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COMPOSITE LAYERS WITH CERAMIC MATRIX MODIFIED WITH GLASSY CARBON DESTINED FOR OIL-LESS SLIDING PAIRINGS**WARSTWY KOMPOZYTOWE Z OSNOWĄ CERAMICZNĄ MODYFIKOWANE WĘGLEM SZKLISTYM PRZEZNACZONE NA SKOJARZENIA BEZOLEJOWE**

The paper presents basic knowledge about producing and some results of tribological and metallographical research on composite layers with porous, anodic hard coating matrix which were modified with glassy carbon nanotubes. These composite layers were formed as surface layers of machine parts operating under conditions of sparse lubrication (limited lubrication) and friction in air. The layers were tested at sliding mating with EN-GJL-350 cast iron used for piston rings in combustion engines and air compressors. On the basis of the metallographical tests was the structure of the composite layer described. It was found that on the surface of the oxide is a glassy carbon layer and in the pores of oxide are regular carbon nanotubes. On the basis of the obtained results of tribological tests it was found that glassy carbon layer on the oxide surface shorts the wearing-in time, and the glassy carbon nanotubes formed inside the pores of anodic hard coating upon EN-AW-6061 aluminum alloy prove to be effective solid lubricants and complement lubrication function of the graphite in cast iron. Consequently the coefficient of friction was lower than in case of nanotubes-free oxide layers.

Keywords: composite layer, carbon nanotubes, sliding, lubrication, anodic hard coating

W pracy przedstawiono podstawy wytwarzania oraz wyniki badań metalograficznych i tribologicznych warstw kompozytowych na osnowie porowatej, anodowej warstwy tlenkowej modyfikowanej węglem szklстым. Warstwy te zostały wytworzone jako warstwy powierzchniowe części maszyn współpracujących ślizgowo w warunkach ograniczonego smarowania (oszczędnego) oraz w warunkach tarcia technicznie suchego. Warstwy te zostały przebadane we współpracy ślizgowej z żeliwem EN GJL 350 używanym na pierścienie tłokowe silników spalinowych i tłokowych sprzężarek powietrza. Na podstawie przeprowadzonych badań metalograficznych określono budowę i strukturę warstw kompozytowych, stwierdzając że na powierzchni tlenku wytwarza się warstewka węgla szklстого, a wewnątrz porów są regularne nanorurki węglowe. Na podstawie badań tribologicznych stwierdzono, że znajdująca się na powierzchni warstewka węgla szklстого skraca czas docierania skojarzenia a nanorurki węglowe wytworzone w porach anodowej warstwy tlenkowej na stopie aluminium EN-AW-6061 są skutecznym środkiem smarowym i wspomagają funkcje smarne grafitu znajdującego się w żeliwie. Współczynnik tarcia w skojarzeniu z warstwą kompozytową był mniejszy niż w skojarzeniu z warstwą tlenkową.

1. Introduction

Machine parts, the surfaces of which are destined for tribological mating, are covered with anodic hard oxide layers and find their wide application in mechanical engineering [1,2,3,4]. These coverings operate under conditions of limited lubrication and friction in air. The structure and properties of the layers applied seem to depend crucially on the technology and parameters of the oxidation process. There is a general principle which states that the layers upon machine parts which operate under low load such as slideways of car sun

roofs, rail coach cabin windows or elements of deck and coach fittings, are formed in sulphuric acid based electrolytes. However, machine parts operating under higher loads e.g. sliding surfaces of cylinder liners in oil-less compressors or pneumatic servo-motors oxidize in oxalic acid electrolytes.

Composite layers with anodic hard coating are formed for some specific tribological applications. Friction reducing agents such as soft metals are introduced into oxide coating on the result of which the composite coating of AHC+Me type (oxide coating + metal) [1,2,5,6] is generated, coating surface is spread with

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films of plastic and AHC+P (oxide coating + polymer) [7,8] is formed.

In the Polish industry conditions, the solutions where AHC+P type composite layer is formed only when friction appears in the process known as friction plating, proved to work really well [8]. Such process found its application in oil-less air compressors where sliding surfaces of cylinder liners made of aluminium alloys are covered with anodic hard coating whereas piston rings mating with them contain substances which form a sliding film [9] known as transfer film upon the oxide sliding surface. The film reduces the friction coefficient and the wear intensity, which in turn lowers energy consumption and prolongs the machines durability.

All layers mentioned above feature their advantages and disadvantages. Only thorough understanding of the layers properties enables their proper application. The paper discusses the technology of producing and chosen properties of the new generation of composite layers with the anodic hard coating matrix ie. layers which contain amorphous glassy carbon functioning as solid lubricant. As the result of glassy carbon being formed in the pores

of oxide layer, the composite layer ceramics-glassy carbon (AHC+GC) is obtained which features absolutely unconventional properties never met in the solutions applied so far.

