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New generation of protective coatings intended for the power industry

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Abstract: This article presents the fundamentals of the production technology of multi component composite coatings of a zonal structure designed for the protection of components and appliances against corrosive and erosive wear at elevated and high temperatures. They can be also applied to seal the surfaces of thermally sprayed coatings. In a technological variant of the process, an external ceramic coating containing aluminium and chromium oxides was produced. An aluminium phosphate binder was used as a component of ceramic seal and of the coating. Flow charts of the binder and ceramic coatings fabrication are presented here. The structure and phase composition of selected coatings have been determined and some examples of their application in the domestic power industry have been presented.

Keywords: Coatings, Thermal spraying, Sealing, Aluminium phosphate binder

1. INTRODUCTION

In the power industry, for the protection of water walls of boilers against intensive wear, coatings and layers produced by pad welding and thermal spraying are applied. For pad welding of water walls, metallic materials are used, e.g. Inconel 625. The process itself, expensive as it is, requires specialist tools and can be effectively applied only in actual production conditions [1] . The thermal spraying methods, such as arc spraying or high velocity oxygen fuel spraying, have found numerous applications in the Polish power industry. A certain limitation of wider application of the supersonic method are its relatively high costs (although, in many cases economically viable), whereas coatings obtained by arc spraying, due to their porosity, require the fabrication of layers of a considerable thickness. An alternative that allows a reduction of the production costs of effective protective coatings is the application of metal/ceramic coatings. Ceramic coatings can be used either to seal thermally sprayed coatings or as an independent protective cover. Such coatings contain both ceramic and metallic reinforcing particles in the binder, e.g. in an aluminium phosphate binder. Such binder is also applied for the manufacture of refractory ceramic materials, sealing of thermally sprayed coatings and ceramic coatings themselves. Information concerning this issue in the literature is limited for commercial reasons [1-12].

2. PURPOSE AND SCOPE OF THE RESEARCH

The main purpose of the research was to develop a production technology to obtain a multi component 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. Another purpose was to develop a method of sealing the thermally sprayed coatings as well as the fabrication of an "independent" ceramic coating. In the conception of fabrication of such coating, it was assumed that the coating would meet the following conditions:

- it can be deposited by means of spraying onto a sand-blasted, etched or thermally sprayed surface,
- the coating material must be water-dilatable, without chemical solvents or liquid organic matter,
- the necessary thermal treatment must be simple and convenient; it can be applied in power facilities during their operation.

It was assumed that based on the inorganic aluminium phosphate binder, a coating material could be fabricated to be used for the modification of the thermally sprayed coatings surface structure, the material being an element that would bind the components of the ceramic coating. Furthermore, it was assumed that the phosphate binder applied in the process of coatings' sealing would form a passive surface and next, in consequence of the phase composition and volume change during thermal treatment, it would seal the porosity of the coatings resulting from the technological process. The scope of the research presented covers part of the research carried out under earlier works of the authors.

The scope of the research encompassed:

- the development of a material and technological conception of the fabrication of sealing and multi component composite coatings,
- the selection of appropriate components and technological processes to fabricate the material,
- the development of the conditions and technological parameters for the production of al aluminium phosphate binder and coating material,
- the determination of the structure and phase composition of the binder and the coatings.

Currently, wide research is conducted on utilitarian properties and performance of the coatings. In order to meet the target and cover the scope of the research, the following methods were applied:

- light microscopy, to determine the composite coatings' structure (Reichert MFZ),
- scanning microscopy and EDX analysis, to evaluate the structure and chemical composition of the materials used,
- X-ray radiography analysis by means of a Philips X-Pert diffractometer, to determine the phase composition of the binder.

The metallic coatings were thermally sprayed by arc (Smart ARC) and HVOF spraying methods (JET Kote II, Diamond Jet 2600), whereas the ceramic coating was sprayed by classical pneumatic method.

3. RESULTS AND DISCUSSION

The first stage of the research carried out was the determination of the factors that influence the properties of the aluminium phosphate binder. The applied technological procedures for binder production are shown in figure 1.

