XRF Analysis of the Seated Shaka Nyorai Statue of Kaniman-ji at Kyoto

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The Japanese National Treasure, “Seated Shaka Nyorai bronze statue of Kaniman-ji” at Kyoto is 250.4 cm tall, weighs 2,172 kg, and is one of the largest bronze statues made by a single casting in ancient Japan. The statue was assumed to have been made over half a century between the late-7th to the mid-8th century A.D. Since the statue has been a Buddhist object of worship, no scientific research has been conducted on it to date. Fortunately, reconstruction of the hall in which the statue is housed meant that a scientific investigation of the Kaniman-ji Shaka Nyorai bronze statue could be conducted from March 2008 to June 2009. The authors investigated the chemical composition of the statue using a portable XRF spectrometer. The Kaniman-ji statue was found to be made of a copper alloy that contained arsenic, tin and lead. The composition was similar to that of Daibutsu of Todaiji. Using the analyzed data, we made an experimental cast sample to estimate the physical and mechanical properties of the alloy.

KEY WORDS: seated Shaka Nyorai statue; casting; X-ray fluorescent analysis; arsenic bronze; DTA; Vicker’s hardness; elastic modulus.

1. Introduction

The seated Shaka Nyorai bronze statue of Kaniman-ji at Kizugawa in Kyoto, hereafter referred to as the “Kaniman-ji statue”, was designated a Japanese national treasure in 1953. The statue, which is shown in Fig. 1, is 250.4 cm tall, weighs 2,172 kg, and is one of the largest bronze statues made by a single casting in ancient Japan. The history of the statue remains an enigma and the techniques used for the casting the statue has not yet been clarified in detail. There has been vigorous debate for many decades about when and where the statue was cast. Judging from its design, the statue is thought to have been constructed between the late-7th to the mid-8th century A.D. We are specifically interested in whether the statue was constructed before or after the Yakushi Nyorai Triad of Kondo at Yakushi-ji (the history of the Yakushi Nyorai also remains an enigma).

Although a detailed scientific investigation could have clarified some of the questions related to the statue, no scientific research on the statue was previously conducted as the statue is a Buddhist object of worship.

Taking advantage of the recent reconstruction of the main hall in which the statue was housed, a scientific investigation of the Kaniman-ji statue was carried out from March 2008 to June 2009. Specifically, 3D laser scanning, X-ray transmission imaging, fluorescent X-ray (XRF) analysis and carbon-14 dating tests were performed. Using carbon-14 dating, Yoshida dated the ash of straw contained in the core.
mold of the Kaniman-ji statue to be from the late-7th century A.D. with 58.2% reliability.\textsuperscript{1)}

As composition data is considered important for understanding the production history, the present authors examined the chemical composition of the statue using a portable XRF spectrometer. Here, we report the XRF analysis results and discuss differences with other bronze statues, including the Yakushi Triad of Kondo in the Yakushi-ji temple (Yakushi Triad) and the Rushana Butsu of Kondo in the Todai-ji temple (Todai-ji Daibutsu), both of which are considered to be made in the period from the 7th to the 8th century A.D. We also attempted to cast a bar with the same composition as the Kaniman-ji statue. The physical and mechanical properties of the cast bar were investigated.

Fig. 2. Measurement points (reprinted from Ref. 1)). (a) front view, (b) back view, (c) side view, (d) upper view, (e) bottom view.
2. Method

2.1. Chemical Composition Analysis

Chemical analysis was carried out using a portable XRF spectrometer (101FA, OURSTEX Osaka, Japan) which employed an energy dispersive detection system. The target material used to generate the X-rays was silver. The filament current and accelerating voltage were 20 μA and 20 kV, respectively. The X-ray beam was approximately 2 mm in diameter. Quantification analysis was carried out by the fundamental parameter (FP) method. The sensitivity coefficient of each element for the FP calibration was determined using three standard samples.

We analyzed 256 points on the surface of the outside and inside of the statue (Fig. 2). The obtained data were sorted by casting sites including the main body, chaplet, tinkering and inlay. A chaplet is a small metal spacer that supports the core to form a space with a sand mold. Using visual observation, 134 chaplets were found in the Kaniman-ji statue. A tinkering is a site made by casting onto the main body to repair shrinkage, porosity or cracks. There were 60 tinkering sites on this statue. The inlay is a metal piece inserted by hammering to repair defects in the main body. About 80 inlays were found in this statue.

