International Journal of Chemistry and Technology

http://dergipark.gov.tr/ijct

Research Article

Effect of nanoparticles on mechanical and tribological properties of composite friction materials

Fikrat YUSUBOV*

Department of Mechanical Engineering, Azerbaijan State Oil and Industrial University, 16/21 Azadliq Avenue, Baku, Azerbaijan

Received: 11 October 2017, Revised: 19 October 2017, Accepted 26 October 2017

*Corresponding author's e-mail address: fikratyusub@gmail.com (F. Yusubov)

ABSTRACT

Wear mechanism of newly developed asbestos-free frictional materials (i.e. brake pads material) was investigated by physical-mechanical experiments. The suitability of the developed these new composite materials were investigaed by firiction testes at the different temperatures. Thermal investigation was performed by a differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Stability and mechanical properties at different temperatures of the brake pad materials were comparatively evaluated. Testing results showed that under the given conditions, new developed frictional material has the advantages of the good tribological properties over the widely used commercial asbestos enhanced material as a FK-24A (Retinax, mark B). The research of the thermal and wear behaviour of materials indicates that brake pair has better frictional characteristics and wear resistance performance at high temperature. With use of new friction brake pads materials will be improved the safety of braking processes, and the quality in drilling will be increased. There is also an environmental and economic advantages in using the new asbestos-free materials in the break pads.

Keywords: Composite material, Brake pads, Friction, Thermal analysis

Nanoparçacıkların kompozit sürtünme malzemelerinin mekanik ve tribolojik özelliklerine etkisi

ÖZ

Yeni geliştirilen asbest içermeyen sürtünme malzemesinin (yani fren balataları malzemesi) aşınma mekanizması, fiziksel mekanik deneylerle incelendi. Geliştirilen bu yeni kompozit malzemesinin uygunluğu farklı sıcaklıklarda sürtünme deneyleri ile araştırıldı. Isı analizleri, diferansiyel tarama kalorimetresi (DTK) ve termogravimetrik analiz (TGA) ile yapıldı. Fren balata malzemelerinin dayanıklılığı ve mekanik özellikleri farklı sıcaklıklarda karşılaştırmalı olarak değerlendirildi. Test sonuçları, verilen şartlar altında, yeni geliştirilen sürtünme materyalinin, FK-24A (Retinax, mark B) gibi yaygın olarak kullanılan ticari asbest katkılı materyalden daha iyi tribolojik özellik avantajlarına sahip olduğunu gösterdi. Malzemelerin ısı ve aşınma davranışlarının araştırılması, fren çiftinin yüksek sıcaklıkta daha iyi sürtünme özelliğine ve aşınma direnci performansına sahip olduğunu göstermektedir. Yeni sürtünme fren balatası malzemelerinin kullanımı ile frenleme işlemlerinin güvenliği iyileştirilecek ve tüm sondajlamada kalite arttırılacaktır. Fren balatalarında yeni asbest içermeyen malzemelerin kullanılmasında çevresel ve ekonomik avantajlar da vardır.

Anahtar Kelimeler: Kompozit malzeme, Fren balataları, Sürtünme, Isı analizi

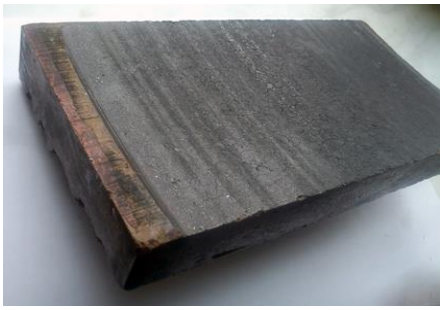
1. INTRODUCTION

Modern drilling equipments and parts are characterized by problems such as heat and wear due to friction. While lifting and lowering operations, the working surface parts of disc-brake system generates intensively heat due to the increase of the temperature of the sliding bodies and therefore causes the rise of the surface temperature, even its temperature can reach above 1000°C. Temperature flash originating temperature gradient and the result of this disorder occurs a thermal stress. The temperature gradient rise at the contact between sliding bodies can have an important influence on the tribological behaviour of the contacting components such as friction and also mechanical properties of brake block material.[1]

