoxidizers of deposited metal, belong to alloys with a low activation energy. The tendency of their powders to oxidation in the pre-inflammation heating period (from 300 to 600, 700, and 1000 °C, respectively) is estimated from the values of $T_{s.e}$ and V_{ox}, obtained by the DTA method. The fractions with a particle size of 0–40 μm were investigated, which evolved by screening of powders produced by crushing and vibration grinding in laboratory installations. The heating rate of a sample in the DTA definitions amounted to 10 °C·min^{-1}. The oxidation rate was determined by graphical differentiation of DTA- and DTG-diagrams at a preset temperature of material heating.

The results of $T_{s.e}$ determination are presented in Table 1, and the dependence of their oxidation rate on temperature is shown in Figure 1.

From the abovementioned data it follows that the studied ferroalloys differ in their resistance to oxidation during the period of pre-inflammation heating. The process of ferromanganese oxidation, the most active among the tested ferroalloys, begins at the lowest temperature. Ferrosilicon is the most resistant to oxidation. Ferrotitanium takes intermediate position.
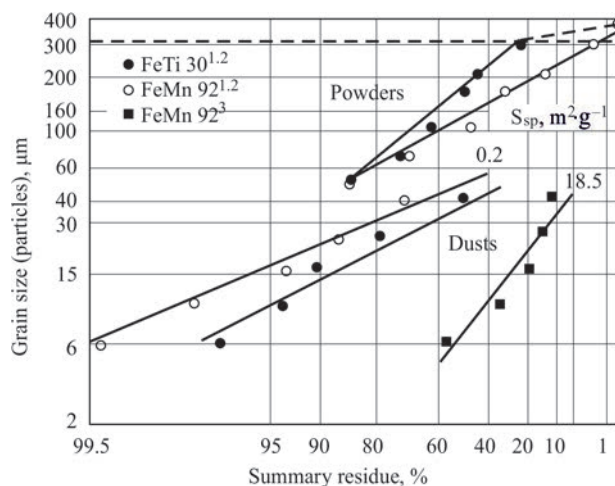

Figure 3 Grain compositions of powders of ferromanganese, ferrotitanium (*1*), dust deposits of ferromanganese in the air ducts of grinding installation (*2*) and dust fractions sieved from powders (*3*) of ferromanganese and ferrotitanium [7]

It is characteristic, that ferromanganese and ferrotitanium powders, produced by vibrating grinding, are more active than powders crushed by grinding. At the same time, the methods of ferrosilicon grinding do not affect the values of the temperatures of the exothermic reaction beginning.

With increase in temperature, the rate of oxidation is growing. Moreover, for ferromanganese powders it is so intensive, that when the inflammation temperature is reached, the crushed particles become more active than those produced by vibration grinding. The oxidation rate of ferrotitanium particles is growing with a rise in temperature to a lesser extent, and that of ferrosilicon particles is growing even more slowly. Moreover, their dust particles retain activity which is lower than that of their vibration grinded analogues throughout the whole pre-inflammation period.

Alongside with the powders prepared in laboratory conditions, at the MISiS [1], the samples were

Table 3 Effect of grinder type on indicators of fire and explosion hazard of powders [1, 8]

Ferroalloy	Fraction, μm	LFCL, g/m^3	$T_{s.ig}$, °C	T_{int}, °C
Laboratory ball mill*				
Ferromanganese	0–50	69	370	350
	50–100	106	540	420
Ferrosilicon	0–50	n.v	n.v	n.v
Ferrotitanium	0–50	n.v	590	470
	50–100	n.v	635	450
Laboratory disintegrator D95*				
Ferromanganese	0–50	190	600	450
	50–100	n.v	790	550
	Polydispersed	280	630	470
Ferrotitanium	0–50	n.v	n.v	n.v
	50–100	n.v	n.v	n.v
*Inert mixture of argon with air.				

