Defects of copper patina

Vady měděných patin

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The paper is focused on analyses of dark copper patina defects that were formed on one sheet under the same conditions. Roofs of ten historical buildings were studied by image analysis and samples of two roofs were subjected to more detailed destructive analysis. These samples were studied by means of scanning electron microscopy with energy dispersive X-ray spectroscopy, X-ray diffraction and infrared spectroscopy. Both types of patina are composed of brochantite. Green patinas consisted of a pure brochantite and they had a flat and compact surface. Conversely, black patina contained a high degree of impurities (ammonia cations, nitrates, silicates) and the surface was rough. The proportion of dark patina was higher in south and east facing surfaces, where washing by rainfall is more difficult.

Tato práce byla zaměřena na analýzu defektů patin, které vznikly na jednom plechu za stejných podmínek. Střechy deseti historických objektů byly studovány pomocí analýzy obrazu a vzorky ze dvou střech byly podrobeny detailnějším destruktivním typům analýzy. Vzorky byly sledovány pomocí scanovací elektronové mikroskopie s energiově disperzní rentgenovou analýzou, rentgenové difrakce a infračervené spektroskopie. Oba typy patin se skládaly výhradně z brochantitu. Zelené patiny se skládají z čistého brochantitu a mají hladký a kompaktní povrch. Na druhou stranu tmavá patina obsahuje vysoké množství nečistot (ammoný kationt, dusičnany, křemičitany) a má drsný povrch. Podíl tmavé patiny je vyšší ve směru jižním a východním, kde je obtížnější omývání srážkami.

INTRODUCTION

Natural copper patina is mostly composed of basic copper sulphate (brochantite) with the chemical formula $Cu_4(OH)_6SO_4$. Brochantite is well known due to its pastel green colour, but there is also a dark variant with rough morphology. The formation of these patinas has been well described **[1-6]**. Another stable corrosion product based on sulphate is antlerite with the chemical formula $Cu_3(OH)_4SO_4$. Antlerite is typically formed in acidic environments, in areas with a lack of rinsing by rainfall and in sheltered areas or in contaminated spots on a surface. The dark (rough) variant of brochantite is also formed at these sites **[1]**. Antlerite has a higher solubility constant (2.53×10^{-48}) than brochantite (1.01×10^{-69}) **[7]**, and therefore has a less protective effect. Antlerite and rough brochantite have also higher “runoff”, due to the erosion impact of rainfall **[1, 8]**. Many cases were observed where green and dark patina were present on the same sheet and in the same site (see Fig. 1), i.e. where the conditions for patina formation are the same. Sites were also observed where initial dark patina had become flattened and turned green. Determination of the origin of these patina defects was the scope of this paper.

Fig. 1. The tower of the church of the Birth of the Virgin Mary in Písek
Obr. 1. Věžička kostela Narození panny Marie v Písku

EXPERIMENTAL

Patina characterisation

Samples of two objects were provided for detailed destructive analyses. Those were roof sheets of Queen Anne's Summer Palace (approx. 150 years old) and roof sheets of the University of Chemistry and Technology building (approx. 70 years old). Samples were cut and both types of patina (green and dark) were subjected to scanning electron microscopy imaging and energy dispersive X-ray spectroscopy (*VEGA3 LMU*, TESCAN), X-ray diffraction (*X´Pert Pro*, PANalytical) and infrared spectroscopy (*IFS 66v*, Bruker).

Image analyses

Pictures of ten objects were taken from each cardinal direction. The analysed objects were in the district of Prague: the Church of Saint Bartholomew, the Church of Saint Wenceslas, the Monastery of Premonstratensians, the Archbishop´s Seminary, the Benedictine Archabbey, a house in the Wolker street, the Saint Maria Magdalena Chapel, the Church of Saint Thomas Episcopal, the House Na Valech, and a house on Wenceslas Square. Images were converted to binary files and the ratio of dark/green area was calculated. Three objects (the Church of Saint Bartholomew, the Church of Saint Thomas Episcopal, and the Church of Saint Wenceslas) allowed also estimation of the influence of roof angle, because they were composed of two or three different angles.

