MATEC Web of Conferences **129**, 02008 (2017) DOI: 10.1051/matecconf/201712902008
ICMTMTE 2017

Developing of porous composites on the basis of bi-polymers with aluminum particles and AlOOH nanoparticles for getting antifriction coatings

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Abstract. Porous composites on the basis of bi-polymer of natrium-carboxymethylcellulose containing aluminum powder and nano-particles of aluminum oxohydroxide have been developed. With the help of electronic microscopy the sizes of the formed pores were defined: 600 – 1000 µm; the surface porosity of the coating was defined as well, it made 65%. Using methods of x-ray diffraction analysis and infrared spectroscopy it was stated that the phase composition of porous composites remains unchanged in the process of forming. The possibility to form antifriction coatings by filling porous matrixes with solid lubricants is shown on the example of molybdenum disulfide. When applying the coatings to steel surfaces the friction coefficient reduces by 60%. With the help of differential scanning calorimetry the limit of coatings thermo destruction was defined: 300 - 306° C.

1 Introduction

Highly porous materials with cell structure are demanded as filters, catalyst bearers, parts of light constructions, coatings with functional properties. Technologies of getting foamed metals on the basis of nickel, iron, copper, titanium, aluminum are developed. In production scales porous structured metals are produced by injecting inert gases into the melt, stimulating gases generating by using gas emitting reagents, doubling porous polymers structures with metals [1-4]. Polymer net structures, which do not contain metals, may be got easier as a result of systems self-organising [5, 6]. However, approaches, which help to form composite functional materials with cell structure on the basis of polymer matrixes with metal powders using controllable self-organisation, are not studied properly nowadays.

We got [7] porous film materials from water suspensions of natrium- carboxymethylcellulose bi-polymer (Na-CMC) with aluminum powder as a filling and nanoparticles of aluminum oxohydroxide (AlOOH) as microadditives in a relatively cheap and ecologically safe way. Changes in AlOOH quantity let us control the generated cells sizes within the diapasone of 100 – 1000 µm [8]. Biodegradable Na-CMC polymer is nowadays widely used in production and attracts researchers' attention as the basis for developing membranes and packaging films [9-11]. There are almost no works devoted to using porous organic films as antifriction materials. Such composites, produced with the help of using ecologically safe Na-CMC bi-polymer, were of great interest as porous matrixes suitable to develop materials which being combined with different solid lubricants let provide resistanse of the coating under the conditions of environment impact and contact strain. So arose the idea of the work presented: to use film pores for filling them with solid lubricants of different origin and dispersion and to form antifriction coatings to protect metal surfaces under friction conditions.

The powder of molybdenum disulfide (MoS_2) was chosen as solid lubricant. This lubricant is widely used and the results of the researches in the sphere of its antifriction properties are being published during the last 40 years. The friction coefficient of MoS_2 under vacuum conditions is within 0,005 – 0,05 limits [12], it increases when in the air and makes 0,15 – 0,3 due to the possibility of the lubricant to absorb moisture and oxygen [13-14]. To reduce adsorption the authors of the work [14] recommend increasing the density of coatings and decreasing free surface energy. Inserting MoS_2 powder into porous materials supposes becoming the lubricant in the pores more solid when the friction pair contacts dry and reducing the friction coefficient.

The aim of the work presented is to reveal the peculiarities of structure forming and antifriction properties of composite porous coatings developed on the basis of Na-CMC with Al and MoS_2 powders and designed to protect metal surfaces.

2 Materials and Methods

2.1 Materials

Porous films were got by mixing gel-like solution of purified Na-CMC polymer (with the concentration of 2,8%) and aluminum powder particles of spheric shape, the size of particles less than 40 µm. Distilled water was the solvent. Glycerin was used as plasticizer,

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microadditives were nanoparticles of aluminum oxohydroxide – (AlOOH), which were synthesized in accordance with the technique [8]. Forming of samples was made in “wet” way on fluoroplastic wafers with the temperature of (55±1) °C. Films were dried until getting constant mass. The composition of the suspension used for films production is represented in table 1.

Table 1. The composition of the suspension for porous films production.

