REINFORCED WITH FULLERENES COMPOSITES BASED ON METALLIC MATRICES

Prof. Dr. O.Sizonenko[1], Prof. Dr. S.Prokhorenko[2], Dr. A.Torpakov[1],
Dr. D.Żak[2], Dr. Y.Lypian[1], MSc. R.Wojnarowska-Nowak [2,], Prof. Dr. J.Polit[2] and Prof. Dr. E.M.Sheregii[2]

[1] Department of Disperse Systems Pulse Treatment, Institute of Pulse Processes and Technologies, National Academy of Science of Ukraine, Mykolaiv 54018, Ukraine
[2] Center of Microelectronics and Nanotechnology, University of Rzeszow, 1 Pigonia Str., 35-959 Rzeszow, Poland

sheregii@ur.edu.pl

Abstract. *A new technological approach to obtain anti-friction dispersion-hardened by nanoparticles materials based on of TiC – AlC – and FeC alloys with inclusions of the C_{n0} (n=6 or 7) phases which characterized by high heat resistance, strength and durability for use in aircraft and rocket technology, is presented. Elemental powders of Al–Ti–C and Fe–Ti–C systems are used as base objects for development of new composite materials by high voltage electric discharge treatment in kerosene (dispersion, activation and synthesis). In effect, as shown micro-Raman data, these systems contain refractory components (fullerenes, carbides), MAX-phases of Ti-Al-C system with increasing thermo-stability, strength and wear resistance while maintaining ductility how can it be predicted.*

Keywords: HIGH VOLTAGE ELECTRIC DISCHARGE; COMPOSITE MATERIAL; RAMAN SCUTTERING; FULLERENCE.

1. Introduction.

Considerable number of fabrication methods have been proposed to develop metal matrix composites containing carbon nano-materials, nanotubes for example, using the liquid-state techniques[1-6] as well as solid-state techniques[7-13]. Spraying processes[6-8], squeeze casting[9], disintegrated melt deposition[10,11] processes (also electrolytic[12]) and milling fabrication[13-16] have been introduced to fabricate the composite at temperatures above the melting temperature of the matrix. On the other hand, metal matrix composites containing such carbon nanoparticles as fullerenes are less known, although the properties of these objects with predominant *sp*^{2} bonding[17] extend their use also in composites.

Dispersion-hardened composites, based on titan-iron-carbon alloy systems are widely used in aviation and aerospace industry due to the properties combining characteristics for metals (significant ductility and fracture toughness) and ceramics (high strength, high thermal resistance and elastic modulus). If they could consist of titanium and iron carbide matrix and hardening inclusions –as fullerenes (C_{60} and C_{70}) decreasing coefficient of friction, such nano-composition besides large strength will be characterized by high thermal resistance in the wide range of temperatures and low coefficient of friction. Therefore, method to obtain such composite would be irreplaceable.

A new method of the metal matrix composites containing carbon nanoparticles preparing – high voltage electric discharge treatment in kerosene (dispersion, activation and synthesis) is proposed in present work.
The measured micro-Raman scattering confirm the present of fullerenes in fabricated composites while mechanical properties shown considerable increasing of strength and wear resistance.

