Fluorocarbon Production Residue in Composite Coating Used for Protecting Heat-and-Power Equipment from Damage

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Abstract. Most often breakage in heat-and-power facilities is caused by decomposition of heating elements while in process. The reason of it is a thick layer of boiler scale on their surface caused by hardness salts and ferric carbonates in industrial water, as well as by roughness of the surface of the heater. The quality of the surface is improved by polishing and covering it with a layer of nickel. The above-mentioned processes could be replaced by covering the surface with a composite electrochemical coating (CEC nickel-fluorocarbon) using fluorocarbon production residue which contains a mixture of fluorocarbon and carbon black. Estimate of the parameters of the process of getting CEC nickel-CFx showed that nickel current output does not depend on presence of a dispersion phase (CFx) in conditions of high current density. Throwing power is even, so that it is possible to get uniform nickel coatings and CEC nickel-CFx. It was stated that the physical characteristics, as well as anti-scaling and anti-corrosion characteristics of CEC nickel-CFx are higher than those of nickel coating. CEC nickel-CFx is recommended for using in heat-and-power equipment.

1. Introduction

The researchers are much working over getting composite coatings with tribological, anti-corrosion, anti-stick, and anti-scaling properties. Long-term exploiting of a coating without any deterioration of the above-mentioned properties is possible if the coating is got when metals serve as the matrix (nickel, copper, chrome, cobalt) and dispersion particles of inorganic compounds (molybdenum disulfide, mineral carbon, boron nitride, cadmium halides, silver iodide, plumbous oxide, etc.) or polymers are used as the second phase. When mineral carbon is used compact layers get as hard as nickel. Their wearability increases 3 - 5 times. Polytetrafluorethylene (PTFE) is widely used as it has all the necessary properties.

2. Relevance, scientific significance, literature review

Development is to out the conditions for getting CEC nickel- fluorinated carbon with stable chemical and physical characteristics in a broad interval of surface-active substances (SAS) and a dispersion phase.

The advantages of composite electrochemical coatings (CEC) over metal coatings are evident, both at low and high temperatures. Heat treatment contributes to wearability, corrosion resistance dynamic durability increase [1].

CECs on the basis on nickel are the most widely-spread, they have lubrication properties. As a dispersion phase fluorinated carbon (CFx) could be used as it is physically and chemically stable. CFx has the same
ability of to form CEC with metals as PTFE. CECs with CFₓ as the disperse phase have a low friction ratio and are high anti-corrosion properties. So they have a high potential in different spheres of industry.

CFₓ is highly resistant to most of corrosive mediums because of the C-F connection is the strongest of all the connections of carbon with other elements known of in organic chemistry. A big size and a special composition of fluor atoms around carbon make the C-C link unavailable for any attack of chemical reagents. A symmetrical composition of fluor atoms presupposes weak intermolecular forces, insolvability in all the solvents, and low adhesiveness of fluorine derivatives to other materials [2-3].

Fluorine derivatives are chemically clean and inert; they do not have any additives and do not influence process fluids [4].

3. Problem statement, theoretical part
For getting CEC nickel-CFₓ fluocarbon production residue containing a mixture of fluocarbon and technical carbon T900 was used. Electric-chemical precipitation of nickel coating was made on samples of copper М1 sized 0.05 or 1.00 dm² and n electrolyte the content of which is presented in Table 1.

| Component       | Formula                  | Concentration , г/л | Electrolyte №1 | Electrolyte №2 |
|-----------------|--------------------------|---------------------|----------------|----------------|
| Nickel chloride hexaqua | NiCl₂ ×6H₂O             | 126                 | 126            |                |
| Mixture: fluocarbon-82.04 %; technical carbon T900 -17.96 % | CFₓ + C               | 0                   | 4.5            |                |
| Saccharinose    | C₇H₅NO₃S                | 1.4                 | 1.4            |                |

Electrolyte pH is 4.0-4.5. The temperature of the process was 50-55 °C. Current efficiency of nickel (BΤₐₙ) was calculated according to Faraday’s second law [5]. Internal stresses were calculated by the method of flexible cathode deformation [6]. Throwing power was assessed according to distribution of coating thickness in Moler’s electrolytic cell, current force was 1 А, electrolysis time was 0.5 hour, then deflection of coating thickness distribution from primary current distribution on the collapsible cathode was calculated [7].

Anti-scaling properties of CEC КЭП Ni-CFₓ were tested in an evaporating system [8], samples in the form of pipes which were 0.04-0.05 m long and with the outer diameter of 0.012-0.013 m with a different state of the effective surface: either coated with CEC Ni-CFₓ or coated with nickel. The samples were kept in boiling water for 100 hours. For estimating anti-scaling properties of the surfaces water with hardness according to calcium ions and magnesium ions equal to 3.0-6.0 mg-eq/l was used. To shorten the time of assessing anti-scaling properties of nickel and composite coating of copper pipes calcium and magnesium ions concentration was increased 5 times. Boiling lasted 100 hours. Each 10 hours the amount of scale which appeared on the samples surface during the period of time was assessed.

Scale mass was found out as a difference in mass of the samples after and before the process of boiling.

Anti-corrosion properties were tested in a 3% solution of sodium chloride at 20 °C in a salt-spray chamber. Mass of the samples was measured and the appearance of the surface was estimated every 10 hours. The number of corrosion points on 1 sm² of the surface was fixed. Mass coefficient of corrosion speed was calculated according to the formula Кₘ=Δm/(S×τ), with Кₘ as a mass coefficient of corrosion speed, g/dm²×h; Δm – mass change in the sample, g; S – the sample area, dm²; τ – corrosion time, h.
4. Practical significance and results of experimental studies
The main condition of getting CEC Ni-CFₓ on products contacting with hot water and steam is a constant composition of CEC and constancy of its mechanical, physical, and chemical properties, it strongly reduces a possibility of corrosion and scale on the heating part surface of heat-and-power equipment.

