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Study on Ru ware glaze of the Northern Song dynasty: One of the earliest crystalline-phase separated glazes in ancient China

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Abstract

Ru Guan kiln is the most famous imperial kiln in the Northern Song dynasty (960–1126 A.D.) of ancient China. In this study, green-glazed porcelain shards excavated from Qingliangsi Ru Guan kiln site in Henan province were adopted as test samples. Based on the physicochemical foundation for crystallization and phase separation of Ru glaze, the correlation among composition, microstructure, firing technique and visual appearance has been investigated by means of energy-dispersive X-ray fluorescence, X-ray diffraction, high temperature microscope, field emission electron microscopy and transmission electron microscopy. For the first time, the study demonstrates that Ru glaze is typical of crystalline-phase separated glaze with a dual coloring mechanism.

Keywords: B. Microstructure-final; C. Color; D. Glass

1. Introduction

Over the ancient Chinese ceramics history, the simple but refined green-glazed porcelain has always been regarded as the most important genre, in accordance with the implicit character of Chinese people. The Song dynasty (960–1279 A.D.) was culturally the most brilliant period in imperial Chinese history, a time of great social and economic change, an era when the values of a cultivated scholar class guided taste as never before. Green-glazed Ru ware from Qingliangsi Ru Guan (imperial) kiln in Henan province, the rarest of the Song wares, comes first on the list of the ‘‘five classic wares’’ of the Song dynasty in China. Ru ware is distinguished for its thin body, fine and smooth glaze, graceful figure and elegant color, which inaugurated a new era of green glaze aesthetics. Ru ware is very evenly and thinly enameled and most of the pieces are fully glazed, in the kiln Ru wares were placed on tiny supports which left only minute ‘‘sesame-seed’’ marks on the glaze. The restrained monochrome effects were preferred which imitated or harmonized with those of nature such as the evanescent shades of foliage, water or sky [1,2]. The manufacture of Ru ware thrived for about only 20 years to the order of the imperial court as tribute in the late Northern Song dynasty (960–1126 A.D.). Being invaluable rareness, barely about 70 handed-down intact Ru wares have been collected all over the world today.

It is obvious that potters in the Northern Song dynasty were already proficient in firing such kind of opaque glazes, although they did not understand the inherent reasons behind the appearance at that time of over eight hundred years ago. Some researchers have studied the chemistry and microstructure of Ru ware, giving a generally correct description of the phases present [3,4]. In this study, glaze formulation requirements were placed on a physicochemical foundation. The glaze and body compositions and microstructures were studied by means of EDXRF, XRD, HTM, FESEM/EDS and TEM/SAD/EDS, aiming at investigating the correlation among composition, microstructure, firing technique and

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glaze appearance, disclosing the scientific rules behind the aesthetically pleasing appearance of Ru glazes.

2. Experimental

Six opaque green-glazed shards N1–N6 excavated from the fourth firing zone of Qingliangsi Ru Guan kiln site were provided by the historical relic and archaeology research institute of Henan province. Glaze and body composition was examined by energy-dispersive X-ray fluorescence (EDAX Eagle-III μProbe, USA). Apparent porosity of body was measured by Archimedes' principle. X-ray diffraction (D/max 2550V, Japan) using Cu Kα radiation was employed to identify the crystalline phases in glaze. Glaze maturing range was estimated according to the temperature interval between FP (flowing point) and HP (hemisphere point) measured using high temperature microscope (MHO-2, Germany). Microstructure and phase composition was studied using field emission electron microscopy (JSM-6700F, Japan) and transmission electron microscope equipped with EDS and SAD (JEM-2100, Japan). FESEM samples were obtained by etching polished cross sections of glazes in dilute HF solution at room temperature. TEM samples were acquired by argon ion tapering method.

3. Results and discussion

3.1. Characteristics and chemical compositions of Ru guan ware shards

The outward appearances of the Ru guan ware shards observed with a stereo-microscope are listed in Table 1. The glazes are attributed to calcia–silicate glazes. The glaze composition range written in a seger formula is as follows:

$$\left.\begin{array}{c}0.13-0.23\mathrm{KNaO}\\0.63-0.73\mathrm{CaO}\\0.14-0.17\mathrm{MgO}\\0.03-0.04\mathrm{Fe_2O_3}\end{array}\right\}0.46-0.53\mathrm{Al_2O_3}\{3.41-4.52\mathrm{SiO_2} \qquad (1)$$

