

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Multilayer Metal Material with Special Properties and The Production Technology.

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ABSTRACT

A new class of multilayer materials with high corrosion resistance and internal protector has been proposed. Authors have suggested a fundamentally new principle of pitting corrosion protection. The choice of layers in multilayer materials, designed for use in oxidizing and non-oxidizing environment, has been justified. The areas for multilayer materials' use have been specified.

Keywords: multilayer material, internal protector, corrosion, sacrificial protection against pitting.

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RELEVANCE

Currently, annual direct metal losses resulting from corrosion make up 12% of the total weight of metal in stock in Russia, which corresponds to the loss of up to 30% of the metal produced annually (Kablov, 2012). Global corrosion losses account for 4-6% of the national income in developed countries (Ivanovsky, 2010). Indirect losses associated with the structural failure, process shutdown and depressurization of equipment cause even greater economic damage. This leads to the necessity of improving the methods of protection against corrosion and developing new corrosion resistant materials and products.

Modern nuclear, chemical, petrochemical and oil refining industries are characterized by engineering units of high capacity and processing medium that is highly corrosive. This leads to the use of equipment with an increased metal content. According to the estimates made by Japanese experts (ESPEC Technology Report Test Navi Report No. 21, 2014) and data provided by the NACE International (2011), more than 60% of the engineering units' failures occur due to the influence of temperature and corrosive environment, and the annual cost of corrosion is estimated at \$ 2.2-2.5 trillion. In particular, in 2014, they amounted to about \$ 445.0 billion in the USA, \$ 95.0 billion – in Germany, more than \$ 50.0 billion – in Russia. This corresponds to the loss of up to 30% of the metal produced annually. It should also be noted that the main corrosion damage is caused not only by the metal loss, but also by high value of the products destroyed by corrosion, high cost of corrosion preventing measures, equipment downtime, product loss, disruption of technological processes, and environmental problems.

The problem of corrosion damage remains extremely topical worldwide. Presently widely used mono- and bimetallic corrosion-resistant materials cannot increase the material's operational life to the full extent in corrosive and highly corrosive environments. The development of new steels and alloys that is based on increasing the content of alloying elements (molybdenum, nickel and chromium) has almost exhausted its potential.

In this regard, multilayer metallic materials with internal protector (Rozen et al., 2012) that are able to increase the operational life in corrosive environments by 10 times and more may be of interest.

METHODS AND METHODOLOGY

The key point of the technical solution is a multilayer material containing components with different electrochemical potential, which transform the corrosion processes when the corrosion shifts from one layer to another. Pitting corrosion of the outer layer shifts to the contact corrosion of the specific sacrificial layer.

In case of unilateral action of the corrosive environment, four- and three-layer compositions are used. For products subject to heavy internal or external loads and high pressures, a four-layer composition is used (Figure 1a). The first three layers, the overall thickness of which is not more than 5 mm, provide corrosion protection, and the fourth layer – the mechanical strength (used to calculate the structural strength of the entire construction). If there are no heavy loads, a three-layer composition is used. In this case, the thickness of the third layer is defined by strength calculation (Figure 1b) (Rozen et al., 2010).

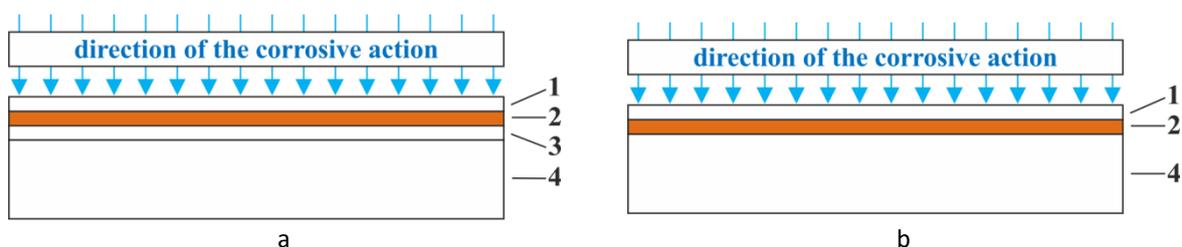


Figure 1. Four-layer (a) and three-layer (b) multilayer metallic materials with internal protector: 1 – layer with high electrochemical potential providing mainly pitting; 2 – layer with low electrochemical potential (“sacrificial layer” – the internal protector) – brown color; 3 – layer with high electrochemical potential; 4 – layer used to calculate the structural strength of the entire construction (base layer).

