Transparent Protecting Film Deposited Using the Method of Ion-Plasma Deposition in Low Pressure Arc Discharge

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Abstract – The technologies of transparent protecting and decorative films deposition were elaborated and tested. Films based on AlN and Al_2O_3 as well as amorphous hydrocarbon films were analyzed. The results of films' microhardness, corrosion, chemical and mechanical resistance analysis are obtained. It was revealed that deposited film protects metals from active oxidation and from influence of sulfur-bearing medium. The film also protects from mechanical effect in the case of light load. The research into phase content and defective substructure of the film and substrate material was carried out applying the methods of diffraction electron microscopy. Regardless of substrate type, the deposited carbon film is amorphous and contains nanosize particles of graphite which crystal lattice is of hexagonal-modification.

1. Introduction

Recently the problem of transparent protecting and decorative film deposition has been considered more topical. Thin transparent film could be applied for protecting metals from corrosion serving as metal preservative coating. In jewelry industry the coating is used to provide protection for soft noble metals such as Ag, Au and Pt from scratches. Besides, such film provides chemical protection of silver preventing it from darkening as the result of oxygen effect as well as from sulfur and alkaline medium influence. Transparent films could be used as decorative coating in order to obtain interference color.

Such color could be reached depositing films which thickness vary from ten to hundreds nanometers. Present paper describes the methods of transparent protective and decorative AlN and Al_2O_3 films deposition, amorphous hydrocarbon films, as well as gives the analyses of their structure, corrosion and wear resistance.

2. Description of the Transparent Films Deposition Technology

Within the framework of performed research two kinds of films were obtained: hydrocarbon films and films on the base of aluminum nitride and oxide. The research was carried out using vacuum plasma setup "DUET" [1]. General view of the setup is shown in Fig. 1.

Fig. 1. General view of "DUET" setup

Plates made from stainless steel, silver and jewelry alloys were used as the substrate, and glass objects – as testing samples. Before starting the process samples were washed in alcohol by ultrasound and clean by coarse calico.

The deposition process started from ion-plasma cleaning of the samples. "PINK" source was used as plasma generator [2]. The working gas was argon, discharge current was $I_{DP} = 2–20$ A, cleaning period was $t = 10–30$ min. The details were under floating potential in order to prevent ion etching of the surface and increase of its roughness. The cleaning was made under 0.05–0.08 Pa pressure in working chamber.

For hydrocarbon film deposition gas plasma generator based on vacuum arc with hollow cathode was used [3]. The source operation principle is the following: Cathode spot appears on the inside surface of water-cooled cylinder hollow cathode with the help of igniter rod and remains on the place in axial magnetic field. The axial magnetic field is generated by magnetic coil in such way so that cathode spot will be able to rotate on the inside cathode surface and not to reach end surface. Electrons generated by cathode spot move by crossed electric and magnetic fields, and provide ionizing of working gas which is supplied through cathode cavity. Diaphragm transmits discharge current and screens microdroplet fraction which comes out of cathode spot.

For hydrocarbon films deposition methane and its blends with argon were used. In order to reduce discharge current and limiting temperature for heating substrate, the inductance throttle $L = 4.6$ MHz was included into the cathode chain of the plasma generator. Throttle inclusion allows reducing current of plasma generator stable operation up to 10 A. Hydrocarbon films were deposited under the pressure 0.3–0.4 Pa. Deposition rate was up to 300 nm/hour.

Aluminum oxide and nitride films deposition was made applying the method plasma-assisting deposition. Passive screen was used as separator of dot fraction. The screen had semi-cylinder surface of 400 mm diameter and 270 mm height.

Nitride aluminum coating was made using arc cathode evaporator and plasma generator "PINK". Discharge current of arc evaporator was $I_{DAl} = 150$ A, discharge current of plasma generator "PINK" was $I_{DP} = 5–8$ A. Deposition was made in nitrogen atmosphere, working pressure was 0.11 Pa, deposition rate was 140–130 nm/hour. Research revealed that obtained AlN film is unstable to the alkaline and sulfur medium effect. The aluminum nitride film was protected by aluminum oxide film in order to prevent such effect. To deposit Al_2O_3 film the nitrogen was replaced by oxygen and the pressure in vacuum chamber was set to 0.3–0.4 Pa. Plasma generator current remained the same. However, plasma generator could not operate in alkaline medium for the long period due to heated cathode poisoning of "PINK", and after each hour of operation it was switched off. Al_2O_3 deposition rate in such system comes to 60–70 nanometers per hour. Total thickness of the film was chosen aiming at deposition of clear film or color film of required color.

