PROCEEDINGS

2020 7th International Congress on Energy Fluxes and Radiation Effects (EFRE)

Tomsk, Russia, September 14 – 26, 2020

SPONSORED BY

IEEE Nuclear and Plasma Sciences Society

Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences

National Research Tomsk Polytechnic University

Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences

Chairman

Nikolay Ratakhin
Institute of High Current Electronics, Tomsk, Russia

Co-Chairman

Andrey Yakovlev
National Research Tomsk Polytechnic University, Tomsk, Russia

Alexey Markov
Tomsk Scientific Center SB RAS, Tomsk, Russia

Program Chairman

Alexander Batrakov
Institute of High Current Electronics, Tomsk, Russia

Program Co-Chairman

Edl Schamiloglu
University of New Mexico, Albuquerque, USA

Inffluence of Ion Beam Implantation on the Corrosion Properties of Stainless Steel

Maria S. Dorofeeva
National research
Tomsk State University
36 Lenin Ave., 634050,
Tomsk, Russia
dorofeevatomsk@gmail.com

Tatyana A. Gubaidulina
Institute of Strength Physics and
Materials Sciences SB RAS
2/4 Akademichesky Ave., 634055,
Tomsk, Russia
goub2002@mail.ru

Victor P. Sergeev
Institute of Strength Physics and
Materials Sciences SB RAS
2/4 Akademichesky Ave., 634055,
Tomsk, Russia
vs@ispms.tsc.ru

Tamara I. Dorofeeva
Institute of Strength Physics and
Materials Sciences SB RAS
2/4 Akademichesky Ave., 634055,
Tomsk, Russia
dorofeeva@ispms.tsc.ru

***Abstract*—A modified surface layers with high resistance were successfully prepared on corrosion stainless steel by Ion Beam Implantation (IBI). These layers contain oxides of chromium, aluminum, iron, and boron. It was revealed that the implantation of oxygen and aluminum with boron has a positive effect to the characteristic of the formed layers. In order to confirm this phenomenon, scanning electron microscopy (SEM), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy were carried out to investigate the morphology and composition of this layer after ion implantation process. The corrosion behavior of the implanted stainless steel was investigated in NaCl solution by electrochemical system and long-term salt spray (NSS) tests. The modified surface layer has been demonstrated to improve the corrosion resistance of stainless steels, even in the long standing corrosion influence. Finally, the corrosion of the stainless steel with implantation was discussed.**

Keywords—ion beam implantation; stainless steel; corrosion resistance.

I. Introduction

Surface treatment is an effective method to improve the poor corrosion resistance of construction metal alloy. Typical surface modification techniques include anodic oxidation [1–3], microplasma oxidation [4, 5], electroplating [6], physical vapor evaporation [7, 8], chemical vapor deposition [9], and ion implantation [10–13]. Ion beam implantation is one of the most favorable technologies for stainless steel protection [14–16]. It is necessary to select such ions and the implantation mode to do not to change the product dimensions (it is typical for threaded joints) and to increase their service life.

II. Experimental

Specimens were cut from an as-extruded stainless steel plate (Si: 1.12wt.%, Ti: 9.69wt.%, Mn:0.65 wt.%, Cr: 16.99wt.%, Ni: 9.57wt.%, Fe: 61.9 wt.%) with sizes of 10×10×0.5 mm. They were ground with emery paper and polished with Al_2O_3 paste (average size 1 μm). Surface profiler (Alpha-Step IQ profiler) analyzed surface roughness. After polishing process, morphology of the surface was characterized by SEM (LEO EVO-50XVP).

The work was performed under the government statement of work for ISPMS Project No. III.23.2.1.