2. Materials

2.1. Fundamentals of AHC+GC coatings formation

The basic fundamental of the production of composite layers with anodic hard coating matrix is its porous structure (Figs 1 and 2). Electrolytically obtained aluminium oxide is composed of hexagonal cells of 250-300 nm diameter with 15-50 nm diameter pores in their axis. It is possible to obtain hard coatings with the pores of diameter bigger than 50 nm, but their usability for tribological purposes is limited due to their low hardness which is a decisive factor of wear resistance as well as the value of transferred loads. Therefore the coatings with pores diameter of 15-50 nm seem to have wider practical application.

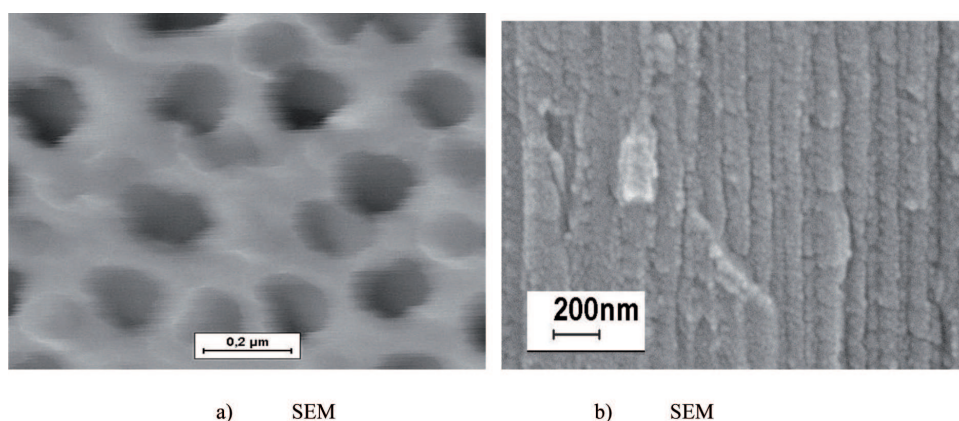


Fig. 1. Surface view (a) and fracture (b) from anodic hard coating used as matrix of composite layer AHC+GC, nanopores as dark near circle shaped dots – Fig a – and vertical canals – Fig b

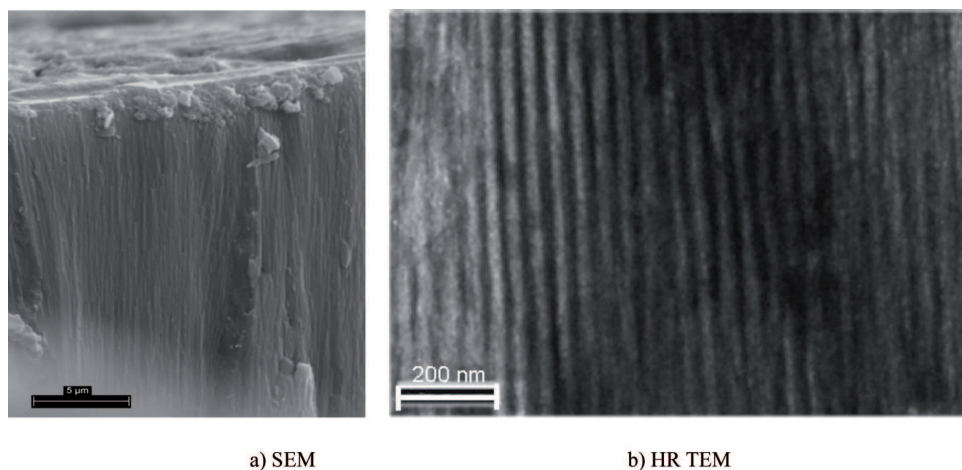


Fig. 2. Cross view of fracture from AHC+GC-composite layer: a – macro roughness of surface destined for sliding – upper part and oxides cells area-bottom part, b – nanopores filled with glassy carbon as solid lubricant

While discussing the core of the process of producing composite hard layers for tribological purposes it is essential to focus on the problem of introducing carbon containing substances (precursor) inside the pores of the

existing anodic hard layers and subjecting the substances to the process of carbonization in the atmosphere of argon or nitrogen, Fig. 2.

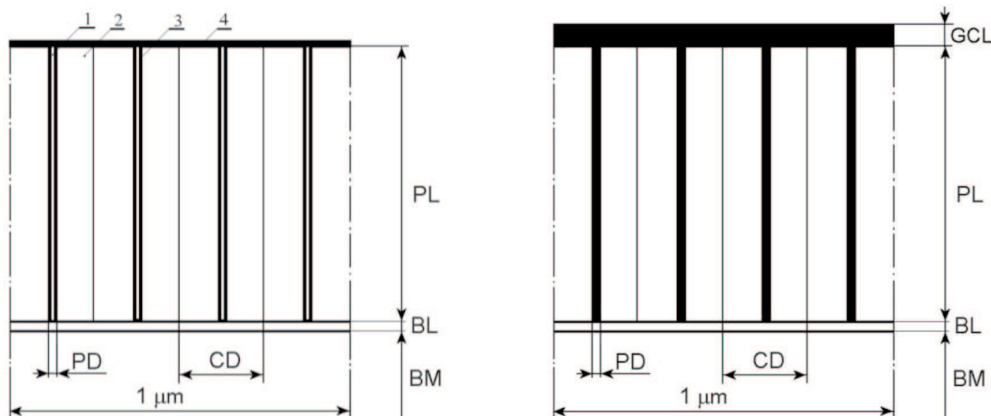


Fig. 3. Composite layer AHC+GC with GC-nanotubes and thin outer layer (a) and with nanowires with thick outer GC-layer (b): 1 – pore filled with nanotubes, 2 – wall of oxide cell, 3 – nanotubes on aluminium oxide, 4 – continuous layer of glassy carbon generated in mikroroughness and in depth of oxide surface; PD- Pore diameter, CD- oxide cells diameter, PL- porous part of oxide layer, BL – barrier part of oxide layer, BM – basic material

