Measurement of transient thickness between the body and graze layers of ancient porcelains using microprobe EDXRF technique

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Abstract The oxide contents of TiO_2, MnO, SrO and Fe_2O_3 in the body and graze layers of the Jiao-Tan-Xia (JTX) and Lao-Hu-Dong (LHD) porcelains in Southern Song Dynasty (1127-1279 A.D.) have been determined using an International Eagle-II μ-probe EDXRF spectrometer. The results show that the contents in the body are much different from those in the graze one. Therefore, the transient thickness (TT) between the body and graze layers can be measured through determination of a distance of the drift change in the chemical contents. The TT average for the JTX porcelains is 161μm, while that for the LHD porcelains is 258μm, which are consistent with a range of 0.15-0.3mm in the Ru-Yao porcelains. The different TT is related to the variances in firing temperature and raw material for manufacturing the respective porcelains.

Keywords Southern Song Dynasty porcelains, Microprobe EDXRF technique, Micro-structural analysis

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1 Introduction

Application of energy-dispersive X-ray fluorescence (EDXRF) analysis to the chemical composition of ancient porcelains shows the rapid, multi-elements and non-destructive characteristics. By using EDXRF techniques, we have determined the major and minor element contents in the porcelains (618-1368 A.D.) from the Linjiang, Jizhou, and Hutian Kilns, Jiangxi Province and the Changsha Kiln, Hunan Province and discriminated their provenance.[1] We have also analyzed the white porcelains (800-1600A.D.) from Dehua Kilns, Fujian Province and discussed the commercial channels of the Chinese wares to the Southeast Asian countries along the south oceanic road, so called "South Silk Road".[2] However, the general EDXRF technique is not suitable for the micro area and thin section analysis due to the large incident X-ray spot, e.g. ϕ6~22 mm.

Currently, there are many studies related to the microanalysis. Ro et al [3] described an approach, which allows to apply computer controlled-electron probe X-ray microanalysis (CC-EPXMA) to the estimation of the chemical homogeneity of the powder samples as candidate reference materials. Spolnik et al [4] analyzed the ultra-thin metallic film, artificial particles and aerosols using grazing-exit EPXMA, which is beneficial to the measurement of the characteristic intensity emitted from those specimens at very small exit angles. Campos et al [5] presented an experimental procedure to determine metallic thin film thickness by using EPMA. Several monoelemental films of Al, Ti, Cr, Cu, Nb, Mo and Au with different thickness were characterized by Rutherford back-scattering spectrometry for the thickness determination. Engi et al [6] explained an improved probe XRF instrument, which

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could be used to extend single grain chemical dating to Tertiary monazite as small as 50 μm with a few percent precision.

In this paper, the microprobe EDXRF technique is described as a tool for determination of the transient thickness between the body and graze layers in the ancient porcelains in comparison with the other results.

2 Experimental

2.1 Samples

The Chinese Imperial kilns in Southern Song Dynasty (1127-1279 A.D.) were divided into two series: Jiao-Tan-Xia (JTX) Kilns and Lao-Hu-Dong (LHD) Kilns at a distance of about 30 km apart in Hangzhou City, Zhejiang Province, China. Those kilns produced famous celadon as a kind of porcelains with green graze and dark body, which played an important role in the Chinese ceramic development. The JTX wares obtain 1~3 mm thickness for the body layer and ~1 mm thickness for the graze one, while the LHD wares have 4~ 5 mm thickness for the body layer and 1~2 mm thickness for the graze one. The transient thickness between the body layer and graze layer in the JTX and LHD samples will be determined as described in the following.

2.2 Equipment

An International Eagle-II μ-probe EDXRF spectrometer with a Rh target and Si(Li) detector was used in our study. It has a set of capillary optics for producing ϕ 40 μm X-ray beam, with working voltage of 40 kV, current intensity of 520 μA, target angle of 45º, exposed time of 5000 ms and energy resolution of 0.16 kV.