The ion implantation was performed step by step. First, an oxygen (O) was implanted. Then, aluminium (Al^+) and boron (B^+) were implanted together. The specific parameters of implantation of oxygen are shown as follows: the base pressure of 1×10^{-8} A, the work pressure of 1×10^{-6} A, the power of 10 keV at fluences of 10^{18} ions/cm^2. Aluminum and boron implantations were performed at fluences of 10^{17} ions/cm^2 to increased penetration of implanted ions into the sample using 136 keV and 80 keV, respectively After implantation, surface morphology was investigated by SEM.

The SIMS (MS-7201M, Selmi UA) determined the elemental composition of this layer. The SIMS technique involves continuous bombardment of the sample surface with a focused high-energy beam of Ar^+ primary ions. This results in sputtering of the upper surface. Then ejected secondary ions were collected and analyzed. The mass/charge ratios of these secondary ions are measured with a mass spectrometer to determine the elemental, isotopic, or molecular composition of the surface layer to a depth up to 300 nm.

For the electrochemical investigation, the experiments were controlled by potentiostat PI-50-1 complete with compensation two-axis potentiometer N307/1 advanced electrochemical system, using the conventional three-electrode technique. Polarization curves were obtained at room temperature (25 C) under static conditions (without aeration), using a cell with a working electrode of 1cm^2 exposed area, Ag/AgCl (3.33 M KCl) reference electrode and a stainless steel sheet counter electrode under a 3.5 wt.% sea salt solution with deionized water at pH 6.2. The sample was observed by SEM after corrosion. In addition, the corrosion behaviors of non-implanted and implanted materials were comparatively evaluated by long-term corrosion tests in a salt spray chamber (Model CSS-2).

III. Results and discussions

Within the 50nm layer, the damage level and the local O concentration are controlled by the ion energy. The O implantations were performed using the low-energy ions. Therefore, ion fluences 10^{18} ions/cm^2 was chose for the implantation process of oxygen. From the SIMS calculations it

978-1-7281-2686-9/20/$31.00 ©2020 IEEE

was determined that an ion energy of 10 keV at fluences of 10^{18} ions/cm^2 would result in the implanted O concentration being contained within the 50 nm layer, without significant spillover into the 200 nm layer.

It is worth noting that a few experimenters are made: if boron and aluminum are implanted at the first step and oxygen at the second step, the depth of the implanted ions is decreases to 60nm during the implantation process (results of SIMS).

Depth profiles of implanted stainless steel are shown in Fig. 1. After ion implantation, concentrations of O, B, Al in the range from 0 nm to 270 nm decreases. The O, Al and B have been introduced into stainless steel samples by ion implantation. In addition, Fig. 1 shows the composition profile analysis from SIMS taken in depth for ion modified layers. From the SIMS results, it is possible to observe that the surface had a layered distribution of elements. Oxygen was implanted to a depth of not more than 25 nm, aluminum and boron are implanted to a depth of more than 200 nm. The O modulation signal was greater than the Al and B signals, for this case; however, the O signal could reach up to 30 times the Al and B signals in bilayers with 10nm thicker.