2.2. Evaluation of Physical and Mechanical Properties

We tried to make a cast sample with the same composition as the main part of the statue. The density of the cast sample was measured by the Archimedes method. The melting temperature was measured by differential thermal analysis (DTA). Vickers hardness was measured under a load of 500 gf. The test piece used for hardness measurements was annealed at 500°C for 30 min before the measurements were taken. Elastic modulus was measured by ultrasonic pulse testing. The microstructure of the cast sample was observed by a scanning electron microscope and energy dispersive X-ray spectrometer (SEM-EDX).

3. Results and Discussion

3.1. Chemical Compositions of the Kaniman-ji Statue

Using the portable XRF spectrometer, we successfully obtained over 250 chemical composition data points for the statue. Table 1 shows selected data of the quantification analysis; more comprehensive coverage of the data was reported.1) The average compositions for each casting site are also shown in Table 1. Although the surface was covered with a layer of natural oxide, we were able to collect standard data from the knee of the statue (No. 67) where the surface had been polished by devotees touching over a long period. The average data for the main body were close to the values expected as chaplets become part of the statue after casting.

| No. | Si   | S    | K    | Ca   | Fe  | Cu  | As  | Sn  | Pb  | Sort of casting site |
|-----|------|------|------|------|-----|-----|-----|-----|-----|----------------------|
| 1   | 0.1  | 0.1  | 0.9  | 1.0  | 0.8 | 91.2| 3.6 | 1.5 | 0.7 | main body            |
| 2   | 0.1  | 0.1  | 0.8  | 0.8  | 0.6 | 91.1| 4.2 | 1.6 | 0.7 | main body            |
| 3   | 0.1  | 0.1  | 1.0  | 1.1  | 1.0 | 89.1| 4.2 | 2.3 | 1.0 | main body            |
| 7   | 0.1  | 0.1  | 0.3  | 0.1  | 0.1 | 96.6| 1.9 | 0.9 | 0.2 | inlay                |
| 17  | 0.1  | 0.1  | 0.2  | 0.1  | 0.1 | 95.7| 3.0 | 0.6 | 0.1 | tinkering            |
| 67  | 0.1  | 0.1  | 0.9  | 2.8  | 0.9 | 89.2| 2.8 | 2.4 | 0.9 | main body (bare metal)|
| 139 | 0.1  | 0.0  | 0.6  | 0.3  | 0.5 | 94.0| 2.3 | 1.4 | 0.7 | tinkering            |
| 255 | 0.1  | 0.0  | 0.2  | 0.3  | 0.1 | 94.5| 3.9 | 0.6 | 0.3 | tinkering            |
| 256 | 0.1  | 0.1  | 0.9  | 0.5  | 1.2 | 90.5| 4.3 | 1.3 | 1.0 | chaplet              |
| Ave | 0.1  | 0.1  | 0.8  | 1.3  | 0.6 | 92.4| 2.6 | 1.5 | 0.6 | main body            |
| Ave | 0.3  | 0.0  | 0.9  | 1.1  | 0.6 | 92.5| 2.3 | 1.7 | 0.6 | chaplet              |
| Ave | 0.1  | 0.1  | 0.8  | 1.5  | 0.6 | 91.8| 2.9 | 1.5 | 0.7 | tinkering            |
| Ave | 0.1  | 0.1  | 0.7  | 1.4  | 0.5 | 93.9| 1.6 | 1.2 | 0.5 | inlay                |

The main hall of the Kaniman-ji Temple was once almost entirely destroyed by fire after the mid 9th century. It is considered that the Kaniman-ji statue was damaged by that fire and that it was then repaired by tinkering. The tinkering at the lower back was judged to be made after the fire. Data No. 139 shown in Table 1 shows the composition of the Kaniman-ji statue using XRF.
increases, hardnes of the alloy increases drastically due to work-hardening. It is appropriate to use a softer material for the inlay containing a smaller amount of arsenic. Although arsenic was an impurity, people in ancient Japan could control the amount of impurities by refinement if the raw material of the inlay also came from Naganobori.

