

ASSESSMENT OF CLEANING THE CORROSION LAYER OF PLATED BRONZES WITH A COMPLEX GEL OF POLYVINYL ALCOHOL AND CARBOMER

Pujun JIN^{1*}, Fanghong RUAN², Xiaogang YANG³,
Kaiqiang LIU⁴, Houxi ZOU³, Lin YE³, Laiyuan GU³

¹ School of Materials Science and Engineering, Shaanxi Normal University, Xi'an, 710119, China

² Chongqing Institute of the Dazu Rock Carvings, Chongqing, 402360, China

³ Chongqing Cultural Heritage Research Institute, Chongqing, 400013, China

⁴ School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China

Abstract

When unearthed from soil, many plated bronzes were covered with a thick layer of patina that hid their original shiny lustre. A sandwich structure is observed in their cross-section including superficial patina, plated layer and inner patina. In this paper, a hydrogel cleaner, composed of polyvinyl alcohol (PVA) and Carbomer, and added by formic acid and cysteine, is introduced as de-rusting agent which can not only remove the patina from the surface of plated bronzes successfully, but also keep their original lustre.

Keywords: *Plated bronze; Patina; De-rusting; Gel cleaning; PVA; Carbomer.*

Introduction

Metal plating is an important invention in human history providing many benefits to artefacts made from metal and other materials. As a manufacturing process, plating refers to coat a thin layer of metal on a substrate that can be achieved through fire-plating, leaf-plating or electrochemical plating, etc [1]. Notable advances in the economical use of gold can be seen in the introduction of gold leaf in the second millennium BC, the later invention of fire-gilding about 2000 years ago, and the recent development of electroplating in the middle of 19th Century [2]. The first use of fire plating was reported in ancient China, where a case, a dagger with a plated surface excavated from a tomb (M1) at Jiao village in Gansu province [3], was thought to be produced by fire gilding technology as early as the West Zhou Dynasty Dynasties. In the following dynasties, some plated bronzes appeared via fire gilding technology and sprout up in the Han dynasties [4-6].

Most metals can form an amalgam with mercury, among which mercury gold plating is known as fire plating because of the manufacturing process. When baked under a charcoal fire [7, 8] at a temperature about 500–600°C [9, 10], a thin gold film can be formed on the surface of artefacts due to the evaporation of mercury after a layer of amalgam was applied [11-13]. After enduring in a long-time burial circumstance, the plated artefacts are usually completely covered with a thick patina [14-17] without any shiny appearance, as shown in Figure 1. It is

* Corresponding author: jinpj@snnu.edu.cn

usually mixed with other contaminants, such as soil crust, causing physical damage to the plated bronze [1]



Fig. 1. Two plated bronzes covered with a layer of patina were unearthed in Wushan County in the Three Gorge District

Many methods have been tried to descale the patina above the plated layer and make them exhibit a shiny appearance, which can be achieved with a scalpel while being observed microscopically causing little damage to the gilding surface besides the appearance of minor scratches [13], and with some chemical solvents including alkaline Rocelle salts or formic acid [11, 18-21] resulting in the partial separation of plated layer. Recently, laser cleaning was introduced as an effective method [1], but which could lead to a rapid increase of surficial temperature and release of Hg from the plated layer [22] resulting in a reddish colour of the plated layer.

As shown in Figure 2a, SEM images demonstrate a sandwich cross section of a plated bronze fragment including a superficial patina layer, a plated layer and an inner corroded layer. A similar structure was observed by Lee [1, 23] who also reported a decreased content of Cu with increasing O, indicating a reduced tendency of copper oxides from the inner patina to the superficial patina. Many holes and cracks are observed on the surface of fresh plated layer as the migratory tunnels of alloy elements, as shown in Figure 2b. Therefore, the subsequent growth of inner patina can cause the upper plated layer to detach [24-26]. The sandwich structure makes it difficult to remove the superficial patina without any detachment of the plated layer by those mentioned normal methods. For example, the leakage of chemical agent will corrode the inner patina resulting in the peeling of the plated layers, and the mechanical method will be dangerous for the superficial patina that adheres to the plated layer strongly.

