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TRIBO-SPECTRAL METHOD AND IDENTIFICATION OF THE MICROMECHANICAL CHARACTERISTICS OF THE EXFOLIATED GRAPHITE BASED MATERIALS

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The results obtained in the experiments allow us to demonstrate the successful application of the tribo-spectral method deforming and tribo-spectrum analysis for the identification of tribo-spectral characteristics of lightweight exfoliated graphite based materials in the wide range of their density. This undoubtedly a favor in upgrading of the quality of the control of both technological processes of lightweight powder material production and property degradation processes in materials and products. Some parameters of the tribo-spectral characteristics may be used as a criterion for a comparative estimation of the powdered material production, that may be exploited in order to increase the efficiency of the moulding materials quality control. Tribo-spectral method can be used for the estimation of oxide stability of lightweight materials for the optimization of the composite material content. Tribo-spectral characteristics are sensitive to the processes of thermo-oxide destruction of the structure and can be applied for the optimization of the content of parts made of the lightweight graphite composite materials.

Introduction

Exfoliated graphite (EG) is made of the powdered natural crystalline graphite that can form intercalation compounds, anions or metals that are intercalated between the layers of carbon. The thermal shock of such a graphite intercalation compound leads to the strong «swelling» of the graphite particles that is the result of the vaporisation and decomposition of the intercalated molecules.

In patent and information literature the graphite obtained by means of this treatment is also referred to as expanded, delaminated, bloated, swelled, vermicular graphite [1].

Electron microscope studies of EG and natural graphite give evidence that a qualitative distinction between the morphologies of their particles can be draw. The crystallite sizes along c-axis and the degree of crystallinity of the exfoliated graphite are lower, and the structural anisotropy and interlayer spacing is higher in comparison with the natural graphite. The technological conditions of the EG preparation induce a special type of the deformation of the carbon layers, that leads to the formation of the particles of both cylindrical and vermicular shape with the cellular structure, which is attributed to the presence of the specific defects in the graphite crystal lattice. Unlike graphite-based material prepared according to the proper technology (by mixing with binders followed by pressing and thermal treatments), the exfoliated graphite lends itself to forming without binders. It has been found, that the role of an out-of-ordinary binder is dictated by products, formed in the of process EG preparation. This eliminates delimitation, ensures the sliding of the material layers and their adhesion during the moulding [2].

Special interest is given to application of exfoliated graphite (EG) in the areas of high temperatures. One of the possible ways in erasing of thermo-oxide strength of composite parts made of EG is the use of the modification process which includes the synthesis of simple or complex compounds on the surface of EG powder particles for composite material formation. Our studies show that the modification of the EG powder leads to inhibition of the oxidation process by means of durable chemical compounds creation on ready to reaction carbon atoms which are called active centres. This process considerably increases thermo-oxidation stability of parts made of EG composite materials [3].

Methods

The material tested by the tribo-spectral method involves the penetration of a loaded indentor into the specimen surface and motion of the specimen in the regime of the elasto-plastic strain (fig. 1).

In the process of the specimen motion, the indentor performs the forced vibrations, whose character is caused by different physical resistance of the structural components of the material surface layer.

The change of the resistance to the development of the elasto-plastic, strain within the fragments and on the fragment boundaries of the structure is random in its behaviour and corresponds to the instantaneous change of the forces P_t and P_h (fig. 1) which is measured in a real time scale and is transformed by means of laser sensor into electrical signal.

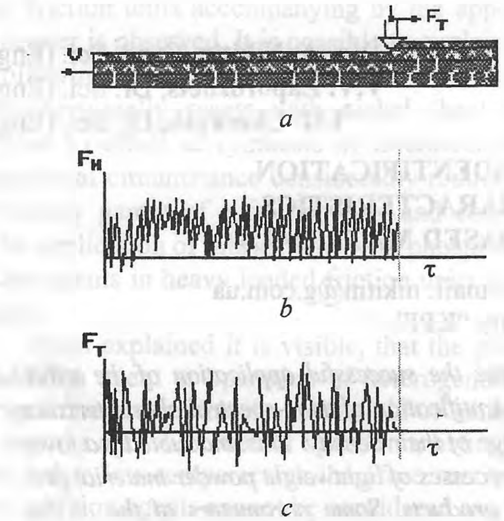

Fig. 1. Physical background on the tribo-spectral method:
a– the process of the indentor material surface formation during scanning; *b* – normal tribogram of the material surface layer; *c*– tangential tribogram of the material surface layer

As a result, the process of the forces change in the course of time may be thought as a set of polyharmonic vibrations processes with periods which are related to the sizes of fragments, blocks, and other structural components of the material.

