

Transformation of Polymers in a Stream of Low-Temperature Arc Discharge Plasma

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SYNOPSIS

Spraying of polymer materials in a low-temperature plasma stream is a very efficient way of depositing polymer coatings on large surfaces. The deposition of powdered polymers by an arc discharge plasma flow and spraying from the bulk have been compared. The properties of powdered polymers do not change considerably during transportation by the stream because of the short residence of the particles in the plasma. When spraying from the bulk, polymers are transported in the form of melt droplets (polyethylene, polycarbonate) or in gaseous phase (polytetrafluoroethylene); autohesion of the droplets or secondary polymerization occurs, respectively, on the substrate surface. This process offers high-quality thin films and coatings whose structure depends significantly on the characteristics of the substrate as well as on the structure of the source polymer. Obtained polymer coatings contain nitrogen and oxygen entrapped from the atmosphere as well as (on the glass surface) the products of glass etching. This fact enables one to vary widely the properties of the coatings. Furthermore, the problem of obtaining combined protective coatings in which polymer melt fills the pores between metal particles can be solved successfully in a united technological cycle including plasma spraying of the polymer and the metal. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

When one speaks about plasma application for polymer coatings deposition, glow discharge plasma is usually implied. However, the possibilities of this method are limited by natural factors: a discontinuous coating process, small size of workpieces being treated, thin coatings obtained, and a relatively long time required for the polymer deposition. At the same time, the protection and reclamation of large-sized articles (in particular, those working in corrosive media) remains a problem of high priority. To solve this problem, the deposition of protective coatings by a stream of arc discharge plasma is used. Traditionally, only inorganic coatings (metallic, ceramic) are obtained in this way because the conditions in a high-enthalpy flow are believed to be too hard for organic polymers. However, ceramic and metallic coatings deposited by an arc discharge

plasma stream include a lot of pores, which reduces considerably their protective ability and lifetime. In this respect, the use of polymer materials for the design and production of composite metal-polymer systems is promising. It is possible to obtain combined coatings, which offer the advantages of each component, in a united technological cycle.

Unfortunately, information about the arc discharge plasma effect on polymer materials is scarce. The aim of this article is to study the behavior of polymers in a plasma stream as well as the structure and properties of deposited coatings.

EXPERIMENTAL DETAILS

The arc plasmotron was used (Fig. 1) with the following working parameters: the arc current 320 A, the arc voltage 30 V, and the gas (argon) flow rate ≈ 0.9 g/s. The plasma temperature was estimated as follows: First, the ion concentrations were measured with a probe¹ for different points in the stream. Second, their values were substituted in the kinetic

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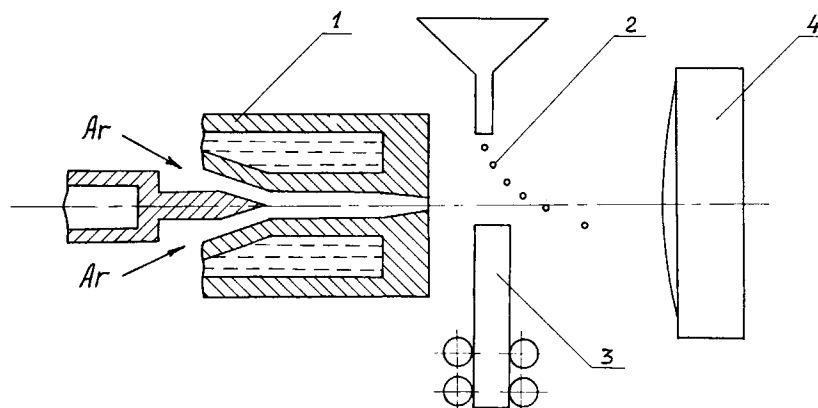


Figure 1 Deposition of polymers by an arc discharge plasma stream: (1) arc plasmotron; (2) polymer powder; (3) polymer bar; (4) substrate.

equation taking into account the processes of ionization, three-particle recombination, and radiative recombination. The profile of plasma temperature along the stream axis is presented in Figure 2.