Heavily loaded friction contacts with high temperature gradient makes growth of physical-chemical-mechanical formations, and pair materials and structure changes causes abrasion and decomposition of contacting materials.[2,3] These temperature increases can often cause to oxidation and even possibly the melting of the contacting solids or friction burn. Also, this increase in temperature causes enlargement of microcracks which leads directly decomposition[4], as illustrated in Figure 1. This figure shows thermal worn of

front and back surfaces of the asbestos-containing friction material (FK-24A (Retinax, mark B).

a) front



b) back

Figure 1. Thermal worn surfaces of the asbestos-containing friction materials FK-24A (Retinax, mark B).

Progress of stress realated microcracks strongly arises as a result of thermal-physical properties of material.[5] Wear rate of brake pair materials increases with friction temperature rising, and tribological-mechanical performance becomes poorer. As damaged brake pads are changed with new pads after worn every time, driving efficiency and productivity decrease. The brake block material must have some properties such as higher thermal conductivity, wear resistant, stable friction coefficient and better mechanical properties. Resistance to humidity, good heat and electrical conductivity, low noise, stable friction, reliable mechanical performance and the absence of harmful environmental impact are important requirements for friction materials. Because of thermal, electrical resistance and tensile strength characteristics, asbestos are used widely in industry, especially in brake pads development. But due to its association with lung disaeses, like mesothelioma and different disorders in human body, new uses of asbestos have been banned in many countries. However, the use of asbestos material was inevitable for a long time as new materials were either economically not profitable, or could not exceed the quality of the asbestos based materials. But rapidly progress of nanotechnology also influences the development of composite materials. Composite materials are used in braking systems due to several reasons such as heat resistance, high endurance, good resistance to wear.[6] Recently, the use of nanoscale particles in composition materials has caused to arise of new development approaches and methods which is providing new materials with different properties and better quality indicators. In obtaining of the brake pads material with desirable tribomechanical properties, polymer based composite materials included different fillers, modifiers can be used. For this reason, we are offering new durable materials filled with nanoparticles and suggesting the help of various modifiers to get suitable and more stable composition for the purpose of obtaining economically and environmentally friendly materials. Removal of the asbestos from composition and replacing it with new materials will ensure a continuous and at the same time safe working regime in the driving process. Also, due to excellent heat conductivity and adhesive performance, the use of phenolic resin are the reason for preference as a binder or matrix in the development of friction brake composites.[7,8] Therefore, in this study, we aimed development new friction brake block material for oil drilling rigs brake system (friction pair materials for disc brake of drilling rig). For this purpose, we have developed two new friction materials.

The first is phenolic resin-containing material without asbestos. The second is inorganic nanoparticles-containing material besides phenolic resin without asbestos. At the same time, thermal and mechanical propeties of these new composite materials are compared with that of widely used friction material Retinax (FK-24A - Retinax, mark B).

2. MATERIALS AND METHODS

2.1. Materials

FK-24A (Retinax, mark B) was received from Suraxani Oil Company. This material is widely used as friction material in post Soviet countries. FK-24A (Retinax, mark B) contains 40% asbestos, 35% barite, and 15% phenol-formaldehyde. Herein, this material was named as sample A, and used as reference.

Chemicals and materials required for the production of sample B are graphite, silica, phenol-formaldehyde, and barit. These materials were received from Department of “Organic substances and technology of high molecules compounds” (Azerbaijan State Oil and Industry University). The material produced was named as sample B.

Chemical and materials required for the production of sample C are inorganic fibre (Ceramic fiber), silicon dioxide, heat resistant adhesives (epoxy), zinc oxide, short glass fibers, modified phenol-formaldehyde, phenolic resin (Phenol formaldehyde resin), and Cu-graphite nanoparticles. The materials were received from Department of “Organic substances and technology of high molecules compounds” (Azerbaijan State Oil and

Industry University) and Institute of Polymer Materials (Azerbaijan National Academy of Sciences).

Size of Cu-graphite nanoparticles produced with mechanical-chemical methods in Department of Machine-building and Materials Science, Azerbaijan State Oil and Industrial University is 70 μm. The material produced was named as sample C.

