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Plasma Methods of Obtainment of Multifunctional Composite Materials, Dispersion-Hardened by Nanoparticles

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Abstract: High voltage electric discharge (HVED) in disperse system "hydrocarbon liquid - powder" due to impact of plasma discharge channel, electromagnetic fields, shock waves mechanical impact, hydro flows and volume microcavitation leads to synthesis of nanocarbon, metal powders dispersion and synthesis of micro- (from 10^{-6} to 10^{-7} m) and nanosized (from 10^{-7} to 10⁻⁹ m) composite powders of hardening phases. Spark plasma sintering (SPS) of powder mixtures allows targeted control of grain growth rate and thus allows obtainment of multifunctional composite materials dispersion hardened by nanoparticles. Processes of HVED synthesis of micro- and nanosized powders of new compositions from elemental metal powders and their mixtures with the subsequent application of high-speed SPS of obtained powders create conditions for increase of strength (by 10-20%), hardness and wear-resistance (by 30-60%) of obtained materials.

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Introduction

Nuclear energetics is one of the most dynamic sectors of the world economy. Each new generation of nuclear plants becomes more efficient and safe, but demands the use of materials that have high strength, wearresistance and are capable of working in aggressive environments. Thus, development of construction materials for nuclear plants is important scientific and technical task.

Creation of heterogeneous structure in material, which is a plastic matrix with hard inclusions, is a necessary condition to ensure materials strength and wear-resistance. Heterogeneous materials include metal-matrix composites of Fe – Ti – C system, obtained with methods of powder metallurgy. These materials have high strength, hardness, their wear resistance is close to tung-sten-containing alloys and their modification by boron carbide leads to increase in corrosion and radiation resistance [1].

Present methods for obtainment of highly durable and wear resistant materials in powder metallurgy need a new complex approach, which would unite the processes of powders preparation with methods for their effective consolidation.

It is known that high voltage electric discharge in disperse system "hydrocarbon liquid – powder" is used for dispersion, activation and synthesis of bimodal micro-(from 10⁻⁶ to 10⁻⁷ m) and nanosized (from 10⁻⁷ to 10⁻⁹ m) composite powders. HVED in disperse system "hydrocarbon liquid – powder" leads to a synthesis of nanocarbon due to pyrolysis of liquid, and the impact of plasma channel, electromagnetic fields, mechanical impact of shock waves, hydro flows and volume microcavitation

leads to dispersion of metal powders and formation of their carbides [2, 3]. SPS of composite powders allows to control the targeted grains growth rate and thus to form microheterogeneous structure of multifunctional composite materials with high physical-mechanical and performance properties.

Unlike conventional methods, in developed plasma method dispersion-hardening additives are not mechanically added to powder mixture as additional component, but are instead synthesized during powders HVED treatment. Subsequent SPS consolidation of HVED treated powders ensures preservation of ultrafine structure.

The aim of present work is an analysis of possibilities of HVED and SPS plasma methods with means of obtaining multifunctional composite materials, dispersion-hardened by nanoparticles, based on Fe - Ti - C system.

Methods of studies

HVED treatment of powders of initial mass composition 75 % Fe - 25 % Ti, 50 % Fe - 50 % Ti, 25 % Fe - 75 % Ti and 75% Fe - 20% Ti - 5% B_4C was performed on experimental stand, which is described in detail in paper [2]. Galvanic contact of point-electrode with layer of processed powder was ensured during treatment. Specific treatment energy of micropowders of different mass composition was chosen in accordance to condition of full carbidization of titanium to obtain blend of Fe -Ti - C system with hardening TiC phase content from 25 to 75% (see Table 1) [4, 5].

Computer granulometric and X-ray diffraction analysis were used to study the impact of HVED on dispersity, form and phase composition of powder mixtures.

Specific electrical resistance of powder mixtures before and after HVED treatment was determined on experimental stand based on MCP "BR 2820" LCR METER device, which is described in detail in paper [2].

After HVED treatment, powder mixtures were separated from hydrocarbon liquid using centrifuge and oven drying.

Table 1: Powder mixtures treatment regimes.

Number of regime	Mixture composition	Specific treatment energy (MJ/kg)
1	75 % Fe – 25 % Ti	6.25
2	50 % Fe - 50 % Ti	12.5
3	25 % Fe - 75 % Ti	18.75
4	75 % Fe – 20 % Ti – 5 % B ₄ C	6.25

Consolidation of powder mixtures was performed by method of spark-plasma sintering on experimental complex «Гефест – 10» ("Gefest – 10"), which allows to consolidate powders at mechanical load in vacuum with superposition of direct and alternating currents with amplitude of 1.1 kA and frequency of alternating component of 10 kHz [6, 7].

Hardness of consolidated specimens was measured according to [8]. Wear resistance was studied on friction machine CMU - 2 (SMC - 2) with roller - block scheme. Diamond circle 1A1 with AC4 80/63 grain was used as counter-body. Mechanical properties of obtained specimens were determined on P-5 (R-5) research machine by TRS method of determining strength limit [9].

