Vacuum Plasma-Arc Metallization of Metals and Dielectrics

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Abstract

This paper gives the results of vacuum plasma arc metallization of metals and dielectrics. The advantages of this method are presented together with the main properties of «metal-dielectric» and «metal-metal» systems.
The contribution of constituents of vacuum arc discharge plasma to the adhesion strength of the coatings is pointed out.
The mechanism of interaction of the substrate with ions and droplets of metals appeared in the arc discharge is proposed.

Riassunto

In questo articolo sono riportati i risultati della ricerca dei processi di applicazione sottovuoto al plasma-arco sui rivestimenti per i materiali dielettrici e di metalli.
Sono indicate le possibilità ed i vantaggi di questo metodo di metallizzazione ed anche le proprietà principali dei sistemi «metallo-dielettrico» e «metallo-metallo». È stato sottolineato il ruolo delle singole componenti del plasma della scarica dell'arco a vuoto e la loro influenza sulla resistenza di adesione dei rivestimenti.
Viene proposto un meccanismo di interazione con substrato di ioni e gocce di metallo che sorgono nella scarica dell'arco.

Introduction

Thick films attaining 10-50 μm are employed for metallization of dielectrics which is made by covering the substrates with metal — bearing pastes and their subsequent firing into these substrates for the production of vacuum — tight seals, for the use as electrode and contact layers and also for the production of corrosion — resistant and decorative coatings on metals, that are usually deposited by electroplating.

The purpose of this report is to present information about vacuum plasma arc metallization effected by high current vacuum arc discharge in the vapours of the evaporated material.

The investigation of erosion products from cold cathodes of vacuum arcs showed that these products involved neutral components consisting of atoms, clusters of material and droplets, as well as ion components consisting of metal ions (multiple-charged ions included) [1].

Droplet velocities and temperatures of some materials have been investigated. Hg droplets which had the velocities about 10 m/s were found to be present [2] with their probable speed of escape reaching 3 m/s. According to calculations presented in [3], the speeds of escape of Hg droplets of 10^{-3} cm were estimated to be 15 m/s. The steady — state droplet temperature in stationary vacuum arc [4] estimated on the balance of droplet energy between the inflow of energy to the droplet from the arc plasma as a result of ion — electron collisions and the escape of energy as a result of evaporation reached 2000-2600 K under the assumption of plasma homogeneity and quasi-linearity.

The heating of substrate was effected by the considerable power emitted from the cathode area. The substrate temperature depended on the action of electric circuit arc source electrodes and in the majority of cases the minimal temperature was chosen.

The high temperature of the cathode spot initiated flash evaporation, which enables to obtain good reproducibility of the evaporated material (alloy) in the resultant coatings.

Experimental procedure

The quality of the film to substrate adhesive bonding is responsible for the strength properties of the investigated systems. The adhesive bonding σ_{ad} was estimated from the ratio of the force necessary to strip the film from the substrate to the unit surface area of the film separated by the action of this force.

Surface morphology of the condensate films was investigated with a scanning electron microscope.

Analysis of element composition of the films was performed by Auger Electron spectroscopy, secondary ion mass-spectrometry and electron probe x-ray scanning electron microscopy.

Experimental results

The adhesive bondings of the films produced by the condensation of ion σ_{ion} and neutral σ_{neutr} components of the arc discharge erosion products were compared (Fig. 1).

The plasma components flow separation was carried out in the electrostatic field of the plate capacitor during the deposition of Mo and Ni films on the alumina ceramics (with Al_2O_3 content of 99,7 per cent). The adhesive strength of the films produced by metal ions condensation was 2-7 times higher than that of the films produced by the deposition of the atomic-droplet component of the flow.

The investigation was made to find out the effect of the droplet component of a stationary vacuum arc exerted on the properties of «film-substrate» systems.

Various types of droplet solidification on the substrates were noted (Fig. 2). For Cu they were classified to have the following forms: 1) semispherical; 2) semispherical with ring-shaped extensions; 3) semispherical changing into toroidal; 4) toroidal having craters; 5) exclusively toroidal. Relative quantity of Cu for each group resulted 40, 20, 18, 16 and 6 per cent respectively. Mo was characterized by semispherical droplets.

Investigations of film composition revealed that at the condensation boundary a transition zone was formed the width of which varied from some fractions to several micrometers according to the kind of material and deposition mode (Figs. 3 and 4).