Table 4 Specified characteristics of fire hazard of powders of ferroalloys, produced in grinding installations in electrode production

Ferroalloy (and additive, 5 %)	Medium	Holding, days[*]	Fraction, µm	LFCL, g·mm^{-3}	$T_{s.ig}$, °C	T_{inf}, °C
Slotted ball mill						
Ferromanganese (marble 15)	Air	3	0–50	740	430	620
			Polydispersed	n.v[*]	460	760
Ferrotitanium (marble 7)			0–50	n.v	740	520
			Polydispersed	n.v	930	590
Ferromanganese (magnesite 10)	Nitrogen (92 %)	10	0–50	n.v	430	760
			Polydispersed	n.v	450	780
Ferrotitanium (marble 10)		–	0–50	740	420	600
			Polydispersed	n.v	850	640
Vibration rod mill						
Ferromanganese FMn 92	Nitrogen (92 %)	7	0–50	690	420	510
			Polydispersed	760	460	570
Ferrosilicon Fs 45			0–50	n.v	620	n.v
			Polydispersed	n.v	790	n.v
Ferrotitanium FTi30			0–50	n.v	710	520
			Polydispersed	n.v	870	610

[*]In accordance with plant technology to brake the chemical interaction with liquid glass in coating.
[**]n.v — value of LFCL exceeds 1000 g/m^3, and T_{inf} exceeds 1000 °C.

investigated, taken during grinding of ferroalloys in industrial vibratory mills PALLA. The fractions with a particles size of 0–50 and 0–100 µm were investigated. The results of investigations of ferromanganese powders are shown in Figure 2. They correlate with the abovementioned data, which characterize the kinetics of oxidation of dust particles of this ferroalloy, which were produced in grinders of a laboratory type. Indeed, a coarse disperse sample, as well as its laboratory analogue, is less active; therefore, it begins to oxidize noticeably at a higher temperature than the fine disperse one. With rise in temperature, the rate of its oxidation increases steeper.

Comparing Figures 1 and 2, it is seen that the increase in the oxidation rate of particles of 0–40 µm in size, caused by heating, which are taken from ferromanganese powders grinded in the laboratory, is the same as of the particles of 0–50 µm in size, taken from the powder produced in the industrial mill PALLA. Fractions with a particle size of 0–100 and 0–50 µm from the powders produced in the mill PALLA, as to oxidative ability, are qualitatively related to each other in the same way as the particles similar in size, which are taken from the powders produced by grinding and, accordingly, vibrating milling in laboratory installations.

By the nature of change in the relative position and inclination angle of the compared curves relative to the temperature scale, it may seem that the size of the particles affects their oxidation capacity more than the activation of their surface by vibration grinding, which should have occurred. Since the compared ferroalloys differ in density, the oxidation rate of the powders should be normalized, in our opinion, by the specific volume surface of particles, but not by the mass of the sample.

Regulatory characteristics of fire and explosion hazard of ferroalloys, established in laboratory conditions. The values of the pyrophoric and explosive indicators of the powders of ferromanganese, ferrosilicon and ferrotitanium are given according to the data of IPMS of the NAS of Ukraine in Table 2. For comparison, it also includes indicators of powders of metallic manganese and silicon.

The grain characteristics of the used powders of ferromanganese and ferrotitanium are compared in Figure 3.

Indexation of samples accepted in Table and in Figure 2 is the following: 1 — polydispersed powders of studied ferroalloys; 2 — fractions with particles sizes of less than 50 µm, screened from polydispersed powders; 3 — dust deposits in the air duct; d_{av} is the average weighted diameter of particles.

The mentioned data show that ferrosilicon powders are characterized by the highest resistance against inflammation and explosions. They are not ignited either by heat or pyrotechnic source of inflammation, neither in a layer, nor in a state of aerosol.

Ferromanganese and ferrotitanium powders in the layer are characterized by approximately the same values of T_{ig}. However, in the state of air suspension they differ significantly. Thus, with an increase in the share of tiny particles from 15 to 100 %, for ferrotitanium powder the values of LFCL (initially about 2 times higher than that of ferromanganese), almost 5 times decrease, and that of ferromanganese, only 3 times. At the same time, the MSOC value of the compared objects decreases only 1.5 times.

The explosion pressure of the aerosol of ferrotitanium and ferromanganese powders and especially the rate of increment of pressure during an explosion is changed at the same increase in the degree of dispersion to a much higher level. Thus, the value P_{max} of the compared ferroalloys in the state of aerosol increases by 2.5–3.0 times. Similarly, the value of the aerosol V_{max} of ferromanganese increases (from 3 to 5 MPa/s). At the same time, V_{max} of aerosol of ferrotitanium increases by 10 times (from 0.9 to 8 MPa/s).

