

Investigation of new antifrictional/frictional nanocomposites based on PTFE matrix filled with Fe-doped carbon nanoparticles

Elguja Kutelia^{1*}, David Gventsadze², Olga Tsurtsunia¹, Leri Rukhadze¹, Nikoloz Jalabadze¹, Tengiz Kukava¹, Teimuraz Dzigrashvili¹

¹Republic Centre for Structure Researches of Georgian Technical University, 77 Kostava str., Tbilisi 0175, Georgia.

²R. Dvali Institute of Machine Mechanics, 10 Mindeli str., Tbilisi 0186, Georgia

*Corresponding author

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Abstract

The present work is dealing with the study of a nano-compositional material which was obtained on the basis of PTFE with 2.5÷10wt% of core-shell type Fe-doped carbon nano-tubes and carbon nano-particles as fillers. The PTFE samples without the fillers were prepared too. Weight wear, friction coefficient and temperature were measured after passing some velocity steps, and afterwards the linear wear was calculated. The obtained results have shown that the incorporation of about 2.5÷5wt% of Fe-doped CNTs into PTFE matrix drastically improves the antifrictional properties in comparison to the unfilled PTFE. Namely, the wear resistance of these nanocompositions increased by the factor of 500-150 in the range of friction velocities 0.25÷1.25 m/sec. Increase of the filler portion up to 10wt% transforms the obtained nanocomposite from antifrictional to friction material with the enhanced coefficient of friction up to 0.32, but with the unexpectedly ultra-low wear. SEM-EDX analyses of the worn surfaces of the tested nanocomposites and the cast iron samples after working as a tribological pair, revealed some favorable effects of the Fe-doped CNTs filler on the formation mechanism of a transfer film and its role in promoting very low wear of the obtained new nanocomposites. Copyright © 2018 VBRI Press.

Keywords: Nanocomposite polymer, PTFE, Fe-doped CNT, transfer film.

Introduction

The idea of adding fillers to polymers in order to improve their physico-mechanical properties has been successful for many decades since a virgin (single) polymeric material generally does not possess the right set of properties to be used for particular applications. Currently, improvement of physico-mechanical and tribological properties of polymeric materials by incorporation of small amounts of various micro/nano solid particles (carbides, borides, nitrides, oxides and carbon nano-forms) into the polymer matrix is well known [1-8]. It is also known that the Polytetrafluorethylene (PTFE), as a tribotechnical material, is a unique among the existing polymers, as a solid body having the lowest coefficient of friction (0.05÷0.1) at temperatures up to 300°C, and which is distinguished by its lowest ratio of surface shear strength to volume shear strength ($s/\tau = 0.2$). However, this material has four main deficiencies as a tribotechnical material. Notably, insufficient mechanical strength, low thermal conductivity, high thermal expansion coefficient and increase in friction coefficient up to 0.3 at high speeds of sliding [1]. Alteration of a coefficient of friction along with the increase in sliding speed is

definitely related to the increase in temperature of the material with the low thermal conductivity, and is caused by friction self-heating. The latter unambiguously points at the viscous-elastic nature of the friction mechanism of the PTFE. Consequently, a direct influence on the viscous-elastic features of the material through modifying its matrix may be a key to the purposeful control of friction and wear of the PTFE-based nanocomposites.

The conventional approach to the strengthening and improvement of tribological properties of the polymer matrix via incorporation of micro/nano-ceramic particles (oxides, nitrides, carbides etc) in the matrix, in spite of a considerable strengthening, does not lead to the stability of friction and wear parameters of the nanocomposite polymer in wide range of temperatures during friction at high speeds and under heavy load. Notwithstanding the strengthening of the polymer matrix, the above is caused by the fact that the ceramic nanoparticles as fillers (modifiers) do not provide a considerable increase in the intrinsic low heat conductivity of the matrix. The solution to this problem occurred after the development of the technology of the synthesis of nanopowders composed of carbon nanoparticles of different nano-forms, such as carbon nanotubes (CNTs), carbon nanoparticles (CNPs) and carbon nanowires (CNWs) [2]. It was expected, that