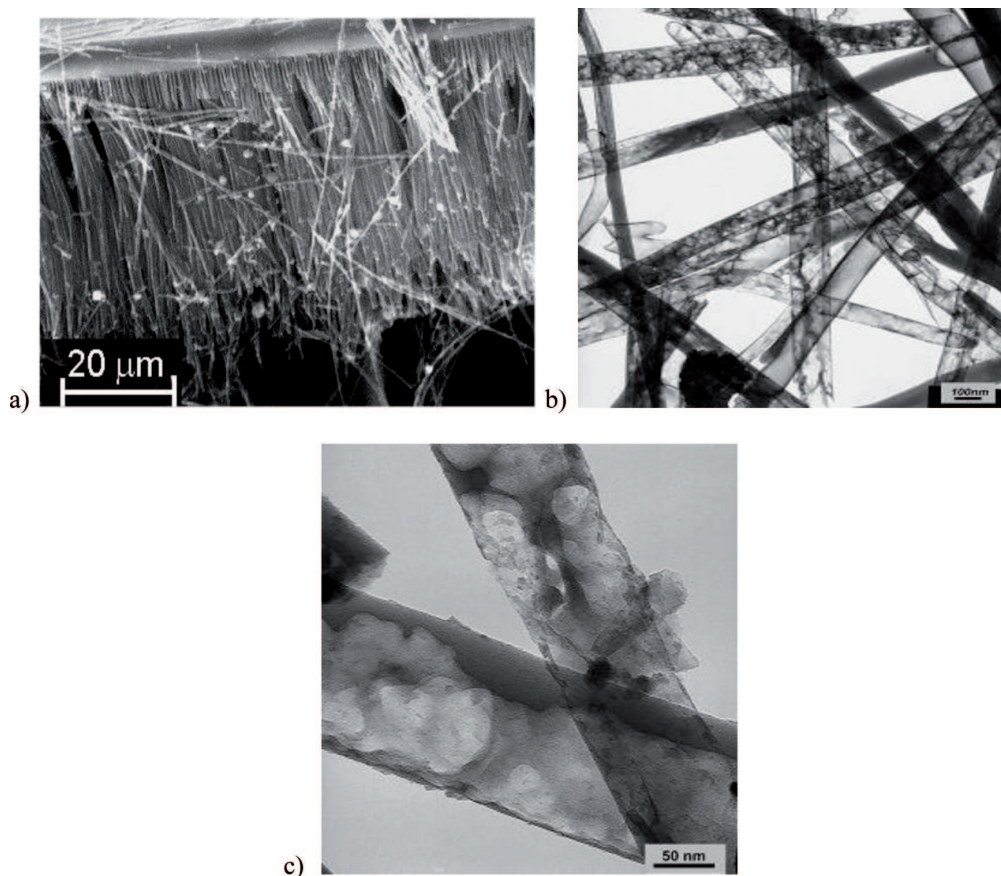


Fig. 4. Composite layer AHC+GC after dissolution of aluminium oxide layer: a – nanotubes from top joined with glassy carbon film, b – bunch of nanotubes, c – simple nanotubes

The amount of the introduced precursor depends upon the saturation time. The shortest possible time of saturation is required to deposit the precursor over entire wall of the pores and generate continuous nanotubes (Figs 3(a) and 4). Non-continuity of nanotubes might worsen the tribological properties of the layer. The longest possible time is necessary to fill the pores entirely and to form nanowires from glassy carbon (Fig. 3(b)). Only these carbon containing substances the particles parameters of which are smaller than the parameters of the pores, can be introduced into the pores of hard anodic oxides. Therefore the selection of substances for filling in the pores is not simple and does not constitute the subject of this paper.

The parameters of precursor carbonization process significantly affect the structure and tribological properties of composite layers. The process temperature determines the degree of carbonization as well as coefficient of friction. Since EN-AW 6061 alloy was used in the

research with its melting temperature of about 650°C, the carbonization process had to be carried out in such temperatures which would not pose any hazard for the alloy to soften.

