NUKLEONIKA 2002;47(3):119–122

ORIGINAL PAPER

An apparatus for sequential pulsed plasma beam treatment in combination with Arc PVD deposition

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Abstract A hybrid type of apparatus is described which enables one to form a thin multi-layer film on the surface of any kind of solid substrate. In one process, the surface is treated with a high intensity pulse plasma beam which introduces the chosen kind of atoms into the near-surface layer of the substrate. In the second process, following the first without breaking the vacuum, the coating is formed by arc PVD (physical vapour deposition) process. Two examples of coatings formed on metallic and ceramic substrates are presented.

Key words Arc PVD • interlayer • pulse plasma treatment

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Received: 8 August 2001, Accepted: 18 February 2002

Introduction

Frequently, the surfaces of engineering materials are subjected to treatment by more that one process in a hybrid type of equipment in the common process chamber. Good examples of such an approach are, for instance, an apparatus that combines PVD coating with ion implantation [4], an apparatus that combines the plasma immersion ion implantation with RF/DC sputtering [1] or a facility composed of two opposing arc evaporation sources and two opposing sputter sources [2]. The present work falls into this group of approach. Our key concept is to form a novel kind of interlayer on top of the substrate prior to its coating with a chosen film by means of Arc PVD process. Both processes are carried out in sequence, without breaking the vacuum. They are executed in a common chamber. The interlayer is formed with the use of high intensity pulsed plasma beams generated in a rod plasma injector type of device, run in so called deposition by pulsed erosion mode (DPE) [5]. Most characteristic feature of the DPE relies upon the fact that metallic atoms eroded from intentionally chosen electrodes are alloyed into the substrate when its top layer (0.1–2 μm) is in the liquid state induced by heat deposition during the initial phase of the plasma pulse. In subsequent paragraphs we describe the apparatus and examples of application of the hybrid process mentioned above.

Set-up of the apparatus and principle of the processes

Figure 1 shows a schematic presentation of the set-up of the apparatus. Its three main components are as follows: a process chamber with a volume of 40 l evacuated with diffusion pump, a source of high intensity plasma pulses and an arc cathode PVD source. The source of plasma pulses is based on a rod plasma injector type accelerator described elsewhere [5]. Briefly, the plasma pulses are gen-

erated as a result of the low-pressure high-current discharge between two concentric sets of electrodes. High voltage pulses ignite the discharge producing the plasma pulses delayed for a certain time with respect to the moment of injection of a working gas into the inter-electrode space (delay time τ_D). An energy density of plasma pulse in the 1–5 J/cm^2 range and duration in the μs scale are sufficient to raise the temperature of the near-surface layer (from a fraction to few μm) of most solid substrates up to the melting point or above. When this region is molten, a rapid inward diffusion of pulse-delivered and/or pre-deposited atoms into the liquid can occur, leading to formation of new phases, alloys or compounds. If τ_D is set long enough to allow the injected gas to expand over the whole inter-electrode space, the plasma pulse contains exclusively elements of the working gas with ion energies covering a wide spectrum from few to several keV. This mode of operation is referred to as pulse implantation doping (PID). For significantly shorter τ_D, when there is a step gradient of the gas concentration in the inter-electrode space, effective erosion of the metallic electrodes occurs. In this mode a pulse of vapour or/and low energy ions of the electrode material is produced together with the plasma pulse like in PID mode. Unlike the working gas atoms, the metal atoms do not undergo acceleration during the discharge. Having a kinetic energy in the range of tens to hundreds eV they travel much slower than the working gas ions and reach the substrate when its surface is already re-solidified (after being melted by gaseous plasma pulse) and condense on it as a thin film of thickness 10–20 nm. This film can be regarded as the "pre-deposited" one before subsequent pulse, which melts it together with top layer of the substrate and which constitutes an intermediate layer for further coating.

The typical parameters of the DPE source are as follows: energy density 3–6 J/cm^2, pulse duration about 1 μs, beam diameter 3 cm, source-substrate distance 25 cm, nitrogen or oxygen as working gas, delay time τ_D=160 and 170 μs for N_2 and O_2, respectively, outer and inner electrodes – 32 metallic rods of 2 mm in diameter and of 250 mm in length.

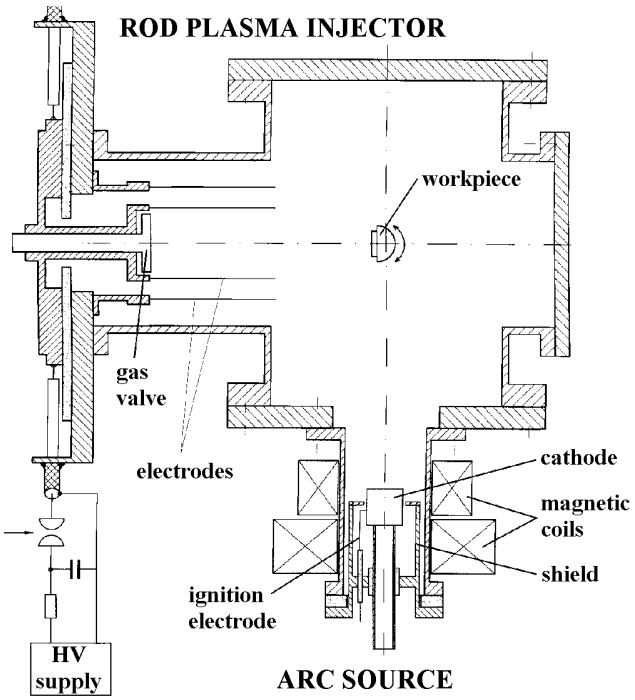

Fig. 1. Schematic cross-section of combined pulse plasma treatment and PVD deposition apparatus.