Gradual change of film and substrate elements concentrations which usually characterizes the process of interdiffusion could be upset (Fig. 3c); it reveals that new phases were formed in the transition zone.

Investigations were carried out that gave rise to the development of systems characterized by high adhesive strength including the formation of fundamentally new «metal-dielectric» systems (Ti - AlN, Ti - Y_2O_3) as well as «metal-metal» systems (Ti-steel, Mo-steel) which were characterized by high strength and could not be developed by universally adopted standard methods. The technical data at newly developed systems are listed in the following Table 1.

Table 1 - Technical data for «film-substrate» systems produced by plasma arc metallization

Designation of metal coatings	Substrate	Metal to be applied	Coating thichness, μm	Results
		Metal-dielectric systems		
Metal coatings for hermetic seals	Alumina ceramics with 94-99% Al_2O_3; Sitall, quartz, sapphire	Mo, W, Ni, Fe, Cu, Ti, Ni - Cu alloy	2 - 20	For Mo metallization: bending strength of seals is 250 MPa; seals remained hermetic at thermoresistance tests up to 190 thermocycles

(continue)

Electrode coatings	Lead titanate-zirconate	Ni - Cu alloy, Ni - Cu	4 - 20	Adhesive strength of the Ni - Cu alloy coating, 30-50 MPa
Contact coatings	Alumina ceramics with 94% Al_2O_3	Ni - Cu, Ni - Fe alloys, Ni	0,5 - 5	For nickel coatings: tensile strength of brazed contact seal 90-120 MPa
Current conducting coatings	Alumina ceramics with 94% Al_2O_3 and mullite-siliceous ceramics	Cr, Ti, Al, Ta, stainless steel; Ti-Al, Ni-Cr, Fe-Cr-Al, Si-Cr-Al alloys	0,5 - 1	For Ni - Cr coatings: resistance 0.1-150Ω temperature resistance coefficient 100 10^{-6} 1/K; resistance stability 0,5%
Newly developed «metal-dielectric» systems	AlN, Y_2O_3 - based ceramics	Ti, Mo	5 - 15	Crystal dielectric metallization with pure metals for hermetic seals production. The adhesive strength of Ti coatings is 50 MPa
		Metal - metal systems		
Current conducting coatings	Steel, Kovar, Mo	Cu	5 - 10	Tensile strength 200-300 MPa
	Steel	Ni - Cu alloy	5 - 10	Tensile strength 300-330 MPa
	Kovar	Ni	5 - 10	Tensile strength 300-400 MPa
Corrosion-resistant coatings	Steel	Ti, Ni, Cr, stainless steel, Ni - Cr alloy	4 - 10	Adhesion strength for all enlisted coatings is 60 MPa. The coastings were weather - proof for 96 days at the relative humidity of 96±3% and the temperature of 40°C.

Discussion of experimental result

Chemical interaction between the components of the substrate and the film at the interface of a dual-phase structure, as well as diffusion processes are responsible for a high strength bonding of a metallic or dielectric substrate with an applied coating [5].

Chemical interaction occurs between a metal coating and substrate constituents in any of several ways: either as an exchange reaction or as the formation of binary compounds (for a dielectric substrate) and intermetallic compounds (for a metal substrate).

In terms of thermodynamics chemical exchange reaction is possible if Gibbs energy is below zero. This condition is met when the matter is deposited in the form of neutral particles for a limited number of film and substrate materials in narrow temperature interval, e.g. for «titanium-aluminium nitride» system in the temperature range 500-1800 K.

Phase composition of the material evaporated in the arc discharge and the occurrence of high energy metal ions with multiple charges (the number of charges per ion is from 1 to 3) enable their interaction with substrate components. Ions present in the arc discharge plasma enhance the thermodynamic probability of the exchange reaction with dielectric components, decreasing the value of Gibbs energy by the ionization potential that makes the interaction possible even for those reagents which usually don't enter into reaction [6].

Experimental studies of interaction of some erosion products from arc discharge with a ceramic substrate confirmed the theoretical estimates concerning thermodynamic probability of the studied systems interactions induced by the action of ion component of plasma flow with the simultaneous activation of the substrate surface, enabling its chemical bonding with the coating.

In the «metal-metal» systems the situation is different; the formation of the intermetallic compounds in the interface sometimes causes the brittleness of the systems. Therefore the number of materials which can be used in the process of electroplating is limited. These materials include such metals as copper, nickel, chrome, zinc, cadmium etc.

