Diffusion Degradation of Carbon Coatings on Various Metallic Substrates

B. Straumal[1,2], N. Vershinin[2,3], A. Asrian[2,3] and M. Friesel[4]

[1] Institute of Solid State Physics RAS, Chernogolovka, Moscow District, 142432 Russia

[2] I.V.T. Ltd., P.O. Box 47, 109180 Moscow, Russia

[3] SONG Ltd., P.O. Box 98, Chernogolovka, Moscow District, 142432 Russia

[4] SIMS Laboratory, Chalmers University of Technology, Fysikgränd 3, 41296 Gothenburg, Sweden

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Abstract. Carbon belongs to the class of materials with large field of potential applications. Particularly, the novel forms of carbon can be very advantageous in form of rather thin coatings deposited on various substrates. Unfortunately, in case of metallic substrates the carbon diffusion into the substrate during the deposition and during the life-time of the coated part can deteriorate drastically its properties. For the deposition of diamond-like coatings the novel industrial vacuum arc apparatus «Nikolay» was used which allows one to coat the large area parts with dimensions up to 2100x1400 mm. This apparatus comprises the novel Hall current accelerator for ionic cleaning and implantation of substrates. The accelerator has a large aperture of 1400 mm and a power up to 10 kW. The diamond-like coating was deposited simultaneously in the identical conditions on the polished substrates of polycrystalline austenitic stainless steel (with fcc structure), ferritic low-carbon steel (with bcc structure), copper and (for comparison) on silicate glass. Depth profiles measured with the aid of secondary-ion mass spectroscopy are presented. The carbon profile on the silicate glass remained unchanged. In case of copper substrate only slight diffusion broadening of the carbon profile was observed. On the contrary, the diamond-like coatings on both steel substrates were almost completely dissolved in the substrates. Therefore, the special interlayers has to be deposited on the steel substrate in order to prevent the duffusion deterioration of carbon coatings. The role of the grain boundary diffusion and grain boundary phase transformation is also discussed.

Introduction

Diamond and diamond-like (DLC) films are of interest for many technological applications as a consequence of their outstanding combination of properties such as very high hardness, low coefficient of friction, high wear resistance, high thermal conductivity and chemical inertness. In particular, diamond film coatings for tribological applications have a high technological potential. However, to realize these applications, excellent adhesion of the films to the substrate and controlled deposition onto complex geometries are required. The novel vacuum arc technology for deposition of hydrogen-free DLCs was developed recently [1–10]. The deposition of diamond and DLC films on various metallic substrates or interlayers like Cr [11,12], Ni [13–15], Pt [16–21], Ti [22–24], Ir [2530], Cu [31], W [32] evoked the big interest due to the important technological applications of DLCs and diamond. During the deposition of diamond and DLC various problems arize, in particular poor adhesion and diffusion of carbon into metallic substrate. Nevertheless, the data on the carbon diffusion into metallic substrates during and immediately after the deposition are very scarce (especially for Fe and Cu). However, it has been shown recently, that the (interstitial) nitrogen diffusion in fcc-steels can be anomally high under the influence of low-enenrgy high-density ionic flux [33]. Therefore, in this work the diffusion influence on composition of DLC deposited onto polycrystalline austenitic stainless steel (with fcc structure), ferritic low-carbon steel (with bcc structure), copper and (for comparison) silicate glass is studied.

Experimental

The diamond-like coatings were deposited on polycrystalline austenitic stainless steel (with fcc structure), ferritic low-carbon steel (with bcc structure), copper and (for comparison) silicate glass substrates with the aid of the installation "Nikolay" which comprises the vacuum arc unit and Hall current accelerator [34]. Hall current accelerator described elsewhere [35,36] has a form of elongated loop with vertical aperture of 1400 mm and horizontal aperture of 55 mm. No additional heating of the samples was used. Deposition time was 30 min. The composition of the steels was controlled by the spark spectral analysis according GOST 22536.13 "Carbon steel and cast iron. Methods of spectral analysis". The carbon content was measured coulombometrically according GOST 22536.1. The 12X18H9T austenitic stainless steel contains (in wt. %) 0.11 C, 17.0 Cr, 8.8 Ni, 0.35 Ti, 0.28 Mo, 0.55 Si, 0.35 Mn, Fe (matrix). The VSt-3-kp ferritic low-carbon steel contains 0.19 C, 0.12 Cr, 0.05 Si, 0.30 Mn. Samples having dimensions 20×15 mm were cut from the rolled steel strip of thickness 2 mm, ground and polished.

