DOI 10.52209/1609-1825_2023_2_34 UDC 621.2.082.18

Thermodynamic Analysis of a Composite Obtained Using a Mixture of Copper and Molybdenum Oxides and Sulphides

[1]**ZHUMASHEV Kalkaman,** *Dr. of Tech. Sci., Head of Laboratory, innovaciya_zh@mail.ru,*
[2]***NAREMBEKOVA Aitbala,** *Cand. of Tech. Sci., Associate Professor, cpk-kru@mail.ru,*
[3]**ZHARMENOV Abdurassul,** *Dr. of Tech. Sci., Director General, nc@cmrp.kz,*
[4]**MAMYACHENKOV Sergei,** *Dr. of Tech. Sci., Professor, svmamyachenkov@yandex.ru,*
[3]**TERLIKBAYEVA Alma,** *Dr. of Tech. Sci., First Deputy Director General, nc@cmrp.kz,*
[1]*Zh. Abishev Chemical-Metallurgical Institute, Kazakhstan, Karaganda, Ermekov Street, 63,*
[2]*NPJSC «Abylkas Saginov Karaganda Technical University», Kazakhstan, Karaganda, N. Nazarbayev Avenue, 56,*
[3]*RK National Center of complex processing mineral raw materials, Kazakhstan, Almaty, Zhandosova Street, 67,*
[4]*Ural Federal University named after the First President of Russia B.N. Yeltsin, Russia, Yekaterinburg, Mira Street, 19,*

**corresponding author.*

Abstract. *The purpose of the study is selecting the optimal composition of antifriction composites alloyed with refractory metal sulfides in copper-based systems and developing the design of a laboratory plant for the production of sinter by pyrolysis of coke chemistry production resins. The object of the study is antifriction composites based on rare metal sulfides and coke chemistry production resins. The methodology of the work is determined by the use of modern physical and chemical research methods and modern software systems. As a result of the studies, the probable chemical reactions between compounds of copper and rare metals: molybdenum, tungsten with and without the participation of carbon, have been compiled. The optimal compositions of antifriction composites based on copper and rare metal sulfides have been determined, and a laboratory plant has been designed for the production of sinter by pyrolysis of coke chemistry production resin. The scope of the results is materials science and technology of new materials. Based on the thermodynamic analysis of various reactions that are likely to occur during the preparation of the cladding carbon lubricant composition based on powdered copper and carbon with the addition of rare metal sulfides (MoS_2), the most appropriate component composition of the charge has been selected. In this case, a reducing agent is used: soot obtained from resins of coke production that has an amorphous structure and does not have solid impurities. The main choice was made on the formation of metallic copper and disulfides of rare metals in the presence of active carbon. The most probable reaction is the formation of metallic copper and molybdenum disulfide in the presence of carbon. Carbon and copper are macro-components of the lubricant, and rare metal sulfides are additives that improve its plasticity. It is also important that carbon does not contain abrasive impurities and has certain hardness and fineness. These qualities are ensured in the production of black carbon using coke chemistry resins. To obtain black carbon, a laboratory plant has been designed that will be used for the pyrolysis of resin from the coke chemistry production.*

Keywords: *tribotechnical properties, copper sulfide, molybdenum sulfide, copper oxide, coke resin, antifriction composites, thermodynamic analysis.*

Introduction. It became possible to develop a material with a set of specific properties for a specific friction unit through the use of a compositional approach in the formation of a future material. The analysis of this problem shows that there are no industries in the country that provide modern mechanical engineering with such materials.

In the overwhelming majority of cases, to improve the tribotechnical characteristics of copper-based materials, various additives (titanium, nickel, chromium, and iron compounds) and graphite, molybdenum disulfide, and fluorides are introduced into their composition. To improve the characteristics of iron-based alloys, graphite, copper, molybdenum, phosphorus, and sulfur are added to them. Sulfides, selenides, fluorides, etc. are also introduced into the composition. These measures make it possible to expand the boundaries of using such materials, to increase their wear resistance and load capacity [1, 2].

In mechanical engineering an urgent task is to improve the tribotechnical properties of these materials. This is achieved by selecting the optimal chemical composition, introducing solid lubricants, etc.