2. High voltage electric discharge method.

Electric discharge treatment is unique complex method of impact combining the physical and mechanical action and it is based on utilizing high voltage electric discharge (HVED) in liquid. HVED in liquid is essentially an electric explosion, characterized by rapid energy excretion (during microseconds) in initially small volume of discharge channel, paved by streamer, appeared under the influence of high electric potential between the opposing electrodes. HVED allows obtaining dense low temperature plasma[18]; its temperature reaches up to 5.104 °C. The high energy concentration, high pressures (about 1 GPa) and temperatures, developed within the channel, lead to rapid (from 500 up to 2000 m/s) expansion of channel and appearance of shock waves, transformed into acoustic with wide frequency specter, powerful hydro flows, cavitation, electromagnetic and thermal fields[18,19] Studies have shown that the dispersion process involves the shock wave with a front of 10^{-10} m thickness[18] (or compression wave, depending on circuit parameters), cavitation, destruction of particles during their collision with the rigid wall of the chamber and their mutual attrition throughout the chamber during expansion and collapse of the vapor-gas cavity in varying degrees. Use of a hydrocarbon liquid as the working medium during processing of powder mixtures avoids their oxidation without substantially reducing the hydrodynamic characteristics of the discharge. The case of using a hydrocarbon liquid with *sp*^{2}-hybridization (kerosene) is characterized by carbon of graphite type short-range order, and the case of using a fluid with sp^3-hybridization (dodecane, cyclohexane, hexane), by a diamond-like[20-23]. Therefore, it is advisable to use kerosene as the working fluid at HVED treatment of metal powders. The processes occurring in the consolidation of micropowder particles have significant influence on the properties of the material. Application of method of sintering, such as a spark-plasma sintering (SPS), which allow the preservation of the ultrafine structure of the initial powders, leads to the possibility of obtaining high-density powder composites with improved physical and mechanical properties as well as SPS allows purposeful control of grain growth speed and thereby generate nanostructured microheterogeneous structure of multifunctional composite materials with high physical-mechanical and performance properties[20]. Besides that, high pressure zone enables the formation of fullerene particles. Last one is particularly important the last one is especially important because of the huge mechanical strength of fullerenes and their property to lower the coefficient of friction[22].

2.1. The experimental complex

The experimental complex of HVED (see electrical scheme Fig.1), located at the Institute of Pulse Processes and Technologies, National Academy of Science of Ukraine, was used for studies. As shown below, the connection between sufficiently strong and stable. The enzyme catalytic activity is also confirmed, which means that the method applied to construct the nanobiosystem was effective.

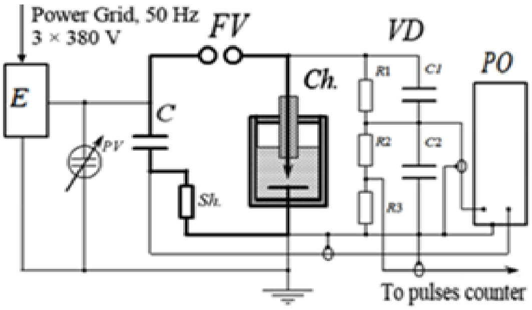
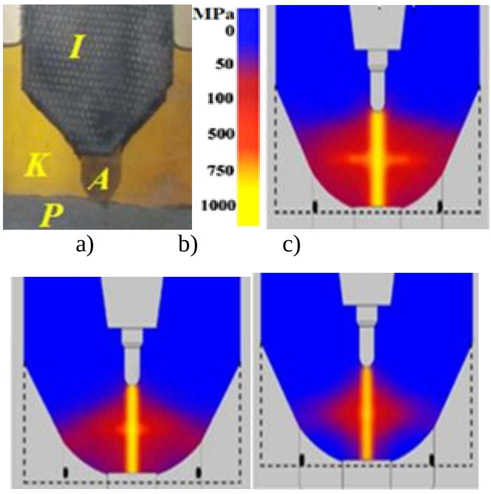


***Fig. 1**. Electrical scheme of HVED*



a) b) c)

d) e)

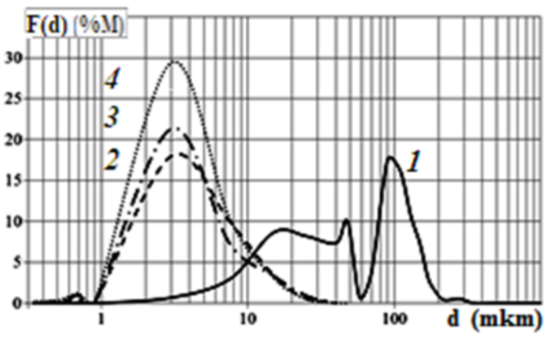
***Fig. 2**. a) - working chamber: I – isolator; F – anode; K– kerosene; P – research powder, b) - pressure scale, c, d, e) pressure wave peaks during HVED treatment with single discharge energy of 1, 0.5 and 0.25 kJ, respectively.*

Since at the high voltage electric discharge (HVED) pressure in the discharge channel reaches 1GPa (Fig.2 a,b,c,d,e) the temperature in the discharge channel can reach 50 000K and at the interface between the plasma channel and environment it is down to 1000 K, the transition layer thickness is 2 mm, pyrolysis of kerosene, with the formation of solid carbon and atomic and molecular hydrogen gas, is possible[24,25].

