Impulse Plasma In Surface Engineering - a review

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Abstract. The article describes the view of the plasma surface engineering, assuming the role of non-thermal energy effects in the synthesis of materials and coatings deposition. In the following study it was underlined that the vapor excitation through the application of an electric field during coatings deposition gives new possibilities for coatings formation. As an example the IPD method was chosen. During the IPD (Impulse Plasma Deposition) the impulse plasma is generated in the coaxial accelerator by strong periodic electrical pulses. The impulse plasma is distributed in the form of energetic plasma pockets. Due to the almost completely ionization of gas, the nucleation of new phases takes place on ions directly in the plasma itself. As a result the coatings of metastable materials with nano-amorphous structure and excellent adhesion to the non-heated intentionally substrates could be deposited. Recently the novel way of impulse plasma generation during the coatings deposition was proposed and developed by our group. An efficient tool for plasma process control, the plasma forming gas injection to the interelectrode space was used. Periodic changing the gas pressure results in increasing both the degree of dispersion and the dynamics of the plasma pulses. The advantage of the new technique in deposition of coatings with exceptionally good properties has been demonstrated in the industrial scale not only in the case of the IPD method but also in the case of very well known magnetron sputtering method.

1. The role of electric energy in nonconventional synthesis of materials

The use of plasma in vapour deposition methods of surface engineering is a consequence of the efforts to increase the efficiency of the process. This approach concerns a typical technological aspect of the process (for example, obtaining vapours from a solid phase through the use of an arc discharge instead of thermal evaporation or the possibility of sputtering dielectric targets by applying rf power).

Another tendency seems to be even more important: Application of plasma is providing new possibilities of influencing material parameters, such as morphology (e.g., achieving a greater dispersion of the crystallites, or “designing” the mixing zone at the interfacial boundary) or to form metastable phases such as DLC, c-BN etc. even in a relatively low temperature of the substrate.
The role of the particle energy during the formation of film morphology together with the substrate temperature is reflected in the well known film morphology models of Movchan-Demchishin (M-D) [1], Thornton [2], Messier [3] or Anders [4]. An underlining assumption of these models was to generalize the relationship between energy conditions of layer synthesis and the morphology of these layers, especially in view of the possibility to obtain fine crystalline structures instead of columnar structure.

In this context attention should be paid to the replacement of the pressure effect in the Thornton model by kinetic energy of particles in Messier and Anders models. The M-D model refers to the thermal evaporation and does not consider the role of pressure in the creating the morphology of the layers, while the Thornton model refers to magnetron sputtering when the gas under the pressure of about $10^0$-10$^1$ Pa plays a crucial role. However, the pressure in the second model represents a measure of the nonthermal kinetic energy of the vapour phase particles. In this way, the linear M-D model with the layer structure dependent solely on the temperature is transformed into the Thornton model in which the film structure is described in a two-dimensional space (T, p), reflecting thereby the dependence of the structure on the gas phase particles (plasma) kinetic energy.

The role of the plasma in the development of the phase composition of a layer material in surface engineering with gaseous methods is vividly reflected by spectacular example of the DLC layers synthesis. It seems that the importance of the electric energy in the synthesis of carbon-linked sp$^3$ hybridization is not in doubt. This problem was launched with the publication of Aisenberg and Chabot [5]. It is interesting that in the cited work the authors restricted themselves to the kinetic energy obtained by the ionized atoms during their acceleration by the electric field, and the interaction of these ions with the substrate where nucleation of a "diamond" carbon phase occurred.

A different and original view of the DLC synthesis has been expressed by Sokolowski and Sokolowska [6,7]. These authors substantiated the formation of sp$^3$ bonding by carbon phase nucleation on plasma ions. The essential potential energy is supplied to the nuclei of this stage as a result of inelastic collisions with electrons. The role of the potential energy seized from the electric field applied in the nucleation zone has been demonstrated for example in [8] and [9] for the synthesis of an aluminium oxide and boron nitride, respectively. In this second paper taking the electric field into account it was explicitly proposed to define something like a new state parameter related to the potential energy of the plasma particles which, along with pressure and temperature determines the phase composition of the BN layers.

2. IPD – Impulse Plasma Deposition method

In the 1980’s in the Faculty of Materials Science of Warsaw University of Technology the Impulse Plasma Deposition (IPD) method has been proposed. This method has no counterpart among other contemporary methods of surface engineering. As already mentioned above, it is based on the assumption that homogeneous nucleation takes place on plasma ions which have been formed by inelastic collisions with electrons.