Components proportion, g.			
Water solution, Na-CMC	Glycerin	Al	AlOOH
100,00	3,00	2,50	0,20

In the process of work the possibility of using the formed porous films as buffer matrixes for developing antifriction materials was determined. It is known that purified watersoluble polymer Na-CMC, used as bond for aluminum powder, possesses adhesive properties. That is why the obtained porous coating after being moistened with water was spread onto samples surfaces made of 40Xsteel which had been degreased with acetone and afterwards hold inside the oven under the temperature of 25°C within 2 hours to provide the adhesion of the film to the metal surface. The lubricant was spread onto the surface of the film with open pores with a brush.

2.2 Techniques

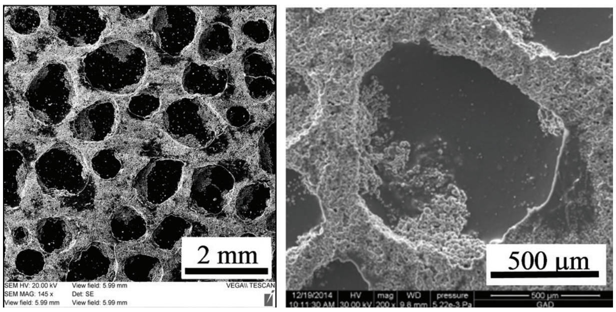
Films morphology was studied with the help of electronically scanning microscopes Quanta 200 in the *Common Use Center* (*CUC*) *Nanotechnologies*, SRSTU (NPI) named after M.I. Platov, VEGA II LMU in the CUC *Mineral Raw Materials and Environment Condition Study Center*, SFU. Dispersion of aluminum powder and molibdenum disulphide powder was defined with the help of MicroTrac Bluewave analyser (*CUC Nanotechnologies*, SRSTU (NPI). X-ray diffraction analysis (XDA) of porous films was made with the help of diffractometer ARL X’TRA within the anglular spacing of 2θ from 5° to 80° with the interval of 0.05°, emission – $CuK_{\alpha 1}$, $K_{\alpha 2}$ (*CUC Nanotechnologies*, SRSTU (NPI). Infrared spectra (IR-spectra) of the films were registered by spectrophotometer FT-08, *Lumex*, within the spacing of 600÷4000 cm^{-1} using the technique of DFIR (disodered full inside reflection).

Antifriction properties of the materials were studied with the help of stand friction unit TMT-25 under the load up to 500 MPa and sliding speed 0,04 m/sec. The experiment lasted for 2 hours. The work environment was air. Termostability of obtained porous films was defined by the technique of differantial scanning calorimetry (DSC), with the help of METTLER TOLEDO calorimeter DSC-1 within the temperature spacing 30,00 - 600,00 °C with the sample heating speed of 20°C min^{-1} and air discharge of 50 ml/min^{-1} in a standard aluminum crucible.

3 Results and Discussions

3.1 Morphology and Structure of Porous Films

Figure 1a shows SEM-picture of composite film surface with cells, obtained on fluoroplastic wafer from Na-CMC suspension with Al and AlOOH powders. Typical pore fragment is shown in Figure 1b. Pores are of domed shape formed mainly by the polymer film with the thickness of 30 µm. Spaces between pores are filled with aluminum microparticles, the diaphragm thickness is about 300 µm. Pore bases are open; cell sizes reach 1000 – 600 µm. In the process of cells forming aluminum particles remained unchanged in thier size and shape. The thickness of porous film is about 100 µm. Total surface porosity of the film, defined with the help of Tescan software *Morphology*, made 65%.



a) b)

Fig. 1. Surface of porous film with Al powder and AlOOH additives – (a), pore fragment – (b)

Results of dispersion analysis of Al and MoS_2 powders are given in histograms in Fig.2 where N means the total amount of enumerated particles, ΔN – the number of particles which got into the diameters spacing, d – particle size. Flat particles of molybdenum disulphide tend to agglutinate; Al and MoS_2 particles distribution according to their size is close. In both cases submicron fraction takes place, particles and agglomerates with the size of 10 – 20 µm prevail. Sizes of the cells, formed in the film, reach 1000 µm which supposes dense packaging of MoS_2 particles having smaller sizes into pore cells.

