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Investigation of anti-corrosion properties of Ti:C gradient layers manufactured in hybrid deposition system

D. Batory · T. Blaszczyk · M. Clapa ·
S. Mitura

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Abstract Excellent properties of hard carbon layers and especially, the unique combination of tribological, chemical and physical properties make them a popular coating material for use on surgical prosthesis, biomedical implants, and machine tools. However, their well-known poor adhesion and high internal stress disqualifies them in many possibilities of industrial applications. These drawbacks were improved by deposition of Ti buffer layer. By a combination of Radio Frequency Plasma Assisted Chemical Vapor Deposition (RFPACVD) and DC magnetron sputtering methods, thick carbon films were manufactured on Rex 734 steel. Structure and chemical composition of deposited layers was determined by scanning electron microscope and energy dispersive spectrometer analysis. The main purpose of this work was to determine the corrosion properties of Rex 734 alloy in a typical 0.5 M NaCl solution and to find the influence of Ti:C gradient layers on these properties. Anti-corrosion behavior was measured by the detection of corrosion potential in open circuit and the registration of potentiodynamic characteristics according to Stern–Geary and Tafel methods. Five different types of samples were studied: for full analysis the investigation was conducted for every structural component of the layer: for pure Ti deposited on Rex 734 as well as for Ti containing carbon layer and carbon layer deposited subsequently, and finally the corrosion resistance of Rex 734 steel was measured for comparison. As a result of the investigation it was noticed that the Ti–C interlayer enables to maximize the thickness of DLC films and Ti:C gradient layers have the good influence on the corrosion features of Rex 734 alloy.

Introduction

Rex 734 (ISO 5832-9) and AISI 316L (ISO 5832-1) have been very often used as biomaterials for orthopedic implants. The chemical composition of the Rex 734 alloy is presented in Table 1 [1].

Although it is one of the best austenitic FeCrMo alloys, then also for this biomaterials localized corrosion such as pitting, crevice, and stress corrosion cracking can be observed. Investigations of corrosion features of this alloy have been widely performed in different solutions using electrochemical methods [1–3]. One way of improving both mechanical and corrosion features of biomedical materials is the deposition of carbon layers using the Radio Frequency Plasma Assisted Chemical Vapor Deposition method (RF PACVD) [4–6]. Intensive scientific researches concerning carbon layers were performed for more than 25 years and found many possibilities for their industrial application. Due to their excellent correlation among mechanical, physical, and chemical properties, they became a promising material for medical, optical, mechanical, and tribological applications. Chemical inertness and good corrosion resistance became attractive parameters for wide range of technologies [7]. They are

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D. Batory (✉) · M. Clapa · S. Mitura
Institute of Materials Science and Engineering, Technical University of Lodz, 1 Stefanowskiego St., 90-924 Lodz, Poland
e-mail: damian.batory@p.lodz.pl

T. Blaszczyk
Department of General and Inorganic Chemistry, University of Lodz, 68 Narutowicza St., 90-136 Lodz, Poland

Table 1 Chemical composition of Rex 734 alloy (wt %)

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Nb	Fe
Rex 734 (ISO 5832/9)	Max. 0.08	Max. 0.75	2.00–4.25	Max. 0.025	Max. 0.01	19.5–22.0	9.0–11.0	2.0–3.0	Max. 0.25	0.25–0.50	0.25–0.80	Rest

used for corrosion protection and wear resistance improvement of magnesium alloys recently widely used in mechanical industry because of their high strength/weight ratio [8, 9] and also as an improvement of biocompatibility, mechanical, and corrosion properties of austenitic, Ti and C alloys used in medical industry for implants and surgical prosthesis [10–13]. However, there are also many widely discussed weak points of carbon coatings. Among them the most problematic is poor adhesion to the substrate surface caused by high internal stress. Thereby the attempt to deposit thick layers on some substrates results in layer self-delamination. There are many methods of improving adhesion of carbon layers. One of them is the deposition of gradient layers using Ti to decrease internal stress and improve adhesion to the substrate surface. This combination results in thick and well-adherent DLC layers useful in many special, technical applications [14, 15].

