On using of gas detonation for spraying of biocompatible films onto the carbon nanocomposites

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Abstract. The paper presents the experimental study of the using of gas detonation for spraying of hydroxyapatite (HOA) particles onto the carbon nanocomposites. The characteristic parameters of the heterophase detonation flows were defined. The prepared films (with a thickness of 80…100 μm) were polycrystalline with Ca and P concentration ratio of ≈1.67 as for raw HOA. It was noted about the prospects of gas detonation for HOA spraying.

1. Introduction

The one of main problems of the modern engineering is designing of biocompatible materials for the bone substitutes [1]. Nowadays the films of hydroxyapatite (HOA) \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \) onto SiC and Ti substrates are under consideration [2]. Carbone nanoimplants (CNI) [3] are more perspective due to the structure features.

The commercial technologies [4] of HOA spraying are plasma and high velocity oxygen fuel spraying. The using of such methods is limited [2] because of poor adhesion, imperfection of structures etc. Therefore nowadays the application of gas detonation [5] for this aim is under studying [2]. The detonation provides pulsed action onto a substrate for minimization of abrasive wear and increasing of the adhesion.

2. Experimental set

Based on commercial CCDS 2000 equipment [5] the experimental set was designed (see figure 1). Gas detonation generated within a cylindrical barrel (1) with a diameter \( d_b \) of 1.6 cm in a stoichiometric acetylene-oxygen mixture by a spark (2). The mixture was supplied via controlled solenoid valves by a gas feed system (3). A portion of the mixture \( \eta \) within the barrel was varied from 0.6 to 0.95. Nitrogen flow was used for the blowdown among shots. The injection of fine (\( d_p \leq 100 \mu m \)) HOA particles was realized into the direction normal to the barrel axe by a pneumatic feeder (4). A volume flow rate of HOA was about of 0.3…1.0 mm\(^3\) per a shot. Piezometric sensors were used for control of the pressure dynamics \( p(t) \) and estimation of average velocity \( \bar{D} \) at different distances from the spark. The one (5) was built in the barrel at the injection zone at the distance of \( a=56 \) cm from the spark and the other (6) was embedded into a substrate (7). A distance \( \delta \) between the muzzle and the substrate was varied from 2.5 up to 23.0 cm. The length of the particle acceleration zone was of \( l=40 \) cm. The recording of data from the sensors was realized by a digital oscilloscope (8). A system of laser Schlieren photography...
was used for the visualization of the detonation flow (9). This system consisted from a Nd:YAG laser (10) and a high-speed camera (11). The red (\(\lambda=670\) nm) and the green (\(\lambda=532\) nm) lasers were used. The polarizing filter (12) regulated an intensity of the laser radiation. The system consisting of an interference filter (13) with \(\lambda_{\text{max}}=532\) nm and \(\Delta\lambda=11\) nm for the green laser and with \(\lambda_{\text{max}}=670\) nm and \(\Delta\lambda=11\) nm for the red laser and a diaphragm (14) was used for cutoff of the flow (9) radiation and visualization of flow disturbances. The laser beam was collimated by lenses (15) and (16). Synchronizing unit BNC 575 (17) delayed a picture capturing by the camera relatively to the spark (2).

The study of the detonation dynamics was done both for the non-dusty flows and heterophasic flows with HOA particles with an average size of \(d_p=70\) nm and 100 μm.

![Figure 1](image)

**Figure 1.** Experimental set: 1 – barrel; 2 – spark; 3 - gas feed system; 4 – pneumatic HOA feeder; 5 and 6 – piezometric sensors; 7 – substrate; 8 – oscilloscope; 9 – detonation flow; 10 – Nd:YAG laser; 11 – high-speed camera; 12 – polarizing filter; 13 – interference filter; 14 – diaphragm; 15 and 16 – lenses; 17 – BNC 575 synchronizing unit.

The prepared films and initial CNI were characterized by SEM (Zeiss Ultra plus 55), EDX (INCA Energy 350 XT), XRD (DRON 3M) and profilometry (FRT MicroSpy). The film adhesion was measured by ISO 13779-4 technique.

### 3. Results and discussion

The main features of the dynamics of non-dusty and heterophasic flows were defined. In figure 2 the dependences of pressure \(\tilde{p}(\tilde{t})\) are presented. Here \(\tilde{p} = p / p_0\) - dimensionless pressure and \(\tilde{t} = t / t_0\) is dimensionless time, where \(p_0 = 3.1\) MPa and \(t_0 = 440\) μs.

