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A Materials Investigation into the Metal Composition and Coating Structures of Four Ming Dynasty Cast Iron Statues, with Subsequent Discussion and Development of a Treatment Protocol

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ABSTRACT

Four iron statues dated by inscription to the Ming Dynasty, China, (1491 A.D.) were investigated for their metal composition and coating structures. The investigation was initiated with the intent of ascertaining whether any prior treatment had been done and to determine the present condition of the object. During visual examination and simple surface cleaning, it became apparent that the objects had some form of surface decoration and polychrome. On closer examination, gilding, lacquer, and traces of pigment around the hat, eyes, and garment were visible. A sample of the metal was taken for metallography and chemical compositional analysis. Samples were taken from the surface of the four objects to identify the composition of the observed decoration and corrosion. The results revealed that the statues are white cast iron and were fully decorated with multiple colours and gilding as well as being sequentially lacquered. Recommendations for the cleaning and conservation of these objects are given.

INTRODUCTION

In the spring of 1999, the Royal Ontario Museum (ROM) acquired funding for the 'Levy Sculpture Court', which would house the ROM's collection of Chinese cast iron statues. These statues had been in storage since the late 1970s and therefore required conservation before they could be displayed. The statues are from the Ming Dynasty and their production can be dated to approximately 1491 A.D. Inscriptions incorporated into the casting provide details as to their date of production and the temple that commissioned their manufacture.

The statues investigated here are so-called '*Judges of Hell*', and are one of the main types of figures associated with the Chinese Buddhist temple. Other types are lohans, buddhas, bodhisativas and attendants. Their purpose in the temple was to watch over and care for the religious welfare of the participants and generally protect the spiritual interests of Buddhism [1].

These statues were produced of cast iron in piece moulds as indicated by the various casting seams surrounding the objects (Figure 1). Cast irons are alloys of iron and carbon which contain, when cast, more than 1.7% carbon (generally 2.4 to 4%). Silicon, manganese, sulphur and phosphorous are usually present in various amounts as well [2]. Casting iron was well know in China as early as the 5th century BCE, based on a sample dated from a grave site in Luhe, Jiangsu [3]. By the Ming Dynasty the technique was so well evolved and formulated that even monumental cast iron statues were produced [4].

INITIAL OBSERVATIONS AND CLEANING

The statues were covered in a thick layer of dirt and dust on their arrival in the Metals Conservation Lab at the ROM. The upper layer of dirt was fairly compact and adhered to the

Figure 1: Judge of Hell no 921.1.59. The cast iron statue produced in piece moulds as visible in various casting seams surrounding the body (statue is approximately 27-29 inches in height). Photo copyright of R.O.M. photo by Brian Boyle.

surface. The most effective method of removal was to gently lift the dirt with a soft sable brush, while vacuuming the residue with the nozzle placed at right angles to the surface. Caution had to be taken because although the surface looked smooth, flakes of corrosion were easily detached, leaving tiny pits or craters characteristic of iron corrosion. Under the upper layer of dirt, the surface was black and appeared waxed or oiled. There is a possibility that the black surface residue could be partially composed of incense and other residues generated in the Temple and during open air exposure during the life of the pieces. Certainly, display and storage in the ROM contributed to the uppermost layers heavy dirt layers. During cleaning, decorative features including gilding became apparent. Other decorative elements became visible at the edge of the first tier of the robe. These appeared to be built up with an impasto effect leaving a sense of brocade. Careful examination also revealed not only a black hair-like pattern at the back of the neck, but also a deep, smooth, purple finish which resembled lacquer.

Although there are several contemporary ornately decorated ceramic and wood statues, very little information has been published on similar cast iron statues and no references were found to suggest the possibility of such a highly decorated polychrome surface. Samples were taken from the statues to identify any original surface coatings, the ubiquitous black coating, orange areas of corrosion and small spots of white efflorescence. In addition a sample was taken to determine the metallurgical structure and chemical composition of the object.