The variety of matrix binders, fillers, and multifunctional additives makes it possible to control the properties of the developed composites [3-5].

The purpose of the work is to carry out a thermodynamic analysis for the preliminary selection of the most optimal composition of the initial mixture with the formation of the necessary interaction products at the temperature of the friction units of various aggregates, as well as to predict possible side reactions leading to undesirable products in the presence of impurities.

The novelty of the work is the use of a reducing agent based on the pyrolysis products of coke chemistry resin and their impact on the copper oxide reduction process, as well as the expected formation of complex thiosalts based on copper and rare metal sulfides, which can give new properties to the cladding lubricant or require adjustment of the heat treatment condition and composition of the mixture.

There are many works where graphite and such additives as molybdenum sulfide are used as the main component. However, graphite is a high-temperature reducing agent and can contain foreign inclusions of an abrasive nature. It is also known the use of finely dispersed copper powder in composition with graphite and lubricating oils [6-8]. Carbon and copper are macro-components of the lubricant, and molybdenum sulfide is an additive that improves its plasticity. It is also important that carbon does not contain abrasive impurities and has certain hardness and fineness. These qualities are ensured in the production of black carbon using coke chemistry resins. Therefore, to obtain a reactive reducing agent, carbon black and pitches obtained from the resins of Shubarkulkomir JSC have been proposed.

In the production of coke chemistry, resins are formed that, despite the possibility of obtaining a variety of compounds, are not widely used. At the same time, resin and some products of its pyrolysis (soot, pitch) could be used as a pure reducing agent for the reduction of metals at lower temperatures. This would make it possible to use them to obtain pure metals, their powders (copper, noble metals), since the excess can be removed by raising the temperature. Therefore, in this work, this possibility is used, taking into account the fact that an excess of finely dispersed carbon (pitch, soot) is also included in the composition of the lubricant. Copper oxide, being the main component of the initial mixture, is needed to obtain finely dispersed copper under the reducing action of the sinter. The composition of the sinter includes hydrocarbons and other organic compounds that are oxidized by copper oxide oxygen, forming at certain ratios black carbon or hydrocarbons that are poorer and have a high evaporation temperature.

Research methods. In this work, with the use of the HSS-5.1 Chemistry (Outokumpu) software package, a thermodynamic analysis of a series of reactions that are assumed to occur during the heat treatment of reaction mixtures has been carried out, the results of which are probabilistic in nature [4]. The possibility of adjustments is also related to the fact that the formation of basic thiosalts based on copper and rare metal sulfides is allowed, which could not be thermodynamically assessed due to the absence of their initial thermodynamic functions.

The probable chemical reactions involving compounds of copper and rare metals: molybdenum, tungsten and vanadium with and without participation of carbon, are presented below (reaction equations 1-6):

$$2Cu_2O + MoS_2 = MoO_2 + 2Cu_2S, \quad (1)$$

$$6CuO + 2MoS_2 = 3Cu_2S + 2MoO_2 + SO_2(g), \quad (2)$$

$$4CuO + MoS_2 + C = 2Cu_2S + CO_2(g) + MoO_2, \quad (3)$$

$$4CuO + MoS_2 + 2C = 2Cu_2S + 2CO(g) + MoO_2, \quad (4)$$

$$2CuO + MoS_2 + C = 2Cu + CO_2(g) + MoS_2, \quad (5)$$

$$2CuO + MoS_2 + C = 2CuS + CO_2(g) + Mo. \quad (6)$$

Research results. The results of the thermodynamic analysis, the probable chemical reactions involving compounds of copper, molybdenum and carbon are shown in Figure 1.

Taking into account the conditions of heat treatment of charge mixtures up to 300°C, Table shows the results of the thermodynamic analysis of probable chemical reactions.

The most probable is the reaction of metallic copper and molybdenum disulfide formation in the presence of carbon (reaction 3). The reduction of molybdenum to metal is undesirable, since molybdenum sulfide has a layered structure and greater ductility. It is more expedient to use a mixture according to reaction 3.

According to the obtained data, the probability of molybdenum disulfide oxidation in the presence of copper oxide is high and the formation of copper molybdate is possible. Such a transformation is possible at the stage of obtaining a cladding lubricant, and it is not known what effect it will have when using it.

