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The Inelastic/Elastic and Tribological Properties of PTFE-Based Nanocomposites Filled with Co Cluster-Doped CNTs

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The elastic/inelastic behavior and tribological properties of new PTFE-based nanocomposite materials filled with 5wt% and 10wt% Co atomic cluster-doped carbon nanotubes (CNTs) was investigated using low-frequency amplitude-independent (AIIF) and amplitude-dependent (ADIF) internal friction measurements, compressive deformation and tribological test methods. It was shown that the Co atom cluster-doped CNTs filler provides a considerable positive effect on the physicomechanical characteristics of the respective PTFE-based nanocomposite materials used for tribological applications. The obvious effectiveness of the externally applied gradient magnetic field in the process of mixture preparation has been established for sintering of the PTFE-based nanocomposite materials modified by carbon nanotubes doped with the ferromagnetic atom (Co) clusters, finally resulting in the improvement of wear- and creep resistance of the obtained nanocomposites. *© 2020 Bull. Georg. Natl. Acad. Sci.*

PTFE, co cluster-doped CNTs, nanocomposite, internal friction, wear

The survey study of many decades show that polytetraflouroethilene (PTFE) has been widely used as an engineering plastic because of its outstanding thermal stability, good solvent resistance and lowest friction coefficient among the existing tribotechnical materials [1-3]. However, PTFE exhibits a high wear rates under normal sliding conditions, bad heat- and electric conductivities, low compressive resistance and also a cold-flow phenomenon (low creep resistance) under load. These main deficiencies of virgin PTFE become limiting factors for numerous engineering applications in automotive, aerospace, petro-chemical and other industries. On the other hand, the unique combination of physical-mechanical properties of virgin PTFE, that distinguish it from other polymeric materials [4], creates big potential for the development of a wide spectrum of advanced PTFE-based composite/ nanocomposite materials with excellent functional characteristics, using a modifying of the matrix by several micro/nanoparticles of fillers. The reviews of the last decade literature [5-7] showed that a distant effect on friction and wear behavior of PTFE may be caused by micro-scale as well as nanoscale ceramic fillers. Along with the development of nanoparticles production technology during the last decade, mostly on carbon nano-forms (CNTs, CNPs, CNBs, CNWs), the interest in them as the PTFE matrix modifiers have also considerably raised. From this point of view, use of the nanoparticles of CNFs as a filler for the PTFE matrix would provide a considerable improvement in the heat- and electric conductivities coupled with the increase in its strength that is impossible in the case of ceramic filler nanoparticles. The existing researches on this matter [8-9] have already revealed a very high potential of carbon nanoforms as the filler of the PTFE matrix for the production of multi-functional nanocomposites for diversified applications. Along with the development of nanocompositional CNFs production technology, preferably of core-shell-type carbon nanotubes (CNTs) and carbon nanoparticles (CNPs) doped with the ferromagnetic (Fe, Co, Ni) atom clusters [10, 11], as the unique hybrid fillers for PTFE matrix, has deserved a considerable attention. The new PTFE-based trial nanocomposite materials filled with the Fe atom cluster-doped CNTs were first studied in the authors' recent works [12, 13], where a drastic improvement of physical, mechanical and functional properties of the obtained nanocomposites in comparison to virgin PTFE were demonstrated. However, to date, few data have been reported on the structure-properties relation in the PTFE-based nanocomposites filled with the ferromagnetic atom cluster-doped CNTs. Consequently, for further development of the above-type advanced multi-functional PTFE-based nanocomposites for the diversified applications a complex study of their properties in the wide range of temperatures and deformation rates is important, using structure-sensitive, multi-parametric measuring/ testing techniques. Thus, the aims of the proposed work are: comparative study of elastic/inelastic behavior and tribological properties of new trial PTFE-based nanocomposite materials filled with 5wt% and 10wt% of Co atomic cluster-doped CNTs using the AIIF and ADIF measurements, compression deformation and tribological tests methods.

Experimental

The choice of the PTFE-based nanocomposite materials filled with 5wt% and 10wt% of Co-cluster-doped CNTs was conditioned by the authors' recent results obtained for the new PTFE-based nanocomposites filled with different amount (2.5, 5, 7.5, 10 wt%) of nanopowders composed of Fe-cluster-doped CNTs [12, 13]. The standard bulk test samples for each method of experimental study were synthesized via powder metallurgy route similar to the diagram of main steps of the preparation process described by the authors in [13]. The synthesis of the magnetic carbon nanopowders composed of Co-cluster-doped CNTs as a nanocompositional filler was performed in the ethanol vapor pyrolysis experimental set-up described in [10]. For the comparative study of the filler's dispersity influence on the properties of the nanocomposite under study, two batches of the nanocomposite test samples with the same content of the filler (5wt%) were obtained by sintering of a conventionally dry blended mixture and the mixture suspension blended in the external gradient magnetic field. The compression resistance was measured at 30 MPa pressure with the linear deformation mechanism. The study of the tribological parameters was conducted on the friction machine where the test samples of the developed new nanocomposite materials were torsionally worn against the tubular gray cast iron counter body at 0.7 MPa pressure, with the sliding velocity of 0.25÷0.87 m/s. The low-frequency

