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Study on surface properties of gilt-bronze artifacts, after Nd:YAG laser cleaning

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ABSTRACT

As numerous pores are formed at plating gilt-bronze artifacts, the metal underlying the gold is corroded and corrosion products are formed on layer of gold. Through this study, the surfaces of gilt-bronze are being investigated before and after the laser irradiation to remove corrosion products of copper by using Nd:YAG laser. For gilt-bronze specimens, laser and chemical cleaning were performed, and thereafter, surface analysis with SEM-EDS, AFM, and XPS were used to determine the surface characteristics. Experimental results show that chemical cleaning removes corrosion products of copper through dissolution but it was not removed uniformly and separated the metal substrate and the gold layer. Nevertheless, through laser cleaning, some of the corrosions were removed with some damaged areas due to certain conditions and brown residues remained. Brown residues were copper corrosion products mixed with soil left within the gilt layer. It was due to surface morphology of uneven and rough gilt layer. Hence, they did not react effectively to laser beams, and thus, remained as residues.

The surface properties of gilt-bronze should be thoroughly investigated with various surface analyses to succeed in laser cleaning without damages or residues.

1. Introduction

Gilt-bronze is the application of a layer of gold onto the surface of bronze. There are several gilding methods such as fire-gilding, leaf-gilding or electrochemical gilding. Amongst the methods, fire-gilding, also known as the gold amalgam process, was invented in China around the 4th century B.C. and had been used as the most common gilding method until the mid 19th century [1]. It is a method whereby the mixture of gold and mercury is spread on the metal for gilding and the mercury evaporates when heated. However, as time passes, with remaining mercury gradually evaporating, numerous gas pockets or cracks are formed in the gold layer. As moisture infiltrates into formed gas pockets or cracks, the corrosion of bronze, the inner metal, progresses, and copper compounds start to cover the top of gilt-bronze [2]. These copper compounds are mixed with contaminants such as soil and dust, covering the surface of gilt-bronze thickly and causing physical damage to gilt-bronze. Conservation treatment of gilt-bronze differs according to the state of artifacts. Copper corrosion products on gilt layer are removed by scalpel based on observations through microscope, at a level which would not cause damages to gold layer [3]. For copper corrosion products, there are methods of using chemical solvents such as alkaline Rocelle salts or formic acid [4,5]. However, such methods may damage the gold layer and substrate metal, and, thus, it is rarely used [6].

In general, laser cleaning holds a range of exposure parameters where selective removal of dirt is feasible to preclude object damages [7]. When Au is reflected in more than 95% at 700 nm or higher laser wavelength [8], it is possible to use 1064 nm Nd:YAG laser. Although there are not many studies on laser cleanings related to gold artifacts, there are some researches such as the study on using the Nd:YAG laser equipment according to manufacturing methods of gilt-bronze [9] and the study on identification of optimal cleaning conditions combining the existing methods based on observations of surface change after laser cleaning applications on gilt-bronze statues [10].

This study is to investigate the stability of gilt layer when corrosions products of copper are removed from the surface of gilt-bronze with the Nd:YAG laser. In addition, by conducting chemical cleanings, comparative analyses were performed for laser cleaning. Topography of the surface before and after cleaning was checked through SEM-EDS, atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS) in investigating the surface oxidation.

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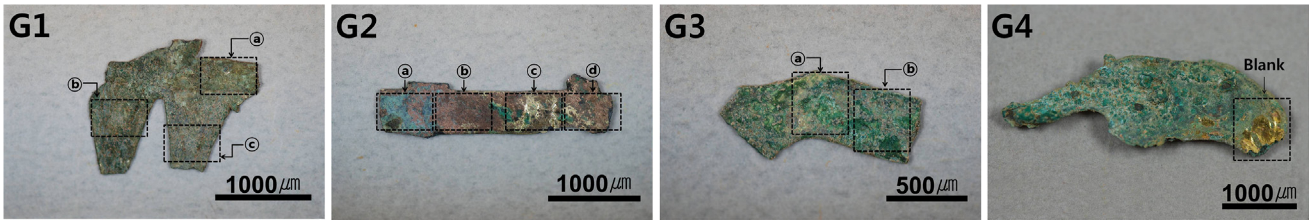

Fig. 1. Samples for laser cleaning (G1, G2), chemical cleaning (G3), blank (G4).

2. Material and methods

2.1. Samples

There were four samples in total and they are from gilt-bronze artifacts of the Proto–Three Kingdoms Period of Korea in the 4C–5C. Gilt-bronze specimen of this experiment uses the amalgam technique of about 1–3 μm thickness of gold layer [11]. Fig. 1 is an image of the gilt-bronze samples. Laser cleanings for G1 and G2, and chemical cleanings for G3 were done. As for G4, since part of gold layer was already exposed when it was first found, it was selected as blank. (a)–(d) of Fig. 1 was investigated regions with optical microscopy after laser and chemical cleaning. The size of samples was listed in Table 1.

