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Field electron emitters made of plasma sprayed layers

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An alternative to the Spindt-type cold cathodes are the layered ones made of composite materials. The classical example are nanostructured diamond and diamond-like carbon (DLC) layers which can be very good emitters. Nanostructured diamond and DLC layers are composed of two clearly distinguishable phases: the boundaries of the diamond nanocrystals or graphite in DLC are electrically conductive, while the bulk of the diamond is a dielectric. This overview deals with various composites made with several kinds of plasma spraying techniques and tested as the cold electron emitters. Following composites were made by the atmosphere plasma spraying (APS): Cr_2O_3 (additionally laser engraved and coated with Ti layer), Al_2O_3 + 13 wt% TiO_2, Al_2O_3 + 40 wt% TiO_2 and TiO_2 (additionally laser engraved), Cr_2C_3–NiCr and Cr_2C_3–NiCrAlY. Deposited with the suspension plasma spray (SPS) were titania coatings. Layers of ZrB_2 and ZnO + 3 wt% Al_2O_3 were deposited with controlled atmosphere plasma spray (CAPS). The parameters of these cathodes are comparable with DLC ones. One of the cathodes was successfully used in a prototype light source.

Keywords: field electron emitters, plasma spraying, composite materials.

1. Introduction

Thin film field emitters, invented by Charles A. Spindt in the sixties of the last century, made possible the construction of microdevices with free electron flow [1]. In spite of their dimensions, these emitters could be integrated with classical integrated circuits [2, 3]. From the very beginning it was expected that they could be used as electron sources in flat displays (field emission display, FED) and substitute thermocathodes in electron tubes [4, 5]. Financial perspectives of these FED mass production and of breaking technological limits in the electronics of highest frequencies (especially for military applications) gave a great impulse stimulating the growth of vacuum microelectronics. These expectations have been cooled by very complicated techniques of the Spindt emitters and the tremendous development of liquid crystal and plasma displays. Such situation forced a search for more simple solutions of the field emitters production. Composite emitters and quasi one dimensional structures (quasi 1-D) seem to be particularly interesting. The most popular composite cathodes are diamond-like carbon (DLC) emitters and cathodes made of nanocrystalline

diamond. The most known 1-D emitters are carbon nanotubes [6]. Composite field emitters are layers containing two, electrically different material phases. The bead consists of dielectric or poorly conducting phase and is mixed with the conducting or semiconducting phase. For good emission properties, the conducting phases should form structures with nanometer dimensions and should be dense enough to form conducting paths under the electric field penetrating the layer [7]. In the DLC cathodes there are conducting paths in the surfaces of nanocrystals, where the conducting paths are due to the defects creating surface states or graphite inclusions [8, 9]. In the DLC layers, the conducting paths are graphite phases [6, 10]. The nanostructured 1-D emitters show very high field enhancement factors of several thousands due to their proportions. This results in very low electric field threshold values, some several V/μm [6, 11], which makes possible the application of such techniques like screen printing, ink-jet deposition or spraying of liquid suspension [6, 11–13].

The author has been involved for some time in the investigation of field emitters deposited by the atmosphere plasma spraying (APS). This technique is well known in mechanical and chemical industries where it is used for deposition of protective or decorative layers as well as special tribological ones [14]. The principle of APS technique is shown in Fig. 1.

From the plasma source (usually Ar + H_2) the stream is directed onto the substrate to be covered. The material to be deposited, usually in the form of powder (Fig. 2), is

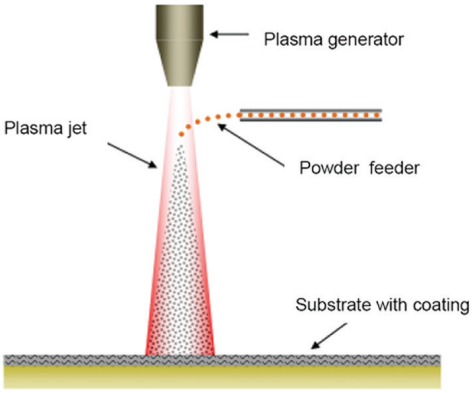

Fig. 1. The principle of plasma deposition of layers.