Diffraction pattern of the porous film is given in Fig 3. X-ray diffraction analysis of the formed porous composites showed the presence of metal aluminum in them (Al cubic cell, space group Fm-3m, elementary cell parameter *a*= 4.0494 Å, PDF card000-04-0787). Absence of AlOOH and aluminum oxides, taking place on the aluminum powder particles in the form of films, may be explained by their low content in the initial composition. Interplanar line spaces in the diffraction pattern of cell composite point at zero-valent condition of metal in the sample. Reflex in the 2θ=18-20 ° field, according to the data [13], is characteristic to cellulose

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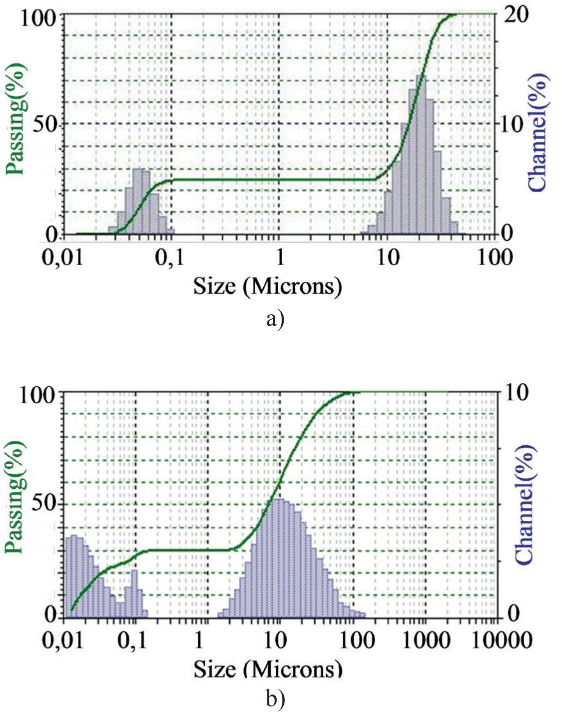
crystallites. There were no structural changes of aluminum in the process of porous composite forming.



a)

b)

Fig. 2. Histograms of particles distribution according to their size: Al powder – (a); MoS_2 powder – (b)

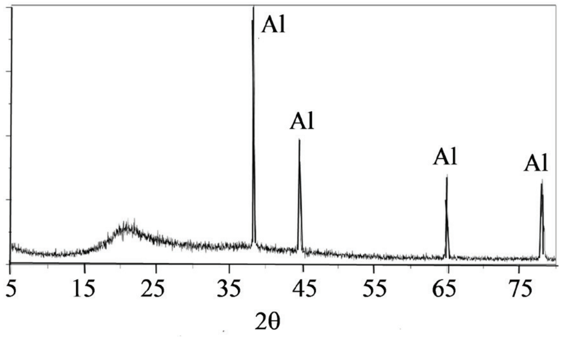


Fig. 3. Diffraction pattern of cell film: Na-CMC+Al

Diffraction pattern of the porous film is given in Fig 3. X-ray diffraction analysis of the formed porous composites showed the presence of metal aluminum in them (Al cubic cell, space group Fm-3m, elementary cell parameter a= 4.0494 Å, PDF card000-04-0787). Absence of AlOOH and aluminum oxides, taking place on the aluminum powder particles in the form of films, may be explained by their low content in the initial composition. Interplanar line spaces in the diffraction pattern of cell composite point at zero-valent condition of metal in the sample. Reflex in the 2θ=18-20 ° field, according to the data [13], is characteristic to cellulose crystallites. There were no structural changes of aluminum in the process of porous composite forming.

Changes in the organic component of porous composites in the process of forming them from solutions were analysed with the help of IR-spectroscopy. Fig. 4 shows IR-spectra of Na-CMC powder, film with empty pores and film with pores filled with molybdenum disulfide. Broad intensive stripe in 3600 – 3000 cm^{-1} field characterises frequencies of valent fluctuations of OH-groups, involved into intramolecular and intermolecular bonds. OH-groups' taking part in forming intermolecular hydrogen bonds shows itself in shifting of absorption stripe towards smaller frequencies [15]. For Na-CMC powder characteristic stripe of absorption makes 3550 cm^{-1}, for the film sample without lubricant – 3500 cm^{-1} and its intensity increases abruptly. Na-CMC macromolecules posess ionised groups which promote Na-CMC macroions repulsing each other. Staying by their conformational structure polyanionic Na-CMC macromolecules mutually repulsing form a space polymer net with distributed aluminum microparticles in the suspension. As a result hydrogen bonds between active hydroxyl groups of macromolecules and oxide shells of aluminum particles are formed. The set of stripes in 1350-700 cm^{-1} field is an individual characteristic for each substance [16]. For Na-CMC powder and porous composite films they are practically identical. Molybdenum disulfide, densely filling pores of the coating, forms tight solid film. IR-diffraction pattern is of little use for defining disulfides which is also proved by spectrum obtained for film with lubricant – absorption stripes almost do not exist in this case.

