Formation, Structure, Phase Composition and Physicotechnical Attestation of Protective Coating with Cr-Y Composition[1]

D.S. Vershinin, N.V. Gavrilov*, I.M. Goncharenko,
Yu.F. Ivanov, Yu.A. Kolubaeva, O.V. Krysina, N.N. Koval

Institute of High Current Electronics, 2/3 Akademichesky ave., Tomsk, 634055, Russia,
Tel.+7-3822-491713, Fax +7-3822-492-410, E-mail: potter@opee.hcei.tsc.ru
**Institute of Electrophysics UD RAS, Ekaterinburg, 620016, Russia,*

Abstract – The uniform chromium coatings with a thickness of ~1,0 μm and different concentration of an yttrium (from 1 up to 15 %), that uniformly distributed in bulk, were formed by plasma-assisted deposition in low-pressure arc discharges plasma. It was shown that the coating consists of submicron chromium crystallites and nanocrystalline yttrium particles distributed on borders. The obtained results of investigations and described construction of the electrophysical device for a deposition of protective Cr-Y coatings from low pressure arc discharges plasma are the fundamentals for broad usage of perspective technology of surface modification of materials and articles.

1. Introduction

It is known [1–5], that small additions of rare earth and other actively oxidable elements (including yttrium) increase high temperature oxidation resistance of alloys making Cr_2O_3 compound. Due to these additions entire oxide layer is formed at smaller chromium concentration in the alloy, speed of oxide film growth decreases, adhesion of scale and bulk improves, Cr_2O_3 scale grain size decreases.

The purpose of these investigations were: 1) the development of formation technique of dense, high-adhesion and homogeneous (in volume and surface) coatings such as Cr-Y type; 2) the attestation of physical-mechanical properties, structure and phase composition of these coatings; and 3) an expert evaluation of the promise of arc-discharge plasma-assisted deposition of dense, high-adhesion coatings with a homogeneous surface and consistency. These coatings can have a thickness up to several microns on metals and alloys. The metals and alloys on which these coatings reside can include steel up to a several hundred square centimeters, along with metals and alloys with anticorrosive properties.

2. Materials and methods of investigation, plating method

The subject of investigation was Cr-Y coatings (thickness not less than 1 μm). These coatings were formed on steel substrate by deposition from dense homogeneous plasma in big vacuum volumes that is generated by high current low pressure arc discharges.

Coating investigations were carried out by methods of SIMS, optical, SEM and TEM, X-ray diffraction. Coating mechanical properties were investigated by scratch-test at increasing normal load from 0,1 up to 2,0 N during 1 minute of diamond indenter with a radius of 400 μm to investigated samples surface. The speed of sample lengthwise movement regarding diamond needle was 8 mm/min.

Coating formation was carried out on modernized technological installation for a vacuum – arc deposition NNV 6.6-I1. The work space of chamber has ~0,25 m^3 and it is pumped out up to limiting pressure of 10^{-3} Pa; chamber internal walls are made of stainless steel and used as an anode. Installation gas feed was carried out by two-channel automatized precision system. We used argon for work. The chamber is equipped by electromechanical manipulator for replacement of treated samples with sizes of 25×25 mm^2, made of polished steel with thickness of 1 mm. that samples were located on the manipulator in work chamber centre on the distance of ~300 mm from arc evaporators from which we made coating deposition. At deposition that samples turned and it allowed improving of coating deposition homogeneity. For preliminary cleaning and activation of samples surface "PINK" source of low temperature gas plasma [6], located on the work chamber top flange was used. Due to argon flooding to "PINK" source the pressure in chamber was ~10^{-1} Pa. The non-self maintained arc discharge with current of 30–50 A at burning voltage of 30 V was initiated in plasmagenerator electrode system. The discharge generated argon plasma with the concentration of 10^9–10^{10} cm^{-3} in work chamber. The negative bias was given to the treated samples. Power supply provided stepless control of negative bias voltage on treated samples regarding anode up to –1500 V. It was equipped by arc blowout system, preventing microarcs functioning