METHODS OF ANALYSIS

The surface coating samples were analyzed by X-ray microanalysis, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) at the Canadian Conservation Institute. X-ray microanalysis was performed using a Hitachi S-530 SEM integrated with a lithium-drifted silicon X-ray detector with a beryllium window and a Noran Voyager II X-ray microanalysis system. XRD was performed using a Rigaku RU200-BVHF 12 kW rotating anode generator equipped with a PSPC microdiffractometer and a Co anode. For FTIR, the sample was analyzed using either a Bomem MB-100 spectrometer or a Spectra-Tech IR-Plan research microscope interfaced to a Bomem MB-120 spectrometer. A Leica DMRX polarizing light microscope was used to identify pigments in selected paint samples. Cross-sections were prepared by embedding the samples in polyester casting resin and grinding and polishing them. The samples were then examined using incident light microscopy (LM), fluorescence microscopy (FM), SEM and X-ray microanalysis. The metallographic sample was etched using a 4% nital etchant and analyzed by optical microscopy and compositional data was acquired using a JEOL JXA 8600 superprobe (EPMA) with an accelerating voltage of 25 keV at the Institute of Archaeology, London.

RESULTS AND DISCUSSION

Metal

Metallographic investigation confirmed that the statues were produced as a white cast iron consisting of a fine dendritic network of pearlite with cementite intergrowth with some iron sulphide inclusions (Figure 2). White cast iron is extremely hard and cannot be easily filed or chiselled. The hardness comes from the carbon content forming iron carbide Fe_3C (cementite) which is harder than quartz [4]. It has typically not been considered a useful material since most iron must be finished after being removed from the mould but evidence has been found for its use in weaponry and as farming implements [5]. It is therefore not surprising that these statues were found to be exquisitely finished.

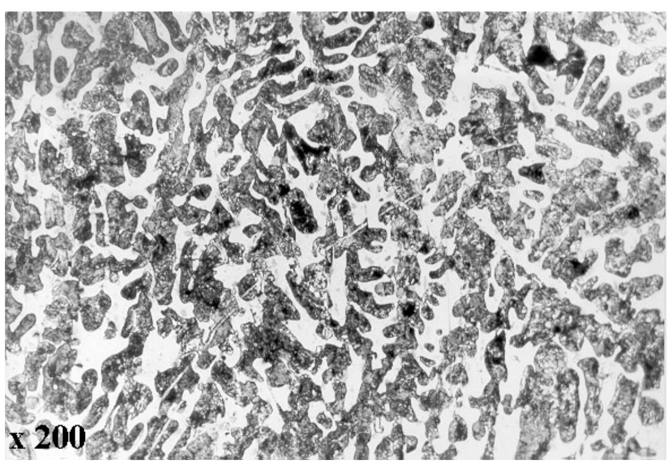

Figure 2: Micrograph of metallurgical structure showing fine dendritic network of pearlite (dark) with cementite intergrowth (white) with some iron sulphide inclusions (dark spots in cementite) (width = 50 µm). Photo copyright of R.O.M. photo by Aaron Shugar

Decorative Elements

All the *Judges of Hell* were originally fully coated with multiple lacquer layers, probably composed of urushi. The lacquer was then covered with preparation layers that ranged in colour from white, through to beige, yellow, brown, orange and red, depending on the area sampled. The preparation layers were, in general, composed of pigmented kaolin, often with large mineral inclusions such as quartz or calcite. Different colours of paint were applied over the preparation layers.

The robes were decorated with red paint and lacquer layers over which gilding was applied in some places. The hats were coloured green, the hair coloured black and the faces and hands were coloured beige. The colours were applied using multiple layers.

The lacquered surface typically showed different layer structures for each colour. For example, in a green sample from the hat a green pigment layer containing copper oxalate hydrate, atacamite, cupric chloride and kaolin, was applied over a yellow-brown preparation layer. The cross-section showed that these layers were applied over an irregular, translucent brown layer.