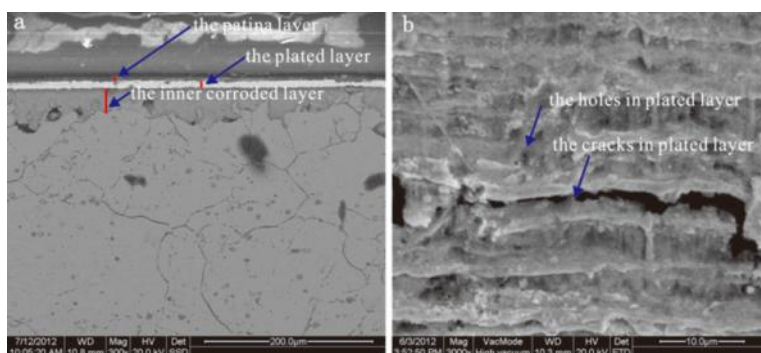


Fig. 2. Back-scattered images of a section of a plated layer and a fresh surface:

- a) A sandwich structure of the plated layer section was observed.
- b) After the patina was removed, the fresh surface shows a porous structure with multiple cracks

A hydrogel forms a crosslinked network with a water dispersion medium which is largely used as a carrier release agent [21, 26, 27]. Since 1988, the Getty Conservation Institute has an ongoing research project on gel cleaning for murals, rock, wood, metal and oil paintings [28, 29]. In 2010, a peeling high viscoelastic gel was introduced to clean varnish from the surface layer of cultural relics [30].

In this study, a complex hydrogel of polyvinyl alcohol and Carbomer 940 containing formic acid and cysteine has been prepared, characterized, and applied to descale the plated artefacts. Solutions of polyvinyl alcohol (PVA), in the presence of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) as a cross-linker, are known to form an aqueous dispersion with a high elastic modulus [31-33]. Carbomer 940 (Cb940), comprised of acrylic acid, has an extremely efficient rheology modifier allowing it to form a highly viscous hydrogel in water [34, 35]. Based on PVA and Cb940, a complex hydrogel with a medium viscoelasticity was prepared, which could remove the covering patina from the plated artefacts and keep their original shiny lustre.

Methodology

Samples

A plated bronze fragment (M5:2, numbered as No.1) collected in Wushan County Museum, and some plated bronzes from the Chongqing Cultural Heritage Research Institute were prepared for this de-rusting procedure, including a bronze ewer (No.2) that was used to hold liquor and water, and two small boxes (No.3 and No.4) used as containers, as shown in Figure 3. The plated bronzes were restored from many fragments with many losing parts instead of new substitutions.



Fig. 3. Four plated bronze pieces that were de-rusted

Instruments and methods

A Quanta 200 scanning electron microscope (FEI Company, Netherland) equipped with an X-ray energy dispersive spectrometer (EDS) was used to explore the sandwich-type structure and detect the elements in the patina and the treated de-rusting hydrogel, under a high vacuum

mode ($<5.0 \times 10^{-3}$ Pa). A TM3030 (Hitachi High-Technologies Corporation, Japan) tabletop microscope was used to observe the network of complex hydrogels.

A SmartLab high-resolution diffraction system (Rigaku, Japan) X-ray diffractometer equipped with Cu K radiation were applied to identify the corrosion compounds of patina with 2 range from 10° to 70° , the tube voltage about ca. 40 kV, and the current about ca. 30 mA.

An AR-G2 rheometer (TA Company, USA) was applied to detect the storage modulus (G') and the loss modulus (G'') of complex hydrogels with a 1.0g sample in an oscillation strain sweep mode at a constant temperature (25°C) and frequency (1rad/s), and in an oscillation temperature ramp and sweep mode from 10 to 70°C , using 40mm steel parallel plates with a gap of 1.0mm.