The design of arc cathode PVD source similar to that described in the rich literature e.g. [3, 8] is schematically shown in Fig. 1 also. It contains a cylindrical cathode (connected to an arc power supply), surrounded by the electrostatic shield, magnetic coils, and arc initiating electrode. The surface of the vacuum chamber serves as the anode. Both the cathode and anode are water-cooled. The supply system of the source contains three main DC supply units with parameters as follows: 100 V, 200 A – for the arc discharge; 60 V, 5 A – for the magnetic field; and 2 kV, 1 A – for the bias of the irradiated substrate. In the present construction, two magnetic coils of different functions are located side by side. The coil which surrounds the cathode supplies a magnetic field which stabilizes the arc discharge. It forms a magnetic trap on the cathode front-surface, which prevents to some extent a cathode spot escape outside the working area. Additionally, the magnetic field allows minimum current of arc stable burning to be decreased; that leads to a considerable reduction of the macro-particles emitted within the ionized vapour. The second coil supplies a magnetic field focusing the metallic plasma stream, which leads in turn to an increase of the deposition rate and to more effective use of the evaporated material. As mentioned above, a magnetic trap on the cathode surface prevents to some extent, but not fully, the spot escape from the front to cylindrical part of the cathode. Such an escape can damage the insulator. Therefore, additional electrostatic shield has been applied. A shield is on the floating potential, which extinguishes the cathode spots occasionally dropping on its surface. For initiating a vacuum arc, an electric explosion of the current-conducting film deposited on the insulator was used. The ignition unit operates as follows. High voltage pulse is applied to the additional initiating electrode in which there is a dielectric insert coated with a conductive film. The film is in an electric contact with the lateral surface of the cathode. The pulse causes evaporation of the film and creation the local plasma cloud at the surface of cathode, which is sufficient for initiation of an electric arc. In the present design of the conductive film is grown as a product of the main coating process. Figure 2 illustrates the particular phases of plasma treatment and Arc PVD process.

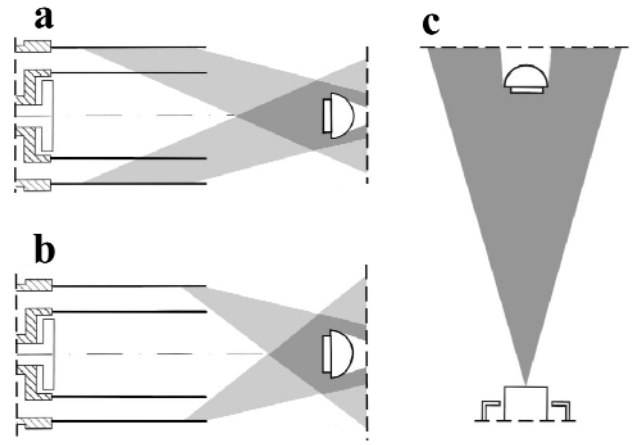

Fig. 2. Schematic illustration of consecutive phases of combined plasma treatment (a, b) and PVD deposition process (c). a – melting of the work piece surface by the plasma pulse; b – deposition of the metal eroded from the electrodes; c – arc PVD deposition.

Examples of application

Interlayer for TiN coating on tool steels

Two kinds of tool steel were subjected to coating with TiN. They were: HSS SW7M (AISI M2) and NC10 (AISI D3). After quenching and tempering to final hardness of 64HRC SW7M and 60HRC for NC10, the samples were divided into two batches A and B. The series type A was coated using the apparatus described above and for comparison the series type B was coated by a commercial manufacturer. In our experiments the coating was performed in three steps. In the first step, the samples were irradiated with 5 plasma pulses in DPE mode with titanium electrodes and pulse energy density of 3.5 J/ cm^2 without additional heating. In the next step, the samples were exposed to Ti ion sputter etching for 2 min with 500–1000 V substrate bias. Titanium ions were generated by vacuum arc process. In the third step, TiN was deposited from arc source at 0.7 Pa nitrogen pressure for 10 min. For SW7M substrate temperature was kept at 450°C whereas for NC10 the temperature was reduced to 250°C, i.e. still 30°C above the tempering temperature for this steel. Thickness of TiN coating was similar in A and B batches; it amounted 2.5–3.0 μm.