Thermoplastic polymers of Soviet production were as follows: high-density polyethylene (HDPE), with a molecular mass (MM) of 1.2×10^5 ; polytetrafluoroethylene (PTFE, MM = 3.50×10^5); polycarbonate (PC, MM = 3.3×10^4); and polysulfone (PSF, MM = 3.0×10^4). These were in powder form (with particle size of 60–100 μm) and bars ($5 \times 10 \times 200$ mm) and were introduced in a high-temperature zone (≈ 8700 K) of the plasma stream. The substrates of aluminum, KBr, and glass were placed at a distance of 200 ± 5 mm from the edge of the plasmotron nozzle. The temperature of the substrates was measured by means of a thermocouple fixed on their back; it did not exceed 120°C .

The structure of powders and coatings was investigated with the optical microscope NU-2 (Carl Zeiss, Germany). The thermograms were obtained with the DSM-2M microcalorimeter (U.S.S.R.) at scanning rates of 8 to $16^\circ\text{C}/\text{min}$. The thermogravimetric analysis was carried out with the OD-102 derivatograph (Hungary) at a heating rate of $2.5^\circ\text{C}/\text{min}$ and the specimen mass 500 mg. For infrared spectra registration, the UR-20 infrared spectrophotometer (Carl Zeiss, Germany) was used. For coatings deposited on KBr plates, infrared spectra were registered directly from the plates. Coatings obtained on other substrates were stripped off, ground, and molded with a KBr pulver to transparent tablets of which infrared (IR) transmission spectra were easy to obtain. The X-ray photoelectron spectra were obtained with the ES-2401 device (U.S.S.R.).

Coating resistance to corrosion was estimated by measuring the corrosion rate of aluminum samples (coated and uncoated), which was defined as a decrease of the sample mass after a 240-h exposure to 45% H_2SO_4 at 50°C .

RESULTS AND DISCUSSION

Powdered Polymers

When powdered HDPE, PC, or PSF was introduced in the plasma flow, a porous, partially fused coating was formed on the substrate surface. According to our previous observations and calculations,^{2,3} the particles are melted only to a depth of about 8 to 10% of their radius. The reason for this is the low thermal conductivity of polymers as well as the process of ablation in the plasma flow. The polymer deposition on hot substrates and/or additional thermal treatment result in coatings whose structure and properties are practically identical with those of source polymers. For example, the IR spectra and

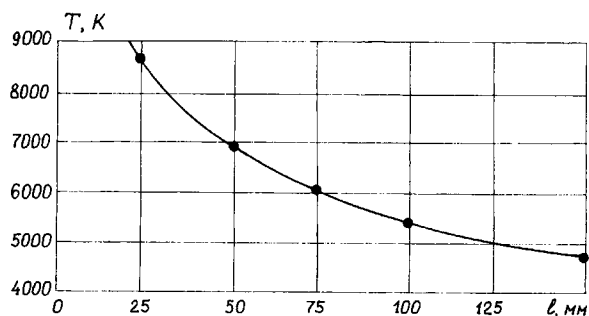


Figure 2 Ion plasma temperature versus the distance from the plasmotron edge.

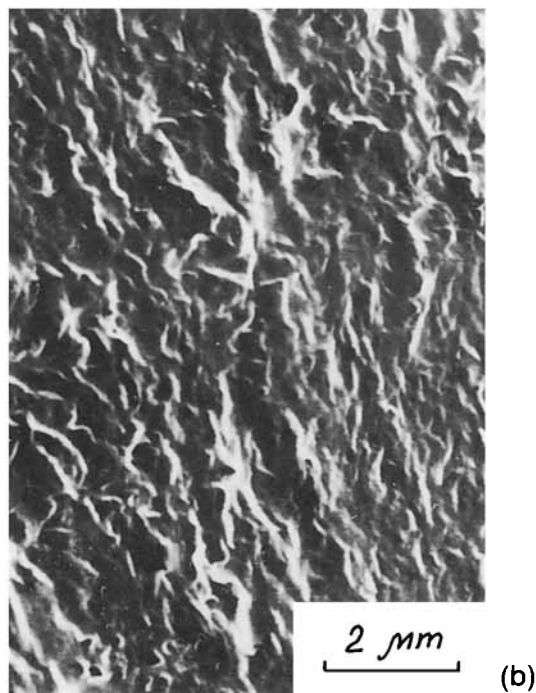
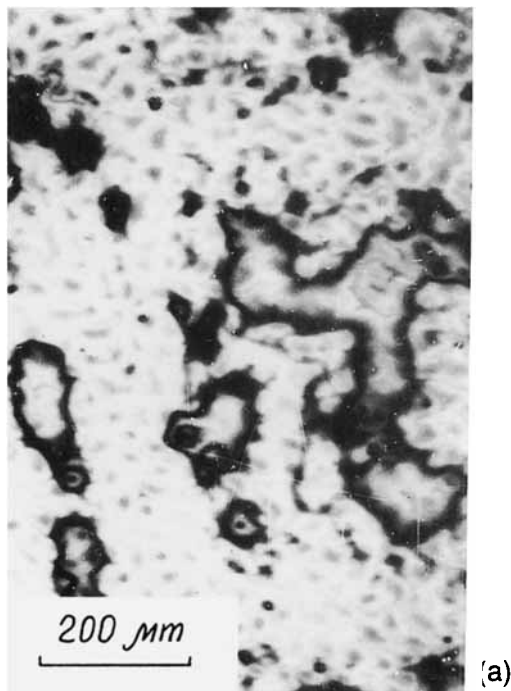


