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CORROSION RESISTANCE AND MECHANICAL PROPERTIES OF MULTILAYER METALS

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Abstract

The authors described the results of their studies of corrosion resistance and mechanical properties of multilayer metal materials. They carried out experiments on deliberately pitted samples in various media (sodium and ferric (III) chlorides, sodium hypochlorite, and sodium dichromate). They show that anodic dissolution of the sacrificial protector occurs in non-oxidizing media and that the outermost layer metal is passive in oxidizing media. Samples of a multilayer 08X18H10T - steel 10 - 08X18H10T materials were made for layer by layer shear test that showed the breaking stress to be equal to between 190 and 215 MPa. Bending of 08X18H10T - steel 10 - 08X18H10T samples until their opposite ends were in parallel caused no rupture, layer separation, or cracking. These multilayer materials have high mechanical and technological properties.

Keywords: corrosion, multilayer material, electrochemical potential, pitting, explosive welding.

1 Introduction

Processing equipment in the chemical, oil refining, and paper industries, power engineering, transportation, and shipbuilding must be operated in a safe and reliable environment. Corrosive media cause general and local corrosion of metal structures, affect the service properties of materials, and increase equipment manufacture, installation, and repair costs.

It is an object of this study to explore a new class of multilayer metal materials combining high corrosion resistance, and high mechanical and service properties.

Multifunctional multilayer metal materials can be used instead of widely applicable bimetals and corrosion resistance high-alloy steel or alloys [1, 2].

Multilayer corrosion-resistant metal materials have high corrosion resistance to general corrosion and localized corrosion. The high-alloy steel or alloys provide their corrosion resistance to general corrosion. Multilayer structure provides their corrosion resistance to localized corrosion. The pitting corrosion is one of dangerous varieties of localized corrosion [3, 4]. The pitting corrosion makes on passive metal surface and develops in the form of deep pits. Well-known methods of corrosion protection to pitting corrosion are inhibitors, alloy composition (doping of Cr and Mo for steels) and electrochemical protection [2, 5].

Multifunctional multilayer corrosion-resistant metal materials are obtained on the «sacrificial pitting protection» principle [6]. The international application PCT WO2010/036139 A1«Multilayer material with enhanced corrosion-resistance (variants) and methods for preparing same» was filed. The patent of Eurasian Patent Organization was taken out [7]. The idea is that a multilayer material has at least three layers that are chosen depending on the medium composition and values of stationary electrochemical potentials [8-12]. The authors' material is distinct from any other in that its protective layer is placed between the layers it protects.

The external layer is made of a material that has a sufficiently high corrosion resistance and is passive in the surrounding medium. The material of the second internal layer is chosen to have its stationary electrochemical potential when brought into contact with the working medium below the stationary electrochemical potential of the first layer material. As pitting reaches the second layer material the latter turns into an anode and the first layer material becomes a cathode. The anode, or sacrificial protector, dissolves gradually. Anode dissolution reaction may continue until a cavity, or lens, of considerable size is formed in the protector. Depending on medium composition, material of the first layer releases hydrogen, reduces oxygen, or sustains other electrochemical reactions. The third layer is similar to the first layer in composition. The ratio of the stationary electrochemical potentials of the first and second layer materials is suitable for mediums that do not contain oxidizing agents. The schematic polarization curves in

Fig. 1 show the case when medium does not contain oxidizing agents.

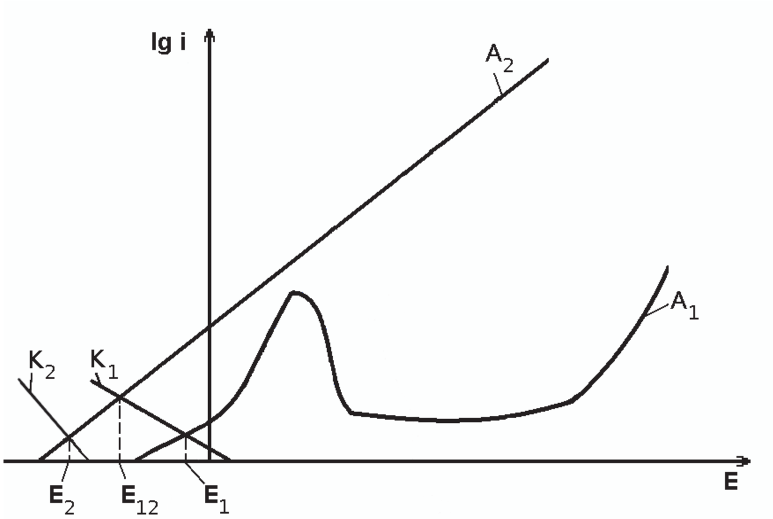


Fig. 1 Schematic polarization curves of the first outermost layer and the second internal layer in non-oxidizing media

