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PHYSICOCHEMICAL AND ELECTROCHEMICAL PROPERTIES OF AISI 316L STAINLESS STEEL USED FOR IMPLANTS IN HUMAN URINARY SYSTEM

OCENA WŁASNOŚCI FIZYKOCHEMICZNYCH I ELEKTROCHEMICZNYCH STALI AISI 316L STOSOWANEJ NA IMPLANTY W UROLOGII

The main purpose of this study was to evaluate physicochemical and electrochemical properties of AISI 316L stainless steel with modified surface, used for implants in human urinary system. In order to simulate conditions, which occur in the tissue environment of the urinary system, the test pieces were exposed in a urinary solution at temperature of $T=37\pm 1^{\circ}\text{C}$, for a period of 30 days. Evaluation of physicochemical properties of biomaterial was made on the basis of surface chemical analysis (XPS). To evaluate the effects which occur on the surface of the examined steel, Electrochemical Impedance Spectroscopy (EIS) method was also employed. Analysis of test results shows favourable influence of the suggested surface treatment of AISI 316L stainless steel. Samples having electrolytically polished and chemically passivated surface featured the best physicochemical and electrochemical characteristics.

Keywords: AISI 316L stainless steel; electrochemical impedance spectroscopy (EIS), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM)

Podstawowym kryterium przydatności biomateriału metalowego na implanty urologiczne (stenty urologiczne) jest biokompatybilność. Jest ona w głównej mierze związana z własnościami fizykochemicznymi powierzchni implantu, które powinny być dostosowane do cech środowiska tkanek układu moczowego człowieka. W celu poprawy biokompatybilności stali Cr-Ni-Mo ustalono warunki wytwarzania warstw pasywnych na jej powierzchni. Wytworzenie warstwy pasywnej obejmowało etap polerowania elektrolitycznego i pasywowania. Taki sposób obróbki powierzchniowej zapewnił chropowatość $R_a < 0,16 \mu\text{m}$ wymaganą dla tego rodzaju implantów. W pracy tej szczególną uwagę skoncentrowano na analizie długotrwałego oddziaływania środowiska sztucznego moczu na własności fizykochemiczne wytypowanej stali.

Zasadniczym celem pracy była ocena własności fizykochemicznych i elektrochemicznych stali AISI 316L o modyfikowanej powierzchni stosowanej na implanty w układzie moczowym człowieka. W celu zasymulowania warunków występujących w środowisku tkankowym układu moczowego próbki poddawano ekspozycji w roztworze sztucznego moczu o temperaturze $T=37\pm 1^{\circ}\text{C}$ przez okres 30 dni. O przydatności zaproponowanej warstwy pasywnej do uszlachetniania powierzchni stali w znacznym stopniu decyduje jej skład chemiczny. Dlatego w pracy wykonano badania składu chemicznego metodą spektroskopii fotoelektronów (XPS), z użyciem wielofunkcyjnego spektrometru elektronów PHI 5700/660 firmy Physical Electronics, podczas których zidentyfikowano i wyznaczono stężenia atomowe pierwiastków w badanych warstwach pasywnych. Dla próbek przeprowadzono pomiar widma fotoelektronów w szerokim zakresie energii wiązania od $0\div 1400 \text{ eV}$ oraz dokładne pomiary linii widmowych poszczególnych pierwiastków składowych z warstwy powierzchniowej. Dla oceny zjawisk zachodzących na powierzchni badanej stali zastosowano również metodę elektrochemicznej spektroskopii impedancyjnej (EIS). Pomiary przeprowadzono z wykorzystaniem systemu pomiarowego AutoLab PGSTAT 302N wyposażonego w moduł FRA2 (Frequency Response Analyser). Badania przeprowadzono w alternatywnym roztworze symulującym środowisko moczu człowieka. Zastosowana w pracy mikroskopia skaningowa pozwoliła na ocenę stanu powierzchni stali AISI 316L przed i po ekspozycji w sztucznym moczu.

Analiza wyników badań wskazuje na korzystny wpływ zaproponowanej obróbki powierzchniowej stali AISI 316L. Najkorzystniejszą charakterystykę fizykochemiczną i elektrochemiczną miały próbki o powierzchni polerowanej elektrolitycznie i pasywowanej chemicznie. Przeprowadzone w pracy badania stanowią podstawę do dalszych analiz związanych z zagadnieniem biokompatybilności stali Cr-Ni-Mo stosowanej na implanty w urologii.