Figure 3 The initial stage of PC (a) and PTFE (b) film formation when a polymer bar is dispersed by the plasma flow.

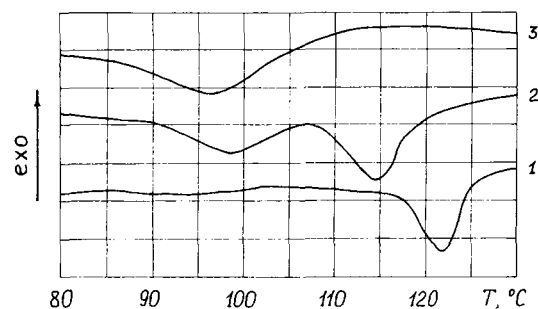


Figure 4 Thermograms of source (1) and plasma deposited (2) HDPE and of low-molecular-weight products of HDPE destruction (3).

thermograms for source and plasma-treated powdered HDPE are practically the same. A slight difference—the consequence of the surface oxidation of the particles—manifests itself through the peaks at 1720 cm^{-1} in IR spectra ($\nu_{\text{C=O}}$).

Polyethylene

When polymer bars are treated, a substantial difference in the behavior of different polymers is observed. For instance, a thin film of the melt is formed quickly on the surfaces of HDPE and PC bars; the plasma flow disperses it into small droplets and transports the droplets to the substrate surface, where they fuse to form a transparent, colorless coating 50 to $200\text{ }\mu\text{m}$ thick [Fig. 3(a)]. The IR spectra comparison for source and plasma-treated HDPE reveals the polymer oxidation (intensive peak at 1720 cm^{-1}) with carbonyl group formation. The rise in the intensity of the peak at 910 cm^{-1} evidences the growth of the double bonds as a result of HDPE destruction.⁴ The thermogram of plasma-treated HDPE (Fig. 4) demonstrates a wide endothermic peak at 85 to 115°C which corresponds to the melting of low-molecular-weight products of destruction. The content of these products (soluble in boiling hexane) is about 25% by mass. The coatings' extraction by boiling xylol revealed the absence of the gel fraction. Thus, the transport in a plasma stream and following film formation do not result in crosslinking.

Polycarbonate

Polycarbonate is characterized by similar behavior in an arc plasma flow (i.e., oxidation, destruction, no crosslinking). The estimation of the PC molecular weight (M_n) performed according to the viscosimetry technique⁵ gave $M_n = 2.4 \times 10^4$ for the

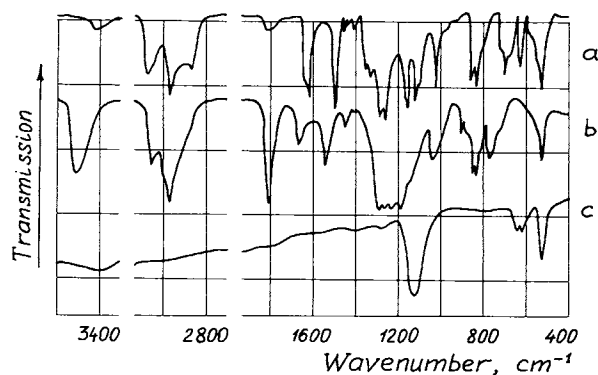


Figure 5 Infrared spectra of polysulfone: source polymer (a), soluble part of the plasma deposited coating (b), material of the coating (c).

coating material, while M_n for the source PC was 3.3×10^4 .