A1 – anodic curve of the first external layer

K1 – cathodic curve of the first external layer

A2– anodic curve of the second internal layer

K2 – cathodic curve of the second internal layer

E1 – stationary electrochemical potential of the first external layer

E2 – stationary electrochemical potential of the second internal layer

E12 – stationary electrochemical potential in contact condition of first external layer and second internal layer in non-oxidizing media

The corrosion rate of the second layer may increase and the reaction continues until the sacrificial protector is dissolved completely. Where the reaction products are insoluble substances they can clog individual pits and, therefore, slow down the corrosive destruction rate of the multilayer material as a whole.

If the working medium contains an oxidizing agent, the material of the first external layer is also chosen on the condition that it is in a passive state and has a high resistance in contact with the medium. The material of the second internal layer is chosen on the condition that its electrochemical potential in the medium is higher than the potential of the first layer material. Eventually, pits develop in the first layer and reach the second layer. The resulting contact difference between the potentials is sufficient for slow-solving products to form on the surface of the first layer metal in a reaction of anodic dissolution of the first layer metal resulting in its passivation and, therefore, end of pitting. In this case, the second layer serves as the cathodic sacrificial protector. The corrosive potential of the first layer steel maintains its steadily positive value conforming to its passive state and high corrosion resistance. The schematic polarization curves in **Fig. 2** show the case when medium contains oxidizing agents.

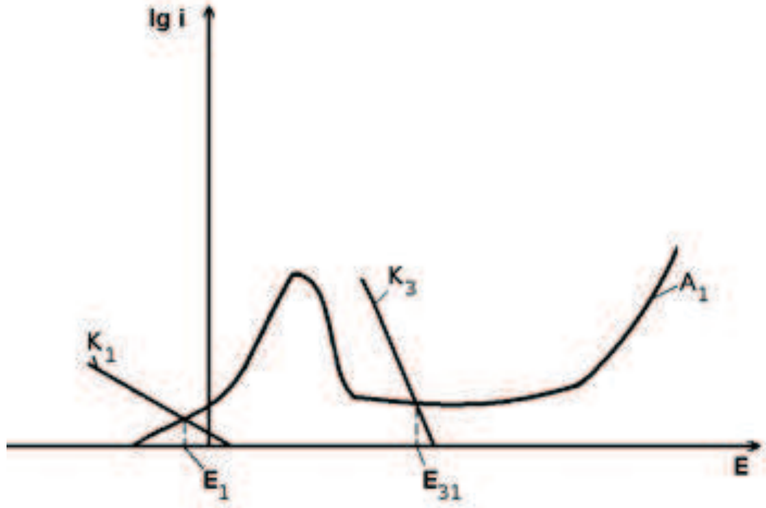


Fig. 2 Schematic polarization curves of the first external layer and the second internal layer in oxidizing media

A_1 – anodic curve of the first external layer

K_1 – cathodic curve of the first external layer

E_1 – stationary electrochemical potential of the first external layer

K_3 – cathodic curve of the second internal layer

E_{31} – stationary electrochemical potential in contact condition of first external layer and second internal layer in oxidizing media

A layer of structural steel of required thickness may be welded as a supporting layer to the multilayer material to give it high structural strength.

Explosive welding was used to produce three- and four-layer materials comprising 08X18H10T - steel 10 - 08X18H10T (analog AISI 321 - ASTM 1010 - AISI 321) and 08X18H10T - steel 10 - 08X18H10T - 09G2C (analog AISI 321 - ASTM 1010 - AISI 321 - A 516-55) as intermediate sheet products measuring 1,000 × 1,500 mm. Explosive welding is well-known technology which are used for manufacturing of bimetal and multilayer metal materials [13, 14]. The layers of steel 08X18H10T and steel 10 were 2 mm thick. This welding technique was also used to obtain a three-layer material 08X18H10T - M1 - 08X18H10T (analog AISI 321 - C11000- AISI 321) in which technical copper M1 was used as the second layer.

