



Oxidation resistance of surface-modified coatings for energy boilers

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ABSTRACT

Purpose: definite the oxidation resistance of the new obtained multicomponent coatings of a zonal structure and properties enabling its long-term work at an elevated temperature and in an environment of aggressive products of fuels combustion

Design/methodology/approach: The selected results of high temperature corrosion resistance of HVOF sprayed coatings with binder composition are presented. The temperature of cyclic oxidation test was 887 K and the exposure time was 500 h. The macro and microstructure of coatings after and before corrosion test were analyzed by optics and scanning microscopy. The structure of binder composition and filling component, like chooses oxides are presented. The structure and chemical composition of coatings are investigated by SEM and EDX energy dispersive analysis method.

Findings: The corrosion resistance of new elaborated coating with binder is presented. The multicomponent new elaborated coating can be applied in elevated temperature and aggressive environments for protection of water walls boilers or waste combustors

Research limitations/implications: If research is reported in the paper this section must be completed and should include suggestions for future research and any identified limitations in the research process.

Practical implications: The new elaborated and presented coatings use to basic protection to wear and corrosion condition or modified surface of multilayer coatings in the energy boiler. The results of example application of presented sealing in 2012 year are shown.

Originality/value: The elaboration of new corrosion resistance coatings with the modification of surface for the application in high temperature and corrosion environments and the presentation a degradation of new elaborated coating during the corrosion test.

Keywords: HVOF; ARC coating; Corrosion resistance; Surface modified

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PROPERTIES

1. Introduction

The development of technology, especially power engineering and petrochemical technologies, is heading towards the

improvement of efficiently, reliability and productivity of facilities in these industries, coupled with a reduction of the emission of harmful pollutants. The basic parameter which enables enhancing the functional properties is the growing

operating temperature of devices and installations. The development of material engineering, thereby enabling higher thermal efficiency, and in the chemical industry, better productivity [1-3]. New or improved materials, which unlike those so far used, provide better stability of material properties during the long-time service, play an important role in the construction of modern power units with supercritical parameters or units incinerating waste or biomass, as well as in the modernizing of conventional facilities. This is because the construction of modern power units is conditional upon the creep resistance and the erosion-corrosion resistance of individual structural components. Hence, the distinctly increasing interest in high-chromium steels and intermetallic phase alloys that has been noted the past decade. The information published in the recent years, among others in: [1-8] indicated that the improvement of corrosion resistance through a modification of steel structure with appropriate chemical elements may be responsible for the decrease in the creep resistance of the discussed steels, which is not recommended for construction elements operating under variable loads.

The results of laboratory research and expert evaluations corroborate the usefulness of applying protective coatings in such case. Materials are selected based on their properties and the technological-economic factor, which is an equally important criterion. The basis for the selection of the technology to produce the upper layer, including the application of a protective coating and the material of which the upper layer is supposed to be made, is the cost calculated not based on the initial cost of protection, but on the anticipated life of the product. The selection of the appropriate technology with the appropriate coating material is therefore an important issue for the power engineering development [1-8]. Protective multicomponents and multilayers coatings, like CMCs, IMCs with high dispersion structure, create considerable opportunities in this scope. The sealing process and easy modification improves their properties [11-20].

2. Purpose and scope of the research

The main purpose of the research was to define the oxidation resistance of the new obtained multicomponent coating of a zonal structure and properties enabling its long-term work at an elevated temperature and in an environment of aggressive products of fuels combustion. The scope of the research presented covers part of the research carried out under earlier works of the authors [8, 19]. The scope of the research included:

- the selection of appropriate components and technological processes to fabricate the material,
- the oxidation periodical test in high temperature to obtain the corrosion resistance of new elaborated multilayer composite covers materials.

3. Materials for research

The materials for research are composite powders (CMCs, IMCs) obtained by MA (Mechanical alloying) and SHS (self

propagation high temperature synthesis) process [5]. The obtained powders were analyzed by light and scanning microscopy observation. The composite materials were not homogenous in the capacity, the size of powder particles characterized different dispersion (Fig. 1), according to materials conception.

The obtained composite powders were thermally sprayed on the carbon-steel rolls by thermally method, like: HVOF- High Velocity Oxy Fuel (JET Kote II, Diamond Jet 2600) and arc (Smart ARC) spraying methods.