The production of samples B and C are given in methods section of the article.

Devices used for the measurments are as follows: A thermogravimetric analyzer (TGA Q50,TA Instrument) was used for thermal analysis. A differential scanning calorimetry (DSC) (Mettler Toledo DSC 823e) was used for specific heat capacities of sample materials. A band-block machine (developed in base МДП-I) was used for the determination of friction coefficients. Brinell hardness 20 device was used for hardness measurements. A pycnometer was used for the estimation of the densities of sample materials.

2.2. Methods

In the laboratory, two new materials (samples B and C) have been developed. These samples were obtained using hot press method.

First material was named as sample B. This material was produced using certain amounts of graphite and silica, and also modified phenol-formaldehyde oligomer without asbestos. In order to obtaine sample B, the used solid materials was firstly powdered and then all materials was mixed well. The resulted mixture was kept under 25 kpa press at 100-120°C temperature for 3,5 h.
In the production of sample B, barit still remained in the composition of sample B. On the other hand, modified phenol-formaldehyde was used instead of raw phenol-formaldehyde included in the sample A .

Second material was named as sample C. This material was developed without reference material A. Sample C is a completely new material produced by using reinforcing inorganic fibre (Ceramic fiber), silicon dioxide, heat resistant adhesives (epoxy), zinc oxide, short glass fibers, modified phenolic resin (Phenol formaldehyde resin) and small amount of Cu-graphite nanoparticles. The used solid materials was firstly powdered and then all materials was mixed well. The resulted mixture was kept under 30-35 kpa press at 135-175°C temperature for 4 h, and at the final stage sample was subjected to vulcanization (dry insulation) for 25 min.

So, these two new materials (Samples B and C) produced have become ready for all analyses.

On the other hand, the percent proportions the materials used in the production of the samples A, B, and C are given in Table 1.

2.2.1. Thermogravimetric analysis (TGA)

When the temperature increases the weights of samples changes due to decomposition.[9] For example, At very high temperatures, the covalent bonds between the atoms in the linear chain may be destroyed, and the material pair may burn or char.[10]

Thefore, thermal experiments has been done to determine the decomposition mechanism of materials and to estimate their thermal stability at the temperatures up to 1000°C.

Table 1. The portions of different categories of polymerbased composition materials used in experiments

Proportions (wt%)	Sample (A)	Sample (B)	Sample (C)
Matrix	40 (asbestos)	15	23
Modifiers	-	25	15
Filler	35	35	25
Binders	25	25	35
Friction modifiers	-	-	2

TG analyses of sample A, B, and C was conducted using a thermogravimetric analyzer (TGA Q50,TA Instrument). For accurate measurements, all test runs were performed under the same experimental conditions. As a specimen holders platinum crucible was used and re-zeroed after each run. During experiments, high purity nitrogen (the flow rate 60 ml $min^{-1)}$ was used as the inert gas. Each of the three sample materials are powdered (weight: 25 mg) and were heated at 10°C/min, from 45 to 1000°C and hold for 49 min. The decomposition and weight loss by temperatures of the three samples is shown in Figure 2.

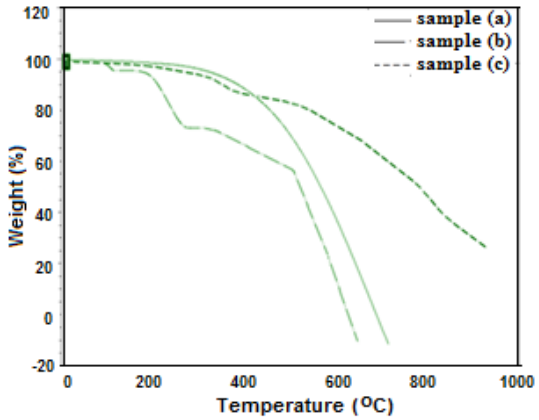


Figure 2. Thermogravimetric analysis (TGA) curves for sample materials.