Composition of the layers depends on the composition of media and on the electrochemical potentials of the constituent metals. Applying a protector between the protected layers is principally new.

We have considered two cases:

- when a multilayer material contacts with the processing medium containing aqueous solutions of alkalis, acid salts or acids, whose anions are not oxidizing agents;
- when a multilayer material contacts with the processing medium containing aqueous solutions of alkalis, acid salts or acids, whose anions are oxidizing agents.

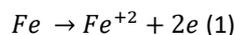
This allows of further discussion of the first and second type multilayer composite.

Multilayer composite of the first type

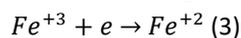
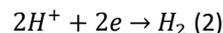
For the first (outer) layer contacting the processing non-oxidizing medium, a material that has a sufficiently high corrosion resistance and passivity in such environment should be selected. When the layer contacts with the corrosive environment that does not contain oxidants, a fixed potential E_1 is set on the layer. As a result of the medium action, corrosion spots in the form of pitting appear in the outer layer. These corrosion spots deepen over time and penetrate into the second layer. The material of the second layer is selected so that the value of its steady-state electrochemical potential E_2 in contact with the processing medium be lower than the steady-state electrochemical potential of the first metal layer.

When pitting reaches the second layer metal, the steady-state potential E_{12} is set due to the contact potential difference of the first and second metal layers. When this happens, corrosion spots located within a radius of protector protection from pitting (that has corroded the first layer) become passivated, and their further growth does not occur. The second layer metal becomes the anode, and the first layer metal becomes the cathode. The second layer becomes the protector, i.e. a sacrificial electrode, and gradually dissolves. Anodic dissolution reaction can proceed until the formation of a sizable cavity – a lens – in the protector. These cavities may reach tens of centimeters, depending on the ratio of electrochemical potentials of the layers. On the first layer material, depending on the composition of the medium, the evolution of hydrogen, the reduction of oxygen or other electrochemical reactions take place.

Anode:



Cathode:



Composition of the third layer is similar to the first one. When the depth of the cavity in the protector becomes equal to its thickness, the third layer also becomes the cathode – the same as the first layer. The corrosion rate of the second layer may increase, and corrosion may take place until the complete dissolution of the protector. If the reaction products are insoluble materials, they can slag individual pitting sites and reduce the rate of destruction of the three-layer material as a whole.

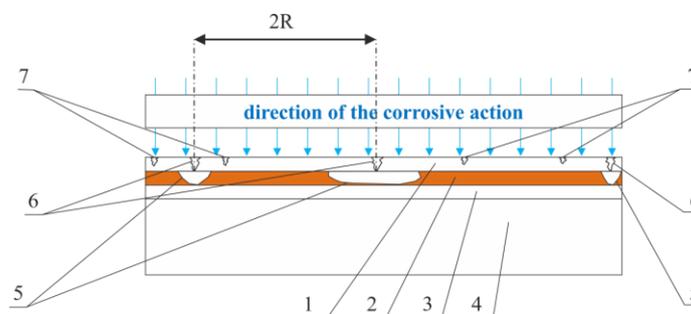


Figure 2. Corrosion dynamics in the multilayer material in the medium that does not contain oxidizing agents: 1 – outer layer in contact with the processing medium; 2 – internal protector; 3 – third layer; 4 – base layer; 5 – lens of the corrosion products in the protector; 6 – pitting in the outer layer, through which the corrosive environment affects the internal protector; 7 – pitting, which became passivated as a result of electrochemical action of the internal protector; R – radius of the internal protector’s action.

