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Plasma chemical reduction of model corrosion brass layers prepared in soil[*]

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Abstract. The brass plates of $(50 \times 10 \times 1)$ mm^3 were prepared with model corrosion layer because the real archaeological artifacts could be damaged during the method optimization. Samples corroded naturally more than 2 years in the soil. Excavated samples were treated in the low pressure (150 Pa) quartz glass plasma reactor (90 cm long and 9.5 cm in diameter) which was surrounded by two external copper electrodes supplied by radio-frequency generator (13.56 MHz). The experiments were carried out in a hydrogen-argon gas mixture at mass flows of 30 sccm for hydrogen and 20 sccm for argon for 90 min. The plasma power was 100, 200, 300 and 400 W in continuous and pulsed mode. Maximum sample temperature was set at 120 °C. The whole process was monitored by optical emission spectroscopy and the obtained data were used to calculate the relative intensity of OH radicals and rotational temperature. The results showed that the higher power had the greater maximum intensity of the OH radicals and rapidly degraded the corrosion layer. Corrosion layer was not completely removed during the reduction, but due to the reactions which occur in the plasma corrosion layer became brittle and after plasma chemical treatment can be removed easily. Finally, the SEM-EDX analysis of the surface composition confirmed removal of chlorine and oxygen from the corrosion products layers.

1 Introduction

Excavated archaeological artifacts contain on their surface very complex corrosion layers reflecting conditions of the environment [1]. The corrosion process continues also after the excavation from the soil or water. But corrosion layers are undesirable and also they support further degradation of any object, so their removal is necessary. There are several methods applicable for the cleaning of archaeological artifacts, e.g. air clearing, mechanical cleaning with hand instruments (scalpel . . .), cleaning using heat (mainly removing old paint), cleaning with pressurized water or steam, cleaning in an ultrasonic bath. Also application of other mechanical techniques like blasting, grinding, polishing, brushing or wet way chemical cleaning with solvents, solutions and complex forming agents, or direct chemical reactions and electrolysis is widely applied [2].

Besides the classical conservation techniques mentioned above, the plasma chemical reduction is another way which can be used to remove corrosion products.

Despite to fact that this method obviously does not completely eliminate the corrosion layer, the corrosion layer becomes more brittle after the plasma chemical treatment, so it can be more easily removed by hand mechanical instruments. The reduction of chlorides during the plasma chemical treatment, which causing the secondary corrosion, is another very important advantage [3].

A few research groups have used plasma chemical treatment for tarnished or corroded metals, mainly iron and silver, during the last 40 years, for example groups of Daniels et al. [4,5], Veprek et al., Patscheider and Veprek [6,7], Schmidt-Ott [8,9].

In Czech Republic, method of plasma chemical reduction of archaeological artifacts has been used by Perlik [10] at Central Bohemian Museum in Roztoky at Prague, by Klima at Masaryk University in Brno, Faculty of Science [11], by scientists at Technical Museum in Brno [2] and also by our group at Brno University of Technology, Faculty of Chemistry [9,10].

The plasma chemical process monitoring procedure was developed under close cooperation of groups at Masaryk University and Brno University of Technology [12]. It is based on the plasma chemical treatment principle. The active particles generated by low pressure plasma, mainly atomic hydrogen neutrals and ions and molecular hydrogen species, excited by the low pressure discharge

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in hydrogen or hydrogen/argon mixture react with oxygen or chlorine containing compounds as typical corrosion products. Thus OH and HCl molecules are effectively produced. Because OH is created directly using oxygen contained in corrosion products, OH radical intensity well reflects efficiency of corrosion layers reduction. Thus it is possible to use OH radical spectra as the finger print of plasma chemical process efficiency. OH radicals have intense emission spectra with maximum in the range of 305–312 nm. The spectroscopic observation (described in detail by paper [13]) showed that the optimal moment for the plasma treatment stop came when more or less constant relative intensity of OH radical was reached and the duration of the relative intensity of OH radical decrease to the value of 10% of its maximum during the particular plasma treatment stage [12].

Recently, the plasma chemical reduction of archaeological artifacts was studied at Brno University of Technology, Faculty of Chemistry in detail and data for the most common archaeological metals have been collected. The basic experimental context was similar as in the case of Veprek, see below [6]. The model samples were used to be able compare different plasma process conditions influences on the corrosion products removal efficiency and also applicability for the sensitive materials like bronze. Moreover, copper based artifacts contain also very specific corrosion layer named patina that must be kept on the surface, so processing conditions must be set and monitored extremely carefully. Several objects/materials were treated, for example iron [14], copper [13], bronze [15] or brass [16].