Hardness of the films was measured using Akashi HM-114 measuring device by Vickers scale. Film thickness was measured using microscope Nanopics 1000, NPX 100, Seiko Instruments Inc.

3. Results and Discussion

Below the results of research are described.

In Fig. 2 the dependence of the hydrocarbon film microhardness on the indenter load is demonstrated.

Maximum hardness 900 kg/mm^2 could be reached when the indenter load is 3 gram, but at 25 gram indenter load microhardness is similar to substrate hardness. It depends on the substrate softness, and at increased load the film becomes crumpled. It is necessary to point out that in the case of hydrocarbon films the correct change of microhardness could be the problem due to film elasticity and resilience.

Figure 3 shows the analysis results of the hydrocarbon films resistance to ozone effect (oxidation). After 30 minutes oxidation in ozone the film remains the same, but non-coated section of the silver becomes dark. The conclusion is that such film is able to protect effectively the silver details from oxidation.

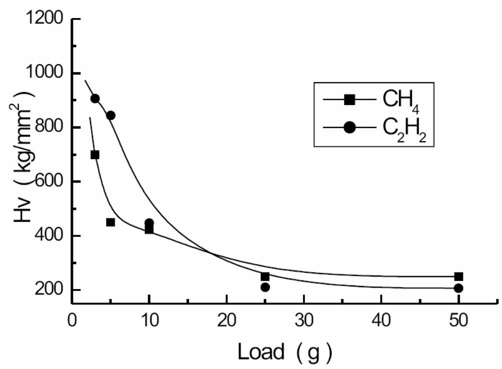
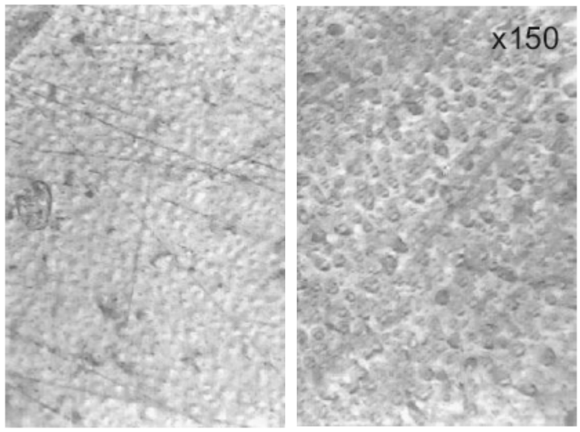


Fig. 2. CH film microhardness dependence on indenter load



a b

Fig. 3. CH-film testing results in ozone: a – after 15 minutes of ozone treatment; b – after 30 minutes of ozone treatment

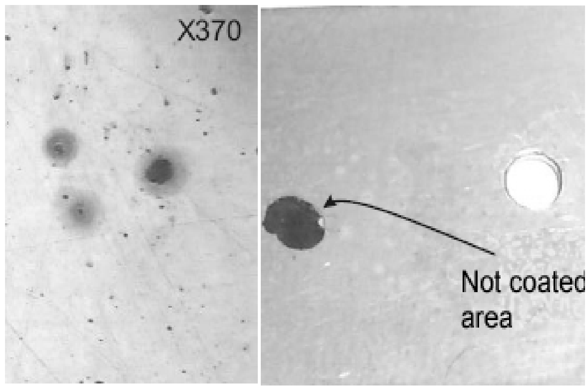


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Fig. 4. CH-film testing in blend $(NH_4)S+H_2O$ at the temperature $t = 80$ °C: a – in 120 minutes after testing; b – general view of the sample in 30 minutes after testing

Figure 4 demonstrates the testing results of hydrocarbon films chemical resistance in sulfur medium.