The body compositions have high alumina (25.91–28.95 wt.%) and relatively low silica contens (62.48–65.95 wt.%) with some impurity iron oxide and titania, manifesting typical of the body from North China. Body composition formula is as follows:

$$\left.\begin{array}{c}0.12-0.22\mathrm{KNaO}\\0.03-0.05\mathrm{CaO}\\0.29-0.56\mathrm{MgO}\end{array}\right\}\left.\begin{array}{c}0.89-0.91\mathrm{Al_2O_3}\\0.09-0.11\mathrm{Fe_2O_3}\end{array}\right\}\left.\begin{array}{c}6.90-7.59\mathrm{SiO_2}\\0.01\mathrm{P_2O_5}\\0.05-0.06\mathrm{TiO_2}\end{array}\right\} \qquad (2)$$

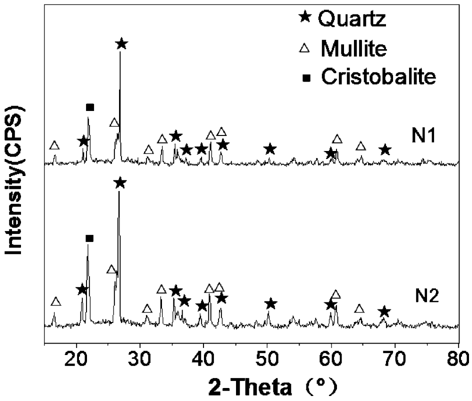

Fig. 1. XRD spectra for Ru ware bodies.

3.2. Glaze maturing range, physical properties and phase attributes

Heating behavior measurement shows that DP (deformation point), HP (hemisphere point) and FP (flowing point) of N1–N6 glazes are 1120 ± 10 °C, 1170 ± 10 °C and 1350 ± 10 °C, respectively, indicating that the maturing range for Ru Guan glaze is quite wide as higher than 1170 ± 10 °C and lower than 1350 ± 10 °C.

Although N1–N6 glazes were correctly fired, yet the apparent porosity range for the bodies is as high as 11–18%, an indication of under-firing of bodies due to the high alumina concentrations.

XRD patterns show that main crystalline phases present in N1 and N2 bodies are quartz, mullite and cristobalite (Fig. 1), while in the glazes are anorthite and unmelted quartz (Fig. 2).

As firing approached peak temperature, glaze would become fluid and react with the underlying body. The interdiffusion of ions between glaze and body can result in a change in the distribution of elements over the interface. The glaze–body interactions which took place during glost firing

Table 1
Appearance description of the green glazed Ru ware shards

No.	Glaze	Body
N1	Celeste blue opaque glaze, semi-lustrous surface, fine crackles, 0.5–0.8 mm in thickness	Loose gray body, dull fracture
N2	Celeste blue opaque glaze, semi-lustrous surface, fine crackles, 0.5–0.7 mm in thickness	
N3	Bean green opaque glaze, lustrous surface, fine crackles, 0.2–0.4 mm in thickness	
N4	Bean green opaque glaze, lustrous surface, fine crackles, 0.5–0.7 mm in thickness	
N5	Moon white opaque glaze, semi-lustrous surface, fine crackles, 0.4–0.8 mm in thickness	
N6	Celeste blue opaque glaze, semi-lustrous surface, fine crackles, 0.3–0.8 mm in thickness	

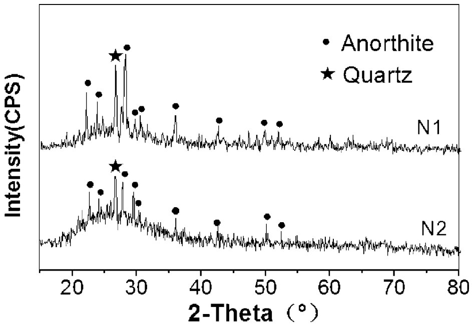

Fig. 2. XRD spectra for Ru ware glazes.

depend mainly on the viscosity of the glaze melt and the mutual solubility of body and glaze components. As for Ru shards, an interaction layer can be observed with denser anorthite microcrystal growth reaching out into the glaze at the glaze–body interface than within the glaze layer, an indication of the diffusion of aluminum ions from body into glaze (Figs. 5a and 6a). Ru glazes are heterogeneous, showing the presence of bubbles, unmelted quartz particles, many acicular or columnar anorthite crystals precipitated within the glaze layer, and the liquid–liquid phase separation occurring between the anorthite precipitates with considerable variations in pattern (Figs. 5 and 6).

