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GRAPHITE AS A PROSPECTIVE MATERIAL FOR METALLURGICAL APPLICATION

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ABSTRACT

2019 will mark the 85th anniversary of Krasnoyarskgrafit. Today, it is a production complex comprising an ore stock yard, a crushing circuit, an ore delivery tunnel, a milling plant with a kiln, a mill and vertical elevators; a production line for antipenetration coatings and other graphite products; a packaging line. The current assortment of Krasnoyarskgrafit's products includes cryptocrystalline graphite powder, sorbent agents, composite lubricants, leads, brushes, antifriction products, antipenetration coatings. The results of the research carried out by Krasnoyarskgrafit in cooperation with Siberian Federal University show that the optimum ratio between natural and activated graphite in antipenetration coatings is 50 : 50. Today, Krasnoyarskgrafit is a dynamically growing company that holds a firm market share as a producer of cryptocrystalline graphite and products made with it and that is constantly working on finding new operational formats and techniques.

The domestic foundry industry heavily relies on the use of carbon and carbon-bearing materials, which can be either manmade (e.g. coal cokes, charcoal, different grades of graphite) or of natural origin (e.g. graphite, different kinds of coal, including anthracite, heat-treated anthracite or thermoanthracite) [1].

Due to a unique combination of its physical, mechanical and chemical properties, graphite offers an important and singular material for many industries. Graphite is used in antipenetration and release coatings [2–4], graphite forms [5], crucibles [6], antifriction parts [7], etc. And natural cryptocrystalline graphite, which, compared with crystalline graphite and other kinds of graphite, has a lower price and higher thermal expansion ratio, resistance to thermal stresses, non-wettability with metals and slags and strength at high temperatures, helps obtain parts with enhanced properties [8–12].

Krasnoyarskgrafit is the only producer in Russia that makes cryptocrystalline graphite for ferrous metallurgy application and, in particular, for casting application. The site's current graphite production capacity is 15–20 thousand tons per year. Since 2002, the raw materials for graphite production have been supplied from the Kureyka deposit. The mining site is located in Svetlogorsk poselok of the Turukhansk area, 100 km from the point where the Kureyka river flows in the Yenisey. Before 2002, the ore was delivered from the underground mine of the Noginsk deposit situated on the Lower Tunguska river. The unique characteristic of these ores is that they contained up to 80% of carbon. Consequently, the obtained graphite requires no beneficiation, which significantly cuts the cost of such product compared with the other kinds of graphite.

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In its 85-year long history, the company went through ebb and flow, but the graphite production has never actually stopped. Due to the unique properties of graphite materials, steel makers can make products of excellent quality. They include rebars, pipes, rolled products, castings and so on. Also today, Krasnoyarskgrafit consistently supplies its products to foundries in Russia and the former Soviet Union republics. Krasnoyarskgrafit has supply contracts with steel makers from Lipetsk, Magnitogorsk, Nizhniy Tagil, Novokuznetsk, with Severstal, Friteks and others. The producer is constantly working on improving its customer relations and finding new operational formats and techniques [13].

The current assortment of Krasnoyarskgrafit's products includes cryptocrystalline graphite powder, sorbent agents, composite lubricants, leads, brushes, antifriction products, antipenetration coatings.

The GLS-3 and GLS-2 grades (**Fig. 1**) of natural graphite powder are produced by Krasnoyarskgrafit per GOST 52729-2009. The minimum carbon concentration in the graphite is 83%, the average particle size does not exceed 60 μm, as measured with the FRITSCH ANALYSETTE 22 MicroTec PLUS laser particle sizer.

The techniques to improve the quality of natural graphite: desulphurization, mechanical, chemical and chemo-mechanical activation were developed through collaboration with professor L. I. Mamina,

Table 1. **Relationship between elemental and phase composition of graphite and the preparation method**

Preparation Method	Ash Content,%	Chemical Element,%							Phase Composition
		Fe	S	Si	Al	Ca	K	Ti	
GLS-3 Graphite									
Primary	20–25	4.2	1.00	5.5	1.4	2.5	0.8	0.25	Quartz; calcite; pyrite; chalcopyrite; montmorillonite; kaolinite; greenalite
Mechano-thermochemical	4–6	1.5	0.90	6.0	1.9	1.0	0.3	0.20	Quartz
Microbiological	11–13	0.8	0.75	6.5	2.2	2.0	0.4	0.25	Quartz; whewellite; albite
Mechano-microbiological	6–12	0.5	0.85	7.7	0.9	1.5	0.5	0.25	Quartz; whewellite
Mechano-thermochemo-microbiological	3–5	0.5	0.80	7.0	0.9	3.7	0.4	0.29	Quartz
GLS-2 Graphite									
Primary	15–20	5.6	1.00	1.8	1.1	2.2	0.7	0.16	Quartz; calcite; iron sulphite; muscovite; kaolinite
Mechano-thermochemical	2–4	0.2	0.85	1.0	0.2	0.5	0.4	0.22	Quartz

Table 2. **Relationship between the sulphur concentration in the GLS-3 graphite and the desulphurization technique**