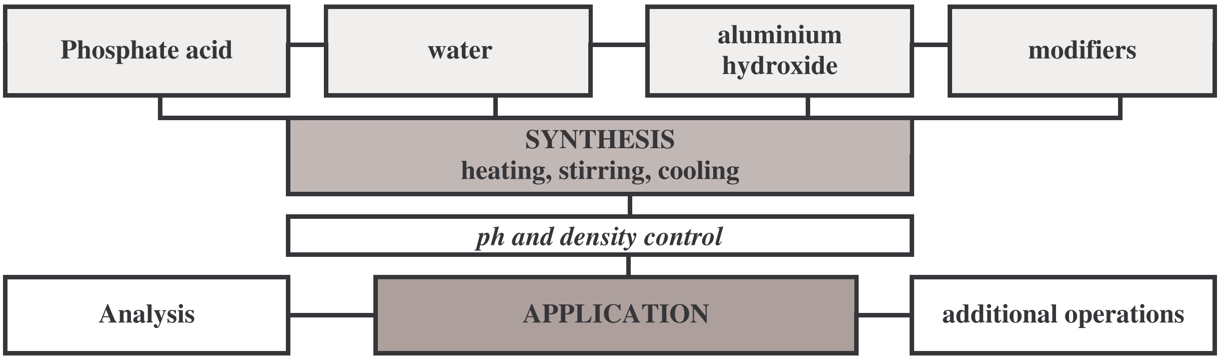


Figure 1. Scheme of the aluminium phosphate binder synthesis

The binder produced as a result of the above procedure constitutes one of the fundamental components of the coating material to be obtained. After a number of technological operations presented in figure 2, a finished coating material is obtained. It can be either used to seal thermally sprayed coatings or serve as an independent cover.

The coating material after its application requires thermal treatment in order to remove water from it. During the thermal treatment, a transformation of hydrated phosphates to a hexagonal and regular lattice $Al(PO_4)_3$ was found as well as a transformation of aluminium phosphate $AlPO_4$ from a tetragonal lattice to a rhombohedron one. Changes of the binder phase composition during soaking are shown in Table 1.

The thermal treatment process is not complicated and can be conducted under actual operating conditions.

Table 1.
Phase composition of a modified aluminium phosphate binder in the temperature range 293-1073 K

Temperature [K]	Phase composition
353	Amorphous structure $AlH_3(PO_4)_2 \cdot 3H_2O$
393	Amorphous structure $AlH_3(PO_4)_2 \cdot 3H_2O$ $Al(H_2PO_4)_3$ hexagonal
473	$Al(H_2PO_4)_3$ hexagonal
523	$AlPO_4$ tetragonal, $AlH_2P_3O_{10} \cdot 2H_2O$
683	$Al(PO_3)_3$ hexagonal, $AlH_2P_3O_{10}$
773	$Al(PO_3)_3$, $Al_2P_6O_{18}$
873	$Al(PO_3)_3$, $Al_2P_6O_{18}$, $AlPO_4$ tetragonal
1023	rhombic $AlPO_4$, $Al(PO_3)_3$

The aluminium phosphate binder, after adding special ceramic fillers which give different colours to the mixture, can be applied for the production of ceramic coatings. Two types of fillers were tested, one with a higher content of Al_20_3 and the other, Cr_20_3.