Urushi

In "Urushi the Technology of Japanese Lacquer" [6] originally published in 1882, a method for the lacquering of metal is given. The layer structures of the lowest layers observed in some of the cross-sections match the description from this book (see Figure 3). The following passage describes the technique for lacquering a metal surface:

"The method for applying lacquer to metal is to smooth and polish the metal and then give it a coating of lacquer. The article is put over a charcoal fire and the lacquer is burnt onto the metal till all smoke ceases to escape. After the lacquer has burnt quite hard, the surface is rubbed smooth. These operations are repeated 3 or 4 times till a good foundation of lacquer has been obtained…"

The lower layers observed in the cross-section were multiple, thin layers applied over the metal surface. They did not contain any particulate matter and appeared to be composed of a similar material, as they were not distinguishable with incident light microscopy or fluorescence microscopy only through backscattered electron imaging.

Over these lower lacquer layers were the preparation layers for the polychrome decoration. The green and black areas had only one pigment layer above the ground. The red areas had a more elaborate sequence of layers.

Red Areas

The layer structure(s) of the polychrome are best described using the example of the red coloured robes which extensively cover each statue. A lower red preparation layer with coarse particles was present in two red cross-sections. In a sample from the lapel, a deep red transparent layer containing fibres was present over the preparation layer followed by another yellowish preparation layer and a particulate red layer, most likely composed of clay minerals (e.g. kaolin) and red iron earth minerals (e.g. iron oxide and oxide hydroxides) (Table 1). An intermittent lacquer layer covered the red clay layer and acted as a mordant for the gilding. Traces of gold leaf were detected on top of this (see Figure 4).

Description	**Results**
Judge of Hell, acc. no. 921.1.59	
black paint from hair + corrosion	poss. akaganéite (β-FeOOH), kaolin ($Al_2(Si_2O_5)(OH)_4$), calcium oxalate hydrate (whewellite $CaC_2O_4XH_2O$ or weddellite $C_2O_4X2.375H_2O$)
green paint from the hat	atacamite ($Cu_2Cl(OH)_3$), cupric chloride ($CuCl_2$), copper oxalate hydrate, kaolin
red “lacquer”	kaolin, calcium oxalate hydrate
red paint - right side of neck	cinnabar/vermilion (HgS), barium sulphate ($BaSO_4$), quartz (SiO_2), calcium oxalate hydrate
Judge of Hell, acc. no. 921.21.139, 921.21.138	
translucent red	probably urushi, calcium oxalate hydrate
red pigment/paint	cinnabar/vermilion, poss. minium (Pb_3O_4), quartz (SiO_2), calcium oxalate hydrate, trace kaolin
Judge of Hell, acc. no. 921.21.137	
deep red layer - gilded red cross-section	quartz, calcium oxalate hydrate, trace kaolin, cinnabar/vermilion
beige preparation layer red cross-section	kaolin, calcium carbonate ($CaCO_3$), calcium oxalate hydrate, trace lead white ($Pb_3(CO_3)_2(OH)_2$)
Red “lacquer”	probably urushi, calcium oxalate hydrate, akaganéite

Table 1: Detailed results of the surface analysis for three of the four judges.

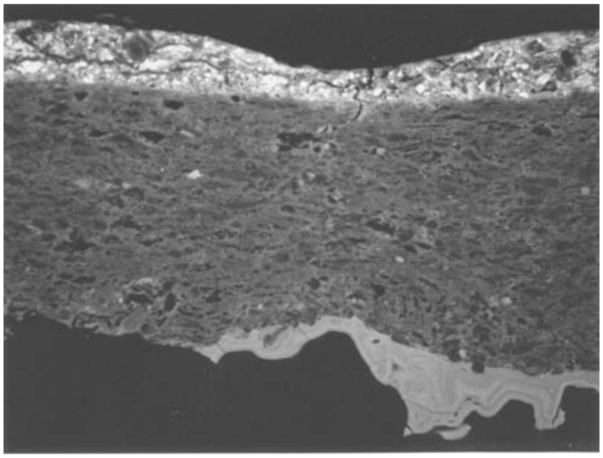

Figure 3: Backscatter electron micrograph, magnification: x600. The top layer contains red lead pigment. The striated appearance of the lowest layers suggests multiple applications of lacquer. Photo copyright of CCI photo by Jane Sirois.

