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Specific sintering by temperature impulses as a mechanism of formation of a TiN layer in the reactive pulse plasma

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A layer of separate TiN particles was fabricated and temperature pulsed in order to determine whether the short lasting intense heat of the deposited clusters can lead to their sintering. It was found that a specific sintering process is inseparably involved in the process of crystallization of the layer from the pulse plasma. The pulse heating also causes an increase in the adhesion of the layer to the substrate.

1. Introduction

For several years the pulse plasma has been satisfactorily used to obtain layers of high-melting materials [1]. As in the case of all impulse effects, the pulse plasma is of high power and is a source of temperature, light and electromagnetic fields. Thus, at high power impulses, some periodic processes can be expected both in the medium of plasma propagation and on the substrate the plasma is acting on.

It has been established [2] that the TiN layer in the reactive pulse plasma is formed of the clusters and ions formed already in the plasma itself. The layer is formed on the substrate being heated exclusively by plasma up to the maximum temperature of 500 K. In the process of the layer growth it seems difficult to explain the association of the deposited clusters by means of coagulation or sintering at such a low temperature as 500 K.

The aim of this paper was to determine whether the short-lasting intense heating of the deposited clusters can lead to their sintering. The experiment was composed of two stages. The first one consisted of the obtaining of a layer of separate TiN particles (a "powder layer"). In the second stage, this "powder layer" underwent the impulses of temperature simulating exactly the conditions of the layer's crystallization process.

2. Methods

2.1. "Powder layer" formation

The TiN "powder layer" for investigation was deposited using the reactive pulse plasma method. In this case, titanium was used as the central electrode in the coaxial plasma accelerator, which, being due to electroerosion, served as a source of material for the plasmo-chemical reaction. Nitrogen was used as the reactive gas. The substrate was placed at an appropriate distance from the source of the plasma (the accelerator) and thus the influence of the plasma temperature field was reduced and the TiN powder was obtained on the substrate.

Two kinds of layers were prepared for examinations: thick ones, of thickness of an order of 1.5 μm, were deposited on the carbon steel substrate (0.45% C); and thin ones, of thickness up to 100 nm, were deposited on the amorphous carbon films. The carbon films were evaporated on a freshly cleaved NaCl single crystal. The conditions of the "powder layer" deposition are presented in Table I, column A.

2.2. Generation of the impulses of temperature

In order to generate the impulse temperature field on the substrate with the deposited "powder layer" again the pulse plasma method was used. The apparatus for the generation of the temperature impulses is schematically depicted in Fig. 1. Plasma is generated as a result of the electric discharge of the battery of capacitors, C, in the coaxial accelerator. The period of

TABLE I The conditions of powder layer deposition (A); and generation of the argon plasma packet (B)

	A	B
Distance of the sample from accelerator (cm)	30	8
Hot internal electrode	Ti	Ta
Atmosphere	N_2	Ar
Pressure (Pa)	130	20
Electric discharge voltage (kV)	3.5	4
Electric discharge energy (J)	2600 1100	1600
Repetition frequency of the temperature impulses	0.25	0.25
Number of electric discharges:		
steel substrate	1800	1240
amorphous carbon substrate	15	100

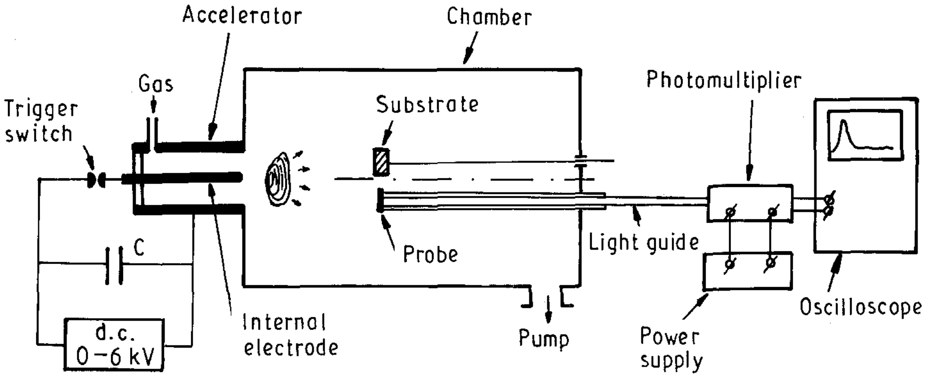

Figure 1 Scheme of the apparatus for the impulse heating of the "powder layer" sample and for the measurement of the probe temperature.

discharge of the capacitors between the electrodes in the coaxial plasma generator does not exceed 250 μs. Owing to the electrodynamic force, the plasma packet is expelled from the accelerator at a high velocity of the order of 10^4 km s^{-1} [3]. If a sample is placed on the path of plasma propagation at a suitable distance, then its surface becomes heated. During plasma generation the central (hot) electrode in the accelerator can undergo electroerosion and the electrode material may be transferred onto the layer and disturb observation of the results. In order to minimize this effect, a tantallum electrode highly resistant to erosion and the non-reactive argonum were used in the accelerator. Moreover, the substrate was not placed opposite the central electrode (Fig. 1). The "powder layer", prepared as described, was pulse-heated. The parameters of the generation of the argonum plasma packet are listed in Table I, column B.