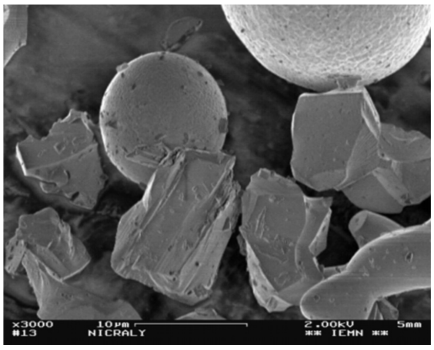

Fig. 2. The mixture of Cr_3C_2 NiCrAlY powders: Cr_3C_2 microchips and NiCrAlY microspheres.

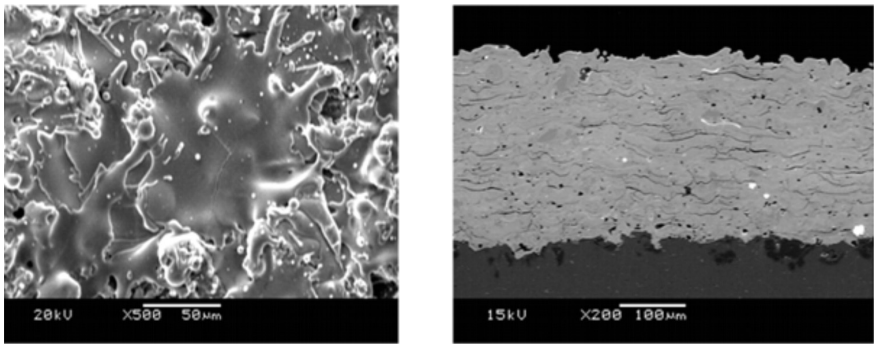

Fig. 3. Splats and cross-section of Cr_3C_2–NiCr layer deposited with APS.

introduced into the plasma stream. The powder is injected by means of a special feeder and the powder's particles are melted in the plasma stream. The deposited layer consists of microdroplets solidified on the substrate. The thermodynamic processes in plasma and on the covered surface influence the layer properties. The APS layers show micropores, microcracks and so-called lamellar structure, which results from the deposition of flat pancake-like forms (splats) (Fig. 3). As a rule, properties of these deposited layers are different from those of initial materials. Typically, thickness of such layers varies from hundred to several hundred micrometers.

2. Experimental results

Several kinds of layers, deposited with various atmospheric plasma spraying methods (APS, SPS and CAPS), were investigated. Some of these layers were additionally laser engraved using anilox rolls techniques, employed for preparation of the surface of paint transporting cylinders in printing machines [14]. Such honeycomb pattern increased the electric field enhancement factor β. The field enhancement factor may be calculated from the engraving profile: its depth H, and curvature radius R of the ridge between adjacent cells: $\beta \sim H/R \sim 4$ (Fig. 4).

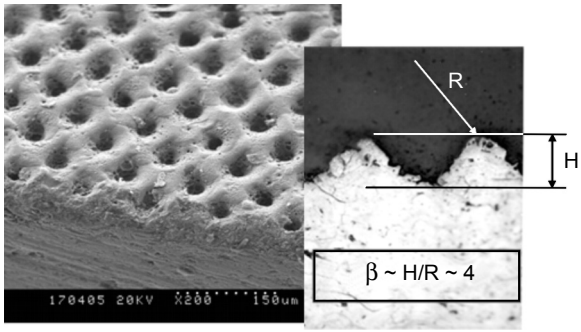

Fig. 4. Laser engraved Cr_2O_3 layer and its cross-section.