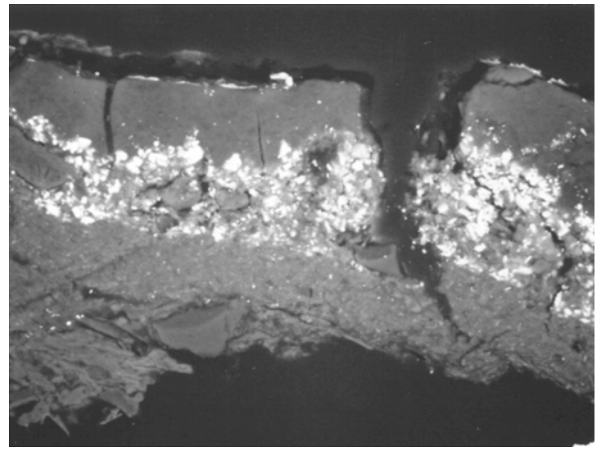

Figure 4: Backscatter electron micrograph, magnification: x600. The thin, bright layer on the top is gold leaf. Vermilion particles in the red paint layer appear white. Photo copyright of CCI photo by Jane Sirois.

The red sample from the lining of the cuff was identified as cinnabar/vermilion, minium/ red lead, quartz, calcium oxalate hydrate, and a trace of kaolin. In another sample from the skirt a deep red paint layer containing cinnabar/vermilion, quartz, calcium oxalate hydrate and a trace of kaolin was present directly under the lacquer and over an orange-red preparation layer. The two examples given above illustrate different approaches taken in red areas — gold leaf over lacquer, an iron oxide paint layer and a yellow preparation layer vs. lacquer over a cinnabar/vermillion paint layer on a red lead ground.

Surface Residues

Calcium oxalate hydrate was identified in almost all samples from the black oily/waxy surface accretion through to the preparation layers and in the surface accretions from the inscription. While some authors have attributed the presence of oxalates to a microbiological origin, *i.e.* the production of oxalic acid by lichens followed by the reaction with a calcium-containing substrate [7,8,9] others have favoured a treatment origin [10]. There was no evidence in the analysis to indicate the source of the oxalates in the samples from the statues

Akaganéite (β-FeOOH) was identified in lacquer and paint samples and as small yellow-brown corrosion particles present on the surface. Akaganéite usually forms at the metal surface when there are high chloride levels [11].

A white efflorescence present on the surface of the lower back part of the sculpture was identified as sodium sulphate (Na_2SO_4) by XRD. Sulphur and chlorine were detected in many of the samples, predominantly in the surface layers: in the black paint, the brown preparation layer under it, the green paint, the red lacquer, transparent lacquer layers and the corrosion particles. Typically no chlorine was detected in the lowest preparation layers from the red painted samples. The presence of sulphur and chlorine in the surface layers, could indicate an earlier conservation treatment, or contamination from dust and dirt in a previous storage environment.

Treatment Decisions

With the presence of urushi, gilding and paint determined, the decision was made to remove both surface dirt and the black surface residue to reveal the polychrome surface using a volatile solvent. Organic solvents, such as ethanol, acetone and toluene, were tested but were ineffective. Ammonium hydroxide, a known degreaser, was selected after testing proved it effective in removing the black oily residue. Urushi lacquer that is not light degraded is unaffected by ammonium hydroxide [12] as are the gilding and the iron. Since ammonium hydroxide is volatile, it should reduce the likelihood of 'wetting' the ground layer, dissolving it or disrupting it. By carefully rolling a lightly wetted swab over the area of fragile gilding, the black residue was removed, exposing and making the gold detail more visible while ensuring the urushi, paint and preparation layers were not damaged. The swabs were visually checked to determine if they were removing anything other than the black accretion.

CONCLUSIONS

The examination and cleaning of the *Judges of Hell* was another reminder that one cannot always know either through a review of the artifact's documentation or careful visual examination, what lies beneath layers of dirt and corrosion. The *Judges of Hell* were fully polychromed white cast iron sculptures. The surface coatings consisted of various layers of urushi, kaolin-type preparation layers, paint layers and gilding. Some residues identified on the surface (sodium sulphate) suggested an earlier treatment had been performed.

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