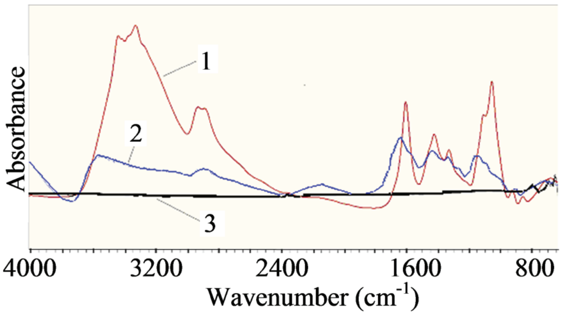


Fig. 4. IR-spectra of samples: Na – CMC powder – (1); Na-CMC+Al porous film – (2) ; Na-CMC+Al+MoS_2– (3)

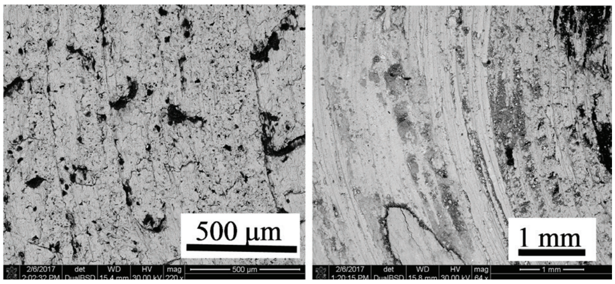
Analyses of IR-spectra and diffraction pattern allow to conclude that initial components in films with generated cells retain their chemical composition unchanged.

3.2 Antifriction Properties of Porous Coatings with Molybdenum Disulfide

Friction pairs were tested dry. The counterbody was made of 47GT steel.

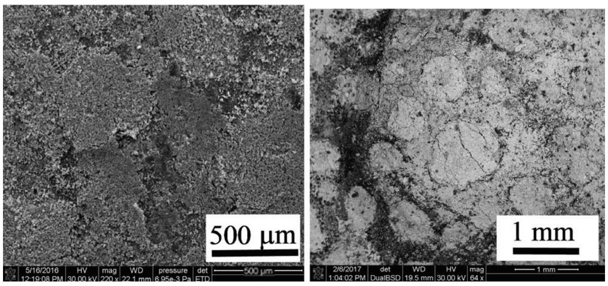
Two types of samples were studied:
- steel uncoated sample after being lathed;
- steel sample with porous coating containing MoS_2.

SEM–pictures of sample surfaces before tests are shown in Fig. 5A, 6A. Sample surfaces after tests on the friction unit are shown in Fig. 5b, 6b. The wear of the steel sample after the tests has mainly adhesive character. In the coated sample in the initial state the pores on the film surface are densely filled with the lubricant – MoS_2. Molybdenum disulfide has laminated structure which provides ‘easy’ glide of friction surfaces against each other, helping to lower friction coefficient and to increase wear resistance of friction-pair parts surfaces. In the process of friction pair work as the temperature gets higher, molybdenum disulfide powder is extruded from the pores and fills the surface of composite matrix on the basis of Na-CMC containing aluminum powder with lubricant film. After tests on the friction unit samples with composite coating obtain smooth shiny surface. Pores-cells with compacted lubricant are clearly seen on the sample surface, nevertheless there are no traces of solidification which, in turn, leads to wear resistance increase (Fig. 6b).



a) b)

Fig. 5. The steel surface: before – (a) and after – (b) friction tests

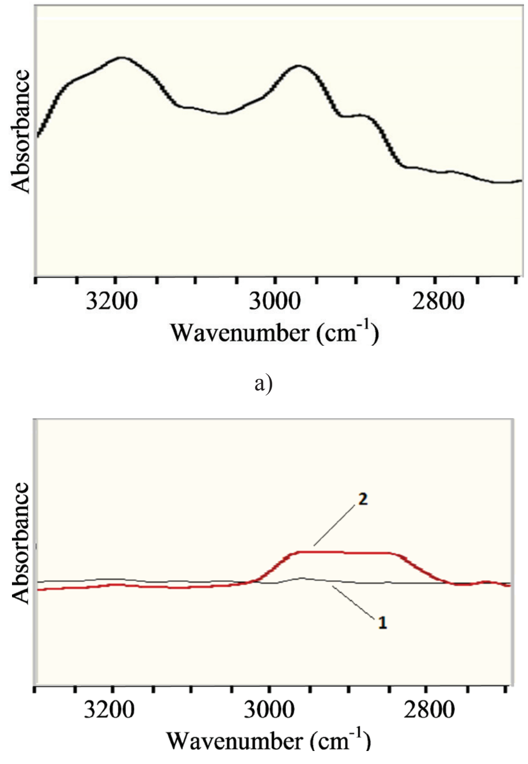


a) b)