Activation Technique									Sulphur Content, %
Mechanical			Electric explosion pulse		Chemical				
					Air-steam		Oxidation Leaching		
Type of Activation Agent	Medium	Activation Time, min	Power (10–100 MW)	No. of Explosions	Temperature, °C	Soak Time, min	Oxidizer Content, %	Leaching Time, h	
Primary									1.00
AGO-2	Air	30	–	–	–	–	–	–	0.32
AGO-2	Water	30	–	–	–	–	–	–	0.26
DTsM	Air	8	–	–	–	–	–	–	0.36
D-100	Water	5	–	–	–	–	–	–	0.26
–	–	–	Medium	2	–	–	–	–	0.26
–	–	–	–	–	800	20	–	–	0.16
–	–	–	–	–	–	–	10	2	0.26
AGO-2	Air	30	–	–	800	20	–	–	0.05
AGO-2	Water	30	–	–	800	20	10	2	0.11
–	–	–	Medium	2	–	–	10	Instant.	0.21
AGO-2	Air	30	Medium	2	–	–	10	Instant.	0.16

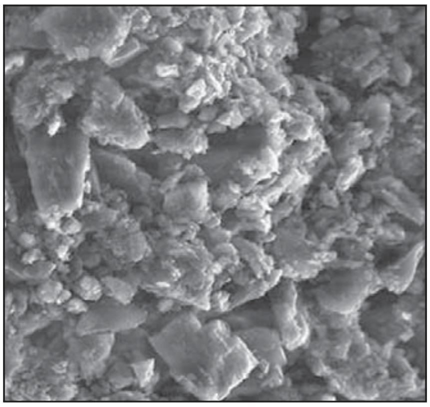

Fig. 1. Natural graphite

DSc (Eng.), from Siberian Federal University (**Table 1**) [14–17].

The quality of cast graphite is characterized not only with the ash content but also with the composition of the ash components. It is a fact that sulphur is the most harmful impurity that can be found in graphite. To reduce the concentration of sulphur, a number of desulphurization techniques was developed (**Table 2**).

The choice of the technique is dictated by the graphite's application. For example, to obtain high-quality graphite with a low sulphur concentration, one can use a mechano-thermo-chemo-microbiological technique, which helps reduce the ash content to 3–5%, followed by an air-steam processing,

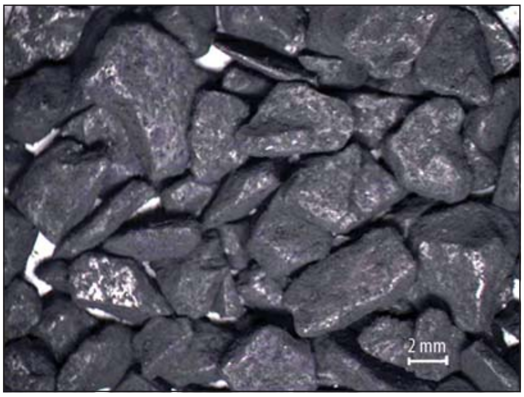

Fig. 2. Carburizer

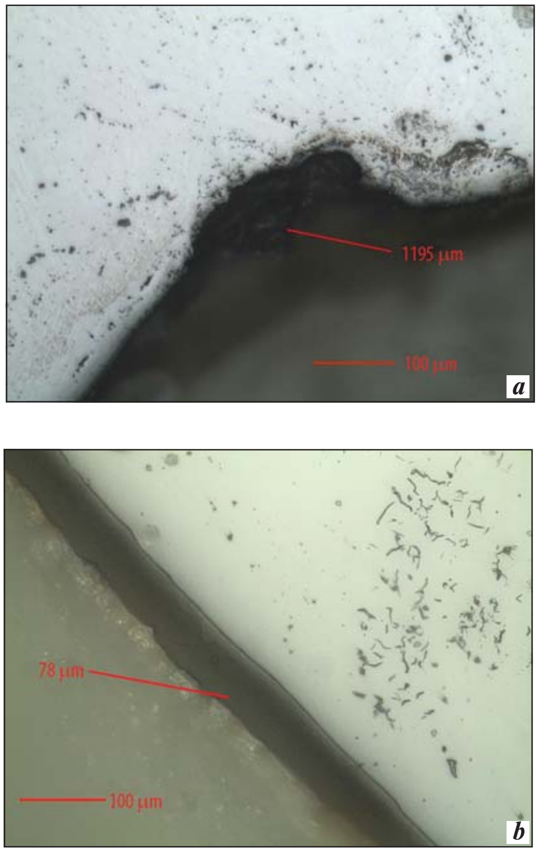

Fig. 3. Burn-ons on SCh20 iron castings.
Filler: *a* — natural graphite; *b* — activated graphite [18]

which helps bring the sulphur concentration down to 0.05%.

The use of concentrated and activated graphites does not only contribute to the properties of final graphite products, but such graphites can also be used to substitute costly materials, thus expanding the graphite's application scope. For example, concentrated and activated graphites have been successfully used in the production of lubricants, brushes, crucibles and other products meant for foundries.

