Improvement of the Cavitation Erosion Resistance of Titanium Alloys Deposited by Plasma Spraying and Remelted by Laser

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The paper analyses the effect of oxides powder deposition by plasma spraying and remelting with laser beam on the cavitation resistance of Ti-6Al-4V biphasic alloy. The deposited and remelted coatings were tested for cavitation erosion on the magnetostrictive vibratory apparatus with nickel tube. Using optical and scanning electron microscopy, were obtained qualitative informations about the degradation mechanism and the cavitation erosion evaluation was done by comparing the specific erosion curves of Ti-6Al-4V substrate with those of coated layers.

Keywords: Ti-6Al-4V, cavitation, characteristic curves, oxide ceramic powders

Due to a relatively low density, good corrosion resistance and good creep properties, titanium and its alloys have been extensively used since 1950 in aerospace, chemical, military, the naval and maritime components construction, medical applications, etc [1, 12, 13].

One of the major factors limiting the life of titanium alloys in service is their degradation due to gaseous environments. When titanium alloys are heated to temperatures above approximately 800°C, oxygen, hydrogen and nitrogen are adsorbed and diffuse into the surface layer. This phenomenon is undesirable because it increases hardness and brittleness of the material [2].

Ti-6Al-4V is the most used biphasic titanium alloy. This material has low tribological properties, reducing performance of the components which are working in wear conditions. For this reason, it is subjected to surface treatments mainly aimed for increasing of the abrasive wear resistance under high load exploitation conditions [3-5].

Coatings with powdery materials proved to be the most efficient and economic methods to increase the erosion resistance to different temperatures without destroying the mechanical properties of the substrate. These hard layers can be obtained either by Electron Beam Physical Vapour Deposition (EB-PVD) or by plasma spraying [6-8].

Plasma Spraying is a thermal deposition process that allows the coating of a substrate with a protective layer, at high temperatures, layer that can be either ceramic or metallic. The transporter gas, often argon, carries the pulverized material in the formed plasma beam, where the partial or complete melting of particles occurs. Particles in this state will be projected on the titanium alloys surface. Cooling on the substrate surface occurs very quickly so the melt droplets are solidified at high speeds and the heating of substrate is limited [9]. The main problem with plasma spraying for such coatings is the high porosity, sensitivity to microcracks appearance, and non-bonded interface areas between lamellae existing in the coatings, which reduce thermal insulation and corrosion performance. In order to reduce the porosity and to obtain a coating with a better chemical homogeneity combined with the increasing of the protective properties a remelting of the deposited layer was performed [10]. The remelted coatings are usually more isotropic and free of the laminar architecture which is responsible for higher susceptibility to spalling and delamination.

Ceramic materials deposited on metallic or polymeric substrates offer many advantages due to the high hardness, good resistance in corrosive and high temperatures conditions and also relatively low densities. Oxide ceramics such as Al_2O_3, ZrO_2, TiO_2, SiO_2 and Y_2O_3 have been widely used as surface coating materials to improve wear, corrosion and fatigue resistance and also to provide good lubrication and thermal insulation properties [7]. Nowadays, zirconia (ZrO_2) is considered one of the most important ceramic materials used in modern technology. It has a wide range of industrial applications because of the excellent combination of high bending strength (~1 GPa) and good fracture toughness (~10 MPa $m^{1/2}$), together with its stability at high temperature. The transformation of ZrO_2 from tetragonal in stable monoclinic phase with volume modification occurs when the temperature changes [8]. This transformation is not desired during coating deposition and therefore in order to stabilize the monoclinic polymorphic phase, oxide compounds as Y_2O_3, MgO, CaO, CeO are added. These are leading to appearance of cubic zirconium oxide phase and prevent cracking. Moreover, the addition of calcium oxide makes that the obtained mixture to be used as an excellent heat insulator with good thermal shock resistance.

This paper aims to analyse the cavitation behaviour of some ceramic oxide coatings deposited by plasma spraying onto the surface of Ti-6Al-4V alloy and then remelted by laser beam.

Experimental part

Coating-substrate materials

The material used in this experimental program is Ti-Al-4V alloy whose chemical composition is presented in table 1. From this material, cavitation samples were worked in shape and dimensions shown in figure 1. Some of these samples were coated by plasma spraying process:

- 100% Al_2O_3, granulation -62+11μm;
- 95% ZrO_2 + 5% CaO, granulation -45+15μm;

Before spraying, the substrate surface was sandblasted and degreased to increase the adherence between substrate and coating and to remove any impurities from the surface.