[1] The work was supported by RFBR grant (05-08-18068-a)

on treated samples surface and keeping them from erosion and damages. Due to samples bombarding by argon ions having energy corresponding negative bias of –700 V, we made finish cleaning and activation of substrate surface. It contributed to adhesion of surface to substrate. Then were switched on two arc evaporators simultaneously, their first cathode was made of chromium, another- of yttrium. Deposition was fulfilled due to cathode spot shifting in magnetic field on water-cooling cathode surface [7]. We set arcs currents according to necessary yttrium concentration in coating and made conduct deposition. Arc current of evaporator with a chromium cathode was varied in range of 70–90 A, yttrium evaporator arc current was in range of – 15–60 A. Argon work pressure was 10^{-1} Pa.

Surface thickness was determined by arc evaporators current and deposition time, which approximately was 1 hour. Changing of element composition of Cr-Y coating in range from 15 % and less is provided by variation of these elements ion currents ratio due to changing in discharge currents of both evaporators of pure metals. For improvement of coating structure and density the bias of –600 V was given to the sample during deposition. Plasma assistance was made due to argon plasma generated by "PINK" plasmagenerator. Discharge current of "PINK" plasmagenerator was no more than 10 A.

3. Investigation results and its discussion

It was established by methods of optical and scanning electron microscopy that coating structure in volume is dense and visually looks like homogeneous (fig. 1). Defects in form of columnar structure, interstices or delaminations are not observed. We can make a conclusion according to fracture pattern that coatings are plastic and have a good adhesion with the steel substrate. Independently on used at work deposition regimes the definite quantity (1–3 %) of microdrop fraction is fixed on surface and in volume of coating. Inclusion volume fraction and average sizes of drops are the controlled parameters and depend on deposition regime and way of sample protection from drops.

Investigations of coating integral elemental composition were carried out by SIMS methods, also using EDAX ECON IV microanalyzer (attachment to SEM 515 Philips scanning microscope). Using EDAX ECON IV microanalyzer we analyzed besides of it the elemental composition of microdrop fraction. Analyze results of coating integral elemental compositions showed that used here deposition method leads to chrome-yttrium coating formation and average yttrium concentration in it changes according to deposition regime from ~1 up to 14 at. %. At that high bound of yttrium content in coating practically is not limited and can be increased significantly. Low bound of yttrium content in coating is limited by microdrop fraction inclusion volume, which, as it was shown by EDAX analysis made, is formed by yttrium in most of cases (~90 %). Drop fraction presence is a consequence of using of coating getting arc discharge method, at which microdrops are present as well at direct flow of plasma passing from arc cathode area, as due to their numerous reflections from vacuum chamber walls, accessory, screens and other elements of installation construction [8]. In this case different variants of drop fraction formation suppression in coating are possible. For example, using of filters of different construction and actions preventing from drop ingress to the sample [9–11].

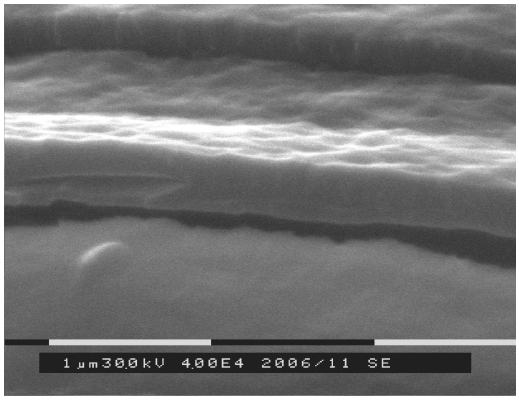

Fig. 1. SEM fracture cross-section of chrome-yttrium coating formed on steel substrate by plasma-assisted deposition in low pressure arc discharges plasma