This might lead to specimen's deformation and layer cracking. Figs 5, 8(b) and 8(f) show an exemplary composite layer after carbonization process in lower temperature. On the specimen surface there are slight cracks – the effect of the difference in thermal expansion of the alloy and oxide coating ($\alpha \approx 22 \times 10^{-6}$ 1/K for the EN-AW6061 alloy and $\alpha \approx 6-7 \times 10^{-6}$ 1/K for aluminium oxide). Fig. 6 shows the coating surface formed in higher temperature with visible large cracks. Such changes in the oxide layer lower the tribological properties of composite layers and tacking might occur. During sliding mating with cast iron some wear debris such as carbon might appear inside cracks (Fig. 6(b)) which can reduce the negative effects of tacking.

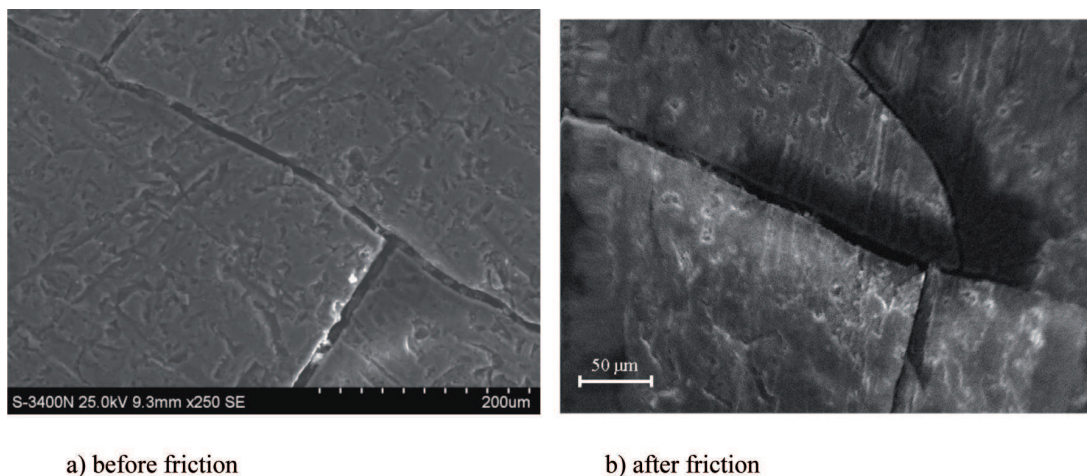


Fig. 5. Small macro-cracks in oxide layer after carbonizing process at lower temperature (a – sharp edges; b – edges smoothed during friction)

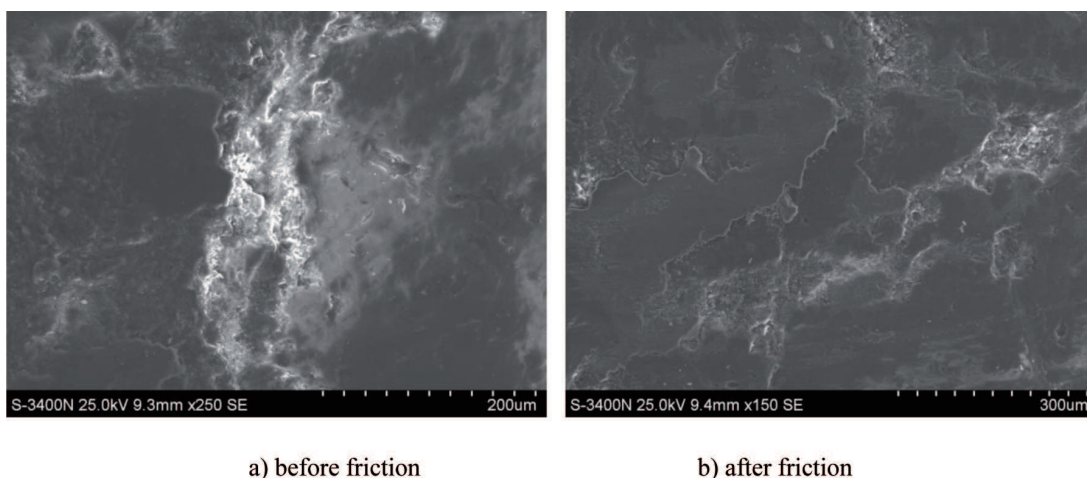


Fig. 6. Big macro-cracks in oxide layer after carbonizing process at higher temperature before (a) and after friction (b: small scratches in friction direction made by sliding cast-iron pin)

2.2. The structure of AHC+GC coatings

Generated composite layers have been subjected to microscopic and tribological tests to analyse their structure and functional properties. In order to view the layers structure AHC+GC the matrix ie. oxide coating has been dissolved and carbon nanotubes extracted [13]. Aqueous solution of hydrofluoric acid has been used. Figure 4(a) presents a view of some nanotubes clung to the layer of glassy carbon on the oxide surface. Figure 4(b) shows a view of separated glassy carbon nanotubes. The number of nanotubes and their dimensions depend upon the parameters of hard oxide layer production as well as upon oxide saturation conditions with furfural acid and carbonization of carbon coating compounds found inside pores.

Taking into account the cellular structure of anodic hard layer, we obtain the following proportions in the composite layer between the filling material and oxide ie. the cylindrical pore with the diameter of 15-20 nm filled with the modifying material and the ceramic sleeve with the inner diameter of 15-20 nm and the outer diameter of 250-300 nm (a shape resembling that of a hexagon, Fig. 1).