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Tabel 1
EMICAL COMPOSITION OF THE ANALYSED ALLOY

Material	Chemical composition, %								Observations
	Al	V	C	N	H	O	Fe	Ti	
Ti-6Al-4V	6.2-6.3	4.0-4.1	0.007-0.012	0.006-0.008	0.002-0.003	0.156-0.180	0.16-0.18	Rest	prescribed values
	6.2	4.05	0.011	0.01	0.002	0.16	0.174	Rest	actual values

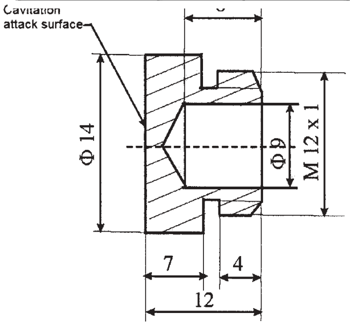


Fig.1. Shape and dimensions of the cavitation samples


Fig. 2 Spray gun 3MBM

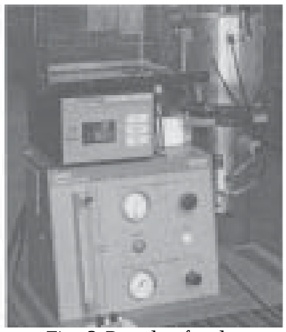


Fig. 3 Powder feeder

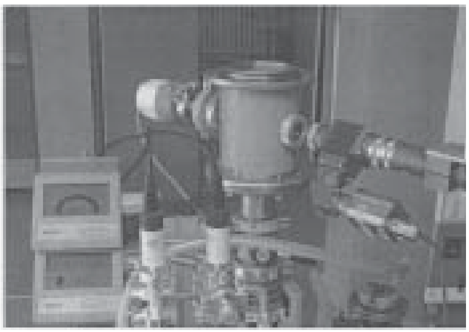


Fig. 4. Laser HL 124P LCU equipment

The plasma spraying equipment used to obtain the coatings deposition of the ceramic materials consists of: power source, control module, powder feeder, cooler, spray gun and the gases exhauster. The spraying of the ceramic powders was done using the Sulzer Metco 3MBM Spray Gun (fig. 2) and as plasma gas a mixture of Ar + 6% H_2 was used. The powder dosage was realized with the equipment from figure 3.

The plasma spraying parameters used for deposition of the ceramic materials were:
- plasma intensity, I_p=320-330 A;
- arc voltage, U_a=90-100 V;
- plasma gas flow, Q_p=40-45 L/min;
- carrier gas flow, Q_{tr}=6-7 L/min;
- spraying distance, d_p=150±5 mm

The thickness of the deposited layers was between 200÷300 μm.

In order to remove the above drawbacks, the coatings were remelted with laser beam. This process was made on Laser HL 124P LCU installation (fig. 4), whose system parameters are:
- pulse duration, d_p=0.6 ms;
- frequency, f=34Hz;
- pulse power, P_p=5000W;
- average power, P_m=102W;
- working pressure, p=1.5 bar.