(~1Hz) AIIF and ADIF measurements were performed in vacuum ~10^{-3} torr at the frequencies of 0.5÷5 Hz, the amplitude of deformation 10^{-5}÷10^{-3}, and the rate of heating/cooling ~2˚C/min, over the temperature range 20÷300˚C.

Result and Discussion

Fig.1 shows the AIIF $Q^{-1}(T)$ temperature spectra (a) and shear modulus G~f^2(T) temperature spectra (b) for the two new trial PTFE-based nanocomposite materials filled with 5 wt% (curve1) and 10 wt% (curve 2) nanopowders, composed of monomodal Co atom cluster-doped CNTs. The chosen magnitude of deformation (**ε** ≤ $2{\cdot}10^{-5}$) ensured the measurements of internal friction to be performed in the AIIF range. Two relaxation regions were revealed on the $Q^{-1}(T)$ curves in the temperature range 20 ÷ 300˚C which are well known as β- and α-peaks for the unfilled (reference) PTFE and the PTFE-based nanocomposites filled with the Fe atom cluster-doped CNTs of the same concentration. However, in the cases of the PTFE-based nanocomposite samples filled with 5 wt% and 10 wt% of Co atom cluster-doped CNTs, the positions of β- and α-peaks are shifted to 38˚C and 50˚C for β-transition, and to 135˚C and 144˚C for α-transition in comparison to those of the unfilled PTFE [13]. The activation energies of β- and α-transformations were derived from the frequency shift of the Q^{-1} peaks. The frequency factors of relaxation were determined from the exponential dependence of relaxation time on the absolute temperature. Fig. 1. b demonstrates that the relaxation processes in the investigated nano-composites under investigation are accompanied by the clearly defined decays in the shear modulus on the G~f^2(T) curves, coinciding with the temperatures of IF peaks on the $Q^{-1}(T)$ curves (Fig.1.a).

In the process of cooling of the examined samples to room temperature with the rate of ~2˚C/min, an almost complete recovery of shear modulus and the trend of the $Q^{-1}(T)$ curve were observed. The experimentally determined and

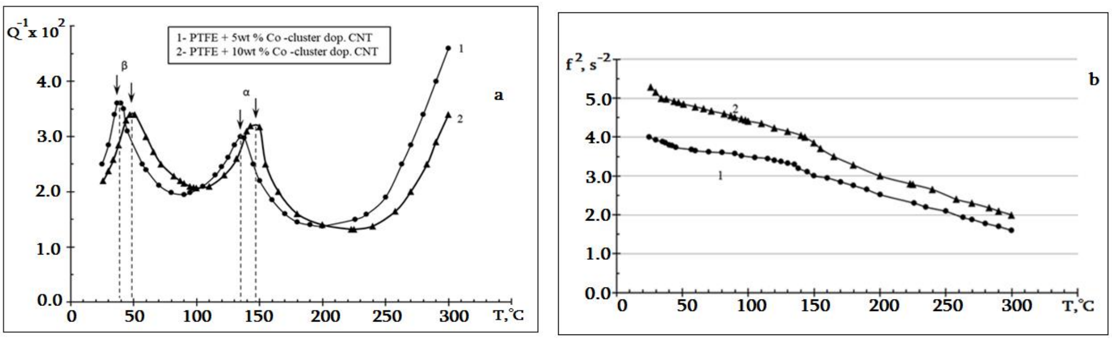

Fig.1. The amplitude-independent internal friction $Q^{-1}(T)$ – (a) and shear modulus G ~ $f^2(T)$ – (b) temperature spectra of the two new trial PTFE-based nanocomposite materials, filled with 5 wt% (curve 1) and 10 wt% (curve 2) nanopowders composed of Co-cluster-doped CNTs.