RESULTS AND DISCUSSION

Patina characterisation

The surface of the samples was first observed by SEM. The surfaces of both green patina samples (from the University of Chemistry and Technology building and Queen Anne's Summer Palace) are flat (see Fig. 2 and 4) when compared to dark patinas (Fig. 3 and 5). The EDS analyses presented in Tab. 1 show the elemental composition of patinas. Dark patinas contain more impurities, silicon and aluminium (dust), and less of the main elements for patina formation, copper and sulphur.

X-ray diffraction confirmed that both crystallographic lattices are based on brochantite. Infrared spectra are given in Fig. 6 and 7. FTIR showed the green patina is composed of pure brochantite while dark patina contains significant amounts of impurities (Fig. 7). Inert silicates were identified, but aggressive ions such as nitrates or ammonia cations were also present. These species are very aggressive to the copper surface. They work as chelating agents and they may have their origin in bird excrement. Nevertheless, these species were present in insoluble form. The increased presence of dust particles in dark patinas could be a consequence of their rough morphology. Conversely, the presence of insoluble nitrates and ammonia cations in the lattice of brochantite is evidence of their long period of formation.

Tab. 1. SEM-EDS analyses of the samples / *SEM-EDS prvková analýza vzorků patin*

Element	UCT		Summer palace	
at. %	black	green	black	green
Al	9	3	19	6
Si	39	6	30	13
P	4	7	7	3
S	12	20	3	15
Fe	5	3	7	2
Cu	31	62	34	60

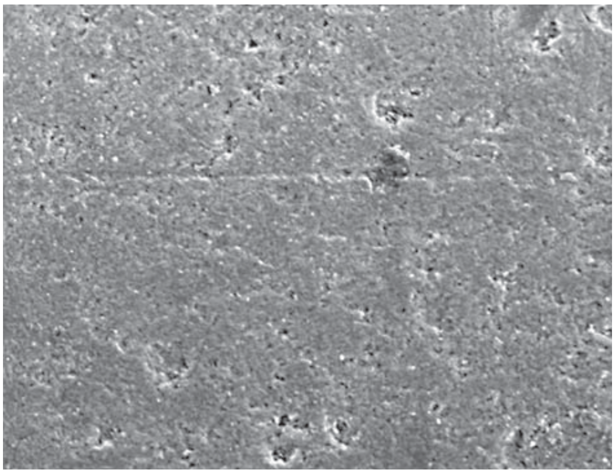

Fig. 2. SEM image of the UCT green patina surface
Obr. 2. SEM snímek povrchu zelené patiny z VŠCHT

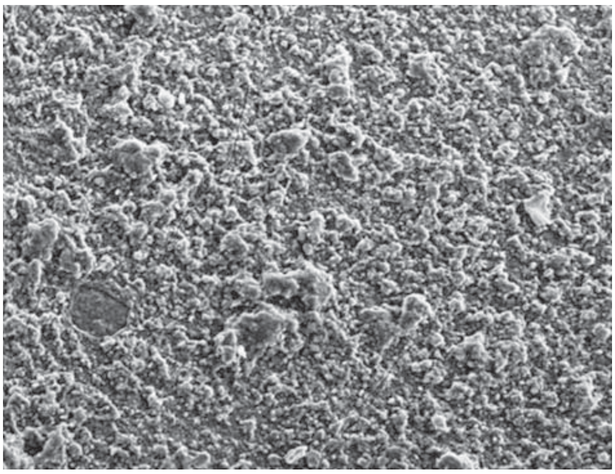

Fig. 3. SEM image of the UCT black patina surface
Obr. 3. SEM snímek povrchu černé patiny z VŠCHT