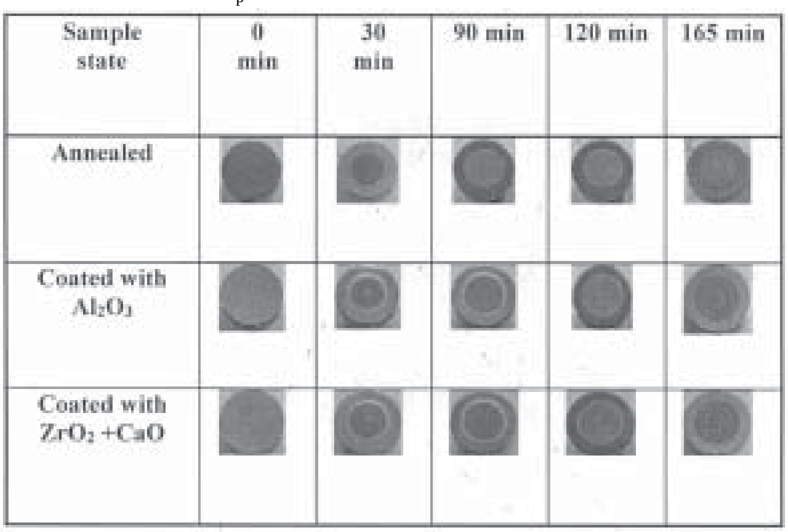
Thus prepared, the samples were subjected to vibratory cavitation on a magnetostrictive apparatus [11] with nickel tube, for 165 min divided into time periods of 5, 10 and 15 min. The test procedure is specified to the Cavitation Laboratory of the University Politehnica Timisoara and is made according to ASTM G32-1985 norms (updated through G32-2010 [14]). Before and after the cavitation tests, the samples were washed in water, alcohol and acetone. After each tested period, the mass loss was measured with an analytical balance with an accuracy of 0.01 mg. The mass losses were converted to volume losses and presented as average erosion depth. The reason was that the materials with different densities can have the same mass losses, but different volumes and erosion rates. The eroded surfaces by cavitation during the exposed 165 min time were examined using scanning electron microscopy.

Results and discussions

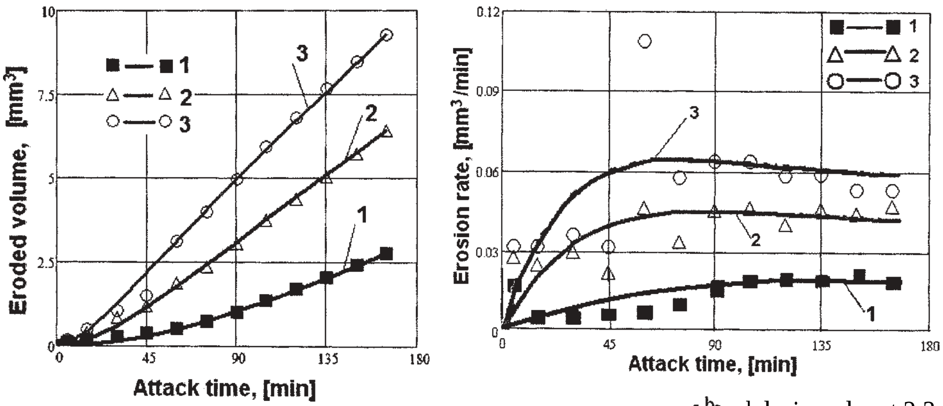
Table 2 shows the deterioration depth modification and the diameter of the affected area during the cavitation erosion testing of the 3 sets of samples from the considered titanium alloys.

It is observed that after the first 30 min testing time, the coated samples show slightly higher values of depth destruction (the cavity is darker, with the formation of the second ring, well visible after 165 min time) and of the

Tabel 2
THE EVOLUTION IN TIME OF CAVITATION EROSION



Sample state	0 min	30 min	90 min	120 min	165 min
Annealed					
Coated with Al_2O_3					
Coated with ZrO_2 +CaO					



- a -   - b -

Fig.5 Comparison of the cavitation resistance of the annlead Ti-6Al-4V alloy with of the standard steels (1- annelead Ti-6Al-4V alloy; 2- 41Cr4; 3- X5CrNi13-4): a) – volumic losses; b) – erosion rate

cavitation surface diameter; probably caused by tearing of fragile oxide particles remained unmelted on the coated surface layer.

In figures 5a and 5b are shown the variation curves of volume losses and erosion rates with the cavitation attack duration, for the alloy Ti-6Al-4V samples having biphasic $\alpha+\beta$ structure obtained after annealing heat treatment, these are compared with those of the standard steels 41Cr 4 and X5CrNi13-4 considered as materials with good resistance to cavitation erosion. The alloyed steel 41Cr 4 (approx. 0.40% C and 1% Cr) is considered as standard steel for cavitation erosion measured with a magnetostrictive vibrator device simulated in the Laboratory of the cavitation from University Politehnica Timisoara. The stainless steel X5CrNi13-4 (approx. 0.05%C, 13%Cr and4%Ni) having „soft" martensitic structure is the selected material used by casting of the Kaplan rotor blades from CHE Iron Gates I, Romania.