3.3. Physico-chemical foundation for crystallization-phase separation of Ru glaze

The principal constituents in Ru glaze are SiO_2, Al_2O_3, CaO, MgO, K_2O, and Fe_2O_3, which could be roughly represented with the SiO_2–Al_2O_3–CaO ternary system by merging MgO into CaO and ignoring KNaO and Fe_2O_3. As marked in Fig. 3, the overall glaze compositions of N1–N6 concentrate in the primary crystalline phase region of anorthite, possessing thermodynamic qualification for the crystallization of anorthite. N1–N6 correspond to compositions in the phase triangle bordered by three crystalline phases: anorthite ($CaAl_2Si_2O_8$), tridymite (SiO_2), and pseudowollastonite ($CaSiO_3$), as illustrated in the CaO–Al_2O_3–SiO_2 phase equilibrium diagram [5] (Fig. 3). While limited to the un-equilibrium thermodynamic conditions during the firing process, anorthite is the only crystal precipitated from the molten glaze. With further growth of anorthite, Al_2O_3 in the circumjacent glass should be consumed greatly followed by a rapid compositional shift into the metatable liquid–liquid immiscibility region above 950 °C with a dramatic rising of SiO_2/Al_2O_3 ratio (assumably marked with an arrow in Fig. 3). In the local region of low Al_2O_3 concentration, the tendency towards liquid–liquid immiscibility increases with increasing SiO_2/Al_2O_3 ratio.

Due to the chemical heterogeneity in glazes resulting from the anorthite crystallization, especially in the interspaces of crystal clusters or the peripherial regions around crystals, the dynamic equilibrium process of anorthite crystallization versus fusion is always accompanied by another process, viz. the dynamic equilibrium process of liquid–liquid immiscibility versus miscibility. With nucleation and growth of anorthite, liquid–liquid immiscibility develops simultaneously with coarsening of the phase separation structure.

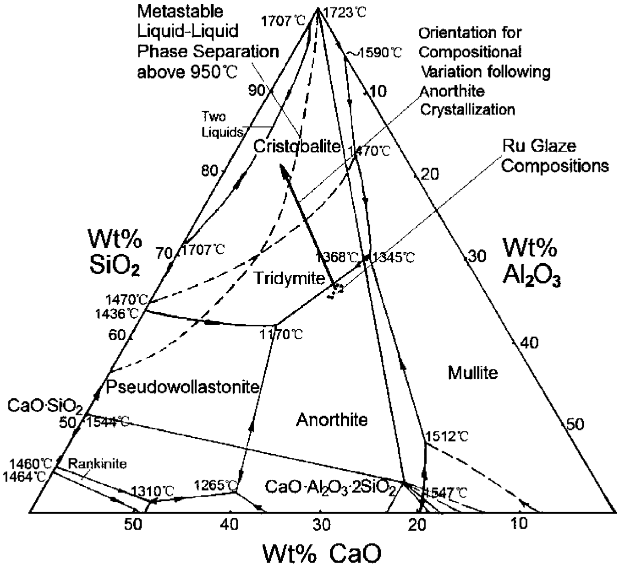

Fig. 3. Ru glaze compositions fall in the anorthite primary crystal region in CaO–Al_2O_3–SiO_2 equilibrium phase diagram, indicating that anorthite precipitates followed by a glaze composition shift into the metatable liquid–liquid immiscibility region above 950 °C.

Based on the ideas of crystallochemistry, the struggle for oxygen between metal ions and silicon ions, and structural compatibility or incompatibility of various cation–oxygen polyhedra is responsible for liquid–liquid immiscibility of glass. The greater the difference in ionic field strength between a silicon ion with an oxygen ion and a modifying ion with an oxygen ion, the stronger the tendency towards immiscibility [6]. The inter-crystal phase separation in Ru glazes should be primarily determined by the strong immiscibility tendency between SiO_2 and CaO. Considering the higher polarizability of nonbridging oxygen atoms compared to that of bridging ones, other modifier iron and magnesium ions locate preferably in the phase enriched by CaO oxides with a large number of nonbridging oxygen atoms, consequently favoring phase separation.

The crystallization mechanism for Ru glaze is different from that in bulk glasses because Ru glaze is quite heterogeneous. There are several possibilities of nucleating interfaces, namely air/glaze surface interface, body/glaze interface, quartz particle or other inclusions/liquid interface, air/liquid interface offered by bubble and crack. With the involvement of the above-mentioned nucleating interfaces and limited by the dynamic conditions, crystallization of anorthite in Ru glaze should be unbalanced thermodynamically and inhomogeneous. Ru glaze crystallization is a course based on a high glass viscosity, during which anorthite growth is mainly controlled by the interface rearrangement and ion diffusion. Embedded in the glass matrix, anorthite generally exists in the shape of dendritic crystal resulting from the big composition difference between crystal and glass melt. Anorthite turns out to be needle or short column determined by firing conditions. The presence of extensive anorthite crystal growth and the associated phase separation is a demonstration of the long duration, high-temperature firing, and slow cooling of Ru wares.