2.2.2. Determination of weight loss

Weight losses of Sample A, B, and C were calculated according to ISO 7111 standards of 1987 (Plastics Thermogravimetry of Polymers - Temperature Scanning Method). After decomposition with the effect of the temperature, the mass losses and the remnant masses of

the materials were determined using Equations (1) and (2), respectively.

$$m_1 = \frac{m_B - m_A}{m_0} \cdot 100 \quad (1)$$

$$R = \frac{m_A}{m_0} \cdot 100 \quad (2)$$

where, m_1 is mass loss percentage, m_B is sample mass before loss, m_A is sample mass after loss, m_0 is beginning mass of sample, R is remnant mass percentage.

2.2.3. Differential scanning calorimetry (DSC) analysis

One of the most important demand while developing friction material is transforming energy to the heat at the short time period without any damage to material.[11] Herein, DSC analyses to determine the heat capacities of sample materials were performed by differential scanning calorimetry (DSC) analysis (a Mettler Toledo DSC823e brand) which is calibrated with indium as a standard. To calculate the heat capacities of the samples, calorimetric measurements were performed in the dynamic mode. The experiments were conducted in dynamic nitrogen atmosphere environmental a flow rate of 40 ml min^{-1} with a heating rate of 10°C/min and heated up to 500°C. All powdered samples (weight 8.1 mg) were loaded into alumina crucible. With the aim to measure the heat flow difference, first pan was filled with the sample material and second pan kept empty.

Specific heat capacities of sample materials in the temperature range 250 to 500°C were determined from this equation using DSC method: [12]

$$C_s = \frac{q}{m \cdot \Delta T} \quad (3)$$

where, q is units of heat, m is mass of the sample, ΔT is change in the temperature. DSC curves for the sample materials shown in Figure 3.

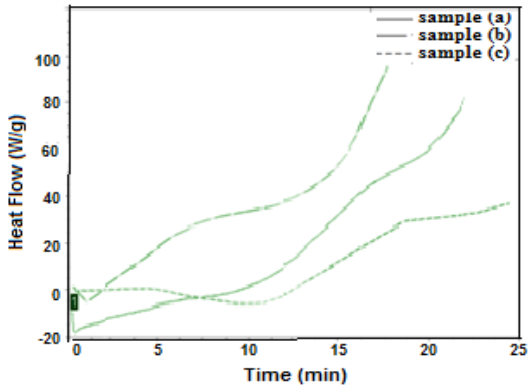


Figure 3. Differential scanning calorimetric (DSC) curves for the sample materials.

2.2.4. Determination of friction coefficients

Determination of friction coefficients of sample A, B, and C were explained in the following.

Tribological test devices such as pin-on-disk can give useful information about friction and wear behavior of materials.[13] All materials were tested in pairs under nominally non-abrasive conditions. Tests was conducted with laboratory procedure by using a band-block machine (developed in base МДП-I)[14](Figure 4).

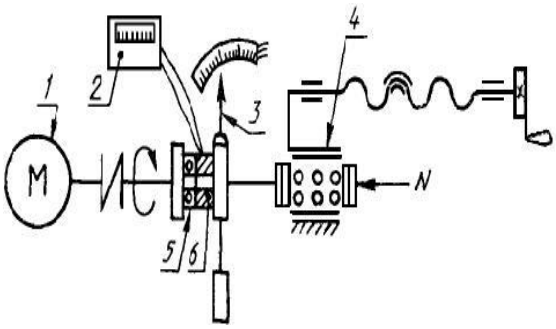


Figure 4. Device for measuring the friction under laboratory conditions.

where, 1- engine, 2- potentiometer, 3- force meter, 4- loader, 5- friction material sample, 6- metallic material sample.

The tribological tests for all specimens was conducted with same experimental parameters: under loads of 30 N and a sliding velocity of 4 m s^{-1}. The pin dimensions was 40 mm in length and 10 mm in diameter.[15,16] Friction measurements were conducted at the temperatures up to 700°C. During experiment, friction coefficients were recorded with sliding distance. The obtained results is shown in Figure 5.