Figure 2 represents the corrosion dynamics in the four-layer material in the medium containing aqueous solutions of alkalis, acid salts or acids, whose anions are not oxidizing agents.

Multilayer composite of the second type

For the first (outer) layer contacting the processing oxidizing medium, a material that has a sufficiently high corrosion resistance and passivity in such environment should be selected. The second layer's steady-state electrochemical potential should be higher than the first layer's electrochemical potential; moreover, the material of the second layer should have lower hydrogen overvoltage than the material of the outer layer.

While in operation, pitting is formed in the outer layer and penetrates into the second layer in the course of time. The contact potential difference between the layers appears. The second layer metal retains its passive state. Anodic dissolution of the first layer metal is inhibited due to the formation of the reaction products that are slightly soluble. The potential of the first layer metal shifts to more positive values of E_{31} potentials; this leads to additional passivation and, as a result, stops the growth of pitting.

In this case, the corrosion potential of the outer layer steel maintains a stable positive value corresponding to the passive state. While in operation, the passive film on the outer layer may dissolve due to the chemical reaction.

Figure 3 represents the corrosion dynamics in the four-layer material in the medium containing aqueous solutions of alkalis, acid salts or acids, whose anions are oxidizing agents.

Composition of the third layer material is identical to the material of the first outer layer.

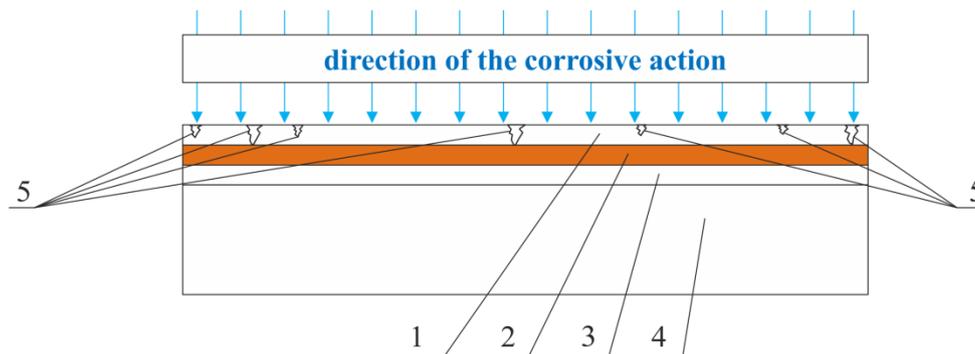


Figure 3. Corrosion dynamics in the multilayer material in the medium that contains oxidizing agents: 1 – outer layer in contact with the processing medium; 2 – internal protector; 3 – third layer; 4 – base layer; 5 – pitting in the outer layer, including pitting passivated as result of contact with the internal protector.

Table 1 shows structural metals and alloys in the order of increasing E_{cor} corrosion potential in sea water (Tomashov, 1986). Data in the table indicate that the grades 10, 15, 20 low-carbon steels have a more negative potential compared with the 12X17, 12X18H9, 10X17H13M2T high-alloy steels in the passive state. This means that low-carbon steels may be used as a protector in combination with the corrosion-resistant high-alloy steels in media containing aqueous solutions of alkalis, acid salts or acids, whose anions are not oxidizing agents.