Experimental part

Materials

Carbomer 940, polyvinyl alcohol 1799 (99.8~100% alcoholysis, Shanghai Aladdin Biochemical Technology Co., Ltd.), triethanolamine (AR, Sinopharm Chemical Reagent Co., Ltd.), sodium tetraborate decahydrate (AR, Sinopharm Chemical Reagent Co., Ltd.), formic acid (AR, Tianjin Fuyu Fine Chemical Co., Ltd.), and cysteine (AR, Shanghai Lanji Technology Development Co., Ltd.) were used to prepare the de-rusting hydrogel. In this study, a complex gel with carbomer and polyvinyl alcohol is prepared as a hydrogel carrier with an excellent three-dimensional network structure and a suitable viscoelasticity.

Analysis of the patina above the plated layer

The XRD patterns of superficial patina are shown in Figure 4. Peaks occur at 29.6° , 36.5° , 42.4° , 61.5° due to Cu_2O (JCPDS Card No.77-0199), at 23.4° , 25.5° , 29.7° , 34.5° , 36.7° , 43.3° , 49.7° corresponding to PbCO_3 (JCPDS Card No.03-0358), at 5.03° , 5.02° , 3.68° , 2.85° , 2.50° , 2.17° , 2.12° , 2.06° , 1.42° , 1.28° , 1.25° corresponding to $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (CPDS Card No.41-1390), at 22.04° , 30.95° , 37.36° , 41.14° , 44.95° , 51.53° corresponding to dolomite $[\text{CaMg}(\text{CO}_3)_2]$ (CPDS Card No.75-1759), at 23.00° , 29.37° , 39.37° , 43.12° , 48.45° , 56.51° , 60.60° , 64.59° corresponding to CaCO_3 (CPDS Card No.72-1937) and at 4.21° , 3.33° are attributed to SiO_2 (CPDS Card No.46-1045).

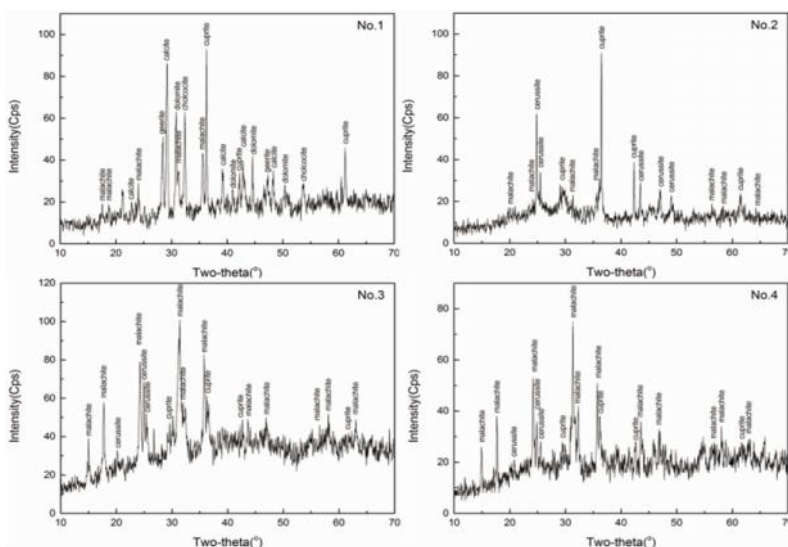


Fig. 4. The XRD pattern of the superficial patina collected from No.1-4 showing the existence of malachite $[\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2]$, Cuprite (Cu_2O), cerussite (PbCO_3), dolomite $[\text{CaMg}(\text{CO}_3)_2]$, calcium (CaCO_3) and quartz (SiO_2)

When buried in soil circumstance, the superficial patina is usually comprised of the patina and soil crust [36]. As shown in Table 1, element Si, Al, Ca, Mg, Fe, K, and P mainly were originated from the soil. Furthermore, 34~58% Cu was detected in the samples showing the predominance of copper salts in these covering patina. On the other side, element Hg, Au and Ag were not detected in the superficial patina indicating the relative stability of the mercury Au/Ag layer under a soil burial condition. This is why these plated layers will keep a shiny lustre after the descaled treatment.