The data evidenced about the presence of a fully developed detonation which was visualized as a strong shock wave (1) with amplitude of \(\tilde{p}_{\text{max}} \approx 1...1.25\) and a further rarefaction (2). The main energy releasing occurred in a deflagration zone (3). The following pressure decreasing (4) was bound with the product cooling. The wide pressure peaks (5) were caused by a deflagration afterburning of the mixture. Further the rarefaction (6) caused by leaving of products from the barrel was recorded. Characteristic velocities \(\overline{D}\) between the spark and the injection zone were varied from 0.7 up to 1.5 km/s. Such dispersion is explained by an irregularity of the valve operation, inhomogeneity of the mixture etc.
Figure 2. Typical $\tilde{p}(t)$ data for non-dusty (a) and heterophasic flows (b) at the injection zone (A) and on the substrate (B) at $\eta=0.95$ and $\delta=2.5$ cm

The impulse amplitude recorded by the sensor (6) and the flow structure were depended on $\delta$ (see figure 3). At $\delta=2.5$ cm the substrate was undergone by an action of strong shock wave (1) with amplitude of $p_{\text{max}} \approx 1...3.2$. Maximal characteristic velocities (at $\eta=0.95$ and $\delta=2.5$ cm) for the non-dusty and heterophasic flows outside the barrel were $D \approx 2.30...2.76$ km/s. Further the shock amplitude was decreased due to $\delta$ increasing. Note that HOA injection with the relative weight content $g$ of 1.25-2.50 % did not lead to a significant changing of a motion law for the flow. For this law it was established $x(t) \propto t^{0.15}$. On the other hand HOA injection caused a increasing of the transmitted on to the substrate impulse in $\approx 1.5...3.5$ times than of non-dusty flows. This fact was linked with action of the dispersed phase.

Figure 3. Typical $x-t$ diagram of a detonation wave within (zone I) and outside (zone II) the barrel and characteristic $\tilde{p}(t)$ patterns at $\eta=0.95$ and $\delta=2.5$ cm

In figure 4 Schlieren photos of a motion of the detonation flow are presented at $\eta=0.95$ and varied delay time $t_d$. It was shown that the moving right to left the shock front was undergone diffraction at the muzzle ($t_d=650$ $\mu$s). The shock (1) and combustion (3) fronts moved jointly at reaching of the shock wave with amplitude $p_{\text{max}} \approx 3.2$.
substrate (2). At the periphery of the muzzle (4) the vortexes (5) and rarefaction waves (6) were registered. Further ($t_d=680 \mu s$) the detonation deceleration occurred. The formation of high density shadowed region (7) and wave interference (8) between the substrate and the barrel were detected. At the larger times ($t_d=720 \mu s$) the vortex growth was detected. This phenomenon resulted to the further «spreading» of the flow and stabilization of high pressure field over the substrate during of 50–70 $\mu s$. This fact was recorded by the piezometric sensor too (see figure 2).

**Figure 4.** Schlieren photos of a motion of the detonation flows visualized by the green $\lambda=532$ nm (a–c) and the red $\lambda=670$ nm lasers (d–f)

Study of the HOA films on CNI allowed to define the main features. The films (see figure 5) had a non porous structure without visible defects. It was showed that the coatings are polycrystalline with Ca and P concentration ratio of $\approx 1.67$ that corresponds to raw HOA.
The adhesion of the films depended non-monotonically on $\eta$ and $p$ respectively (see figure 6). Here $A = A / A_{\text{max}}$ is dimensionless adhesion and $A_{\text{max}}$ is maximum measured adhesion at $l \approx 5$ cm and $d_p \approx 70$ nm. Initially the increasing of $p$ led to $A$ growth due to effective HOA acceleration but further increasing of $p$ (higher than of 0.85) caused the CNI micro crashing and $A$ decreasing.

**Figure 5.** SEM image of the sample: 1 – carbon substrate; 2 – HOA film

**Figure 6.** Dependences $\tilde{A}(\eta)$ (1) and $\tilde{p}(\eta)$ (2) at $\delta=5$ cm and $d_p \approx 70$ nm

4. Conclusion

Gas detonation flows are suitable for spraying of HOA onto CNI. The prepared films (with a thickness of 80…100 μm) have the close packed structure as raw HOA. It was demonstrated that the flow dynamics has an effect on the adhesion. The optimal conditions of the film spraying were defined.
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