The investigation of droplet component of a stationary vacuum arc was carried out together with the estimation of temperature and size of droplets in the process of motion involving the equation of thermal balance, based on the assumption that the energy to the droplet is transferred from a point source which has the temperature equal to that of a cathode spot of small linear dimensions and which measures the energy inversely proportional to the square of the distance.

According to the calculations it was found out that when a drop travels at velocities of 5-150 m/s and the initial temperature is equal to the melting point of the material, the droplet temperature in the process of motion can reach an extremum approximating the boiling point and sometimes exceeds the melting point when the distance from the source is increased (even up to 0.5 m). This estimation is far below the temperature listed in [4].

The experimentally determined variety (Fig. 2) of droplet forms results from various modes of interactions with the substrates. At the moment when a molten droplet contacts the cold substrate the form of this droplet is changed due to plastic deformation and crystallization.

At non-elastic impact of the drop, mechanical stresses, caused by momentum trasfer, arise in the area of contact producing the pressure at the substrate. This pressure consists of 1) the impact pressure exerted by a water-hammer pressure due to incompressibility of the fluid, this type of pressure amounts to 850 MPa; 2) the pressure produced at the simultaneous flow of fluid and its crystallization; this pressure makes up to 30-50 MPa with a duration of the process of about 10^{-5} s.

The solution of the heat transfer equation for the uniform heat exchange between a molten drop and a cold substrate permitted to conclude that the temperature of the contact at the «drop-substrate» interface remained constant whereas a phase transition energy released over a mobile crystallization front. The solution of the heat transfer equation with the utilization of the imprints of solidified droplets (Fig. 2) showed that the contact temperature at the duration of the process of 10^{-5} s exceeded the droplet melting temperature. The temperature for Cu is in excess of 30-300 K, while the excess for Mo is 220-290 K. For droplets which have the imprints of more complicated configuration (Fig. 2b-f) the estimated values discussed here may be considerably higher.

Thus, when the metallization process is effected by erosion products emitted by a vacuum arc discharge, the substrate is subjected to the action of various factors: it suffers high mechanical loads and considerable temperature gradient leading to release of heat that enables the chemical interaction and diffusion at the "film-substrate" interface. The formation of the resultant transition zone at the phase boundary is confirmed by experimental results obtained for some investigated systems (Figs. 3 and 4).

The location of extreme points found on the curves of concentration variations (Fig. 3c) revealed the existence of the reactive diffusion. The change of phase composition in the boundary «film-substrate» region, which is characteristic of a reactive diffusion, has a decisive effect on the strength of adhesive bonding of coatings.

The problems concerning pretreatment of substrate surfaces are not discussed in this report.

Conclusions

The method of vacuum plasma arc metallization can be used to produce new very adherent systems based on various dielectrics including crystalline ones (AlN, BN, Y_2O_3), as well as on metals for the coating of which such materials as stainless steel, titanium and its alloys are used. The method of vacuum plasma arc metallization is an alternative to the electroplating, but unlike the latter, it is ecologically pure and characterized by low power consumption.