TEM and of X-ray diffraction methods allowed conducting investigations of phase composition, morphology, defective substructure and chrome and yttrium distribution in coating. It was established that at evaporation of two cathodes the coating contents nanosize crystals of two phases-chrome and yttrium is formed on the surface. The main phase under the relative reflections intensity is chrome. Chrome crystallites sizes change in range of 40–50 nm. Yttrium particles are located along chrome crystallites boundaries (yttrium particles are pointed by arrows on the Fig. 2), average sizes of yttrium particles are ~10–12 nm. From analyses of Cr-Y system condition balanced diagram [12] it is following that crystallization from Cr-Y melt leads to firstly formation of practically pure chrome grains with displacement of yttrium atoms to the crystallization bound. At achieving of yttrium concentration in the melt up to ~80 at.% yttrium crystals are formed. Obviously, that changing crystallization conditions it is possible to influence on sizes of chrome and yttrium crystallites and their distribution in coating volume. Such mechanism of crystallization can be realized at arc discharge deposition of Cr-Y type coatings. Probably, due to additional energy deposition of ions accelerated in wall layer of space charge near condensa-

tion surface observed size of yttrium crystallites is less than in case of two-phase structure formation from the melt. Thus using of low pressure arc discharge plasma leads to formation on steel substrate of nano-size coating based on chrome crystallites with distributed along boundaries and in crystallites boundary junction yttrium particles.

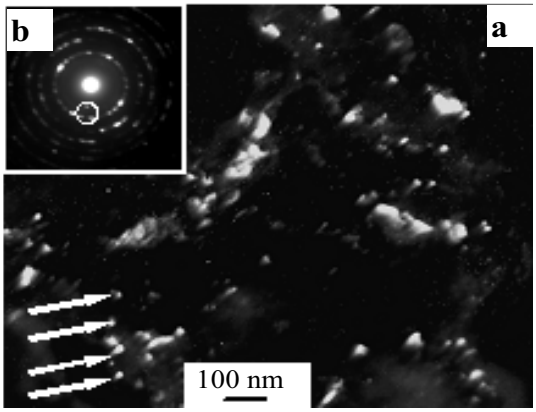

Fig. 2. TEM image of coating formed on steel substrate by plasma-assisted deposition in low pressure arc discharges plasma. a – TEM dark field image, obtained in reflections [100]Y+[110]Cr, b – diffraction pattern (area of reflections, formatting dark field is limited by circle). Yttrium particles are shown by arrows on (a)

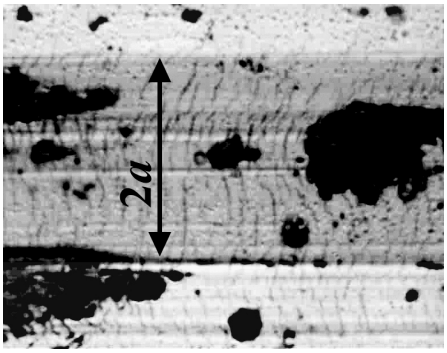

Fig. 3. Optical image of a track part made by diamond indenter during Cr-Y coatings scratch-test

Investigations of adhesive strength of Cr-Y coatings deposited on 12X17 steel substrates by arc discharge method at different regimes were carried out using scratch-test (scratching method). Characteristic optical image of sample surface with a track part made by diamond indenter during Cr-Y coatings scratch-test is given on Fig. 3. Detection of L_c critical load values when an event characterized for failure beginning is registered was carried out by optical microscopy methods. We measured the breaking point of Cr-Y coating deposited at different regimes measuring the width of flute on the track part using optical microscope and upsetson the flute bottom, which show coating failure beginning due to shear deformation. Estimations of breaking point value, made under known correlation [13], show that at load increase on coating surface at indentor movement relatively to the sample it was not observed any visible fluctuations in friction coefficient behavior, frictional force or acoustic signal. Due to Cr-Y plastic coatings they have not a high hardness (~300 kg/mm^2), main creteria for their failure investigation was just one parameter – location of deformation beginning and surface buckle on parts of trackmade by diamond indenter. They become apparent in upsets appearance with increase of normal load value exceeding critical L_c. using experimentally obtained L_c values we calculate shear stress magnitudes which are in range of 40–50 MPa. These values dot show films adhesion to the substrate, just characterize own coating strength. Observing thus coating failure we didn't observed its breakaway from the substrate according to any sctatch-test parameter. Obtained data indirectly characterize high strength of adherence of coatings with the substrate.