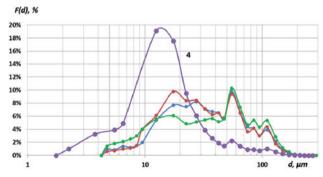
Physical-mechanical properties of obtained specimens were compared with properties of HSS M2 steel.

Results

Initial Fe and Ti powders had similar granulometric composition. Mean diameter of Fe particles was ~ 59 µm, mean diameter of Ti particles was ~63 µm and mean diameter of boron carbide particles was ~ 5 µm. Size distributions of initial mixtures particles are shown on Figure 1.

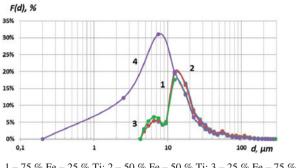
HVED treatment of powder mixtures leads to more than 3 times decrease of mixtures particles mean diameters (to $\sim 20 \, \mu m$) (Figure 2).

Comminution efficiency of Fe - Ti system powder mixtures does not depend on their composition despite the fact that strength of pure Ti is much higher than of Fe. Most likely this is due to embrittlement of Ti because of reaction with H, which is synthesized during pyrolysis of hydrocarbon liquid.



1 - 75 % Fe - 25 % Ti; 2 - 50 % Fe - 50 % Ti; 3 - 25 % Fe - 75 % Ti; 4-75 % Fe - 20 % Ti - 5 % B₄C

Figure 1: Size distribution of initial powder mixtures particles.



1 - 75% Fe - 25% Ti; 2 - 50% Fe - 50% Ti; 3 - 25% Fe - 75% Ti; 4 – 75 % Fe – 20 % Ti – 5 % B₄C

Figure 2: Size distribution of powder mixtures particles after HVED treatment.

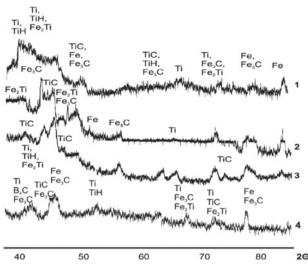
Initial mean diameter of powder mixture that contains boron carbide was ~ 22 µm (Figure 1, line 4) and after HVED treatment it decreases to ~ 17 µm, while quantity of particles with diameter more than 30 µm is less than 5 % (Figure 2, line 4 and Figure 3).

As specific processing energy was selected according to [5] to ensure Ti carbidization conditions, quantity of unreacted carbon in HVED treated mixtures was less than 1% (vol.).

X-ray diffraction analysis of powder mixtures after HVED treatment showed and confirmed the presence of hydrides, carbides and some amount of residual Ti in mixtures composition. Presence of residual Ti indicates that part of nanocarbon reacted with Fe forming Fe₃C. Destruction of boron carbide during HVED treatment in considered regimes have not happened (Figure 4).

Formation of Fe₃C, Fe₂Ti and TiC with size in range from 100 to 600 nm, which are dispersion-hardening phases, occurs in all considered treatment regimes (Figures 3 and 4) [10].

Composition of powder mixtures has significant impact on their specific electrical resistance, which

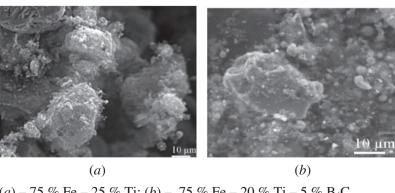


1 - 75% Fe - 25% Ti; 2 - 50% Fe - 50% Ti; 3 - 25% Fe - 75% Ti; 4 - 75 % Fe - 20 % Ti - 5 % B₄C

Figure 4: Phase composition of mixtures after HVED treatment.

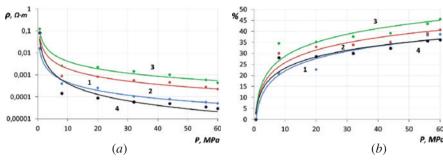
increases in proportion to Fe content from ~ $20 \Omega \cdot m$ (for 25 % Fe − 75 % Ti) up to ~ 610 Ω ·m (for 75 % Fe − 25 % Ti) even while specific electrical resistance of pure Fe powder is significantly lower than of Ti. This can be explained by the presence of oxide films on surface of powder particles, which greatly reduce their conductivity. Addition of 5% B₄C, which is a semiconductor, leads to a ~ 2 times increase of specific electrical resistance (up to ~ 1,100 Ω ·m). Change of powders dispersity and phase composition after HVED treatment leads to decrease of specific electrical resistance by ~ 4 orders of magnitude for 75 % Fe - 25 % Ti

(to ~ 1.6 \cdot 10⁻² Ω ·m) and 50 % Fe – 50 % Ti (to ~ 8 \cdot $10^{-2} \,\Omega \cdot m$) powder mixtures, and to decrease by ~ 2 orders of magnitude (to ~ 0,12 Ω ·m) for 25 % Fe – 75 % Ti powder mixture. Specific electrical resistance of mixture with



(a) -75% Fe -25% Ti; (b) -75% Fe -20% Ti -5% B₄C

Figure 3: Electron microphotographs of powder mixtures after HVED treatment. Magnification ×1700.



