MATERIALS PHYSICS AND MECHANICS RESEARCH ARTICLE

Submitted: October 18, 2025 **Revised: November 11, 2025** **Accepted: December 2, 2025**

Development of theoretical basics and experimental verification of progressive methods of graphite oxidation with simultaneous grinding

S.B. Kargin [1], V.G. Artiukh [2], D.A. Kitaeva [2] ✉, N.V. Korihin [2], A.I. Kruglov [2]

[1] Pryazovskyi State Technical University, Mariupol, Russia

[2] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

✉ dkitaeva@mail.ru

ABSTRACT

The first attempts of scientifically based analysis of grinding process belong to Rittinger and Kik. Results of theoretical and laboratory studies aimed to obtain finely dispersed graphite for manufacture of technological lubricants are presented. Modern very labor-intensive technology for grinding graphite is shown and its shortcomings are indicated. Theoretical analysis of possibility of changing graphite by progressive method of oxidative milling of graphite with help of hydrogen peroxide is given. Original method of laboratory research on oxidative grinding of graphite has been developed. Presented results of laboratory studies fully confirmed theoretical calculations that makes it possible to simplify process of obtaining colloidal graphite for technological lubricants. This eliminates operation of washing colloidal graphite from decomposition products of chromium mixture and sulfuric acid which takes place in manufacture of OGV lubricant.

KEYWORDS

graphite • grinding • acid medium • chromium mixture • lubricant • potassium bichromate • ammonia adsorption • hydrogen peroxide • cation-exchanger

Funding. *This work has been supported by the grant of the Russian Science Foundation, RSF 25-19-00921.*

Citation: Kargin SB, Artiukh VG, Kitaeva DA, Korihin NV, Kruglov AI. Development of theoretical basics and experimental verification of progressive methods of graphite oxidation with simultaneous grinding. *Materials Physics and Mechanics.* 2025;53(6): 44–52.
http://dx.doi.org/10.18149/MPM.5362025_4

Introduction

Graphite lubricants have become firmly established in practice of forging and stamping over past 20–30 years [1–3]. Main dispersion medium for them is water [4–6]. Degree of graphite grinding varies depending on severity of metal deformation conditions and it is in range of 1–30 μm [7–10]. Colloidal graphite in form of single dispersion has proven itself especially well for hot stamping [10–12]. Colloidal state is characterized by particle size of dispersed phase of less than 1 μm. Process of obtaining colloidal graphite is very laborious [13–15]. It should be noted that dispersion of graphite in water is mainly discussed when it is talked about modern lubricants used in stamping [16]. Gaseous products of oxidation which are formed in quantities (that are harmless to worker) are ideally meet requirements for lubrication of dies. Durability of die increases at least twice compared to its durability when lubricated with oils. There have been many publications on this topic since that time. Interest in grinding has especially increased due to sharp

expansion of production and consumption of powders and new technological possibilities for increasing their fineness [17–19].

Simple mechanical grinding of graphite does not lead to production of highly dispersed graphite. An obstacle is its ability to reverse process that is aggregation [20–22]. From our point of view, it is also necessary to chemically treat surface of particles in order to create polar groups of basic and acidic nature on them when crushing graphite. According to our observations, graphite (although quite strongly crushed by swelling (bulk density of 10 g/L) has an inert surface and therefore is not even wetted by water. It was enough to treat expanded graphite in acidic medium at pH = 10 with hydrogen peroxide for 10 h in cold environment so that graphite acquired hydrophilic character and ability to form stable aqueous suspension at 5 % concentration. Even better effect is obtained by oxidizing expanded graphite with chromium mixture.

Water-graphite lubricant OGV ('aquadag' type) is oxidized and crushed graphite with particle size of 1–2 μm in the form of 16–20 % aqueous suspension. Oxidation is carried out by strong oxidizing agent that is potassium bichromate in concentrated sulfuric acid. Aqueous graphite is stabilized with ammonia to pH = 10–11 and it is dispensed as finished lubricant after laborious operation of washing graphite from chromium salts and sulfuric acid. It is obvious that such lubricant can be practically ashless.