because of the unique physico-mechanical properties (high values of heat- and electric conductivities and strength) of carbon nanoparticles (CNT, CNP, CNW etc), their application as fillers in polymer matrix would provide a considerable increase in the heat- and electric conductivities of the obtained nanocomposites; along with the increase in their strength. Currently, the most studied polymer of the above kind is the poly-methyl-methacrylate (PMMA) [2,9], while from the tribotechnical point of view, the study of the most promising polymer PTFE, modified by the carbon nanotubes (CNT), is too limited. Anyway, the existing researches on this matter [2, 10] have already revealed the very high potential of carbon nanoforms (CNT, CNP, CNW) as the fillers of the polymer matrix in order to produce the multi-functional nanocomposites. Preferably, for production of new PTFE-based nanocompositional materials of tribo-technical use, which are capable of excelling in modern machinery and are becoming increasingly complex, imposing a larger number of functional requirements than those possessed by current polymer-based composite solid lubricants. Consequently, the combination of the unique and desirable physical and mechanical properties of the PTFE and the carbon nano-form (CNF) particles (CNTs, CNPs, CNWs), incorporated in the PTFE matrix for production of novel nanocomposites, has already received much attention for their tribological application.

It is generally known that the effective functioning of the polymer-based nanocomposites as solid self-lubricating materials is directly connected to its ability to form on the surface of the counter body during wear a very thin and uniform highly adhesive wear-resistant transfer film. Clearly, despite the type of the polymer, the very important role in the formation of friction properties of the transfer film play the nature of the filler nanoparticles introduced into the polymer matrix, their composition, shape, dimensions, physicochemical properties, distribution in the volume and the degree of compatibility with the matrix [7-10]. Therefore, the role of the filler nanoparticles in preventing wear and improving the physico-mechanical properties of the PTFE-based nanocomposites remains an important topic of debate and the technological experiments. From this point of view, use of nanoparticles of carbon nano-forms (CNTs, CNPs, CNWs), doped with the ferromagnetic (Fe, Co, Ni) atoms (clusters) [11], as the hybrid fillers for the PTFE matrix has deserved a considerable attention.

Thus, the aims of the proposed work are first to study the frictional, wear and transfer responses of the developed new nanocomposites based on the PTFE matrix, filled with the core-shell type Fe atoms (clusters)-doped carbon nanoparticle, and thereafter perform a complex SEM and EDX investigation of the structure transformations and the elemental distribution on the surfaces formed during torsional friction of the pair of cast iron and the tested nanocomposite samples.

Experimental

The nanocomposites based on PTFE matrix filled with the Fe clusters-doped CNTs and the core-shell type CNPs were prepared by the powder metallurgy route. The magnetic carbon nanopowders doped with Fe clusters, as the nanocompositional fillers for the PTFE matrix, were produced using the method developed by the authors and described in the previous works [11,12]. The PTFE powder, with the unit weight of 2200 kg/m³ and the grain size of 0.2 ÷ 0.5 μm, mixed with the different mass fractions of Fe-doped CNTs nanopowders (2.5, 5 and 10 mass %), were produced by blending the constituents followed by cold compaction of the samples in a uniaxial compaction machine under the load of 80 MPa and the holding time 2 minutes. The tubes and the rods were cold pressed with the Ø28/Ø20/20 mm and Ø10/20 mm dimensions respectively. Sintering of the test samples was performed at 360 °C for 2 hours, and then cooled down till room temperature. The PTFE samples without the fillers and the testing samples of one of the best commercial tribological materials, "Superfluvis" [10], were also prepared for a comparative study. The specific weights of the samples were determined using the weight measuring method, while 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 (and the reference materials) were torsion worn against the tubular gray cast iron counter body at 0.7 MPa pressure, with the sliding velocity of 0.25 ÷ 1.25 m/s and gradual increasing. Weight wear, friction coefficient and temperature were measured after passing some velocity steps, each one hour-long, and afterwards the wear rate was calculated. The worn surfaces of the tested nanocomposites and the cast iron samples (counter face), after working as a tribological pair, were analyzed using the SEM and EDX methods. It should be pointed out that in our experiments the new counter faces were used for each test. So, the efforts were made to ensure that each nominally identical counter face (fine-ground surface of a cast iron) was created under the same conditions

Results and discussion

The mean coefficient of friction (*f*), friction speed (*v*), near contact temperature (*T*°C) and wear intensity (*I*) were measured for each sample of the new nanocompositional materials (with 2.5, 5, and 10wt% of the Fe-doped CNPs as the fillers) and the reference materials (unfilled PTFE and one of the best conventional tribo-technical material "Superfluvis"), which were tested against gray cast iron in the mode of rotating torsional sliding friction after the steady-state. The data for each sample, obtained under the identical experimental conditions, are summarized in **Table 1**.