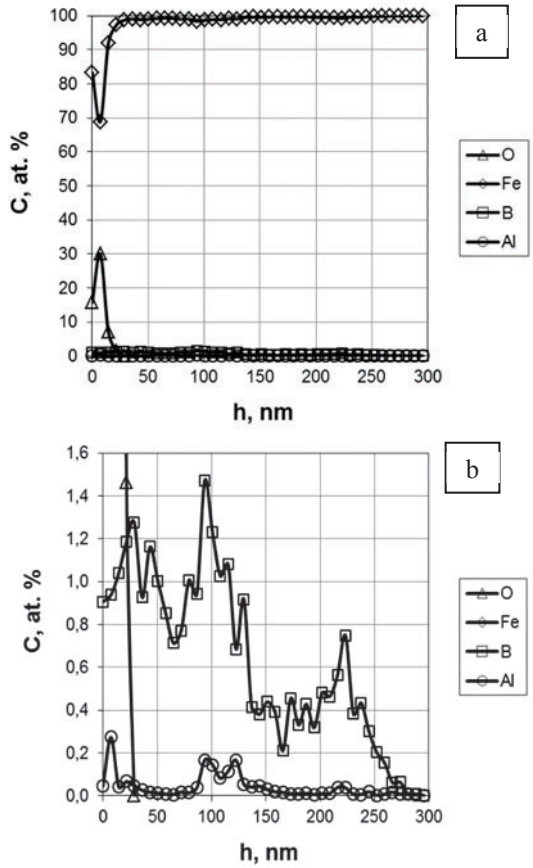

Fig. 1. SIMS depth profiles of stainless steel sample after ion implantation.

The morphology of the surface was characterised by scanning electron microscopy (SEM, LEO EVO-50XVP) (Fig. 2).

Non-implanted samples are more susceptible to corrosion than implanted samples.

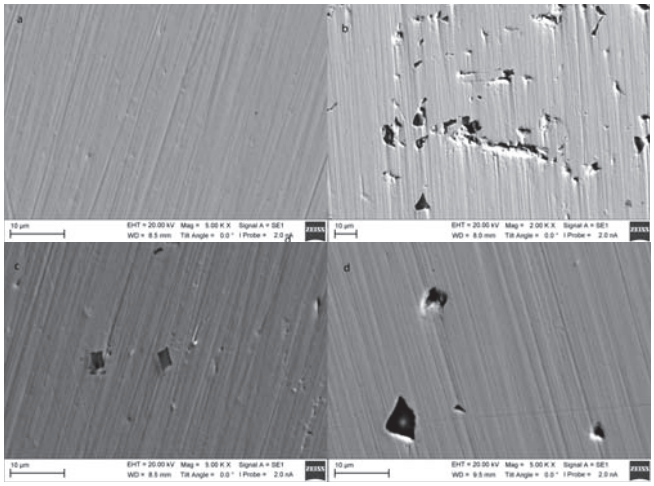

Fig. 2. SEM images non-implanted (a, b) and implanted (c, d) stainless steel samples before (left) and after corrosion tests (right).

The specimens (non-implanted and implanted) were chosen to evaluate corrosion resistance in aggressive medium through long-term corrosion tests in a salt spray chamber. Each sample was masked by paraffin wax with the untreated surface (1.0×1.0 cm^2) exposed in 50 ml of 5 wt.% NaCl solution with acetic acid and deionized water (pH=3). The weight loss of the non-implanted specimen is comparatively high (Fig. 3). The weight of the implanted specimen is practically unchanged. This becomes especially relevant for testing times beyond 480 h. Consequently, it is recommended to avoid the testing without a corrosion protection, especially in long-term tests.

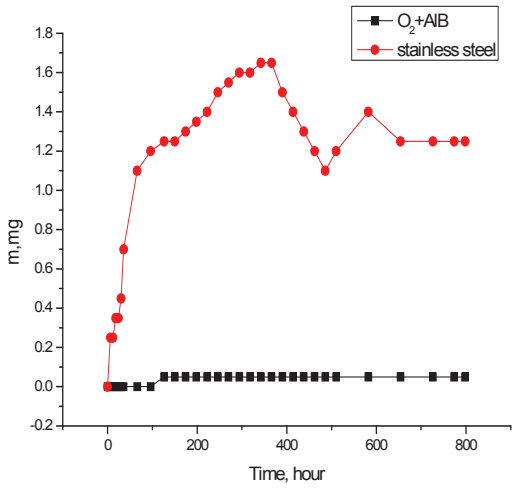

Fig. 3. Corrosion behaviors for the non-implanted and implanted specimens in a salt spray chamber at room temperature (loss mass).

The electrochemical behavior was evaluated in 3.5 wt.% NaCl solution (Fig. 4).