1. Introduction

Dynamic development of urinary system diseases treatment methods brought about a variety of choices related to

diagnostics or treatment for each individual case. At present, it is estimated that urological treatment makes a great part, ca. 30%, of all surgical interventions. They are less and less frequently performed as open surgeries; endoscopic treatment

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or various types of techniques requiring minimum intervention are used instead [1].

In 1988 for the first time metal stent was used in urology. It was used for urethra contraction treatment. At first, stents were used as a part of palliative treatment of people suffering from cancer in its last stage. Now, they are used for treatment in such diseases as: BPH (benign prostate hyperplasia), urethral contraction, contraction of ureteroenterostomy or ureteropelvic junction obstruction [2].

Development of modern urology requires improvement of surgical techniques, which in turn determines the necessity to produce modern equipment and a range of auxiliary materials for treatment. Guide wires must be mentioned here. Their application during operation enables efficient insertion of endoscopes, catheters or urological stents. Both, guide wires and stents, are made of stainless steel. They must show suitable functional properties (among other things: mechanical properties and resistance to corrosion in urinary environment, which features depend to a great extent on wire production technology and determination of physical and chemical characteristics of their surface layer) [3÷8].

General criteria of metal biomaterial applicability for urological implants (urological stents) is biocompatibility [9]. It is mainly connected with physical and chemical properties of implant surface, which should be adapted to the features of human urinary system tissues environment [10]. In order to improve biocompatibility of Cr-Ni-Mo steels, conditions of passive layer creation on their surface were determined [11]. Passive layer creation included the stage of electrolytic polishing and passivation. Such method of surface treatment of the material provided its surface roughness of $R_a < 0,16 \mu\text{m}$ required for this kind of implants. In this study special attention is paid to the analysis of long-term influence of artificial urine environment on physical and chemical characteristics of AISI 316L steel.

2. Methodology and material

Steel selected for the tests was Cr-Ni-Mo steel of AISI 316L type in accordance with the standard PN-ISO 5831-1:2007, supersaturated, widely used for urological stents production. Samples taken from AISI 316L steel were subject the following treatment: mechanical grinding, made by means of water abrasive paper with grain coarseness of $120 \div 500$ grains/mm²; electrochemical polishing for steel was made in the solution with chemical composition presented in Tab. 1 for 4 minutes; chemical passivation was carried out in 40% solution of HNO₃ at temperature $T = 65 \pm 1^\circ\text{C}$ for 60 minutes.

TABLE 1
Chemical composition of the solution polishing for AISI 316L steel

Component	Amount	Conditions
H ₃ PO ₄	55 ÷ 60% mass.	T = 60 ± 1°C, i = 40 ± 1 A/dm ²
H ₂ SO ₄	35 ÷ 45% mass.	
C ₂ H ₂ O ₄	40 ÷ 60 g/dm ³	
C ₈ H ₉ NO	40 ÷ 60 g/dm ³	
Inhibitor of corrosion	3 g/dm ³	

Physical and chemical, as well as electrochemical characteristics was tested in two stages. The purpose of stage one was to determine steel behaviour in urine-like solution – Tab. 2, which the tested biomaterial may come into contact with in clinical practice.

The purpose of stage two was to determine behaviour of biomaterial subjected to 30-day exposure to artificial urine. Therefore, testing station was designed and prepared. The testing station enabled simulation of the conditions present in patient's organism. The flow of physiological medium was maintained by means of a pump that provided proper rate of flow, adequate for physiological conditions. Moreover, this designed testing station enabled permanent control of pH and constant temperature equal $T = 37 \pm 1^\circ\text{C}$.

