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EFFECT OF CHEMICAL REGIMES ON OXIDE LAYERS OF MATERIALS IN POWER ENGINEERING

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Abstract: *Nowadays most commonly used materials in power engineering are stainless steels. Temperatures and pressures in systems are currently increased to achieve higher efficiency. In some plants are applied even supercritical values. This paper is focused on improvement of corrosion protection possibilities. Except new materials (titanium, nickel superalloys), different types of surface treatments or layers are used to reduce problems caused by corrosion. If passive film is formed on treated surface, e.g. nitrided, there can appear differences in its properties. The oxidic layers are common, however in operation of water-steam cycles in power plants arise problems like exfoliation, bigger porosity or disparity of passive layer. Consequence is larger corrosion rate, which leads up to degradation of the material and failure of equipment. In experimental section were created oxidic layers in laboratory conditions and was monitored the behavior of materials used in power industry. Thereafter were evaluated their properties and composition, which permits to analyze what terms are for given materials most suitable. Samples were exposed in autoclave in terms of different cycle chemistry and then analyzed by method of ESCA, X-ray diffraction and metallography.*
Keywords: *corrosion, chemical regimes, oxide layers*

INTRODUCTION

Water treatment in steam-water cycles of power stations especially should ensure functional equipment as long time as possible. Because the construction is made practically only of metallic materials, there is a need to prevent corrosion damage. The choice of suitable chemical regime and its correct regulation are in this issue essential aspect. Appropriately treated environment can considerably reduce material degradation. Dissolved substances increase solution conductivity and promote electrochemical cells formation, which participate at mechanisms of e.g. pitting and crevice corrosion. Species of the reactions taking place on metal surface are thickly affected by pH of environment. This is associated with CO_2 content regulation, which causes solutions acidification and subsequently leads to surface corrosion formation at values pH < 6. Oxygen content has to be controlled as well. It can be cause of pitting corrosion. Moreover is necessary to consider impurities and additives properties, water and steam temperature, velocity and mechanical load of the equipment.

Due to loading turbines construction both tensile and cyclic part of strain, comes up a fatigue corrosion formation risk, frequently initiated by pitting or crevice corrosion. Above that is important to consider blades erosion damage by water droplets cavitation and deposits creation. They can exfoliate from the surface and are dangerous not only for direct parts of the turbine, but can cause also regulation elements failure by clogging them.

Oxidic layers are often used steam turbines corrosion protection type. To be functional, is important to watch their state and prevent undesirable changes, which can be caused by wrong steam quality and inappropriate supply water treatment [1, 2, 3].

RESTRICTION OF STEAM TURBINES CORROSION USING SURFACE TREATMENTS

Surface treatments are effective method to reduce corrosion damage because they constitute solid barrier between the environment and metal. Most commonly are used oxidic layers, organic coatings, electroplating and thermic and vacuum surface treatments.

In this group can be included nitriding as well. However, this technique isn't applied directly as corrosion protection. Metal surface saturation by nitrogen has as a result very tough layer of fine particles alloying elements nitrides. The purpose of nitriding is surface hardness and abrasion resistance increasing while metals original properties remain. This treatment has been carried out on one of tested materials in experimental section [4, 5, 6].

EXPERIMENTAL

To compare corrosion behavior, three types of material for steam turbines construction were tested. The first is martensitic stainless steel X 12 CrNiMoV 12-3 (1.4938) produced by company Böhler. Specimens were taken from a low pressure turbine blade, which was working in Wilson line area. There occurred problems with oxidic layer exfoliation.

Next two samples types are made from nickel superalloy Nimonic 901. Beside nickel (40 – 45 %) it contains approximately 30 % iron and 11 – 14 % chrome. In experiment were tested basic material without surface treatment and nitrided material. Each specimen *except nitrided ones was grinded before testing. Samples designation overview is in Table 1. Numbers are the same as expositions.*

***Table 1**: Designation of samples*

Material	Designation
1.4938 (blade)	L1
	L2
	L3
Nimonic 901 basic	NZ1
	NZ2
	NZ3
Nimonic 901 nitrided	NN1
	NN2
	NN3

All samples were exposed in the autoclave simulating steam turbines operation conditions. Three experiments were performed. Terms were set to locate specimens in the superheated steam environment and their summary is below in tables 2 – 4. Volumetric flow of water was circa 4.6 ml/min. Expositions were implemented due to materials behaviour in terms of different chemical regimes comparison.