The morphology and microstructure of the thin films prior to and after the pulse heating were examined using a Jeol 100B transmission electron microscope (TEM). Samples for TEM observations were prepared in the following way: the carbon thin film with the TiN layer was removed in distilled water from the NaCl crystal. The morphology of the thick layers was observed using a TESLA scanning electron microscope (SEM). Adhesion of the layers was examined by the scratch method, using a diamond pyramid of a 120° angle and 40 μm radius of tip.

2.3. Measurement of temperature impulse

Thermodynamic temperature is a parameter characterizing the thermodynamic state of the plasma. This temperature was indirectly determined by pyrometric measurement of the temperature of the probe being affected by the impulse of plasma packet [4]. The system for the measurement of the probe temperature is schematically depicted in Fig. 1. The idea of this measurement is as follows: The probe, being placed in the way of plasma propagation, is heated as a result of absorption of energy of the impulse plasma packet. The hot probe becomes a source of electromagnetic radiation. The light emitted by the probe is then guided by the quartz light-pipe to the photomultiplier and the current changes are observed on the oscilloscope. A molybdenum sample, heated in a vacuum resistance furnace with controlled temperature, was used as the reference source of light emission. In order to determine the intensity of light emitted by the probe and the reference source, the output voltage at the photomultiplier was measured. Using the linear part of the dependence of the output voltage at the photomultiplier on the light intensity, the ratio of the output voltage for the reference source to that of the probe was taken as a measure of the impulse of temperature.

The probe used for determination of the impulse temperature was of low thermal capacity. It was made of the molybdenum foil 0.05 mm thick and 5 mm diameter. Molybdenum was chosen due to its high thermal conductivity and high melting temperature and also because it is non-transparent in the range of the spectral sensitivity of the photodetector. The photomultiplier with an AgOCs photocathode (MF12 F35-type) with spectral sensitivity in the range 300–1100 nm was used for detection.

3. Results

3.1. Temperature of the sample (powder layer)

The changes in temperature of the molybdenum probe heated by the plasma packet during one pulse are presented in Fig. 2. The maximum temperature, T_{max} (i.e. the highest temperature recorded in the conditions of the impulse heating) was about 2075 K. The lower limit of the measured temperature (800 K) results from the limit of light detection ⩾ 2 μm.

It can be assumed, in the case of the pulse heating of the substrates covered with a powder layer, that the temperature of the substrate surface for a time shorter than 1 ms is not lower than the probe temperature. Thus the TiN powder on the substrate should be

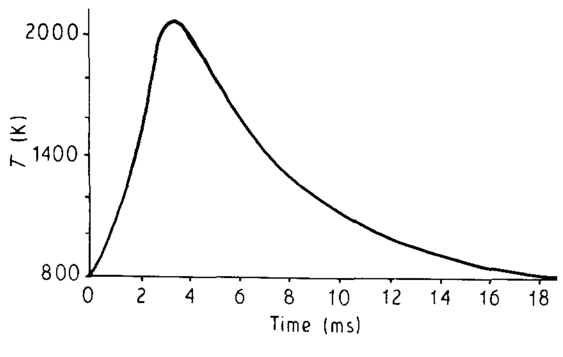

Figure 2 Changes in the temperature of the molybdenum probe during the single plasma impulse.

pulse-heated at last to the temperature 2075 K for 1 ms, at a frequency of 0.25 Hz. The averaged temperature of the substrate heated by several hundred pulses, measured inside the substrate using a Ni–NiCr thermocouple does not exceed 500 K [4].

3.2. Powder layer not being pulse heated

The thick powder layer on the steel substrate, prior to heating in the impulse temperature field, consists of loosely distributed grains spherical in shape, of grain size ranging from 0.2–2 μm. The grains are separated one from another by 0.3 μm wide channels. A SEM image of the layer is presented in Fig. 3a.

The adhesion of the "powder layer" to the steel substrate is equal to 0.3 N. The thin films obtained on the amorphous carbon film are ultra-fine crystalline (7 nm on average) compact, with a small amount of larger grains. A TEM image of the film is presented in Fig. 4a.