It must be assumed that surface of graphite particles in this case is dotted with carboxyl groups that is $COONY_4$ which can strongly decompose into ions: $COONY_4 \rightarrow COO^- + NH_4^+$, while negative charge remains on graphite particles value of which depends on depth of grinding and oxidation. Presence of negative charge on sufficiently small colloidal particles imparts stability of dispersion without additional stabilizer.

High lubricating properties of colloidal graphite are probably also associated with presence of polar groups on particle surface. Thanks to these groups, graphite acquires φ° ability to adsorb and even to chemically interact with the thinnest oxide film which is always present on surface of metal stamp [15,16,23]. Thus, graphite covers surface of stamp with even film that is well retained by chemisorption forces. The film is certainly destroyed when hot object touches this surface but graphite performs its separating function between metal and tool [24–27]. Moreover, graphite contributes to creation of gas cushion which enhances lubricating effect thanks to oxidizing due to oxygen of oxide film of workpiece [28–30].

Materials and Methods

Oxidative grinding of graphite using hydrogen peroxide

It has already been noted that oxidation and grinding of graphite during production of OGV lubricant is very laborious operation accompanied by production of toxic washing water when graphite is washed from chromium salts. Therefore, it is desirable to find out possibility of fine grinding of graphite in presence of "pure" oxidizing agent such as hydrogen peroxide or ozone. In case of positive result, it can be possible to get rid of washing operation and obtain finished products at the final stage by simply neutralizing crushed mass with ammonia.

Oxidizing ability of hydrogen peroxide, like any other oxidizing agent, is determined by normal potential φ°. Hydrogen peroxide accepts electrons from reducing agent (in acidic environment) according to equation: $H_2O_2 + 2H^+ + 2e = 2H_2O$ where $\varphi^{\circ} = 1.77$. Its oxidizing ability is lower in alkaline environment. Real potential can be kept equal to 1.77 by creating concentration of hydrogen ions equal to 1 g/L and concentration of peroxide equal to 1 mol/L, i.e. approximately 3–3.5 · 100 % solution. It was decided to carry out experiments on oxidative grinding at room temperature because grinding of graphite proceeds at ordinary temperature.

But what will be rate of oxidation reaction under these conditions? It will probably be close to zero. Where activation energy can be got from? There is only one hope left that is on active areas of graphite particles which are formed at moment of breaking bonds during crushing of larger particles.

Laboratory experiment on oxidative grinding of graphite was set up as follows. Metal rod 10 mm in diameter and 75 mm long was placed in glass conical flask with flat bottom. This rod with weight equal to 46 g was sealed inside glass tube. 40 g of graphite grade GS-1 by GOST 7022-76, 400 ml of distilled water, 4 g of concentrated phosphoric acid, and 5 ml of 33 % hydrogen peroxide were loaded into the flask. pH of aqueous pulp turned out to be equal to 1.6–1.7. The flask was placed on magnetic mixer and the rod was rotated at about 300 rpm. Grinding of graphite was carried out by friction of glass on glass. 5 ml of hydrogen peroxide was added to the flask every day. And thus, the mixer totally worked for 82 h. Sample was taken twice to determine nature of oxidation during oxidative grinding. The first sample was taken after 12 h of oxidation, the second one was taken after 65 h.

The sample was taken in the following way. The mixer was turned off, contents were allowed to stand for 5 min and upper dark layer was poured into a beaker. Contents of the beaker were allowed to settle overnight (18–20 h) and in the morning clear liquid returned to the grinding flask again. Precipitate of fine graphite in the beaker was thoroughly washed by centrifuge and test tubes until neutral reaction on universal indicator paper. The neutral sample was subjected to determination of oxidation nature.

Determination of nature of graphite oxidation

Moving equilibrium between solid phase and electrolyte solution was used to determine sign of charge of functional group of surface carbon atoms. If surface belong to hydroxyl groups and surface of particles has sign "+" then pH of aqueous phase shifts towards its increase when sodium chloride is added to graphite mixture:

$$R_{TB}OH + Na^+ + Cl^- \leftrightarrow RCl + Na^+ + OH^-. \quad (1)$$

When there are carboxyl groups on surface of graphite particles it results in pH of aqueous phase shifts to the lower side:

$$R_{TB} - COOH + Na^+ + Cl^- \leftrightarrow R - COONa + H^+ + Cl^-. \quad (2)$$

Thus, shift of pH value when sodium chloride solution is added to graphite suspension indicates nature of graphite oxidation.