The brass is one of the first alloys used in technology. The oldest brass artifacts belong to times before 2000 years and brass exact composition was strongly dependent on manufacturing as well as purpose. The brass state diagram is very complicated and many different forms can be obtained in dependence of the copper/zinc ratio. Moreover, many additives, mainly lead, tin and iron, can be found in historical objects compositions. Based on this, there were described many tens of the corrosion products, mainly oxides and chlorides in dependence on the original object corrosion history. Details about historical brass and its corrosion products can be found across centuries in book of Craddock [17].
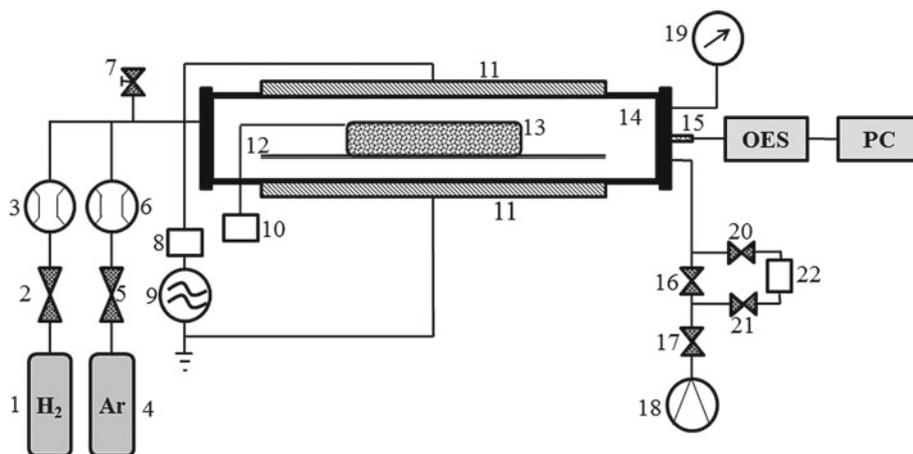
2 Experimental

Archeological artifacts can shelter a lot of information about excavated object, its material, place, where was found or about people who lived at that period. Also, there is nearly impossible to find a big set of artifacts made of the same material that have the same manufacturing and corrosion history. Thus the original objects could not be used for any study leading to optimization of any conservation process. Due to these facts, brass samples with model corrosion layer were prepared. Corrosion layers were prepared in the soil environment in ambient Brno climatic conditions. However, the layer created this way only

approximate corrosion layer of archaeological artifacts, especially it thickness is much smaller.

Brass current production plates of $(50 \times 20 \times 1)$ mm^3 were used for the experimental part of this work. The material composition was 65.11% of copper and 34.89% of zinc without any additives as was determined by SEM-EDX analysis (see later) of the bulk material. The samples were degreased using 50% STAR$^®$ 75P detergent (Everstar Ltd.) solution and in distilled water, both for 1 min in the ultrasonic bath. After that, a mixture of concentrated nitric acid and hydrochloric acid in a volume ratio of 1:3 was used for a few seconds to remove any surface impurities and all samples were finally washed by deionized water and dried by ambient hot air. Model corrosion layers were formed in the ambient soil for 2 years and 1 month. The samples were placed into the soil horizontally. After excavating, the samples were dried in a vacuum drying chamber at 60 °C for 24 h. Finally, the samples were stored in aluminum bags together with the absorbers of moisture and oxygen. The XRD analysis of the corroded samples showed that zinc content was significantly increased in the surface corrosion product layers. Besides the original alloy, the zinc hydroxide chloride (Zn(OH)Cl), cuprite (Cu$_2$O), tenorite (CuO) and simonkolleite Zn$_5$(OH)$_8$Cl$_2 \cdot$(H$_2$O) were determined as the main corrosion compounds at the present case.

