

Positron Annihilation Doppler Broadening Spectroscopy Analysis of Korea Celadon Body from Gunsan

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1. Introduction

Positron annihilation spectroscopy (PAS) has been recognized as a non-destructive technique for investigating materials at the atomic scale. Its effectiveness arises from its high sensitivity to microdefects and variations in electron density distributions. Potential applicability has been suggested in the study of cultural heritage materials such as Korean celadon pottery. In such cases, preservation is maintained in the process of identifying production technologies.

Although firing conditions are known to be a crucial factor in the production process of Celadon pottery, direct analyses are often limited by the nature of cultural heritage artifacts. It has been reported that PAS can be effectively employed to analyze temperature-dependent pore structures in aluminum oxide-based ceramics. The pore characteristics of boehmite (AlOOH) ceramics under varying firing temperatures have been systematically examined using positron annihilation lifetime spectroscopy and coincidence Doppler broadening spectroscopy. Corresponding changes in positron lifetimes and intensities have been identified [1, 2].

Among the components of Goryeo Celadon, aluminum oxide (Al_2O_3) is known to undergo phase transitions from boehmite to gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) and then to alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) as the firing temperature increases. Phase transformations and pore formations have been shown to affect electron density and defect-related properties. Such variations are detectable through spectral differences in PAS. The phase transition mechanism of Al_2O_3 is believed to provide important clues for interpreting the firing conditions of Celadon.

Although no prior PAS analyses have been reported on Korean Celadon, previous studies on similar ceramic materials have offered valuable insights into the microstructure and firing conditions of such artifacts. In the present study, Doppler broadening spectroscopy (DBS), a technique within PAS, is applied to investigate Goryeo celadon pottery excavated in Gunsan. The aim is to explore the firing conditions and production techniques of these artifacts.

2. Materials and Methods

2.1 Celadon Samples

Six celadon shards excavated from the Gogunsan-do were analyzed and referred to as 'Gunsan Celadon' for convenience in this study (Fig. 1). The glaze layers were removed by polishing, and the clay bodies were subsequently measured. Among the six samples, Gunsan 34 and Gunsan 76 exhibited yellowish-brown glazes, while the remaining four had light bluish-green glazes (Gunsan 54, Gunsan 101, Gunsan 114, Gunsan 115).



Fig. 1. Goryeo celadon specimens excavated from Gogunsan-do.

2.2 Doppler Broadening Spectroscopy

DBS was employed to investigate pore structures and electron momentum distributions by measuring the energy shift (ΔE) of 511 keV γ -rays emitted during positron-electron annihilation. Due to the inherent difficulty in preparing standardized reference materials for cultural heritage samples, high-purity aluminum (Al) was used as a comparative and calibration standard, reflecting the presence of Al_2O_3 as a component of Celadon. The S-parameter was defined as the ratio of counts within the central region of the 511 keV peak. A 1 keV window was used in this study, corresponding to annihilation with low-momentum (primarily valence) electrons. This parameter was utilized to compare firing conditions and microstructural characteristics of the celadon samples.

DBS measurements were carried out using a high-purity germanium (HPGe) detector (pop top p-type, GEM-F704094) with a diameter of 69.4 mm and a length of 44.1 mm. The detector was connected to a spectroscopy amplifier (Ortec 672, USA) with a shaping time of 3 μ s and a digital spectrometer (Ortec DSPEC PLUSTM, USA) for energy spectrum acquisition. The detector was housed in a lead shielding enclosure to minimize background. The energy resolution of the HPGe detector was 1.87 keV at the 1.33 MeV γ -ray of Co-60, and the relative efficiency was approximately 40%.

A positron source of $^{22}\text{NaCl}$ (30 μCi) was encapsulated in a polyimide film (10 mm $\times$ 10 mm $\times$ 7.6 μm) and directly attached to the surface of the celadon samples for measurement. During all measurements, the dead time was maintained below 5%.