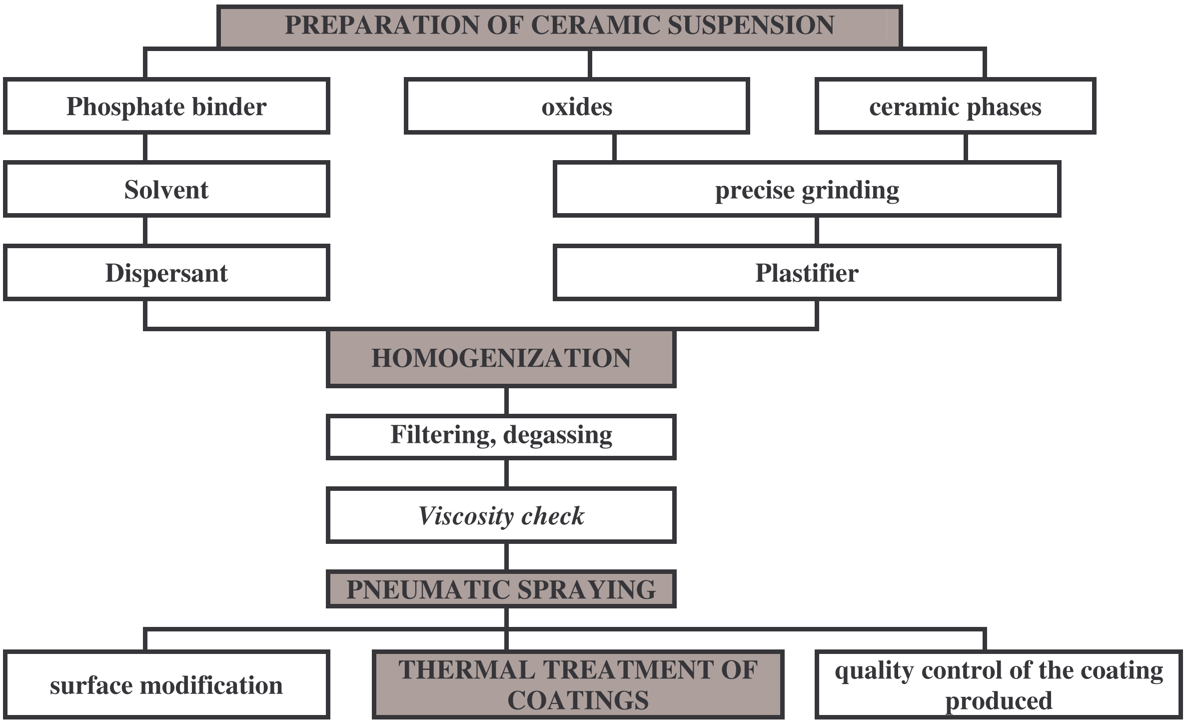


Figure 2. Scheme of the ceramic sealing or coating preparation

The X-ray diffraction pattern of ceramic coating is presented in figure 3. Structures of selected ceramic/metallic coatings and their chemical compositions are presented in figures 4.

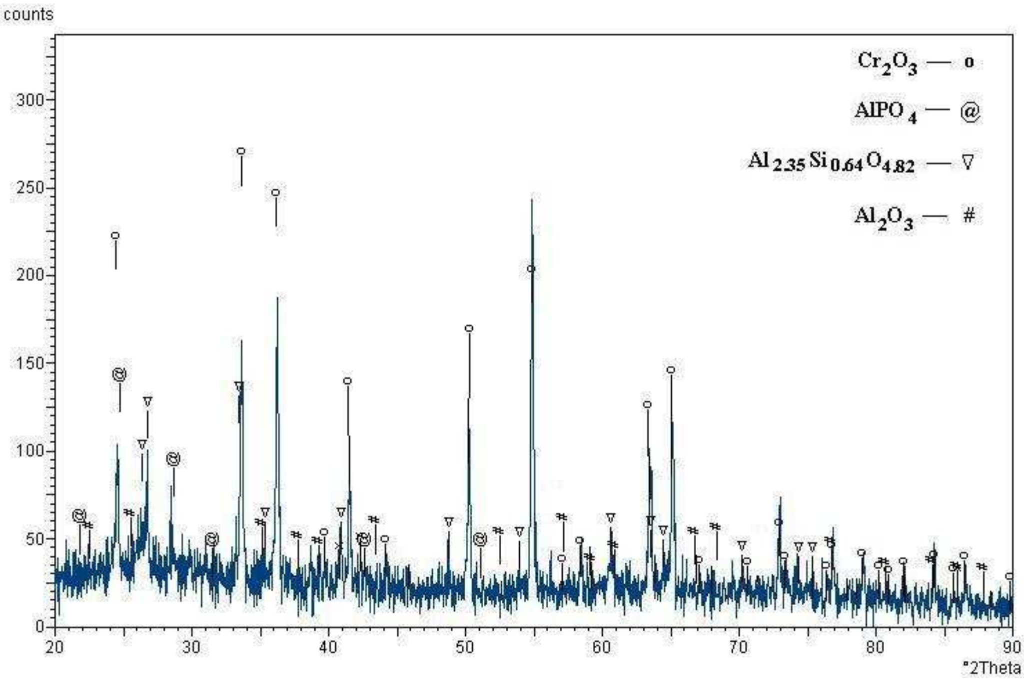
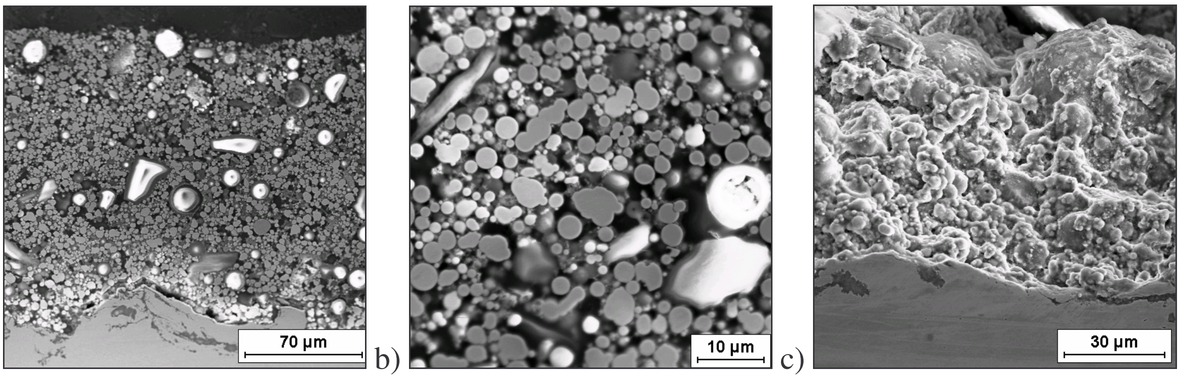