Determination of pH shift of graphite suspension

After carefully washing out about 20 ml of graphite pulp its pH was determined on pH meter. pH of 5 % sodium chloride solution was determined in separate beaker. Then 2–3 ml of sodium chloride solution was poured into a cup with graphite pulp and pH meter electrodes lowered into it and pH of which was controlled. Pulp pH shift was noted. Experiments carried out with the first sample of graphite taken after 12 hours of oxidative milling showed upward shift of pH. Data is given in Table 1.

Table 1. Upward pH changes

pH graphite pulp	7.3
pH of NaCl solution	7.1
pH of pulp mixture and NaCl	8.2–8.4–8.5

Slowly (within 2 min) pH of solution increased while contents were mixed by gently shaking the glass. Experiments carried out with the second sample of graphite (taken after 65 h of oxidation and grinding) showed opposite picture where pH shift was obtained to a lower side. Results of experiment are given in Table 2.

Table 2. pH changes downward

pH graphite pulp	4.4
pH of NaCl solution	4.75
pH of pulp mixture and NaCl	3.8–3.7–3.6

It results in over time depth increase of graphite oxidation and surface carbocation atoms of graphite are transformed into carbanion ones. Presence of positive charge at nodal carbon atoms can be assumed due to benzene structure of six-membered graphite rings where carbon is in SP^2 hybridization.

Conjugation of P-electrons in benzene rings leads to their “contraction” to the center of the ring and, thus, electron density on nodal atoms that are common to two rings is depleted. Further oxidation leads to formation of carboxyl groups and graphite is converted into a cation-exchange substance. Schematically, this can be represented by following fragments in Fig. 1.

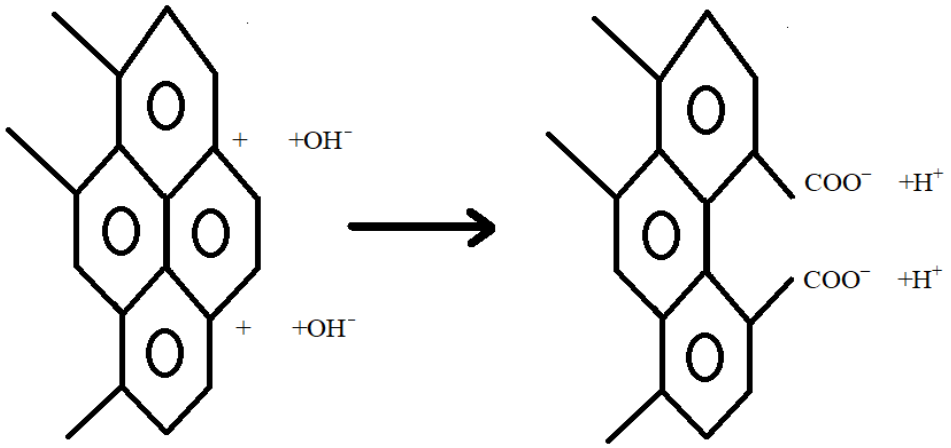

Fig. 1. Cation-exchange formation scheme

Determination of cation-exchange capacity of oxidizen graphite

Cation-exchange capacity was determined by method for determining capacity of ion exchange resins. Sample of graphite taken after 82 h of oxidative grinding (with weight equal to 1.212 g and pulp volume equal to 30 ml) was washed with hydrochloric acid and then with water until pH = 4.7. pH was measured in 5 % NaCl solution. It was equal to 4.5. Preliminarily, readings of pH meter were checked against standard buffer solution with pH = 6.86.

10 ml of sodium chloride was added to a cup with graphite pulp and lowered electrodes of pH meter. pH changed from 4.7 to 3.46 within 2 minutes. 0.100 N sodium hydroxide solution was added dropwise from the buret to the pulp. Results of titration are presented in Table 3.

