Thermal physical processes during forming of biocompatible Ca-P coatings by detonation spraying

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Abstract. Carbon-carbon composites with calcium phosphate (Ca-P) coatings (with a thickness up to of ≈100 μm) are considering as prospective grafts for defect bone substitution. Detonation spraying of Ca-P layers allows to fulfil a deposition mode with relative low temperature loads (up to a temperature of the processed surface of ≈850…1100 K) under a pulsed pressure of ≈2…6 bar. Such deposition conditions could promote to minimal thermal decomposition of feedstock HAp.

1. Introduction

Currently calcium phosphate (Ca-P) coatings based on hydroxyapatite (HAp) are under studying for osseointegration stimulating for both metallic (titanium and its alloys) [1] and carbon-carbon (C-C) composite implants [2, 15]. Among the most promising deposition techniques, detonation spraying is being considered nowadays [3, 4]. It could be noted that the process of formation of coatings occurs due to the braking of heated (up to ≈0.8…0.9 from the melting point) and highly accelerated (up to speeds of ≈0.6...0.9 km/s) particles [5]. As a result, the thermal loads in the coating are significantly lesser than in the case of plasma spraying [6], which minimizes the decomposition of hydroxyapatite with the formation of undesirable compounds and promotes the formation of highly adhesive coatings.

Obviously thermal and gas dynamic processes and heat fluxes into the substrates at the “coating-substrate” interface define the rates of chemical and phase transitions and the final composition. A correct estimation of chemical and phase transitions is only possible with an account of a interface thermal resistance of the coating $R_c$, a heat conductivity of $\lambda_c$ and the other properties. On the other hand, detonation deposition differs from the others by a high and pulsed pressure $p$. So, there are two main mechanisms of influence on the coating properties: a non-stationary heat flux into the substrate and pulsed mechanical loads because of an exposure of heterophase detonation flows with fine HAp particles (with a diameter of $d_p \leq 100 \mu$m). Moreover, the indicated processes could show some features at low-scales during coating deposition. These circumstances with a complex irregular edge of the covered surfaces could cause an uncertainty in chemical and phase composition of the coatings. Chemical transitions could lead to appearance of the species which cause unwanted biological responses [7].

2. Experimental techniques
Deposition of Ca-P coatings was fulfilled by a commercial CCDS2000 setup [8] with the procedure [4, 9]. The coating was deposited almost continuously for a series of 500 shots (with the frequency of 4 shots per second) when a varying of a distance between the barrel and the substrates. Cylindrical carbon-carbon (C-C) composites (“NTM+” Ltd., Vsevolozhsk, Russia) [2] with the diameter of $d_c=17$ mm and the length of $l_c=11$ mm were used as substrates. The coating was deposited on the end face of the samples. Temperatures of the substrates were measured in two points by K-type thermocouples. The first sensor was mounted inside the sample at the distance $l_s=3$ mm from the processed surface (the temperature $T_s$). The second thermocouple was fixed at the opposite surface (the temperature $T_o$). The temperatures waveforms were recorded with USB9211 input device (National Instruments) connected with PC. A dynamics of pressure $p(t)$ on the substrates and in the barrel (near the HAp injection zone) were measured by piezo sensors calibrated with a shock tube (within an overpressure range of 0.5…10 bar). Disposition of piezo sensors calibrated with a shock tube (within an overpressure range of 0.5…10 bar). Disposition of the barrel and the sensor mounted in an aluminum plate is presented in figure 1. Non-stoichiometric HAp in the form of fine particles (with a diameter of <50 μm) was used as feedstock. SEM image (TESCAN VEGA 3 XMU electron microscope; 30 keV; 10⁻³ Pa) of deposited HAp particles is shown in figure 2.

A porous nature of the substrates and the inner non-uniform columnar structure introduce uncertainty to data on thermal properties of C-C composites. Measuring of heat conductivity of the C-C substrate and the Ca-P coating was fulfilled with a steady state Joule heating of the one side and a passive cooling (through a wall to water) at the other side under vacuum. The coating thickness was $\delta_c=80…100$ μm. A heat power $Q$ was 0.07…1.03 W. The temperatures of the “hot” and “cold” sides were controlled by K-type thermocouples. A measurement accuracy of temperature was $\approx \pm 1$ K.

3. Results and discussion

Obtained experimental data indicated that the heat conductivity of the composite was $\lambda_s=9.73$ W/(m·K). Deposition of the Ca-P coating led to an appearance of an additional thermal resistance $R_c$. In this case an effective heat conductivity of the coating was $\lambda_c=0.05$ W/(m·K).

With data on temperature $T_s$ a heat flux into the from the heterophase detonation flow was estimated as

$$q_s = \rho_c C_p l_s \frac{dT_s}{dt}.$$  (1)
Here $\rho_s=2.25\cdot10^3$ kg$\cdot$m$^{-3}$ is graphite density and $C_s=711$ J$\cdot$kg$^{-1}\cdot$K$^{-1}$ is its heat capacity [10]. In the present study a temperature rise was $\frac{dT}{dt} \approx 5$ K$\cdot$s$^{-1}$. In this case characteristic $q_s$ values were $q_s=2.6\cdot10^2$...$3.2\cdot10^2$ kW$\cdot$m$^{-2}$. Such heat fluxes were close to the data of the other authors [11].

The heat flux $q_s$ and the temperature $T_s$ could be considered as boundary conditions for the one-dimensional nonstationary heat conduction equation [12]

$$\frac{\partial T}{\partial t} = a \frac{\partial^2 T}{\partial x^2}. \quad (2)$$

Here $a = \frac{\lambda_s}{\rho_s C_s}$ is the thermal diffusivity. When solving (2) it was assumed about the adiabaticity of the processes at the substrate generatrix.