For the presented work, 13 samples were chosen and subsequently they were treated in the low pressure low temperature RF plasma (13.56 MHz) created in the hydrogen-argon gas mixture. The maximal temperature of the object during the reduction was set at 120 °C. Scheme of the plasma chemical reactor is shown in Figure 1. The treatment was carried out in the cylindrical Quartz reactor (i.d. 95 mm, length 900 mm) with a pair of external copper electrodes connected via the matching network to a radiofrequency generator. The flows of both working gases were set by independent mass flow controllers. Rotary oil pump was separated from the discharge reactor by liquid nitrogen trap with aluminum chips eliminating dust and reactive species (mainly HCl created by reaction of hydrogen with chlorine contained in the corrosion layers) from the gas flow. Each sample was placed on a glass holder at the reactor center. Thermometer optical probe (Optocon FOTEMP1-H, Fiber Optical Standard Temperature Probe TS2) was connected to the sample surface by a small stainless plate and allowed continuous sample temperature monitoring. Whole process was monitored by optical emission spectroscopy using Ocean Optics HR4000 spectrometer with 2400 g/mm grating. Relative intensities of OH radicals in counts per second averaged over 10 s in the interval of 305–312 nm were measured to avoid the changes due to fast power modifications (see later). The used interval was selected because there is no significant overlapping by other potentially presented bands like nitrogen second positive and NO$^\beta$ [12]. The rotational temperatures were calculated from OH radical high resolution spectra according to Boltzmann plot procedure. The OH radical was selected for the process monitoring because hydrogen atoms and ions generated by the discharge react with oxygen bounded in corrosion layers

Fig. 1. Schematic drawing of the experimental set-up: 1, 4-hydrogen/argon bottles; 2, 5-on/off valves; 3, 6-mass flow controllers; 7-venting valve; 8-matching network; 9-RF power supply; 10-system for sample temperature monitoring; 11-outer copper electrodes; 12-sample glass grid holder; 13-sample; 14-quartz discharge reactor; 15-optical fiber; 16, 17, 20, 21-valves; 18-rotary oil pump; 19-capacitance pressure gauge; 22-liquid nitrogen trap with aluminum chips.

Table 1. Sample treatment conditions.

Total power [W]	Mode	Effective power [W]	Effective power after reach 120 °C [W]
100	Continual	100	Max. temperature 117 °C
200	Continual	200	107
200	Pulse	198	141
300	Continual	300	123
300	Pulse	297	175
400	Continual	400	134
400	Pulse	396	198

during the plasma chemical treatment and thus OH radical reflects oxygen [12].

The experiments were carried out at pressure of 150 Pa at mass flows of 30 sccm for hydrogen and 20 sccm for argon for 90 min. The samples were treated at 200, 300 and 400 W in pulsed and continuous mode. Additionally, power of 100 W in the continuous mode was used, too, but temperature in that case was lower when set 120 °C and reduction was not successful due to too low supplied energy, so this power was not used for the further experiments. The rests of the corrosion product layers was carefully removed by pulp after the plasma treatment without any additional cleaning procedure. Thus not all the corrosion products residua were removed from the sample surface. The SEM-EDX analysis using Philip XL30 microscope with EDAX analyzer was carried out as integral over three different areas of (3.45×4.45) μm^2.

Based on various precedent studies, the sample temperature must not exceed temperature of 120 °C due to potential metallographic structural changes. Thus according to the monitored sample surface temperature, the supplied power was automatically modified during the measurement. Two ways of power automatic variation were used. The supplied power value was modified (decreased) at the continuous discharge regime. In the case of pulsed regime, the supplied power value was constant and the mean power was changed by the duty cycle. In this case, the maximal value was 99% because generator is not

able work in pulsed mode with 100% duty cycle. The duty cycle frequency was fixed at 1000 Hz.

3 Results and discussion

The treatment conditions of each sample are listed in Table 1. In addition to the set conditions and effective power, the mean plasma power after reaching the maximal allowed temperature of 120 °C is given.

