

Stripping of copper coatings from steel in Cr(VI)-free commercial bath

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ABSTRACT

In this work the electrochemical characteristics of copper and steel in chromate, cyanide, and phosphate baths as well as in a commercial bath (ENSTRIP S-180), in the absence of chromium and cyanides were determined. Average rates of copper coatings stripping from steel in the above mentioned baths and the baths influence on the morphology of steel surfaces were described. It was found that the commercial bath ENSTRIP S-180 could be successfully used for stripping of copper coatings from steel elements.

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1. Introduction

Steel is the most frequently applied construction material. In order to provide steel with the adequate mechanical properties, it is subjected to thermo-chemical treatment, i.e. it is heated in a specially adapted medium with the purpose of changing its chemical composition in the surface layer [1]. The aim of such a procedure is to obtain a high hardness of the surface layer of the object while keeping its ductile core.

From various methods of thermo-chemical treatments, carburization, nitration and carbonitration, ensuring a high resistance to abrasion, dynamic loads and corrosion are the most often used ones. Carburization is carried out at a higher temperature than the temperature of the austenitization of steel, generally within the range of 880–950 °C. In this medium, carbon forming the carbonized surface is separated, and the carbonized parts are quenched. During this procedure mainly the carbonized layer becomes harder with an increased concentration of carbon [2]. Such a procedure is applied in the case of the parts that require a hard surface, resistant to abrasion, high pressure and fatigue, maintaining however a ductile and elastic core of high impact strength. There are situations in which some parts after their carburization and quenching must display locally a reduced hardness, equal to that of the core, for instance when these parts are subjected to a local machining (e.g., drilling holes). In such cases there are parts of the machines subjected to carburization where diffusion of carbon in the surface layers is not admissible. These parts of the elements are protected against the diffusion of carbon by coatings prepared by electroplat-

ing method [3,4]. Most often this is a copper coating, serving as a barrier between carbon and metal. Practically, even a thickness of only 3 μm prevents the penetration of carbon into steel, thanks to the weaker affinity of copper for carbon than the affinity of other metals [5]. After the process of carburization and quenching, the copper coating must be stripped without damaging the substrate. For this purpose very often a chemical method is applied, consisting of the digestion of copper in a solution containing 250–300 g dm⁻³ CrO₃ and 100–120 g dm⁻³ (NH₄)₂SO₄, or in a solution containing 120 g dm⁻³ CrO₃ and 1.5 g dm⁻³ H₂SO₄ [6]. This process yields large amounts of sewage sludge [7].

Compounds of chromium(VI), being very strong oxidizers, cause negative changes in living organisms, affecting DNA in cells, which leads to the development of cancerous diseases. In the industrial world scale these compounds may occur in the form of vapor and smog, so that they can be easily inhaled by living organisms. In the case of mercury, cadmium and hexavalent chromium the strictest standards are applied concerning sewage sludge discharged to the environment, because they belong to the most dangerous metals in the environment [8,9].

The aim of these investigations was to determine the possibilities of applying a commercial bath that does not contain any chromium compounds for the purpose of stripping copper coating from steel.

2. Experimental

2.1. Investigations concerning the corrosion resistance of copper and steel

The investigations of corrosion resistance of copper and steel were carried out using pure copper and 316L stainless steel, of

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Table 1
Chemical composition of stainless steel 316L.

Element	C	Si	Mn	Cr	Mo	Ni	Fe
Mass fraction/%	<0.03	1.0	2.0	16.5–18.5	2.0–2.5	11.0–14.0	Rest

chemical composition presented in Table 1. The copper and stainless steel samples used in these investigations were 5 cm long rods, of 3.0 mm diameter.

Before measurements, the copper samples were ground with 320 and 600 grit SiC paper, followed by etching for 10 min in 1:1 diluted nitric acid. The stainless steel samples were ground with 320 and 600 grit SiC paper and then degreased in acetone.