Figure 3. X-ray diffraction pattern of ceramic coatings witch Cr_2O_3.

The phase composition of the coating contain: Cr_2O_3, $AlPO_4$, $Al_{2,35}\ Si_{0,64}O_{4,82}$, Al_2O_3.



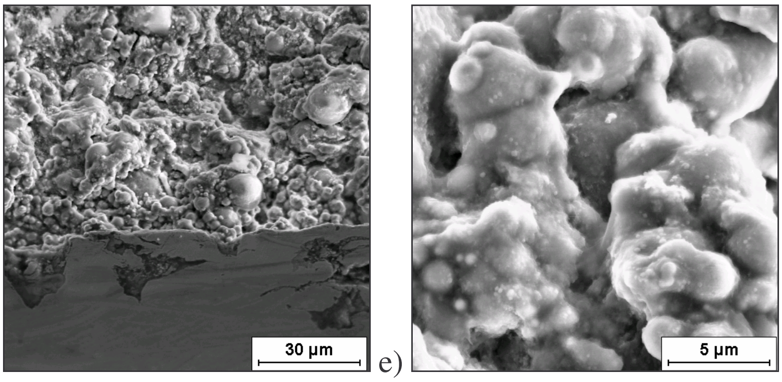


Figure 4. Structures and chemical compositions of coatings: a-b) phosphate binder – ceramic and metal particles; c-e) phosphate binder – oxides.

Chemical composition from Fig. 4c	
element	**wt.-%**
Fe	82.17
Si	10.36
Cr	4.72
Al	2.69
Chemical composition from Fig. 4d	
element	**wt.-%**
Cr	91.06
Si	4.29
Fe	4.66

Ceramic coatings were also deposited on thermally sprayed coatings. The laboratory corrosion tests have corroborated the significant increase of corrosion resistance after the application of ceramic sealing.

The morphology of composite coating with and without phosphate sealing after oxidation test are presented in fig 5. The sealed coatings have better protective properties comparable to the coatings without phosphate seal. The corrosion products on the surface of the coatings with phosphate seal after 48 hours oxidation test contain only the Al_2O_3 phase. The corrosion products structure of there coatings is nodular (fig 5B) The whiskers structure of corrosion products after 48 hours exposure time can be observed only on the coatings without phosphate seal and they corrosive layer contain the iron and aluminium oxides.

The sealing process increases the corrosion resistance of coatings in air as well as in aggressive environment. The morphology after corrosion test in gases contains chlorine and sulphur is presented in fig. 6. The layer of corrosion products on the coatings without seal contains sulphides and iron and aluminium oxides. The homogenous structure of phosphate phase can be observed only on the sealed coatings (fig 6 B).

The results of this research are presented in publications [8-12].

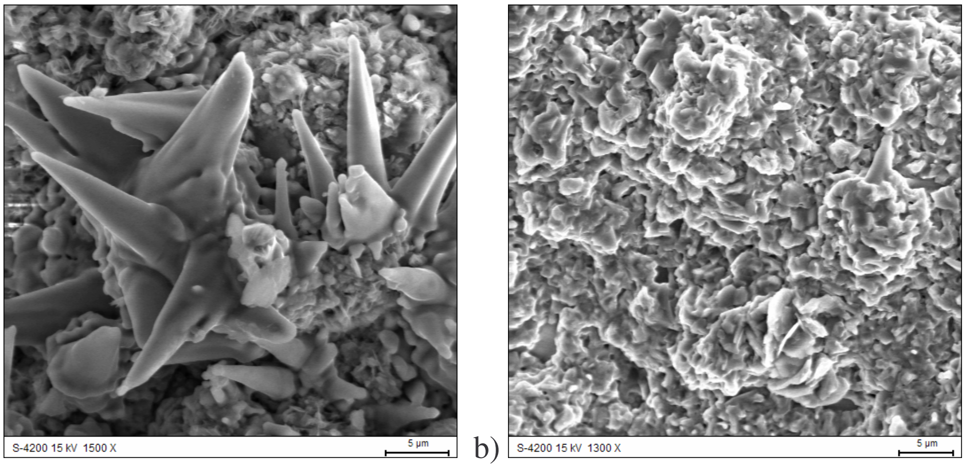
a) b)