From the point of view of increase in the V_{max} indicator, the role of dust particles in the composition of the depositions, the samples of which were taken for testing in the air duct, is especially dangerous As follows from the Table 2, the values of V_{max} of deposits of aerosol are 4 times, and those of ferrotitanium are 1.5 times higher than those of aerosols of under-sieve fractions of polydisperse powders of these ferroalloys.

Effect of type of grinder on fire explosion hazard of ferroalloy powders. In the works [1, 8], fire and explosion hazard of powders produced by dispersing the ferromanganese, ferrosilicon and ferrotitanium in a ball mill and a disintegrator of laboratory type D95 with shielding gas environment was considered. From the manufactured powders, two fractions (0–50 and 0–100 μm) were selected and tested. For comparison, a ferromanganese powder of polydispersed composition, made in the disintegrator D95, was used. The results of investigations are summarized in Table 3.

The given data show that the powders of compared fractions produced by grinding in a disintegrator are less active than in a ball mill. This is explained by their greater oxidation due to a higher energy of the grinding process in the disintegrator. With the increase in the share of large particles, the fire and explosion hazard of the powders of all the tested ferroalloys decreases.

From the results of studies of the dust fraction evolved from ferromanganese powders, MISiS [5] ranked the used laboratory grinding units according to LCLS as follows: KID (280), disintegrator D35 (190), ball mills ShB of drum type (70) and of vibration type VM (50 g·m⁻³).

Comparative evaluation of industrial grinding installations used in electrode production. The general situation with preparation of ferroalloy powders, as well as actual values of their fire and explosion hazard indicators achieved in the technology of welding electrodes production can be characterized by the data given in the works [5, 8, 9]:

● extensive range of grinders types (chamber, bypass, slot-hole and vibratory ball and rod mills, as well as roller, hammer and cone crushers);

● variety of grinding schemes (with an inert additive, in a controlled gas or water environment);

● variety of ways of taking the target product (screening, continuous sieving together with screening, separation or centrifugation);

● different methods of interoperational transport of the finished powder in the technological cycle (Kibble, pneumatic transport, etc.).

The simplest and often a quite reliable technique for preventing explosion hazard situations during fine grinding of ferroalloys in batch mills is the loading of the so-called inert additive into the grinding chamber together with pieces of ferroalloy. This product can be any of the ore mineral components of the coating, added in the amount of at least 8 % of the mass of the ferroalloy being grinded. Even with this variant of grinding, to prevent the explosion, the mill can be depressurized only after a preliminary exposure for at least 15 min from the moment of stopping to guarantee the dust deposition.

Nowadays, mainly mills of continuous action are used, providing a high efficiency of the process and operating per pass with continuous sieving of the crushed product or its subsequent screening. In these mills, grinding is realized mainly in shielding gas media and the scheme and modes of supplying shielding gas (nitrogen or carbon dioxide with a regulated oxygen concentration) are selected taking into account:

● chemical activity of grinded ferroalloy;

● their dispersion in a grinded state;

● design of grinding installation, including the possibility of sealing the mill housing, as well as the path of the further movement of the finished powder outside its borders;

● design features of aspiration suctions, as well as opportunities of optimizing their aerodynamic interactions with the protective environment in order to maintain the partial pressure of oxygen in the protective atmosphere of the grinder at a preset level, necessary for the formation of a phlegmatizing oxide film on the newly formed surface.

In this regard, the characteristics of fire and explosion hazard of industrial powders of ferroalloys produced by different electrode making enterprises vary within fairly wide limits (Table 4). Evaluating them, it can be concluded that the powders produced in laboratory installations have a higher fire and explosion hazard than those produced in industrial installations.

Despite a fairly high degree of oxidation of the surface of particles, they, nevertheless, retain the ability to burn and explode. Especially ferromanganese powders, the LCLS values of which do not reach 1000 g·m⁻³, and $T_{s.ig}$ and T_{inf} of polydispersed powders are 460 and 570 °C, even if they are produced

in a protective medium of the necessary condition. Particularly dangerous are the fractions of industrial powders smaller than 50 μm. From Table 4 it follows that the LCLS values of this fraction are 690 g·m^{-3}, and $T_{s.ig}$ and T_{inf}. are 420 and 510 °C, respectively. The efficiency of inert additive is low because it is more easily grinded and leaves the slotted mill chamber faster than the particles of ferroalloy powder.