Table 1. E_{cor} potential value in sea water

Metal	$E_{cor. B}$	Metal	$E_{cor. B}$
Magnesium	-1.45	Brass (40 Zn)	-0.20
Magnesium alloy (6 Al, 3 Zn, 0.5 Mn)	-1.20	Bronze (6 Mn)	-0.20
Zinc	-0.80	Nickel (active state)	-0.12

Aluminum alloy (10 Mg)	-0.74	Brass (30 Zn)	-0.10
Aluminum alloy (10 Zn)	-0.70	Bronze (5-10 A1)	-0.10
Aluminum	-0.53	Copper	-0.08
Duralumin	-0.50	Corrosion-resistant steel 20X13 (passive state)	+0.03
Iron	-0.50	Nickel (passive state)	+0.05
Carbon steel	-0.40	Corrosion-resistant steel 12X17 (passive state)	+0.10
Gray cast-iron	-0.36	Corrosion-resistant steel 12X18H9 (passive state)	+0.17
Corrosion-resistant steel 12X13 and 12X17 (active state)	-0.32	Hastelloy (Ni, 20 Mo, 18 Cr, 6 W, 7 Fe)	+0.17
Corrosion-resistant steel 12X18H9 (active state)	-0.30	Corrosion-resistant steel 10X17H13M2T (passive state)	+0.20
Corrosion-resistant steel 10X17H13M2T (active state)	-0.30	Silver	+0.12...+0.20
Lead	-0.30	Titanium	+0.12...+0.20

According to the Table 1, the 12X17, 12X18H9, 10X17H13M2T high-alloy steels in active state have a more negative potential compared with copper, titanium, and Hastelloy. This means that high-alloy steels can be used as a protector in combination with the indicated metals and alloys in media containing aqueous solutions of alkalis, acid salts or acids, whose anions are oxidizing agents.

In the case of bilateral action of the corrosive environment, multilayer compositions may consist of five, seven and more layers (Figure 4), given that there are at least two internal protectors (Kireyev et al., 2012).

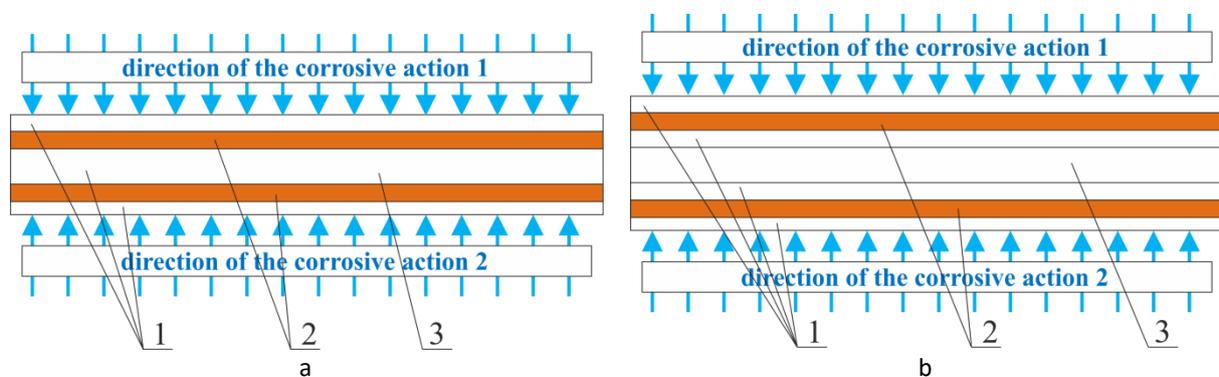


Figure 4. Multilayer materials with five (a) and seven (b) layers in case of bilateral action of the corrosive environment: 1 – layers with high electrochemical potential; 2 – internal protectors; 3 – layer used to calculate the structural strength of the entire construction.

If it is necessary to increase the operational life of the multilayer material with an internal protector for an indefinite period, a construction with two, three and more internal protectors may be applied (Figure 5). The sequence of the corrosion propagation in each of the layers will be similar to the previously mentioned, respectively increasing the operational life by a factor of 10, 100 and more.