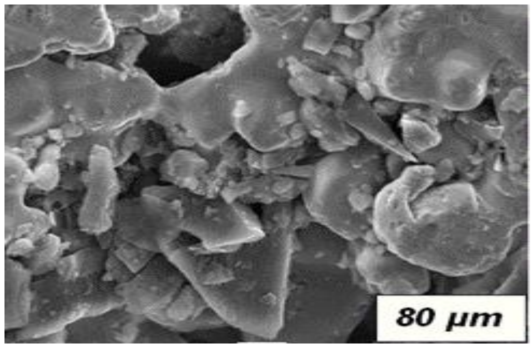
For example, treatment of 75%Fe–25%Ti powder mixtures was performed with specific energy of $W_{s\Sigma=const}$ =25 MJ/kg, which ensures synthesis of necessary amount of carbon for formation of stoichiometric Ti carbide. Current rise rate varied from 13 up to 24 GA/s, which provided different intensity of pressure waves impact (see Fig.1d,e,f). Frequency of pulses passing was f = 0,6 Hz.

2.2. Distribution of particles by diameter values.

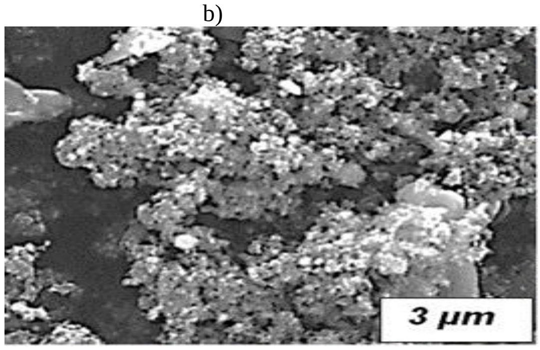
Mean diameter of powder particles after treatment in all studied modes decreased from 80 to ~3 µm (see Fig. 3a).



a)



b)



c)

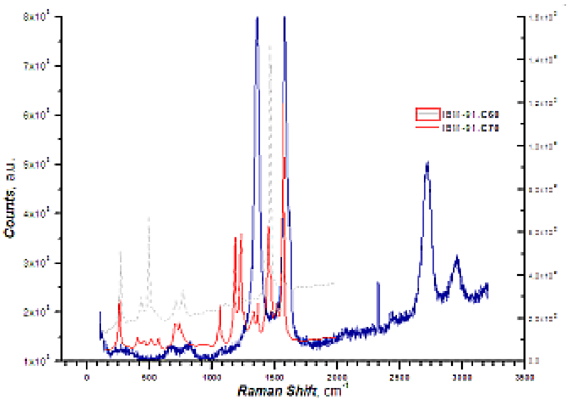
***Fig. 3**. The 75%Fe–25%Ti mixture. a) - Distribution of particles percentage F(d) by diameter values (1– initial mixture; 2– after HVED treatment with di/dt = 13 GA/s; 3– di/dt = 19 GA/s; 4– di/dt= 24 GA/s), b)- Mixtures micro-photo-graphs: initial mixture, c)– after HVED treatment with WsΣ = 25 MJ/kg and di/dt = 24 GA/s.*

