The potentiodynamic polarization using PIGE – testing of a method that helps identify historical metallic materials

Potenciodynamická polarizace s využitím PIGE – ověření metody pro identifikaci historických kovových materiálů

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The potentiodynamic polarization using a paraffin impregnated graphite electrode (abbreviated as PIGE) is an analytical electrochemical method suggested as an alternative to commonly used procedures of identification of historical metallic materials. The principle of the method consists in potentiostatic reduction of a small amount of the sample's corrosion products deposited on a PIGE and subsequent potentiodynamic oxidation of the reduced metals. The obtained potential/current density potentiodynamic curve is the starting point for determination of a metal present in the alloy (based on peaks' positions on the curve). The aim of the study was to test the methodology for identification of historical metallic materials and to monitor parameters that might impact the results of the analysis (polarization rate, size of particles, electrolyte de-aeration). The study also aimed to test suitability of the method for a quantitative analysis. Having applied the procedure on selected samples of alloys (solder and copper alloys), traces of silver, copper, tin and lead were identified in the samples, however, the possibility of using the method for quantitative analysis was not proven.

Potenciodynamická polarizace s využitím parafínem impregnované grafitové elektrody (zkráceně PIGE) je analytická elektrochemická metoda, navrhovaná jako alternativa k běžně používaným postupům identifikace historických kovových materiálů. Princip metody spočívá v potenciostatické redukci nepatrného množství korozních produktů vzorku přenesených na PIGE a následné potenciodynamické oxidaci takto vyredukovaných kovů. Získaná závislost potenciálu na proudové hustotě v podobě potenciodynamické křivky je výchozí informací pro určení přítomnosti kovů ve slitině (na základě poloh píků na křivce). Cílem práce bylo ověření použití této metodiky pro identifikaci historických kovových materiálů a sledování parametrů, které mohou mít vliv na výsledek analýzy (rychlost polarizace, velikost částic, odvzdušnění elektrolytu). Součástí práce bylo také zkoumání vhodnosti použití metody pro kvantitativní analýzu. Aplikace postupu na vybrané vzorky slitin (slitiny mědi, pájky) vedla k identifikaci přítomnosti stříbra, mědi, cínu a olova. Možnost kvantitativní analýzy potvrzena nebyla.

INTRODUCTION

Analysis plays an important part in conservatory and restoration practice. Identification of the material character and the type of damage is crucial for quality, sensitive and effective treatment. For the time being, there are various methods and procedures available to conservators and restorers helping them identify the state and composition of historical objects [1]. Obviously, not all of them are available on a daily basis. Moreover, if the method is supposed to meet other requirements, such as a non-destructive character and in-situ utilization, the group of actual alternative analytical tools narrows significantly [2].

Therefore, new analytical procedures combining the aforesaid properties are being searched for and tested. Electrochemical methods representing the already traditional specialisation of stabilisation, cleansing and conservation of metallic historical objects offer an opportunity where such analytic instrument could be found. One of the tools is measurement of open circuit potential in carbonate and nitrate solutions [3]. More apparatus demanding techniques involve a method of direct potentiodynamic anodic dissolution of a product and direct potentiodynamic cathodic reduction of a product [4-6]. Another method of potentiodynamic polarization consists in two consecutive steps: at first, a subtle amount of corrosion products deposited on

a paraffin impregnated graphite electrode (PIGE) is potentiostatically partly reduced to metal and the particles are subsequently oxidised at a continuously changing potential (potentiodynamically). Composition of the sample is identified from the recorded curves representing the dependence of potential over current density – the decisive aspects are the positions of curve peaks vs. potential representing particular metals. In our case, the silver-related peak corresponded approximately to the potential of 0.5 V/ACLE, as for copper the peak was around 0 – 0.1 V/ACLE, as for tin the peak was -0.45 V/ACLE and as for lead the peak was -0.5 V/ACLE.