Investigations concerning the corrosion resistance of copper and stainless steel were carried out using the potentiodynamic method. The main element of the apparatus was a typical double-chamber electrolyzer with three electrodes. The test electrode, the auxiliary platinum electrode and the Haber–Luggin capillary with a reference electrode, viz., the saturated calomel electrode (SCE) were immersed inside. The electrolyzer was powered by a potentiostat (AUTOLAB POSTAT 30), which was controlled by the program GPES (General Purpose Electrochemical System). The investigation comprised the measurement of the: corrosion potential, E_{corr} , the relation $j = f(E)$ determining the value of the corrosion current, j_{corr} , the polarization resistance, R_p and the linear rate of corrosion, V_p , characterizing the corrosive wear of the material in mm year^{-1} . The measurements of the corrosion resistance were run at 40°C in the following solutions:

- chromate bath; CrO_3 , 250 g dm^{-3} ; H_2SO_4 , 40 g dm^{-3} ,
- cyanide solution; KCN, 200 g dm^{-3} (pH 13),
- commercial bath ENSTRIP S-180, containing diethylenetriamine, sodium 3-nitrobenzenesulfonate and NH_4Cl .

The corrosion resistance of stainless steel in the tested solutions was also determined gravimetrically. Cylindrical stainless steel samples 5 mm high and 2 cm in diameter, were weighed, placed in a 250 cm^3 beaker and inundated with the tested solutions. After 24 h the samples were taken out, rinsed and again weighed. In this way the weight loss of the stainless steel was determined.

2.2. Investigations concerning the stripping of copper coatings from stainless steel

Samples of stainless steel in the form of 5 cm long rods of 3.0 mm diameter, coated with a layer of copper about $40 \mu\text{m}$ thick, were tested. The copper plating was carried out in a pyrophosphate bath of the following composition:

- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 35 g dm^{-3} ,
- $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, 140 g dm^{-3} ,
- $\text{Na}_2\text{HPO}_4 \cdot 10\text{H}_2\text{O}$, 95 g dm^{-3} .

The applied parameters were:

- -temperature, 40°C ,
- -cathode current density, 1 A dm^{-2} .

The copper coatings were stripped from the stainless steel chemically in the chromate bath, cyanide bath and in the commercial ENSTRIP S-180 bath at 20, 40, and 60°C . The apparatus in presented schematically in Fig. 1.

About 250 cm^3 of solution was poured into 500 cm^3 flasks; the flasks were placed in the water bath and heated up to the required temperature. As soon as the required temperature was achieved, samples of copper-plated stainless steel were immersed into the

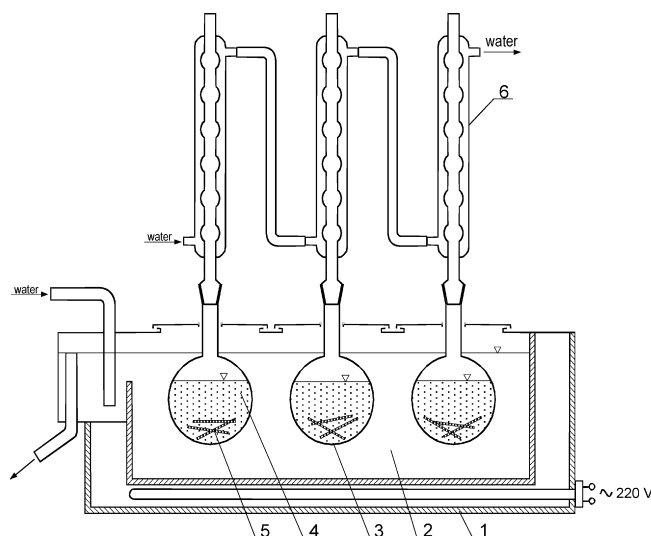


Fig. 1. Diagram of the test stand for the stripping of copper coatings; 1, water bath; 2, water; 3, round bottom flask; 4, bath; 5, samples; 6, reflux condenser.

flasks. The process was continued until all the copper coating was stripped. The samples were weighed before and after the tests in order to determine the average rate of stripping the copper coating. The mean value of the rate of stripping the coating was calculated by means of the formula 1:

$$a = \frac{\Delta m}{dst} [\mu\text{m h}^{-1}] \quad (1)$$

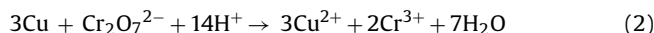
where: a is the average rate of stripping the copper coating, $\mu\text{m h}^{-1}$, Δm , decrease of the mass of the copper coating in the time t , g, d , density of copper, 8.92 g dm^{-3} , t , duration of the stripping of the coating, h, s , exposed surface area of Cu, cm^2 .