In figures 6 and 7 are presented in comparison the specific cavitation curves of the investigated titanium alloy coated by plasma spraying with 100% $Al_2O_3$and 95% respectively 95% ZrO_2+ 5% CaO, followed by laser remelting with those of the standard steel 41Cr4 and X5CrNi13- 4. These comparisons provide information about the cavitation erosion resistance of the ceramic oxide coatings, related to that offered by standard steels.

The analysis of these results allows the following observations:

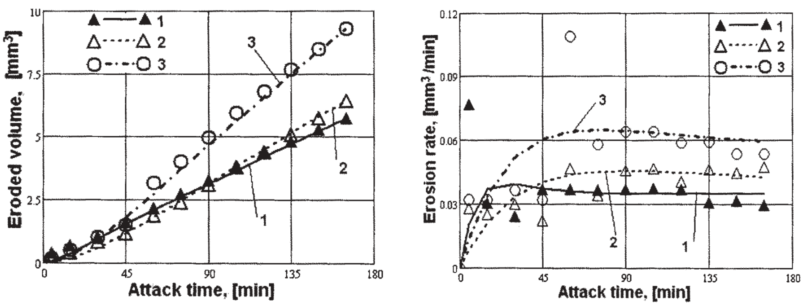
- samples from titanium alloy Ti-6Al-4V, show a superior cavitation resistance compared to those of the standard steel, being about 2.3 times higher than that of 41Cr4 steel and about 3.4 times higher than that of stainless steel X5CrNi13-4 (no matter the used criterion, respectively the eroded cavitation volume after 165 min (fig. 5a), or erosion rate, which tends to the approximation curve of the experimental data points at 165 min time (fig. 5b);

- cavitation resistance of the sprayed 100% Al_2O_3 coating is slightly higher than that of 41Cr4 steel (approx. 20% after attack time of 90 min.) and approx. 1.7 times higher than that of the X5CrNi13-4 stainless steel (fig. 6);

- compared to the standard steel (41Cr4 and X5CrNi 13-4), the ceramic mixture, 95% ZrO_2 + 5% CaO, deposited by plasma spraying followed by remelting, offers a cavitation resistance of about 3÷4 times higher.

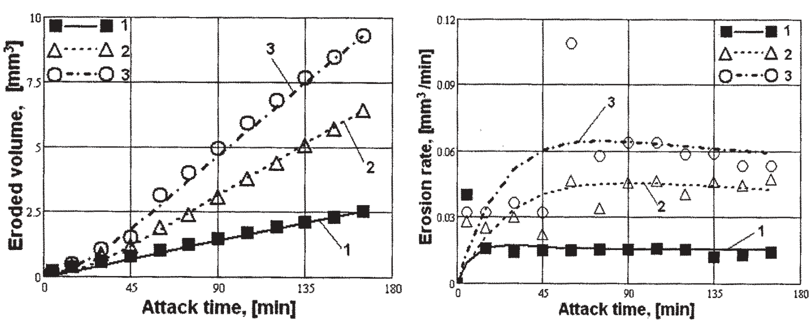
The evolution in time of the curves given in figure 8 shows that regardless the structural state of the surface zone, the considered titanium alloy has superior cavitation erosion resistance compared with those of the 41Cr4 alloyed steel and of the "soft" martensitic structure X5CrNi13-4 stainless steel.

However, in the first part of the erosion attack (until the minute 90), the annealed titanium alloy Ti-6Al-4V resists slightly better to cavitation compared with both types of plasma sprayed and laser remelted coatings, the phenomenon being justified by the better surface roughness. Instead, in the last part of erosive attack, the ceramic oxide powders 95% ZrO_2 + 5% CaO deposited on the exposed surfaces offers a higher resistance than the annealed base material. It is considered that these differences are caused by deposition technology of the ceramic oxide powders and of the surface unevenness which are destroyed in the first minutes of the attack.



a)   b)

Fig.6 Comparison of the cavitation resistance of the coated titanium by 100% Al_2O_3 spraying and followed by remelting with those of the standard steels (1-coated titanium alloy by 100% Al_2O_3 spraying and followed by remelting; 2-standard steel 41Cr4; 3-standard steel X5CrNi13-4). a) – volume losses; b) – erosion rate



a)   b)