Microstructure of the Rex 734 surface was widely investigated [2, 16, 17]. Pan et al. [2] report the presence of precipitates on the nitrogen and niobium enriched surface. They suggest that this fact has no influence on corrosion resistance of the alloy. Giordani et al. [16] demonstrate scanning electron microscope (SEM) micrographs with coarse niobium-rich precipitates, associated with alumina-rich non-metallic inclusions. They made a hypothesis that non-metallic inclusions were the reason of corrosion, especially the fatigue kind. The full role of different precipitates, inclusions, etc., in localized corrosion is not known.

The main purpose of this work was to determine the corrosion properties of Rex 734 alloy in a typical 0.5 M NaCl solution and to find the influence of Ti:C gradient layers on these properties. The corrosion investigations were performed using electrochemical methods. A SEM with energy dispersive spectrometer (EDS) was used for microstructure and element analysis.

Experimental details

Manufacturing

Ti:C gradient layers were deposited on 3-mm thick Rex 734 samples having 25.4 mm in diameter which were mechanically grinded and polished with water-based, 3 μm diamond suspension. Specimens were ultrasonically cleaned in acetone for 20 min and placed on the RF electrode opposite to the magnetron sputtering system. A combination of two different deposition techniques DC Magnetron Sputtering and Plasma Assisted Chemical Vapor Deposition let to obtain gradient Ti:C layers. In order to improve the adhesion of DLC film, the Ti interlayer is deposited first. During the sputtering process, the carboniferous gas is introduced into the reaction chamber, its flow is controlled by the computer. Next, parameters of sputtering process are being decreased. When the sputtering process is finished, thick carbon layer is deposited. The deposition process was preceded by 10 min etching in RF discharge in argon with 600 V negative bias voltage. Precise information concerning technical and process parameters can be found in works [14, 15].

Coatings characterization

The thickness of deposited layers was determined on a SEM cross-sectional view and measured on a profile measurement gauge.

Gradient of chemical composition was measured on a SEM with EDS. The analysis was made on the profile of the cross-section.

Anti-corrosion behavior characterization

Corrosion measurements were carried out using PGSTAT 30 Autolab EcoChemie potentiostat/galvanostat. A glass electrolytic cell with volume ca. 25 cm^3 had a sample as working electrode E_w, Pt foil as counter electrode E_c, and calomel electrode in saturated NaCl solution as reference electrode E_{ref}. The reference electrode was connected to the cell by Lugin capillary, which was placed close to E_w. All potentials in this paper are given versus this calomel electrode ($E^0 = 0.236$ V vs. SHE). The sample was mounted on supporting plate with flat silicon gasket between the sample and the glass cell. Exposed area of each sample was ca. 3.1 cm^2 [3].

Corrosion measurements were done at 25 ± 1 °C in deoxygenated 0.5 M NaCl solution prepared with reagent without additional purification (POCH Gliwice) in triple distilled water. All sample surfaces were cleaned with ethanol and dried with argon before each experiment. The measurements were taken simultaneously on three identical samples and the results were averaged. The detection of corrosion potential in open circuit (OCP), the registration of potentiodynamic characteristics according to Stern–Geary and Tafel methods, and the electrochemical impedance spectroscopy EIS were used as experimental techniques (the results from the last method require additional analysis and are not presented in this paper). For one of the samples, the registration of potentiodynamic characteristic was done for a wide range of anodic polarization voltages [3]. Subsequently, the sample surfaces were analyzed using a metallographic optical microscope and a SEM with an EDS analyzer.

Results

Ti:C gradient layers were deposited in hybrid deposition system, which is the connection of RF PACVD and DC magnetron sputtering methods. Thickness of Ti intermediate layer was ~0.1 μm, subsequent deposition of Ti:C gradient layer resulted in total thickness ~0.2 μm, the deposition of final carbon layer gave 0.55 and 1.7 μm thick coatings.

Figure 1 presents the cross-sectional view of Ti:C gradient layer obtained on SEM and the direction of chemical composition analysis. Unfortunately poor resolution of the measurement method makes it hard to show the composition in the interface areas accurately (Fig. 2).