TABLE 2

Chemical composition of artificial urine

Component	Amount of distilled water, g/l
Solution A	
CaCl ₂ · H ₂ O	1,765
Na ₂ SO ₄	4,862
MgSO ₄ · 7H ₂ O	1,462
NH ₄ Cl	4,643
KCl	12,130
Solution B	
NaH ₂ PO ₄ · 2H ₂ O	2,660
Na ₂ HPO ₄	0,869
C ₆ H ₅ Na ₃ O ₇ · 2H ₂ O	1,168
NaCl	13,545

2.1. Electrochemical impedance spectroscopy (EIS)

In order to obtain information concerning electrochemical characteristics of AISI 316L steel, electrochemical impedance spectroscopy (EIS) tests were made. Measurements were made by means of Auto Lab PGSTAT 302N system equipped with FRA2 module (Frequency Response Analyser). The applied measurement system enabled to perform tests within frequency range of $10^4 - 10^{-3}$ Hz. Impedance spectra of the system were determined and obtained measurement data were matched with equivalent circuit. On this basis, numeral values of resistance R and capacity C of the analysed systems were determined. Impedance spectra of the tested system were shown in the form of Nyquist diagrams for various frequency values and in the form of Bode diagrams. Obtained EIS spectra were interpreted after matching to the equivalent electric circuit by means of the least square method. Thanks to this method it was possible to characterise the impedance of biomaterial – passive layer – solution phase boundary by means of approximation of impedance data, with application of electrical equivalent circuit.

2.2. X-ray Photoelectron Spectroscopy (XPS)

The tests were made by means of multi-functional electron spectrometer made by Physical Electronics PHI 5700/660. X-ray Photoelectron Spectroscopy (XPS) was used, with application of monochrome radiation $AlK\alpha$ with energy of 1486,6 eV. The tests were made on samples taken from AISI 36L steel with varied way of surface preparation. Measurement of photo-electron spectrum in the wide range of binding energy from 0÷1400 eV was made for the samples, as well as precise measurements of spectral lines of the respective compound elements of the surface layer. For the applied excitation energy, average free path of electrons was determined within the range of ca. $5\div 20 \text{ \AA}$. Information about chemical composition obtained from the spectra refers to the surface layer with such thickness. Chemical composition was determined by integration of the respective photo-emission lines with application of MULTIPAK software, made by Physical Electronics. Analysis of spectral lines of the respective elements enabled to assess chemical composition of the surface layer.

2.3. Scanning Electron Microscope (SEM)

Scanning microscopy, applied for the tests, enabled to evaluate the morphology of modified surface of AISI 316L steel after 30-day exposure in artificial urine. By means of electron scanning microscope with field emission FE SEM S-4200 HITACHI and spectrometer Voyager 3500 NORAN INSTRUMENTS, qualitative and quantitative analysis of chemical composition of the surface layer was made.

3. Test results and discussion

3.1. EIS test results

During stage one of the tests, impedance spectra were determined for the samples with electrochemically polished surface – Fig. 1. Nyquist diagrams determined for such prepared surfaces show fragments of large incomplete semicircles that are a typical impedance response for thin oxide layers – Fig. 1a. Maximum values of phase angles within a wide range of frequencies, presented by Bode diagrams, are similar and equal $\theta \approx 75^\circ$. Slopes of $\log|Z|$ in the whole range of frequency changes are close to -1, which proves capacitive character of passive layer – Fig. 1b.

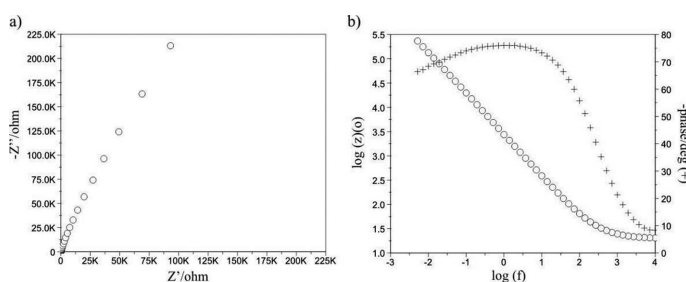


Fig. 1. Impedance spectra for AISI 316L steel (electrochemically polished): a) Nyquist diagram, b) Bode diagram

It was proved that the best matching of experimental impedance spectrum with generated by the programme model

curve for real and imaginary component impedance of the circuit, according as changes of measuring signals, is obtained with application of electric equivalent circuit that consists of a parallel Constant Phase Element (CPE) connected with resistance of ions transition through phase boundary: electrode - solution R_{ct} and resistance at high frequencies, that can be attributed to electrolyte resistance R_s – Tab. 5 [12÷14].