Somewhat more passive are ferrotitanium powders of the same fraction, the value of LCLS of which exceeds 1000 °C, and $T_{s.ig}$ and T_{inf} is 710 and 520 °C, respectively.

Explosions of ferroalloy aerosol particles, occurring in grinding equipment with the participation of combustible gases, represent a particular danger [9].

Hydrogen evolved from the grinded ferroalloy together with hydrogen, acetylene, methane, arsenites and phosphines, formed as a result of interaction of alloys with moisture, which for any reason got to the grinding chamber, significantly decrease LCLS and MSOC, and also increase P_{max} and V_{max} of aerosols. It was established, that to reach an explosive hazard of the hydrogen concentration, which is accumulated in the grinding chamber as a result of desorption from ferroalloy particles and their interaction with moisture, it may take no more than 1 min [9]. In such conditions, the required efficiency of quick response of emergency gas analysis systems and timely blocking of equipment operation is not achieved.

Additional danger is represented by microparticles (satellites), which, accumulating on the surface of coarser ferroalloy grains, increase their specific surface. As a result, the value of LCLS of polydispersed powders may decrease by 1.5–2.0 times. In order to prevent the adverse effect of this factor, phlegmatizing additives of bonding and enveloping liquids are injected into the grinding equipment. They agglomerate microparticles into larger aggregates covered with a protective film of a chemically inert liquid [8, 10, 11]. On the example of ferromanganese powder, vibro-crushed for 3 h, it is shown that the fraction of free particles with a size smaller than 40 μm can be 5 times reduced in it, and its LCLS density — by 3 times [10].

The abovementioned results show that the fire and explosion hazard of each ferroalloy powder used in electrode technology should be determined for each type of grinding equipment, its operation mode, sampling place, as well as technological methods used to prevent inflammations and explosions. In other words, regular certification of each specific technology of grinding ferroalloys is necessary, just as it is done in the technology of welding production in order to regularly confirm the quality of manufactured products.

1. Toleshov, A.K. (2009) Method of evaluation of fire and explosion hazard of production processes of metal and alloy powders. *Metallurg*, **6**, 30–33 [in Russian].
2. Nedin, V.V., Nejkov, O.D., Alekseev, A.G. et al. (1971) *Fire hazard of industrial powders*. Kiev, Naukova Dumka [in Russian].
3. *(1990) GOST 12.1.044–89 SSBT*: Fire and explosion hazard of substances and materials. Range of blast data and methods of their determination. Moscow, Standarty[in Russian].
4. Toleshov, A.K. (1995) Standard characteristics of fire and explosion hazard of ferroalloys powder made in electrode production. *Metallurg*, **4**, 19–21 [in Russian].
5. Babajtsev, I.V., Toleshov, A.K., Derzhavets, A.A. (1995) Evaluation of inflammability of powders of metals and alloys. *Ibid*., **9**, 26–27 [in Russian].
6. *Rules of arrangement of electric units PUE7* [in Russian].
7. Nejkov, O.D., Vasilieva, G.D., Kuzub, A.P. et al. et al. (1971) *Examination of explosibility of ferrosilicon, ferromanganese, ferrotitanium, ferrochrome, silicocalcium and manganese powders. Prevention of sudden explosions of gas-dispersed systems*. Kiev, Naukova Dumka, 36–44 [in Russian].
8. Gridin, A.A., Serebryakova, V.V., Babajtsev, I.V. et al. (1985) Study of disintegrator processes of dispersion and activation of explosion and fire hazardous ferroalloys. *Stal*, **11**, 36–37 [in Russian].
9. Strizhko, L.S., Babajtsev, I.V., Toleshov, A.K. (1998) Prevention of explosions in refining of ferroalloys. *Metallurg*, **9**, 27–28 [in Russian].
10. Babajtsev, I.V., Gerusova, V.P., Delyan, V.I. (1983) Passivation of powders of silicocalcium. *Izv. Vuzov. Chyorn. Metallurgiya*, **5**, 151–152 [in Russian].
11. Babajtsev, I.V., Toleshov, A.K., Shchepelev, A.V. (1996) Decrease of explosion hazard of ferroalloys powders during vibrogrinding. *Ibid.*, **1**, 73–74 [in Russian].