2 Experimental materials and methods

The complexity of a problem consists in absence standard tests for resistance to pitting corrosion which intend for multilayer materials. Standard tests GOST 9.912-89, BS EN ISO 11463:2008, ASTM G48 – 11 [15, 16, 17] intend for monometallic materials.

The first external layer must contact with corrosive medium in the course of prolonged period to such an extent that pitting corrosion penetrated into its full thickness. Then the deep foci come up to second layer. The second layer becomes a protector because of the difference of electrochemical potentials. Methodology with a man-made pit was used in order to reduce the test time [18].

Multilayer materials were tested in oxidizing media ferric chloride ($FeCl_3$), potassium chlorate and dichromate, and sodium hypochlorite and in non-oxidizing media (sodium chloride) to verify our hypothesis. The samples were plates measuring 40×25 mm 6 mm thick obtained by explosive welding. A hole 1 mm in diameter was drilled at the sample centre to the middle of the sacrificial protection layer to provide a man-made pit. The end surfaces of the sample were coated with heat-resistant adhesive as insulation.

An experiment was conducted on a 08X18H10T - steel 10 - 08X18H10T sample in a medium containing no oxidizing agents. Corrosion tests were conducted in a sodium chloride solution at a concentration of 0.1 mol/liter at room temperature for 4,100 hours. At the end of the test, the sample was cut across the hole center. **Fig. 3** and **fig. 4** shows photographs of the sample removed from the solution, with corrosion products cleared away. **Fig. 5** shows distinctly that a cavity extending to the full depth of the layer was formed in the protector due to anodic dissolution. The dissolution boundary runs along the weld of wavy configuration that is typical of explosive welding.

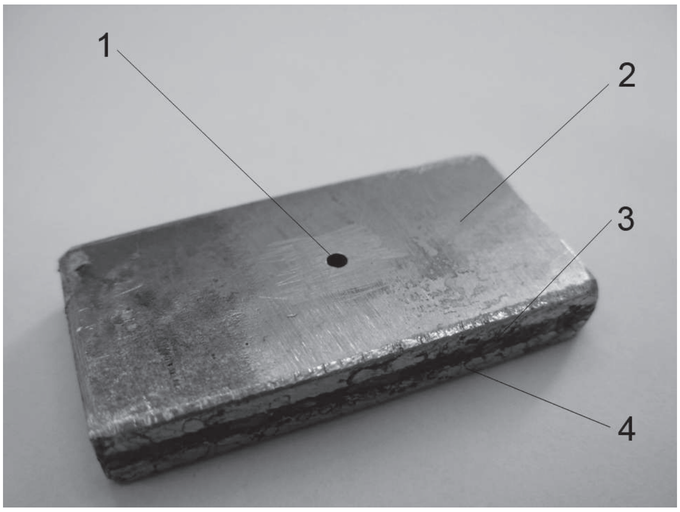


Fig. 3 Plan view of 08X18H10T - steel 10 - 08X18H10T sample:
1 – the man-made pit; 2 – the external layer; 3 – the second layer - sacrificial protector; 4 – the third layer

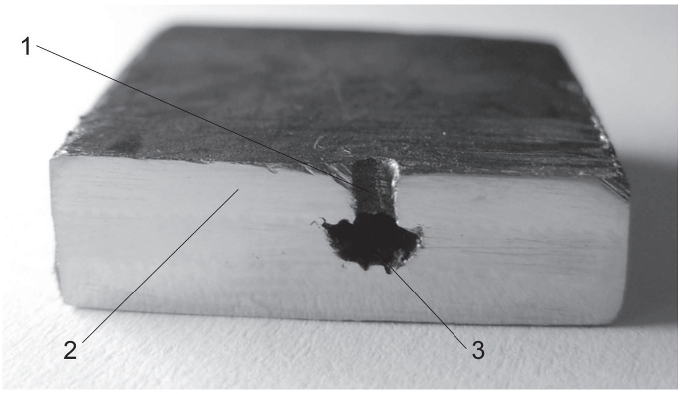


Fig. 4 Cross-sectional view of 08X18H10T - steel 10 - 08X18H10T sample
1 – the man-made pit; 2 – the external layer; 3 – the lens in sacrificial protector