The need to take into account the low cost and availability of raw materials and reagents requires consideration of the possibility of using different component composition of the reaction mixture. Therefore, based on the thermodynamic analysis of various reactions that are likely to occur during the preparation of the cladding carbon lubricant composition based on powdered copper and rare metal sulfides (MoS_2, WS_2 и V_2S_3), the most appropriate component composition of the charge was selected. In this case, there is used a reducing agent, soot obtained from resins of coke production, which has an amorphous structure and does not have solid impurities. The main choice was made on the formation of metallic copper and molybdenum disulfide in the presence of carbon (reaction 3).

Carbon and copper are macro-components of the lubricant, and molybdenum sulfide is an additive that improves its plasticity. It is also important that carbon does not contain abrasive impurities and has certain hardness and fineness. These qualities are ensured in the production of black carbon using coke chemistry resins.

There has been designed a laboratory plant (Figure 2) for the production of pitch by pyrolysis of resins from the coke chemical production. The material of the pyrolysis plant is iron. Body (1) has the shape of a round or rectangular tube, which is heated by open resistance furnace (7) with a thermostat. Liquid or solid lump resin is fed through hopper (2) and the performance is adjusted to determine the optimal melt heating temperature. The temperature of the

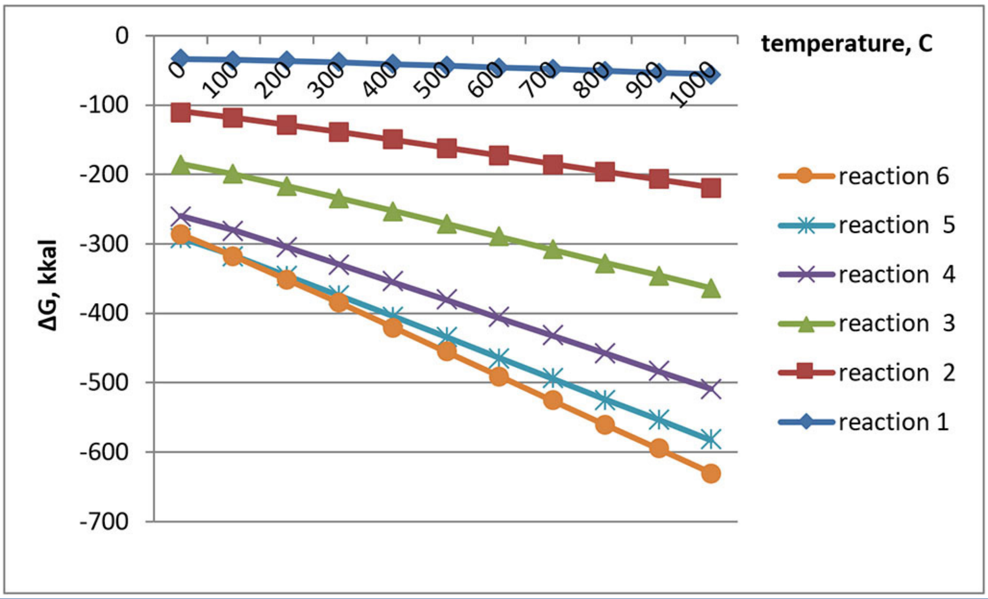
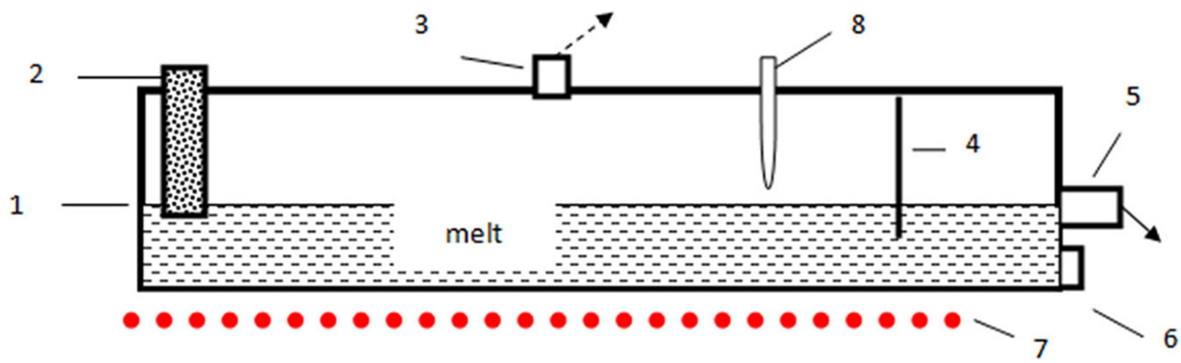