To stabilize the exchange of ions between samples and electrolyte, the sample was immersed in 3.5 wt.% NaCl solution for 15 min before electrochemical measurements. The potential was swept at the rate of 1 mV/s for potentiodynamic polarization measurements. The corrosion potentials before and after implantation were 50mV and 150mV, respectively. The latter

moved to a more positive position, which indicated that the structural stability of stainless steel in corrosive medium was improved by ion implantation treatment.

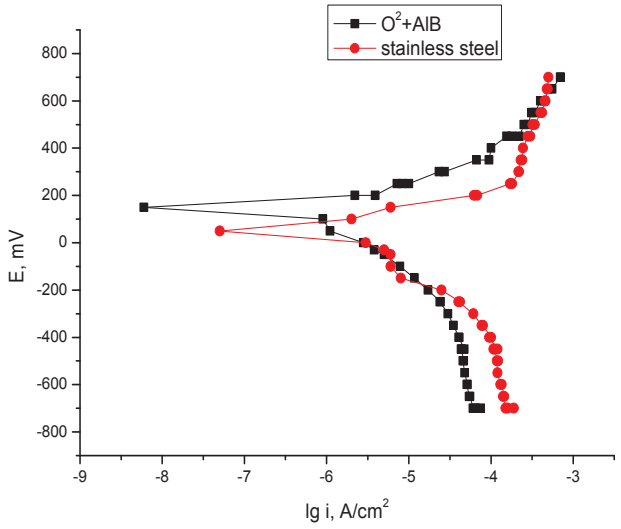

Fig. 4. Potentiodynamic polarization curves of the stainless steel substrate and implanted specimens.

During a corrosion test, the corrosion current density decreased from 1.26 to 0.708 μA/cm^2. The corrosion potential of the implanted specimen is comparatively high; in particular, the corrosion potential of stainless steel shows 50 mV. Unlike the case for stainless steel addition, the corrosion potential shifted toward the less noble side and both the activation current density and reactivation current density increased significantly in the case of implanted sample. The probable explanation for this phenomena is the boride formation such as $(Cr,Fe)_2B$, $(Cr,Fe)_{23}B_6$ and AlB_2, spinel compounds of the type Fe_xCr_yO and formation of oxide [17] and non-crystal layers on the surfaces [15]

Therefore, ion implantation could effectively improve the corrosion resistance of metal materials, which was mainly related to its surface stability during the process of restraining the corrosion initiation point

IV. Conclusions

It is expected that ion implantation can be a valuable tool to provide corrosion resistance of metal materials, both current and future. Although the present study focused on the O/AlB system, it is expected that other ion implantation layers can be formed similarly. A deeper understanding of the corrosion characteristics of ion modified layers is essential for their development and testing if they are to contribute to the continued reduction of environment impact on the mechanical devices. This work demonstrates how ion implantation can be a powerful tool to further this effort.

In the future, a number of strategies will be explored to control the amount of ions required for corrosion resistance of stainless steels to make this material more stable and thus increase the economic benefits of using these alloys.

Acknowledgment

The work was performed under the government statement of work for ISPMS Project No. III.23.2.1.

References

[1] K. An, C. An, C. Yang, Y. Qing, *et al*., "Effect of phosphating and post-sealing on the corrosion resistance of electro-galvanized steel," *Int. J. Electrochem. Sci*., vol. 12, pp. 2102 – 2111, 2017.

[2] A.-K. Mortaga, A. Fawzi, A. Omer, A. Abdelrahman, El-S. Fatma, "Corrosion behaviour of electrodeposited Zn–Co–Fe alloy," *Indian Journal of Chemical Technology*, vol. 23, pp. 271–278, 2016.

[3] Y. Konno, E. Tsuji, P. Skeldon, G.E. Thompson, and H. Habazaki, "Factors influencing the growth behaviour of nanoporous anodic films on iron under galvanostatic anodizing," *J. Solid State. Electrochem*., vol. 16, p. 3887–3896, 2012.