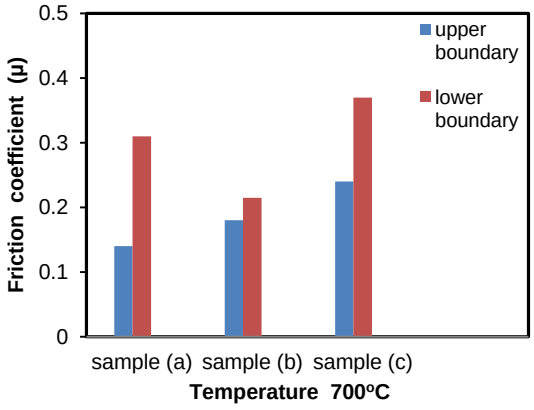


Figure 5. Friction coefficients for upper and lower boundary of the reference area by pin-on-disc wear up to 700°C.

2.2.5. Hardness measurements

For the hardness measurements of all samples, Brinell hardness tester was used.[17] Brinell hardness process was conducted in a period of 25 seconds using a 10 mm diameter-steel ball by applying a 500 kg-load.

2.2.6. Denstiy measurements

In order determine densities of sample materials, pycnometer method was used.[18] Materials were divided to small parts and measured by pycnometer using water.

3. RESULTS AND DISCUSSION

Results show that the sample A undergoes thermal degradation beginning at 310°C with a mass loss of 19.6%, when the temperature is >310 °C do its weight-loss rates increase slightly (to 0.3 wt %/°C). Sample B loses about 1,7% of its mass about 114°C.

This effect occurs mainly because silica desorbs into the gas phase during the initial stages of passive oxidation.[19] As can be seen from Figure 2, TGA curve shows that there are two mass losses at 114 °C and 326 °C and starting from 326°C to 520°C the sample decomposes completely. Measurements showed that the sample C was more thermally stable than other materials. The weight loss at 374°C represents the decomposition of the sample C when the material have absorbed certain amounts of heat energy. No drastic change in the sample mass was observed for temperatures up to 400°C.

The statements about friction are evidenced in Figure 4, where it can be observed that the temperature increases determined both the sliding speed and nominal contact pressure increase. According to the analyses, the surface friction temperature of the brake pair at beginning of the wear is low and with temperature rising surface layer begins to soften. After temperature rises much higher micro crack enlargements leads decompositon of material. Common method to improve the mechanical properties or performance at wide temperature range is to include a glass fiber as filler or binder in the polymer. Reinforcement material shall have characteristics which improve the stiffness and well relation tie to the matrix.

Glass fiber also has advantages from an economic point of view.[20] Compared to the Retinax material, the sample C showed an important improvement of the overall thermal stability profile. The increasing in thermal stability was found in all decomposition stages. The results indicates that the decomposition of the sample C occurs at a higher temperature than that for other compositions, showing greater degree of thermodynamic stability. Also the results reveal that sample C has higher friction coefficient than other sample materials.

The coefficient of friction between two surfaces is influenced by the mechanical properties of material, the surface sturucture, temperature and other parameters. Braking materials must ensure a stable friction with a high friction coefficient.[21,22] The coefficient of friction increases as disc temperature is increased from 29°C to 200°C and phenolic resin does not affect disc temperature sensitivity of coefficient of friction. During the study of tribological behaviors, it became clear that glass fibers increased hardness and thermal conductivity depending on load percentage. On the average, the friction coefficient in the 5-10% glass fiber material has decreased due to the increase in load. The friction coefficient of 0.1 kg under normal load rises at the initial stage, then gradually rises to 0.50. In the later stages, the slowly begins to decrease. When we look at the overall frictional activity of the material, we have the same mechanism as the smallest difference for all cases. However, the effect of load percentage on friction behavior cannot be overlooked. The friction coefficient in the material consisting of glass fiber particles under all loads are the lowest.