Fig.7 Comparison of the cavitation resistance of the coated titanium by 95% ZrO_2+ 5% CaO spraying and followed by remelting with those of the standard steels (1-coated titanium alloy by 95% ZrO_2+ 5% CaO spraying and followed by remelting; 2-standard steel 41Cr4; 3-standard steel X5CrNi13-4). a) – volume losses; b) – erosion rate

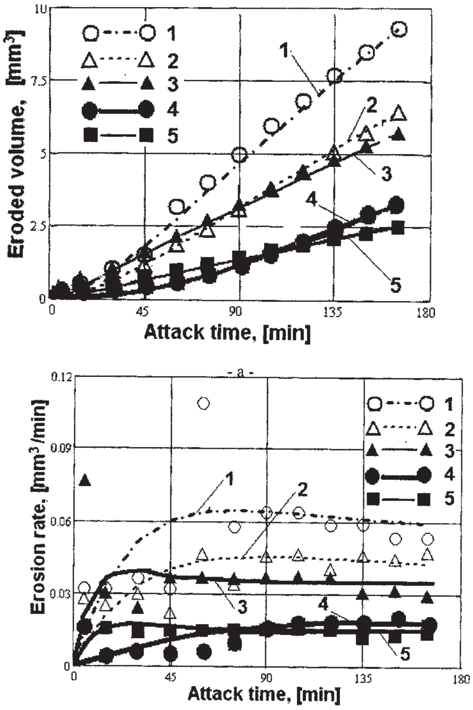


Fig.8 Comparison of the cavitation resistance of titanium after the surface status with those of the standard steels (1- standard steel X5CrNi13-4; 2 –standard steel 41Cr4; 3- coated titanium alloy by 100% Al_2O_3 spraying and followed by remelting; 4- annealed titanium alloy; 5-coated titanium alloy by 95% ZrO_2 + 5% CaO spraying and followed by remelting. a) – volume losses; b) – erosion rate

Cavitation attack surfaces of the stabilized zirconia coated samples and of the annealed samples are characterized by extremely fine and uniform “pinching” of material particles, phenomenon explained by homogeneous microstructure resulted after laser coating remelting.

The coating deposition by plasma spraying differs from other methods of thermal spraying (flame, electric arc) by the reached temperatures. Plasma is produced by a gas ionization, such argon or hydrogen, and provides temperatures of approx. 20000°C. As a result, this method is appropriate for the processing of materials with very high melting point. Ceramic powders can be melted only in the plasma beam to obtain a dense coating with adherence to the substrate. By laser remelting is favoured both the removing of any metal continuity defect and alloying of the coating with a small area from the substrate. Macro- and micrographic image of the marginal layer structure after its remelting is given in figure 9.

Due to its reduced thickness (fig. 9a) and high cooling speed from the elevated temperature, the conditions for producing of a martensitic transformation, $\beta \rightarrow \alpha + \beta_{rez}$ (fig. 9b,c) are created.

Phase α is an oversaturated solution of dissolved alloying elements in the polymorph form of Ti_a. It has a hexagonal crystal lattice easily disturbed and needles like microstructure similar to the martensite from steels. Hardness and mechanical strength of the phase $\alpha$are even higher as the concentration of alloying elements is higher.

Scanning electron microscope examination of the cavitation tested surfaces provided from samples heat treated by annealing (fig. 10) and covered with zirconia and calcia (95% ZrO_2 + 5% CaO) (fig. 12) and subsequently laser remelted reveals an uniformly material degradation, with reduced size of the formed craters.

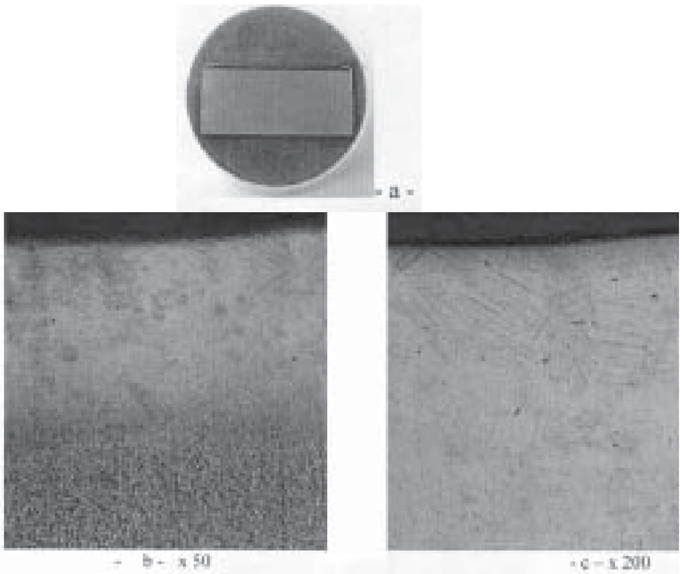


Fig. 9 Macro (a) and microstructure (b,c) of the sprayed (95% ZrO_2 + 5% CaO) and remelted coating