The high modulus (ceramic) TiC (with homogeneity area up to TiC0,92) and FeC (with size varying from 10 up to 600 nm) phases are synthesized at this time. Worth noting that maximum amount of powder with ~ 3 µm diameter (~ 30 %) was obtained after treatment with maximal considered current rise rate of di/dt=24 GA/s (see Fig.3a, curve 4). Most of initial mixture particles had irregular fragmental shape (see Fig.3b), but after processing they have shape, close to spherical (see Fig.3c) – this shows, that they were synthesized due to impact of discharge channel current (ablation and electric erosion). Thus, due to the combined action of simultaneously mechanical (forced compaction during processing), spark plasma (electric discharge between particles), plasma (local heating after the breakdown of the oxide films on the surface of powder particles) it is possible to receive composite material with improved physical and performance properties at sufficiently low temperature compared to traditional approaches.

3. The Raman scattering results.

In order to control the chemical composition of components during SPS, the Raman spectroscopy analysis was applied using micro-Raman system based on Renishow inVia spectrometer. In Fig.4, micro-Raman (with spatial resolution of 1 µm) spectrum of individual grain (is shown in center in Fig. 3c) for the 75%Fe – 25%Ti mixture obtained by HVED treatment is presented. The sharp strong line at 1583 cm^{-1}, observed on the curve in Fig. 4, is attributed to C_{70} molecules[26], undoubtedly while the line at 1355 cm^{-1} is close to the one related to the C_{60} molecules. The deviation from the classic position will be explained later in Table 1.

In Fig. 5 the detail results about micro-Raman spectra refer to individual grains of the 50% Al – 50% Ti powder are given.



d)

***Fig. 4**. Raman spectra: blue for above mixture; red for C_{60} and C_{70} mixture [26].*

The shape of the spectra is changed with each step but two lines at 1355 cm^{-1} as well as at 1596 cm^{-1} are clearly shown on each presented in Fig. 5 spectra. A large variety of the C_n fullerene molecules could be attributed to the wide line at about 1360 cm^{-1} (see Table 1) while line at about 1590 cm^{-1}, is referred to C_{70}, and is the strongest one in the 24 point. The lines observed in the region from 2300 cm^{-1} to 3000 cm^{-1} refer, probably, to Ti–C alloy (with the exception of the line at 2720 cm^{-1}, which is certainly the overtone of the line at 1355 cm^{-1}) and the lines observed in the region from 500 cm^{-1} to 900 cm^{-1} – to Al – C alloy.

4. Conclusion.

Therefore, the new method of the metal matrix-carbon nanoparticles composite fabrication based on the HVED treatment of the initially prepared powder is proposed. Proposed method of preparation of powders for consolidation differs from known methods[7-16] by the fact that hardening particles are not mechanically added to powder mixture, but are instead