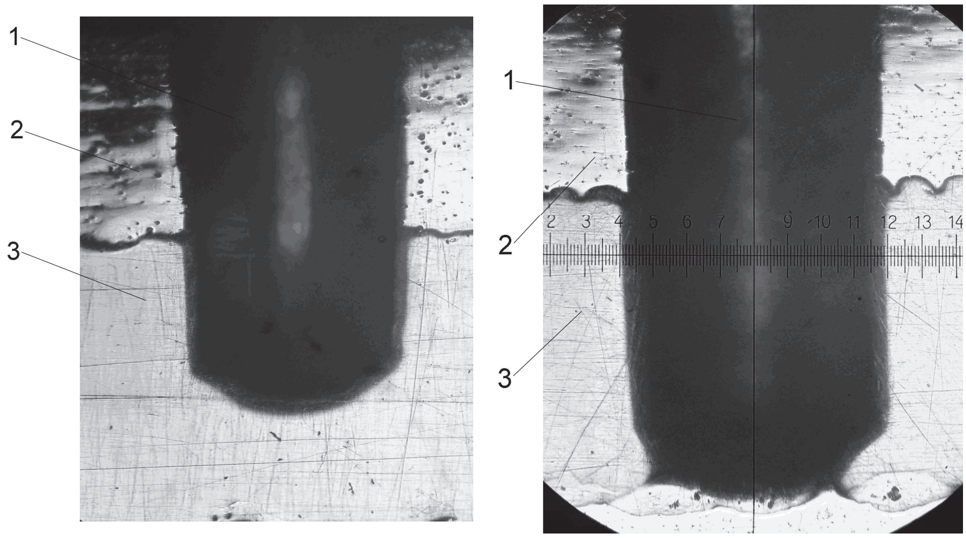
Experiments were carried out in a medium containing oxidizing agents on samples:

Sample 1: 08X18H10T - copper M1 - 08X18H10T; and

Sample 2: 08X18H10T - steel 10 - 08X18H10T.

Corrosion tests of Sample 1 were carried out in solutions of potassium chlorate (*a*) and potassium dichromate (*b*) at a concentration of 0.1 g-equiv/liter at room temperature for 4,700 hours. **Fig. 5** shows photographs of the samples after the tests. No traces of corrosion were found on the stainless steel and copper surface. The hole walls retained their original shape, and no pitting occurred on the outer surface of steel 08X18H10T.

The ratio of the areas of the protector and the surface protected was calculated to be 1:250.

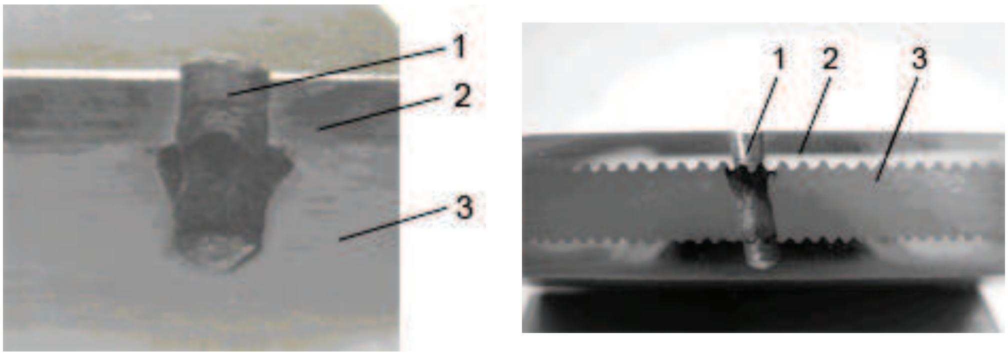


a *(b)*

Fig. 5 08X18H10T - M1 - 08X18H10T samples after immersion in solution of potassium chlorate (*a*) and solution of potassium dichromate (*b*): 1 – the man-made pit; 2 – the external layer; 3 – the second layer

Corrosion tests of Sample 2 were carried out in a solution of sodium hypochlorite at room temperature for 580 hours and a solution of ferric chloride at a 10% concentration at room temperature for 1,900 hours.