Assessing $B_{T,Ni}$ in electrolytes №1 and №2 in the interval of cathode current density 1.5–2.5 A/dm$^2$ showed that in getting nickel it accounts for 97.6–99.1 % and in CEC Ni-CFₓ precipitation – 91.3 – 99.0 %. The results of researching morphology of surfaces, nickel and CEC Ni-CFₓ, are shown in picture 1.

![Figure 1. Morphology of surfaces: nickel (a) and CEC Ni-CFₓ (b). Zoom 1000×](image)

Picture 1a with zoom 1000×demonstrates that nickel surface has defects, i. e. points placed around the perimeter of grains. CEC Ni-CFₓ (pic.1b) consists of homogeneously enclosed fluorocarbon particles stuck to the surface with as-deposited layers of nickel. CEC Ni-CFₓ actually has no mechanical defects. Inclusions of technical carbon Т900 were not noticed. High internal stresses of stretch of nickel coating precipitated from electrolyte № damage its structure and cause scaling and flaking off. To lessen or fully stop internal stresses of stretch of nickel coating and CEC Ni-CFₓ is possible by means of sustaining optimal acidity of the electrolyte, by appending SAS by regulating current density. To avoid any fault of the surface chloride-containing electrolytes №1 and №2 were used (Table 1). Electrolysis last 20 min. Current density was 2.0 A/dm$^2$. The results are presented in picture 2.

![Figure 2. Dependence of internal stresses of compression from deposition time of nickel (●) and CEC nickel-CFₓ (▲).](image)

Picture 2 shows that irrespective of electrolytes’ content and electrolysis time (coating thickness) precipitation always appears caused by internal stresses of compression. If internal stresses of compression grow, mechanical properties of CEC nickel-CFₓ increase more than those of nickel coating.
Visual observing showed that there is no flaking-off or micropits on the surface of CEC. Dissipative ability of electrolytes calculated by coating relative mass change to anodic slit are shown in picture 3.

**Figure 3.** Relative distribution of mass of nickel coating (●) and CEC nickel-CF₆ (▲)

The picture shows that relative distribution of coatings mass decreases if the distance to the anode grows and it becomes actually constant at the distance of 3 sm or more from the anode, which allows getting homogeneous nickel coating and CEC nickel-CF₆.

The results of calculating relative add-on of the samples in the process of boiling from the time of treatment are given in picture 4.

**Figure 4.** Relative add-on of scale on nickel coating (●) and CEC nickel-CF₆ (▲) depending on the time.

It appeared that the amount of scale on nickel coating grows every 10 hours of boiling, while the amount of scale on CEC nickel-CF₆ is considerably less and it is actually constant. So anti-scaling properties of the composite coating are higher and products coated with CEC nickel-CF₆ can be used in heat-and-power equipment.

Corrosion research after 400 hours of contact with aggressive substance showed that corrosion mass index of steel samples coated with nickel was not more than $1\times10^{-3}$ g/dm², and that of samples coated with CEC nickel-CF₆ was zero. Thus CEC nickel-CF₆ remains corrosion-resistant for a long time and it can be used as a surface coating of equipment contacting with aggressive substances and working at high temperature.
5. Conclusions
Assessing the parameters of getting CEC nickel-CFx from chloride electrolyte using flourcarbon waste contaminated with carbon T900 as a dispersion phase showed that current efficiency of nickel in conditions of low current density is lower within a dispersion phase (CFx) and it does not depend on its presence when current density is high.

CEC nickel-CFx has no mechanical defects such as deep pitting, flacking-off, cracks, and chips.

Dispersion ability of electrolytes in a broad interval of current density remains actually the same, so that it is possible to get CEC nickel-CFx homogeneous in thickness and physical properties.

Anti-scaling and anti-corrosion properties of CEC nickel-CFx are considerably higher, so that this coating could be recommended for using in heat-and-power equipment.

6. References
[1] Tang Hongke, Zhao Wenzhen and Yang Yan 2006 Mechanism of electrodeposition of a Ni-Co-PTFF composite with rare earth elements 4 Dep VINITI 2009-01 6
[2] Khitrin S V, Fuchs S L, Devyaterikova, S V, Agalakova N V and Samara V A 2005 Experience of separation, processing and utilization of waste from the process of synthesis of F-4D fluoroplasts Mir nefteproduktov 1 pp 39-41
[3] Zelenkova T N and Kalinina B Yu 1978 Environmental protection in the production of plastics and hygiene of the use of plastics (L.: Mysl.) p 128
[4] Devyaterikova S V, Khitrin S V and Fuks S L 2003 The use of mother solutions for the production of fluoroplast for the production of composite coatings Journal of Applied Chemistry vol 4 pp 690 – 692
[5] Antropov L I 1984 Theoretical electrochemistry Textbook for universities (M.: Higher school) p 518
[6] Popereka M Ya 1966 Internal voltage of electrolytically deposited metals (Novosibirsk: Zap. sib. Book. Ed.) p 336
[7] Antonov V T, Fomichev V A and Zybin E N Kutygin Publ. 07.11.82. Bulletin No 41
[8] Mashtalyar D V 2007 Antinakipin Formation of composite layers on the heat transfer elements of ship power plants Author. dis. Cand. tech. Sciences Institute of chemistry, far East branch, Russian Academy of Sciences (Vladivostok) p 25