Polysulfone

Transformations of PSF in a stream of low-temperature arc discharge plasma are much deeper. The thin melt film on the surface of PSF bar grows dark and is transported to the substrate in the form of small particles. The obtained coatings have an intense brown color; their surfaces formed by carbonized inclusions are rough. Infrared spectra of the source PSF and the material of the coating (Fig. 5) show deep chemical changes. The presence of only a few absorption bands at 1100 to 1250, 1500, and 1600 cm^{-1} , assigned to C—C and O—S—O groups and the C=C bond in a core, evidences the breaks of molecular chains with subsequent crosslinking, resulting in formation of graphitelike honeycomb structures. Extraction by chloroform gives the content of the gel fraction of 50 to 60%. The infrared spectrum of the soluble part of the coating is similar to that of source PSF, and the former is distinguished by lower intensity of the signal at 837 cm^{-1} and by prominent absorption at 3300 to 3500 cm^{-1} . These differences indicate the lower molecular weight of the polymer as well as preferential spending of C—H core bonds in oxidation and crosslinking processes.

Thus, PC and PSF, similar in their chemical nature, reveal substantially different behavior under the effect of arc plasma flow. Destruction of PSF is more intensive than PC decomposition, and it is not thermal destruction. Because PSF is known to be very sensitive to ultraviolet (UV) radiation,⁶ it may be the UV component of plasma flow radiation that causes the difference in the behavior of these polymers and in the properties of deposited coatings.

Polytetrafluoroethylene

The mechanism of PTFE transformation in arc discharge plasma is different. The polymer melt on the bar surface does not disperse into droplets; instead, gaseous products of plasmolysis are transported to the substrate. The growth of the depositing film is a result of the complex process, including condensation of gaseous products on the substrate surface and chemical interactions. In this way, 1- to 5- μm -thick coatings are deposited [Fig. 3(b)]; after this, the thickness does not increase with time. The structure of the coatings differs markedly from that of the source PTFE. The IR and XPE spectra (Figs. 6 and 7) show that they are determined, to a great extent, by the nature of the substrate. We may conclude that co-polymerization of PTFE destruction products with particles of other chemical natures takes place on the substrate surface. For instance, Si—F [IR peaks at 400 to 800 cm^{-1} ; Fig. 6(a)] and Si—C [XPE spectrum, Fig. 7(a)] bonds were registered in the coating on glass. This coating is hydrophobic ($\vartheta = 102^\circ$) and stable: Its IR spectrum and wetting angle are constant in time.

The coating on KBr contains nitrogen and oxygen atoms [Figs. 6(b) and 7(b)] in the form of amino-, amido-, and nitrosogroups. It is known⁷ that nitrogen and oxygen entrapped from the atmosphere by an argon plasma flow form various active particles (in particular, the nitroxyl radical NO). Because the structures of coatings on glass and KBr are different, the interaction of these particles with PTFE plasmolysis products likely takes place on the substrate surface rather than in a stream. An important role in the process described can be the catalytical properties of the KBr surface; it is known, for ex-

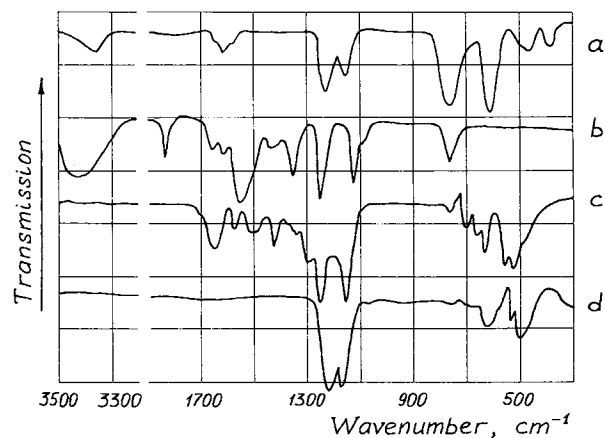


Figure 6 Infrared spectra of PTFE deposited by arc discharge plasma on glass (a), KBr (b), and aluminium (c) and of the source PTFE (d).