Table 1. Composition of the patina samples obtained by EDS analysis (wt%)

Element	C	O	Si	Pb	Fe	Cu	Ca	K	Al	Sn	P	S
No.1	/	30.61	5.96	/	1.17	57.55	1.05	0.48	3.02	/	/	0.15
No.2	27.28	27.91	/	8.43	0.33	35.43	/	/	/	/	0.61	/
No.3	14.2	25.17	1.56	3.43	0.7	53.85	0.32	/	0.77	/	/	/
No.4	13.76	27.84	1.64	20.03	/	34.41	/	/	0.73	1.59	/	/

Cleaning components

Cu(I) and Cu(II) salts detected in this study, such as cuprite (Cu_2O) and malachite [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$], which are common corroded productions of archaeological copper artefacts [14-17]. Therefore, formic acid and cysteine were considered as the cleaning components in the de-rusting hydrogel. As a weak acid, formic acid (HCOOH) can react with copper salts in a mild process besides softening the soil crust. Cysteine, with the chemical formula [$\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$], contains two coordination ions (ammonia nitrogen and carboxyl oxygen) and sulfhydryl groups that can remove Cu(II) salts via coordination reaction with Cu(II) [37].

Preparation of de-rusting hydrogels

Firstly dissolve PVA1799 in the 85~90L distilled water with a constant stirring, then cool this solution to 55L, add Cb940 gradually and stir them to dissolve. Then add triethanolamine, borax, formic acid and cysteine, mix them to uniform until the aqueous solution becomes transparent. The de-rusting hydrogel can form the crosslinked polymer network absorbing substantial amounts of aqueous solutions which will accomplish the controlled release of chemical agent into the artwork and provide a simple and non-invasive treatment [38].

The properties of de-rusting hydrogels

Viscosity test

Table 2 shows the viscosity data, measured with a NDJ-8S rotational viscometer, of seven de-rusting hydrogels with different PVA/Cb ratios: PC1 (PVA:Cb=1:1), PC2 (PVA:Cb=1:2), PC3 (PVA:Cb=1:3), PC4 (PVA:Cb=1:4), PC5 (PVA:Cb=2:1), PC6 (PVA:Cb=3:1) and PC7 (PVA:Cb=4:1). The results show these hydrogels with high viscosity, especially for those with PVA/Cb ratios ranging from 1/2 ~ 1/4, among which PC4 show the largest viscosity, even exceeding the measurement range of the NDJ-8S rotational viscometer.

Table 2. The viscosity data of derusting hydrogels by a NDJ-8S rotational viscometer

Samples	1	2	3	4	5	6	7
Velocity (rpm)	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Viscosity (Pa·s)	594	1312	1812	over	726	850	990

RPM is rotating speed.

SEM images of the interior morphology

The interior morphology of de-rusting hydrogels was observed by SEM after the freeze drying process. Freeze drying is the process of dehydrating frozen hydrogels under a vacuum so the moisture content changes directly from a solid to a gaseous for maintaining their original 3D network structure, specifically preventing the moisture damage of the SEM accessories [39, 40]. As shown in Figures 5, the de-rusting hydrogels demonstrate the 3D networks similar to a porous structure whose size and quantity greatly affects the absorption of water and cleaning agents. Sample PC1~4 acquire a highly porous 3D hydrogel with open and interconnected pores with diameters below 20 μm . Especially for PC4, the small and uniform pores were observed with diameter less than $\sim 6\mu\text{m}$ displaying a foamy structure. PC5~6 had larger pores in their networks and a few pores were observed in PC7. Gel PC4 was confirmed as a practical de-rusting hydrogel. Comparing the viscosity values of these gels listed in Table 1, it also had highest viscosity value and even exceeds the detection limit of the NDJ-8S rotational viscometer.