Characteristics of phase boundaries: metal – passive layer – solution, after the process of steel electrochemical polishing, was made with application of approximation of experimental data obtained with physical model of electric equivalent circuit – Fig. 2.

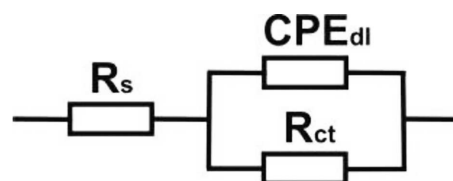


Fig. 2. Physical model for AISI 316L – passive film – artificial urine

Mathematical model of impedance for the system: AISI 316L – passive layer – artificial urine (after electrochemical polishing) has been shown in the equation (1):

$$Z = R_s + \frac{1}{1/R_{ct} + Y_0(j\omega)^n} \quad (1)$$

where: Z – impedance, Ωcm^2 , R_s – electrolyte resistance, Ωcm^2 , R_{ct} – resistance of ions transition, Ωcm^2

Y_0 – admittance to relevant variable $j\omega$, $1/\Omega\text{cm}^2$, ω – angular frequency, rad/s, n – coefficient of imperfection element

Subsequently, tests of samples after chemical passivation were performed. Chemical passivation influenced the change of character of the layer.

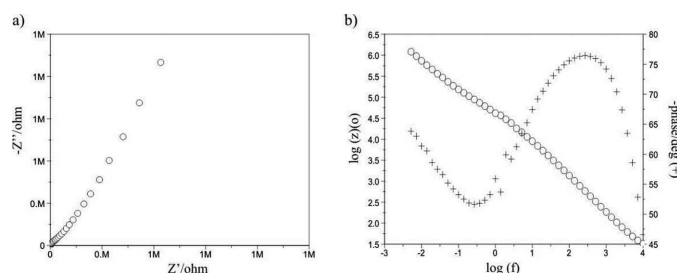


Fig. 3. Impedance spectrums for AISI 316L steel (electrochemically polished and passivated): a) Nyquist diagram, b) Bode diagram

It was found that the best matching of experimental impedance spectra (Fig. 3) is obtained when using electric equivalent circuit that consists of two consecutive parallel systems of CPE element connected with resistance of transition and resistance at high frequencies, that can be attributed to ohm resistance of electrolyte – Fig. 4.

In Fig. 4 R_{ct} means resistance of charge, and CPE_{dl} capacity of a double layer, whereas R_p and CPE_p – resistance and capacity of passive layer.

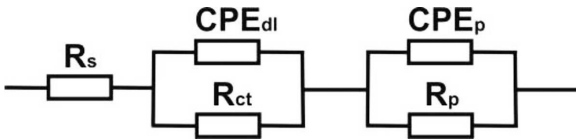


Fig. 4. Physical model for AISI 316L – double layer – artificial urine

Mathematical model of impedance for the system: steel – double layer – solution (after chemical passivation) has been shown in the equation (2):

$$Z = R_s + \frac{1}{1/R_{ct} + Y_{01} (j\omega)^{n_1}} + \frac{1}{1/R_p + Y_{02} (j\omega)^{n_2}} \quad (2)$$

where: Z – impedance, Ωcm^2 , R_s – electrolyte resistance, Ωcm^2 , R_{ct} – resistance of ions transition, Ωcm^2 ,

R_p – resistance of passive layer, Ωcm^2 , Y_{01}, Y_{02} – admittance to relevant variable $j\omega$, $1/\Omega\text{cm}^2$, ω – angular frequency, rad/s, n_1, n_2 – coefficient of imperfection element

Exposure of samples with polished as well as polished and passivated surface to artificial urine influenced the character of registered spectra – Fig. 5 and 6. Values of typical parameters describing electrical characteristics of the analysed systems have been shown in Tab. 3. For samples electrochemically polished samples that have been exposed to artificial urine for a prolonged period of time it was found that phase angle θ decreased in low frequencies. It may prove the decrease of protective properties of the passive payer created during polishing – Fig. 5. It was found that the best matching of experimental spectra with generated by the programme model curve for real and imaginary component impedance of