Table 3. Results of titration

No	V_{NaOH}, ml	pH
1	0	3.46
2	0.2	4.0
3	0.3	4.4
4	0.4	5.0
5	0.5	5.8
6	0.6	6.8
7	0.7	7.4

Equivalent volume was taken to be equal to 0.5 ml. Pulp was washed twice with water, evaporated and dried in weighed beaker to determine mass of taken graphite. As a result, mass of graphite was equal to 1.212 g. Cation-exchange capacity of graphite Q was calculated by equation:

$$Q = \frac{V_{NaOH} \cdot N_{NaOH}}{m} = 0.041 \text{ mg·equal/g}, \quad (3)$$

where V_{NaOH} is volume of caustic soda used for titration, N_{NaOH} is normality of sodium hydroxide solution, m is mass of graphite.

Results of experiments convincingly indicate effect of oxidative grinding on quality of resulting material. Cation-exchange graphite with a clearly defined capacity is obtained as a result of oxidative grinding.

Results and Discussion

Calculations of state of oxidized graphite particles size and its maximum cation-exchange capacity

Main assumption. Maximum cation-exchange capacity will be if all corner and edge carbon atoms in graphite microcrystals contain carboxyl groups. One plane of graphite flake with scale of 1 Å: 1 cm can be taken. Carboxyl groups on extreme carbon atoms can be placed in Fig. 2:

1. Number of carboxyl groups is equal to number of units consisting of 4 C atoms along length of flake.
2. Along width, number of carboxyl groups is equal to twice number of units of 6 C atoms.
3. There are no carboxyl groups on the upper face of the flake.

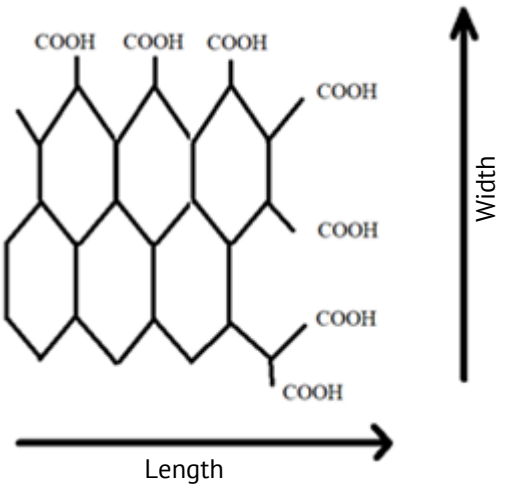

Fig. 2. Carboxyl groups

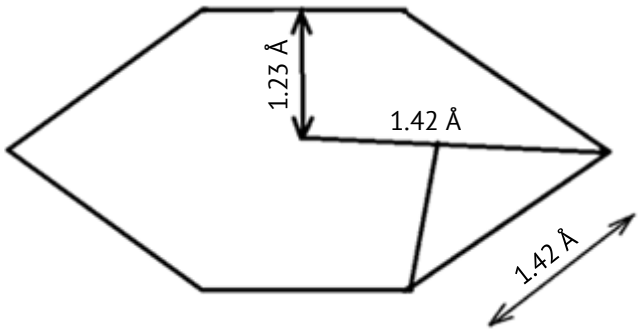

Fig. 3. Dimensions of six-membered ring of carbon atoms in graphite

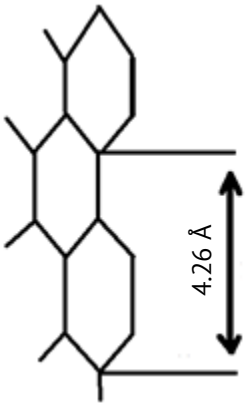

Fig. 4. Carboxyl groups

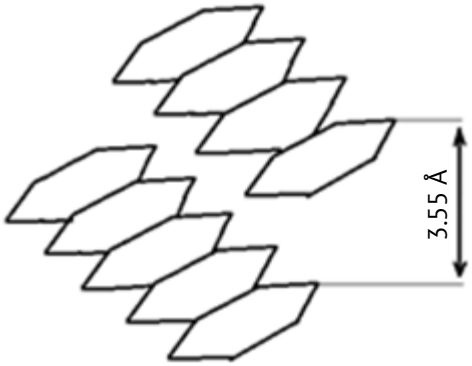

Fig. 5. Dimensions of six-membered ring of carbon atoms in graphite

Dimensions of six-membered ring of carbon atoms in graphite (Fig. 3) can be set to: length of C–C bond is 1.42 Å, width of six-membered ring is 2.46 Å. Distance between six-membered rings is 4.26 Å (Fig. 4). Fragment of graphite flake (Fig. 5) can be considered. Distance between planes in graphite is 3.55 Å. Calculations of ratio between carbon atoms and limiting number of carboxyl groups are described below.