Table 1. Activation characteristics of the relaxation processes near the β- and α-peak temperatures in the PTFE-based new nanocomposites with 5wt% and 10wt% content of Co-cluster-doped CNTs as filler

Composition of samples	Relaxation process's type		IF peaks T_{max}, ˚C	IF peaks f_{max}, sec^{-1}	Activation energies H, kcal/mole	Frequency factor τ_o^{-1}, sec^{-1}
PTFE+5wt%Co-dop.CNT	β		38	1.80	18.4	$1{\cdot}10^{14}$
		α	135	1.65	26.5	$1{\cdot}10^{15}$
PTFE+10wt%Co-dop.CNT	β		50	2.0	19.3	$1.3{\cdot}10^{14}$
		α	144	1.80	27.7	$2.5{\cdot}10^{14}$

calculated values of activation characteristics (activation energies, frequency factors) of β- and α-relaxation processes near temperatures corresponding to the β- and α-peaks of the new PTFE-based nanocomposite materials, filled with the Co atom cluster-doped CNTs are shown in Table 1.

relaxation processes. Measurements of amplitude-dependent internal friction (ADIF) for the above nanocomposite materials show that above certain critical magnitude of deformation the intensity of IF strongly increases along with the increase in amplitude of vibration deformation. Fig. 2 shows the results of amplitude-dependent internal friction

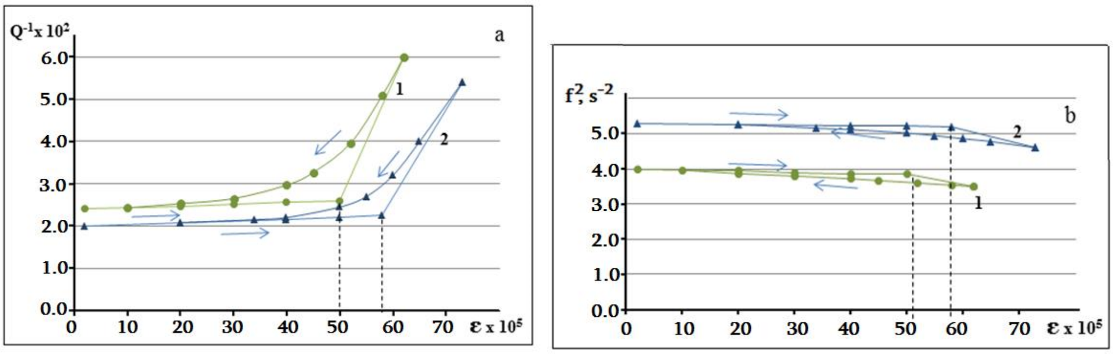

Fig. 2. The amplitude-dependent internal friction $Q^{-1}(\varepsilon)$ – (a) and shear modulus $G \sim f^2(\varepsilon)$ – (b) spectra of the two new trial PTFE-based nanocomposite materials, filled with 5 wt% (curve 1) and 10 wt% (curve 2) nanopowders composed of Co-cluster-doped CNTs.

Table 2. Summary of tribological and mechanical test results for the two pilot samples of nanocomposite material PTFE + 5 wt% Co-cluster-doped CNTs, prepared by sintering of a conventionally blended mixture (N:2 – 5wt%Co) and sintered from a mixture blended in the external magnetic field (N:2M – 5 wt% Co)

Composition of nanocomposite and Test samples N:	Friction speed V, m/sec	Temperature T, °C	Friction coefficient f	Wear intensity I, 10^{-9}	Compression under 30 MPa, %
PTFE + 5wt% Co-cluster-doped CNTs N:2 – 5wt% Co	0.25 0.38 0.62 0.87	70 125 185 205	0.21 0.23 0.28 0.27	1.8 1.2 0.4 2.0	9.2
PTFE + 5wt% Co-cluster-doped CNTs N:2M – 5wt% Co	0.25 0.38 0.62 0.87	75 100 160 230	0.23 0.27 0.27 0.31	1.8 1.2 0.7 2.0	4.5

The comparatively high values of the relaxation frequency factors indicate at the reversible processes of reconstruction in the sub-systems of defects in the localized areas (pinning centers) of the nanocomposite material's structure. The observed tendency to increase the temperature of the IF β- and α-peaks along with the amount of a filler apparently is a result of a considerable influence of quantity of the Co-cluster-doped CNT nanoparticles, incorporated in the matrix that increases the activation energies of β- and α-