The cross section of samples before the experiment was analyzed by SEM-EDS to obtain chemical compositions of each layer (Fig. 2, Table 2). From contaminant on the gold layer, 42.39 wt% Cu, 31.69 wt% O and small amounts of Si, P, Al, Fe, and Ca were detected, and it seemed that the copper oxides and soil were mixed. The gold layer was analyzed to 64.39 wt% Au, 23.78 wt% Cu, and 2.61 wt% O, in that copper oxides were within the gold layer. The substrate metal under the gold layer was detected to 49.73 wt% Cu and 41.59 wt% O, while 78.23 wt% Cu and 12.13 wt% O was found in the section further down. Consequently, the content of Cu was deceased with increasing O from the core toward the surface; showing that the content of copper oxides was increased.

Copper corrosion products which were mostly green on the gold layer in G1 were analyzed by using Raman spectroscopy, and as a result, their Raman shift was equally matched to that of malachite. It was confirmed that green copper corrosion products were malachite, copper carbonate (Fig. 3).

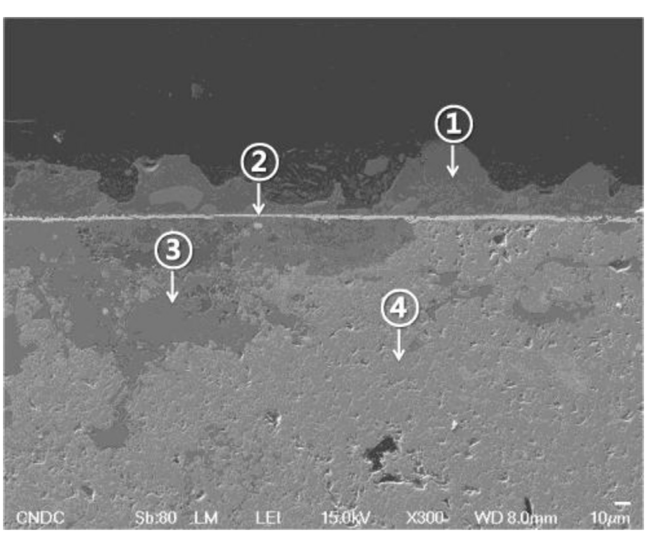

Fig. 2. SEM image and EDS points of the cross section of G1 before laser irradiation.

2.2. Experimental procedures

Laser used for this experiment was Nd:YAG laser (iMT800MV, IMT) with Q-Switch attached and its laser energy output is 160–800 mJ with 1064 nm wavelength and 10 ns of pulse length. The laser beam was circular shaped with 0.13 cm^2. The angle of incidence was 90° with 1.59–2.39 J/cm^2 of laser fluence and 3–5 laser pulses were applied depending on removal response of contaminants. As for chemical method, 5% formic acid (in distilled water) was absorbed into super absorbent polymer and then it was placed on top of gilt-bronze sample until the corrosion product was removed [12] (Table 1).

2.3. Analysis methods

From the experiment of removing copper corrosion products on the surface of gilt-bronze, the surface and cross section before and after treatment were magnified by using stereoscopic microscope (MZ75, LEICA) and thereafter, observed, and photographed by digital camera (D200, Nikon). In addition, surface micro-morphology and identification were analyzed by SEM-EDS (LYRA, TESCAN), and Raman spectroscopy (LabRam HR, Horiba Jobin-Yvon). The AFM (XE-150, PSIA) images were collected in non-contact mode. X–Y scan size of AFM was 10 μm and resolution was below 0.15 nm. Z

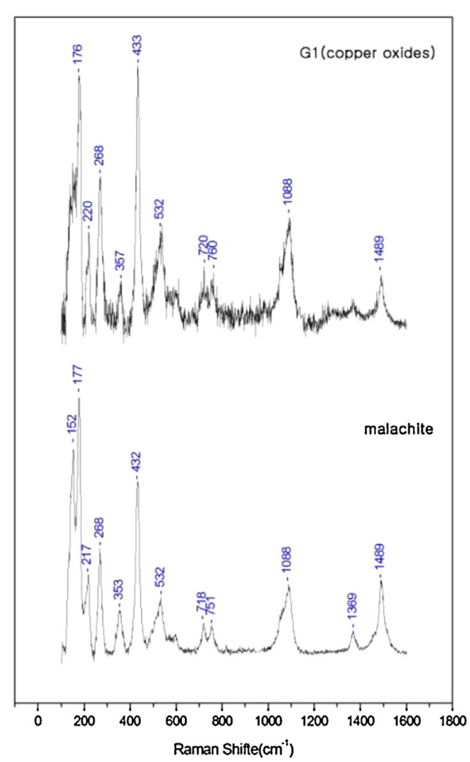

Fig. 3. Raman spectroscopy of corrosion products on gold layer of G1.