The spectral dens structural components of the materiality S_t and S_h of such a process will have maximum at the frequencies which correspond to the sizes of fragments, blocks and others [4].

Before testing, specimens were sequentially fixed in holders on the anvil. A tetrahedral diamond indentor was forced into the material tested at the load of 10–50 mN.

After holding under the load for 10–15 s, the specimens moved at the speed of 20–80 mm/s, and the value of the tangential force (P) acting on the indentor vibrated at the frequency of 20 Hz was registered.

The information obtained was stored on a magnetic disk of the control computer complex.

The amount of the experimental performance for the probability process was more than 1200 values. The tests were made on different areas of the specimen surface layer in order to obtain all possible characteristics.

The treatment of the experiments were out using the Fourier transformation method which allows us to perform a simple interpretation of the results obtained through their spectral analysis with the help of a computer.

The result of the experimental studies are the values of the tribo-spectral characteristics $S = F$, where S is the spectral density, F is the frequency of the indentor vibrations.

From the physical point of the spectral density S characterizes the frequency (size) of the contact strain energy distribution for individual structural components of the material surface layer.

One of the important features of the spectral analysis is also the value of the dispersion which characterizes the strength property inhomogeneity of the structure fragments of the material surface layer and is determined on the basis of the area under the spectral density curve.

The compression tests were conducted in air at room temperature. The speed of the loading was 20 mm/min.

The experiments allow to demonstrate the successful application of the “Nano/Micron-Gamma” (Ukraine) device which realises the tribo-spectral method deforming tribo-spectrum analysis for the identification of tribo-spectral characteristics of exfoliated graphite based materials in a wide range of their density.

Materials

Exfoliated graphite composite materials have been made by means of thermal treatment at 900 ^{0}C for 2 min of the mixture of graphite intercalation and oxide aluminum solution.

The composite materials have been obtained in the form of a powder with 1 to 10 % of aluminum oxide.

Small-sized test specimens, manufactured from the powders foamed material and exfoliated graphite outlined above, were shaped into a cylinder of 20 mm in diameter and 20 mm in height.

These small-sized specimens were subjected to tests that involved the forcing of an indentor into their surface and also testing in the conditions of the uniaxial compression in a standard test unit with standard attachments.

Every point of the strength characteristic obtained is the average result of the testing of not less than five specimens.

The specimens were subjected to the original test which shows the surface layer conditions.

The tribo-spectral method with a step-by-step control in the process of specimens calumniation in the range of 500 to 1000 ^{0}C (every 50 ^{0}C) and time interval of 10 min has been used. Simultaneously, the estimation of thermo-oxidation stability of specimens has been carried out by means of determination of specimen mass loss (Δ m/m) at 100 % of the same density with different initial mass.

Results

Our studies of the process of the lightweight exfoliated graphite materials moulding made it possible to detect the various changes of the surface layer tribo-spectral characteristics for the specimens with the increasing density (fig. 2).

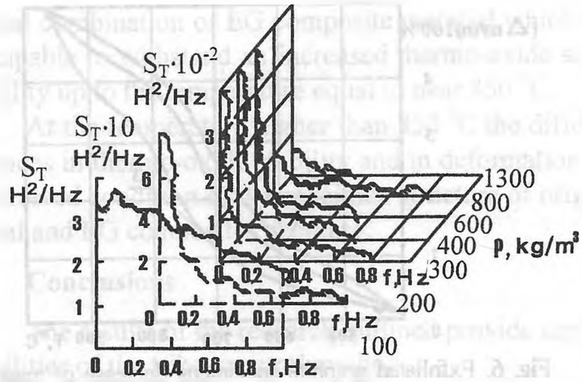

Fig. 2. Tribo-spectroscopic characteristics of the lightweight exfoliated graphite material surface layer in the process of its formation

The analysis of the surface layer structure by the visual optic method showed that at the stage of the initial moulding at the density of 100 kg/m^3 the vermicular particles of powder exfoliated graphite were plastically strained against the background of the developed system of the continuity disruptions in the form of pores.