1-75~% Fe -25~% Ti; 2-50~% Fe -50~% Ti; 3-25~% Fe -75~% Ti; 4-75~% Fe -20~% Ti -5~% B₄C

Figure 5: Change of specific electrical resistance (a) and shrinkage (b) of HVED processed powders under mechanical pressure.

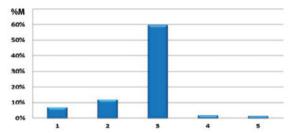
addition of boron carbide decreases by ~ 5 orders of magnitude (to 1,6 \cdot 10⁻² Ω ·m) (see Figure 5(a)). Change of specific electrical resistance occurs due to increase of contact surface and destruction of oxide films, which is confirmed by results of X-ray diffraction analysis.

Mechanical load on powder leads to decrease of specific electrical resistance of blend – as the pressure was increased to $10\,\text{MPa}$ specific electrical resistance of the mixtures decreases ~ 40 times (Figure 5(a)), and at pressure of $60\,\text{MPa}$ it decreases by 3–4 orders of magnitude.

Mechanical load on blend during SPS leads to its shrinkage, which occurs abruptly when pressure increases up to 10 MPa and totals from 20 to 30 % due to the removal of the arch effect (stable large voids) in the filling (Figure 5(b)), and then shrinkage increases monotonically and at a pressure of 60 MPa is from 35 to 45 %, due to plastic deformation of the particles. Increase of mechanical pressure over 60 MPa is inappropriate because it is limited by strength of matrix.

Analysis of dispersity, phase composition and specific electrical resistance of powder mixtures after HVED treatment allows choosing the regime of their SPS consolidation. Fe – Ti system phase diagram [11] shows that in area of Ti concentration near 53–77% there is a low-temperature eutectic zone with melting temperature of 1,085 °C. If the mixture is heated over given temperature the melt will consist of FeTi intermetallic and Ti. If nanocarbon, which could not react during HVED, is present in system, then, given the high affinity of carbon to titanium and its solubility in iron, favorable conditions for active interaction of components with synthesis of Fe and Ti carbides are created during sintering.

SPS regime was chosen in accordance to phase diagram – 1,100 °C temperature with subsequent isothermal



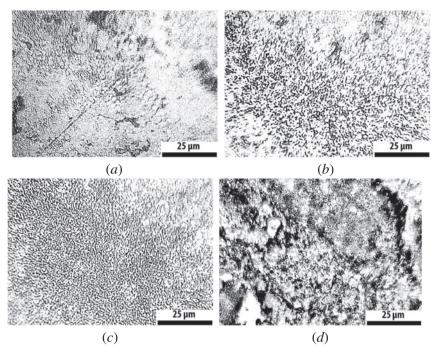
1 – sample, consolidate from HVED treated mixture № 1 (see table 1); 2 – from mixture № 2; 3 – from mixture № 3; 4 – from mixture № 4; 5 – HSS M2 steel

Figure 6: The weight loss of the samples in contact with the diamond wheel 1A1 of AC4 80/63 grain.

holding during 3 min, which allows obtaining materials with high density and wear-resistance (Figure 6).

Samples of initial mass composition $25\,\%$ Fe $-75\,\%$ Ti show the highest mechanical characteristics after SPS among all considered mixtures of Fe - Ti - C system after HVED treatment. Their bending strength was 800 MP, hardness was 48 HRC, and weight loss of the samples in contact with the diamond wheel 1A1 of AC4 80/63 grain was $\sim 7\,\%$ of sample mass for 1km of way. Increase of carbide content in system composition leads to their concentration across grain boundaries and thus to embrittlement of material (Figure 7).

Addition of 5% B₄C to mixture leads to its decomposition during SPS and formation of Fe and Ti borides in consolidated samples, which significantly increase their mechanical properties: weight loss was $\sim 1.8\%$ (which is comparable to wear resistance of tungstencontaining HSS M2 steel – weight loss of $\sim 1.4\%$ for 1 km), bending strength increased up to 1,100 MPa. X-ray diffraction of sintered samples showed presence of carbides and borides. No sign of unreacted carbon was noticed.



- (a) sample, consolidate from HVED treated mixture №1 (see table 1);
- (b) from mixture № 2; (c) from mixture № 3; (d) from mixture № 4;

Figure 7: Microstructures of consolidated materials. Magnification × 250.

Conclusions

- It is shown that plasma methods of HVED powders preparation for consolidation and their subsequent SPS allows obtaining multifunctional dispersionhardened by nanostructured particles composite materials, based on Fe - Ti - C - B system.
- Use of HVED in disperse system "powder hydrocarbon liquid" allows performing dispersion of particles (mean diameter of Fe and Ti powders decreases ~ 3 times) and synthesis of TiC, Fe₂Ti and Fe₃C dispersion-hardening additives with size from 100 up to 600 nm in them.
- Consolidation of blend after HVED treatment by SPS method allows obtaining material of Fe - Ti -C system with bending strength of 800 MPa and weight loss during contact with diamond circle of 7% for 1km.
- Modification of Fe Ti C system by boron carbide leads to increase of bending strength up to 1,100 MPa and to decrease of weight loss to 1.8%, which is comparable to wear resistance of tungsten-containing HSS M2 steel.

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