Phenolic resin do not affect the trend of increasing of coefficient of friction toward disc.[23] For retinax material (sample A), when the temperature increases from 100°C to 700°C, friction coefficient changes from 0,270-0,605 to 0,200-0,387. It is observed that friction coefficient decreases with the increase of temperature from starting point. After 380-440°C phase, no changes has been dedected, and thus the friction coefficient becomes constant. Friction coefficient starts to increase significiantly after 480°C, but it never reaches to higher numbers. Same temperature effect to the friction has also been observed for other materials, but the obtained results indicates that the sample B has lowest (0,115-0,237) and the sample C has highest friction coefficient (0,264-0,400) at the highest temperatures. During the measurement of the friction coefficient of Cu-graphite in dynamic conditions, the values varying under different loads have reached the highest value of 0.4. Since graphite has good antifriction properties, the high friction coefficient of the sample C can be explained by the role of Cu-graphite particles with increasing the heat conductivity of the material. Also, one of the reasons why the sample C shows good mechanical perfromance is the use of modified phenol-formaldehyde. Overall physical-mechanical measurement results and other parametres are summarized in Table 2.

Table 2. Physical-mechanical properties of materials

Properties	Sample (A)	Sample (B)	Sample (C)
Thermal decompost. (°C)	>310	114->336	>374
Density (kg m^{-3})	2134	2112	2238
Hardness (HB20/500/25)	32	29	38
Specific heat cap.(kJ/kg°C)	0.96	0.77	1.32
Mass loss (1000°C)	82%	97%	43%

Figure 6 shows scanning electron microscopy (SEM) surface images of the sample C. It can be clearly observed structural formation of cu-graphite and modified phenol-formaldehyde which is played significant role on mechanical properties.

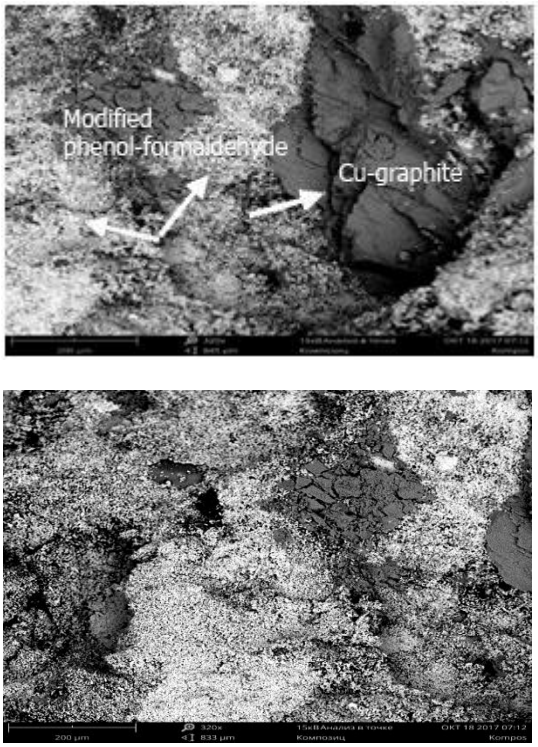


Figure 6. SEM images of the sample material C.

In addition, a large amount of frictional dance was observed in the sample material B with a barite mass percentage, and some signs of damage on the friction surface of contact appeared. Rising temperature also affected frictional stability in sample materials where barite mass percentage is high. From the results, it can be seen that the density of silica dioxide leads a high density of materials. Besides, it should be noted the effect of silica dioxide on mechanical properties. One of the reasons why the hardness of the sample material C is not too low is due of silica dioxide.

4. CONCLUSIONS

Based on the experimental investigation and analysis, conclusions are drawn that the sample C has better tribological performance compared to the samples A (FK-24A, Retinax material) and B materials. Friction and wear performance of the sample materials has improved with addition of nanoparticles to material content. From experiments, it is found that sample C has highest friction coefficient. Both sample materials which are reinforced with inorganic fibres, heat resistant adhesives and different nanoparticles has higher mechanical characteristics. The effect of modified phenol-formaldehyde on mechanical performance of the sample materials are considerably high. But due to poor heat conductivity, the sample B showed 97% mass loss at 1000°C. Thanks to Cu-graphite particles and fillers, the mass loss of the sample material C was only 43% at 1000 °C following the decomposition starting at 374°C. Results indicates that polymer based composite material C can be used as brake block material instead of asbestos. By providing reliability and stability of the braking process with newly developed composite friction materials, high efficiency and economic advantage in driving process can be achieved.