In order to determine the effect of the bath used for the stripping of copper coatings on the morphology of the surface of stainless steel, selected samples were examined using a scanning electron microscope Hitachi S-3400N, and the chemical composition of their surface was subjected to the microanalysis applying the EDS method (a system of X-ray microanalysis of the firm Thermo Noran, equipped with the software System Six).

3. Results and discussion

Copper can be oxidized using the whole volume of the solution by means of chemical oxidizer (mediator) and then submitted to reduction. The reduced mediator (load transmitter) then regenerates (oxidizes) electrochemically on the surface of the anode and again participates in the basic reaction (being reduced during the process of oxidation). The system applied so far ($\text{Cu} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cu}^{2+} + \text{Cr}^{3+}$) is an electrochemical system, but without any external supply of electricity. It can be absolutely applied reciprocally. This system may be described by means of the following partial processes:

1. Oxidation of metallic copper to divalent ions by hexavalent chromium compounds, which are reduced to trivalent chromium:



The partial reactions of the redox system are:

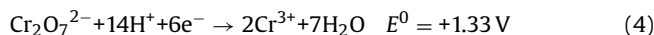
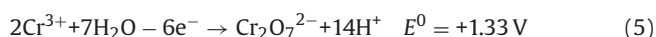


Table 2

Parameters of the corrosion resistance of copper and stainless steel in solutions applied for stripping of copper coatings.

Kind of bath	$j_{\text{corr}}/\text{mA cm}^{-2}$	$R_p/\text{k}\Omega \text{ cm}^2$	$E_{\text{corr}}/\text{mV}$	$V_p/\text{mm year}^{-1}$
Copper				
Chromate	24.99	1.34×10^{-3}	370.0	290.9
Cyanide	0.14	86.13×10^{-3}	-1598.9	1.576
ENSTRIP S-180	7.11	4.10×10^{-3}	-560.9	82.77
Steel				
Chromate	0.78×10^{-3}	284.93	85.6	0.008
Cyanide	0.38×10^{-3}	158.04	-570.8	0.004
ENSTRIP S-180	0.32×10^{-3}	296.18	-438.8	0.003

2. So far, the post-reaction solution has been discharged to the sewage treatment system and rendered harmless, although it might be electrochemically regenerated to compounds of hexavalent chromium on the anode (e.g. lead anode):



As the oxidizer, which is the load transmitter, any other substances may be used that do not react with stainless steel. Of essential importance is the choice of the proper substance to complex the copper ions, preventing the reaction of free copper ions with stainless steel. The fundamental condition due to the absence of any effect to copper ions on the surface of stainless steel is an adequately high durability of the complex compound binding the ions of the digested copper. The concentration of free copper ions resulting from the dissociation of the complex compound determines the value of the potential of the copper electrode submerged in this solution.

Based on the observed results, it has been found that the steel in the investigated baths is highly corrosion resistive. The corrosion current density reaches about $0.3 \times 10^{-3} \text{ mA cm}^{-2}$ in the case of the ENSTRIP bath, and to about $0.8 \times 10^{-3} \text{ mA cm}^{-2}$ in case of the chromate bath. The corrosion potential of stainless steel reaches its highest value in the chromate bath, amounting to about 86 mV. The linear rate of corrosion is equal to 0.003–0.008 mm year^{-1} (Table 2). In the case of copper the linear rate of corrosion, the density of the corrosion current and the polarization resistance in the chromate bath are equal to about 300 mm year^{-1} , about 25 mA cm^{-2} and $1.3 \times 10^{-3} \text{ k}\Omega \text{ cm}^2$, respectively. These results prove that in a medium containing chromic(VI) acid no corrosion resistance of copper can be detected at all (Table 2). Copper is characterized by a slightly higher resistance in the commercial bath ENSTRIP S-180 (linear rate of corrosion ca. 85 mm year^{-1} ; density of the corrosion current about 7 mA cm^{-2}).