Figure 5. Morphology of coatings after 24 hours oxidation test: a) Fe_xAl_y-Al_2O_3
b) Fe_xAl_y-Al_2O_3 with phosphate seal

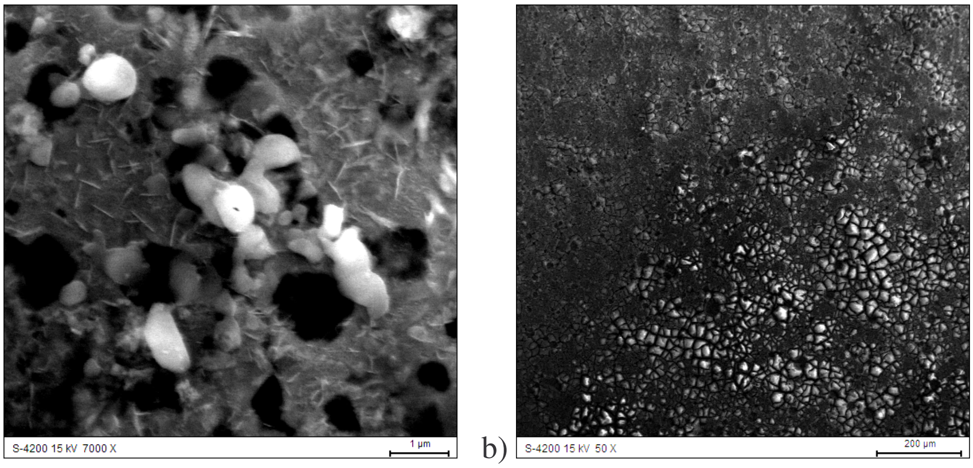
a) b)


Figure 6. Morphology of coatings after 24 hours corrosion test: a) Fe_xAl_y-Al_2O_3
b) Fe_xAl_y-Al_2O_3 with phosphate seal

4. CONCLUSION

The aluminium phosphate binder after thermal treatment forms effective sealing and is a component of ceramic coatings applied for the modification of surfaces of thermally sprayed coatings. The chemical and phase compositions as well as the properties of the sealing and coatings ensure their high protective properties at elevated temperatures and in complex aggressive corrosion atmospheres. Owing to a fraction of hard phases, e.g. Al_2O_3 or Cr_2O_3, in their chemical composition, ceramic coatings are also characterized by resistance to abrasive wear. They can work at temperatures of up to 1900°C. They are resistant to thermal shocks and have very high emissivity (at a temperature of above 800 ^{o}C for technically useful wave lengths).

The developed material and technological conception, which takes into account a modification of thermally sprayed coatings' surfaces and the fabrication of layered multi component coatings, was applied to protect the surface of power boiler water walls. Figures 7 and 8 present examples of coatings applied for the protection of water walls of pulverized-fuel power boilers.