Referring to the works published so far, the method was applied when studying various historical metallic objects [7,8]. The aim of this work was to test and assess the possibility of using the potentiodynamic polarization as a simple, non-invasive method of identifying composition of historical metallic objects (including their assessment in terms of their qualifications for a quantitative analysis) and also to describe the impact of testing conditions (polarization rate, the size of particles transferred upon the PIGE and their reducibility, the impact of de-aeration) on the results.

EXPERIMENTAL

Samples of alloys (namely CuPb20, CuPb5, CuZn40, CuSn6, AgCu7.5, SnPb40, SnCu1) representing metals usually present in historical objects were selected to test the method of potentiodynamic polarization. Having been grinded and rinsed the samples were exposed to specific conditions for a period of 14 days to have a layer of corrosion products formed. There were two types of exposure conditions:

- Exposure to an atmosphere saturated with hydrogen sulphide vapours (2 % solution of Na_2S was used) at 100 % relative humidity and a laboratory temperature (AgCu7.5, CuPb20, CuZn40, SnPb40 and SnCu1).
- Exposure to an atmosphere of sulphur dioxide (200 ml of SO_2 in a condensation chamber of 300 dm³) at 100 % relative humidity and the temperature of 40 °C (CuPb5, CuSn6, CuZn40).

After the exposure, samples covered with a layer of corrosion products were rinsed with distilled water and ethanol and dried. Composition of corrosion products was identified by the SEM-EDS analysis. This piece of information was inevitable for confirmation that the identification was correct and determination which metals from the sample end up in corrosion products and what their ratio is.

The potentiodynamic method requires only a small amount of material for the analysis, therefore, only a negligible amount of corrosion products was scratched by a scalpel from the surface of exposed samples, and

deposited on the tip of the graphite electrode. The test was performed in a three-electrode arrangement with a reference silver-silver chloride saturated electrode (ACLE) and a platinum counter-electrode (Fig. 1). The potentiodynamic curves were recorded by Gamry PCI4 electrochemical system, 0.1 mol.dm⁻³ oxalic acid was used as the testing solution. The graphite electrode with a small amount of corrosion products of the analysed material connected as a working electrode touched the level of the solution so that the largest area of the immersed electrode consisted of the surface of particles of a sample of the analysed material corrosion products.

Using the Gamry electrochemical system, potentiostatic reduction was applied in the first phase of the analysis in order to reduce corrosion products at PIGE to a metal. The reduction proceeded for 5 minutes at a negative potential of -2 V/ACLE, and in the next step was followed by potentiodynamic polarization in the direction of oxidation with a rate of 10 mV.s⁻¹. The starting potential E_o corresponded to the potential used at the reduction, i.e. -2 V/ACLE, the terminal potential E_k was 1.5 V/ACLE. Reduced metal particles from the first step of the method thus oxidised and the potentiodynamic curve representing the dependence of current density on potential was recorded. Oxidation of the metal showed as a peak on the curve. The potential corresponding to such peak was characteristic for the metal concerned and its existence could be considered evidence of the metal being present in the sample material.

Prior to the analysis of another sample, it was necessary to rinse the surface of the working graphite electrode and grind it smoothly with a grinding paper. When monitoring the impact of the polarization rate on

Fig. 1. Setup arrangement
Obr. 1. Uspořádaní aparatury

the analysis result, a slower alternative with a rate of 1 mV.s^{-1} was tested in addition to the basic polarization rate of 10 mV.s^{-1} and the recorded curves were compared.

In order to identify the impact of the size of particles, the size of particles scratched by a scalpel from the exposed sample was compared under a microscope with the particles carefully crushed by a glass stirring bar on a watch glass after being scratched from the surface. After that, crushed particles were deposited on the PIGE and analysed under identical conditions as uncrushed samples. The recorded potentiodynamic curves of both crushed and uncrushed samples were compared then.

So as to be able to assess the impact of the presence of oxygen in the solution, the solution was deaerated by nitrogen bubbling for a period of 30 minutes. During the deaeration process and the subsequent measurement, the apparatus arrangement (the beaker with the testing solution and electrodes) was isolated from the external environment by parafilm. Potentiodynamic curves recorded for measurements in both deaerated and aerated solutions were compared.