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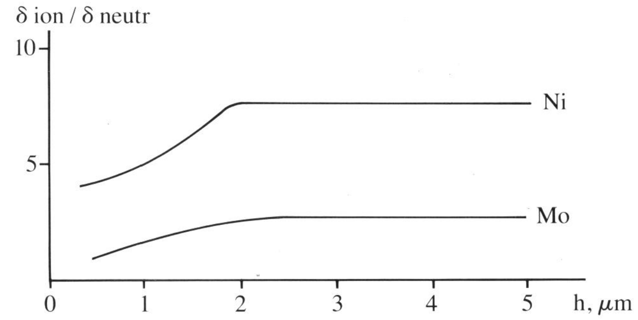
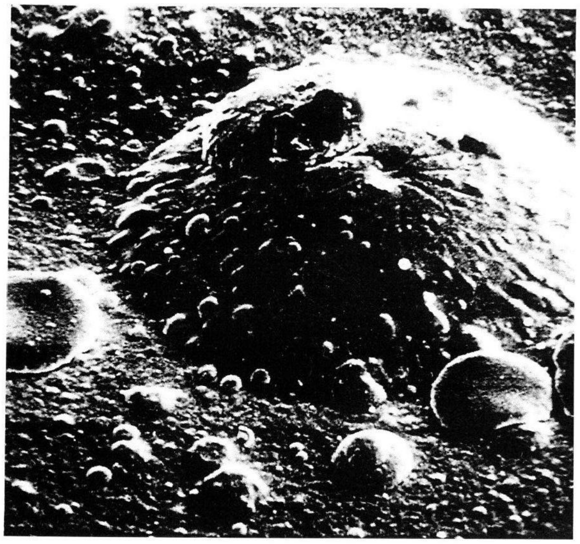
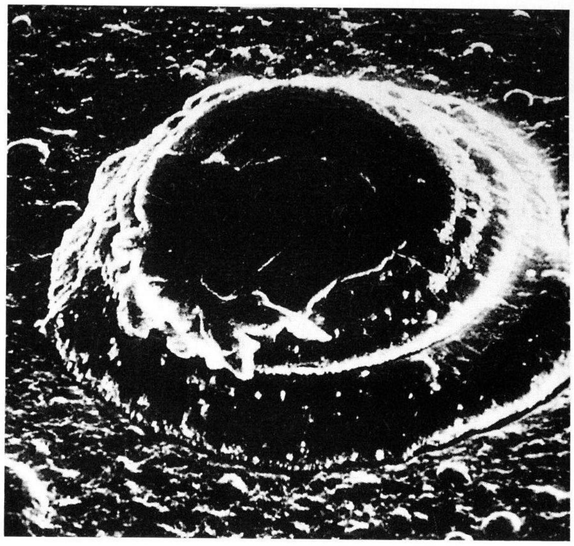


Fig. 1:

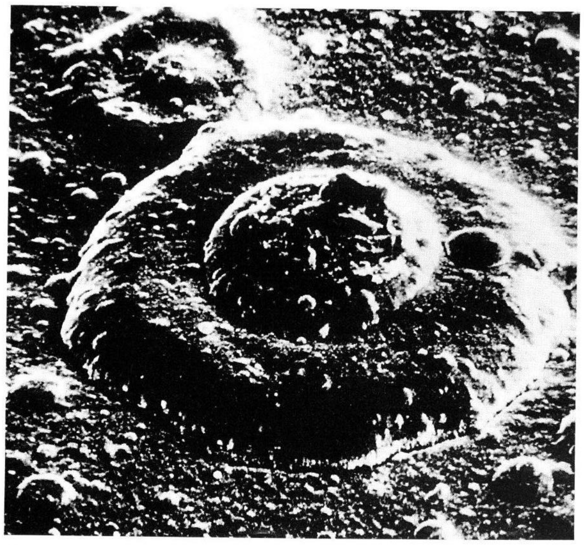
Adhesive strength of Mo and Ni coatings deposited on alumina ceramics at the condensation of the flow of neutral and ionized particles as a function of films thickness *h*.



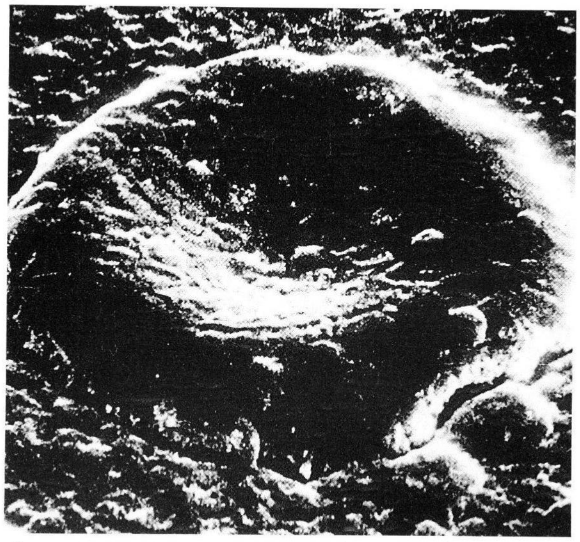
a) semispherical, × 1000;