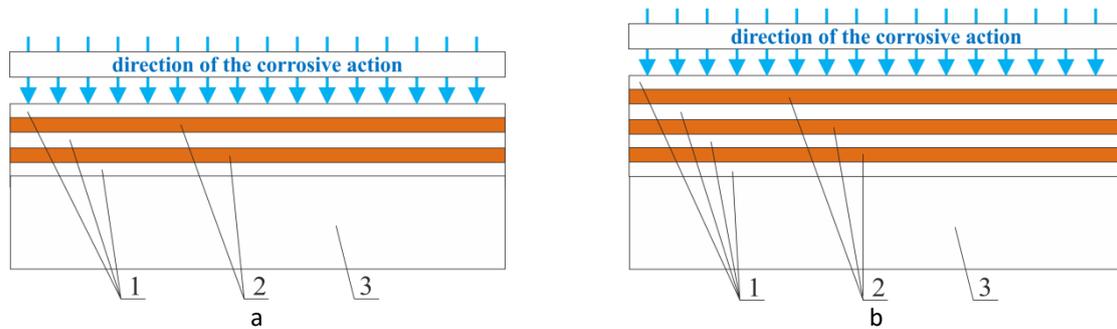


Figure 5. Multilayer materials with two (a) and three (b) layers of internal protectors in case of unilateral action of the corrosive environment: 1 – layers with high electrochemical potential; 2 – internal protectors; 3 – layer used to calculate the structural strength of the entire construction.

RESULTS

As a result of the research, we have created a material with adjustable operational life.

The created material is designed and suitable for manufacturing tanks, containers, barrels, cylinders, reservoirs, vessels, including vessels, caskets and reservoirs for nuclear power plants, equipment and pipelines, shells and elements of boilers, reactors, turbines, pumps for corrosive liquids and gases, furnace heating chamber covers, elements of heat-exchange and heat-recovery equipment, submerged hulls of river- and sea-crafts, structural elements of the drilling equipment and platforms, and other products that are exploited in corrosive environments, in particular at elevated temperatures (Los et al., 2010).

Materials, containing two or more layers of different composition, may be prepared by various techniques. These include foundry plating, hot batch rolling, cold plating, explosion welding, surfacing ("Production of layered composite materials", 2002). Explosion welding is one of the most efficient industrial ways for their production, especially in the case of joining dissimilar materials (Kobelev et al., 2002).

Explosion welding is a high pressure welding method, wherein a permanent connection is formed as a result of collision of welded elements. The energy source is a high explosive (HE) serving as an energy source. When initiating, a detonation front extends over the high explosive (HE), and the front decomposes into gaseous products. There is a pressure surge under the effect of which a thrown-off element develops a high speed and collides with a fixed element. The pressure in the collision zone can reach 10 to 20 GPa. There occurs a joint plastic deformation of the metal in a relatively thin layer of up to 1 mm thick. A high-temperature plasma formed during a high-rate collapse, clears them from the oxide films, adsorbed gas and activates atoms of the surface layers, while a high contact pressure crushes all the roughness and irregularities, providing a high strength permanent connection.

Advantages of the explosion welding could be formulated as follows:

1. The possibility of preparing compounds of homogeneous and heterogeneous metals and alloys, including those with sharply differing physical and mechanical properties (melting temperature, coefficient of linear thermal expansion, strength, ductility).
2. Primary and cladding layers during explosion welding do not alter the chemical composition, whereas mechanical properties vary within a narrow band of 3 ... 6 mm wide, being adjacent to the joint line.
3. Explosion welding is carried out in the solid phase, which allows connecting the materials forming brittle intermetallic compounds.
4. The possibility of obtaining compounds of the area up to 20 m² or more, with the thickness of the base layer being limited only by the thickness of rolled products, by the thickness of the cladding layer of a millimeter to several millimeters.
5. The possibility of obtaining multilayer materials per welding cycle.
6. Absence of the need for complex and expensive equipment.
7. Relatively low cost of consumables and low energy consumption.
8. The possibility of obtaining flat, cylindrical billets and cladding curved surfaces.

For the production of three-layer materials welding circuit shown in Figure 6 was used. The plates 3 and 4 were successively adjusted to the technological supports on the fixed plate 5. The height of the poles corresponded to the value of gaps h_1 and h_2 . V-shaped brackets (chaplets) made of metal were used as supports; the metal was similar in composition to one of the materials to be welded.