2.3 Method

A piece of porcelain sample was put in the low vacuum chamber. The CCD cameras with high and low magnification were used for setting a measured profile as shown in Fig.1. The profile indicates the body layer (B), transient layer (T) and graze layer (G) of the sample. The measurement modes include the facial scan in an area of about 1mm×1mm in the body and graze layers and the linear scan in a length of about 1~1.5 mm along the body layer through the transient layer to the graze layer for the determination of TiO_2, MnO, SrO and Fe_2O_3 contents (Fig.1). The former scan can supply the average values of the oxide contents in the body and graze layers, respectively, while the latter scan can reveal variability of the oxide contents from the body layer to the graze one. The X-probe points irradiated at the profile surface must be high enough to overlap the measured area or line for avoiding loss of the compositional signals. In principle the XRF standardless software (SW) used for the Eagle II system is a Fundamental Parameter modeling program described by Bertin.[7] The SW program itself is the same from the International DX-95 to the current version of Eagle II-SW. We have made the comparison of the standardless results with the standard ones. The correlative coefficients between the two data banks ranged from 0.95 to 0.99. Table 1 shows the content averages of TiO_2, MnO, SrO and Fe_2O_3 in the JTX and LHD porcelains and Fig.2 indicates the variability of those oxides from the body layer, across the transient layer, to the graze layer. The relative standard deviation (RSD) for TiO_2，Fe_2O_3 was generally in the range of 5%~10%, that for SrO, MnO in 10%~15% in the body layer; while the RSD for Fe_2O_3 in 5%~10%, and that for TiO_2, MnO, SrO in 10%~15% in the graze layer.

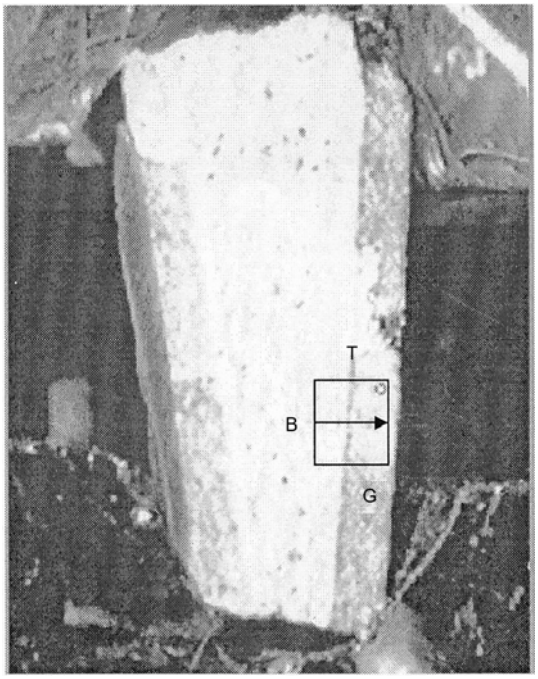

Fig.1 A porcelain profile with the body layer (B), transient layer (T) and graze layer (G). The arrow line shows the linear scan.

Table 1 The averages of chemical contents in the JTX and LHD porcelains

Samples		TiO_2 (%)	MnO (%)	SrO (%)	Fe_2O_3 (%)
JTX samples (*n*=6)	Body	2.54	0.02	0.02	2.44
	Graze	0.38	0.72	0.21	1.12
LHD samples (*n*=8)	Body	2.47	0.02	0.02	3.02
	Graze	0.21	0.23	0.17	0.82