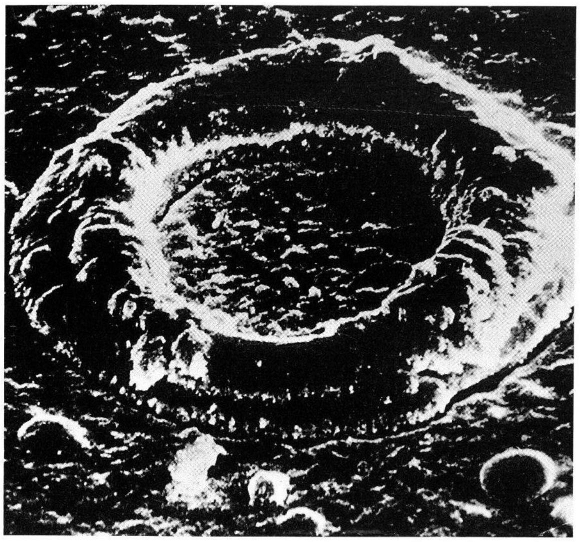
b) semispherical with ring - shaped edges, × 1000;



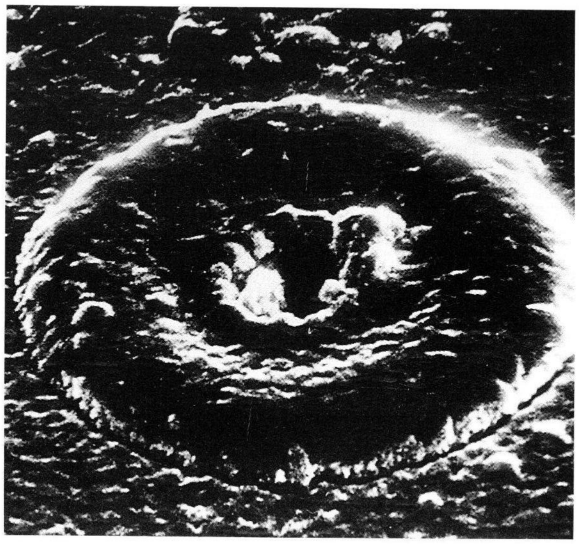
c) semispherical with ring - shaped edges, × 1000;



d) semispherical trasforming into toroid, × 4500;