The five preparation stages of the samples for the corrosion test included:

1. Formation of substrate for coatings (rollers from low carbon steel: $\Phi 12.2 \times 21$ mm)
2. Pressing and SHS- synthesis of material for coatings
3. Powder preparation for thermal spraying - crushing, separation
4. The thermal sprayed method - HVOF or ARC.
5. Cutting the samples for corrosion test.

The procedure were presented in [8, 22]. The structure of sprayed coatings has porous. The special combination of group paints are sprayed on the surface of composite coating. The ceramic coating (the paints) was sprayed by classical pneumatic method. The paints were prepared special for the obtained resistance coatings worked in corrosion and wear at elevated temperature.

One part of the inorganic-ceramic composite coatings are modified by anemometric phosphates binder with connection designed chemical and phase composition of powder mixture. The second part was strengthened by fine dispersive Al_2O_3 or modified by Cr, Si oxides and sealed by alumina phosphate binder (Fig. 2.)

The author's technology of obtained the phosphate or alumina phosphate binder base on the procedure presented in Fig. 3.

The presented in Fig. 3. conception of the materials and technology to be applied to fabricate a multiphase composite hybrid coating resistant to corrosion and erosion wear at elevated and high temperatures. Based on the analysis of the reference literature, it was assumed that [11-18]:

- organic-inorganic materials or inorganic-ceramic materials have a set of advantageous properties, including high abrasion and high-temperature corrosion resistance.
- nanodispersion ceramic particles of the oxides, like Cr_2O_3 , SiO_2 type should make up an effective and functional composition of the composite mixtures fabricated, by ensuring appropriately high resistance to abrasion coupled with resistance to elevated and high temperatures.
- ceramic powders are characterized by thermodynamic stability at a high and elevated temperature [12-16].

Ceramic composite coatings are developed in two variants (Table 1):

- with a high corrosion resistance at elevated and high temperatures (the multilayer coatings - signify A1, Z1, Z2 - Table 1) with the aluminum or phosphate binder.
- with a high protective properties resistance to erosive and corrosive wear at elevated temperature (the multilayer coatings - signify AZ1, C2 - Table 1) with the modification of alumina-phosphate binder.

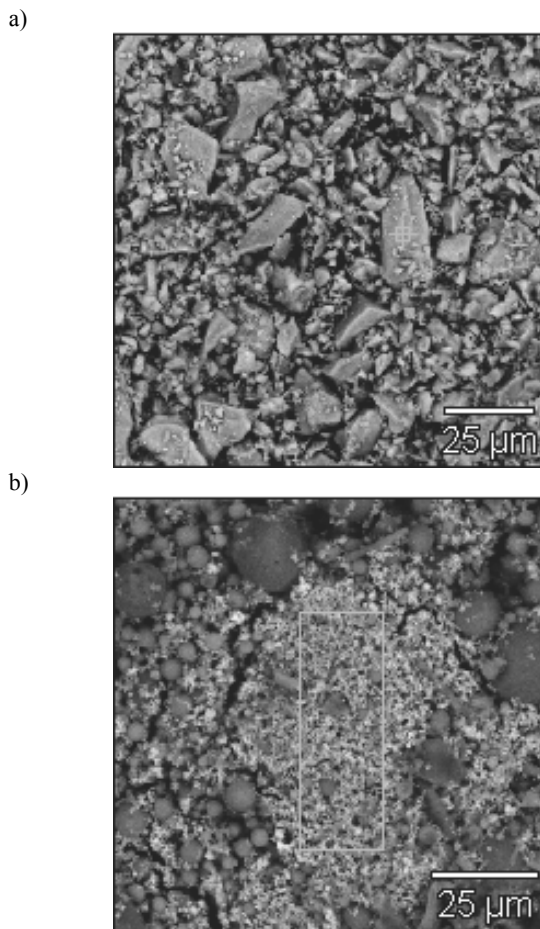


Fig. 1. Morphology of composition with Si and Cr oxide particle powder

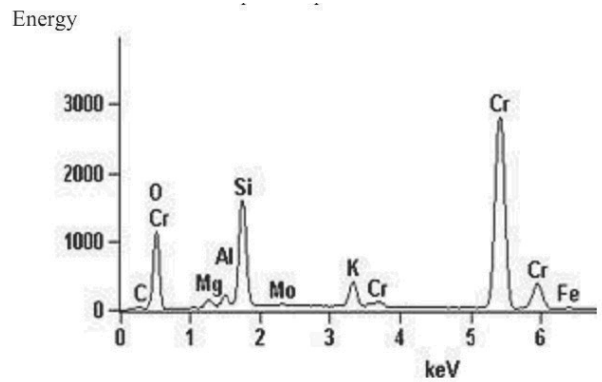


Fig. 2. Chemical composition of particle presented in Fig. 1 b

Table 1. Signify of multilayer coatings with binder obtained in thermally sprayed process