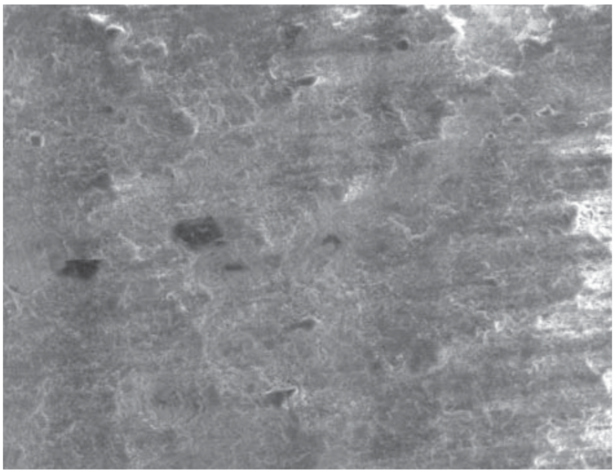

Fig. 4. SEM image of the Summer Palace green patina surface
Obr. 4. SEM snímek povrchu zelené patiny z Letohrádku královny Anny

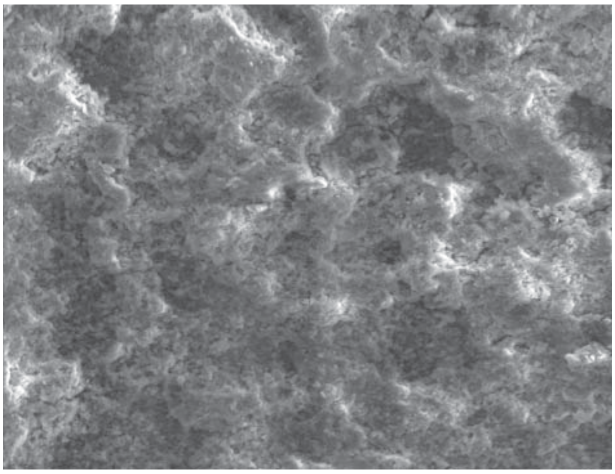

Fig. 5. SEM image of the Summer Palace black patina surface
Obr. 5. SEM snímek povrchu černé patiny z Letohrádku královny Anny

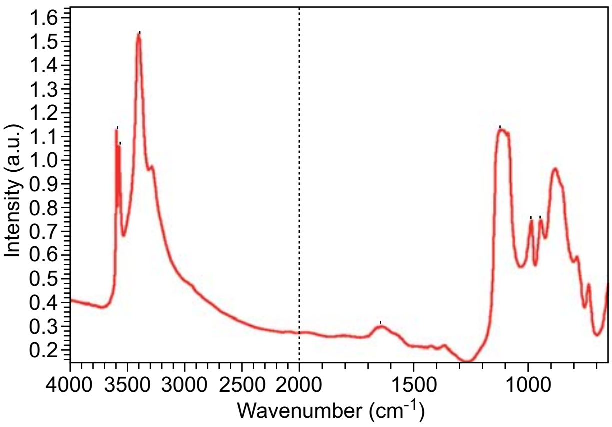

Fig. 6. FTIR spectrum of the Summer Palace green patina sample
Obr. 6. Infračervené spektrum zelené patiny z Letohrádku královny Anny

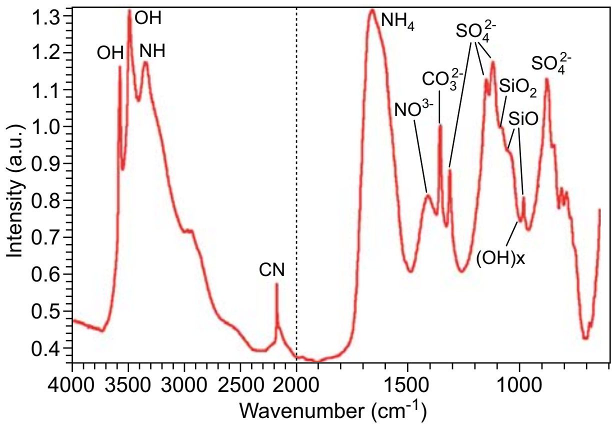

Fig. 7. FTIR spectrum of the Summer Palace black patina sample
Obr. 7. Infračervené spektrum tmavé patiny z Letohrádku královny Anny

These species were probably present on the surface and they are the reason for the easier dissolution of substrate copper and consequently the rough morphology of the dark patinas.