It is nearly impossible exactly define the point when 120 °C were reached because the mean power modification started before this temperature reaching based on the temperature grow slope (see Fig. 2). The temperature over 120 °C is absolutely unacceptable because metallographic structural changes can be initiated and also surface can be locally overheated at heavy particles bombardment. Thus the power modification had to start at temperature of 100 °C. An example of the sample temperature evolution with applied power and relative intensity of OH radicals is given in Figure 2. It is clearly visible that no temperature oscillations were measured. The initial increase of OH radicals intensity is mainly due to removal of the surface adsorbed oxygen at the beginning of the process that accelerates by elevating temperature. After this, the OH radicals are created mainly by reaction of atomic neutral hydrogen with oxygen contained in the corrosion products [16].
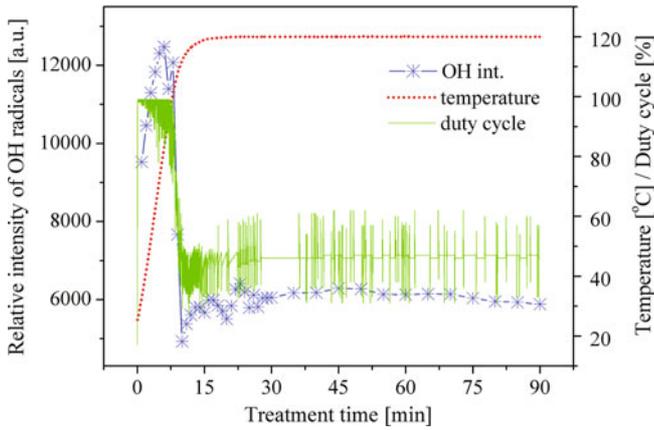
Fig. 2. Time evolution of sample temperature, duty cycle and OH radicals relative intensity during the treatment of sample in pulsed mode at the initial power of 400 W.
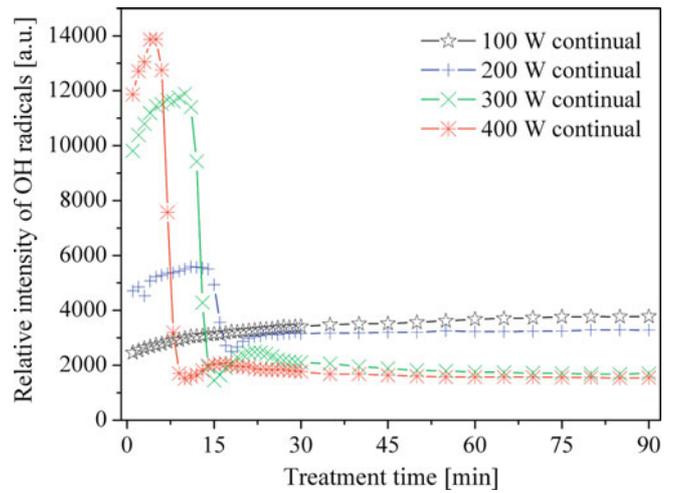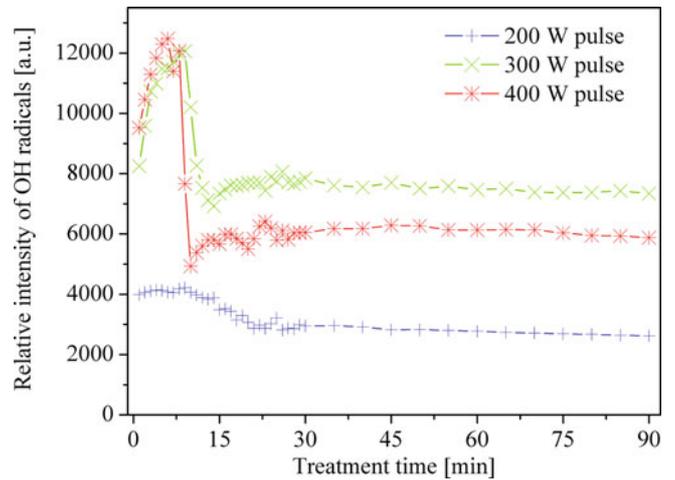

**Fig. 3.** Time evolution of the OH radical relative intensity during the plasma treatment in continual mode.

The maximal temperature of samples during the measurement was 120 °C; however sample treated at 100 W in continuous mode was only one exception. In this case the temperature reached only 117 °C and stayed constant. The relative intensity of hydroxyl radicals was very low and the OH radical intensity maximum was not as significant as in the case of other measurements. For these reasons, the same treatment conditions were not used at 100 W power and pulse mode, too.

Relative intensities of OH radicals during the plasma chemical treatment of samples are presented by Figures 3 and 4. As it was pointed above, the relative intensity of OH radical usually initially increased, then reached its maximum and consequently decreased due to the mean applied power decrease and after that it is nearly constant. The OH radical intensity at that phase of treatment process is lower if continual mode is used. OH is excited by electron collisions and thus intensity (averaged over 10 s) reflects the mean power and OH species concentration. The effective power is about 50% higher in the pulsed mode (see the left column in Tab. 1). This is clearly reflected by higher OH radical intensity, but relation is not direct because more hydrogen active species are generated at higher applied power and they can react with surface during the discharge off period, too. Thus OH radical is produced more efficiently in pulsed mode that is also reflected in the total OH radical intensity. This means that plasma chemical reduction of corrosion products is faster using the pulsed regime. Different shape of the OH radical time dependences has no significant influence on the process monitoring described in [12] because there decrease down to 10% of maximal OH radical intensity or stable conditions for at least 30 min are recommended as the stop value of the plasma treatment process.