As the **Table 1** shows, the wear intensities of all the three new nanocomposites, produced by filling the PTFE matrix with the Fe-doped CNTs nanoparticles, are

Table 1. Summary of tribological test results for the three developed new (PTFE + Fe-dop.CNPs) nanocomposites and the two reference materials.

Friction speed V, m/s	Unfilled (PTFE)			PTFE + 2.5 mass% Fe-dop.CNT			PTFE + 5 mass% Fe-dop.CNT			PTFE +10 mass% Fe-dop.CNT			“Superfluvis”		
	T, °C	f	I,10 ⁻⁹	T, °C	f	I,10 ⁻⁹	T, °C	f	I,10 ⁻⁹	T, °C	f	I,10 ⁻⁹	T, °C	f	I,10 ⁻⁹
0.25	40	0.14	892	50	0.21	1.79	45	0.18	1.82	45	0.19	1.84	70	0.18	10.0
0.38	62	0.14	310	70	0.23	1.20	60	0.19	1.21	100	0.23	1.22	75	0.13	9.0
0.62	85	0.13	123	135	0.25	1.44	90	0.19	0.73	160	0.25	0.5	125	0.15	12.0
0.87	120	0.13	158	200	0.25	2.56	200	0.21	1.56	215	0.26	1.57	180	0.15	11.0
1.25	180	0.14	330	240	0.21	28.76	230	0.21	6.90	280	0.32	5.89	180	0.14	6.0

drastically reduced in comparison to those of the unfilled PTFE. This effect is maximally revealed at comparatively low speeds of friction. Namely, in spite of some increase of friction coefficient at 0.25 m/s of friction speed, the wear intensity of all the three nanocomposites are 500 times lower than that of the unfilled PTFE, and 260 times lower at 0.38 m/s of friction speed. Further increase of friction speed up to 0.62, 0.87 and 1.25m/s makes the tendency of improvement the wear resistance weaker than it was at low speeds.

Here should be noted an interesting feature of the new nanocomposite materials (mainly with 5 and 10 wt% of filler), they all have the lowest value of wear intensity at 0.62 m/s than at the lower and higher speeds of friction. The latter may be related to the fact that the unfilled PTFE also has the lowest value of wear intensity at exactly 0.62 m/s of friction speed. A comparison of the tribological test results of the three new PTFE-based nanocomposites and one of the best commercial self-lubricating reference material “Superfluvis” (Table 1) leads to the conclusion that wear resistance of the new nanocomposites considerably (5–7 times) exceeds that of the reference material at low speeds (0.25–0.87 m/s) of friction. However, this preference is specifically exhibited at a friction speed of 0.62 m/s. Thus, the lowest values of wear intensity of the nanocomposites containing 5 and 10 wt% of filler, in comparison to those of the reference composite, are lower by the factors of 16 and 24 respectively, in spite of friction coefficients of the new PTFE-based nanocomposites are higher to some certain degree than those of the reference composite materials.

The noted inverse correlation between the friction coefficients and the wear intensities is more tangible at high speeds of friction. Particularly, the coefficient of friction of the PTFE-based nanocomposite containing 10 wt% of Fe-dop.CNTs is equal to 0.32 at friction speed of 1.25 m/s, while the wear resistance of this material is the same as for the best self-lubricating reference material, and the friction coefficient of which in the same conditions equals to 0.14. Consequently, the above nanocomposite should be considered as the frictional material with the very low wear rate.

The above considerable improvement of tribological properties of the developed new PTFE-based nanocomposites, achieved by the incorporation of the Fe-doped CNPs in the PTFE matrix, in some certain degree, is caused by the polymer matrix strengthening effect by-turn conditioned by the new filler. The direct indicator of the considerable strengthening effect caused by the

incorporation of the Fe-doped CNTs nanoparticles in the PTFE matrix is the increase (more than 2 times) of the compression resistance of the new nanocomposites in comparison to that of the unfilled PTFE, both measured by the authors at 30 MPa pressure with the linear deformation. However, the observed peculiarities of wear rate and friction coefficient, occurring when the content of the nanocompositional fillers increase in the PTFE matrix, and also at high speeds of friction, cannot be unambiguously explained considering only the polymer matrix strengthening effect. Particularly, the above experimentally confirmed facts about the existence of the critical value of friction speed and the optimal content of filler in the new nanocomposite, ensuring the ultra-low wear rate, and for the transformation of its tribological properties from antifrictional to frictional but keeping the unexpectedly low wear rate, is not possible without a complex consideration of the mechanism of transfer film formation [7-9], and the role of the various fillers [13], particularly of the nanocompositional fillers (Fe-dop.CNPs) in the formation of frictional properties of the transfer film, such as “the third phase” between the surfaces of friction pairs. In this relation, the surface morphology and the elemental composition of the worn surfaces of the tested unfilled PTFE samples, PTFE-based 3 new nanocomposite samples and the respective cast iron counterfaces, working as the tribological pairs for steady-state period, were investigated using the SEM and EDX methods.

