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CORROSION INVESTIGATION OF THE PREŠEREN MONUMENT IN LJUBLJANA

KOROZIJSKA PREISKAVA PREŠERNOVEGA SPOMENIKA V LJUBLJANI

Mirjam Bajt Leban, Viljem Kuhar, Tadeja Kosec, Andraž Legat
Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana, Slovenia
mirjam.leban@zag.si

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The investigated monument, erected in honour of the Slovenian poet France Prešeren, was unveiled in 1905 in Ljubljana, and restored in 1970. Its appearance differs considerably from the original as a result of corrosion. The strong interaction between atmospheric pollutants and the bronze alloy in Ljubljana city centre has resulted in the formation of a secondary patina. With the aim to determine the corrosion state of the Prešeren monument and to ensure the data for the next restoration procedure, a chemical and physical examination was performed. The composition of the patina was analysed using energy-dispersive spectroscopy coupled with scanning electron microscopy and a non-destructive method for determining the alloy composition was used. The different types of patina were studied.

Key words: Prešeren monument, bronze, patina, corrosion, urban atmosphere

Spomenik v spomin pesniku Francetu Prešernu v Ljubljani je bil odkrit l. 1905, renoviran pa l. 1970. Danes je njegov zunanji videz zaradi bolezni brona precej drugačen od tistega ob postavitvi. Največji razlog za to je onesnaženje okolja v centru Ljubljane. Da bi ugotovili korozijsko stanje Prešernovega spomenika in pridobili potrebne podatke za predvidene restavratorske posege, smo izvedli kemijske in fizikalne analize brona spomenika. Sestavo patin smo analizirali z energijsko disperzijsko spektroskopijo rentgenskih žarkov, kemijsko sestavo brona pa z nedestruktivno metodo.

Ključne besede: Prešernov spomenik, bron, patina, korozija, mestna atmosfera

1 INTRODUCTION

Artistic sculptures exposed outdoors are subjected to many environmental pollutants and other influences [1]. Bronze is a copper–tin alloy, sometimes referred to as phosphor bronze, and may contain other alloying elements, such as zinc, lead, etc. [2]. Copper is a commonly used material in statuary art, and it is heavily affected by ageing; however, the rate of ageing depends strongly on the exposure conditions. Bronze forms a protective oxide layer, also referred to as natural patina, when exposed to humid aerated environments. Furthermore, harmful factors include humidity, oxygen, UV light, biological pollution, etc., that can change the appearance of sculptures significantly.

The duration of patina [3–6] formation depends on the atmosphere. It can last from 20 to 100 years in rural sites, up to 10 years in urban centres, and up to 1 year in littoral zones [7]. Nowadays, with the aim to achieve the desired visual effect on bronze surfaces, artificial patination [7–11] is used. Bronze-brown or green casts patinas are used on statues exposed to the open air. The desired colours can be obtained by using various recipes and concentrations of one or more chemical compounds [12].

In order to ensure the quality of the maintenance and the long-term protection of outdoor sculptures against corrosion, various parameters should be taken into account. The most important parameters are: bronze quality, type of surface, chemical cleaning and subsequent treatment, and the type of corrosive atmosphere. In addition, the chemical composition of different parts of the bronze sculpture should be determined, as well as the type and intensity of the corrosion processes should be evaluated.

1.1 Prešeren's monument in Ljubljana

The monument erected in honour of the Slovenian poet France Prešeren was unveiled on the 10th of September 1905. The author of the monument was the Slovenian sculptor Ivan Zajec and the architecture for the statue was designed by the architect Maks Fabiani. The monument consists of a statue of the poet (Prešeren) and a statue of his poetic Muse (Muza), in her hand holding a sprig of laurel (**Figure 1**). Two reliefs – "Fisherman (Ribič)" on the north side (**Figure 2**) and "Črtomir's Farewell to Bogomila (Slovo Črtomira od Bogomile)" – on the south side of the pedestal (**Figure 3**) are also constituent parts of the monument. The main statues and both reliefs were cast in bronze in the renowned Vienna foundry.