$Q^{-1}(\varepsilon)$-(a) and shear modulus $G \sim f^2(\varepsilon)$-(b), measured at 20°C for the new two trial PTFE-based nanocomposite materials, filled with 5wt% (curves 1), and 10wt% (curves 2) nanopowders composed of Co-cluster-doped CNTs. It is obvious that, in this case, as well as in the case of the PTFE-based nanocomposites modified by Fe atom cluster-doped CNT nanopowders, increase of filler content leads to the increase in the critical amplitude of microplastic deformation beginning ε_c (see Fig. 2). The measurements of internal friction and shear modulus of the PTFE-based nanocomposite materials filled with the Co atom cluster-doped CNTs at room temperature in the range of amplitudes of deformation $10^{-5} \div 10^{-3}$ (analogous to the nanocomposites filled with the Fe atom cluster-doped CNTs of the same concentration [13]), revealed a critical point (ε_c) from which begins a drastic increase in the intensity of internal friction and the respective linear reduction of shear modulus. The $Q^{-1}(\varepsilon)$ and $f^2(\varepsilon)$ curves (Fig.2.a, b) recorded during the increase and decrease in amplitude of deformation shows, some discrepancy in the form of a closed loop of hysteresis. The samples with a high content of Co-cluster-doped CNTs are characterized with the increased ε_c and a comparatively small area of the hysteresis loop which closes at high values of ε.

The pilot samples of PTFE + 5wt%Co-cluster-doped CNTs, synthesized from the mixtures prepared by a conventional dry mixture blending technique and by mixture suspension blending in the external gradient magnetic field were tribologically tested at different friction speeds on a vermicular cast iron counterbody under P = 0.7 MPa load. Cylindrical samples of the same material were also tested under compression deformation at 30 MPa.

In Table 2 a summary of tribological and mechanical test results for the two pilot samples of the above nanocomposite material is presented. The sample N: 2 – 5wt% Co is prepared by sintering of a conventionally dry blended mixture, while the sample N: 2M – 5wt% Co was sintered from a mixture suspension blended in the external gradient magnetic field.

Thus, a significant effect of external gradient magnetic field on the preparation process of a sintering mixture have been revealed for the PTFE-based nanocomposite materials filled with the ferromagnetic atom (Co) cluster-doped CNTs. In particular, in the case of the PTFE-based nanocomposite synthesized from the mixture containing 5 wt% Co atom cluster-doped CNTs, and prepared in the external gradient magnetic field, the following characteristics were revealed: High wear resistance is retained at the increased coefficient of friction up to 0.31, reduction of compression deformation for ~50% under 30MPa in comparison to the nanocomposite of the same composition but synthesized from the conventionally blended dry mixture.It is obvious that during blending of a mixture suspension of PTFE micro-particles and the nanoparticles of the filler (Co-cluster-doped CNTs) a more uniform (without segregations) distribution of the filler nanoparticles is achieved in the volume of the matrix of the synthesized nanocomposite.

Conclusions

1. The regularities of alteration of activation energies (H), frequency factors (τ) of β(crystalline)- and α(amorphous)-relaxation processes and critical amplitudes of microplastic deformation beginning (ε_c) in the new PTFE based nanocomposite materials, filled with 5 wt% and 10 wt% Co atom cluster-doped CNTs, were determined from the obtained experimental $Q^{-1}(T,\varepsilon)$ and $G(T,\varepsilon)$ spectra.
2. It is shown that the Co atom cluster-doped CNT filler, analogous to Fe atom cluster-doped fillers, provides a positive effect on the physicomechanical characteristics of the respective PTFE-based nanocomposite materials used for tribological applications.

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ფიზიკური ქიმია

კობალტის კლასტერებით დოპირებული CNT-ით შევსებული PTFE-ფუძიანი ნანოკომპოზიტების დრეკადი/არადრეკადი და ტრიბოლოგიური თვისებები

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დაბალსიხშირული ამპლიტუდისაგან დამოუკიდებელი და დამოკიდებული შინაგანი ხახუნის გაზომვების, კუმშვითი დეფორმაციისა და ტრიბოლოგიური გამოცდის მეთოდებით გამოკვლეულია დრეკადი/არადრეკადი და ტრიბოლოგიური თვისებები პოლიტეტრაფთორ-ეთილენის ფუძეზე შექმნილი ნანოკომპოზიციებისა, რომლებიც შევსებულია კობალტის კლასტერებით დოპირებული ნახშირბადის ნანომილაკებით. ნაჩვენებია, რომ კობალტის ატომების კლასტერებით დოპირებული ნახშირბადის ნანომილაკებით შევსება დადებით გავლენას ახდენს PTFE-ფუძიანი ნანოკომპოზიციური მასალების ფიზიკურ-მექანიკურ მახასიათებლებზე. დადგენილია ნარევის შექმნის პროცესზე გარეშე მაგნიტური ველის გავლენის ცხადი ეფექტურობა, ფერომაგნიტური ატომების (Co) კლასტერებით დოპირებული ნახშირბადის ნანომილაკებით მოდიფიცირებული PTFE-ფუძიანი ნანოკომპოზიციების სინთეზისათვის. აღნიშნული ვლინდება მიღებული ცვეთა-ცოცვა მედეგობის გაუმჯობესებაში.

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