Fig. 1.a-d show the SEM images of the characteristic morphology and the corresponding EDX spectra of the worn surfaces of the unfilled PTFE sample (a, b) and the gray cast iron counterface sample (c, d) of the friction pair separated from each other after working as the tribo-pair at temperatures up to 180°C. It is evident that in the process of sliding friction a visco-elastic flow of the PTFE surface layers occur which subsequently brakes because of microcrack formation in the delaminated layers, and tear away from the sliding surfaces in the form of ~100÷500 µm size debris flakes (Fig.1. a, b). On the other hand, SEM and EDX analyses of the surfaces of the cast iron counterface, worked as a tribo-pair with the unfilled PTFE samples, show that (Fig. 1. c, d) the abovementioned debris flake particles, cannot be stuck on the counterface because of their big dimensions, and form a thin transfer film on it during sliding. These result in the very high rate of wear for the unfilled PTFE. Actually, the cast iron counterface worked as a tribo-pair with the unfilled PTFE sample has morphology of clean, fine-

ground cast iron surface (**Fig.1. c**). In the EDX spectra of the latter only the peaks of the cast iron components are shown (**Fig.1. d**). The weak peaks corresponding to fluorine are caused by the small ($\sim 1\mu\text{m}$) individual debris flake particles squeezed in the scratches on the fine-ground surface.

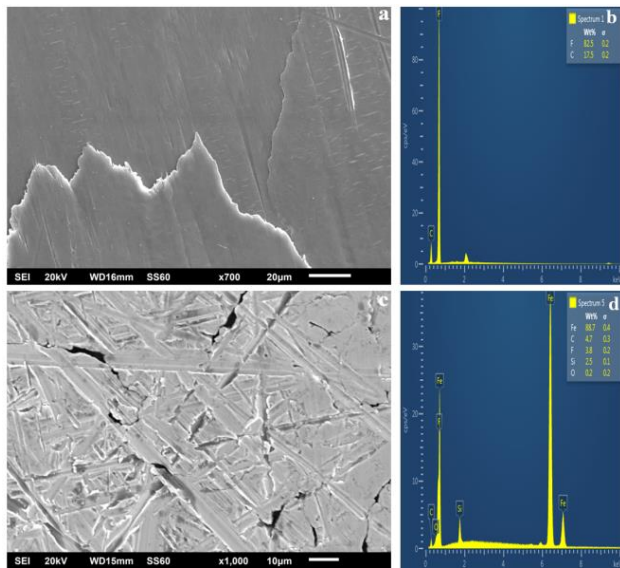


Fig.1. SEM images and the respective EDX spectra of the worn surfaces of the unfilled PTFE sample (a, b) and the gray cast iron sample (counter body) (c, d) after working as a tribological pair at temperatures up to 180°C .

Fig. 2.a-d show the SEM images and the respective EDX spectra of the worn surfaces of the PTFE+2.5wt% Fe-dop.CNTs nanocomposite sample (a, b) and the gray cast iron sample counterface (c, d) after working in the tribo-pair at temperatures up to 240°C . The comparison to the same images taken from the unfilled PTFE samples clearly shows that the incorporation of 2.5 wt% of the filler in the polymer matrix drastically changes its properties as well as the mechanisms of formation of wear products and their transfer to the counterface. Namely, dimensions of the debris flakes formed on the surface of the nanocomposite have reduced by almost two orders of magnitude and reached $\sim 1\div 10\mu\text{m}$ (**Fig.2.a**).

The transfer of the latter to the counterface and subsequent stirring leads to the formation of a very thin ($\leq 100\text{ nm}$) adhesive transfer film. The observed films on the surface of the nanocomposite sample (**Fig.2.a**) as well as on the cast iron counterface (**Fig.2.c**) are formed through the mechanical (frictional) stirring of the crashed and scuffed nanocomposite particles during friction under pressure. The EDX analyses of the superficial surface layers formed on both surfaces (**Fig.2.b, d**) show that their compositions are practically the same, however, slightly enriched with the filler's nanoparticles than in the case of nanocomposite. Since the local ($\sim 1\mu\text{m}^2$) EDX spectrum of the counterface (**Fig.2.d**) is presented by the intensive peaks of fluorine and the elements relevant to their content in the cast iron, one may conclude that the transfer film is of sub-micron thickness. Besides, it is evident that the nanocomposite transfer film is

transmittable for the electron beam of SEM accelerated with the energy of 20 keV, therefore, the thickness of the film should be less than 100 nm.