The use of pulse plasma generated in a coaxial accelerator during short discharge in gas under reduced pressure is most favourable to activate this mechanism. Such conditions were created due to discharge of the capacitor with a capacity of the order of $10^{-4}$ F, cyclically loaded to a voltage of $10^3$ V with a preset frequency of $10^1$-$10^6$ Hz, when peak current value reaches the order of $10^4$ A.

The lifetime of the resulting plasma is of the order of $10^{-4}$ s. Plasma is emitted from the coaxial accelerator in the form of a plasmoid, which is accelerated by the magnetic pressure to speeds of about $10^5$ m/s. During the interaction of the plasmoid with the unheated surface of the substrate a short (of the order $10^{-3}$ s) thermal pulse with a peak temperature of about 2000 K [10] acts on the substrate surface. This heat is dissipated in the substrate material with a velocity in the order of $10^6$ Ks$^{-1}$ which is determined by the thermal conductivity of the substrate. In addition to the thermal effect the
plasmoid interaction with the substrate surface causes subplantation of plasma constituents, which favours the formation of the mixing zone at the interface.

The essential application-related features of the pulse plasma generated in the manner described above were connected with nearly complete ionization and thermodynamic nonequilibrium [11,12]. In such plasma, the probability of inelastic electron collision with the heavier plasma components, including the formation of critical nuclei in the plasma, is particularly high and therefore efficiency of energy exchange between the plasma and the condensed phase formed in plasma is also high.

It should be noted that in the impulse plasma generated during capacitor discharge (as a source of electrical energy) it is possible to induce discharges at voltages which are significantly lower than those described by the Paschen curve [13]. In this way a particularly large amount of energy can be supplied in a relatively easy way and, hence, the internal energy of the gas environment increased to an extent which is impossible to reach by other means. As a result, the mechanism of IPD layer synthesis comprises the following specific elementary phenomena [14]:

1. Generation of practically completely ionized nonequilibrium plasma by high-energy pulse discharge in gas under reduced pressure,
2. Acceleration of the plasmoid with magnetic pressure thus increasing the kinetic energy of the plasma,
3. Nucleation in plasma on ions,
4. Dynamic interaction of the plasmoid with the surface of the unheated substrate, leading to a strong thermal activation of the surface and to subplantation,
5. A cluster growth mechanism, consisting of a limited coalescence of nanoaggregates.

IPD method, although it is still somewhat a niche technique in plasma surface engineering, has demonstrated however its applicability in the synthesis of layers composed of such materials like DLC [15, 16], c-BN [9], Al₂O₃ [8] as well as of multi-component metallic alloys of MCr Al(Y)-type [16]. Industrial use of IPD method for depositing TiN layers on cutting tools in one of the largest Polish machinery works [18] was a spectacular illustration of technique potential. One should keep in mind that, according to our knowledge, this is the only method of plasma surface engineering which allows to obtain nanocrystalline wear resistant layers on unheated and unbiased substrates.

Recently a similar kind of pulse plasma generation was also used in magnetron sputtering technology [19 - 21], namely in form of HIPMS (High-Power Impulse Magnetron Sputtering). It is worth to underline that the essential features of the HIPIMS process, i.e. inducing the gas discharge under reduced pressure, using the capacitor as the source of energy, as well as taking the advantages of high degree of plasma ionization and its nonequilibrium state are similar to the assumptions of the IPD method. The practical achievements of the HIPMS technology application are connected first of all with a significant reduction of substrates temperature and a dramatic improvement of the morphology of the deposited layers, in particular the reduction of the tendency of structure columnarization.

3. Gas injection as a tool of control of plasma process during the coatings deposition

In 2011, Zdunek et al. [22] proposed a novel variant of plasma surface engineering processes, namely to control the plasma process through the use of pulse variable concentration of the working gas. The pressure of the gas injected with a pulse-valve having a low mechanical inertia cyclically oscillated between a value of the order of 10⁻⁴-10⁻⁵ Pa and a value of the order of 10⁻¹-10⁻² Pa.

Work in this regime allows preventing or triggering the electrical discharge in the gas. This idea has been practically proved in the IPD accelerator, previously equipped with continuous dosing of the working gas (standard IPD).