Figure 1 – Results of thermodynamic calculations of chemical reactions with participation of copper and molybdenum at different temperatures

Temperature dependence of the Gibbs energy of the most appropriate reaction in charge mixtures based on black carbon, metallic copper and molybdenum sulfide

Reaction No.	Reaction equation	DeltaH, kcal		DeltaG, kcal	
		100°C	300°C	100°C	300°C
3	$2CuO + MoS_2 + C = 2Cu + CO_2(g) + MoS_2$	-19.752	-20.494	-36.400	-45.164



1 – body of the pyrolysis plant in the form of a pipe; 2 – hopper for loading resin; 3 – pipe for exhaust gases; 4 – partition for isolating gases from adjusting the level of the resin melt; 5 – drain hole for high-temperature melt (sinter); 6 – branch pipe for complete draining of the melt; 7 – heater; 8 – case for thermocouple

Figure 2 – Diagram of a laboratory plant for producing the carbon component of a high-temperature lubricant by means of coke chemistry production resin pyrolysis

melt is controlled using a device with covered thermocouple (8). The gaseous pyrolysis products are discharged through branch pipe (3) that is connected to the condenser. The melt slowly moves to discharge unit (6) and at the outlet should not contain volatile components such as toluene. Partition 4 serves to isolate the volatiles from the sinter and to form vacuum from the side of tube (3), if needed.

When developing a sketch of the plant, the known conditions for the pyrolysis of resins have been taken into account [9, 10].

Resins from coke production have a complex composition and contain various volatile and heavier hydrocarbons. At the same time, heavy hydrocarbons are environmentally friendly reducing agents that interact with oxides to form water and soot. The latter is a macro-component of the cladding lubricant that has a finely dispersed structure.

The pyrolysis plant is designed to carry out the pyrolysis process under continuous conditions with the condensation of volatiles.

It is expected that the use of pyrolysis products of coke chemistry resins will expand the scope of its application not only within the framework of this work but also for other purposes, for example, to obtain pure powders of metals: copper and noble metals.

Conclusion. As a result of the thermodynamic analysis of a number of chemical reactions, the most probable ones have been selected that give a general direction for further experimental study at the next stages of the research.

Coke chemistry production resins containing heavier hydrocarbons are environmentally friendly reducing agents that interact with oxides to form water and soot. Soot is a macro-component of the cladding lubricant that has a finely dispersed structure and replaces graphite.

The pyrolysis plant has been designed to carry out the pyrolysis process under continuous conditions with the condensation of volatile substances.

It is expected that the use of pyrolysis products of coke chemistry resins will expand the scope of its application not only within the framework of this work but also for other purposes, for example, to obtain pure powders of copper and noble metals.

The work was carried out within the framework of the program-targeted financing of the STP «Developing new composite materials with high performance properties based on rare and rare earth elements» of the Committee for Industrial Development of the Ministry of Industry and Infrastructure Development of the Republic of Kazakhstan.