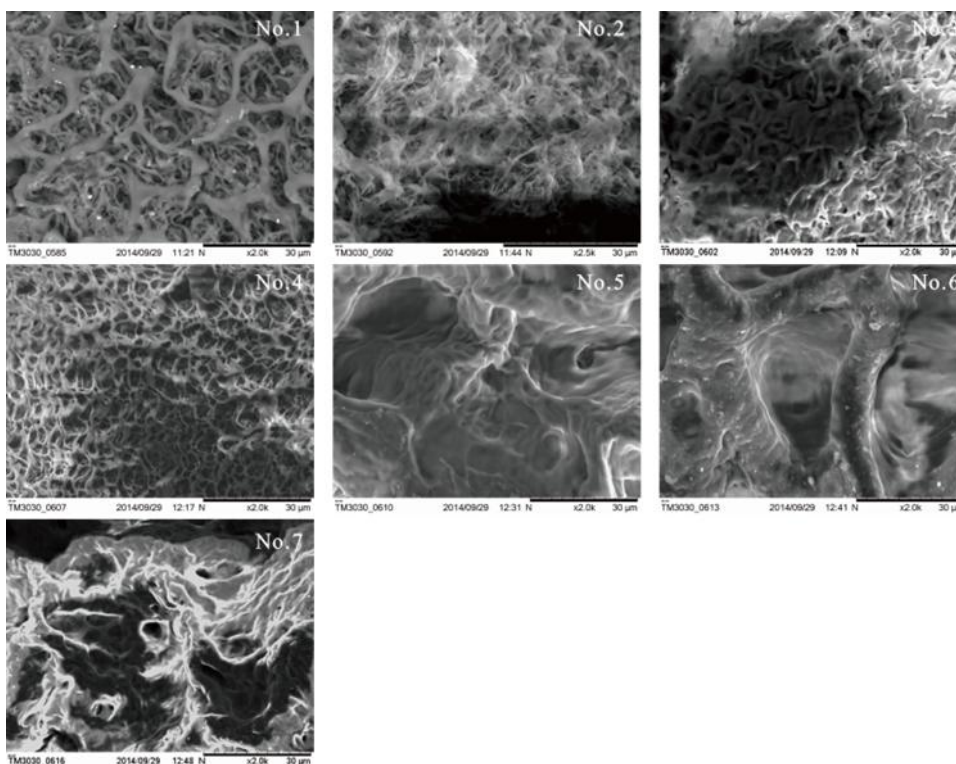


Fig. 5. SEM images of freeze-dried de-rusting hydrogels No.1-7 with porous structure

Rheological characteristics

The rheological characteristics of these hydrogels were investigated using an AR-G2 rheometer (TA Company, USA) in the oscillation mode at a constant temperature (25 $^{\circ}\text{C}$) to evaluate the effects of brushing stress, and in a temperature sweep from 10 to 200 $^{\circ}\text{C}$ to investigate their thermal stability. The values of rheological parameters like the storage modulus (G') indicate the solidity and the loss modulus (G'') indicates the liquidity of the hydrogel [41].

Oscillation stress gives deep insight into the rigidity and strength of the soft-solid structures that impart critical quality attributes to the de-rusting hydrogels. In the oscillation stress model, the sample is subjected an oscillatory shearing force of increasing amplitude until the structure is ultimately disrupted. Figure 6a shows that the parameters G' and G'' decreased with increasing shear stress in a non-linear fashion, indicating that the microstructure of the sample gradually weakened and broke down, exhibiting a more liquid-like behaviour [42]. The structural breakdown of PC3 and PC4 lagged behind the other samples until stress above 1000 Pa at 25°C was reached, which indicated favourable stability during manual brushing and wiping operations.

The temperature effect on gelation of the hydrogels was also studied by oscillatory tests and the results are shown in Figure 6b. As the temperature increased from 10 to 70°C, the linear profiles of both G' and G'' indicate the thermal stability of hydrogels at room temperature, as shown in Figure 6b. In fact, the hydrogels can remain in the wet gel state for several months in a closed container. Thus, the perfect stability of these gels guarantees the convenience of the protective process.