***Table 2:** 1st exposition*

T [°C]	570
p [MPa]	6
τ [h]	59
pH	< 10
Degassed water	Yes

***Table 3**: 2nd exposition*

T [°C]	570
p [MPa]	4
τ [h]	66
pH	< 8
Degassed water	No

***Table 4**: 3rd exposition*

T [°C]	610
p [MPa]	3
τ [h]	66
pH	< 8
Degassed water	Yes

METHODS OF EVALUATION

Photoelectron spectroscopy (XPS) was used for chemical constitution evaluation of oxidic layers formed in autoclave. ESCA (Electron Spectroscopy for Chemical Analysis) is a technique enabling qualitative and quantitative surface analyze into depth 50 – 70 Å. Result is XPS spectrum, which displays radiation intensity as a function of binding energy. Survey spectra analyze was performed in range of binding energies 0 – 100 eV. For evaluation was used program Casa XPS [7].

For analyze and photographic documentation of oxidic layers with microscope, were made metallographic samples. Available optical microscope disposed of magnification 25x and 50x.

RESULTS AND DISCUSSION

After all expositions there was dark grey colored oxide layer on each sample surface. On several places occurred in small amount orange corrosion products (hematite Fe_2O_3). The best properties showed samples after third exposition. All layers were unbroken but thin enough.

On steel (designation L) were formed very fine layers. Nimonic 901 nitrided samples (NN1 – NN3) showed in every exposition terms relatively coherent and compact oxidic layers. Only by NN2 occurred exfoliation. Nimonic 901 basic samples (NZ1 – NZ3) were covered with a passive layer but not such undivided as on nitrided set.

On Figure 1 is survey spectrum of sample NZ3 after 15 minutes sputtering with significant iron and oxygen peaks. Figure 2 shows the same samples fitted spectrum.

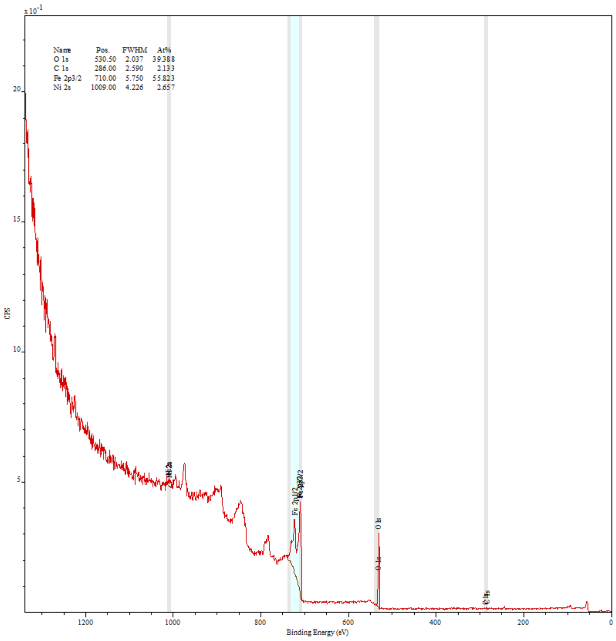

***Figure 1:** Survey spectrum of orbitals of oxidic layer elements, sample NZ3*

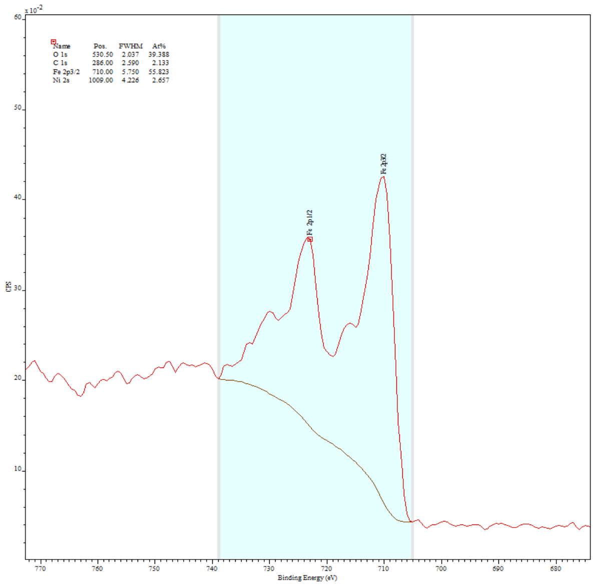

***Figure 2**: Fitted spectrum of Fe 2p1/2 and Fe 2p3/2 orbitals, sample NZ3*

Nimonic 901 basic and nitrided samples have beside original material bigger iron and oxygen content on surface and nickel content is lower as by nitrided samples nitrogen. Next identified in passive layers are chromium, molybdenum and titan, which are alloying elements. However these metals are present only in very small amounts. On surfaces of steel 1.4938 increased iron content and oxygen as well. Before sputtering there was found a low chromium amount on all samples. It is main alloying element for this material. In small amounts were identified also nickel, manganese and other.