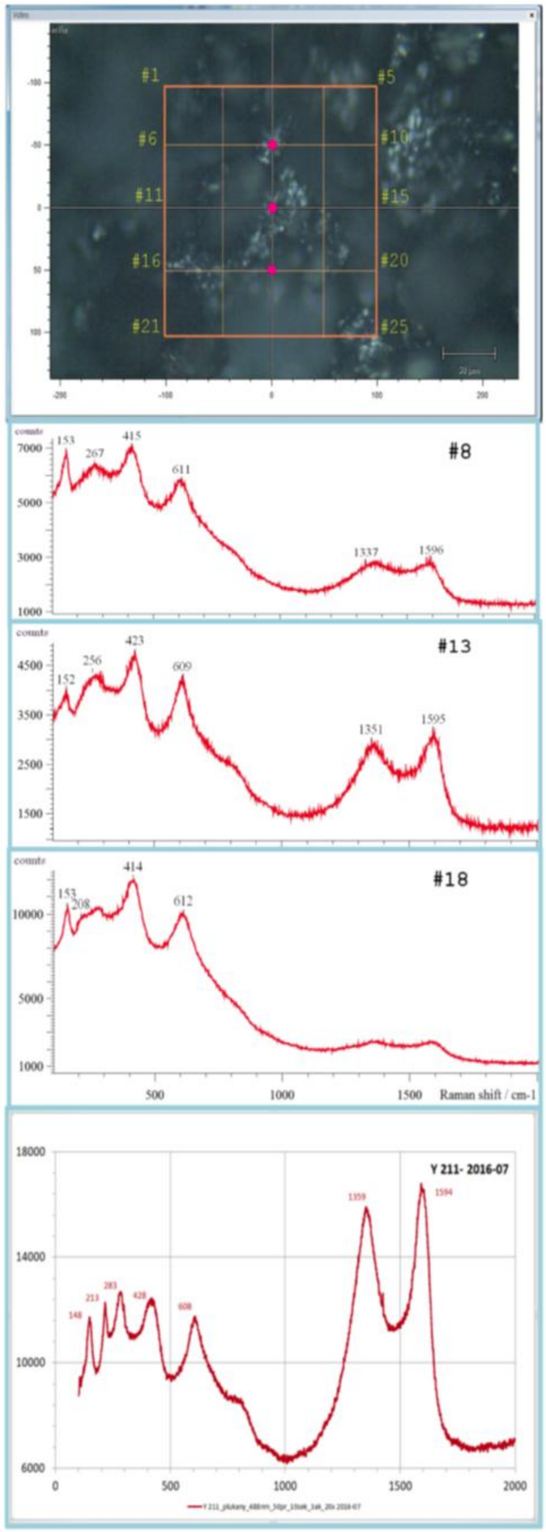


***Fig. 5.** Mapping of Raman spectra on researched grains of the 50% Al – 50% Ti nanoparticles composite. (a) – the map of the surface of powder; (b) – Raman spectra obtained for the points on map: 8, 13, 18 and 24.*

Table 1. Identification of the lines observed in the Raman spectra (s-strong, m-medium, w-weak)

	Position of line or group of lines (cm^{-1})	Raman spectrum designation: point number on the map, line pattern (w - weak, m - medium, s – strong)	Identification	References
1	148 – 154	1s,2(w),8(w), 10(w),13(w),14(w), (18-22) (w)	Al – C alloy	12,14,15
2	208 – 213	5(w),6(w), (10-12)(w), (14-16)(w), (20-21) w	Al (Ti)– C alloy	12,14,15

3	256 – 267	1-3w, 8w, 13w, (16-18)w, 21w	Al (Ti)– C alloy	12,14,15
4	415 – 428	1-3, (5-7)m, 8(-10)s, 13s, 17s,18s, 21m, 23s, 24m, 25w	Al (Ti)– C alloy	12,14,15, 26
5	608 –613	1-3, 6s, 7m, 8s, 9, 10, 13s, 14, 17s,18s, 21, (23 – 25)m	Al (Ti)– C alloy	12,14,15, 27
6	820 – 840	4, (5–9)s, 10 – 14, 15s, 16, 19s, (20-22)m, 23s, 24s, 25m	Al_4C_3	12
7	1355 – 1359	(1-8)m, (9-16)s, (19-22)s, 24sm, 25s	C_{60} including Fe or Al atoms and other allotropic C forms	15, 26, 27
8	1594 – 1596	(1-3)m, (4-6)s, 7m, 8m, (9-16)s, 17w 18w, (19-22)s, 24s, 25s	C_{70}	26, 27
9	2700 – 2720	(3-7)w, (8 – 16)w, (19-25)w	overtone of line at 1355 cm^{-1}	28, 29
10	2930 – 2950	3m, 4m, (5-7)w, (9 – 16)w, (19-25)w	Ti – C alloy	28, 29
11	2320	(1-4)w, (5-7)s, 8w, 9s, (10-16)m,	Ti – C alloy	28, 29

synthesized during HVED treatment of “kerosene – Fe (Al) – Ti powder mixture” disperse system with its simultaneous grinding,
which can be used for creation of composite materials with increased mechanical and performance characteristics.

Raman spectra of obtained composites have shown presence of fullerenes $C_{70,}$ as well as other allotropic forms of fullerenes, which allows us to predict strong thermo-stability in the wide temperature region, strength and wear resistance while maintaining ductility also.

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