The first case. Particle size is 0.1 μm that is equal to 1000 Å. Particle view can be set as cube for simplicity.

1. Number of links along the length = 1000 ÷ 2.46 = 406.
2. Number of links in width = 1000 ÷ 4.26 = 234.
3. Number of planes = 1000 ÷ 3.55 = 2.81.
4. Number of carbon atoms in plane: $406 \cdot 234 \cdot 6 = 5.7 \cdot 10^5$.
5. Number of carbon atoms in cube: $5.7 \cdot 10^5 \cdot 281 = 1.6 \cdot 10^8$.
6. Mass of atoms is $1.6 \cdot 10^8$ 12 = $1.92 \cdot 10^9$ amu.

Number of carboxyl groups:

1. Number of carboxyl groups in face along length and height is $406 \cdot 281 = 114086$.
2. Number of carboxyl groups in face along width and height is $234 \cdot 281 \cdot 2 = 131508$.

3. The total number of carboxyl groups is 114086·2 + 131508·2 = 491188.
4. Their mass is 491188·45 = $2.2 \cdot 10^7$ amu.
5. Cube weight is $1.92 \cdot 10^9 + 2.2 \cdot 10^7 = 1.94 \cdot 10^9$ amu.

It means that in $1.94 \cdot 10^9$ g of graphite there are $2.2 \cdot 10^7$ g of carboxyl groups. Carboxyl group equivalent is 45. Amount $2.2 \cdot 10^7$ can be converted into number of *r*-equivalents: $2.2 \cdot 10^7 \div 45 = 4.9 \cdot 10^5$. It is equal to $4.9 \cdot 10^8$ mg·equal. Proportion can be solved:

$$Q = X = \frac{4.9 \cdot 10^8}{1.94 \cdot 10^9} = 0.25 \text{ mg·equal/g}. \quad (4)$$

Similarly, for particle with size of 1 μm it can be got equal to 0.025 mg·equal.

The second case. Particle 2 μm long, 1 μm wide and 0.5 μm high can be taken. Cation-exchange capacity of 0.02 mg·equal/g can be obtained by repeating calculations. Calculation results for graphite particles of various sizes are summarized in Table 4. From Table 4 it follows that it is really possible to determine cation-exchange capacity of graphite only having particle size of less than 2 μm, i.e. almost practically for colloidal graphite. Cation-exchange capacity indicates the maximum particle size. Smaller particles provide obtained *Q* under condition of incomplete oxidation. So, if figure 0.04 was obtained in experiment to determine *Q* it means that particle size was no more than 1 μm. There may be smaller particles with lower degree of oxidation.

Table 4. Calculation results for graphite particles of various sizes

No	Particle size, μm, cube/plate	Capacity *Q*, mg·equal/g
1	0.1	0.25
2	0.05 × 0, 1 × 0.2	0.20
3	0.5	0.050
4	0.025 × 0, 5 × 1	0.040
5	1.0	0.025
6	0.5 × 1 × 2	0.020
7	2.0	0.012
8	1 × 2 × 4	0.01

Conclusions

1. Possibility of graphite oxidation with hydrogen peroxide of low concentration (0.3 – 0.4 %) at room temperature during its grinding has been proved.
2. Graphite acquires cation-exchange capacity due to formation of carboxyl groups on faces of colloidal particles.
3. Sample of colloidal graphite with cation-exchange capacity of 0.04 mg·equal/g was obtained after 82 h of oxidative grinding under laboratory conditions using magnetic stirrer.
4. Particle size of sample is estimated within limits not exceeding 1 μm using theoretical calculations.
5. These studies outline ways to simplify process of obtaining colloidal oxidized graphite by its oxidative grinding using “pure” oxidizing agents which are hydrogen peroxide and ozone. This eliminates operation of washing colloidal graphite from decomposition products of chromium mixture and sulfuric acid which takes place in manufacture of OGV lubricant.