3.3. Powder layer being heated

The powder layer under the effect of the impulse temperature field (at the conditions as given in Table I) changes its structure considerably. Morphologically, a thick layer consists of large compact regions, involving, however, some pores and micro-cracks. Regions where earlier the individual grains were observed, after the pulse heating, become joined with each other. The shape of the grains and their size (not exceeding 3 μm) indicate that during the pulse heating the particles forming the layer are growing. The micro-cracks in the layer may be caused by thermal shocks within the layer itself as well as at the layer–substrate interface. A SEM image of the layer after pulse heating is presented in Fig. 3b. After pulse heating, the adhesion of the layer to the steel substrate increased to 3 N.

As a result of pulse heating, the thin layers deposited on the amorphous carbon film became transformed into a set of small islands 50 nm in size and of thickness bigger than that of the layer not being

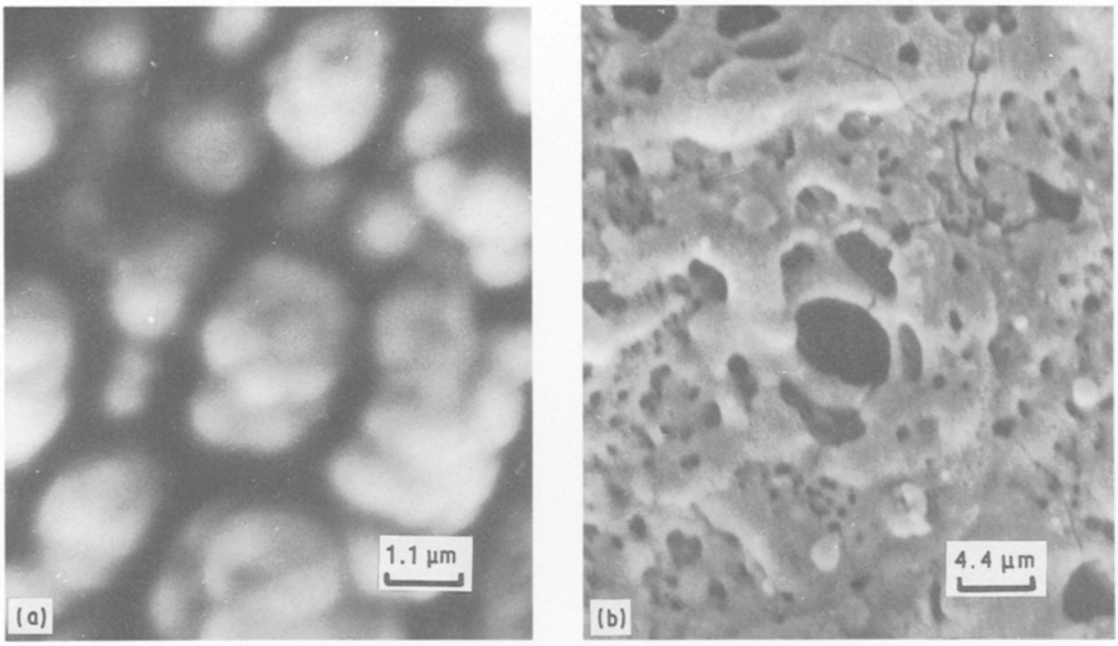

Figure 3 Morphology of surface of TiN "powder layer" (a) prior to and (b) after being under the effect of impulses of the temperature field of pulse plasma (SEM).

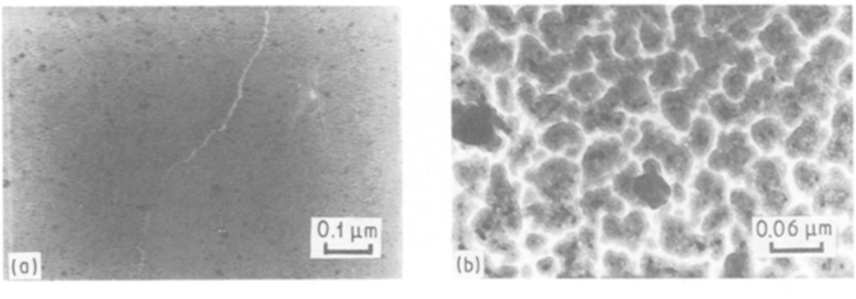

Figure 4 TEM image and electron diffraction of TiN "powder layer" (a) prior to and (b) after effect of impulses of the temperature field of plasma.

heated. Changes in the electron diffraction pattern also indicate the growth of crystallites. A TEM image is presented in Fig. 4b.

4. Conclusion

During the pulse heating of TiN layers in plasma, the process of cluster growth and the formation of the necks specific to the sintering process can be observed. Thus it seems that, in the process of the pulse heating of the TiN "powder layer", a specific sintering process proceeds, leading to the formation of a compact layer.

The pulse heating also causes an increase in adhesion of the layer to the substrate.

It can be concluded that a specific sintering process is inseparably involved in the process of crystallization of the layer from the pulse plasma, while the ions and clusters become condensed on the substrate.

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