2.1. Cr_2O_3 layers APS deposited, laser engraved and covered with Ti

The chromium oxide still showed its insulating properties after plasma spraying, thus it could not be an electron emitter. Therefore the chromium oxide layer was additionally covered with 1 μm titanium layer. So prepared structures appeared to be good electron emitters [15]. From the emission measurements it appeared that the field enhancement factors were about 150 and substantially exceeded the calculated value $\beta_{engr} \approx 4$. A close examination of STM pictures revealed the presence of well developed chromium oxide microcrystals (Fig. 5). The edges and peaks of these microcrystals caused an additional field enhancement $\beta_{crystals}$ with its value estimated to be ~35.

2.2. APS layers: TiO_2, Al_2O_3 + 13 wt% TiO_2 and Al_2O_3 + 40 wt% TiO_2: additionally laser engraved

APS layers: TiO_2, Al_2O_3 + 13 wt% TiO_2: additionally laser engraved are good field emitters in spite of the fact that pure initial materials should be dielectric. Microphotographs of such structures and their emission characteristics are shown in Figs. 6 and 7, respectively [16].

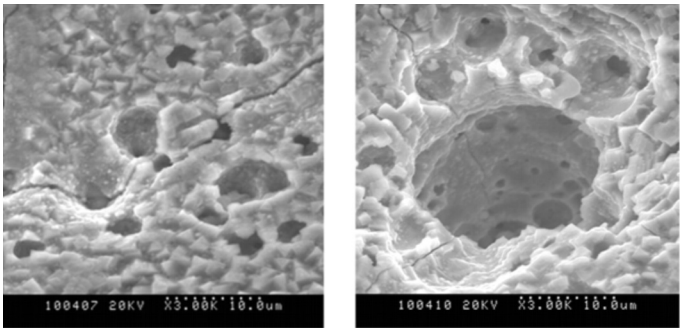

Fig. 5. The SEM picture of APS Cr_2O_3 layer laser engraved.

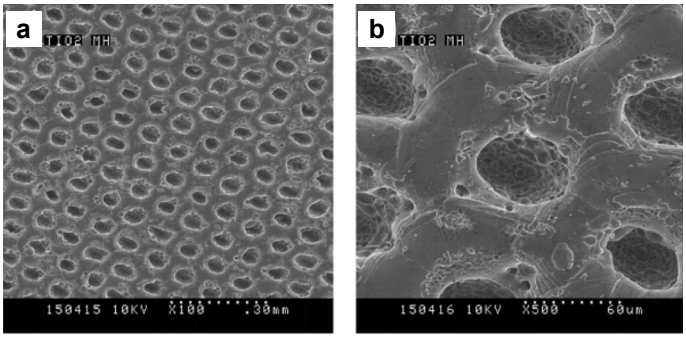

Fig. 6. SEM microphotographs of APS produced emitters. TiO_2 laser engraved with 0.1 mm of the cell density. Overall view (**a**), the cell vicinity (**b**).

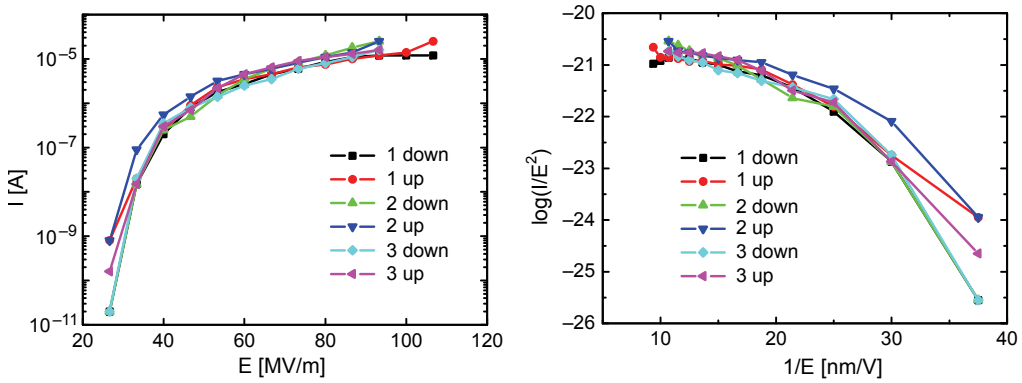

Fig. 7. Emission characteristics and Fowler–Nordheim plots of laser engraved APS layers of Al_2O_3 + 13 wt% TiO_2.