The monument was partly restored after 1970. The old patina was mechanically removed, although not completely. Once this procedure was finished, the monument was most likely artificially patinated with green patina. Subsequently, influenced by the corrosive environment and rinsing by water, at different locations on the monument different types of patina were formed

Figure 1: Statue of the poet France Prešeren, with the statue of the poetry Muse above, holding a sprig of laurel in her hand
Slika 1: Kip pesnika Franceta Prešerna s kipom pesnikove Muze, ki drži v roki lovorjevo vejico

and various colours of green and pale green patinas developed as secondary corrosion products. The purpose of our work was to determine the corrosion state of the Prešeren monument and to provide the necessary data to be used in future restoration interventions.

2 EXPERIMENTAL

In order to identify the corrosion processes on the monument, samples of the corrosion products were mechanically scrapped off selected sites of the monument, as well as off both side reliefs. A non-destructive method of chemical analysis for the bronze was applied on these areas, using a portable instrument, i.e., a *Niton – Xli/XLp 800 Series Analyser and XDXRF – energy dispersive x-ray fluorescence*. A calibration of the *Niton – Xli/XLp 800 Series Analyser* apparatus was made before and after the analysis, using control etalons of the qualities C260C (Cartridge brass), C464 (Naval brass); C443 (Admiralty brass) and C110 (electrolytic copper) – UNS identification – *The Unified Numbering System*. In the laboratory, the corrosion products were examined with a scanning electron microscope SEM (JEOL JSM – 5500 LV Japan (*Japan*)) and analyzed with electron-dispersive spectroscopy (EDX, Oxford Inca, *Oxford Instrument Analytical, UK*) at an accelerating voltage of 20 kV.

Figure 2: Relief "Fisherman"
Slika 2: Relief "Ribič"

Figure 3: Relief "Črtomir's Farewell to Bogomila"
Slika 3: Relief "Slovo Črtomira od Bogomile"

3 RESULTS

3.1 Results of the chemical analysis of the bronze

The results of the chemical analysis of the bronze alloy at different parts of the monument are given in mass fractions (w/%) in **Table 1**.

In addition to a certain content of elements, such as Cu, Sn, Pb, Zn, Ni and Fe, which are prescribed for bronzes, minor quantities of Ag, W, Mn, Cr, V, Ti, Al, Mo, Nb and Co were detected, also. The presence of Fe, Al and Mn confirmed the impurity of bronze. The presence of phosphorus and sulphur is common and expected in such alloys, but cannot be determined by the application of the applied method because the detection of the elements is limited.

3.2 Results of EDS (Energy-Dispersive X-ray Spectroscopy) analysis of patinas formed on the monument

Samples of patinas were taken from different sites of bronze before any renovation on the stone part of the monument. Powder patina samples from internal and external layers were analyzed deposed on a carbon surface. The elemental compositions of the different corrosion layers are reported in **Table 2**. The EDS results of the most representative sites of the monument analyses are given in mass fractions (w/%).

Table 1: Results of the chemical analysis of the bronze (mass fractions, *w*/%)
Tabela 1: Rezultati kemijske analize brona (masni deleži, *w*/%)

Site *w*/%	Cu	Sn	Pb	Zn	Ni	Fe	Rest
Fisherman	87.76	6.37	1.74	3.28	0.18	0.10*	0.57
Farewell	87.25	7.17	1.74	3.07	0.09	0.11	0.57
Prešeren	88.51	4.78	1.34	4.61	0.12	0.19	0.45
Muse	87.03	6.74	1.64	3.72	0.14	0.21	0.97
C922**	86– 90	5.5–6.5	1–2	3–5	0–1.0	<0.25	–
***	<0.10	0.18	0.04	0.20	0.10	0.04	–

Remarks:
* – below the detection limit of the analyser;
** – regulation for C922 bronze quality (UNS identification);
*** – detection limits of Niton – Xli/XLp 800 Series Analyser.