On optical microscope is not significant layer on steel. Nimonic 901 nitrided samples have relatively thick oxide layers on surface, on NN1 even 15 µm. But NN3 only has unbroken, compact and slightly thinner layer. By this set of samples was observed one more layer under oxidic (Figure 3). This is probably the result of material structure changes caused by high temperatures influence.

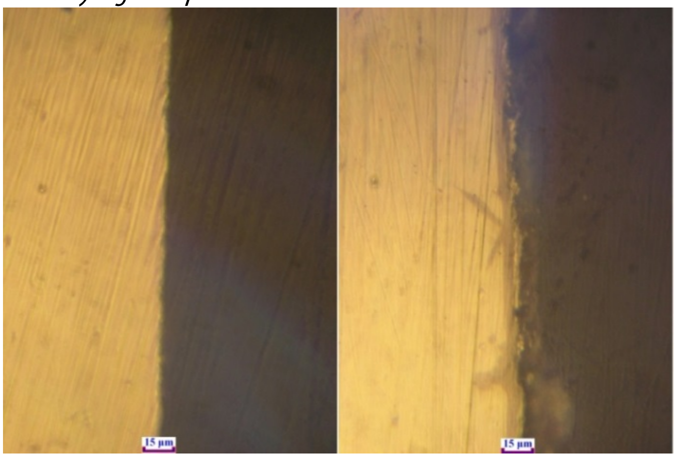

***Figure 3**: Original Nimonic 901 nitrided (left) and NN2 after exposition (right). Magnification 50x*

On Nimonic 901 basic material (NZ1, NZ2, NZ3) are very thin passive layers, visible only with higher magnification.

CONCLUSIONS

Any of samples is not hit by corrosion in a greater degree. The best properties showed oxidic layers formed in the third exposition. They are thin, coherent enough and consisted largely of iron oxides and nickel oxides on Nimonic 901. Terms were in this case set on 610°C, 3 MPa and pH < 8. Water used as medium was degassed with argon.

Each material behavior depends on environment conditions. In general, all samples resisted experiments. Only NN2 has exfoliating layer. This could be dangerous in steam turbines operation, because of mechanical damage and regulation elements blocking. It was probably caused by the water with content of oxygen used in this part of experiment. Structure changes on Nimonic 901 nitrided surface, raised due to extreme terms influence on alloying metals behavior. This phenomenon can cause changes in material properties, for example fragility increase.

Steel 1.4938 samples did not form significant passive layers during any exposition. This material has to resist high temperatures and pressures without hardness and tensile strength changes. In next research is appropriate to study oxidic layers structure and surface material changes as was evident on Nimonic 901 nitrided more in detail.

REFERENCES

[1.] *Karas, F. Koroze energetických zařízení. Úprava kotelní vody a čistota páry, 1st ed.; Státní nakladatelství technické literatury: Praha, 1965.*
[2.] *Brát, M. Koroze turbín a ochrana povlaky. Diplomová práce, VŠCHT v Praze, 2001.*
[3.] *Ahmad, M.; Casey, M.; Sürken N. Experimental assessment of droplet impact erosion resistance of steam turbine blade materials. [Online] 2009, 9-10, 1605-1618.*
[4.] *Vojtěch, D. Kovové materiály, 1st ed.; Vydavatelství VŠCHT v Praze: Praha, 2006.*
[5.] *Souto, R. M.; Mirza Rosca, I. C.; Gonzáles, C. Resistance to Localized Corrosion of Passive Films on a Duplex Stainless Steel. 2001, 4 (57).*
[6.] *Abreu, C. M.; Cristóbal, M. J.; Losada, L.; Nóvoa, X. R.; Pena, G.; Pérez, M. C. The effect of Ni in the electrochemical properties of oxide layers grown on stainless steels. [Online] 2006, 51, 2991-3000. www.sciencedirect.com (accessed Nov 11, 2013).*
[7.] *X-Ray Photoelectron Spectroscopy / Electron Spectroscopy for Chemical Analysis (XPS / ESCA). Evans Analytical Group. http://www.eaglabs.com/mc/x-ray-photoelectron-spectroscopy.html (accessed May 07, 2013).*

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