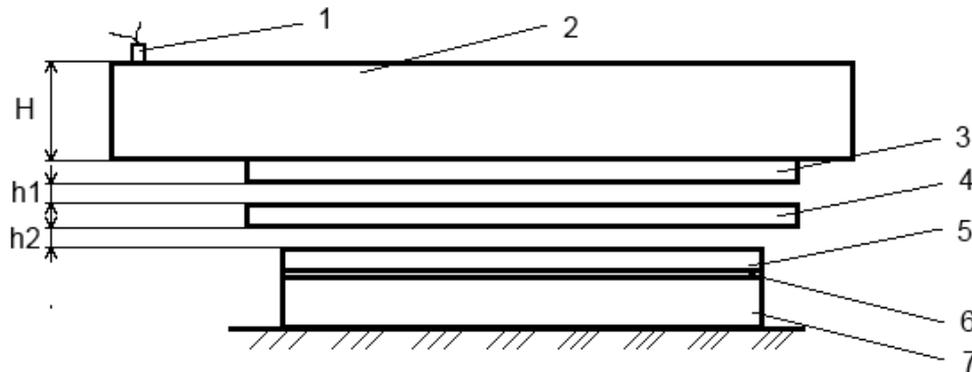


Figure 6. A three-layer material explosion welding scheme: 1 – electric detonator; 2 – HH charge; 3, 4 – thrown-off plates; 5 – fixed plate; 6 – a layer of an inert material; 7 – steel base; H –thickness of the HH charge; h_1 , h_2 – technological gaps.

In order to ensure high quality welding around the perimeter, the plates 3 and 4 had a size of 40 mm larger than the fixed plate. During welding, cutting occurred on the perimeter of the fixed plate. To prevent the fixed plate from setting with the base, an inert material 6, such as polyethylene was laid between them. A HH charge was placed on the outer surface of the upper thrown-off plate in a special container.

At explosion welding of a four-layer material number of the thrown-off plates was increased, whereas the bottom plate served as the fourth layer at the same time. The thickness of the three-layer materials varied from 6 to 24 mm, and the four-layer ones varied from 16 to 75 mm. The area of the billets was within the range from 1 to 9 m² (Perelygin et al., 2014).

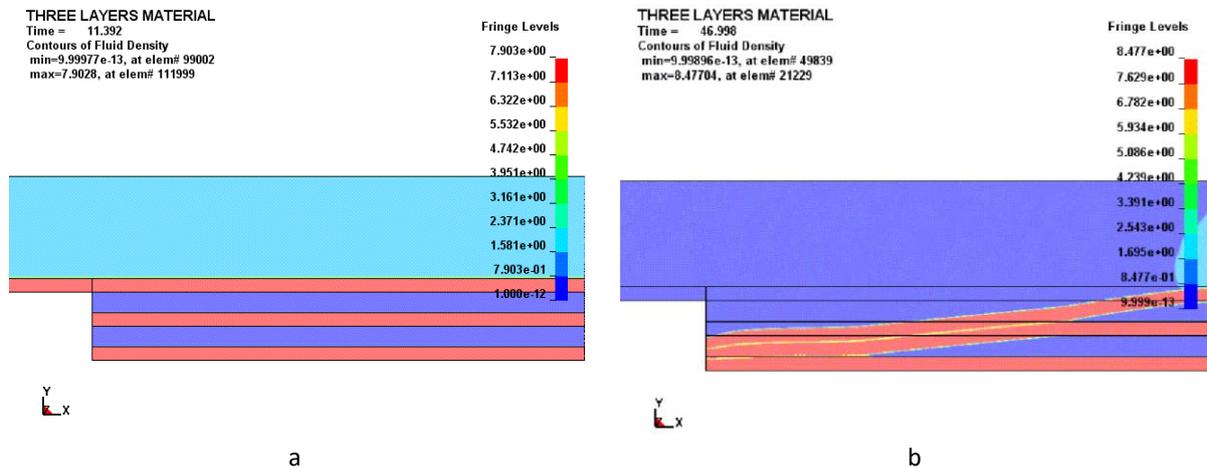


Figure 7. Results of 2D modeling in LS-DYNA explosive welding of a three-layer material at the initial time (a) and after 40 μ s elapsed after the beginning of detonation of the explosive (b).