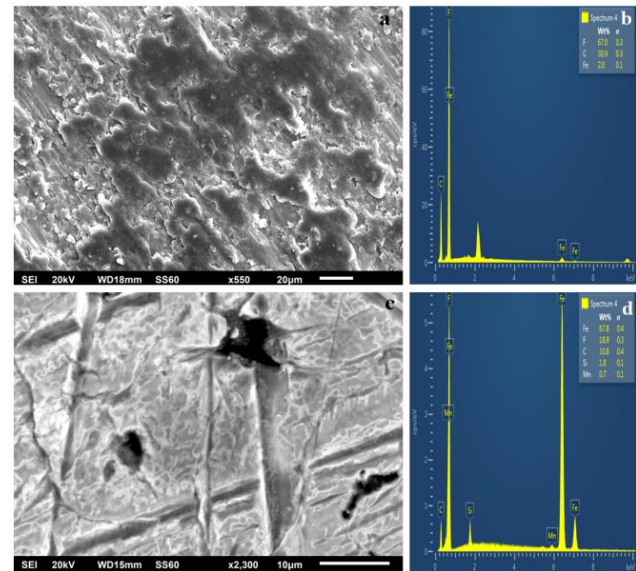


Fig.2. SEM images and the respective EDX spectra of the worn surfaces of the PTFE sample filled with the 2.5wt% Fe-doped CNTs (a, b) and the gray cast iron sample (c, d) after working as a tribological pair at temperatures up to 240°C .

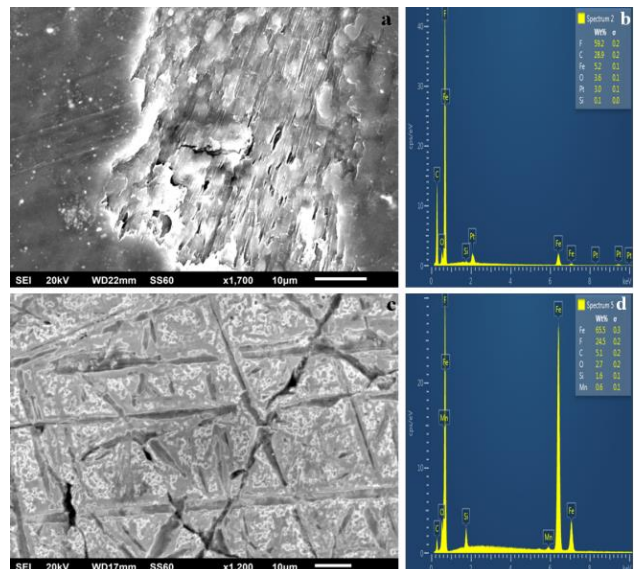


Fig.3. SEM images and the respective EDX spectra of the worn surfaces of the PTFE sample filled with the 5wt% Fe-doped CNTs (a, b) and the gray cast iron sample (c, d) after working as a tribological pair at temperatures up to 230°C .

Fig. 3. a-d show the SEM images and the respective EDX spectra of the worn surfaces of the PTFE + 5 wt% Fe-dop.CNTs nanocomposite sample (a, b) and the gray cast iron counterface sample (c, d) after working as a tribo-pair at temperatures up to 230°C . The matching of these images with those obtained for the nanocomposite containing 2.5 wt% of filler (**Fig.2.a-d**), shows that increase in filler content up to 5 wt% provides a formation

of a transfer film by the practically similar mechanism as described in the above case of 2.5wt%. The only difference is that the lateral dimensions of the debris flakes formed in the process of friction on the surface of the nanocomposite are reduced, while the rate of covering of the smooth areas (without scratches) of the counterface ground surface by the transfer film (with the flat island-like domain morphology of the same <100 nm thickness), increased.

At high speed of friction (1.25 m/s) this naturally results in the considerable (4 times) decrease in wear intensity of the nanocomposite containing 2.5wt% of filler against that containing 5wt%, while the coefficient of friction remains the same for both materials (see Table 1).