Fig. 6 showing photographs of the sample following immersion in the ferric chloride and sodium hypochlorite solutions clearly demonstrates that a cavity was formed in the sacrificial protector because of anodic dissolution. The dissolution boundary runs along the weld at the line of contact between the first layer and the protector. The sample surface has not changed after the tests and no new damage foci in the form of pits have been observed.



(a) (b)

Fig. 6 Three-layer 08X18H10T - steel 10 - 08X18H10T sample after immersion in solutions of ferric (III) chloride (*a*) and sodium hypochlorite (*b*): 1 – the man-made pit; 2 – the external layer; 3 – the second layer - sacrificial protector.

The microstructure of the interlayer boundaries of the 08X18H10T - steel 10 - 08X18H10T material has been studied [19]. The weld line has a distinctly wavy pattern in both instances, which is indication of sufficient strength of the weldment. Double amplitude and wavelength have been determined (**Table 1**). Fusion zones 70 to 110 μm long and 30 to 50 μm thick occur. The difference of parameters λ and 2A was result in changes of collision parameters which modify for every interlayer boundaries [20].

Table 1 Parameters of the Wavy Pattern of Interlayer Boundaries

Interlayer boundary	**Wave period λ, μm**	**Double amplitude 2A, μm**
08X18H10T – steel 10	300-350	90-130
Steel 10 - 08X18H10T	150-80	40-60

The multilayer 08X18H10T – steel 10 - 08X18H10T material was used to make samples for shear tests by layer that showed the breaking stress to be between 190 and 215 MPa. The test results confirm that the layers are joined with a strength conforming to the requirements of the GOST 10885 [21].

Bending of 08X18H10T - steel 10 - 08X18H10T samples until the opposite ends are in parallel in accordance with GOST 14019-80 [22] was carry out. It did not cause rupture, layer separation, or cracks.

The multilayer metal materials of high corrosion resistance may be used in the manufacture of equipment for the chemical, oil refining, and paper industries, power engineering, including nuclear power engineering, and waste processing and disposal equipment [23, 24].

Conclusions

The technique described here is intended for producing multilayer metal materials on the principle of sacrificial pitting protection of materials against pitting corrosion.

A batch of test samples of multilayer materials was produced by explosive welding. The results of sample testing in model media have shown that the principle of sacrificial pitting protection has been verified and is efficient in protecting materials in contact with corrosive media.

These multilayer materials have high mechanical and technological properties.

References

[1] I.I. Reformatskaya, A.N. Podobaev, I.I. Ashcheulova, V.V. Zav'yalov, I.G. Rodionova: Protection of Metals, Vol. 36, 2006, No. 1, p. 46-51, ISSN 0033-1732
[2] I.I. Reformatskaya et al.: Protection of Metals, Vol. 42, 2006, No. 6, p. 521-525, ISSN 0033-1732
[3] I.L. Rosenfeld: *Corrosion and Metal Protection*, first ed., Metallurgiya, Moscow, 1970 (in Russian)
[4] [12.01.2014], http://www.mse.eng.ohio-state.edu/~frankel/fcc/pubs/MetalsHandbookCorrosionchapter.pdf, G. S. Frankel: *Pitting Corrosion*
[5] N.D. Tomashov, G.P. Chernova: *The Theory of Corrosion and Corrosion-Resistant Structural Alloys*, first ed., Metallurgiya, Moscow, 1985 (in Russian)
[6] A.E. Rozen, I.I. Reformatskaya, E.V. Kuznetsov, I.S. Los, P.A. Abramov, I.V. Denisov, A.V. Khorin, A.A. Rozen: *Corrosion Resistance of Multilayer Exploclad Metal*, In.: Explosive Production of New Material: Science, Technology, Business, and Innovations, Bechichi, TORUS PRESS Ltd., 2010, p. 63, ISBN978-5-94588-073-3
[7] Eurasian Patent No. 016878 EAPO: *Multilayer material with enhanced corrosion-resistance (variants) and methods for preparing same*. C23F 13/06 B 32B 7/02. A.E. Rozen, I.S. Los, Yu.P. Perelygin, L.B. Pervukhin, Yu.A. Gordopolov, G.V. Kiriy, P.I. Abramov, S.G. Usatyi. D.B. Kryukov, O.L. Pervukhina, I.V. Denisov, A.A. Rozen. Issued on June 30, 2012. Priority of September 26, 2008
[8] F. Todt: *Corrosion and corrosion protection*, first ed., Khimiya, Moscow – Leningrad, 1966, (in Russian)