No	Signify	Binder
1.	A1	Aluminium binder
2.	Z1	Phosphate binder type A
3.	Z2	Multilayer coating without binder
4.	AZ1	Aluminum phosphate binder with metal and ceramic particles
5.	C2	Alumina phosphate binder with chromium and silicium oxide
6.	S1	Steel without binder

The morphology and the chemical composition of ceramic layer on the surface of composite coating modified by phosphate binder are presented at Figures 4-5 and Table 2. The another chemical composition and morphology of obtained materials are presented in [16].

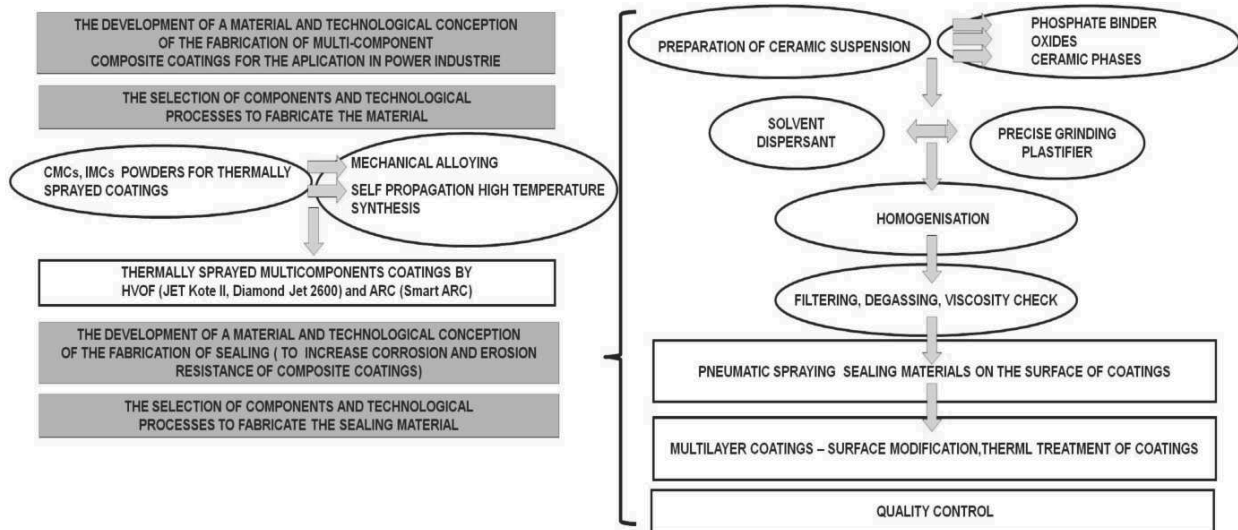


Fig. 3. The procedure of obtained the multilayer composite coatings with phosphate or alumina phosphate binder