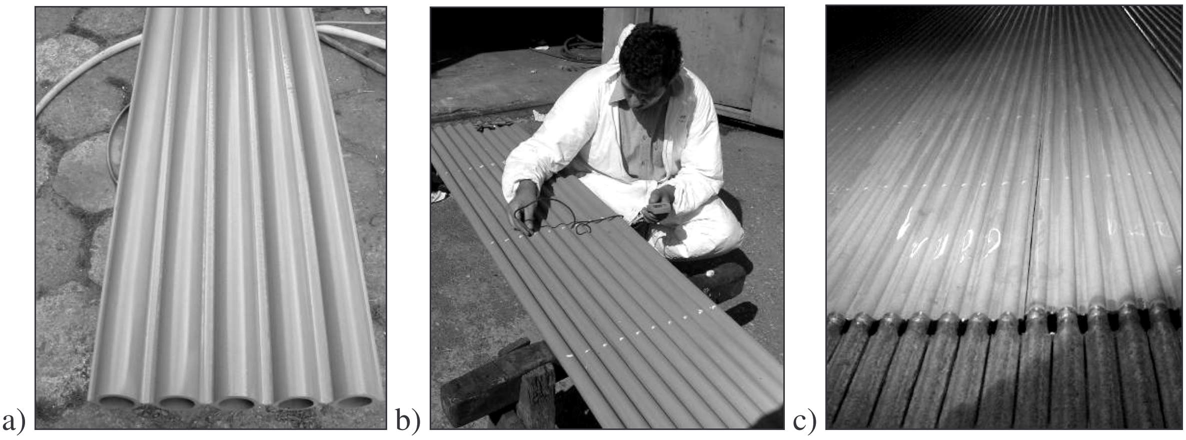


Figure 7. Ceramic coating of type B sprayed on a selected area of water wall: a) coating sprayed by pneumatic system, b) measurement of coating’s thickness after heat treatment, c) screen with a coating installed inside the water wall.

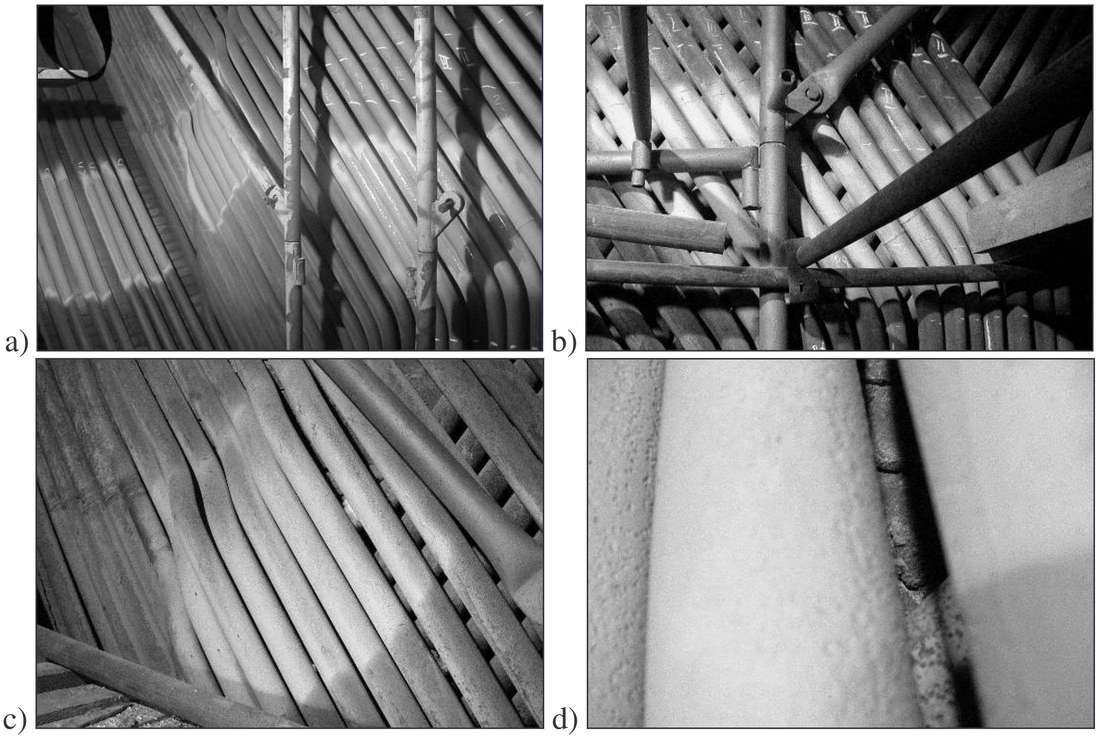


Figure 8. Ceramic coating of type A on the tube in a pulverized-fuel boiler: a) coating sprayed by pneumatic system, b,c,d) coatings after one year exploitation.

The developed variants of the production technology of coatings of the required utilitarian properties take into account the complex conditions of their operation in the power industry. The application of metal/ceramic or ceramic composite coatings can be very wide, owing to their properties.

They can be applied as:

- surface protection against corrosive wear, e.g. of ducts, electrostatic precipitators, chimneys and other installations in power plants, incinerating plants and flue gas desulphurization installations,
- in heat consuming and processing installations; owing to an increase of emissivity, the heat flow effectiveness improves with a simultaneous reduction of the working surface temperature.

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