The obtained films have been tested in water solution (0.025%) $(NH_4)_2S$ during 2 hours at the temperature 80 °C. The corrosion was not revealed on the silver substrates with film protection, while the non-coated surface becomes dark in 5 minutes at room temperature. It is indicated that obtained film is able to reduce significantly the process of sulfur poisoning of the surface.

In Fig. 5 the dependence of surface microhardness on the indenter load is shown in the case of $AlN+Al_2O_3$ coating.

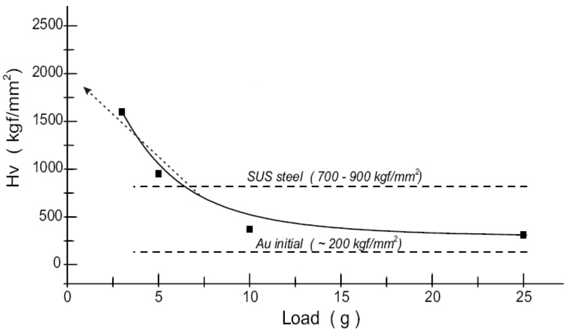

Fig. 5. $AlN+Al_2O_3$ film microhardness dependence on the indenter load. Film thickness is 1.1 mkm

In this case microhardness dependence is similar to the case of hydrocarbon films. However, hydrocarbon film becomes partially crumbled by indenter, but could renew it initial condition. The films based on aluminum nitride and oxide are more hard and fragile, and hard film could become broken on the soft surface. Maximum microhardness is 1600 kg/mm^2 in the case of minimum indenter load. If the load is more than 10 gram, measured microhardness becomes similar to substrate hardness. The conclusion is that described film is unable to protect the details from large mechanical effect, but it is able to protect from small scratches in the case of light load.

In Fig. 6 the images of $AlN+Al_2O_3$ film with chemical corrosion are shown. It is obvious that the film has not been changed since the time of testing. It means that the protection from chemical effect using such films is effective enough.

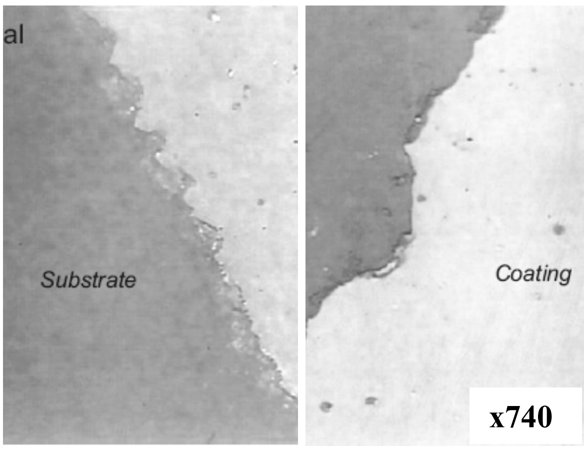

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Fig. 6. $AlN + Al_2O_3$ films testing in the blend $(NH_4)S+H_2O$ at the temperature $t = 80$°C: a – initial surface; b – in 120 minutes after testing

In Fig. 7 the abrasion testing results of aluminum nitride and oxide film are shown. The tests were made using eraser which had soft and hard sides. Mechanical effect on the covered surface was made as alternate motion with equal load.

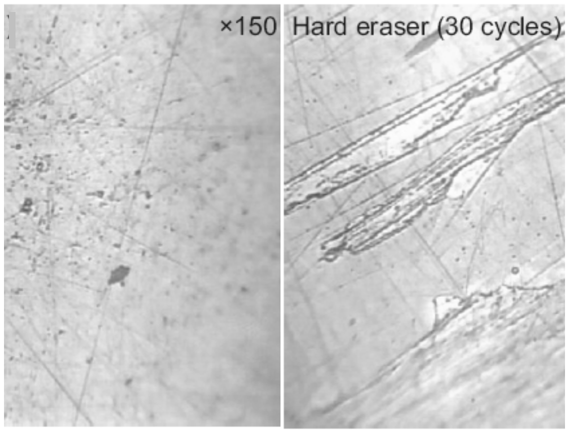

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Fig. 7. $AlN+Al_2O_3$ film abrasion resistance testing: a – after the eraser soft side effect (70 cycles); b – after the eraser hard side effect (30 cycles)

It is evident that in the case of eraser soft side influence on the film, it remains in the previous condition. At the same time 10 cycles of alternate motion effect of the eraser hard side produce many scratches. The explanation is that rubber of the eraser hard side is more elastic and the force of abrasive particles pressure on the film is much higher than of the eraser soft side. Absence of the scratches and chips in the case of the eraser soft side effect proves that the film is able to protect the details only from small and shallow scratches. The conclusion is that the film protects the substrate soft surface only in the case of light mechanical effect.