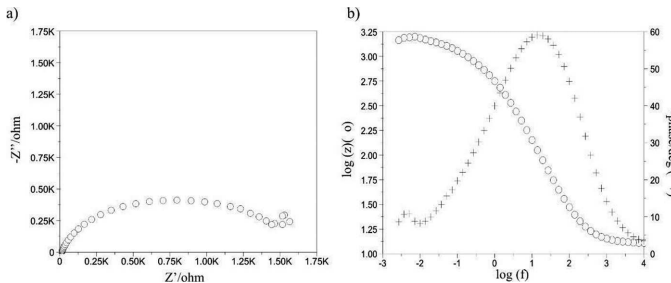


Fig. 5. Impedance spectrums for AISI 316L steel (electrochemical polished) after exposure in the artificial urine: a) Nyquist diagram, b) Bode diagram

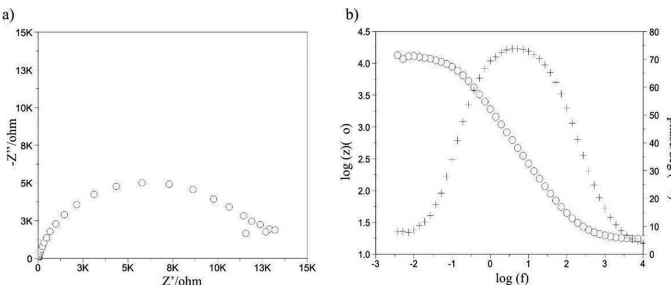


Fig. 6. Impedance spectrums for AISI 316L steel (electrochemical polished and passivated) after exposure in the artificial urine: a) Nyquist diagram, b) Bode diagram

the circuit is obtained when using electric equivalent circuit that consists of a parallel system of CPE element connected with Warburg impedance Z_f together with the resistance of ion

transition through the phase boundary: electrode – solution R_{ct} and resistance at high frequencies, that can be attributed to the resistance of electrolyte R_s – Tab. 3, Fig. 7 [12÷14].

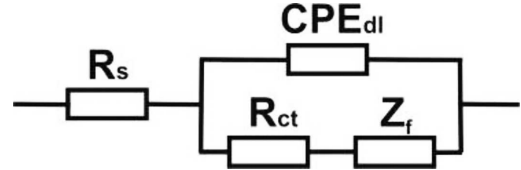


Fig. 7. Physical model for AISI 316L – passive film – artificial urine (after exposure)

Mathematical model of impedance for the system: AISI 316L – passive layer – solution (after exposure to artificial urine) has been shown in the equation (3):

$$Z = R_s + \frac{1}{Y_{01} (j\omega)^{n_1} + 1/(R_{ct} + Z_f)} \quad (3)$$

where: Z – impedance, Ωcm^2 , R_s – electrolyte resistance, Ωcm^2 , R_{ct} – resistance of ions transition, Ωcm^2 ,

Z_f – Warburg element, Ω , Y_{01} – admittance to relevant variable $j\omega$, $1/\Omega\text{cm}^2$, ω – angular frequency, rad/s, n_1 – coefficient of imperfection element

Linear dependence of the real (Z') and imaginary (Z'') impedance component, observed at low frequencies, is a typical feature of passive layer that is created in acid environment (artificial urine). It could be connected with the process of growth or dissolution of the passive layer obtained in the result of either electrochemical polishing or chemical passivation [15].

3.2. XPS tests results

Applicability of the proposed passive layers for the refinement of surface of AISI 316L steel is determined to a great extent by its chemical composition. Therefore, in the next stage of work, tests of chemical composition of surface layer that was created on steel samples after 30-day exposure in artificial urine were made.

Measurement of review spectra for the samples after exposure to artificial urine showed presence of the following elements in the surface layer: C, N, O, Na, Mg, Si, P, Cl, K, S, Ca, Ni, Cr, Fe and Mo – Fig. 8. Spectra shown in Fig. 8 reveal visible lines coming from electron states of the respective elements, and also lines of Auger electrons marked as KLL or LMM. Obtained spectra of the respective elements proved that interaction of artificial urine and the surface of the samples, irrespective of the type of surface modification, caused increase in oxygen concentration, mainly related to iron in Fe_2O_3 oxide, chromium in Cr_2O_3 oxide and nickel in Ni_2O_3 oxide. Also the presence of sulfates, silicates and phosphates as well as compounds CaSO_4 , CaCl_2 and compounds containing NH_3 or $-\text{NH}_2$ groups was found on the surface. Concentration of the respective alloy elements (Fe, Cr, Ni, Mo) in relation to chemical composition of the substrate was substantially decreased – Tab. 4, which should be seen as extremely favourable for biocompatibility.