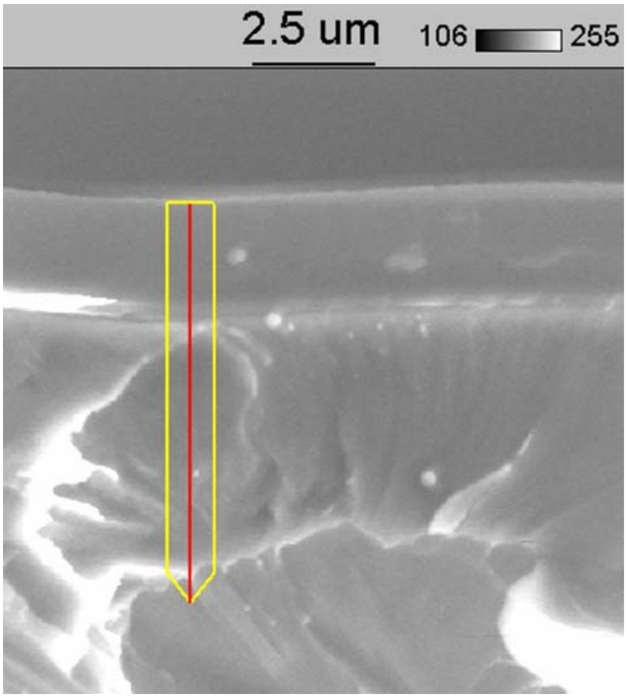


Fig. 1 SEM cross-sectional view of Ti:C gradient layer deposited on tungsten substrate, area, and direction of the chemical composition investigation is marked

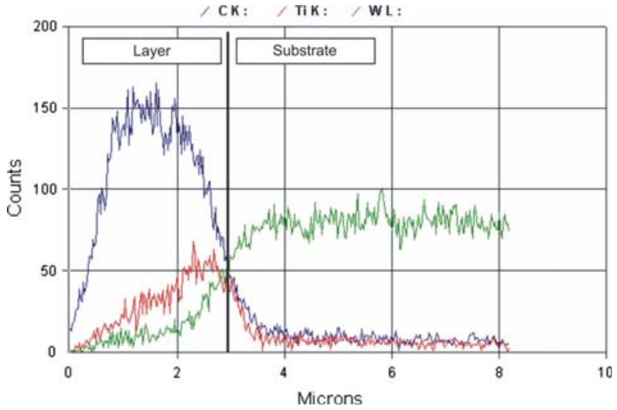


Fig. 2 Results of EDS analysis investigated on the line from the surface into the substrate direction for C, Ti, and W. The acceleration voltage was 25 kV

Corrosion potential, E_{corr}, was determined typically 2,000 s after the electrolytic cell was filled with the corrosion solution. A stable potential of measured sample in open circuit was taken as E_{corr}. The averages and standard deviations of the corrosion potential obtained for the investigated samples are presented in Fig. 3. The corrosion potential for Rex 734 without layers (marked as 0) has a value −0.14 ± 0.05 V which is very close to −0.16 V obtained for this alloy in other investigations [18]. Corrosion potentials for Rex 734 increase together with the types and the thickness of deposited layers. It is still negative for the pure Ti layer but rises considerably with the increasing amount of deposited carbon and reaches 0.22 ± 0.04 V for the thickest layer with about 1.5 μm of pure carbon. Potential E_{corr} for the samples with Ti interlayer is different from E_{corr} of Ti in solutions containing Cl^- ions [4], but E_{corr} for samples with Ti interlayer and Ti containing

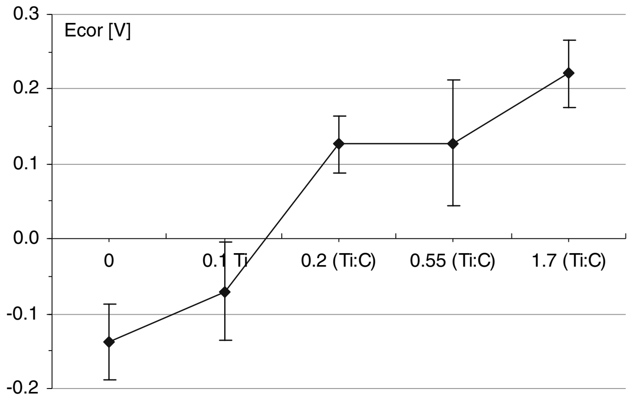


Fig. 3 Corrosion potential of Rex 734 vs. Ti:C gradient layers (averaged over three samples)

carbon layer are very close to potentials of Ti with carbon layers in the same solutions [19]. The corrosion potential for Rex 734 with 1.7 μm Ti:C layer is in agreement with the corrosion potential of Rex 734 with an NCD carbon [18]. Summarizing the results of corrosion potential measurements described above we can state that Ti, Ti containing carbon layers, and pure carbon layers have a good influence on this corrosion parameter of the Rex 734 alloy.