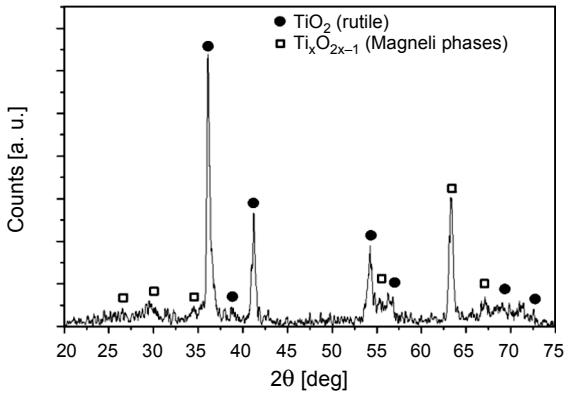

Fig. 8. XRD analysis of APS TiO_2 layer. The Ti_xO_{2x-1} suboxides (Mangeli phases) are visible.

XRD structural analysis of TiO_2 APS deposited showed the presence of titanium suboxides (Magneli phases) which are good conductors and make electron field emission possible (Fig. 8) [17].

The field enhancement factor was also larger than that calculated from the cross--section dimensions (Fig. 4). AFM examination showed the existence of micrometer inclusions on the melted area (Fig. 9). It is possible that these inclusions brought an additional component into the field enhancement factor.

In the case of Al_2O_3 + 40 wt% TiO_2 in spite of the presence of the traces of Magneli phases, and the surface relief similar to that of TiO_2 (Fig. 10), the field electron emission was very poor or none. XRD analysis showed the increased amount of Al_2TiO_5 spinel phase in the laser melted area (Fig. 11) [17].

The investigation of the charge transport mechanism in the APS Al_2O_3 + 40 wt% TiO_2 layer with the impedance spectroscopy method, indicated that the presence of the Al_2TiO_5 spinel phase makes the electron emission impossible [18].

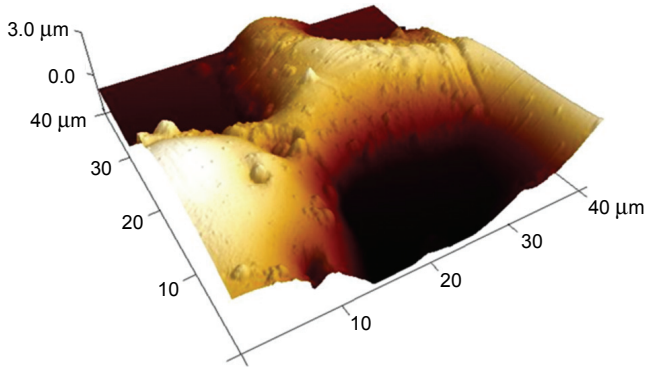

Fig. 9. AFM picture of the surface between two adjacent cells in the APS TiO_2 layer. Visible intrusions on the surface probably responsible for the increase in the field enhancement factor.

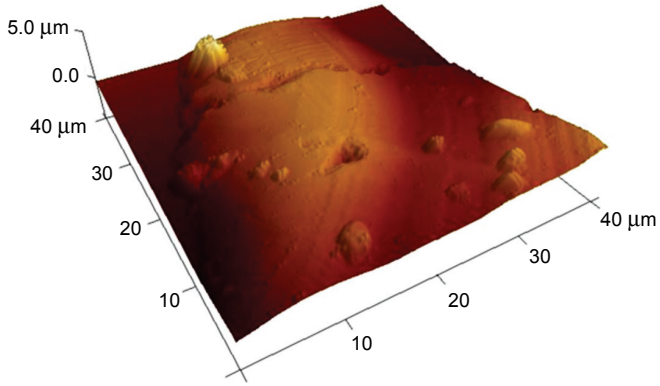

Fig. 10. AFM picture of the surface between two adjacent cells in the APS Al_2O_3 + 40 wt% TiO_2 layer.