The proportion between oxide surface (A_o) and modifying material (A_m) in one cell is 225:1. This way the mating surface between the composite layer and cast iron is obtained. The surface contains 200 times more of extremely hard abrasive aluminum oxide than plastic modifying material which softens the friction.

The surface fraction of the modifying material within friction zone is proportional to the porosity of the anodic oxide coating. According to some literature data the layers formed in electrolytes of sulfuric and oxalic acids feature porosity which amounts to 20%. In electrolytes of more complex chemical composition (polyacid elec-

trolytes) it is possible to obtain layers with porosity over 20% [1]. Assuming the ideal cellular structure of the oxide layer it is possible to determine the surface fraction of the modifying material. To simplify the calculations we assume the outer diameter of the cell $DC=250$ nm which gives 16 cells per square micrometer of the surface ($A_n=16 \times 10^6 \text{ mm}^{-2}$). Assuming the maximum cell diameter $DC=300$ nm we obtain more than 9 cells per μm ($A_n > 9 \times 10^6 \text{ mm}^{-2}$). Such a surface of the composite layer obtained by methods applied so far (oxidation + metallizing) is not favourable – despite many other advantages – from the tribological point of view when they are used at sliding pairings for example in vehicles. Therefore new alternative technology of obtaining both ceramic-metal (Anodic Hart Coating + Metal ie. AHC+M) and ceramic-carbon (Anodic Hard Coating + Glassy Carbon ie. AHC+GC) destined for selected parts of combustion engines operating in conditions of limited lubrication (ultimately oil-less) have been elaborated in Faculty of Transport of the Silesian University of Technology and Faculty of Earth Sciences of University of Silesia. The selected properties of the new layers AHC+GC are being discussed in the course of this paper.

3. Tribological properties of AHC+GC coatings

Since the aim of the research was to generate the composite layers destined for surfaces of machine sliding parts rubbing in the environment of restricted lubrication and friction in air, the authors used anodic hard layers produced in the environment close to hard oxidation [1]. Composite layers discussed have been tested with pin-on-disc tribological tester (Fig. 7) with relative velocity of 1 m/s and unit pressure of 0.8 MPa in the conditions of friction in air.

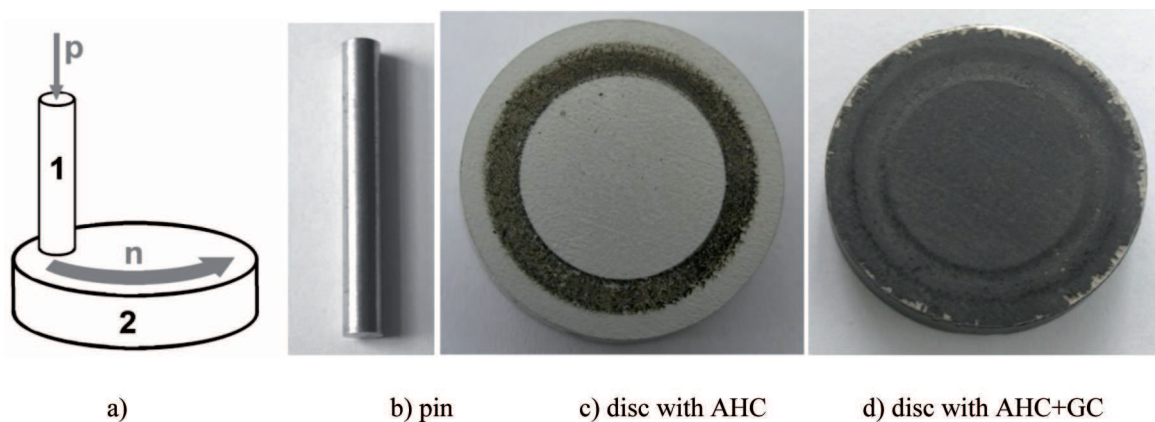


Fig. 7. Friction pair of T11-tester (1 – pin made of EN-GJL-350; 2 – disc made of EN-AW-6061 with AHC and with AHC+GC-composite covering)