The most important result of the analyzing equation (2) was the estimation of the temperature of the processed surface $T_p$. The ambiguity of the calculation was associated with a change of the boundary thermal resistance $R_c$. In the present study the effective heat conductivity $\lambda_{eff}$ of the interface between the processed surface and the first temperature sensor was calculated as

$$\lambda_{eff} = \frac{\delta_p + l_s}{\delta_c / \lambda_c + l_s / \lambda_s}. \quad (3)$$

In our case $\lambda_{eff} = 1.43$ W$\cdot$m$^{-1}\cdot$K$^{-1}$.

Temperature of the processed surface $T_p$ was calculated with the data on special and temporal temperature dynamics at the point of $x=0$

$$T_p \approx q_s \sqrt{\frac{\pi \tau}{\lambda_{eff} \rho_s C_s}} + T_o. \quad (4)$$

Here $\tau$ is the time of temperature rising. In the present study $T_p \approx 850$...1100 K. Temporal dynamics of $p(t)$ is presented in figure 3. It was found that in the case of the heterophase detonation flow the substrate was undergone by exposure of, firstly, shock wave front with the next relaxation (a rarefaction) and, secondly, a HAp particle flow. A contribution of the particles was visualized as an extended “tail” of $p(t)$ waveforms. The overall time of the exposure was $\approx 10^{-2}$...$10^{-1}$ s. The temporary delay between the shock in the barrel and on the substrate allowed to estimate the shock velocity $D$ of $\approx 0.5$...1.0 km/s. Typical average pressure loads on the substrate were $\approx 2$...6 bar.

![Figure 3](image_url)

We consider detonation deposition as an alternative to the other spraying techniques (and especially, plasma spraying [13]) which are characterized by a powerful thermal impact on deposited particles (with a temperature above the HAp melting point $T_m \approx 1523$ K [14]).
4. Conclusions
We noted that the Ca-P coating formation by detonation spraying occurred under relatively low temperatures (below $T_m$) and pulsed pressure loads ($\approx 2...6$ bar). Such conditions could lead to insignificant HAp disproportion with formation of unexpected components.

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References
[1] Demnati I, Parco M, Grossin D, Fagoaga I, Drouet C, Barykin G, Combes C, Bracers I, Goncalves G, Rey C 2012 Hydroxyapatite coating on titanium by a low energy plasma spraying mini-gun Surf. Coat. Technol. 206 (8–9) 2346–2353
[2] Gordeev S K 2001 Nanoporous and nanofragmental carbon composite materials (Nanostructured Carbon for Advanced Applications) ed G Benedek, P Milani, V G Ralchenko, Nanostructured Carbon for Advanced Applications (Dordrecht: Springer) pp. 71–88
[3] Klyui M I, Temchenko V P, Gryshkov O P, Dubok V A, Kladko V P, Kuchuk A V, Dzhanag V M, Yukuymchuk V O, Kiselov V S 2013 Bio-SiC ceramics coated with hydroxyapatite using gas-detonation deposition: An alternative to titanium-based medical implants Funct. Mater. 20 (2) 163–171
[4] Tsygankov P A, Skryabin A S, Krikorov A A, Chelmodeev R I, Vesnin V R, and Parada-Becerra F F 2019 Formation of a combined bioceramics layer on titanium implants J. Phys.: Conf. Ser. 1386 012011
[5] Ulianitskiy V, Shtertser A, Zlobin S, and Smurov I 2011 Computer-controlled detonation spraying: from process fundamentals toward advanced applications J. Therm. Spray Technol. 20 791–801
[6] Xue W, Tao Sh, Liu X, Zheng X, Ding Ch 2004 In vivo evaluation of plasma sprayed hydroxyapatite coatings having different crystallinity Biomaterials 25 (3) 415–421
[7] Heimann R B 2018 Plasma-Sprayed Hydroxyapatite Coatings as Biocompatible Intermediaries Between Inorganic Implant Surfaces and Living Tissue J. Therm. Spray Technol. 27 1212–1237
[8] Smurov I, Ulianitskiy V 2011 Computer controlled detonation spraying: a spraying process upgraded to advanced applications Surf. Eff. Contact Mech. X pp. 265–276
[9] Tsygankov P A, Skriabin A S, Telekh V D, Loktionov E Yu, and Chelmodeev R. Yu. 2018 Interaction between Dusty Shock Waves and Three-Dimensional Scaffolds of Carbon Nanocomposites upon the Deposition of Biocompatible Coatings Bull. Russ. Acad. Sci.: Phys. 82(4) 380–385
[10] Emsley J. 1998 The elements, third ed. (London: Clarendon Press)
[11] Golub V V, Bazhenova T V 2008 Pulsed supersond streams (Moscow: Nauka) [in Russian]
[12] Carslaw H S, Jaeger J C 1959 Conduction of Heat Solids, second ed., (London: Oxford University Press)
[13] Khor K A and Cheang P 1997 Plasma sprayed hydroxyapatite (HA) coatings produced with flame spheroidised powders J. Mater. Process. Technol. 63 (1–3) 271–276
[14] Roopalakshmi S, Ravinshakar R, Belaldavar Sh, Prasad R G S V, Phani A R 2017 Investigation of Structural and Morphological Characteristic of Hydroxyapatite Synthesized by Sol-Gel Process Mater. Today. 4(11) 12026–12031
[15] Wang Ch, Li K, Zhai Y, Li H, Wang J-I, Jiao G 2009 Study of fluoro-hydroxyapatite coatings on carbon/carbon composites Surf. Coat. Technol. 203 (13) 1771–1775