Figs. 4.a-d show the SEM images and the respective EDX spectra of the worn surfaces of PTFE + 10 wt% Fe-dop.CNTs nanocomposite sample (a, b) and the gray cast iron counterface sample (c, d) after working as a tribo-pair at temperatures up to 280°C. The comparison of these images to those of the nanocomposites with the lower content of the filler (**Fig.2, Fig.3**) shows that the increase of filler content in the nanocomposite up to 10 wt% changes the mechanism of debris particles' formation on its surface. Namely the visco-plastic mechanism transforms to more fragile process. Consequently, the lateral dimension to thickness ratio for the particles formed during friction is reduced because of the increase in thickness of the particles (**Fig.4.a**). As a result, their transport to the counterface provides a formation of a transfer layer on the ground surface by a different, so-called "clearcole"-like mechanism of filling the scratches. The thicker layers plus the increased content of filler nanoparticles, and therefore the increased quantity of Fe-clusters of the dopant, result, at higher friction speeds, in the increased values of friction coefficient up to 0.32. However, the wear intensity still remains very low, especially at 0.62 m/s of friction speed (Table 1). To the author's opinion the transfer films of nano/micro thickness, mainly as a nanocomposite worn product which scuff the both surfaces of the tribo-pair, considerably increases the actual surface of the contact between friction bodies provoking the deconcentration of local stresses. Therefore, the interlayer is able to undergo the tangential stresses without formation of microcracks and finally this leads to the work of the tribo-system in the regime of minimal wear with the rheo-dynamics of thermal self-loading, even in the cases of higher values (>0.25) of friction coefficient.

Thus, the tribological tests of the developed new nanocomposite materials (PTFE+Fe-dop.CNT), and the analysis of the SEM-EDX results on the worn surfaces of the tribo-pairs show that under concrete conditions of load and speed of sliding, the transfer films (such as the third phase) create an equivalent of lubricating effect in tribo-pair. Moreover, depending on the morphology, composition and the dynamics of transformation of the transfer film, the antifricition, as well as friction properties of the PTFE-based nanocomposites may be realized, keeping a very low value of wear intensity.

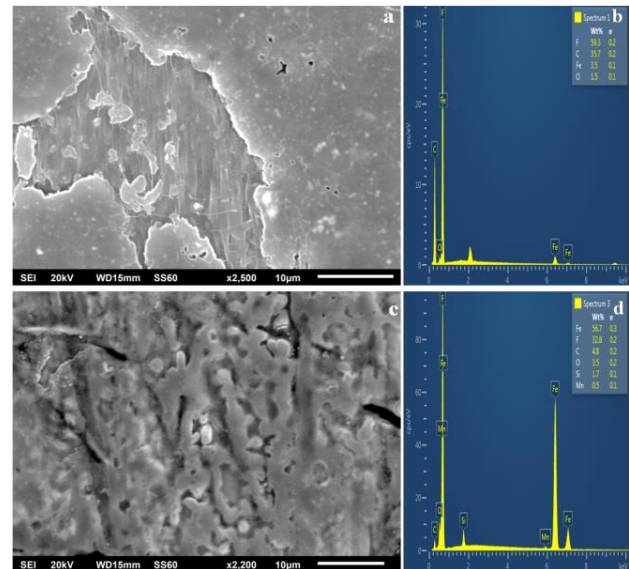


Fig.4. SEM images and the respective EDX spectra of the worn surfaces of the PTFE sample filled with the 10wt% Fe-doped CNTs (a, b) and the gray cast iron sample (c, d) after working as a tribological pair at temperatures up to 280°C.

Conclusion

In this work the frictional, wear and transfer responses of the developed new nanocomposite antifrictional/frictional materials, based on the PTFE matrix filled with 2.5, 5, and 10 wt% of core-shell type magnetic nanoparticles doped with Fe-atoms (clusters), were studied. Particularly, the comparative tribological tests and the SEM-EDX characterizations of the new nanocomposite and the reference materials (unfilled PTFE and the best commercial self-lubricating composite material, "Superfluvis") have been conducted after tests under the constant load and at various sliding speeds against cast iron.

The obtained results made it possible to conclude that the effective mechanism of wear reduction of the PTFE-based new nanocomposites is tied to the incorporated Fe-doped CNTs magnetic nanoparticles' ability to modify the PTFE matrix properties to form a very thin, uniform and tenacious transfer film on the cast iron counterface and to significantly improve its lubricity and wear protection capability in tribological pair.

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