The distribution of C, O and H in the diamond-like coatings was determined using the secondary-ion mass spectrometry (SIMS). A Cameca IMS 6F secondary ion mass spectrometer has been used for in-depth analyses of the films and substrates. O_2^+ ions accelerated with energy 12.5 kV and Cs^+ ions accelerated with an energy of 11.1 keV were used as primary ions. The primary ion current I_p ranged from 250 to 1800 nA. The primary ion beam was rastered over a square area 250×250 μm. The secondary ions, accelerated by 4.5 kV, were collected from a square area 100×100 μm in the middle of the rastered area. The energy band pass filter for the secondary ions was 50 eV, centered at the maximum energy of the secondary ions. The distributions of Fe, C, O and H were studied by profiling the isotopes $^{56}Fe^+$, $^{24}C_2^-$, $^{12}C^-$,$^{16}O^-$ and $^{1}H^-$, respectively. The depth of the sputtered craters was measured with a *Talysurf 10* instrument (Rank Taylor Hobson, UK). Each crater was measured several times in the central region of the crater. The deviation in the average depth ranged from 2 to 11%. The microhardness of the diamond-like coatings was measured at loads from 0.1 to 0.85 N with the aid of a PMT instrument (LOMO, Russia).
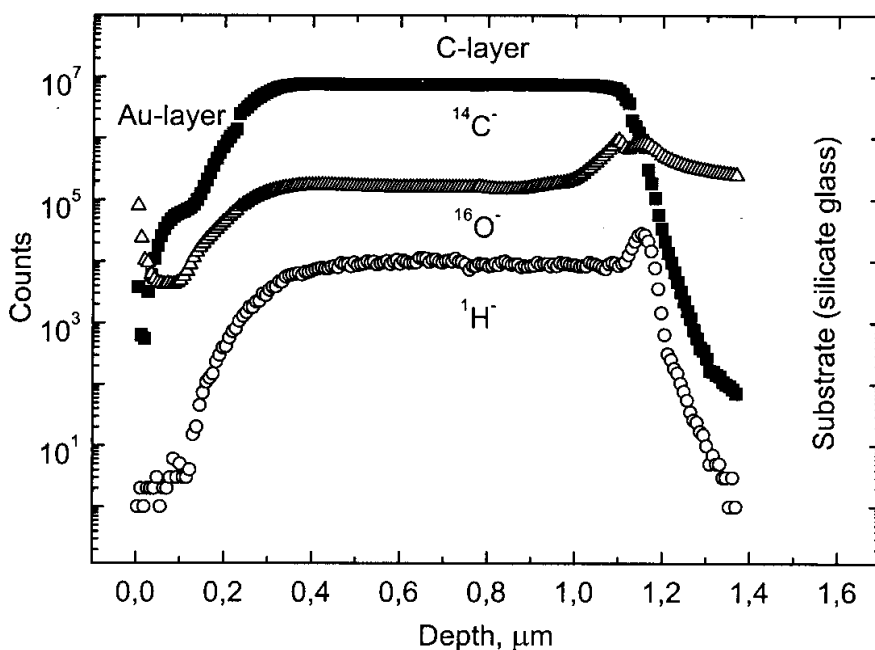

Fig. 1 C, O and H SIMS depth profiles for the DLC coating deposited on silicate glass substrate