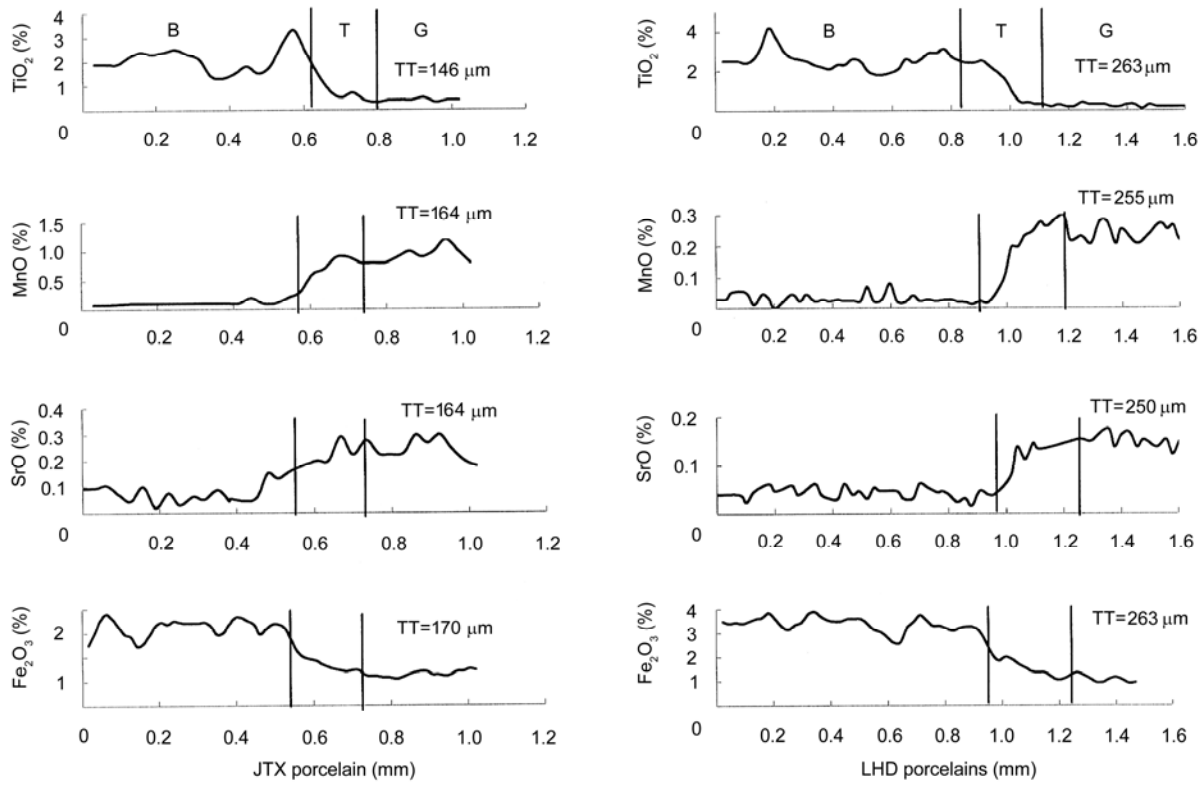

Fig.2 The measured transient thickness (TT) between the body layer (B) and graze layer (G) of the porcelains using the micro probe EDXRF analysis.

3 Results and discussion

Table 1 shows that the averages of TiO_2, MnO, SrO and Fe_2O_3 contents in the body layer of the JTX and LHD porcelains are much different from those in the graze layer. The Fe_2O_3 content in the body layer is higher than that in the graze one. Therefore, the JTX and LHD porcelains have a typical character of the dark body and green graze. That is a kind of famous products in the ceramic history of China. The oxide ratios of body/graze or graze/body for the JTX samples range from 2 to 36, while that for the LHD samples from 4 to 12. This is due to much variant material used for making the porcelain body and graze, respectively. The body is mainly made of natural clay, whereas the graze is mainly made of alkaline-silicic oxides.

On the basis of different composition between the body and graze layers, if a linear scan passes from the body layer to the graze one as shown in Fig.1, the measured signals of the chemical oxides could appear with a drift change in the transient layer. Fig.2 shows that TiO_2 and Fe_2O_3 contents in the body layer are higher than those in the graze layer, while MnO and SrO contents appear in the reverse order, which are in agreement with the facial analysis as shown in Table 1.