4. Conclusion

1. Uniform coatings of chrome-yttrium composition with satisfactory adhesion and different yttrium content (from ~1 up to ~14 at. %) uniformly distributed in volume of solid solution based on chrome were formed by method of vacuum-arc plasma-assisted deposition on steel substrate. Coatings thickness in all cases exceeds ~1,0 μm.
2. It was shown that coating composition is controlled by correlation of each deposited element ion currents due to control of evaporators discharge current in range from 70 up to 90 A for chromium cathode and from 15 up to 60 A for yttrium cathode. Speed of deposition of coating uniformly distributed on the substrate with an area of several hundreds of square centimeters is ~1 m/h. At increase of deposition process time and number of arc evaporators there is a real possibility to get Cr-Y system coatings with a thickness of ~10 μm with satisfactory homogeneity of yttrium distribution in coating volume.
3. In conducted series of experiments we could not obtain coatings with yttrium content less than ~1%. It was expressed an assumption that the last one is caused by absence of effective screening of deposited samples from microdrop flow passing from yttrium cathode.
4. It was displayed that high energy of ions (more than 100 eV), bombarding coating in process of its growth leads to obtaining of dense pore-free without columnar structure chromium coating with distributed in volume yttrium.
5. We displayed the next zoom levels of yttrium distribution in coating. Firstly, submicro- and microlevel are yttrium islands and have a form of drop fraction on coating surface. Secondly, nanolevel is particles of nanometer range and they are

distributed uniformly along chrome crystallites. Thirdly, it should suppose a presence of atomic level-formation of solid solution of yttrium atoms in chrome.

References

[1] *Spravochnik po redkim metallam* / Ed. by. V.E. Plyuscheva, Moscow, Mir, 1965, 945 pp.

[2] F. Riffard, H. Buscail, E. Caudron, R. Cueff, C. Issartel, S. Perrier, Journal of Material Science 37, 3925 (2002).

[3] S.M.C. Fernandes, L.V. Ramanathan, Surface Engineering 16, 327 (2000).

[4] F.J. Perez, M.J. Cristobal, M.P. Hierro, F. Pedraza, G. Arnau, T.P. Merino, Surface and Coatings Technology 126, 116 (2000).

[5] M.J. Cristobal, P.N. Gibson, M.F. Stroosnijder, Corrosion Science 38, 805 (1996).

[6] L.G. Vintizenko, S.V. Grigoriev, N.N. Koval, V.S. Tolkachev, I.V.Lopatin, P.M. Schanin, Izv. Vyssh. Ucheb. Zaved. Fizika 9, 28 (2001).

[7] I.I. Aksenov, V.G. Padalka, V.M. Horoshih, Fizika plazmy 5, 607 (1979).

[8] I.I. Aksenov, I.I.Konovalov, E.E.Kudryavceva et al., ZhTF 54, 1530 (1984).

[9] A. Anders, S. Anders, I.G. Brown, Plasma Sources Sci. Technol 4, 1 (1995).

[10] A.I. Ryabchikov, S.V. Degtyarev, I.B. Stepanov, Izv. Vyssh. Ucheb. Zaved. Fizika, No. 4, 193 (1998).

[11] M. Keidar, I.I. Bellis, R.L. Boxman, IEEE Trans. Plasma Sci. 23, 902 (1995).

[12] *Diagrammy sostoyaniya dvojnyh metallicheskih sistem* / Ed. by. academician RAS N.P. Lyakisheva, Moscow, Mashinostroenie, 1997, 200 pp.

[13] J. Valli, J. Vac. Sci. Technol. A. 4, 3007 (1986).