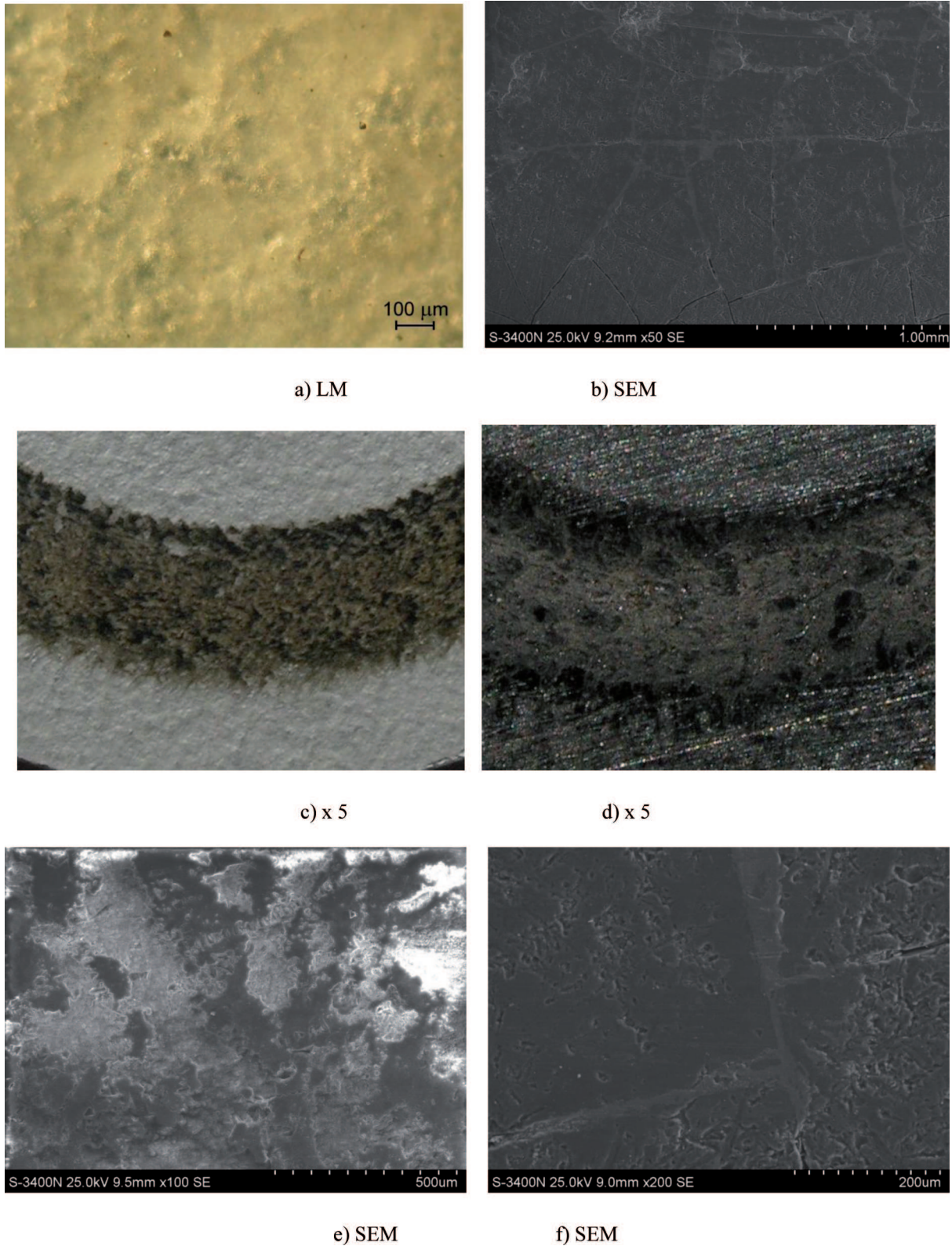


Fig. 8. Surfaces views of AHC (a) and AHC+GC (b) and friction tracks after rubbing of cast-iron pin against AHC (c, e) and AHC+GC (d, f)

The pin used for tests was made of EN-GJL-350 cast iron which is used for piston rings of combustion engines because composite layers can be used for slid-

ing surfaces of cylinder liners. Due to positive insulating properties and high thermal resistance of the hard anodic aluminium oxide, such layers can be used for cylinder

liners in the mixture combustion areas raising the temperature of exhaust gases and facilitating evaporation of injected fuel. Layers were prepared upon aluminum alloy EN-AW-6061 disc. The aluminum alloy is used for parts in low-power engines (up to 50 cm³) only. The tests on Al-Si casting alloys will be performed in the due course.

Testing time was restricted to 12 minutes because the lubricant-free pairing cast iron – anodic oxide layer worked well for about 10 minutes at friction coef-

ficient of 0.15 – 0.23 (Fig. 11). During that time the graphite film from the pin formed upon the oxide surface (Figs 8(c) and 8(e)) and the friction coefficient momentarily decreased from 0.23 to 0.15. Film deposition is possible due to well developed aluminium oxide surface (Figs 8(a) and 8(c)). However, it is too thin and so loosely tied with the bed that rubbing can last for about 10 minutes. After 11 minutes part of the graphite is removed