Table 3

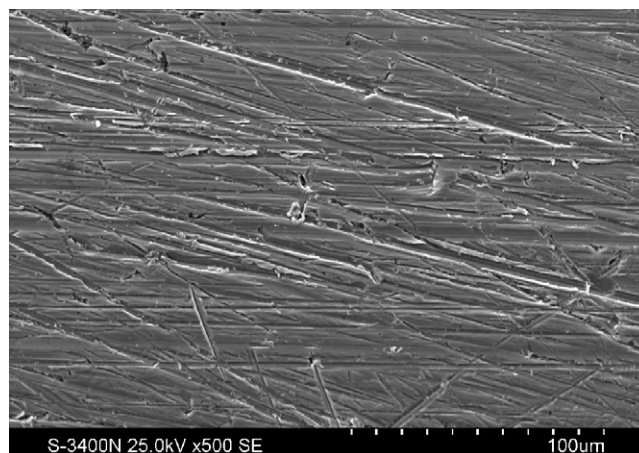
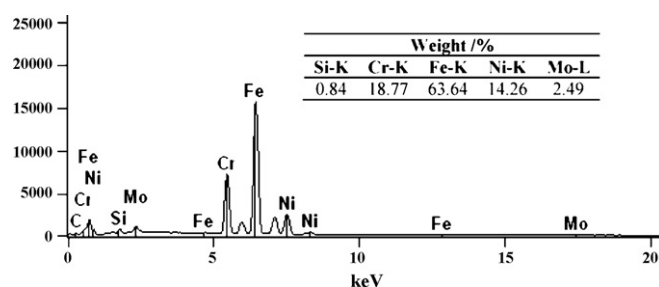
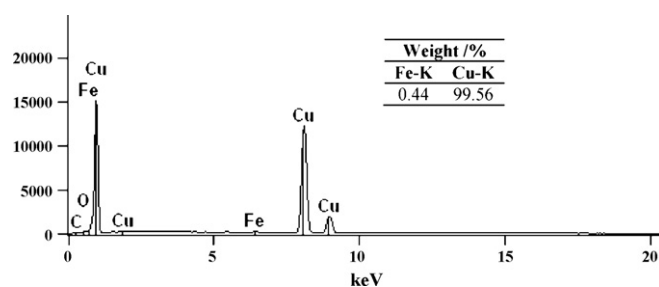
Results of gravimetric measurements of the corrosion resistance of stainless steel.

Kind of bath	Mass of the samples/g	
	Before	After 24 h
Chromate	25.8339	25.8339
Cyanide	25.8456	25.8456
ENSTRIP S-180	25.8387	25.8387

Table 4

Rate of the stripping of copper coatings from stainless steel depending on the applied bath and temperature.

Kind of bath	$a/\mu\text{m h}^{-1}$		
	20 °C	40 °C	60 °C
Chromate	23.9	48.2	44.3
Cyanide	10.8	11.7	25.9
ENSTRIP S-180	8.3	11.0	14.8

**Fig. 2.** SEM image of stainless steel surface.**Fig. 3.** EDS spectra and chemical microanalysis of stainless steel surface.**Fig. 4.** SEM image of copper coating on steel.**Fig. 5.** EDS spectra and chemical microanalysis of surface of copper coating on stainless steel.

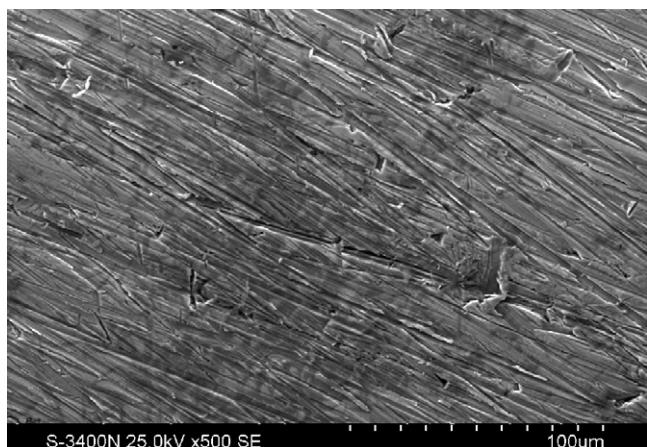


Fig. 6. SEM image of stainless steel surface after stripping of copper coating in ENSTRIP S-180.

Table 5
Chemical microanalysis of stainless steel surface after stripping of copper coating.