The chemical contents in the body or graze layers are not homogenous. Some of small peaks found in the compositional curves (Fig.2) could be attributed to certain minerals or oxides gathered at some areas,

such as the TiO_2 peak in LHD sample at 0.18 mm and the Fe_2O_3 peak in JTX sample at 0.05 and 0.41 mm, etc. It is clear to see that the drift changes of TiO_2, MnO, SrO and Fe_2O_3 contents have happened in the transient layer (TL). The transient thickness (TT) can be measured approximately by the determination of a distance between two vertical lines according to the content averages in the body and graze layers as shown in Fig.2. The TT values are 146~170μm with an average of 161μm for the JTX porcelains, while those are 250~263μm with an average of 258μm for the LHD porcelains. The latter average is about 100μm higher than the former one. The variant extent of the TT values for the JTX and LHD porcelains accord with the criterion for the Ru-Yao porcelains (0.15-0.3mm).[8]

The transient thickness is influenced by many factors, such as diffusive behavior of the chemical elements, graze components and firing temperature. The difference of the transient thickness between the JTX and LHD porcelains reveals that two kinds of ancient porcelains were made using variant materials and manufacturing technology even though all of those wares belonged to the products of the Chinese Imperial kilns.

4 Conlusions

The Chinese Imperial kilns were rapidly developed since the Southern Song Dynasty (1127-1279 A.D.), which was corresponding to the Medieval Warm Period (900-1300 A.D.). The chemical contents of TiO_2, MnO, SrO and Fe_2O_3 in the JTX and LHD porcelains back to Southern Song Dynasty have been determined by use of the μ-probe EDXRF microanalysis. The average of oxide contents in the body layer is much different from that in the graze layer. Therefore, the transient thickness (TT) can be defined by a distance, which reflects a drift change of the chemical components between the body and graze layers. TT is an important index of the porcelain characteristics because it is related to raw material and manufacturing technique. The information is useful for studying the evolution of the Chinese ceramics. Xu et al [9] and Zhou et al [10] performed the thermodifferential analysis[11] of the JTX and LHD porcelains and inferred the firing temperature of 1160℃ and 1205℃, respectively. A higher firing temperature may bring about a bigger transient thickness. Therefore, the results show the microprobe EDXRF spectrometer can become a useful tool for the micro-structural analysis.

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References

1 Leung P L, Stockes M J, Li M T W *et al*. X-Ray Spectrometry, 1998, **27**: 11

2 Leung P L, Peng Z C, Stockes M J *et al*. X- Ray Spectrometry, 2000, **29**: 253

3 Ro C U, Hoornaert S, Grieken R V. Analytica Chimica Acta, 1999, **389**: 151

4 Spolnik Z, Zhang J, Wagatsuma K *et al*. Analytica Chimica Acta, 2002, **455**: 245

5 Campos C S, Coleoni E A, Trincavelli J C *et al*. X-ray Spectrometry, 2001, **30**: 253

6 Engi M, Cheburkin A K, Köppel V. Chemical Geology, 2002, **191**: 225

7 Bertin T P. Principles and practice of X-ray spectrometric analysis, New York: Plenum Press, 1975: 690

8 Li J Z. The volume of ceramics. Beijing: Science Press, 1998: 274

9 Xu J M, Deng Z Q, Li J Z. The international symposium collection of the ancient pottery-porcelain science and technology (ISAC'99), Shanghai: Shanghai Press of Science and Technology Document, 1999: 531

10 Zhou X H, Leung P L, Du Z X *et al*. The international symposium collection of the ancient pottery-porcelain science and technology (ISAC'02), Shanghai: Shanghai Press of Science and Technology Document, 2002: 231

11 Liu Z H. Introduction to thermal analysis, Beijing: Chemistry and Industry Press, 1991: 7