TABLE 3

Results of EIS

Time	$R_s, \Omega\text{cm}^2$	$R_{ct}, \text{k}\Omega\text{cm}^2$	CPE_{dl}		$R_p, \text{k}\Omega\text{cm}^2$	CPE_p		Z_f, Ω
			$Y_{01}, \Omega^{-1}\text{cm}^{-2}\text{s}^{-n}$	n_1		$Y_{02}, \Omega^{-1}\text{cm}^{-2}\text{s}^{-n}$	n_2	
Electrochemical polished								
-	14	1058	0,76E-04	0,8467	-	-	-	-
30	13	1,28	0,33E-03	0,7532	-	-	-	0,16E-01
Electrochemical polished and passivated								
-	14	42,24	0.46E-05	0,8643	5240	0,1173e-4	0,80	-
30	14	12,49	0,10E-03	0,8663	-	-	-	0,62E-02

TABLE 4

Chemical composition of layer formed on the AISI 316L steel

Time	Element, % at.											
	N	O	Na	Mg	P	Cl	K	Ca	Cr	Fe	Ni	Mo
Electrochemical polished												
-	0,42	60,96	0,84	-	0,54	-	-	0,15	14,79	21,00	0,30	0,72
30 days	17,77	65,09	4,11	0,51	3,76	4,00	0,45	0,97	1,63	0,68	0,19	-
Electrochemical polished and passivated												
-	2,03	75,44	0,65	-	0,45	-	-	0,25	9,92	5,51	0,99	0,19
30 days	8,63	62,16	2,51	0,65	6,79	1,29	2,11	1,02	8,26	4,60	0,69	0,23

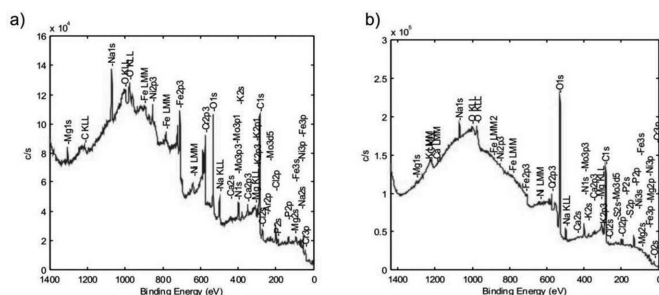


Fig. 8. XPS spectrums of AISI 316L steel after 30 days in artificial urine: a) electropolished, b) electropolished and passivated

3.3. SEM test results

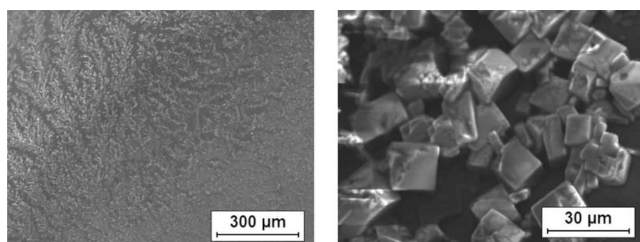


Fig. 9. NaCl crystals created on the surface of steel after 30-day time of exposure in artificial urine

Observation in electron scanning microscope prior to and after 30 time of exposure to artificial urine did not show changes in topography of steel surface. After the exposure,

only fine crystals with regular shapes and various size, that were easily removed in ultrasound washer, were found on polished as well and polished and passivated surface – Fig. 9.

4. Conclusions

On the ground of carried out tests the following generalisation can be made:

1. the process of electrolytic polishing and chemical passivation of steel under conditions shown in the study ensures the required surface smoothness and substantially improves its electrochemical characteristics in the environment of artificial urine,
2. the layer created as the result of passivation on the surface of AISI 316L steel serves as an additional barrier protecting the implant from interaction with the environment of human urinary system,
3. as far as the composition of passive layer obtained after electrochemical treatment is concerned, beneficial decrease of the main alloy elements – Fe, Cr, Ni and Mo in relation to the substrate was observed and the fraction of oxides of those elements increased.

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