[9] K. Vetter: *Electrochemical kinetics*, first ed., Khimiya, Moscow, 1967, (in Russian)
[10] V.F. Kapitanov, O.V. Platonova, V.I. Kovalevskii: Protection of metals and physical chemistry of surface, Vol. 32, 1996, No. 3, p. 331-332, ISSN 2070-2051, (in Russian)
[11] I.I. Zamaletdinov: Protection of metals and physical chemistry of surface, Vol.27, 2007, №5, p. 470-475, ISSN 2070-2051
[12] G.G. Uhlig, R.W. Revie: *Corrosion and corrosion control. Introduction in corrosion science and technology*, first ed., Chemistry, Leningrad, 1989, (in Russian)
[13] Yu.A. Conon, L.B. Pervukhin, A.D. Chudnovsky: *Explosive welding*, first ed., Masinostroenie, Moscow, 1987, (in Russian)
[14] V.R. Ryabov, I.D. Dobrushin, Jung-Gi Moon: *Welding of bimetal*, first ed., E.O. Paton Electric Welding Institute, Kiev, 2003
[15] GOST 9.912-89. *United system of corrosion and ageing protection. Corrosion resistant steels and alloys. Methods of accelerated tests for resistance to pitting corrosion*, Gosstandart Publishers, Moscow, 1989, 18 p., (in Russian)
[16] [30.08.2013], http://standart.normdocs.ru/bs-en-iso-114632008/, BS EN ISO 11463:2008 *Corrosion of metals and alloys. Evaluation of pitting corrosion*
[17] [21.09.2013], http://www.astm.org/Standards/G48.htm, ASTM G48 - 11: *Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution*
[18] Yu.A. Conon, V.N. Fedorov, L.B., Pervukhin, A.A. Bykov: *Corrosion-resistant bimetal for agricultural masinostroenie*, first ed., Masinostroenie, Moscow, 1984, (in Russian)
[19] I.S. Los, A.E. Rozen, Yu.P. Perelygin, S.G. Usatyi, A.V. Khorin: *New Multilayer Corrosion-Resistant Material and Technique for Producing Same*, In.: Resource-Saving Technologies to Repair, Restore, and Reinforce Parts of Machines, Mechanisms, Equipment, Tools, and Accessories from Nano- to Macrosize, In.: St. Petersburg, Polytechnical University Press, Vol. 1, 2010, p. 465-468, (in Russian)
[20] A.G. Kobelev, V.I. Lysak, V.N. Chernyshov, A.A. Bykov, V.P. Vostrikov: *Manufacturing of metal laminated composite material*, first ed., Intermet Inginiring, Moscow, 2002, (in Russian)

[21] GOST 10885-85. *Hot-rolled corrosion-resistant clad steel sheets. Specifications*, Gosstandart Publishers, Moscow, 1985, 10 p.
[22] GOST 14019-2003 (ISO 7438:1985). *Metallic materials. Bend test method*, Gosstandart Publishers, Moscow, 1985, 10 p., (in Russian)
[23] Yu.P. Perelygin, S.Yu. Kireyev, I.S. Los, A.E. Rozen: *A Multilayer Material of High Corrosion Resistance*. Coatings and Surface Treatment, Publishing centre of Russian D. Mendeleyev University of Chemical Technology, Moscow, 2012, p. 95-96, ISBN 978-5-7237-0985-0, (in Russian)
[24] Yu.P. Perelygin, S.Yu. Kireyev, I.S. Los, A.E. Rozen: A New Corrosion-Resistant Multilayer Material. In.: Protection of Metals and Physical Chemistry of Surfaces, 2014, Vol. 50, No. 7, pp. 856-859. © Pleiades Publishing, Ltd., ISSN 2070-2051.
[25] S.Yu. Kireyev, I.S. Los, A.E. Rozen, Yu.P. Perelygin, Kozlov G.V., Kryukov D.B., Rozen A.E.: Fabrication of corrosion-Resistant multilayer materials by explosive welding. In.: Explosive production of new materials: science, technology, business, and innovations. Strasburg, May, 2012. p. 68.