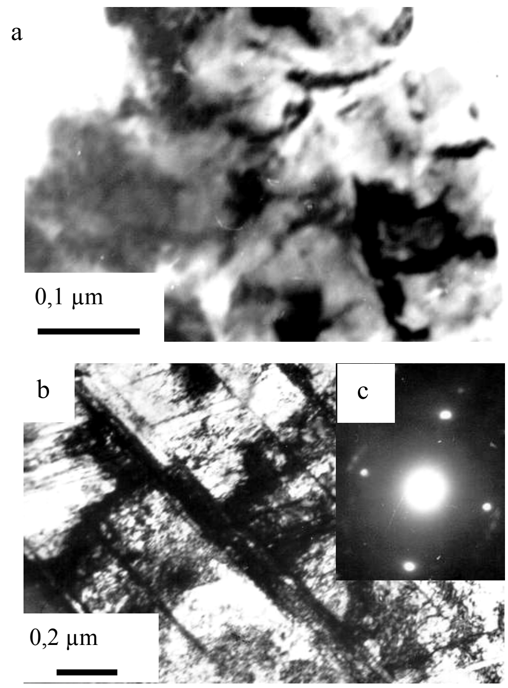

Fig. 8. TEM image of defective substructure, formed in surface layer of Ag substrate (a), stainless steel (12X18H10T) substrate (b) and microdiffraction (c) as a result of CH-film coating

In Fig. 8 are resulted TEM images of a defective substructure of silver substrate (Fig. 8, a) and stainless steel 12X18H10T substrate (Fig. 8, b) coated by CH-films. The microdiffraction analysis shows, that the formed CH-film is amorphous-crystal and contains graphite crystal islands with hexagonal or cubic lattices. Substrates surface layers are deformed during film coating. At silver substrate it expressed as fragment substructures appearance (Fig. 8, b); at steel 12X18H10T substrate – in plural microtweedleduming, essential increase in scalar density of dislocations, bend-torsion of a crystal lattice, metal surface layer chemical compound changing, that indicated by diffusion streaks presence near the matrix reflexes, revealed by microdiffraction analysis method (Fig. 8, c). These facts shows, that the presented process of protective carbon film coating is accompanied by simultaneous hardening of a substrate surface layers. The last is the additional factor of increasing of rather soft precious metals resistance to scratching, deforming and wearing.

4. Conclusion

1. The method of transparent protecting film deposition is developed and realized. The amorphous hydrocarbon deposition provides good adhesion of the film to substrate, and sufficient chemical resistance level. At the same time the film doesn't worsen the appearance of treated details.

2. AlN and Al_2O_3 film deposition could be used for anticorrosion protection of details made from soft metals and alloys. It is preferred to apply such film deposition for the details which are not planned to be used under great mechanical effect. The hardness of the deposited film is up to 1200–1500 kg/mm^2, that is enough for preventing small scratches.

3. Analysis made using diffraction electron microscopy revealed that regardless of substrate type, the deposited carbon film is amorphous and contains nanosize particles of graphite which has crystal lattice of hexagonal-modification.

4. The deposition of protective hydrocarbon film is accompanied by substrate pre-surface layer deformation. Thus, in stainless steel the following processes occur: the formation of deformation microtwins, the increase in scalar density up to $4.6 \cdot 10^{10}$ cm^{-2}, and curve-torsion of crystal lattice which is revealed on light field structure images taking the form of curve extinction contours. Simultaneously with surface deformation, the film deposition is accompanied by change of metal surface layer chemical composition. It is proved by the fact that near matrix reflexes the diffusion streaks which became evident after applying microdiffraction analysis method.

Acknowledgements

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