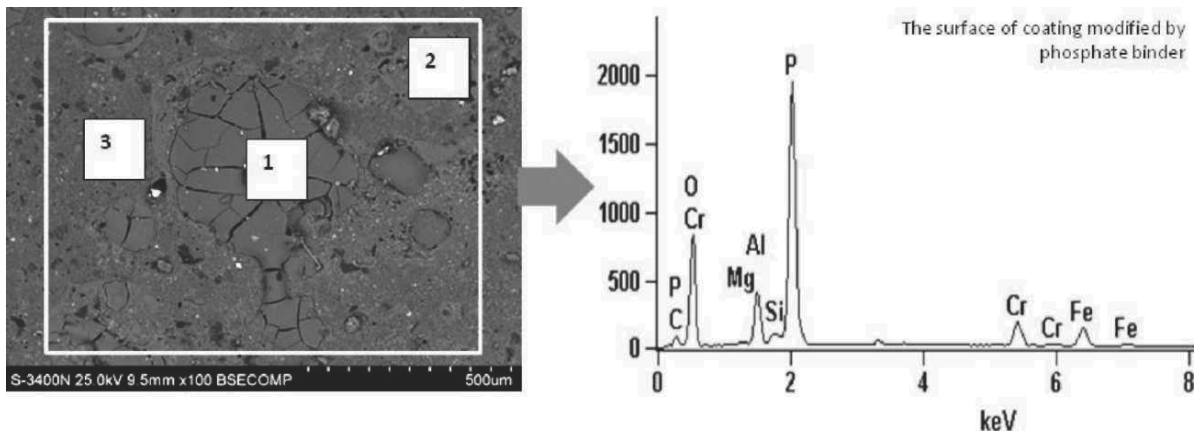


Fig. 4. a) Morphology and b) chemical composition of surface multilayer composite coatings modified by phosphate binder

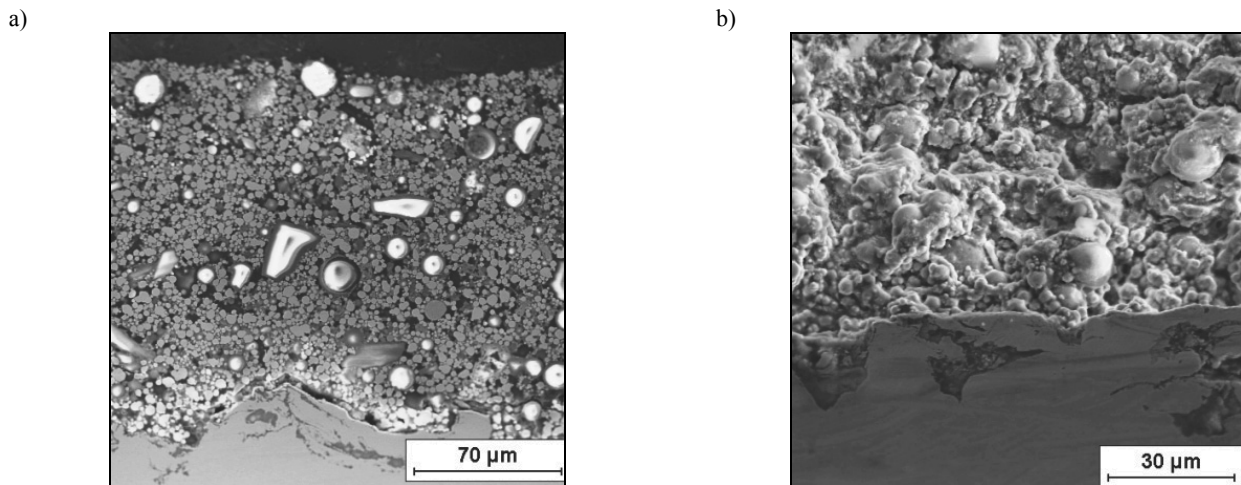


Fig. 5. Structures of coatings: a) phosphate binder - ceramic and metal particles; b) phosphate binder - oxides

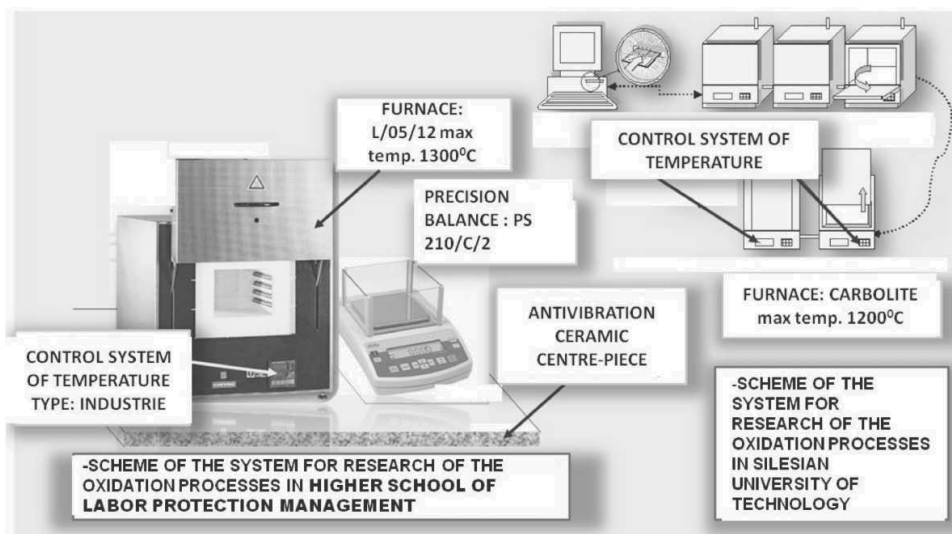


Fig. 6. Scheme of the installation of oxidation test

Table 2.