CRediT authorship contribution statement

Sergey B. Kargin: writing – review & editing, original draft; **Viktor G. Artiukh**: investigation; **Daria A. Kitaeva**: data curation; **Nikolay V. Korihin**: data curation; **Adrei I. Kruglov**: data curation.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Rukhov A, Bakunin E, Dyachkova T, Rukhov A, Istomin A, Obraztsova E, Kornev A, Burakova E, Smirnova A, Usol'tseva N. Graphite nanoplates as grease lubricant additive. *Fullerenes Nanotubes and Carbon Nanostructures.* 2022;30(1): 167–170.
2. Kumar N, Saini V, Bijwe J. Tribological Investigations of Nano and Micro-Sized Graphite Particles as an Additive in Lithium-Based Grease. *Tribology Letters.* 2020;68(4): 124.
3. Kargin S, Artyukh V, Ignatovich I, Dikareva V. Development and Efficiency Assessment of Process Lubrication for Hot Forging. *IOP Conference Series: Earth and Environmental Science.* 2017;90: 012190.
4. Joerger A, Morstein C, Dienwiebel M, Albers A. A numerical approach for the determination of graphite deformation behaviour by using microtribological pressure tests. *Wear.* 2021;476: 203652.
5. Ota J, Hait SK, Sastry MIS, Ramakumar SSV. Graphene dispersion in hydrocarbon medium and its application in lubricant technology. *RSC Advances.* 2015;5(66): 53326–53332.
6. Gotzias A, Lazarou YG. Graphene Exfoliation in Binary NMP/Water Mixtures by Molecular Dynamics Simulations. *ChemPlusChem.* 2024;89(6): e202300758.
7. Chizhevsky VB, Fadeeva NV, Kuranov PV. Processes of secondary enrichment of graphite in the foam layer and the influence of reagents on them. *Mining informational and analytical bulletin (scientific and technical journal).* 2003;(8): 160–162. (In Russian)
8. Pereira K, Yue T, Abdel Wahab M. Multiscale analysis of the effect of roughness on fretting wear. *Tribology International.* 2017;110: 222–231.
9. Vodzianskiy V, Artiukh V, Kargin S, Soloveva E. Machining of bearing trunnions of rolls by heavy lathes in conditions of repair production. *IOP Conference Series: Materials Science and Engineering.* 2020;918: 012129.
10. Mohd Nasir NA, Nazmi N, Mohamad N, Ubaidillah U, Nordin NA, Mazlan SA, Abdul Aziz SA, Shabdin MK, Yunus NA. Rheological Performance of Magnetorheological Grease with Embedded Graphite Additives. *Materials.* 2021;14(17): 5091.
11. Popov EM. Research of possibility of the Rostov region hydrocarbon raw materials usage for creation and manufacture carbonaceous materials. *Mining informational and analytical bulletin (scientific and technical journal).* 2009;(S6): 330–333. (In Russian)
12. Snitko SA, Yakovchenko AV, Sotnikov AL. Influence of wheel billet stamping schemes on power modes of forming press operation and wear of the deformation tool. Izvestiya. *Ferrous Metallurgy.* 2018;61(5): 385–392. (In Russian)
13. Obraztsova EYu, Rukhov AV, Bakunin ES, Bubnova EV, Rukhov AnV, Al-Ameri SNM, Zhabkina IA, Goncharova MS. Methodology and equipment for kinetic studies of electrochemical exfoliation of graphite. *Transactions TSTU.* 2023;29(4): 666–676. (In Russian)
14. Kolobov MYu, Bratkov IV, Gushchina TV, Chagin OV. Energy and resource saving technology production of sferical graphite. *Modern science-intensive technologies. Regional application.* 2023;2(74): 79–87. (In Russian)
15. Stebeleva OP, Kashkina LV, Vshivkova OA, Minakov AV. Application of high-speed hydrodynamic technology for the production of graphene nanosuspensions from natural graphites. *Siberian Aerospace Journal.* 2024;25(4): 521–530. (In Russian)
16. Belov VV, Slukin EY. Protective lubricant material for hot metal forming. Russian Patent RU 2741047 C1, 22 January 2021. (In Russian)
17. Zhang J, Wang A, Yin H. Preparation of graphite nanosheets in different solvents by sand milling and their enhancement on tribological properties of lithium-based grease. *Chinese Journal of Chemical Engineering.* 2020;28(4): 1177–1186.