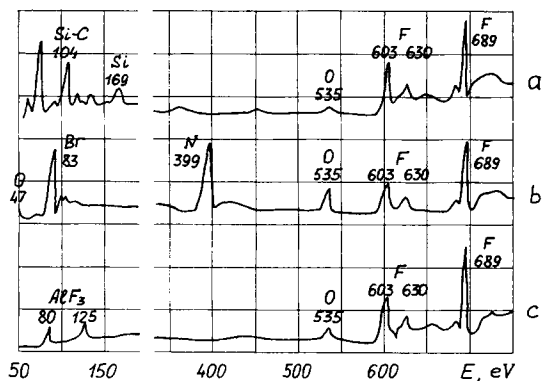


Figure 7 XPE spectra of PTFE deposited on glass (a), KBr (b), and aluminium (c) surfaces.

ample, that LiBr catalyzes the synthesis of nitrosoft fluoropolymers.⁸

The film on KBr is hydrophilic ($\vartheta = 34^\circ$). The peaks at 3300 to 3500 cm^{-1} in the IR spectrum are assigned to H_2O molecules. Water adsorption on the coating surface was observed under the specimen cooling. A characteristic of this coating is its instability: After 2-week storage in air or argon, the wetting angle rises to between 50 and 60°, and the intensity and positions of IR peaks in the range of 1300 to 1700 cm^{-1} change significantly.

IR spectra of the films formed on aluminum substrate [Fig. 6(c)] also have bands assigned to the motion of nitrogen-containing groups (1300 to 1700 cm^{-1}). The stability of these films as well as the wetting angle ($\vartheta = 78^\circ$) is intermediate between those on glass and on KBr.

Combined Coatings

When a metal and a polymer were simultaneously sprayed with the arc discharge, combined coatings were formed. Microscopic study of their sections revealed that pores in the structure of the metal were filled with the polymer (Fig. 8). The possible reason for easy polymer melt permeation into the pores is the improvement of its rheological properties due to polymer decomposition under plasma treatment, resulting in low-molecular-weight product formation.

The corrosion rate in H_2SO_4 for the metal surface protected with the combined coating was only $7.0 \times 10^{-3} \text{ g}/(\text{m}^2 \cdot \text{h})$; in the case of metallic coating under the same conditions, it was $3.07 \text{ g}/(\text{m}^2 \cdot \text{h})$.

CONCLUSION

The application of the arc discharge plasma facilitates the deposition of metal and polymer coatings on large surfaces. Because the properties of the obtained polymer coatings depend on the method of material spraying (in a powder or from a bar) and on the nature of the surface to be protected, it is possible, by varying deposition conditions, to obtain coatings with prescribed properties. Plasma spraying of a polymer and a metal in a united technological cycle offers combined metal-polymer coatings which protect metal surfaces against corrosion.

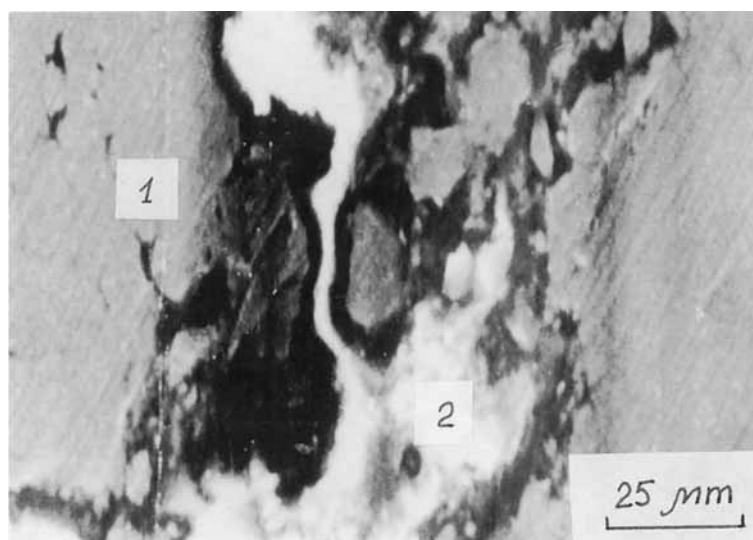


Figure 8 Combined (Ni + HDPE) coating on the aluminium substrate: (1) nickel, (2) HDPE.

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