The following assumption was applied. Operating a valve with the opening time of the order
of $10^3$ s and a frequency of the order of $10^4$ Hz (highly dependent on the pumping system efficiency relation to the volume of the vacuum chamber) leads to the generation of plasma in the coaxial accelerator during the time of pressure rise in the interelectrode space. Since the plasma generation takes place during the pressure increase, the rise of injected gas mass is followed by the current value increase due to the growing concentration of the gas undergoing ionisation. This synchronization should result in strong differentiation of the plasmoid velocities at different stages of its development, thus promoting a greater degree of plasma nonequilibrium in the IPD method. As before valve opening the mean free path of the gas particles many times exceeds the linear dimensions of the vacuum chamber (for a pressure of $10^{-4}$ Pa the mean free path is of the order of $10^1$ m) the plasmoid accelerated with magnetic pressure does not collide with the cold gas in the vacuum chamber volume after leaving the interelectrode space. This and the lower average gas density of the plasmoid in comparison to that generated under continuous gas dosing should favour reducing the dissipation of the kinetic energy of plasma particles during collisions.

This probably reduces the tendency to aggregate nuclei by plasma ion nucleation in comparison to the standard IPD process. As a result, in the ion flux hitting the substrate surface the portion of atomic ions increases and that of cluster ions decreases. Consequently, the whole layer growth mechanism is changed in such a manner that atomic mechanism play a larger role and nuclei formation also on the substrate surface takes place.

The research hypothesis presented above has been verified during subsequent studies. Already published results show that:

- A large increase of TiN coated SW7M HSS tool life, reaching up to 1600% [23], was observed.
- Morphologically, the TiN layer represents a nanograin structure, in contrast to nanoglobular structure in the standard IPD [23].

Unpublished research so far carried out proves that:

- The electron temperature of the plasmoid spreading in a vacuum chamber reaches 10 eV at the substrate (Langmuir probe, computer simulations).
- The plasmoid is almost completely ionized (OES).
- Multiple ionized titanium and nitrogen are present within plasmoid (OES).
- At the surface of the iron substrate influenced by the plasmoid exited atoms of iron are observed (OES). We conclude from this that intensive sputtering and/or evaporation of iron from this surface takes place.
- In the interfacial zone a considerable enrichment of the substrate with the titanium is observed (HRTEM, SIMS).
- Locally the increase of the TiN layer has explicit hetero epitaxial character (HRTEM)
- Adhesion of the TiN layers to the SWAM steel substrate is very good, corresponding to a critical load of 80-100 N (scratch test method).

The use of the mode described above during magnetron sputtering process could be an interesting example of pulse gas concept application in the plasma surface engineering. In [22] preliminary results are presented for the synthesis of AlN layers using this solution (GIMS - Gas Injection Magnetron Sputtering). As a result of pulsed dosing of the working gas, the AlN layers on the surface of monocrystalline silicon substrates do not exhibit a characteristic columnar structure. The growth rate of the layers, however, was decreased by a factor of three compared to the process with continuous dosing of gas.

Technical usability of GIMS was extremely positively verified in industrial conditions. The GIMS
concept was used in a multimagnetron facility for the deposition of Ti and TiO$_2$ layers on large-size unheated windows of 2000x3000 mm, utilizing linear magnetrons with the length of 2200 mm. The Ti layers obtained were distinguished by a much better adhesion (qualitatively tested using adhesive tape) than layers produced with continuous dosing of the working gas. A spectacular result was obtained in the case of TiO$_2$ layers produced on ceramic unheated tiles. Abrasion studies of the tile surface coated with TiO$_2$ proved class II abrasion resistance, enabling the use of coated tiles for lightly loaded floors (e.g. in operating rooms).

4. Conclusions

Non-thermal energy can be utilised in gaseous surface engineering methods as a specific substitute of thermal energy. The synergy of both types of energy in the synthesis of layers is evident and creates new possibilities for control of the process synthesis. Non-thermal energy of the particles is created by the application of electric power in plasma surface engineering. Two cases have to be discriminated, one is associated with the kinetic energy of the particles, the other with their potential energy as represented by ionisation of excitation of particles. The latter aspect seems to be significant because of providing impact on the solid phase composition of the synthesis products occurring in the plasma itself. As a result, it is possible to nucleate condensed phases in the plasma which is otherwise characterized by high barriers of nucleation.

The recently introduced innovative mode of process control in the plasma surface engineering methods through the use of dynamically changing pressure of working gas opens new perspectives in the development of these methods. It seems that the use of this mode allows to increase the efficiency of electric energy transfer to the gas source, which leads for example to an increase in the ionization degree or the electron temperature in comparison to a plasma generated under the same conditions but with continuous dosing of the working gas. Probably the kinetic energy dissipation by collisions of plasma particles decreases, which positively affected the status of layer/substrate interface. This yields better application properties of the layers.

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