REFERENCES

1. Tang Zh., Lia Sh. A review of recent developments of friction modifier for liquid lubricants // Curvent Opinion in Solid State and Materials Science. 2014. V. 18, no. 3. Pp. 119-139.
2. Vidal J., Lany S., d’Avezac M., Zunger A., Zakutayev A., Francis J., Tate J. Band-structure, optical properties, and defect physics of the photovoltaic semiconductor SnS // Applied Physics Letters. – 2012. – Vol. 100. – No. 3. – P. 104.
3. Дамдинов Б.Б., Митыпов Ч.М. Влияние добавок мелкодисперсных частиц металлов на характеристики смазочных материалов // Вестник Бурятского государственного университета. Химия. Физика. 2021. Вып. 1. С. 28-42.
4. Доспаев М.М., Баешов А., Фигуринене И.В., Лу Н.Ю., Доспаев Д.М., Сыздыкова Б.Б., Какенов К.С., Есенбаева Г.А Механизм электрохимического сульфидирования кислородсодержащих соединений меди в составе труднообогатимых окисленных медных руд // IV Международная научно-практическая конференция «Теория и практика современных электрохимических производств», РФ, г. Санкт-Петербург, 14-16 ноября 2016.
5. Ashida M., Hisham S., Awang N.W. and other. Copper (II) oxide nanoparticles as additve in engine oil to increase the durability of piston-liner contact // Fuel. 2018. V. 212. Pp. 656-667.
6. Толочко О.В., Бреки А.Д., Васильева Е.С., Максимов М.Ю. Определение основных трибологических характеристик жидких смазочных композиций, содержащих мелкодисперсные частицы дихалькогенидов вольфрама // Вопросы материаловедения. СПб. – 2011. – № 1 (65). – С. 143-149.
7. Климова О.Г. Структура и свойства спеченных сплавов на основе вольфрама, полученных с использованием наноразмерных порошков: Дисс. … канд. техн. наук: 05.16.01. – С-Пб: СПбГПУ, 2011. – 150 с.
8. Машков Ю.К., Кропотин О.В., Шилько С.В., Плескачевский Ю.М. Самоорганизация и структурное модифицирование в металлополимерных трибосистемах: монография. Омск: Изд-во ОмГТУ, 2013. – 232 с.
9. Бердубанова Е.Г., Лядов А.С., Оганесова Э.Ю. Паренаго О.П. Синтез и трибологическое поведение наночастиц сульфидов металлов, полученных термосольволизом серосодержащих прекурсоров // Нефтехимия. 2019. Т. 59, № 5. С. 580-588.
10. Займовская Т.А., Кузьмина Г.Н., Перенаго О.П. Серосодержащие соединения молибдена как высокоэффективные присадки к смазочным материалам // Нефтехимия. 2017. Т. 57, № 4. С. 367-379.

Мыс және молибден оксидтері мен сульфидтерінің қоспасынан жасалған композиттік құрамды термодинамикалық талдау

[1]**ЖУМАШЕВ Калкаман Жумашевич,** *т.ғ.д., зертхана меңгерушісі, innovaciya_zh@mail.ru,*
[2]***НАРЕМБЕКОВА Айтбала Камзаевна,** *т.ғ.к., доцент, cpk-kru@mail.ru,*
[3]**ЖАРМЕНОВ Абдурасул Алдашевич,** *т.ғ.д., профессор, бас директор, nc@cmrp.kz,*
[4]**МАМЯЧЕНКОВ Сергей Владимирович,** *т.ғ.д., профессор, svmatyachenkov@yandex.ru,*
[3]**ТЕРЛИКБАЕВА Алма Жолдасовна,** *т.ғ.д., бас директордың бірінші орынбасары, nc@cmrp.kz,*
[1]Ж. Әбішев атындағы Химия-металлургия институты, Қазақстан, Қарағанды, Ермеков көшесі, 63,
[2]«Әбілқас Сағынов атындағы Қарағанды техникалық университеті» КеАҚ, Қазақстан, Қарағанды, Н. Назарбаев даңғылы, 56,
[3]ҚР Минералдық шикізатты кешенді қайта өңдеу жөніндегі ұлттық орталығы, Қазақстан, Алматы, Жандосова көшесі, 67,
[4]Ресей Федерациясының бірінші президенті Б.Н. Ельцин атындағы Орал федералды университеті, Ресей, Екатеринбург, Мира көшесі, 19,