3.2. Microstructure, Physical and Mechanical Properties of Materials Used

Table 2 shows the composition of the raw materials used to make the cast samples and the analyzed compositions of the cast samples. We were able to obtain material containing arsenic and lead as we planned, which was almost the same as for the Kaniman-ji statue, even though the tin was lost from the cast alloy. Figure 5 shows the microstructure of the cast sample obtained by SEM-EDX. A spherical lead phase was dispersed throughout the α-phase. Some lead phases contained tin oxide, as shown in Fig. 5(b). Tin was detected only in these lead phases. The question still remains about why tin was not dissolved in the copper matrix but rather collected in the lead phase as tin oxide. Raw tin was preferentially oxidized during the casting process and was mostly ejected from the cast alloy, and residual tin oxides were drawn into the lead phase.

However, since the tin content in the Kaniman-ji statue material was originally small (less than 2%), we decided to evaluate the physical and mechanical properties using this Cu-3As-1Pb cast alloy. In the microstructure, light grayish white dendrites were observed in Fig. 5(a). These dendrites

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**Table 2.** Composition of the raw material and the trial cast sample.

| composition, mass%    | Cu | As | Sn | Pb |
|-----------------------|----|----|----|----|
| Raw material          | Bal.| 2.7| 1.6| 0.7|
| Analyzed value of the trial cast sample | Bal.| 3 | 0.1 | 1 |
Fig. 5. Microstructure of the trial cast sample.

Fig. 6. Cu–As phase diagrams.

Fig. 7. Line analysis of the Cu-3As-1Pb alloy conducted along the horizontal line shown in the composition image.
were formed by initial solidification. As seen in the Cu–As phase diagram (Fig. 6), the solidification temperature range is very wide and micro-segregation could have occurred. However, no significant difference was observed in the quantification for the light grayish white dendrite (initial solidification zone) and the dark grey area (final solidification zone) as shown in Fig. 7. Oxygen was detected more from the dark grey final solidification zone than the light grayish white initial solidification zone. We assume that arsenic micro-segregation may have caused this nonuniform oxidation; however, more research needs to be conducted on this in the future.

The density of the Cu-3As-1Pb cast alloy was 8.82 g/cm³ which is slightly lower than that of pure copper as shown in Table 3. The weight of the statue was 2172 kg and the surface area, estimated by 3D laser scanning, was 21.80 m². The mean thickness for the statue was calculated to be about 11 mm. Yakushi Nyorai of Kondo is 254.7 cm tall (almost the same as the Kaniman-ji statue) and weighs 4947 kg (almost twice that of the Kaniman-ji statue). If the surface area of Yakushi Nyorai was almost the same as the Kaniman-ji statue, the thickness of the Yakushi Nyorai was more than 25 mm. It would thus be more difficult to cast the Kaniman-ji statue than the Yakushi Nyorai statue.

The liquidus temperature of the Cu-3As-1Pb cast alloy was 1055°C, lower by about 30°C than that of the pure copper. Figure 8 shows DTA curves of the specimen. The endothermic reaction starts at 1019°C where the specimen starts to melt. Arsenic and lead addition decreased the melting temperature; however, the corresponding facilitation effect on melting was not drastic.

Vickers hardness of the Cu-3As-1Pb cast alloy was 68 HV. This is a little higher than that of pure copper. The elastic modulus was 156 GPa, about 27% higher than that of pure copper.

4. Conclusion

The material composition of the Kaniman-ji statue was revealed. The statue was made of an arsenic bronze, the composition of which was similar with that of the Todai-ji Daibutsu statue. The mechanical properties and thermal analyses data, which were experimentally determined, are useful for future computer simulations to estimate the casting design. The data are also available to evaluate residual stresses in the structure for conservation of the Kaniman-ji statue.

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Table 3. Comparison of physical and mechanical properties of pure copper and the cast sample.

|                  | Pure copper | Cu-3As-1Pb cast alloy |
|------------------|-------------|-----------------------|
| Density, g/cm³   | 8.93        | 8.82                  |
| Melting point, °C| 1082        | 1055                  |
| Hardness, HV0.5  | 46          | 68                    |
| Elastic Modulus, GPa | 123        | 156                   |

Fig. 8. DTA curves for pure copper and the trial cast sample.