Positron Annihilation Doppler Broadening Spectroscopy of Korean Celadon

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1. Introduction

Positron Annihilation Spectroscopy (PAS) has emerged as a powerful non-destructive analytical technique for investigating microstructural defects, pore sizes, and crystalline structures at the atomic level in various materials. This method is particularly valuable for understanding historical ceramic production technologies, such as those used in traditional Korean Celadon pottery, where information about firing conditions of glaze layers and clay bodies is essential but often difficult to obtain without damaging precious artifacts.

Recent studies have demonstrated the effectiveness of PAS techniques in analyzing temperature-dependent defect structures in aluminum oxide-based ceramic materials. Ghasemifard and Ghamari investigated the porosity changes in aluminum oxy-hydroxide (boehmite) ceramics at different calcination temperatures using Positron Annihilation Lifetime Spectroscopy (PALS) and Coincidence Doppler Broadening Spectroscopy (CDBS) [1-2]. Their findings revealed systematic changes in crystal structure and pore size corresponding to temperature variations, with positron lifetimes and intensities changing accordingly.

Although PAS analysis of historical pottery specimens like Korean Celadon has not been previously reported, studies on similar ceramic materials provide valuable insights for understanding the microstructure and firing conditions of glaze and clay body layers. This research aims to apply PAS techniques, especially Doppler broadening spectroscopy, to Korean Celadon specimens to deduce the firing technologies and conditions employed by ancient potters.

2. Materials and Methods

2.1 Celadon Samples

Six specimens of Goryeo celadon pottery (Daeseom) from the 'Yongunri' type, excavated from the seabed near 'Daeseom' island in Taean, Chungcheongnam-do, were analyzed in this study. For glaze layer analysis, positron sources were directly attached to the pottery surface. To analyze the clay body layer, the glaze layer was additionally removed by grinding, allowing for separate examination of the underlying material.

2.2 Doppler Broadening Spectroscopy

Positron annihilation Doppler broadening spectroscopy (DBS) was employed to analyze the microstructural characteristics and firing conditions of the celadon samples. This technique allows for the investigation of defect profiles and structural information by measuring the energy broadening of the 511 keV annihilation gamma rays, which is caused by the momentum of the electron-positron pair at the moment of annihilation.

The DBS measurements were performed using a high-purity germanium (HPGe) detector with 10% efficiency and ultra-high-rate preamplifier (Ortec GEM10P4-70, USA). The detector was coupled to a spectroscopy amplifier (Ortec 672, USA) with a shaping time of 3 μs and a multi-channel analyzer/analog-to-digital converter (Ortec ASPEC 927, USA) to record the energy spectra.

A Na-22 positron source with an activity of 30 μCi enveloped by 7.63-μm Kapton foil was directly placed on the surface of the celadon specimens for the measurements. The dead time of all measurements were less than 5%.

3. Results and Discussion

3.1 Doppler Broadening Spectroscopy of Korean Celadon Specimens

The Doppler broadening spectrum technique analyzes electron momentum in defects or pores by comparing positron annihilation gamma-ray peak ratios (511 keV) against reference materials. In defect regions lacking atomic nuclei, peripheral electrons with reduced momentum exhibit heightened electron density, producing minimal Doppler broadening and creating observable energy shifts near the 511 keV position.

Given the scarcity of standardized specimens in heritage artifact analysis, we utilized high-purity aluminum as our reference material to establish baseline measurements, acknowledging aluminum oxide as a principal component in traditional Goryeo celadon. Our spectral analyses revealed variable Doppler shifts (below 1 keV) within the 511-512 keV range across examined celadon pieces, with marked differences between clay body and glaze measurements. These variations suggest that thermal gradients during historical firing processes created distinctive defect profiles throughout the ceramic structure.

3.2 Crystalline Phase Transformation and Its Effect on Positron Annihilation

Alumina (Al_2O_3), the predominant component in Goryeo celadon, transforms structurally from boehmite (AlOOH) through γ-Al_2O_3 into α-Al_2O_3 as firing temperatures increase, with the hexagonal α-phase featuring Al^{3+} ions occupying just two-thirds of octahedral positions, thereby reducing electron density. Positrons primarily interact with electrons surrounding cations (Al^{3+}) within celadon matrices, but structural reconfigurations alter ionic distributions, reducing annihilation rates and creating measurable spectral variations.

Formation of pores within α-Al_2O_3's hexagonal framework creates Al^{3+}-depleted regions with -3 charged vacancies, substantially diminishing positron annihilation probability with surrounding oxygen electrons and producing ratio curves below unity.

3.3 Firing Temperature Estimation Based on Doppler Broadening Spectroscopy

Measurements of Daeseom celadon glaze surfaces revealed pronounced low-energy Doppler shifts in blue specimens (samples 36 and 29), likely fired at elevated temperatures, compared to our aluminum standard, while yellowish-brown samples (specimen 7) exhibited considerably reduced shifts. This evidence suggests the blue celadons were fired at temperatures sufficient to form more α-Al_2O_3 with its characteristic hexagonal structure, while the yellowish-brown specimen likely contains more γ-Al_2O_3 phase, indicating a lower firing temperature.

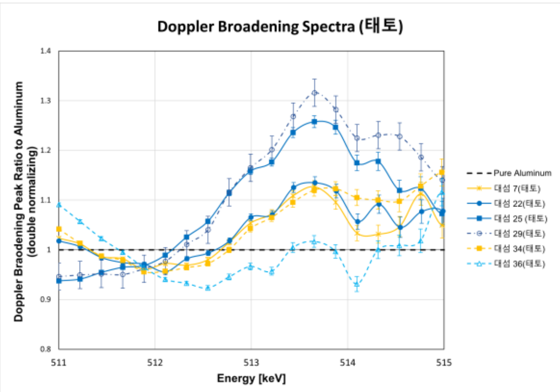

Fig. 1. Ratio of intensities for Doppler broadening spectra for clay body layers of Korean celadon (Daeseom). The ratio curves were normalized by the curve of pure aluminum as reference.

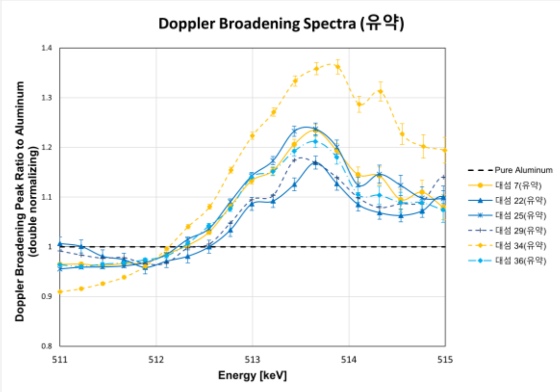

Fig. 2. Ratio of intensities for Doppler broadening spectra for glaze layers of Korean celadon (Daeseom). The ratio curves were normalized by the curve of pure aluminum as reference.

3. Conclusions

This study successfully employed positron annihilation spectroscopy to characterize microstructural features and firing conditions in historical Korean celadon. Positron annihilation Doppler broadening spectra revealed distinct patterns corresponding to color variations, with blue celadons exhibiting signatures of higher firing temperatures and predominant α-Al_2O_3 formation, while yellowish-brown specimens showed evidence of lower firing temperatures with greater γ-Al_2O_3 presence. These findings demonstrate the valuable contribution of non-destructive nuclear analytical techniques to cultural heritage research, offering quantitative insights into ancient ceramic production methods while preserving artifact integrity.

ACKNOWLEDGEMENT

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