Kind of bath	Weight/%					
	Si-K	Cr-K	Fe-K	Ni-K	Cu-K	Mo-L
Chromate	0.70	18.78	63.31	13.84	0.85	2.51
Cyanide	0.79	19.05	63.44	14.12	–	2.60
ENSTRIP S-180	0.79	18.71	63.25	13.90	–	3.35

From the gravimetric investigations concerning the corrosion resistance of stainless steel it has been found that during 24 h the weight of the samples did not undergo any changes independently of the applied bath (Table 3). These results fully confirm the absolute corrosion resistance of stainless steel in the investigated solutions.

The rate of copper coatings stripping from stainless steel depends essentially on the process temperature and the kind of the applied bath (Table 4). The highest rate of copper stripping is achieved in the chromate bath at 40 °C, viz., about 48 $\mu\text{m h}^{-1}$. The rate increases with the rise of temperature from about 11 to about 26 $\mu\text{m h}^{-1}$ in the case of the cyanide bath, and from about 8 to about 15 $\mu\text{m h}^{-1}$ if ENSTRIP is applied. Despite such considerable differences in the rate of copper coatings stripping from stainless steel the application of the ENSTRIP bath should to be selected, because the chromate and cyanide baths contain noxious components.

Figs. 2 and 3 illustrate the surface of stainless steel subjected to copper plating and the microanalysis of the composition of its surface, and Figs. 4 and 5 show the surface and microanalysis of the copper coating composition on stainless steel. The surface and

microanalysis of the composition of the stainless steel surface after the stripping of copper in the respective kinds of baths have been presented in Fig. 6 and Table 5. The obtained results show that in each of the investigated solutions the copper was practically stripped completely. Only in the case of the chromate bath on one of the samples traces of copper (about 0.85%wt.) were detected. Such a low value may, however, result from an error in the chemical analysis of the surface and may be neglected. Neither do the applied baths affect the morphology of the surface of stainless steel in the investigated solutions.

4. Conclusions

From the obtained results it has been found that copper is digested in each of the investigated baths, although at a different rate. Stainless steel, however, is characterized by high corrosion resistance in these baths. Copper coatings can be stripped from stainless steel in baths containing the copper complexing agents, e.g., cyanides (the formal potential of copper amounts in such a solution to 1.271 V) or diethylenetriamine (formal potential of copper -0.285 V). In spite of the slower reactions, these baths constitute an alternative for the solutions containing carcinogenic compounds of hexavalent chromium. The process of copper stripping can be intensified by adding to the solution the compounds which oxidize the copper besides the complexing substances, or by the aeration of the bath. The ENSTRIP S-180 bath has occurred to be a good one for copper stripping from stainless steel. The main component of this bath is diethylenetriamine, a copper complexing agent. The most essential advantage of this bath is that it does not contain any chromium compounds and that it does not attack the steel substrate.

References

- [1] S. Prowans, Materials Science, PWN Polish Scientific Publishers, Warsaw, 1980.
- [2] A. Moszczyński, Gas Carburizing of Steels, WNT Scientifically-Technical Publishing House, Warsaw, 1983.
- [3] J. Siepak, Influence of residual austenite on properties of carburized gear-wheels, *Mechanic* 11 (1979) 5.
- [4] L. Dobrzański, et al., Metal Science and Heat Treatment of Tools Materials, WNT Scientifically-Technical Publishing House, Warsaw, 1990.
- [5] A.A. Appen, Inorganic Heat Resistance Coatings, WNT Scientifically-Technical Publishing House, Warsaw, 1970.
- [6] Multi-author work, Handbook of Electroplating, WNT Scientifically-Technical Publishing House, Warsaw, 2002.
- [7] G. Nawrat, W. Gnot, W. Simka, E. Pol-Sekuła, Best available techniques in the chlor-alkali technology, *Przem. Chem.* 84 (6) (2005) 422.
- [8] A. Bielicka, I. Bojanowska, A. Wiśniewski, Two faces of chromium—pollutant and bioelement, *Pol. J. Environ. Stud.* 14 (1) (2005) 5.
- [9] Z. Kowalski, M. Konopka, Methods of chromic waste waters treatment, *Ecol. Chem. Eng.* 9 (7) (2002) 707.