Image analyses

The results of image analyses are shown in Fig. 8. The highest ratio of dark patina is on roofs facing south and east. A lower ratio was found on north facing surfaces and the lowest in west facing surfaces. This corresponds well with the main direction of wind and rainfall in the district of Prague, west and northwest. Rainfall allows the washing of impurities from the surface of copper sheets.

Even more obvious data was provided by analysis of the roof angle (see Fig. 9). The ratio of dark patina is

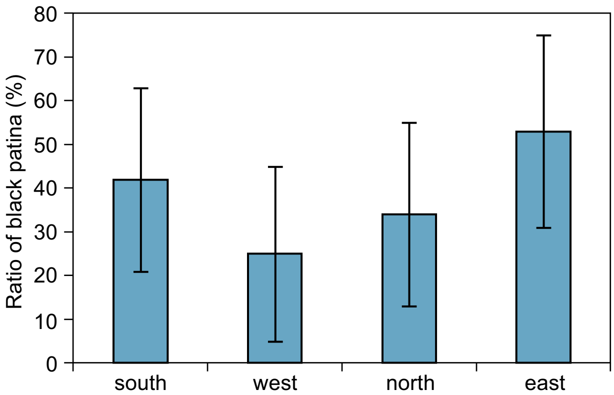

Fig. 8. Ratio of black patina as a function of orientation (the ratio was estimated by image analysis of the roofs of 10 historical objects)
Obr. 8. Závislost podílu tmavé patiny na orientaci střechy (podíl byl stanoven na střechách 10 historických objektů)

the same for low roof angles (close to horizontal). Sheets are well washed regardless of their cardinal direction. When roof angle increases, the ratio of dark patina increases especially in the south and east facing cases where washing is more difficult. A roof angle close to vertical decreases the degree of washing.

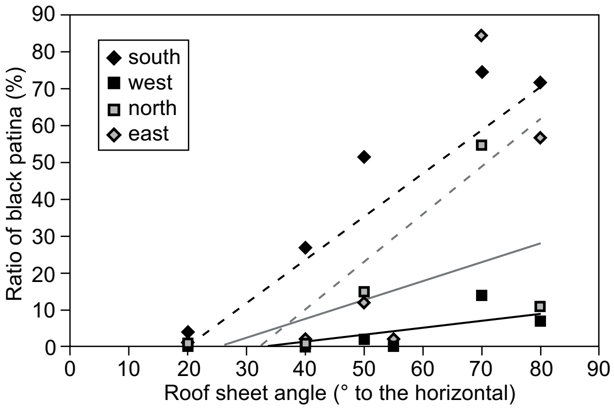

Fig. 9. Ratio of black patina as a function of a roof angle (the ratio was estimated by image analysis of the roofs of 3 historical objects)

Obr. 9. Závislost podílu tmavé patiny na sklonu střechy (podíl byl stanoven na střechách 3 historických objektů)

CONCLUSIONS

Both patinas, green and dark, were based on brochantite. The green patina had a flat surface and it contained only small amounts of impurities (mainly dust). Black patina is rough and it contained significant amounts of impurities. Some of those are inert (dust and soot particles), but some are aggressive to copper (ammonia cations, nitrates). The fact that impurities were in insoluble form led us to assume the rough structure of the dark patina is a consequence of the presence of impurities on the surface of the copper sheet.

Acknowledgement

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