Auger profiles recorded in DPE-treated sample (without TiN) showed Ti-rich layer formed at the surface and long tail of Ti alloyed into steel substrate extending up to 200 nm in depth. Adhesion of the coating was tested using a scratch test method, in which the critical loads CL and non-uniformity NU (standard deviation of the critical load divided by the mean value of CL measured on different samples) were determined. Table 1 summarizes the obtained results. As can be seen, our process with pulse treatment produced poorer adhesion in comparison to conventional procedure applied to NC10 steel. However, both CL and NU have been significantly improved for SW7M steel. These results can be interpreted if we recall that in the former case the TiN deposition was conducted at the temperature higher than tempering temperature for NC10 so some softening of the substrate during the process could not be excluded. On the other hand, adhesion of a hard surface layer depends on the substrate hardness [6].

Table 1. Results of coating adhesion tests.

Measurement no.	Critical load CL (mN)	
	A	B
NC10		
#1	89.4	500.0
#2	149.2	226.9
#3	117.4	363.6
#4	87.9	216.8
#5	39.3	211.9
Mean value	96.6	303.8
Non-uniformity NU(%)	42	42
SW7M		
#1	256.3	88.9
#2	214.1	340.8
#3	215.1	88.7
#4	320.2	335.7
#5	212.7	104.1
Mean value	243.7	191.6
Non-uniformity NU(%)	19	70

Interlayer for ceramic/metal brazing

Obtaining a strong braze joint of ceramic-metal components requires adoption of means that induce wetting either by use of brazes that react chemically with the ceramics or by use of a coating that changes basic chemistry of the ceramics prior to brazing. Metallic coatings are usually fabricated by the PVD, CVD or powder technology. Recently, some novel approach utilizing ion beam technique to brazing alumina with metals was presented [7]. Namely, the reactive element (titanium) was implanted directly into alumina to assure its wetting by conventional copper-silver braze. The key concept of our approach is to manufacture, prior to brazing, an appropriate intermediate layer on the ceramic surface by means of DPE followed by Arc PVD processes using the apparatus described in this work. The experiments were conducted in the full cycle of assembling of a commercial diode housing, which consists of a Al_2O_3 cylinder (of outer diameter 25 mm, inner one 15 mm, and a height of 15 mm) and copper elements. Both flat surfaces of the ceramic cylinders were prepared in the three following ways without applying any pre-cleaning procedures:

(i) DPE deposition of Ti with nitrogen as the working gas using 2, 5 and 10 plasma pulses (with efficiency of about 5 μg/cm^2 pulse) followed by PVD deposition of TiN layer of about 2 μm thick.
(ii) DPE deposition of Ti with oxygen as the working gas using 5 plasma pulses followed by PVD deposition of Ti in presence of oxygen to form TiO_x layer of similar thickness as TiN in (i).
(iii) DPE deposition of Ti as in (ii) followed by PVD deposition of Ti in vacuum of 2×10^{-3} Pa (1.5×10^{-5} Tr).

The brazing of such surfaces to copper was conducted using AgCu19.5Ti3In5 (commercial Degus symbol CB1) reactive braze alloy and AgCu28 non-reactive eutectic alloy for (i) treated surfaces and only AgCu28 for (ii) and (iii) samples. After completing the brazing procedures in the thermal cycles pertinent to these alloys, two parameters of the joints were tested: vacuum tightness and ultimate tensile strength (UTS). The results obtained for (i) treatment were published in [9], whereas only preliminary results are available for (ii) and (iii) samples.

The main results can be summarized as follows. For (i), the ceramic surfaces were non-wettable by non-reactive alloy. For reactive CB1, all joints passed the routine vacuum seal tests, i.e. the leak rate (LR) did not exceed 1.3×10^{-6} Pa $dcm^3\ s^{-1}$ and mean values of UTS for 25 samples amounted to 95.6 MPa. This UTS value is to be compared to 90 MPa obtained in conventional powder process of preparation of alumina surfaces for brazing with non-reactive filler and 87.6 MPa for brazing with CB1 reactive alloy without additional preparation of the ceramic surface. In both cases (ii) and (iii) the ceramic surfaces are well wettable with non-reactive AgCu28 alloy. However, the vacuum tightness and tensile strength are largely dispersed from very good (UTS=92 MPa, LR$<1.3\times10^{-6}$ Pa $dcm^3\ s^{-1}$) to very poor (UTS=3 MPa, LR$>10^{-3}$ Pa $dcm^3\ s^{-1}$). It means those good joints with (ii) and (iii) treatments are feasible but further work has to be done to optimize the process conditions. The experiments aimed at this task are in progress. It is believed that due to their simplicity, after refinement the processes (i) and (ii) may appear competitive to the conventional

time- and energy-consuming powder metallization processes being at present commonly used in the ceramic--metal bonding technology.

Summary

Feasibility of an intermediate layer on a metallic and ceramic surface followed by the formation of various (e.g. TiN, TO_x) coatings in the same processing chamber is demonstrated. The most characteristic feature of such an approach is that an intermediate layer is alloyed in the conditions in which the top layer of the surface is in the molten state. It is also important for potential practical applications that the process inherently obviates the need for tedious and time consuming cleaning of the substrate surface.

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