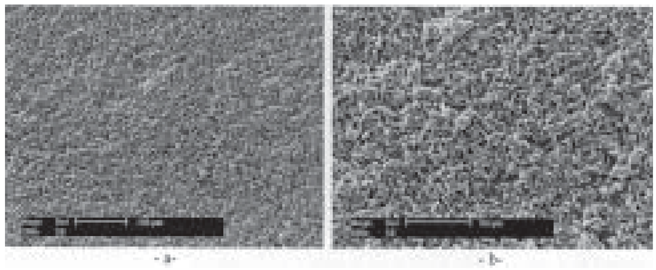


Fig. 10 Microfractographic image of the annealed Ti-6Al-4V alloy the cavitation attack

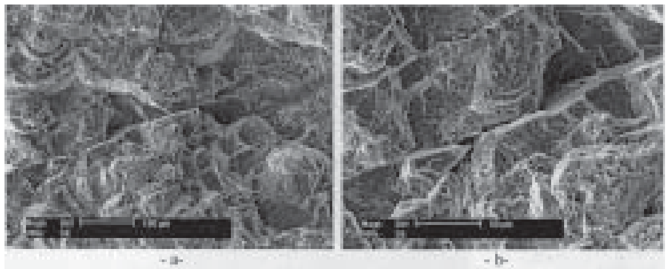


Fig. 11. Microfractographic image of the deposited and remelted Al_2O_3 coating after the cavitation attack

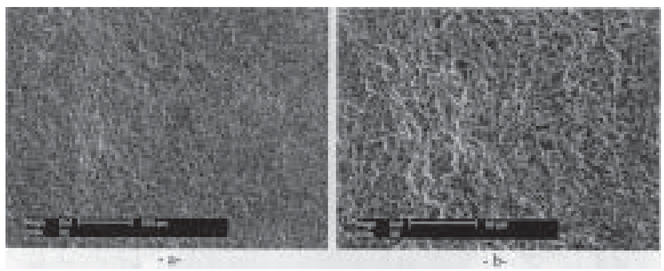


Fig. 12 Microfractographic image of the deposited and remelted 95% ZrO_2 + 5% CaO coating after the cavitation attack

Instead, on the surface coated with aluminium oxide powder (fig. 11) it can be noticed the existence of some roughest micro-zones, with a random distribution, which probably were the headquarters of some chemical combinations with high hardness and also pronounced fragility. From these reasons, overall, the surface roughness of these samples is smaller than of the coated surface with zirconium oxide doped with calcia.

Conclusions

The annealed Ti-6Al-4V titanium alloy shows resistance to cavitation erosion of approx. 2.3 to 3.4 times higher than that of considered standard steels, being used in multiple applications for the manufacturing of machinery parts, such as propellers and river ships, which operate under intense hydrodynamic cavitation conditions.

The coating deposition of 100% Al_2O_3 by plasma spraying on titanium alloy surface followed by laser remelting provides resistance to cavitation erosion comparable to that of the alloyed steels heat treated by hardening - tempering and approx. 1.7 times higher than of "soft" structural martensitic stainless steels.

The powder mixture consisting of 95% ZrO_2 + 5% CaO deposited by plasma spraying and followed by remelting, improves 3÷4 times the cavitation resistance compared to those of considered standard steels and with approx. 20% than that of the annealed titanium alloy.

Beside a finer and refined microstructure of the surface layer, the laser remelting provides a metallurgical bonding between coating-substrate and trigger off a martensitic transformation, induced by cavitation, in the titanium alloy surface.

Optical and electronic metallographic examinations carried out on the coatings obtained from the powder mixture 95% ZrO_2 + 5% CaO and tested to cavitation, show an uniform surface degradation with the formation of shallow and extremely dense micro-craters

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