3. Results and Discussion

The spectrum analysis revealed a distinct difference at the central peak of the Gunsan celadon samples compared to the reference material, pure Al (Fig. 2a). This phenomenon was interpreted as a consequence of the lower average momentum of valence electrons in Al_2O_3 -based ceramics relative to pure Al. The spectrum of pure Al was used as the baseline for double normalization to clarify this difference. This process enabled a clearer distinction of the relative variations among the celadon samples (Fig. 2b). Figure 3 shows that the celadon specimens with bluish glaze exhibit higher S-parameter values (~ 0.602 – 0.606) than those with yellowish-brown glaze (~ 0.596 – 0.600).

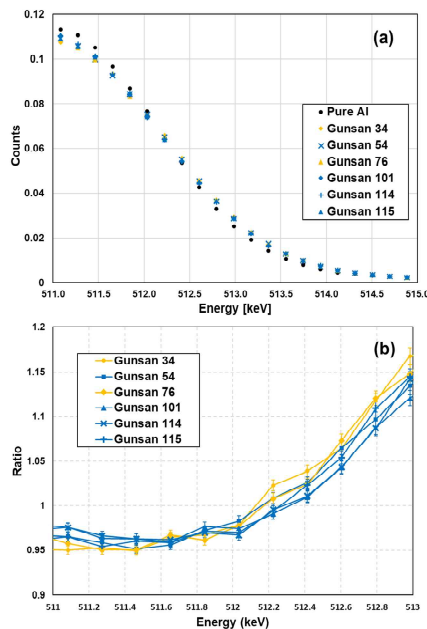


Fig. 2. (a): Normalized Doppler broadening spectra of pure Al and Korean celadon. (b): Double normalization ratio using pure Al as reference.

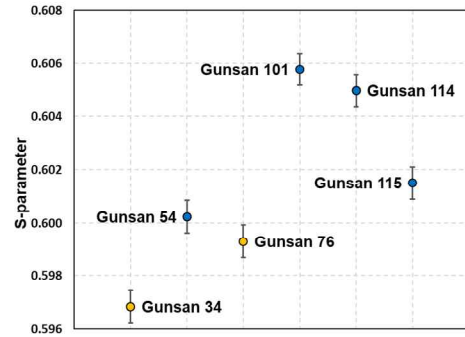


Fig. 3. S-parameters of the Gunsan celadon samples.

The ratio curve was found to be sensitive to changes in electron density associated with pore formation within the α - Al_2O_3 structure. All considered celadon samples exhibited ratio values lower than 1 (Fig. 2b). Significantly, the yellowish-brown celadon samples (Gunsan 34 and 76) consistently showed lower values than the bluish celadon samples. This difference suggests a close relationship with changes in electron density, likely induced by differences in firing conditions or microstructural factors. This observation raises the possibility that the bluish Celadon was fired at relatively higher temperatures, resulting in the dominant formation of the α - Al_2O_3 phase. The yellowish-brown samples were possibly fired at lower temperatures, thereby containing a higher proportion of the γ - Al_2O_3 phase.

The DBS technique alone cannot directly confirm firing temperatures. Therefore, it is suggested that complementary analytical methods be employed in future work to precisely elucidate the correlation between firing conditions and phase transformation.

4. Conclusions

In this study, positron annihilation spectroscopy was applied to investigate the microstructural characteristics and firing conditions of Goryeo celadon from Gunsan. Differences in the Doppler broadening spectra were observed depending on the color of the celadon samples. It was suggested that bluish celadon was predominantly formed with the α - Al_2O_3 phase under relatively high firing temperatures. In contrast, yellowish-brown samples indicated the possibility of lower firing temperatures and the presence of the γ - Al_2O_3 phase. These results demonstrated that non-destructive nuclear analytical techniques can be effectively utilized in cultural heritage research, offering the potential to quantitatively understand the manufacturing techniques and firing conditions of ancient ceramics without compromising artifact preservation. However, due to the limitations of the DBS technique in directly determining firing temperatures, it is recommended that more precise interpretations be conducted in the future through the integration of complementary analytical methods.

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