The investigation of the surface layer of this specimen by the deformation spectroscopy method indicated that the distribution of the spectral density S_t as to frequency had changes in the frequency ranges from 0 to 0,2 Hz and from 2,5 to 4,0 Hz, that corresponded to the dimension distributions of the powder EG particles and of the continuity disruptions in the form of pores.

Besides, the level of the spectral density S_t and the dispersion D_t indicates the nonhomogeneously stressed state of the specimen surface layer.

With the increasing compression pressure (at ρ =200 kg/m^3) one can observe the maximum pacing of the powder EG particles, which is attributed to their relative motion and particle deformation, and the nonhomogeneously stressed state of powder EG approaches its maximum.

During the stage of the density change from 200 to 300 kg/m^3, the process of the EG molding is accompanied with the process of the breaking down of the particles into large fragments. In this case, the values of the spectral density S_t and the dispersion D_t change the magnitude, which gives evidence by of more intensive processes of the material structure reorganization.

At the molding stage during which the density ρ is changed from 300 to 600 kg/m^3, the specimen surface layer does not have any substantial structure reorganization, as is evidenced by a pronounced decrease of the dispersion and by practically constant value of the maximum spectral density S_T^{max}.

In this case, the process of the specimen form change is caused by the compaction within the inner layers under the condition of the homogeneously-stressed state of the large fragments of the powder EG particles.

At the compression pressure corresponding to the specimen density of 600 kg/m^3, the loss of the resistance to the compression of the large-sized fragments of the powder EG particles and a stage of their plastic deformation can be observed.

This stage is followed by the breaking down of the fragments and is completed at ρ = 800 kg/m^3, and is characterized by the appearance of the middle-sized fragment structure in the frequency range from 0,4 to 0,6 Hz.

The analysis of this structure by the visual optic method showed that the appearance of the middle-sized fragment structure is caused by the process of the breaking down of the large-sized fragments of the powder EG particles. During the moulding stage the values of the spectral density S_t and the dispersion D_t are changed by of magnitude.

The decrease of the surface layer resistance to the contact deformation and the decrease of the variance of the structure fragment strength characteristics at the moulding stage from ρ = 800 kg/m^3 to ρ = 1000 kg/m^3 give evidence for the formation of the homogeneous material.

At this stage of the moulding, the deformation process spreads uniformly over practisized fragments of the powder EG particles.

It is necessary to note, that during the moulding process the value of the maximum spectral density $S_T{}^{max}{}_t$ changes nonmonotonously (fig. 3), and the tendency of the change corresponds totally with the succession of the powder graphite molding stages described above and does not correlate with the results of the compression tests of the specimens (fig. 4).

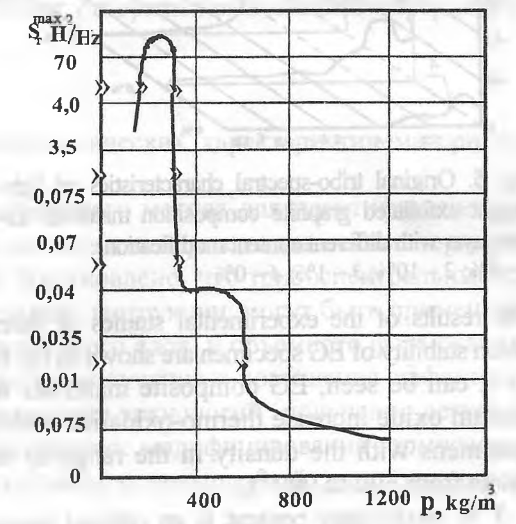

Fig. 3. The variation of the maximum spectral density of the tribo-spectroscopic characteristics of the lightweight exfoliated graphite surface layer in the process of its formation