Chemical composition of layer on the surface of composite coating modified by phosphate binder wt [%]

	Mg-K	Al-K	Si-K	P-K	S-K	Cr-K	Fe-K
Phosphate binder	1.10	11.25	1.40	59.21		13.16	13.89
point 1	2.31	10.54		59.33		17.32	10.49
Point 2		9.76		60.66	0.78	7.48	21.33
Point 3		13.65	1.86	64.27		7.81	12.51

4. Experimental procedure - the oxidation test

Kinetics test of the coatings' mass change was carried out by periodic oxidation method. The exposure time of test was 1000 hours. The materials were heating to the 887 K, annealing in the temperature during 24, 48, 72... hours and cooling after the test time. The full procedure of corrosion resistance test in air and in the elevated temperature are shown in [15, 19]. The scheme of the installation to examine gaseous corrosion is shown in Fig. 6. The corrosion investigation and the presented installation is financially supposed by **Higher School of Labor Protection Management** -grant 8/2009 [19]. The installation to examine oxidation was verified and vilified.

Kinetics of the presented process was analyzed through the analysis of the weight of growing scale after 24, 48, 72...500 h exposition time. The reaction rate constant (k_p) was calculated from the parabolic law ($n=2$) in oxidation test [12]:

$$\left(\frac{\Delta m}{A}\right)^n = k_{c,p} \cdot t + C \quad (1)$$

where Δm - the mass increment after exposure time (t) and C is the free parameter (correlated with initial, non parabolic run-for $n=2$).


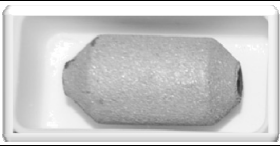

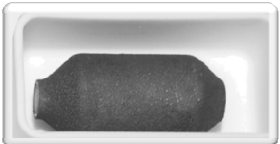


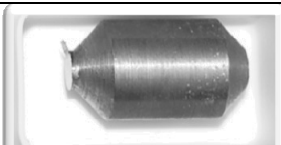
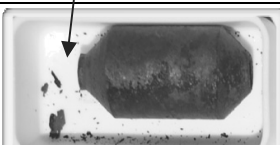
The coating surface after the corrosion test was observed. The materials after 72 hours was selected - only the coatings without spallation, cracks was conformable to the presented procedure investigated. The obtained structure by light microscopy is presented in [15]. The morphology and chemical composition of the corrosion products after the test was determined by Hitachi S-4200 scanning microscopy with a voyager system (Noranalysis system of the characteristic X-radiation of elements). The selected results are presented in this article.

5. Research results

The images of surface of multilayer sprayed composite coatings before and after 72 hours oxidation test is shown in Table 3. The changes of colors, cracks on the all studied surface with phosphate layers in presented tests are not observed on the images. The effect of spallation process was observed as a products in the ceramic-laboratory boat. The mass of the spallation product after the corrosion test is presented in Figure 7.

Table 3.

Examples of the macrostructure of the obtained coatings

	BEFOUR TEST	AFTER 74 HOURS TEST
	A1 - Aluminum binder -	white surface
1		
	C1 Aluminium phosphate binder with Si and	Cr oxides particles- black surface
2		
	Z1 Phosphate binder type A-	green surface
3		
	S1 without sealing - steel surface	effect of spallation process
4		

The highest mass change for the spallation process characterized the materials without coating. The mass change as a function of spallation process was not registered for the composite materials with aluminum phosphate binder modified by oxides.

The microstructure of the surface of composite coatings after 72 and 1000 hours oxidation test is shown in Figure 8. The mass change as a function of the heating time in presented tests are shown in Figure 9. The mass change of the all studied composite coatings with phosphate binder was comparable and the oxidation process of their materials obeys parabolic rate law (Fig. 7.)