Results and discussion

The diamond-like coating is almost uniformly transparent in the visible part of the spectrum (R is about 25 to 40 % in the wavelenghth range between 400 and 800 nm) [10]. The microhardness increases from 8.4 GPa (load $P = 0.5$ N) to 9.7 GPa ($P = 0.2$ N). The microhardness of glass substrate is 6.5 GPa. The SIMS depth profiles for $^{12}C^-$, $^{16}O^-$ and $^1H^-$ in the diamond-like coating are shown in Fig. 1. A gold layer was evaporated on the surface of the coating due to the very low conductivity of the diamond-like coating (left part of the spectrum). The count rate I for the $^1H^-$ secondary ions is about 0.001 I for $^{12}C^-$ and I ($^{16}O^-$) is about 0.01 I ($^{12}C^-$). This feature indicates the low concentration of H and O. I for C, O and H is constant in the whole film. In [10] it has been shown that the Raman scattering spectrum of the diamond-like coating contains two high peaks at 546 and 1086 cm^{-1} and weaker one at 789 cm^{-1}. Neither the characteristic sharp diamond peak at 1332 cm^{-1} nor the broad feature at 1550 cm^{-1} corresponding to the graphitic G band [37] are present in the spectrum. The peaks obtained can be assigned to nanophase diamond [38]. Particularly, the peaks at 1086 and 789 cm^{-1} correspond to the C–C modes in diamandoids like adamantane $C_{10}H_{14}$ and diamantane $C_{14}H_{20}$ [38–40]. On the other hand, the high energy lines (2600-3000 cm^{-1}) corresponding to the C–H modes are not present in the spectra. This fact is supported by the low H content in the coating (Fig. 1).
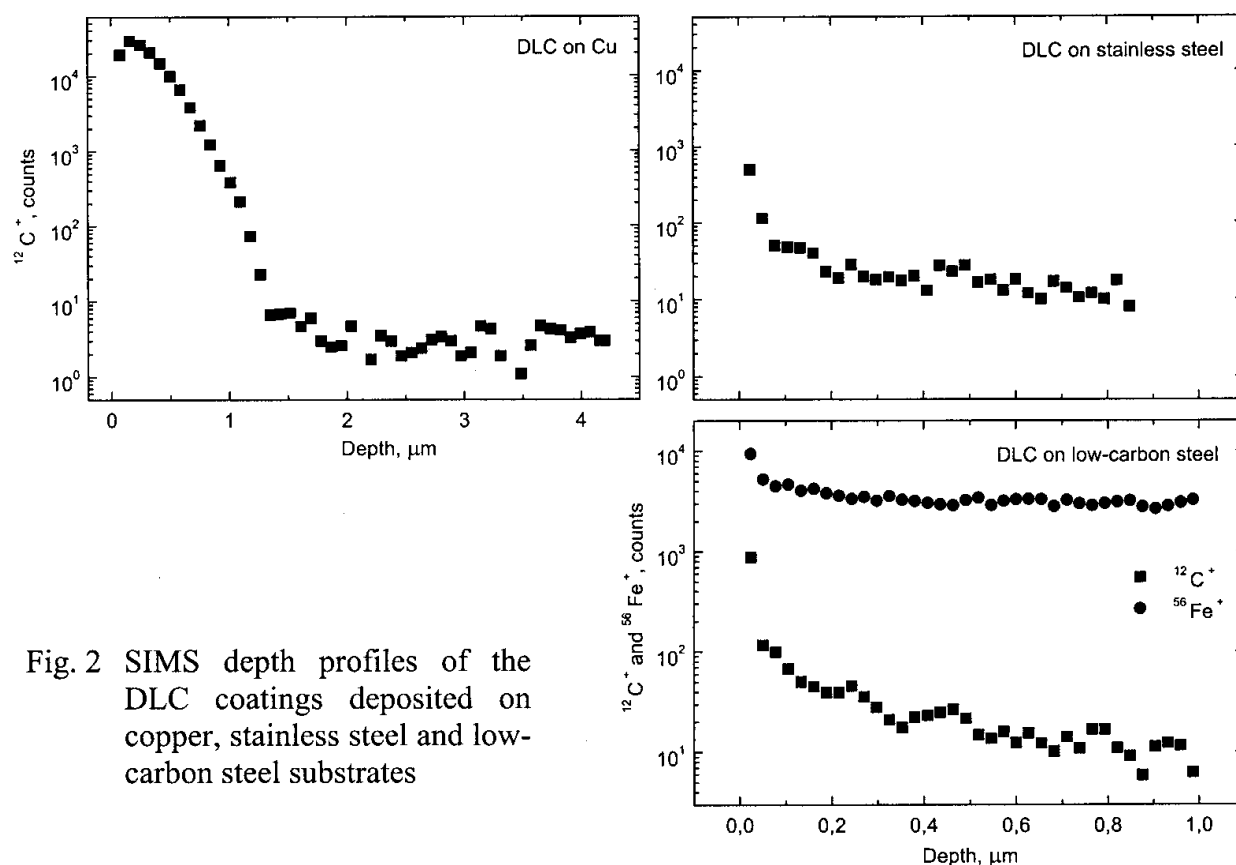