Sample temperatures evaluations during the plasma chemical treatment are shown in Figures 5 and 6. The temperature increased during first 20 min and then it was kept constant by the mean power modulation. It can be clearly seen that higher power leads to faster sample heating.
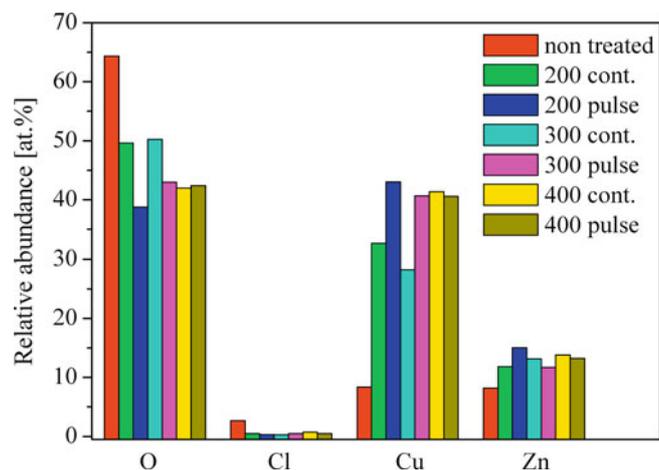

Fig. 4. Time evolution of the OH radical relative intensity during the plasma treatment in pulse mode.
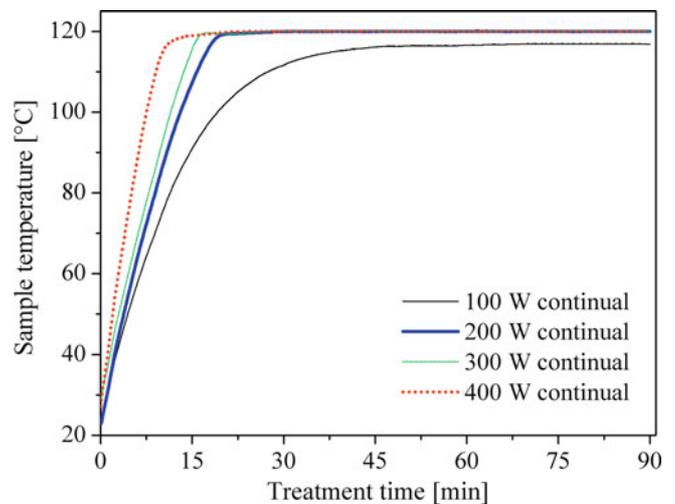
Fig. 5. Sample temperature during the treatment in continual mode.
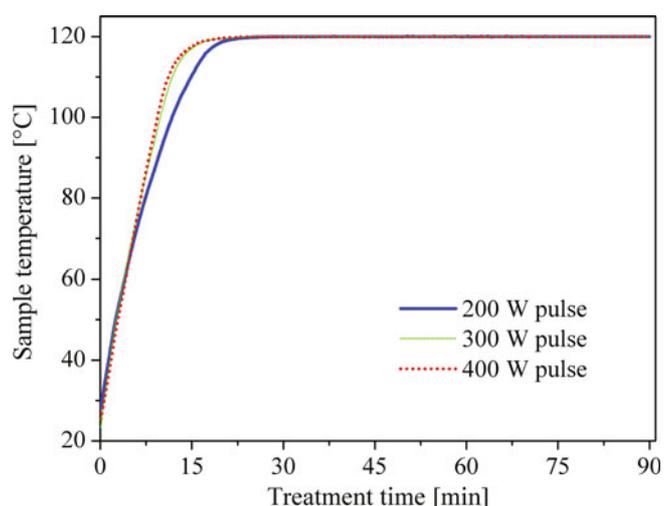
Fig. 6. Sample temperature during the treatment in pulse mode.

Fig. 7. Relative abundance of the main elements in outer corrosion product layers.

The exception was sample treated at power of 100 W in continuous regime (Fig. 5), which did not reach 120 °C because of low power.

Rotational temperature of plasma calculated form OH radical spectra is generally independent on the treatment conditions and reaches (570 ± 70) K.