Table 2: Results of the EDS analysis of the different patinas of the monument and reliefs
Tabela 2: Rezultati EDS-analize različnih patin na spomeniku in reliefih

Site of patina take off	Patina colour, other properties *w*/%	C	O	Si	S	Cl	Cu	Sn	Pb	Rest
Farewell	white – green	26.80	31.76	1.40	3.30	0.25	34.30	0.27	0.43	1.49
Farewell	black – thick layer	4.79	42.58	0.52	6.33	–	42.76	1.16	0.85	1.08
Fisherman	bronze red – brown	46.25	31.82	6.29	0.17	0.25	11.82	1.94	0.63	0.83
Fisherman	green – white	42.47	34.39	7.07	0.24	0.28	12.30	2.19	0.17	0.89
Fisherman	light green – thin layer	6.72	30.26	–	2.03	–	43.68	12.79	2.15	2.37
Fisherman	bronze black – thin layer	4.61	30.75	0.23	1.36	–	49.92	7.71	3.16	2.26
Prešeren	black – thin layer	5.26	43.14	0.39	7.76	0.46	40.06	0.32	1.27	1.34
Muse	black – thin layer	6.61	32.18	1.91	4.97	0.70	49.05	0.01	0.90	3.67
Prešeren	black brown – thin layer	9.16	50.15	0.39	6.02	–	32.10	0.38	0.81	0.99
Prešeren	light green	4.10	48.37	0.29	6.18	–	38.70	1.89	0.44	0.03
Prešeren	black brown – thin layer	4.77	38.37	0.28	2.88	–	41.73	8.89	1.02	2.06
Muse	green-white – thin layer	11.09	34.29	1.11	4.93	0.23	45.62	0.66	0.80	1.27

The corrosion activators (ions that initiate corrosion, Cl^- and S^{2-} in this case) that caused particular patina on different sites of the sculptures and monuments as well as the type of bronze patinas that were formed can be concluded from the composition of the most typical elements of the corrosion products given in **Table 2**.

The content of oxygen was higher in the case of the Prešeren and Muse statues. These patinas were taken from sites that are exposed at different angles of inclination. Moreover, the content of carbon is lower in the case of corrosion products formed on exposed surfaces at different angles of inclination. The content of sulphur is substantially higher in the case of a multi-angle exposure. The presence of zinc in the corrosion products is low and it does not vary on the exposure sites.

4 DISCUSSION

4.1 Visual observations

The visual examination of the monument and the composition of the bronze and the patina indicate that secondary patinas were formed on the sites where there was a non-uniform leaching action of the rain. On the other hand, at sites where the leaching action of the rain is weaker (dark, almost black surfaces), the internal layer of the patina consisted of cuprite (Cu_2O). The external layer consisted mostly of copper sulphates (bronhanite and antlerite), copper chloride–hydroxide (atacamite) and other compounds originating from environmental contamination [13]. On some hardly accessible sites (the Prešeren and Muse statues), where the leaching action of the acid rain (pH < 5) was not as strong, the layer of secondary corrosion products was very thick (up to 0.5 mm).

Only a few corrosion activators accumulated on the dark (green to black colours) surfaces with the thinner patina layer (the bronze shine through the layer is clearly visible). These surfaces are smooth and the bronze is not deeply etched. The leaching action was observed in detail and similar observations were made [14]. On such surfaces the presence of copper chlorides was low or even non-existent, while copper oxides and sulphates were dominant.

On the surfaces with the green-grey and white coloured patina substrate, the secondary patina layer consisted mainly of copper oxides, sulphates, chlorides, carbonates and plaster. As heavily soluble compounds, carbonates were not leached by rain. On the other hand, the secondary layer of corrosion products on the surfaces, affected by the leaching action of the rain, was pale green and had a powdery non adhesive texture.

Flow-off water zones of light green colour were formed on the sites of the intensive corrosion products. A minor area on the south side of the monument, known as *Ribič* relief, has a red-brown bronze surface. The internal patina layer consists mostly of cuprite, whereas the secondary layer is very thin. The patina in the vertical zones is primarily of soluble corrosion products consisting of copper carbonates.

Since many different patinas were formed over the entire surface of the monument and different conditions regulated the water flow-off, it can be assumed that severe corrosion (e.g., bronze disease) was activated because of the relatively aggressive atmosphere. The surface of the reliefs is smoother than the surface of the monument, which is the main reason for the smaller corrosion damage.

The depth of the pitting corrosion on particular sites could not be estimated without a prior patina removal. The damage is not severe, yet it could have a crucial influence on the appearance of the monument details – locally corrosion damage causes an etched appearance of the surface.