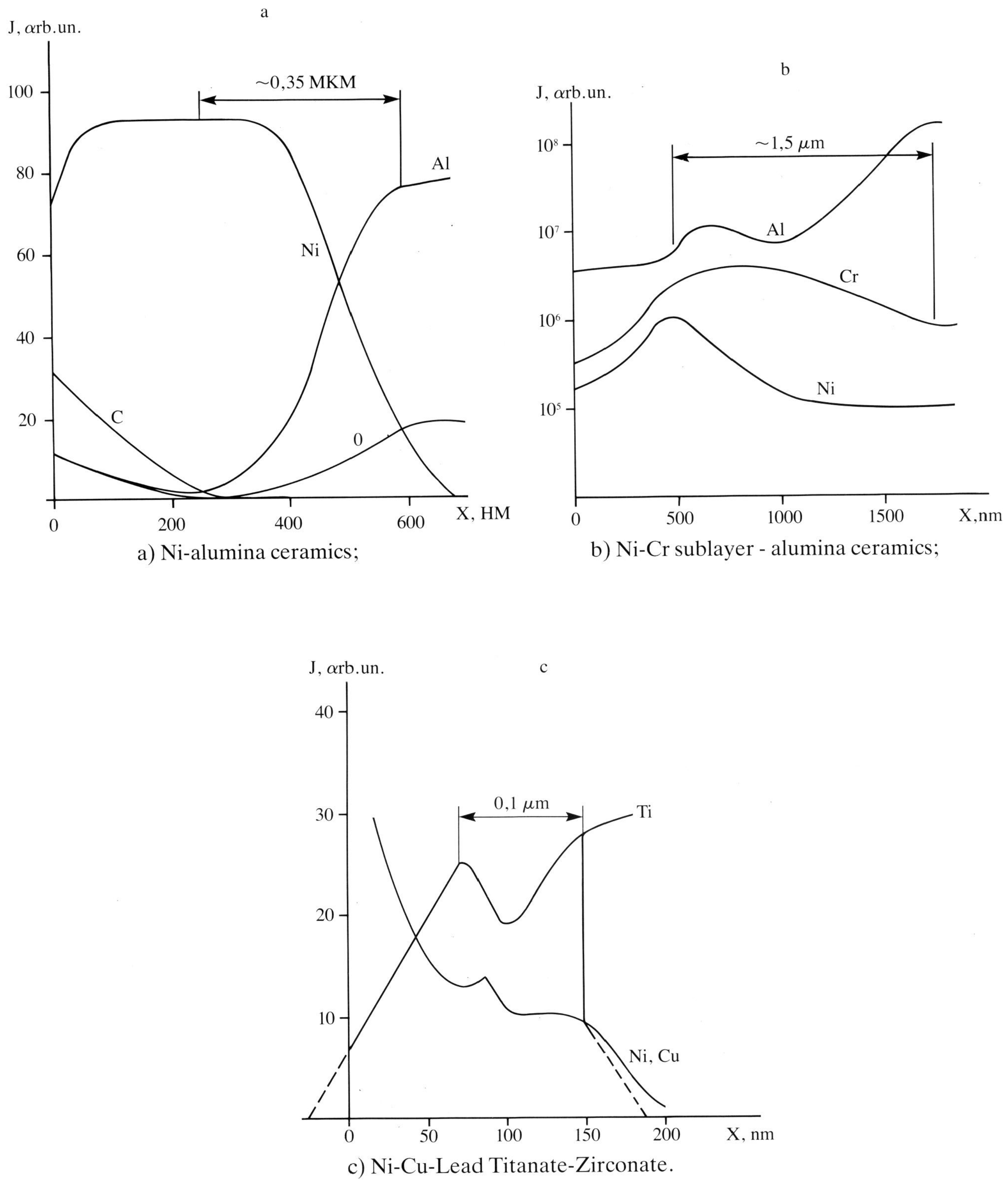


e) toroidal having a crater, × 3000;



f) toroidal, × 2000.

Fig. 2:
Typical forms of Cu droplets on the surface of plasma arc condensates.



a) Ni-alumina ceramics;

b) Ni-Cr sublayer - alumina ceramics;

c) Ni-Cu-Lead Titanate-Zirconate.

Fig. 3:
The variation of intensity I of lines of film and dielectric substrate elements along the thickness of the workpiece with layer composition for different systems.

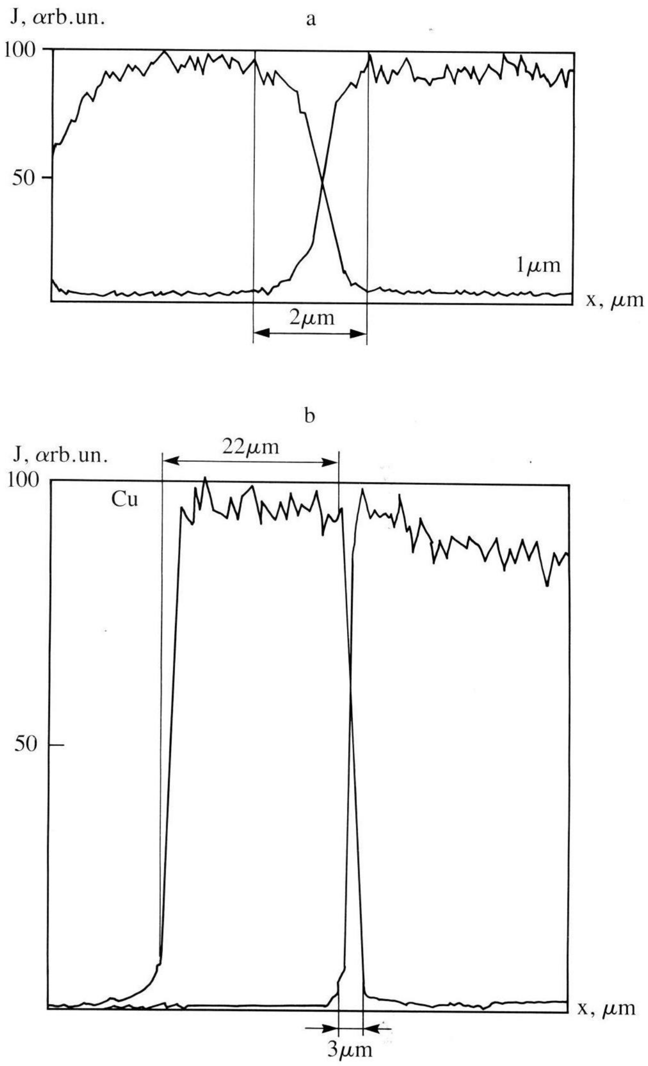


Fig. 4:
The variation of intensity I of lines of main system elements along the workpiece thickness: a) Ti film on a steel substrate; b) Cu film on a Mo substrate.