Fig. 2 SIMS depth profiles of the DLC coatings deposited on copper, stainless steel and low-carbon steel substrates

In the Fig. 2 SIMS depth profiles of the DLC coatings deposited on copper, stainless steel and low-carbon steel substrates are shown. In case of silicate glass the depth profile for C is almost step-like. The width of the transition area from C-layer to silicate glass substrate is about 50 nm and mainly depend on the artifacts like ion mixing during depth profiling and flatness of the crater. The
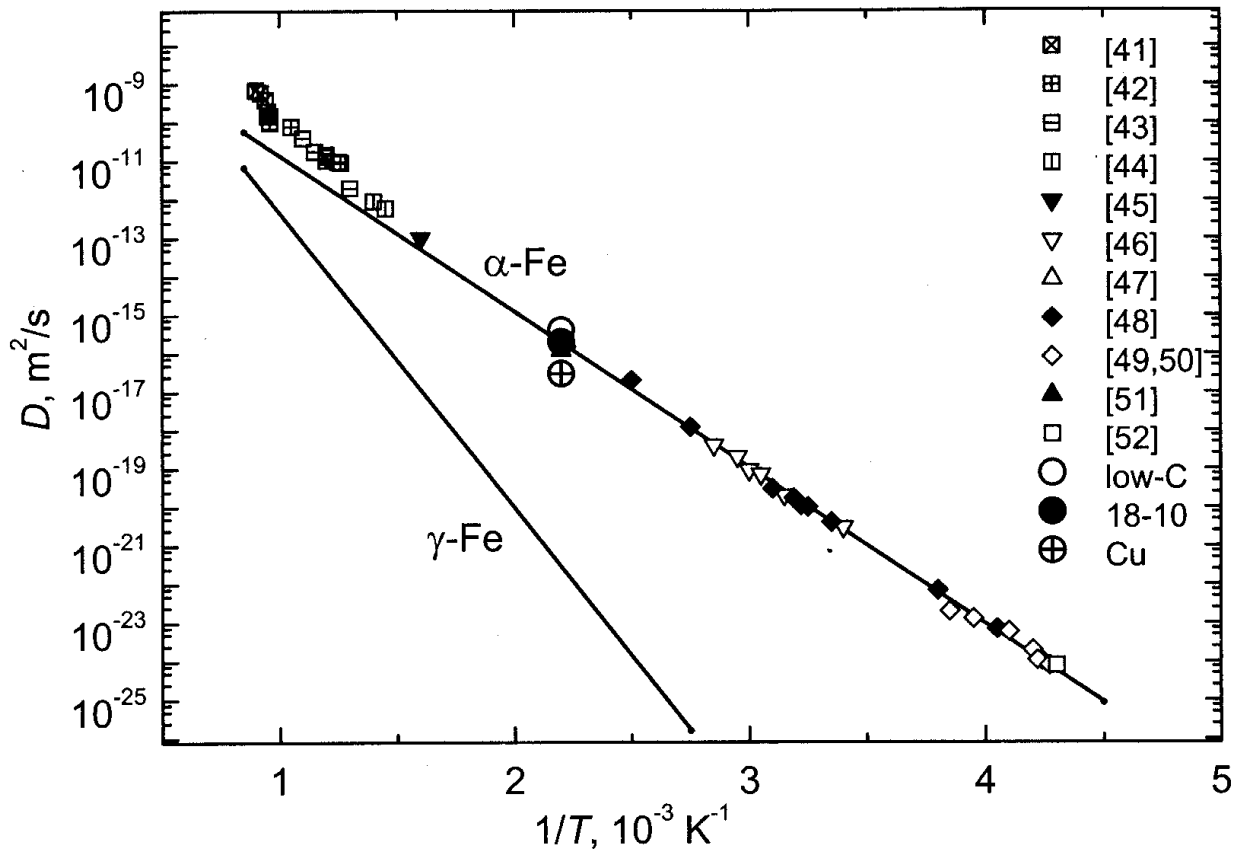
Fig. 3. The temperature dependence (Arrhenius plot) for the diffusion coefficient D of carbon in α-Fe [41–53], γ-Fe [54] and for the effective diffusion coefficient estimated as $D_{eff} = L^2/t$ from the SIMS the depth profiles of DLC layers on low-carbon ferritic steel (low-C), austenitic stainless steel (18-10) and copper obtained in this work