ACKNOWLEDGEMENTS

The author is thankful to his advisor, Associate Professor Guliyev Agali, Department of Machine-building and Materials Science, Azerbaijan State Oil and Industrial University for his valuable comments and encouragement during the investigation.

Conflict of interest

I declare that there is no a conflict of interest with any person, institute, company, etc.

REFERENCES

1. Kragelsky, I. V. ; Alisin, V.V. *Tribology: Lubrication, Friction and Wear, Tribology in practice series*, Wiley, 2001.

2. Bos, J.; Moes, H. *ASME J. Tribol*. **1995**, 117, 4-12.

3. Shpenkov, G.P. *Tribology Series*, Elsevier Science, 1995; Vol. 29, pp 291-296.

4.Kennedy, F.E. *Frictional Heating and Contact Temperatures*, In: *Modern Tribology Handbook*, Bhushan, B. Ed.; *CRC press*, Boca Raton, FL, 2001.

5. Dzhanakhmedov, A.; Gurbanov, R.E.; Aliyev, A.M. *Fundamentals of Tribology*, Baku, Chashıoglu, 2001.

6. Peter, J. B.; *Compositions, Functions, and Testing of Friction Brake Materials and Their Additives*, Oak Ridge National Laboratory, 2001.

7. Jamasri, S.E.; Malau, V.; Ilman, M.N. *ARPN J. Eng. Appl. Sci.* **2014**, 9(11), 2234-2240.

8. Ho, S.C.; Chern Lin, J.H.; Ju, C.P. *Wear*, **2005**, 258, 861-869.

9. Galwey, A.K.; Brown, M.E. *Thermal Decomposition of Ionic Solids.* 1st Ed.; Elsevier Science, 1999, Vol. 86, pp. 62-63.

10. Askeland, D.R.; Fulay, P.; Wright, W.J. *The Science and Engineering of Materials*, 6th Ed.; Cengage Learning, 2010.

11. Stachowiak, G.W. *Wear: Materials, Mechanisms and Practice (Tribology in Practice Series, Book 8*), 1st Ed.; Wiley, 2005, pp 223-225.

12. O'Neil, M.J. *Anal. Chem.* **1966**, 38 (10), 1331-1336.

13. Deleanu, L.; Georgescu, C.; Gheorghieş, C. *The Annals of "Dunarea de Jos Galati. Fascicle IX. Metall. Mater. Sci.* **2011**, 29 (4), 5-15.

14. Friction articles of retinax. Specifications. http://docs.cntd.ru/document/gost-10851-94, 1996.

15. Peter, J. B. *Tribol. Int*, 39 (9), **2001**, 585-591.

16. Bayer, R.G. *Mechanical Wear Fundamentals and Testing*, 2nd Ed.; Revised and Expanded, Marcel Dekker Inc., New York, 2004.

17. Suryanarayana, C. *Experimental Techniques in Materials and Mechanics*, CRC Press, 2011.

18. Hidnert, P.; Peffer E.L. *Density of solids and liquids*, U.S. Government Printing Office:Washington, DC, 1950.

19. Starodub, D.; Gusev, E.P.; Garfunkel, E.; Gustafsson, T.; *Surf. Rev. Lett.* **1999**, 6 (1), 45–52.

20. Eriksson, M.; Lord, J.; Jacobson, S.; *Wear*, **2001**, 249 (3-4), 272-278.

21 Djafri, M.; Bouchetara, M.; Busch, C.; Weber, S. *Mechanika* **2014**, 20 (4), 420-425.

22. Larsen-Basse, J. Basic theory of solid friction, In: Henry, S.D (Ed.), *ASM. Handbook: Friction Lubrication, and Wear Technology*, ASM International, Metals Park, OH. 1992. Voll. 18, p.17.

23. Sundén, B.; Brebbia, C. *AWIT Transactions on Engineering Sciences*, WIT Press, 2014; Vol. 83, pp 203-260.

Note: This work has been presented in 3rd International Turkic World Conference on Chemical Sciences & Technologies (ITWCCST-2017).

ORCID

0000-0002-2095-2469 (F. Yusubov)