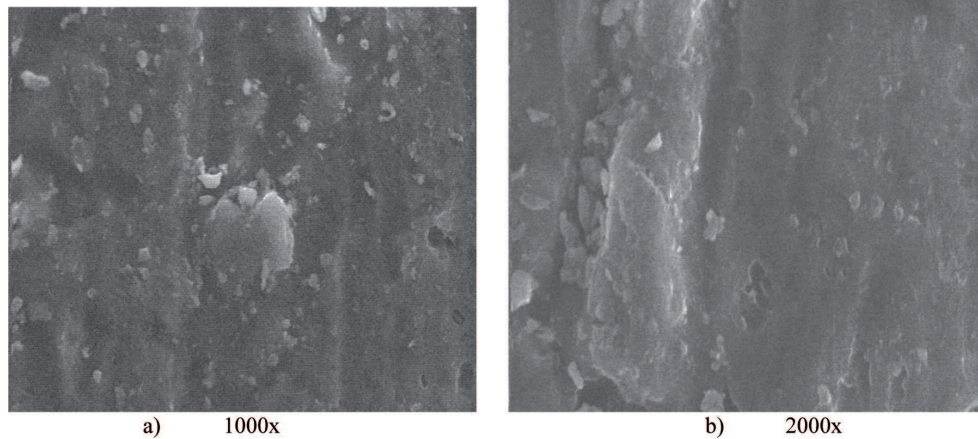


Fig. 9. Surface view of composite layer AHC+GC after sliding against cast-iron pin: a – area without friction containing small pieces of glassy carbon, b – border zone between non rubbed area (left) with stored glassy carbon debris and friction trace with partially worn glassy carbon film (right)

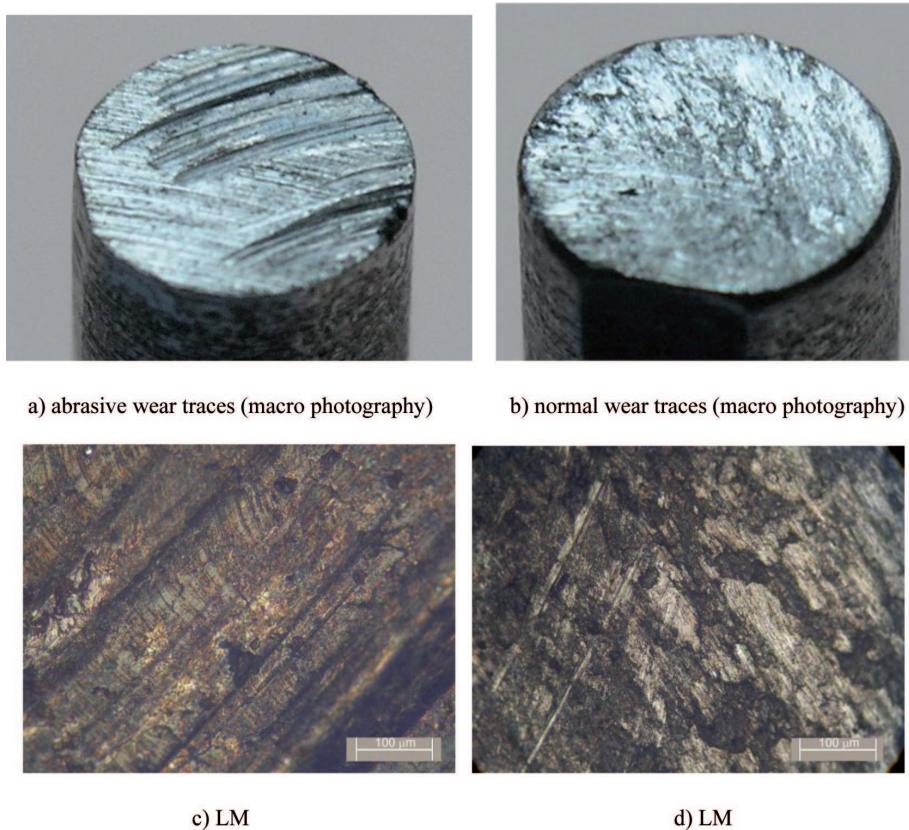


Fig. 10. Working surfaces of pins after friction against AHC (a, c) and AHC+GC (b, d)

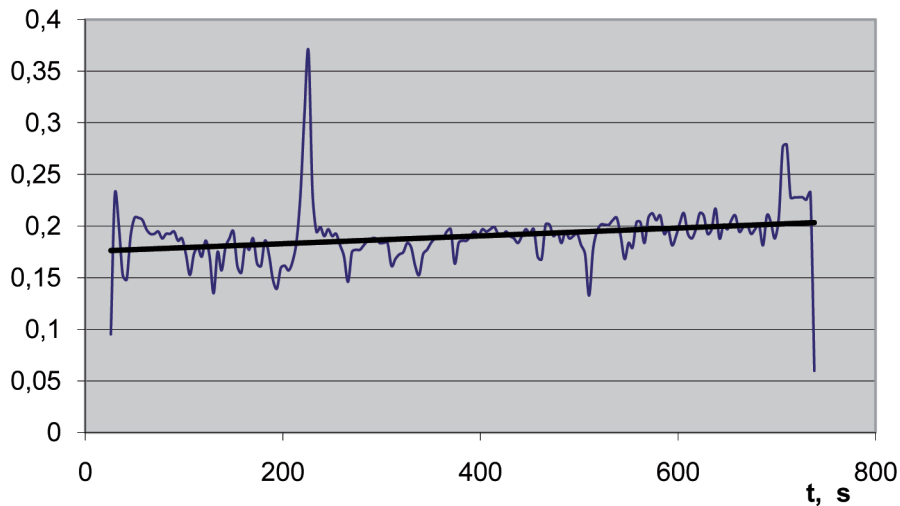


Fig. 11. Friction coefficient in pairing cast-iron EN-GJL-300/AHC v. sliding time ($p = 0.8$ MPa, $v = 1$ m/s; friction in air)