The cracks on the surface of Z2 role after 72 hours was observed, and the materials obeys linear rate low. The obtained values of k_p parameters for oxidation process are comparable for all studied materials (up to $7.8 \cdot 10^{-10}$ [g^2/cm^4s]) and indicate good high temperature corrosion resistance of investigation materials with binder.

The mass changes and the parameters shown, that the multilayer composite sprayed coatings with no-organic phosphate seal have higher corrosion resistance in the laboratory test than the coatings without seal. The presented investigation must be continued. The composite coatings are the perspective materials in applying at elevated temperature.

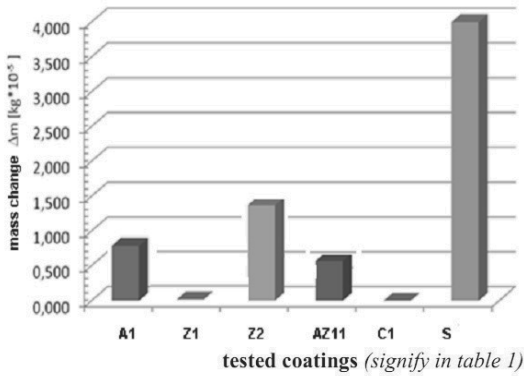
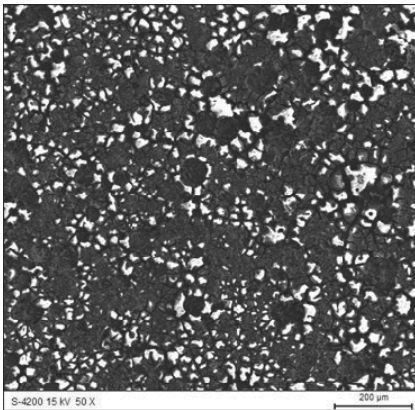


Fig. 7. Mass change as a function of spallation process

a)



b)

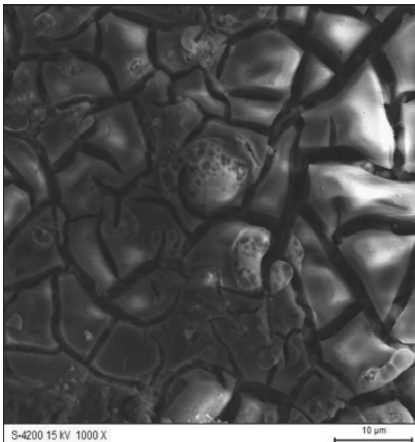


Fig. 8. The morphology of composite surface coating with phosphate binder after 72 and 1000 hours the corrosion test

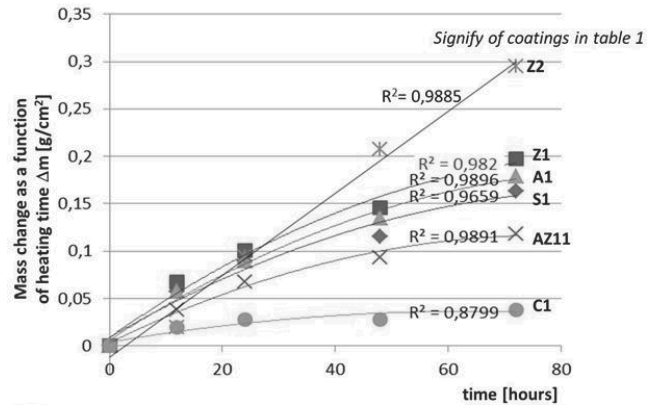


Fig. 9. Mass change of tested coatings as a function of heating time

6. Conclusions

- The composite coatings with inorganic phosphate seal, sprayed by HVOF method have higher oxidation resistant than without seal.
 - The good oxidation resistance of studied multilayer composite materials are the result of the growth of the stable and adherence $\alpha\text{-Al}_2\text{O}_3$ scale on the surface of these composite coatings.
 - The coatings are preferred to application as protection of the water-walls and of boiler tubes for the waste combustion. The results of example application of presented sealing are shown in Figure 10.
- The trends for future research are mainly related to :
- The modeling of high temperature corrosion mechanism of the presented sealing multilayers composite coatings in the oxidation atmosphere.
 - The studied of test corrosion in aggressive environments containing Cl and S.



Fig. 10. The coating with sealing process on the components of power boilers

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