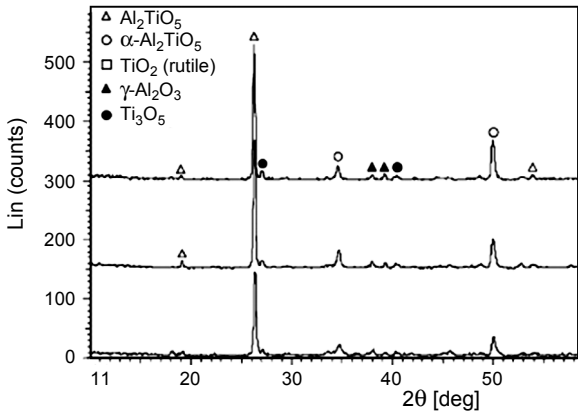

Fig. 11. XRD spectra of the Al_2O_3 + 40 wt% TiO_2 coatings after laser engraving with line densities of 200 lines/cm (top), 100 lines/cm (middle) and 60 lines/cm (bottom).

During investigations of the field electron emission from the APS cathodes, the unusual influence of temperature on emission properties has also been noticed. The increase in the temperature of composites containing TiO_2 caused a decrease in electron emission. It has been explained as the effect of the electrical permittivity ε_{TiO2} with the temperature rise. The permittivity increase caused a decrease in the electric field inside the layer and thus a decrease in the field enhancement factor [19–21].

2.3. TiO_2 layers deposited with APS and SPS

Good properties of APS deposited TiO_2 caused the extension of investigations of this material. A new APS technique with the initial powder applied as liquid suspension has been used. Figure 12 shows SEM microphotographs of TiO_2 SPS layers.

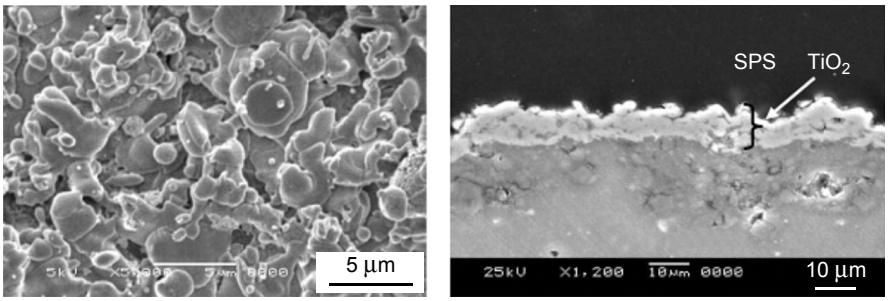

Fig. 12. Splats and the cross-section of SPS TiO_2 layer.

The splats were much smaller as compared with the APS ones. The thinnest possible layers were also thinner than those of APS. The emission properties were as good as the laser engraved APS ones. The XRD spectra reveals that the Magneli phases were also present. It should be pointed out that no laser engraving was applied to these layers [19].

2.4. APS layers: Cr_2C_3–NiCr and Cr_2C_3–NiCrAlY

Carbides are considered as prospective field emitters working in heavy conditions and high currents because of their thermal resistance and chemical inertness. APS layers of Cr_2C_3–NiCr and Cr_2C_3–NiCrAlY were not mechanically stable in high emission current conditions because of mismatching of thermal expansion coefficients between the carbide crystals and alloy matrix [22].