Polarization resistances were measured using the Stern–Geary method with the polarization of the sample changing from E_{corr} through $E_{\mathrm{corr}} - 0.02$ V, $E_{\mathrm{corr}} + 0.02$ V and back to E_{corr} at the rate of 0.5 mV s^{-1}. From the obtained potentiodynamic curves, the polarization resistance R_{p} and corrosion current i_{cor} were calculated using the CorrView (Scribner Associates Inc.) software. As can be seen in Fig. 4, the deposition of a Ti interlayer increases the polarization resistance but the further addition of a Ti:C gradient layer lessens this effect. This can be explained by the higher chemical activity of Ti interlayer with TiC carbides [19]. These carbides can be formed during the deposition process of Ti:C gradient layers. It is worth noticing that the subsequent deposition of a pure carbon layer results in polarization resistances two orders of magnitude higher.

Corrosion currents i_{cor} for the investigated samples are presented in Fig. 5. The course of this parameter is similar to the reciprocal of the course of R_{p}. In this figure, it is visible that thick carbon layers decrease the corrosion current by two orders of magnitude.

Corrosion rate (CR) can only be calculated for the Rex 734 without any layers, from the equation: (ASTM Standard G 102-89, Reapproved 2004 [20]):

$$\mathrm{CR}\left[\mathrm{mm\,year}^{-1}\right] = K_1 \frac{i_{\mathrm{cor}}}{\rho} \mathrm{EW},$$

where coefficient $K_1 = 3.27 \times 10^{-3}$ mm g μA^{-1} cm^{-1} year^{-1}, density of Rex 734 $\rho = 7.80$ g cm^{-3}, equivalent weight for Rex 734 EW = 24.58 (EW is considered dimensionless). In the calculation of EW, only elements above 1 mass% in the alloy were included. The obtained CR value $(4.9 \pm 2.3) \cdot 10^{-4}$ mm year^{-1} is in a good agreement with the CR of $(5.2 \pm 2.5) \cdot 10^{-4}$ mm year^{-1} presented in [18]. For the other samples with Ti layers, it is impossible to correctly calculate the value of CR because of unknown Ti contribution in corrosion current i_{cor}. In general, it can be stated that lower i_{cor} is connected with lower CR. According to this all described layers should give a decrease in corrosion rate and improve corrosion features of the Rex 734 alloy.

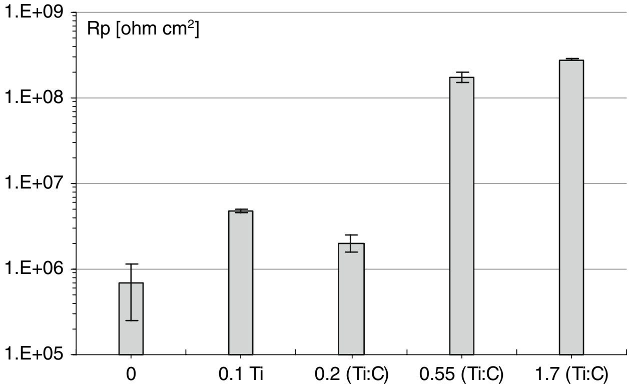


Fig. 4 Polarization resistance of Rex 734 vs. Ti:C gradient layers

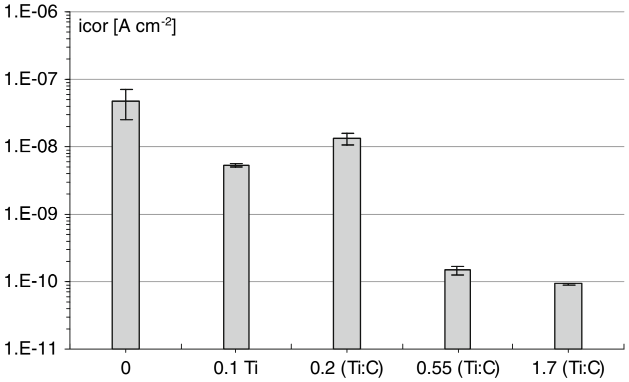


Fig. 5 Corrosion current of Rex 734 vs. Ti:C gradient layers

Tafel characteristics were measured using the potentiodynamic method with polarization in the cycle $E_{\mathrm{corr}} \rightarrow E_{\mathrm{corr}} - 0.20\ \mathrm{V} \rightarrow E_{\mathrm{corr}} + 0.20\ \mathrm{V} \rightarrow E_{\mathrm{corr}}$ at a potential scan rate of 1 mV s^{-1}. The obtained curves are presented in Fig. 6. From these curves, we can draw a conclusion that during the Tafel characteristics measurements for samples with thick carbon layers irreversible electrochemical reactions occurred. From these characteristics, it is impossible to calculate Tafel slope coefficients. The values of potentials confirm the corrosion potentials E_{corr} described above, and values of current densities