4.2 EDXRF analysis

The results of the bronze chemical analysis suggest that both sculptures were made from the bronze C922 according to the requirements of the standard UNS [2]. As presented in **Table 1**, the contents of Sn and Pb in some analyses deviate from their contents prescribed in the standards. However, the chemical composition analyzed on the bronze surface (where the EDXRF analysis was made) can differ slightly from the bulk composition. Regardless of this fact, it can be assumed that the bronze in both sculptures, as well as that in the side reliefs, is homogeneous. Its purity is comparable to currently valid regulations. Therefore, it can be concluded that the casting process of all the component parts of the monument included in this investigation was under quality control.

4.3 EDS analysis

The results of the EDS analyses of the different patinas scraped off different sites of the monument indicate that the main contributions to the corrosion processes and to the formation of patinas are effected by environmental pollution (the pollution in the centre of Ljubljana is an urban atmosphere), acid rain, salt aerosol due to winter salting of the roads, dust, soot and bird excrements. The patina on the bronze statue consists of an internal, usually thinner, layer and a thicker, external layer. A schematic presentation is given in **Figure 4**. The internal patina layer consists of copper and tin oxides. The analyses have also proved the presence of copper carbonate and alloying elements. The thin layers of dark brown-black, red-brown and green patina corrosion products do not contain chloride compounds.

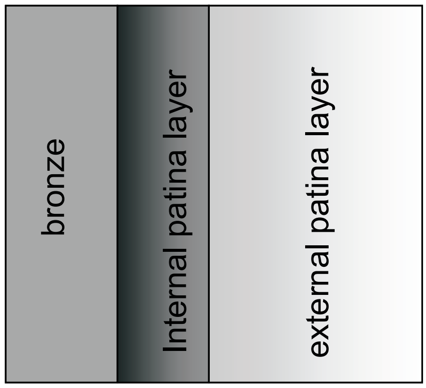

Figure 4: Schematic presentation of patina layers on bronze
Slika 4: Shematska predstavitev plasti patin na bronu

In the secondary-external layer of brown-black, black-green and green-white patina, the following predominant compounds were found: copper oxides, copper hydroxisulphates, as well as sulphides, chlorides and carbonates of copper and its alloying elements.

The sites where the water rinsing was not highly intensive have a relatively stable, predominantly black, patina. The vertical and horizontal surfaces have been affected by intensive rinsing. The leaching activity of the urban rain is therefore stronger and the colour of the patina is pale green-white.

The presence of Cl, Mg, K and Ca in the corrosion products is a consequence of the bronze's contamination with de-icing salts. Although the content of these elements is not high, they are in sufficient quantities to trigger corrosion and "bronze disease". The presence of chlorides and moisture is the cause for copper dissolution. The formation of sulphur compounds of copper and its alloying elements as well as carbonates in corrosion products is probably the consequence of acid rain (carbon and sulphur acid), air pollution (above all SO_2), and moisture. Copper hydroxi-sulphates are soluble in water – they form green-white lines on the sides of bronze sculptures. The content of zinc in the corrosion products is minimal and it can be assumed that the bronze of the sculptures and reliefs is not sensitive to dezincification. However, Bernardi and coauthors found that Cu and Pb in bronze type G85 progressively form insoluble corrosion compounds, while Zn continuously dissolves without forming detectable insoluble products [15]. They also claim that the absence of dissolved tin is remarkable.

Pollution with sand powder and soot might be the reason for the detected presence of Al, Si and C in the corrosion products.

5 CONCLUSION

Based on a visual examination, a chemical analysis of the bronze, and an EDS analysis of the patinas formed on Prešeren's monument in Ljubljana, the following conclusions were drawn:

- The sculptures of Prešeren's monument in Ljubljana were made from bronze C922. The purity of the bronze indicates that the casting process of this monument was strongly controlled.
- Regardless of the corrosion processes and the age of the bronze monument (approximately 100 years), the corrosion damage to the bronze alloy is insignificant, and the patina formation only disturbs the monument's visual/aesthetic appearance.
- The variety of patinas formed on the different sites of the monument under different conditions of wetting/drying/rinsing shows that the corrosion (bronze disease) is a consequence of the aggressive urban atmosphere.
- In order to maintain the bronze statue and to keep the appearance as long as possible, the protection of the bronze prepatinated surface is strongly advised.

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