2.5. ZrB_2 and ZnO + 3 wt% Al_2O_3 layers deposited with CAPS

One of APS techniques is the controlled atmosphere plasma spray. ZrB_2 and ZnO + 3 wt% Al_2O_3 layers obtained with this method show a fine grain structure (Fig. 13) and very good adhesion to ceramic substrates. The emission properties of these layers were comparable with the properties of TiO_2 and Al_2O_3 + TiO_2. This

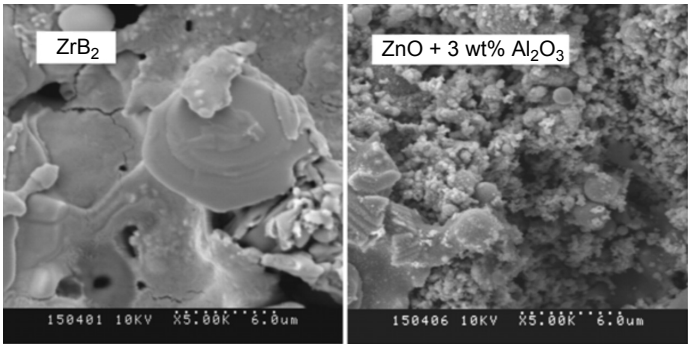

Fig. 13. SEM micrographs of the CAPS ZrB_2 and ZnO–3 wt% Al_2O_3 layers.

method is not so common as APS because of an expensive chamber for atmosphere control [23].

3. An example of application

The photograph in Fig. 14 shows the electroluminescent segment with SPS TiO_2 emitter with the surface of 15×15 mm^2. The segment is made in triode configuration and beside the cold cathode it contains an extracting grid and ITO with phosphor on

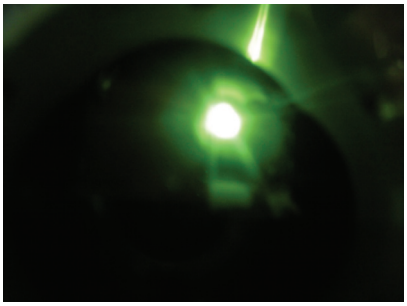

Fig. 14. A light emitting segment with SPS TiO_2 emitter with surface of 15×15 mm^2.

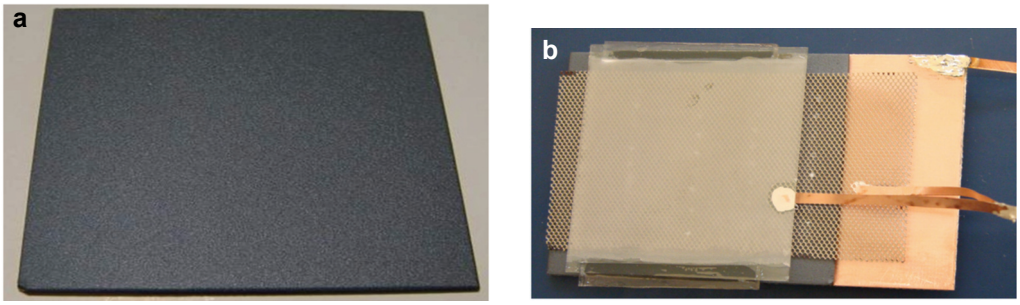

Fig. 15. SPS TiO_2 cathode with 50×50 mm^2 surface area (**a**) and the light source prototype model with such cathode (**b**).

the glass anode. An extracting grid enables luminance of the phosphor control via electron emission modulation [24].

At present, the light source with much larger SPS TiO_2 cathode of 50×50 mm^2 surface is constructed. Figure 15 shows the large area cathode and a prototype model of the light source.

4. Conclusions

The plasma deposited layers appear to be as good as field emitters made from the carbon composites. The plasma spraying technique is well suited for large area depositions. It should be noticed that these layers possess good mechanical strength and being robust they are easy to maintain. The plasma spraying is widely used in mechanical, chemical, energetic and aviation industries. Thus, this method may be promising, especially in the perspective of the application of suspensions with nanopowders [25].

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