**автор-корреспондент.*

Аңдатпа. *Зерттеудің мақсаты – мыс негізіндегі жүйелерде баяу балқитын металл сульфидтерімен қоспаланған антифрикциялық композиттердің оңтайлы құрамын таңдау және кокс химиялық өндірісінің шайыры пиролизімен спек алу үшін зертханалық қондырғының конструкциясын әзірлеу. Зерттеу объектісі сирек металдар сульфидтері мен коксохимиялық өндірістің шайырларына негізделген антифрикциялық композиттер болып табылады. Жұмыстың әдіснамасы қазіргі заманғы физика-химиялық зерттеу әдістерін және заманауи бағдарламалық кешендерді қолданумен анықталады. Зерттеулер нәтижесінде көміртектің қатысуымен және қатысуынсыз мыс пен сирек кездесетін металдар – молибден, вольфрам қосылыстары арасында болжамды химиялық реакциялар жасалды. Нәтижелерді қолдану саласы-материалтану және жаңа материалдар технологиясы. Сирек металдар сульфидтерін (MoS_2) қоса отырып, ұнтақ тәрізді мыс пен көміртек негізінде жалатылған көміртекті майлаудың композициялық құрамын алу кезінде әр түрлі реакциялардың термодинамикалық талдауы негізінде шикіқұрамның ең қолайлы компоненттік құрамы таңдалды. Бұл жағдайда тотықсыздандырғыш қолданылады-аморфты құрылымы бар және қатты қоспалары жоқ кокс химиялық өндірісінің шайырларынан алынған күйе. Негізгі таңдау белсенді көміртектің қатысуымен сирек кездесетін металл мыс пен дисульфидтердің түзілу реакцияларына негізделген. Көміртектің қатысуымен металл мыс пен молибден дисульфидінің түзілу реакциясы ықтималдығы жоғары. Көміртек пен мыс-бұл майлаудың макро компоненттері, ал сирек кездесетін металл сульфидтері – оның икемділігін жақсартатын қоспалар. Сондай-ақ, көміртектің құрамында абразивті қоспалар жоқ және белгілі бір қаттылық пен ірілік болуы маңызды. Бұл қасиеттер кокс химиясының шайырларынан көміртегі алу арқылы қамтамасыз етіледі. Күйе көміртегін алу үшін зертханалық қондырғының конструкциясы әзірленді, ол коксохимиялық өндірістің шайыры пиролизін жүргізу үшін пайдаланылатын болады.*

Кілт сөздер: *триботехникалық қасиеттері, мыс сульфиді, молибден сульфиді, мыс оксиді, коксохимиялық шайыр, антифрикциялық композиттер, термодинамикалық талдау.*

Термодинамический анализ композитного состава из смеси оксидов и сульфидов меди и молибдена

[1]**ЖУМАШЕВ Калкаман Жумашевич,** *д.т.н., зав. лабораторией, innovaciya_zh@mail.ru,*
[2]***НАРЕМБЕКОВА Айтбала Камзаевна,** *к.т.н., доцент, cpk-kru@mail.ru,*
[3]**ЖАРМЕНОВ Абдурасул Алдашевич,** *д.т.н., профессор, генеральный директор, nc@cmrp.kz,*
[4]**МАМЯЧЕНКОВ Сергей Владимирович,** *д.т.н., профессор, svmatyachenkov@yandex.ru,*
[3]**ТЕРЛИКБАЕВА Алма Жолдасовна,** *д.т.н., первый заместитель генерального директора, nc@cmrp.kz,*
[1]Химико-металлургический институт имени Ж. Абишева, Казахстан, Караганда, ул. Ермекова, 63,
[2]НАО «Карагандинский технический университет имени Абылкаса Сагинова», Казахстан, Караганда, пр. Н. Назарбаева, 56,
[3]Национальный центр по комплексной переработке минерального сырья РК, Казахстан, Алматы, ул. Жандосова, 67,
[4]Уральский федеральный университет имени первого Президента России Б.Н. Ельцина, Россия, Екатеринбург, ул. Мира, 19,

**автор-корреспондент.*

Аннотация. *Цель исследования – выбор оптимального состава антифрикционных композитов, легированных сульфидами тугоплавких металлов, в системах на основе меди и разработка конструкции лабораторной установки для получения спека пиролизом смолы коксохимического производства. Объектом исследования являются антифрикционные композиты на основе сульфидов редких металлов и смолы коксохимического производства. Методология проведения работы определяется применением современных физико-химических методов исследований и современных программных комплексов. В результате проведения исследова-*