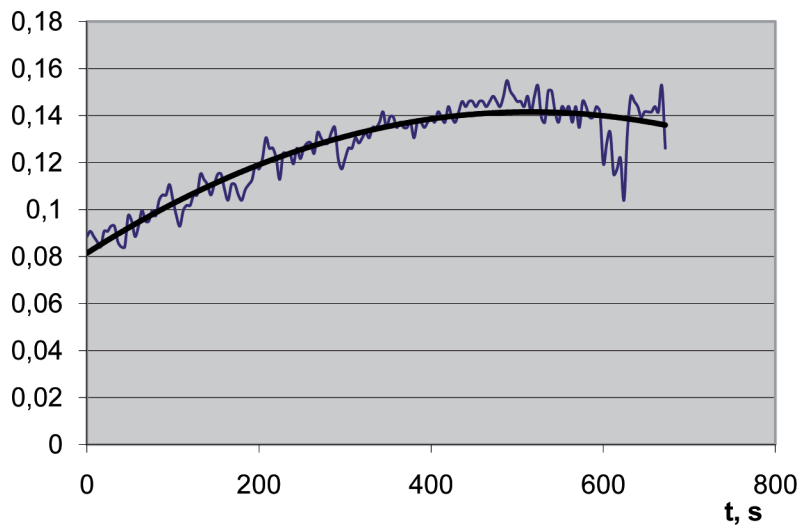


Fig. 12. Friction coefficient in pairing cast-iron EN-GJL-300/AHC+GC v. sliding time ($p = 0.8$ MPa, $v = 1$ m/s; friction in air)

outside the friction zone and intensive abrasive wear of the pin occurs (Figs 10(a) and 10(c)). Since the matrix wear intensity of the cast iron is too weak to uncover new graphite clusters, the friction coefficient increases from 0.25 to 0.3 (wide peak at the end of the diagram, Fig. 11), which corresponds to the values required in frictional pairings eg. brakes. In addition sliding surfaces of cylinder liners in combustion engines are lubricated with oil (four stroke) or air fuel mixture (two stroke) which lowers the friction coefficient. Thus $\mu = 0.3$ has been assumed as maximum level.

Cast iron – composite layer AHC+GC pairing worked well for 30 minutes and the friction coefficient did not exceed 0.15. It is possible due to glassy carbon spread upon the surface (Fig. 9a) and introduced inside oxide layer pores (Fig. 2b). After pairing work for about 10 minutes an excess of glassy carbon (before rubbing in the form of dark strip (4) top of the model in Fig. 3) was removed from the oxide layer surface (Fig. 9b) which

was accompanied by the growth of friction coefficient from 0.08 to 0.14. However the number of glassy carbon particles is big enough to keep the value of friction coefficient below 0.15. Moreover, smaller cracks in the oxide layers are filled with wear debris (Figs 5(b), 6(b) and 8(f)) which lowers the friction resistance. Friction coefficients courses of the tested pairings are presented in Figs. 11 and 12.

When analyzing the diagrams it can be observed that once the glassy carbon is added to AHC the tribological properties of pairing significantly change. Friction coefficient in pairing with GC features clear stabilization area after 300 seconds whereas without GC it increases proportionally to about 600 seconds and then increases dramatically Fig. 11.

Cast iron pin that rubs with oxide layer wears more intensively which is proved by deep grooves upon its working surface (Figs. 10(a) and 10(c)) and starts to seize. Upon the pin working surface at its rubbing with

AHC+GC layer there are slight scratches which are the results of microcutting by protruding roughness peaks of aluminium oxide over glassy carbon (Figs. 10(b) and 10(d)).

4. Conclusion

The worked out composite layers AHC+GC during the friction against cast iron in air feature significantly better sliding properties than oxide layers. Glassy carbon nanotubes (new solid lubricant) formed in oxide layers pores complement the lubricating function of the graphite (traditional solid lubricant) found in the structure of cast iron thus lowering the friction much better than the graphite plated during friction and obtained from the worn out pin.

The time of proper rubbing of cast iron with the tested AHC+GC layer is dependent upon oxide coating structure as well as carbonization parameters. Layers with larger pore diameters let more glassy carbon be introduced which lowers the friction resistance. However, too large pores diameters decrease the thickness of their walls and aluminium oxide hardness. This decreases the load under which the composite layers can work properly. At present some research is carried out to determine the optimum pores diameters and layer porosity which leads to determining the best friction coefficient and layer durability.

Oxide layer cracks, which occur at the tests performed, are definitely their disadvantage resulting from the elaborated process, melting temperature of the alloy upon which the layers are produced as well as the differences in the alloy thermal expansion and oxide coating. Therefore there is strong requirement for further research to be done to determine carbonization parameters which do not cause any cracks in oxide layer and thus prolong its durability.

Usage of metal nanoparticels, for example silver [14] could increase the elasticity of oxide layer and tribological properties of composite layer.

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