18. Rudaev YaI, Kitaeva DA, Kodzhaspirov GE. Superplasticity in bulk forming processes. In: Gubaidullin DA, Elizarov AI, Lipachev EK. (eds.) *Proceedings of the XI All-Russian Congress on Fundamental Problems of Theoretical and Applied Mechanics, 20–24 August, Kazan, Russia.* Kazan: Kazan Federal University; 2015. p. 3252-3254. (In Russian)
19. Ghanbari H, Shafikhani MA, Daryalaal M. Graphene nanosheets production using liquid-phase exfoliation of pre-milled graphite in dimethylformamide and structural defects evaluation. *Ceramics International.* 2019;45(16): 20051–20057.
20. Bragina VI, Baksheeva II. Development of graphite ore beneficiation. *Mining informational and analytical bulletin (scientific and technical journal).* 2012;(9):133–137. (In Russian)
21. Al-Saadi DAY, Pershin VF, Salimov BN, Montaev SA. Modification of graphite greases graphene nanostructures. *Journal of Friction and Wear.* 2017;38: 355–358.
22. Pape F, Poll G. Investigations on Graphene Platelets as Dry Lubricant and as Grease Additive for Sliding Contacts and Rolling Bearing Application. *Lubricants.* 2020;8(1): 3.
23. Nikitchenko A, Artiukh V, Shevchenko D, Larionov A, Zubareva I. Application of Nonlinear Dynamic Analysis for Calculation of Dynamics and Strength of Mechanical Systems. In: Murgul V, Pasetti M. (eds.) *International Scientific Conference Energy Management of Municipal Facilities and Sustainable Energy Technologies (EMMFT 2018). Advances in Intelligent Systems and Computing, vol 983.* Cham: Springer; 2019. p. 496–510.
24. Solomonov KN. Application of CAD/CAM systems for computer simulation of metal forming processes. *Materials Science Forum.* 2012;704–705: 434–439.
25. Burlakov VI, Artiukh VG, Kitaeva DA, Korihin NV. Machinability of nitride ceramics with abrasive powders and their addition to diamond powder. *Materials Physics and Mechanics.* 2025;53(4): 99–110.
26. Gozbenko VE, Korchevin NA, Kargapoltsev SK, Karlina AI, Karlina YuI. Results of Research Replacement of Graphite by Petroleum Coke in Lubricated Compositions. In: *Proceedings of the VIII Science and Technology Conference "Contemporary Issues of Geology, Geophysics and Geo-ecology of the North Caucasus" (CIGGG 2018).* Paris: Atlantis Press; 2019. p. 126–131.
27. Bolotov AN, Novikova OO, Novikov VV. Effect of loading on tribotechnical characteristics of antifriction diamond-bearing mineral ceramics. *Materials Physics and Mechanics.* 2025;53(2): 104–112.
28. Li Z, Lu Sh, Zhang T, Mao Zh, Zhang Ch. A Simple and Low-Cost Lubrication Method for Improvement in the Surface Quality of Incremental Sheet Metal Forming. *Transactions of the Indian Institute of Metals.* 2018;71: 1715–1719.
29. Dan LA, Maslov VA, Trofimova LA, Kargin SB, Artiukh VG, Kitaeva DA, Korihin NV. About possibility of using the Roginsky-Schulz and Avrami-Erofeev equations in topokinetic analysis of carbothermic self-recovery of dispersed iron-graphite waste. *Materials Physics and Mechanics.* 2025;53(4): 111–119.
30. Torres H, Podgornik B, Jovičević-Klug M, Rodríguez Ripoll M. Compatibility of graphite, hBN and graphene with self-lubricating coatings and tool steel for high temperature aluminium forming. *Wear.* 2022;490–491: 204187.