[4] D.-S. Tsai, G.-W. Chen, C.-C. Chou, "Probe the micro arc softening phenomenon with pulse transient analysis in plasma electrolytic oxidation," *Surf. Coat. Technol.*, vol. 357, pp. 235–243, 2019.

[5] V. A. Mamaeva, A. I. Mamaev, T. I. Dorofeeva, Y. Y. Bydnitskaia, "Research cyclic voltammetric dependences during microplasma formation of bioceramic coatings on titanium alloys," *8th Korea-Russia International Symposium on Science and Technology – Proceedings: KORUS 2004*, vol. 3, pp. 133–136, 2004.

[6] Y. Reda, A. M. El-Shamy, A. K. Eessaa, "Effect of hydrogen embrittlement on the microstructures of electroplated steel alloy 4130," *Ain Shams Engineering Journal*, vol. 9, pp. 2973–2982, 2018.

[7] M. Stueber, H. Holleck, H. Leiste, K. Seemann, S. Ulrich, C. Ziebert, "Concepts for the design of advanced nanoscale PVD multilayer protective thin films," *Journal of Alloys and Compounds*, vol. 483.1, pp. 321–333, 2009.

[8] J. Leppaniemi *et al*., "Effect of Surface Wear on Corrosion Protection of Steel by CrN Coatings Sealed with Atomic Layer Deposition," *ACS Omega*, vol. 3, pp. 1791−1800, 2018.

[9] R. Sitek, T. Bolek, J. Mizera, "Microstructure and properties of Ti-Al intermetallic/Al2O3 layers produced on Ti6Al2Mo2Cr titanium alloy by PACVD method," *Applied Surface Science*, vol. 437, pp. 19–27, 2018.

[10] P. J. Evans, T. Vilaithong, L. D. Yu, O. R. Monteiro, K. M. Yu, I. G. Brown, "Tribological effects of oxygen ion implantation into stainless steel," *Nuclear Instruments and Methods in Physics Research B*, vol. 168, pp. 53–58, 2000.

[11] C. Zheng, A. Gentils, J. Ribis, V.A. Borodin, L. Delauche, B. Arnal, "Nano-size metallic oxide particle synthesis in Fe-Cr alloys by ion implantation," *Nuclear Instruments and Methods in Physics Research B*, vol. 409, pp. 333–337, 2017.

[12] A. H. Ramezani, M. R. Hantehezadeh, M. Ghoranneviss, E. Darabi, "Corrosion resistance behavior of nitrogen ion-implanted in tantalum," *Appl. Phys. A*, 122:179, 2016.

[13] S. V. Panin, I. V. Vlasov, V. P. Sergeev, B. B. Ovechkin, *et. al*, "Effect of Vacuum Arc Ion Beam Treatment on the Structure and Mechanical Properties of 30CrMnSiNi2A Steel," *Physical mesomechanics*, vol. 16, N4, pp. 392–406, 2016.

[14] N. V. Pleshivtsev, E. A. Krasikov, "Corrosion protection of metals, alloys and steels by ion bombardment (review)," *Russian Metallurgy*, vol. 4, pp. 64–93, 1995.

[15] T. Poowadin, S. V. Panin, V. P. Sergeev, L. A. Kornienko, L. R. Ivanova, "Wear resistance of UHMWPE-based carbon nanocomposite subsequent AlBx ion implantation," *Proceedings 7th International Forum on Strategic Technology, IFOST 2012*, p. 6357569, 2012.

[16] H.-C. Choe, "Effects of nitrogen ion implantation on the surface characteristics of iron aluminides," *Surf. Coat. Technol*., vol. 148, pp. 77–87, 2001.

[17] R. S. Rajamure, H. D. Vora, S. G. Srinivasan, N. B. Dahotre, "Laser alloyed Al-W coatings on aluminum for enhanced corrosion resistance," *Applied Surface Science*, vol. 328, pp. 205–214, 2015.