For the purpose of technological modes, the explosion welding process was previously modeled using a LS-DYNA multi-purpose program designed to solve the three-dimensional dynamic nonlinear problems of solid mechanics, fluid mechanics and gas, heat transfer, as well as related problems in the mechanics of the deformable solid and heat transfer, mechanics of deformable body and the mechanics of liquid and gas. Modeling was carried out using a multi-component Euler approach. Each element contained a certain part of the material presented in the considered material system. The Wilkins-Giroux model was used to describe the behavior of explosive. It allowed to simulate the detonation of the explosive. In addition, the equation of state was postulated. The MAT_HIGH_EXPLOSIVE_BURN model was used in this solution, including the equation of

Jones-Wilkins-Lee. An irrotational deformation was determined by the natural logarithm of the relative volume. Until the change of compression by expansion, the unloading occurs in a linear fashion with a slope corresponding to the value of the irrotational modulus for the unloaded condition.

The graphic results of modeling of a three-layer material composition of 08X8H10T + steel 10 + 08X18H10T are shown as an example in Figure 7.

Modeling of an explosive welding process has allowed to estimate the size of contact pressure, temperature of heating of contact surfaces as a result of plastic deformation and influence of hot plasma and, respectively, to essentially reduce a number of experiments, to receive steadily qualitative three- and four-layer compositions of a multilayered material with "an internal protector" in a wide range of thickness and sizes.

In particular, the following composite layered materials have been received: 08X18H10T + steel 10 + 08X18H10T, 12X18H10T + steel 20 + 12X18H10T, 12X18H10T + St3 + 12X18H10T, 08X18H10T + steel 08KP (qualitative structural carbon steel) + 08X18H10T, 12X18H10T + St3 + 12X18H10T, 08X18H10T + steel 10 + 08X18H10T + 09G2S, 10X17H13M3T + steel 10 + 10X17H13M3T + 09Г2С, 08X18H10T + steel 08KP + 08X18H10T + 09G2S.



Figure 8. Working on the open testing ground and controlling multilayered materials: a – preparation for welding of a pile; b – blasting; c – loading the obtained metal block for transportation; d – ultrasonic control.

Explosive welding works were performed on specialized grounds of the Penza State University, the Institute of Structural Macrokinetics and Materials Science of the Russian Academy of Sciences, and "Bitrub

International", LLC (Figure 8 a, b, c). 100 percent visual and ultrasonic types of control on all samples (Figure 8 b) were made after explosive welding. The global market size of the created multilayered corrosion-resistant material according to the Center of commercialization of innovations "Skolkovo" in various industries makes more than 900 million dollars. 33% of which are the share of power industry, 25% – of oil-processing industry, 21% – of chemical industry, 14% – of the nuclear industry and 7% – of shipbuilding.

CONCLUSIONS

Depending on the degree of the corrosive power, operational life of the equipment increases 10 times and more in comparison with the austenitic stainless steel. The multilayered metal material includes a possible minimum quantity of expensive components. At the same time, it is possible to carry out inexpensive and safe external diagnostics of corrosion processes, including an ultrasonic control method as well.

The created multilayered material is a brand new product. There have been no direct analogues. The main areas of its application are the chemical, oil and gas industries, nuclear power engineering. For its operational indicators the obtained material is in one segment with tantalum and platinum, and in a price segment it is at the level of traditional Ni-Cr stainless steels.

This work was done under the state grant provided for the project No. 490, dd. September 1, 2014 with the Ministry of Education and Science of the Russian Federation.

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