ний были составлены предполагаемые химические реакции между соединениями меди и редких металлов – молибдена, вольфрама с участием и без участия углерода. Определены оптимальные составы антифрикционных композитов на основе меди и сульфидов редких металлов, разработана лабораторная установка для получения спека пиролизом смолы коксохимического производства. Область применения результатов – материаловедение и технология новых материалов. На основании термодинамического анализа различных реакций, вероятных при получении композиционного состава плакирующей углеродной смазки на основе порошкообразной меди и углерода с добавлением сульфидов редких металлов (MoS_2), выбран наиболее подходящий компонентный состав шихты. При этом используется восстановитель – сажа, получаемая из смол коксохимического производства, которая имеет аморфную структуру и не имеет твердых примесей. Основной выбор остановлен на реакциях образования металлической меди и дисульфидов редких металлов в присутствии активного углерода. Наибольшую вероятность имеет реакция образования металлической меди и дисульфида молибдена в присутствии углерода. Углерод и медь являются макрокомпонентами смазки, а сульфиды редких металлов – добавками, улучшающими её пластичность. Также важно, чтобы углерод не содержал абразивных примесей и имел определенную твердость, крупность. Эти качества обеспечиваются при получении сажистого углерода из смол коксохимии. Для получения сажистого углерода разработана конструкция лабораторной установки, которая будет использована для проведения пиролиза смолы коксохимического производства.

Ключевые слова: *триботехнические свойства, сульфид меди, сульфид молибдена, оксид меди,коксохимическая смола, антифрикционные композиты, термодинамический анализ.*

REFERENCES

1. Tang Zh., Lia Sh. A review of recent developments of friction modifier for liquid lubricants // Curvent Opinion in Solid State and Materials Science. 2014. V. 18, no. 3. Pp. 119-139.
2. Vidal J., Lany S., d'Avezac M., Zunger A., Zakutayev A., Francis J., Tate J. (2012). Band-structure, optical properties, and defect physics of the photovoltaic semiconductor SnS. Applied Physics Letters. Vol. 100. No. 3. P. 104.
3. Damdinov B.B., Mitypov Ch.M. (2021). Influence of additives of fine particles of metals on the characteristics of lubricants. Bulletin of the Buryat State University. Chemistry. Physics. Issue. 1. Pp. 28-42.
4. Dospaev M.M., Baeshov A., Figurinene I.V., Lu N.Yu., Dospaev D.M., Syzdykova B.B., Kakenov K.S., Esenbayeva G.A. Mechanism of electrochemical sulfidation of oxygen-containing copper compounds in the composition of difficult-to-enrich oxidized copper ores // IV International Scientific and Practical Conference «Theory and Practice of modern electrochemical production», Russian Federation, St. Petersburg, November 14-16, 2016.
5. Ashida M., Hisham S., Awang N.W., et al. (2018). Copper (II) oxide nanoparticles as additve in engine oil to increase the durability of piston-liner contact. Fuel. V. 212. Pp. 656-667.
6. Tolochko O.V., Breki A.D., Vasilyeva E.S. and Maximov M.Yu. (2011). Determining the main tribotechnical characteristics of liquid lubricating compositions containing fine particles of tungsten dichalcogenides. Problems of Material Science. SPb. No. 1 (65). Pp. 143-149.
7. Klimova O.G. (2011). Structure and properties of tungsten-based sintered alloys obtained using nanosized powders: Diss. … cand. tech. nauk.
8. Mashkov Yu.K., Kropotin O.V., Shilko S.V., Pleskachevsky Yu.M. Self-organization and structural modification in metal polymer tribosystems: monograph. Omsk: Publishing House of OmSTU, 2013. – 232 p.
9. Bordubanova E.G., Lyadov A.S., Oganesova E.Yu. Parenago O.P. Synthesis and tribological behavior of nanoparticles metal sulfides obtained by thermosolvolysis of sulfur-containing precursors // Petrochemistry. 2019. vol. 59, No. 5. Pp. 580-588.
10. Zaikovskaya T.A., Kuzmina G.N., Parenago O.P. Sulfur-containing molybdenum compounds as highly effective additives to lubricants // Petrochemistry. 2017. vol. 57, No. 4. pp. 367-379. Sciences: 05.16.01. St. Petersburg: SPbSPU, 50 p.