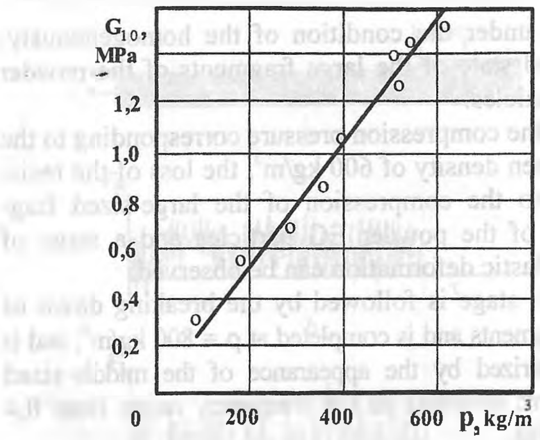

Fig. 4. Dependence's of the compression strength G_{10} on the apparent density ρ of the lightweight exfoliated graphite specimens

On the other side there are interesting results in the estimation of the thermo-oxide destruction process in the surface layer of exfoliated graphite based material modification.

The initial micro-mechanical tests by the tribo-spectral method at 20 ^{0}C allowed us to see non-monotonous changes in tribo-spectral characteristics depending on the percentage of aluminium oxide in EG materials (fig. 5) 3% of modificator corresponding to the maximum heterogeneity of deformation–strength characteristics of modificated specimens surface which is followed by the increased resistance to contact deformation.

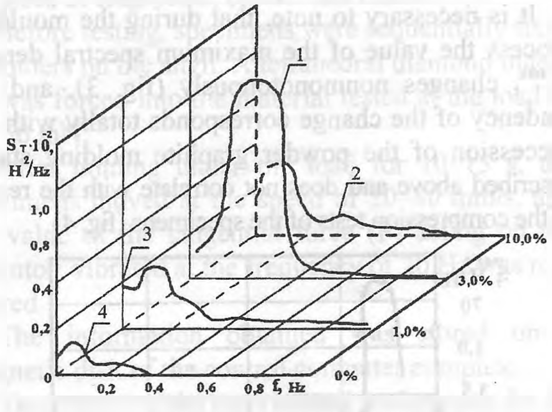

Fig. 5. Original tribo-spectral characteristics of lightweight exfoliated graphite composition materials surface layer with different content modifications:
1 – 3%; *2* – 10%; *3* – 1%; *4* – 0%

The results of the experimental studies of thermo-oxidation stability of EG specimen are shown in fig. 6.

As it can be seen, EG composite materials with aluminium oxide increase thermo-oxidation stability of specimens with the density in the range of temperatures from 600 to 900 ^{0}C.

A 3 % modificator content is an optimal situation when aluminium oxide, which is formed due to the salts pyrolysis is adsorbed on the EG particles active centres.

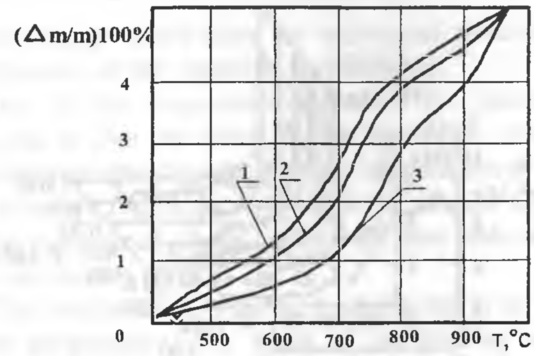

Fig. 6. Exfoliated graphite specimens decrease of mass with different content of the modification:
1 – 0%; *2* – 1%; *3* – 3%

The growing increase of the aluminium oxide percentage in EG does not influence realty the deformation-strength and thermo-oxyde features of EG specimens.

The correlation between tribo-spectral characteristics and the degree of burning out of specimens shows that at 3 % modificator the deformation stress condition of the structure is not changed under the temperatures up to 850 ^{0}C (fig. 7, curve *1*).