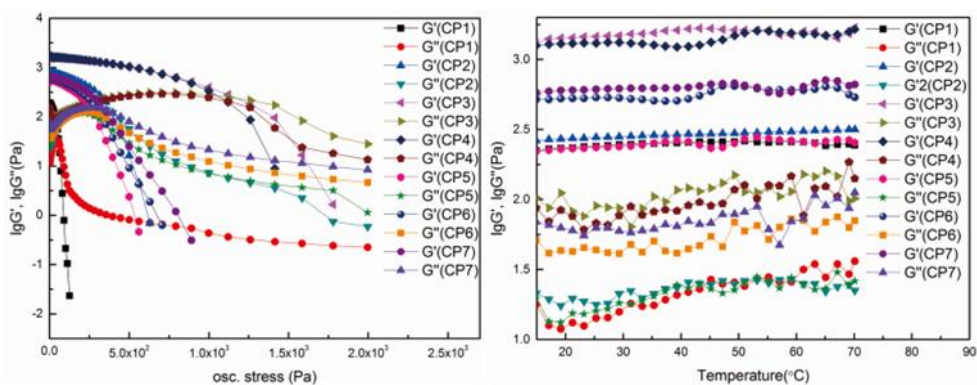


Fig. 6. Storage modulus (G') and loss modulus (G'') modulus of the de-rusting hydrogels were acquired in a stress sweep test and, an oscillation temperature ramp and sweep test

Practical treatment and effective evaluation

Cuprite and malachite powder could dissolved in gel PC4 respectively to form a green or red jellylike substance resulting from its ability to remove Cu(I) and Cu(II) salts in the patina. The practical treatment on cultural relics' samples begins by applying a layer of 3mm gel on the surface of patina for about 10 minutes, then using a cotton swab to wipe off the gel gently when it becomes a green gel, and repeating the process until the patina is clean. Finally, a cotton swab dipped in alcohol to was used to reduce the gel residue in the treatment areas[43]. Compared to the original picture (Figure 3), the treated artefacts show a metallic lustre, as shown in Figure 7. Both No. 1 and No. 2 evidenced a bright golden gloss except for No. 3 and No. 4 showing a little dark hue after their treatment. This colour difference was attributed to the different composition or craftsmanship of the plated layers.

The final treated gel of sample No. 1 was analysed by EDS indicating 59.37% C, 34.61% O, 5.27% Fe, 0.27% Ca, and 0.48% Cu. A higher concentration of C and O than that in the superficial patina is due to the gel. 5.27% Fe, 0.27% Ca and 0.48% Cu correspond to the patina. The elements Au, Ag or Hg of plated layer were not determined in the treated gel, and it shows us a safety of gel on the plated layer.

According to the treatment process, some problems should be further discussed in detail. In fact, it will take a long time to finish the de-rusting process that needs to have more patience for the conservators. Heavy metal ions (Cu^{2+} and Cu^+ , etc.), in particular, can cause

shrinkage of the de-rusting hydrogels corresponding to the new bonds in the hydrogel network in the treatment process [44]. On the other hand, water inside the hydrogel matrix can be classified as free water, free interstitial water or semi-bound water [45] that is the principal component of a hydrogel, and more than 90% of the weight is present in the swollen state. Importantly, free water can be easily removed under higher temperature because it is just physically entrapped within the polymer network [46]. Therefore, the de-rusting hydrogels will also gradually shrink due to losing moisture and adsorbing heavy metal ions gradually, resulting in a tough solid polymer that could adhere to the plated fragments and not be peeled off easily. So, it is very important to remove adhering de-rusting hydrogels in time.

It is difficult to judge the progress of the operation and maintain a uniform colour of the artefact due to the reaction between the hydrogel and the patina. Therefore, artefacts must be determined by imaging techniques including standard X-rays or complementary neutron radiography or tomography (NT), which provide information about the distribution of the plated layers before the de-rusting treatment [46, 48].



Fig. 7. Samples No.1-4 treated with PCb4 show a shiny metallic luster

Conclusion

A complex gel of polyvinyl alcohol and Carbomer with formic acid and cysteine was proposed as a de-rusting hydrogel and to effectively remove the covering patina from some plated bronzes. Gel PC4 (PVA:Cb = 1:4) had a foamy network structure with tiny pores less than $\sim 6\mu\text{m}$ in size. This method exhibited a good aspect for descaling the patina from the surface of plated bronzes.

Acknowledgments

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