3 to 6 experiments were performed for each type of testing depending on reproducibility of the results. Two approaches were considered to assess the method in terms of its suitability for a quantitative analysis: in the first case, maximum current density values in peaks were used and in the other case the attention was focused on the values of charges calculated as an area of the peak (using the trapezoidal method). In both cases, the values obtained were recalculated to the metal per-cent representation in the alloy and compared with the SEM-EDS analysis data.

RESULTS AND DISCUSSION

EDS analysis results are summarized in Table 1, which implies the differences in composition of corrosion products and the basic material of a sample. Potentiodynamic polarization does not provide analysis of the composition of the basic material but that of corrosion products, which further changes according to the conditions of corrosion layers formation, as obvious from the example of brass (CuZn40) – corrosion products on the sample exposure to the atmosphere of sulphur oxide contain twice as much zinc as the sample exposed to the atmosphere saturated with sulphides. Corrosion products on the sample of tin bronze (CuSn6) exposed to sulphur oxide did not contain tin at all.

Considering the character of samples, the following metals could be present in the series of recorded potentiodynamic curves: copper, tin, lead, silver and zinc. Apart from zinc (the sample of brass CuZn40), the metals were visualised by potentiodynamic polarization at given potentials corresponding to their oxidation (Table 2).

The position of a peak corresponding to a specific metal is not bound to an exact value of potential and may differ within the range of tens of mV. Considering this fact, it is rather complicated to distinguish tin and lead, the peaks of which are very close to one another and it is thus not easy to determine, which one from the couple of metals is present in the analysed sample. If both metals are present in a sample, i.e. both tin and lead, both peaks overlap.

It was impossible to unambiguously determine the impact of the polarization rate decrease ($10 \text{ mV.s}^{-1} \rightarrow 1 \text{ mV.s}^{-1}$), as obvious from the comparison of potentiodynamic curves for samples CuPb5 (Fig. 2.) and AgCu7.5 (Fig. 3.). As to the sample CuPb5 , narrower peaks were formed when the polarisation rate was decreased, therefore it was possible to determine more precisely the potential corresponding to the maximum peak. On the other hand, in the case of the sample AgCu7.5 the peaks at lower polarization rate were less significant. In some cases, lower polarization rate could improve resolution of the resulting curves, however, this effect was indefinite.

Fig. 2. Effect of polarization rate decrease (sample CuPb5)
Obr. 2. Vliv snížení rychlosti polarizace (vzorek CuPb5)

Fig. 3. Effect of polarization rate decrease (sample AgCu7.5)
Obr. 3. Vliv snížení rychlosti polarizace (vzorek AgCu7.5)

Tab. 1. Results of EDS analysis and comparison with quantitative evaluation / Výsledky EDS analýzy a porovnání s kvantitativním vyhodnocením

Samples		EDS	Current density ¹	Current density ²	Charge ¹	Charge ²
CuPb20 (sulfides)	Cu	>99 %	92 %	93 %	96 %	96 %
	Pb	<1 %	8 %	7 %	4 %	4 %
SnCu1 (sulfides)	Sn	99 %	77 %	89 %	71 %	83 %
	Cu	1 %	23 %	11 %	29 %	17 %
SnPb40 (sulfides)	Sn	52 %	69 %	62 %	–	–
	Pb	48 %	31 %	38 %	–	–
CuZn40 (sulfates)	Cu	33 %	100 %	100 %	100 %	100 %
	Zn	67 %	0 %	0 %	0 %	0 %
CuSn6 (sulfates)	Cu	100 %	100 %	100 %	100 %	100 %
	Sn	0 %	0 %	0 %	0 %	0 %
CuPb5 (sulfates)	Cu	80 %	44 %	72 %	58 %	71 %
	Pb	20 %	56 %	28 %	42 %	29 %
AgCu7.5 (sulfides)	Ag	78 %	53 %	43 %	61 %	62 %
	Cu	22 %	47 %	57 %	39 %	38 %