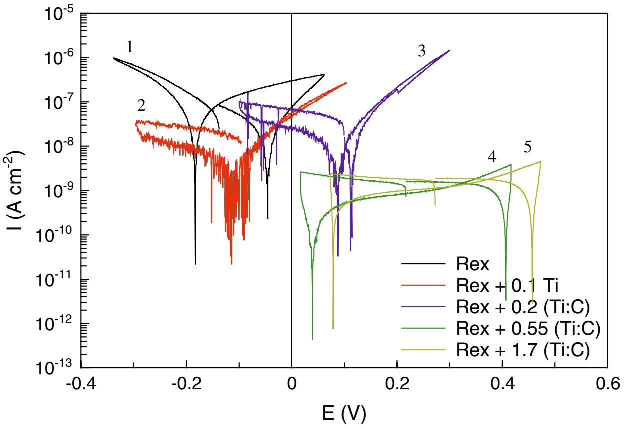


Fig. 6 Tafel characteristics of Rex 734 with Ti:C gradient layers

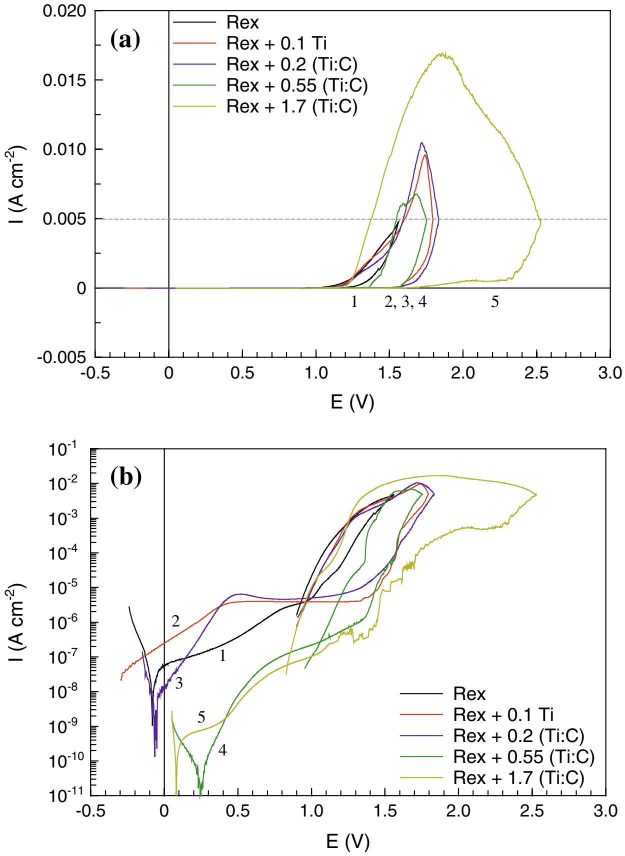


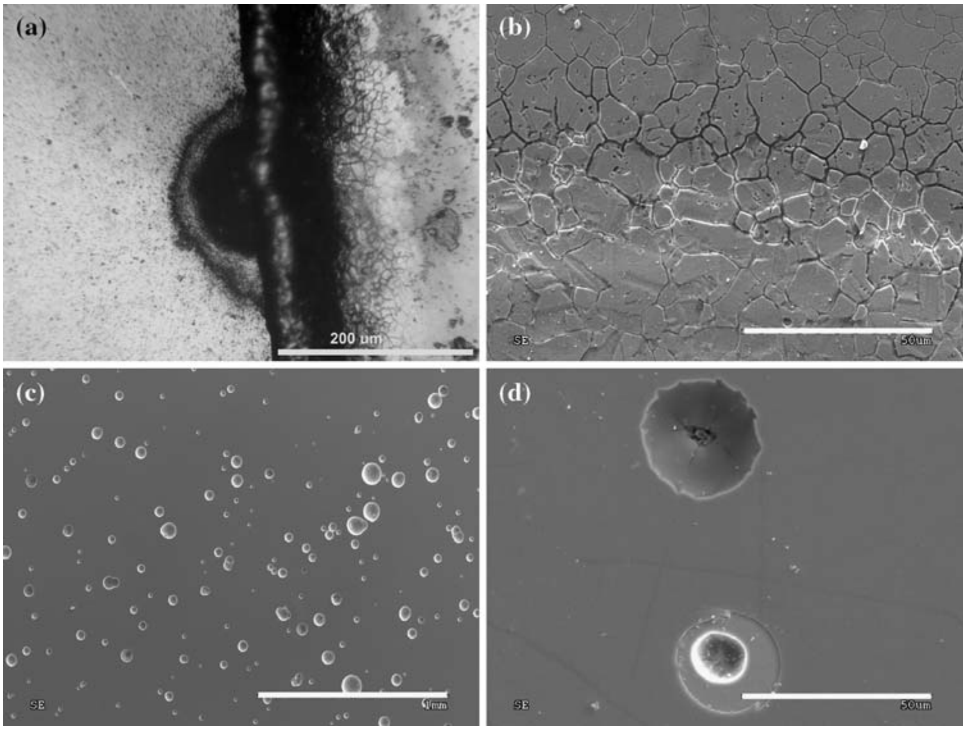
Fig. 7 Potentiodynamic characteristics in wide range of anodic polarization of Rex 734 with Ti:C gradient layers: (**a**) in linear scale (**b**) in logarithmic scale of current density

confirm that the samples with thick carbon layers have the best corrosion resistance.

Potentiodynamic characteristics were measured in a wide range of anodic polarization, starting from a potential more cathodic then E_{corr}, in anodic direction, up to a potential for which the current density achieved the value of 5 mA cm^{-2}. At this potential, the polarization was changed into cathodic direction and returned to start potential. The results are presented in Fig. 7 (without whole recurrent branch in logarithmic scale). Current hysteresis can be seen on each curve which is typical for pitting corrosion with growing of pits. The characteristics in linear scale very distinctly show the differences between the current densities flowing through examined samples. From both linear and logarithmic characteristics, it can be stated that Ti:C layers make a wider passivation range of Rex 734. On the basis of curves shapes, it is impossible to determine breakdown potential and estimate the influence of type of the layer on this parameter. Repasivation potentials for all samples are in the range from 0.84 to 1.06 V.

The wide range of applied anodic potentials produced great changes on sample surfaces. On uncovered Rex 734, only crevice and pitting corrosion close to the cell gasket was detected. For the other samples, the pits were randomly distributed on the whole surface. The crevice/pitting corrosion damages on the uncovered Rex 734 sample are shown in Fig. 8a and b, in Fig. 8c, the pits on Rex 734 with 0.2 (Ti:C) layer, and in Fig. 8d, pits on Rex 734 with 0.55

Fig. 8 Corrosion damages of Rex 734 with Ti:C gradient layers surfaces (see text)