L. I. Mamina passed away in 2013. But V. N. Baranov, A. I. Bezrukikh, E. M. Lesiv, T. R. Gilmanshina took over and continued research in this area.

Another product marketed by Krasnoyarskgrafit includes carburizers (**Fig. 2**). They contain at least 85% of carbon and have a size of 2–5 mm.

The advantages of the graphite carburizer include: its deep and full solubility in metal; low concentration of carbon powder in the working air during storage and utilization; no caking; no ashing during transportation; insoluble in water; resistant to acids; non-explosive.

Since 2017, Krasnoyarskgrafit has been operating a production line for aqueous and self-drying antipenetration coatings (**Table 3**). The production capacity is 4 t/y.

The above antipenetration coatings were successfully tested by foundries in Krasnoyarsk and Krasnoyarsk Krai. The results of the tests show that the coating made with activated graphite outperforms the graphite-bentonite coating in terms of processability and performance: the sedimentation stability of the developed coating is 1.5–2 times higher, the strength is 6–8 times higher, the consumption of dry ingredients is 30–40% lower, the burn-ons on iron castings of different weights are 70–85% less, and the roughness is reduced from Rz40 to Rz20 (**Fig. 3**).

Apart from aqueous antipenetration coatings, the line also produces self-drying coatings (**Fig. 4**).

Conclusions

The results of the research carried out by Krasnoyarskgrafit in cooperation with Siberian Federal University show that the optimum ratio between natural and activated graphite in antipenetration coatings is 50 : 50. The tests conducted at the foundry of the Repair and Maintenance Facility of the RUS-Engineering branch showed that the addition of pre-activated graphite leads to a reduced consumption of the filler and enhanced properties of coatings in solid and liquid states, prevents burn-ons, and reduces the surface roughness of the castings.

Table 3. **Properties of aqueous antipenetration coatings produced by Krasnoyarskgrafit**

Graphite, Activation Technique	Coating Properties		
	Viscosity, cSt	Equivalent Strength, kg/mm of Coating	Sedimentation Stability after 3 h,%
GLS-3(N):	7	1.94	75
Mechanical Activation (20 min)	15	3.48	90
Mechanical Activation (20 min) with surfactant:			
Carboxymethyl cellulose	54	22.27	100
CP lignosulfonate	52	25.10	100
Synthetic detergent	52	4.00	98
Water	62	8.98	100
Liquid glass	66	4.70	99
Ethyl silicate	68	5.00	99
Concentration	23	7.00	97
GLS-2(K):	7	0.34	75
Mechanical Activation (20 min)	13	4.50	97
Chemical Activation	15	5.00	98
Chemo-Mechanical Activation	18	27.20	100

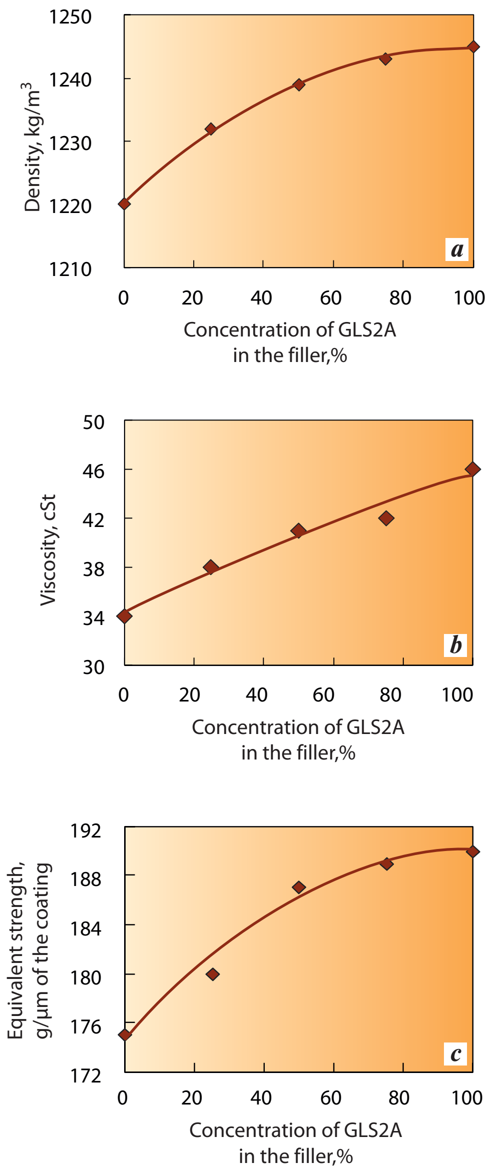

Fig. 4. Properties of self-drying antipenetration coatings:
a – density; *b* – viscosity; *c* – equivalent strength

Today, Krasnoyarskgrafit is a dynamically growing company that holds a firm market share as a producer of cryptocrystalline graphite and products made with it and that is constantly working on finding new operational formats and techniques. In other words, the company has great prospects in developing, implementing and producing products that are and will be in consistent demand and will substitute many of the materials used today.

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