Fig. 4. Alteration of particles size of corrosion products samples

Obr. 4. Změna velikosti částic vzorků korozních produktů

Corrosion products of the samples were simply mechanically crushed into smaller particles (an average size dropped by half) reaching a narrower range of sizes (Fig. 4). In terms of results, smaller particles significantly improved resolution of the curves – as demonstrated on the sample CuPb5 (Fig. 5.), when tests were performed with bigger particles, the peaks obtained were almost unidentifiable compared to the analysis of small-size particles. A similar trend was observed for other samples as well. Since the amount of corrosion products on the surface of the graphite electrode varied from test to test, it was inevitable for the assessment of the impact of the testing conditions to monitor the relative peak height compared to the background rather than absolute values of current densities.

Fig. 5. Effect of particles size decrease (sample CuPb5)

Ob. 5. Vliv snížení velikosti částic (vzorek CuPb5)

The impact of the presence of oxygen on the course of the analysis was not very significant. Comparing potentiodynamic curves in both aerated and deaerated conditions (Fig. 6), slightly improved resolution and definition of the peaks can be observed in the deaerated solution. As the method of PIGE-based potentiodynamic polarization is proposed also as a tool for in-situ analysis, deaeration of a solution outside laboratory conditions would be rather complicated.

Summary of the results (Table 2) and their comparison with the results of the EDS analysis imply that the method is not suitable for quantitative analysis. For each sample, two curves were assessed as per the maximum current density and the by-passed charge (peak area). The assessment of the sample of lead solder

SnPb40 was complicated by a shared peak, therefore, the calculation reflecting charge could not have been used. The sample of tin bronze CuSn6 showed just one peak, therefore, quantitative assessment would make no sense. It was similar in the case of the sample of brass CuZn40 (the only difference was the presence of zinc in corrosion products). The sample CuPb20 showed similar record in the composition identified by the EDS analysis, the method considering the by-passed charge as well as the method considering maximum values of current densities. Considering other samples, the differences ranged within tens of per cent.

Fig. 6. Effect of testing solution deaeration (sample CuPb5)
Obr. 6. Vliv odvzdušňování měřicího roztoku (vzorek CuPb5)

Tab. 2. Values of oxidizing potential for selected metals / Hodnoty oxidačních potenciálů jednotlivých kovů

Metal	E, V/ACLE
Ag	0.5
Cu	0 - 0.1
Sn	-0.45
Pb	-0.5

CONCLUSION

Using the method of potentiodynamic polarization based on the paraffin impregnated graphite electrode, it was possible to identify silver (0.50 V/ACLE), copper (0 – 0.10 V/ACLE), tin (-0.45 V/ACLE) and lead (-0.50 V/ACLE) in samples of alloys simulating metallic artefacts. The proximity of tin and lead peaks in this otherwise universal solution is problematic in terms of identification, which could be solved by choosing another electrolyte (e.g. NaOH-based). As for other testing conditions, the size of particles proved to be the most important parameter – due to better reducibility smaller particles helped achieve much better results.

The impact of slower polarization rate was ambiguous; improvement of the results resolution by narrowing of peaks was observed only for some of the samples. On the other hand, the impact of deaeration of the testing solution was identical for all samples – there was only a minor improvement reported due to better definition of peaks, however, on the account of greater demands on the apparatus and complications, should the method be used in-situ. After comparing the results provided by polarization curves with the results of the SEM-EDS analysis, the method could not have been identified as quantitative.

In terms of quantity, only a small amount of material from each sample was used for testing, i.e. few particles with a size of tens of μm . Provided that the sample is extracted sensitively, the method can be referred to as a non-invasive method. In terms of time, the testing was not demanding (at 10 mV.s^{-1} polarization and with no deaeration), however, it is recommended to dedicate some time to get the command of the method (to estimate the optimum amount of sample to be deposited on the working graphite electrode, etc.).

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