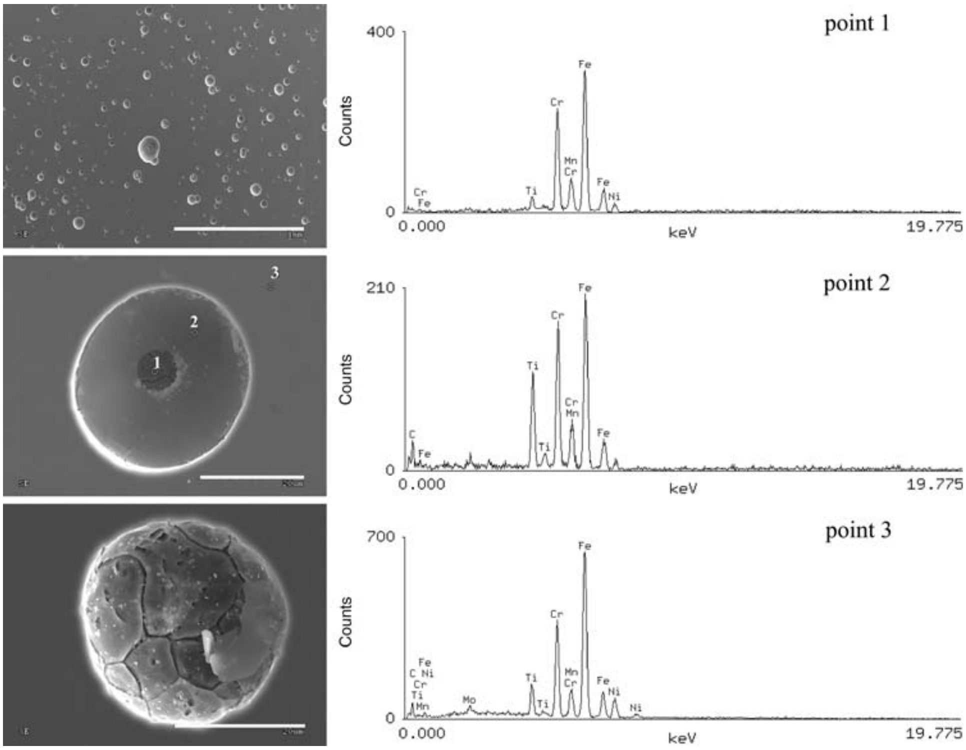


Fig. 9 Corrosion pits on Rex 734 with 0.1 Ti layer and EDS analysis results (see text)

(Ti:C) layer. Pits on Rex 734 with 1.7 (Ti:C) layer were larger and deeper but similar to those observed on Rex 734 with 0.55 (Ti:C) layer. Figure 9 shows three images of the corrosion damages on Rex 734 with 0.1 Ti layer. The first one is an overview of the surface while the other show two pits in more detail. SEM—EDS analyses were performed for three points marked on the second image and their results are presented on the plots. The first point is at the bottom of the pit, the second is on the Ti layer which floats over the pit, and third is on the flat sample surface. The weak Fe line on the second plot confirms that the steel substrate under the Ti layer got etched out. A pit in which this floating Ti layer delaminated is shown on the last image. The bottom of this pit corroded similarly to the uncovered Rex 734 (presented in Fig. 8b).

Choi et al. [9] describe the degradation of anti-corrosion properties of thick carbon layers connected with the appearance of cracks on the surface caused by high internal stress. In the presented research that kind of problems were not observed, which proves the positive influence of Ti inter- and transition-layers on stress intensity. The reasons of the pitting characteristics of the corrosion need further investigations. The EDS analysis unveiled the presence of niobium compounds (probably niobium carbide crystals) inside the pits (Fig. 10). It is possible that these structures cause additional local strain inside the layer which results in the formation of corrosion pits.

Conclusions

1. Ti:C gradient layers were deposited on Rex 734 alloy samples. The gradient of chemical composition made it possible to obtain thick and well-adherent carbon layers without cracks on the surface.
2. The Ti:C gradient layers improve the corrosion features of Rex 734 alloys giving a shift of corrosion potential in anodic direction and increase of polarization resistance.
3. These layers decrease the corrosion current and consequently also the corrosion rate at corrosion potential of the investigated alloy.

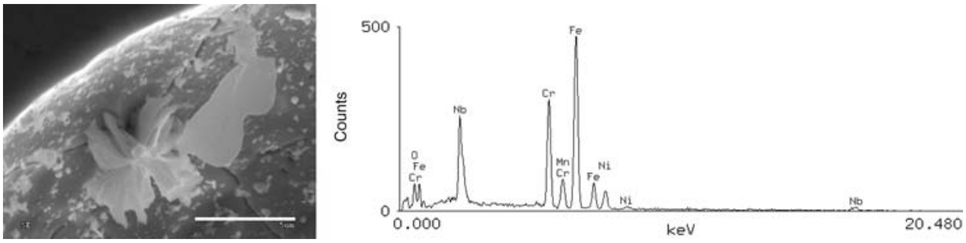


Fig. 10 Bottom of corrosion pit on Rex 734 with 0.2 (Ti:C) layer and EDS analysis results (see text)

4. The Ti:C gradient layers change localization of corrosion damages: from crevice/pitting corrosion failures which are only close to the gasket for uncovered Rex 734 to randomly distributed pits on the whole surface for the Rex 734 with layers.
5. These layers give a wider passivation potential range but do not change the character of growth of pits—for each specimen a hysteresis of current density was occurred.

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