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Mössbauer and Positron annihilation spectroscopy for red pottery bodies from Neolithic and Bronze age in South Korea

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1. Introduction

Since long ago, physiochemical research on pottery excavated from other countries has been conducted, and Zheng et al. [1] studied the firing temperature and manufacturing technique of pottery obtained from Neolithic sites using Mössbauer spectroscopy. Zhang et al. [2] studied coloring and the firing conditions of the celadon from ancient Chinese dynasties using Mössbauer spectroscopy, NAA (Neutron activation analysis) and X-ray diffraction (XRD). However, these previously mentioned have only considered the pigment layer of the pottery for analysis. Thus, this study was focused on the clay used for pottery-making, instead of the pigment layer. Mössbauer spectroscopy using gamma resonance is mainly used for conducting material analysis of cultural assets, such as ceramics, celadon, patterns, and pigments; thus, it should be supplemented with the corresponding Mössbauer spectroscopy data. Further, non-destructive methods are essential for the analysis to ensure cultural property preservation and restoration [3] A non-destructive technique known as positron annihilation lifetime spectroscopy (PALS) is used to evaluate open-volume defects such as monovacancies or dislocations in a variety of materials (metals, semiconductors, and polymers) [4]. The radioactive ^{22}NaCl solution evaporates on the surface of thin foils due to contamination and the short penetration depth of positrons.

2. Experimental Technique

We have investigated three Neolithic red potteries excavated from the Uljin, Tongyeong, and Geoje sites, and four Bronze Age red potteries excavated from the Jinju and Sancheong sites. The Table 1 shows the archaeological site and dwelling point of each excavated pottery samples. This samples are identical to the previously studied. The crystal structures of the red pottery were determined using XRD. The XRD patterns were obtained using a Rigaku Ultima IV diffractometer having a Cu–Kα radiation source (λ = 1.5406 Å), operating at 30 mA and 40 kV. A 30-μCi ^{22}NaCl was dried on both sides of the supporting foil (nickel thickness: 2.5 μm). We covered the support foil with the plates (nickel thickness: 50 μm) because the adhesive should not be contaminated with ^{22}NaCl. Mössbauer spectroscopy was used to determine the phase composition of the iron-containing components of the pottery body. The Mössbauer spectra were obtained for all the samples at 295 K under transmission geometry using a conventional constant-acceleration spectrometer with a ^{57}Co (Rh matrix) source and Wissel transducer. The velocity scale (± 12 mm/s) was calibrated based on the magnetic sextet spectrum of the metallic α-Fe foil absorber, and all isomer shifts were determined with respect to the center of this spectrum.

3. Results and discussion

In this investigation, the body color of the red pottery from the Bronze Age was slightly reddish yellow, whereas that of the red pottery from the Neolithic Age was black. Observations of the color development of the cross-section of red pottery under a stereoscopic microscope revealed the unclear nature of the boundary between the surface and body layer of GJ-1, whereas that of TY-3 was found to be clear. In addition, in spinel and mullite peaks were not confirmed. Thus, the firing temperature of the pottery was estimated to be less than 850 °C.

Hematite and maghemite are found in pottery that has been fired in oxidizing environments, while magnetite and amorphous carbon are typically found when the pottery has been fired in reducing environments due to incomplete combustion with organic fuel materials. The firing environment of red pottery bodies from the Neolithic and Bronze Ages was investigated

Table 1 Age and site of the excavated red pottery

Age	Samples	Site
Bronze	JJ-4	Okbang archaeological site 5, Daepyeong-ri, Jinju
	JJ-7	Dwelling No. 110, Daepyeong-ri, Jinju
	SCG-2	Pit-dwelling No. 4, Maechon-ri, Sancheong
	SCG-5	Pit-dwelling No. 3-2, Maechon-ri, Sancheong
Neolithic	UJ-1	Second layer, Jukbyeon-ri, Uljin
	TY-3	Yondaedo Shell Midden, Tongyeong
	GJ-1	Daepo Shell Midden, Geoje

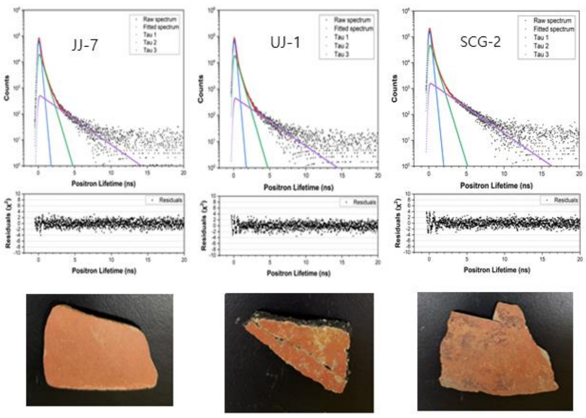

Fig. 1. Positron annihilation spectroscopy for red-pottery

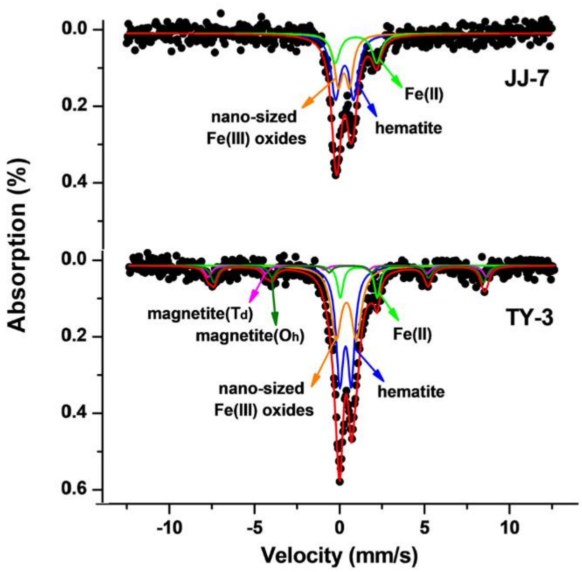

Fig. 2. Mössbauer spectroscopy for red-pottery

Decreasing positron life time exhibits that the crystal structure with decreasing defect structure due to firing condition. From Mössbauer spectroscopy, we confirm that pottery containing magnetite was fired in a reducing atmosphere with insufficient oxygen. The firing method of pottery differed according to the age. The Neolithic and Bronze Ages, which are the periods before the use of kilns, used open-air firing with an uneven firing atmosphere thus, samples of the same object may exhibit differences depending on the firing method. Therefore, rather than considering the individual firing temperature for each pottery, it was concluded that the firing temperature should be distinguished according to the purpose of use and the age.

4. Conclusions

The color factors of the reddish yellow body were estimated to be hematite and maghemite, and those of the black body were estimated to be amorphous carbon and magnetite.

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