The structure of original specimens and specimens with low content of the modificator have some considerable increase in hetero-geneous properties range of temperatures from 500 to 800 ^{0}C. From the point of view of physics it characterises the intensive process of oxidation (destruction) of specimen material in active centres which are badly protected (fig. 7, curve *2*) or which are not protected at all (fig. 7, curve *1*).

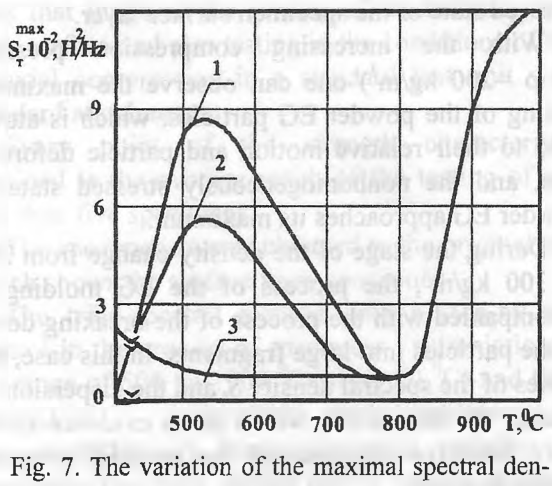

Fig. 7. The variation of the maximal spectral density in the process of thermo-oxide destruction of EG specimens with different content of the modification:
1 – 3%; *2* – 1%; *3* – 0%

So, the application of the tribo-spectral method for the evaluation of heterogeneously stressed condition of composite material surface layer prior to thermal tests (fig. 7) allowed us to choose the optimal combination of EG composite material which is capable to withstand an increased thermo-oxide stability up to the temperature equal to near 850 ^{0}C.

At the temperature higher than 850 ^{0}C the differences in thermo-oxide stability and in deformation – stressed condition of the specimen structure of original and EG composites decrease.

Conclusions

The results of the research outlined provide capabilities of the tribo-spectral method.

1. This is undoubtedly a favor in upgrading the quality of the control of both technological processes of powder porous material production and property degradation processes in materials and products.

2. Tribo-spectral characteristics may be used as a criterion for a comparative estimation of the powdered material production, that may be exploited in order to increase the efficiency of the moulding materials quality control.

3. Tribo-spectral method can be used for the estimation of oxide stability of lightweight aterials for the optimization of the composite material content.

4. Tribo-spectral characteristics are sensitive to the processes of thermo-oxide destruction of the structure and can be applied for the optimization of the content of parts made of the lightweight exfoliated graphite based composite materials.

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Трибоспектральний метод та ідентифікація мікромеханічних характеристик матеріалів на основі терморозширеного графіту

Розглянуто результати використання трибоспектрального методу для ідентифікації трибоспектральних характеристик поверхневого шару легковагих матеріалів на основі терморозширеного графіту в широкому діапазоні їх щільностей. Установлено, що чутливі до процесу термоокислювальної деструкції трибоспектральні характеристики можуть бути застосовані для оцінки процесів структурних перетворень поверхневого шару й об'ємного формування легковагих матеріалів, для порівняння оцінки процесів одержання і підвищення ефективності контролю якості формованих матеріалів, для оптимізації технологій одержування легковагих композиційних графітових матеріалів. Показано, що процес модифікування терморозширеного графіту дозволяє створити композиційні матеріали з підвищеною термоокислювальною стійкістю.

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Трибоспектральный метод и идентификация микромеханических характеристик материалов на основе терморасширенного графита

Представлены результаты использования трибоспектрального метода для идентификации трибоспектральных характеристик поверхностного слоя легковесных материалов на основе терморасширенного графита в широком диапазоне их плотностей. Установлено, что трибоспектральные характеристики, чувствительные к процессам термоокислительной деструкции, могут быть применены для оценки процессов структурных преобразований поверхностного слоя и объемного формования легковесных материалов, для сравнительной оценки процессов получения и повышения эффективности контроля качества формованных материалов, для оптимизации технологий получения легковесных композиционных графитовых материалов. Показано, что процесс модифицирования терморасширенного графита позволяет создать композиционные материалы с повышенной термоокислительной стойкостью.