penetration depth of carbon is for Cu is higher. Carbon concentration decreases 10 times at the distance of about 0.2 μm. Similar distances for low carbon steel and that for stainless steel are 0.5 and 0.7 μm, respectively. Using these data, the effective diffusion coefficient was estimated as $D_{eff} = L^2/t$ for DLC layers on low-carbon ferritic steel, austenitic stainless steel and copper. These data are shown in Fig. 3 together with available data for carbon diffusion in α and γ iron. In Fig. 3 the solid line interpolating the data for α-Fe (pre-exponential $D_o = 1.67 \cdot 10^{-7}$ m²/s, activation energy $Q = 78.08$ kJ/mol) is drawn according to the data [53]. The line for the carbon diffusion in γ-Fe is the extrapolation from high temperature range of existence of γ-phase ($D_o = 2.34 \cdot 10^{-3}$ m²/s, $Q = 147.81$ kJ/mol) obtained in [54] for the limit of zero carbon concentration. The D_{eff} value for low-carbon ferritic steel corresponds to the D value for α-Fe at about 200°C. The respective D_{eff} value for austenitic stainless steel is only slightly lower that that of value for low-carbon ferritic steel, but many orders of magnitude higher than extrapolated value for γ-Fe. Similar behaviour of austenitic stainless steel was observed by us also for low-energy high-current ionic implatation of nitrogen [33]. The high diffusivity in surface layers can be explained by the formation of amorphous or

nanograined material. Recently it was shown that grain boundaries (GBs) in two- or multicomponent systems can contain a stable layer of a GB phase which is unstable in the bulk [55–58]. The presence of such a GB layer can lead to an enhancement of the GB mobility [57], GB segregation [56,58] and GB diffusivity [55]. In nanostructured materials up to 1/3 of all atoms can belong to the GB, and an increase of the diffusivity can be immence in comparison with coarce-grained materials. We can suppose that in the surface layer of stainless steel during DLC deposition and N-implantation the layers of α-phase having higher diffusivity are present in GBs of the γ-matrix. Such layers can be responsible for D_{eff} values which are higher than the D values for γ-Fe but lower than those for α-Fe. The D_{eff} value for copper is more that one order of magnitude lower that that of both α-Fe and γ-Fe. It opens the way to use Cu and other fcc-metals as interlayers to prevent the carbon diffusion during the DLC deposition and the respective dissolution of DLC-films in steel substrates.

Conclusions

The carbon profile of the DLC layer on the silicate glass remained unchanged. In case of copper substrate only slight diffusion broadening of the carbon profile was observed. On the contrary, the diamond-like coatings on both steel substrates were almost completely dissolved in the substrates. Therefore, the special interlayers has to be deposited on the steel substrate in order to prevent the duffusion deterioration of carbon coatings. The grain boundary diffusion and grain boundary phase transformation can contribute significantly to the dissolution of C in steel substrates.

Acknowledgements

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