The surface material composition of samples after the plasma chemical treatment is described by Figure 7 with comparison of the original surface composition. The main elements abundances are described, only. Due to this fact the total amount of corroded non-treated sample is about 80%. The rest were mainly silicon, aluminum and calcium that were built up into corrosion layers as incrustations. These incrustations were fully removed after the post-plasma treatment by pulp wiping and they were not included in Figure 7 because of clarity. Figure 7 clearly shows significant reduction of oxygen and chlorine from the sample surface. The relative copper content increases

after the treatment and copper/zinc ratio is close to original alloy composition. The relatively small amount of copper in the case of non-treated sample is because copper is not so simply corroded and thus it is not presented at the outer corrosion product layers. This phenomenon is well known as dezincification [17].

4 Conclusion

Plasma reduction is one of new advanced methods applicable in the process of corrosion products removal from archaeological artifacts. Corrosion products are not completely removed during the plasma chemical reduction, but due to the reactions of active hydrogen species the corrosion layers became brittle and thus they can be removed easily after plasma chemical treatment. Brass samples with model corrosion layers have been used for this fundamental research, real archaeological artifacts were not used because they have to be destroyed. Corrosion layers were formed in the soil for more than 2 years. Low temperature (rotational plasma temperature was (570 ± 70) K) low pressure (150 Pa) plasma of hydrogen-argon gas mixture was used for reduction. The plasma chemical treatment was carried out in continuous or pulsed mode at various initial applied powers. The maximal sample temperature was set at 120 °C; after that supplied power was decreased (in continuous mode) or duty cycle was modified (in pulsed regime) to keep this maximal temperature. The temperature of 120 °C was generally reached after the first 20 min. The fastest process was observed, as it was expected, at the highest initially applied power in continuous mode but differences were not so critical. The surface material composition changes shown that all applied plasma treatment conditions are applicable. Based on the other results, it can be concluded that the optimal treatment should be done at maximal applied power of 400 W in pulsed regime with mean power adaptation through the duty cycle variation.

References

1. V. Fell, J. Williams, in *Proceedings of Metal, Australia, 2004*, edited by J. Ashton, D. Hallam (National Museum of Australia, Canberra, 2004), p. 17
2. J. Benesova, *Conservation and Restoration of Metals: Preservation of Culture Heritage Objects Made of Metals and Their Alloys*, 1st edn. (Technical Museum, Brno, 2011) [in Czech]
3. V. Sazavska, V. Mazankova, F. Krcma, M. Prochazka, in *Proceedings of Eurocorr, Estoril, 2013*, edited by Edicao Sociedade Portuguesa de Materiais, p. 1
4. V.D. Daniels, L. Holland, M.W. Pascoe, Stud. Conserv. **24**, 85 (1979)
5. V. Daniels, Stud. Conserv. **26**, 45 (1981)

6. S. Veprek, J. Patscheider, J. Elmer, Plasma Chem. Plasma Process. **5**, 201 (1985)
7. J. Patscheider, S. Veprek, Stud. Conserv. **31**, 29 (1986)
8. K. Schmidt-Ott, V. Boissonnas, Stud. Conserv. **47**, 82 (2002)
9. K. Schmidt-Ott, in *Proceeding of Metal, Australia, 2004*, edited by J. Ashton, D. Hallam (National Museum of Australia, Canberra, 2004), p. 235
10. D. Perlik, in *Proceeding of the Conservatory and Restoration Workshops, Ceske Budejovice, 2001*, edited by P. Stohrova (Technical Museum, Brno, 2001), p. 89
11. L. Zajickova, M. Klima, J. Janca, Zeitschrift für Schweizerische Archäelogie und Kunstgeschichte **54**, 29 (1997)
12. Z. Raskova, F. Krcma, M. Klima, J. Kousal, Czech. J. Phys. **52**, 927 (2002)
13. Z. Raskova, F. Krcma, Publ. Astron. Soc. Obs. Belgrade **82**, 159 (2007)
14. V. Sazavska, F. Krcma, T. Simsova, N. Zemanek, J. Phys.: Conf. Ser. **207**, 1 (2010)
15. P. Fojtikova, L. Radkova, D. Janova, F. Krcma, Open Chem. **13**, 362 (2015)
16. L. Radkova, P. Fojtikova, Z. Kozakova, F. Krcma, V. Sazavska, A. Kujawa, Romanian Rep. Phys. **67**, 586 (2015)
17. P.T. Craddock (ed.), *2000 Years of Zinc and Brass* (British Museum London, London, 1998)