Fig. 6. Surface coated with Na-CMC+Al+ MoS_2: before – (a) and after – (b) friction tests

After friction tests IR-diffraction pattern of coated steel sample showed the presence of polymer Na-CMC (3600 – 3000 cm^{-1} field, Fig. 7A). This fact witnesses of retaining of the coating polymer component on protected metal surface. The possibility to re-locate Na-CMC polymer onto the contacting the composite coating counterbody surface was defined. With this purpose IR-spectra of metal counterbody surface were compared before and after the tests (Fig. 7b). IR-spectrum of the initial steel counterbody surface does not have absorption stripe in 3000 – 2800 cm^{-1} field characteristic to OH-groups valence fluctuations, whereas after the tests it appears in counterbody surface spectrum. Consequently, the formation of friction re-location film takes place.

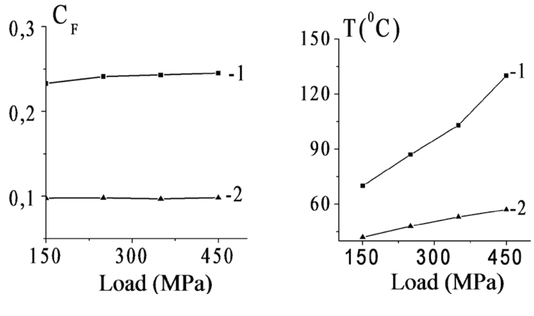
Changes of friction coeffitient C_F for studied samples, depending upon the applied load, is shown in Fig. 8a. For the sample, protected by porous coating with MoS_2 friction coefficient lowers dramatically – by 60% comparing with the friction coefficient for steel surface (Fig. 8a, curves 1 and 2). Its value does not practically change and makes 0,09. While contacting coated samples the counterbody temperature increases only by 15-16%, whereas while contacting steel surfaces it practically doubles (Fig. 8B). It is known that insertion of MoS_2 into antifriction material lets increase materials heat conduction by several times. Aluminum heat conduction is higher than that of steel by 4-5 times. That is why heat is better abducted by means of composite coating Linear wear of uncoated steel sample made 4,7 µm during the test time (2 hours), of coated sample – 12,3 µm. Consequently, after the test more than 80% of initial thickness of composite coating retains. In the process of friction pair work friction re-place of composite coating onto metal counterbody and formation of re-place film takes place.



a)

b)

Fig. 7. IR-spectra: (a) – of coated surface after friction tests; (b) – of counterbody surface before (1) and after (2) the tests



a) b)

Fig. 8. Influence of load, applied to samples 1-2, on: friction coefficient C_F – (a); counterbody temperature T – (b)

3.3 Scanning calorimetry of porous coatings with molybdenum disulfide

In the composite functional coatings under study thermally vulnerable component is biopolymer. Analysis, made by methods of scanning calorimetry showed that relatively small exopick takes place when the temperature is 306°C and corresponds destruction of cellulose components. However thermo destruction of the coating takes place when the temperature is 450°C which does not contradict data about thermal destruction of MoS_2 existing in literature sources.

4 Conclusion

The paper presented shows the possibility to form porous materials from natrium-carboxymethylcellulose suspensions with aluminum microparticles and aluminum oxohydride nanoparticles. In the process of solidification oriented open cells with the size of 1000 – 600 μm are generated in the films. Using methods of X-ray analysis and infrared diffraction pattern it was defined that chemical composition of the composite porous coating remains unchanged in the process of formation.

New porous composite materials perspective as buffer matrixes for creating antifriction coatings are developed. Filling pores with lubricant – molybdenum disulfide – allows to lower friction coefficient by 60% and works towards the increase of coating heat conduction and its wear resistance.

The limit for thermo destruction of antifriction coatings of 450°C is stated.

Authors express gratitude to Alexey Yatsenko, CUC Nanotechnology, SRSTU (NPI) named after M.I. Platov for help with fulfilling SEM-pictures of our materials.

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