3.4. Crystallization-phase separation structure of Ru glaze

Shown in Figs. 4–6, quite a number of acicular or columnar anorthite crystals disperse in glaze layers, ranging in width from a few hundred of nanometers to a few microns, and in length from a few to hundreds of microns. In different glazes or different micro-regions of the same glaze, the nano-sized liquid–liquid phase separation within the interspaces of anorthite clusters or around the brims of anorthite needles or columns turns out diversiform variations in shape, scale and distribution, closely associated with the size and crowding level of crystal crystallization.

In terms of phase separation behavior, a great deal of variability is to be expected. The diversiform phase separation pattern is determined by the chemical heterogeneity of glass. The liquid–liquid phase separation in N1 and N2 glazes appears to consist mostly of different scale interconnected structure, while some discrete droplet structure also exists locally. When glass composition is located in the low calcia content region within the liquid–liquid immiscibility boundary above 950 °C (Fig. 3), the discrete droplet should be rich in CaO (Fe_2O_3, MgO) (Fig. 5g and h), hence the high calcia content and middle calcia content glass should correspond to SiO_2-rich discrete droplet structure (Fig. 5b) and interconnected structure (Figs. 4, 5d–f, i and 6c, d and f), respectively, ion enrichment state in the immiscible phases was determined by EDS. The discrete phase can be in the shape of sphere, ellipsoid or worm in different degree of conglomeration. The formation process of phase separation is complicated, influenced by the variations in chemical composition, viscosity of melt, and firing conditions such as temperature and atmosphere. The glaze microstructure reflects the firing state to some extent.

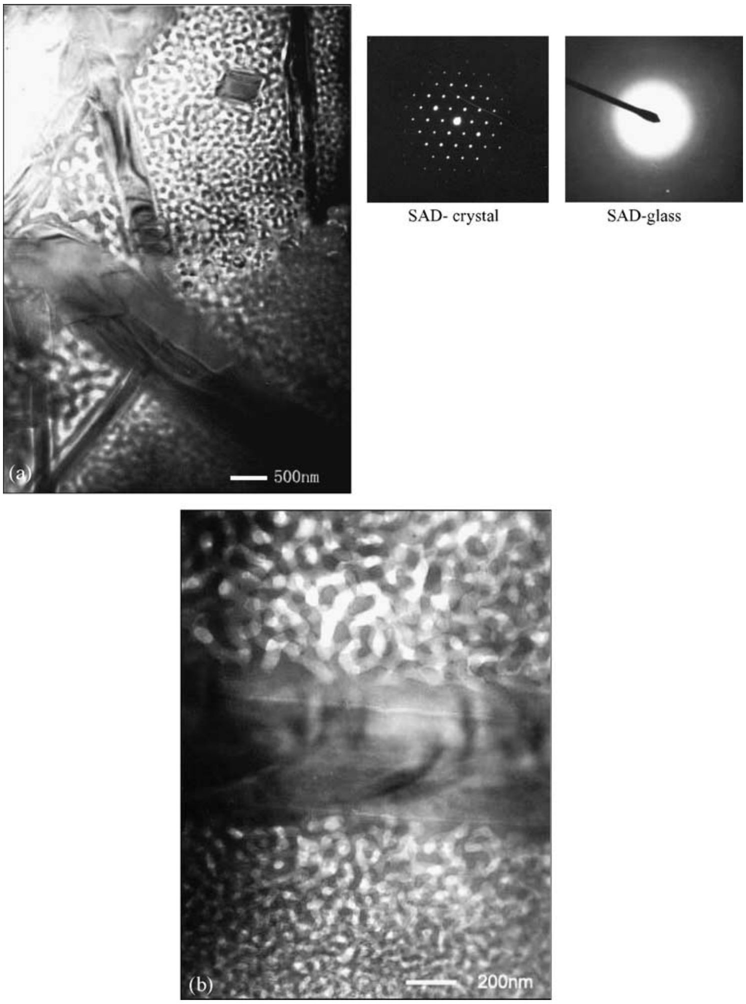

Fig. 4. TEM images of N1 glaze, showing various scale inter-crystal interconnected phase separation, resulting from the chemical heterogeneity caused by anorthite crystals assembling in different density.

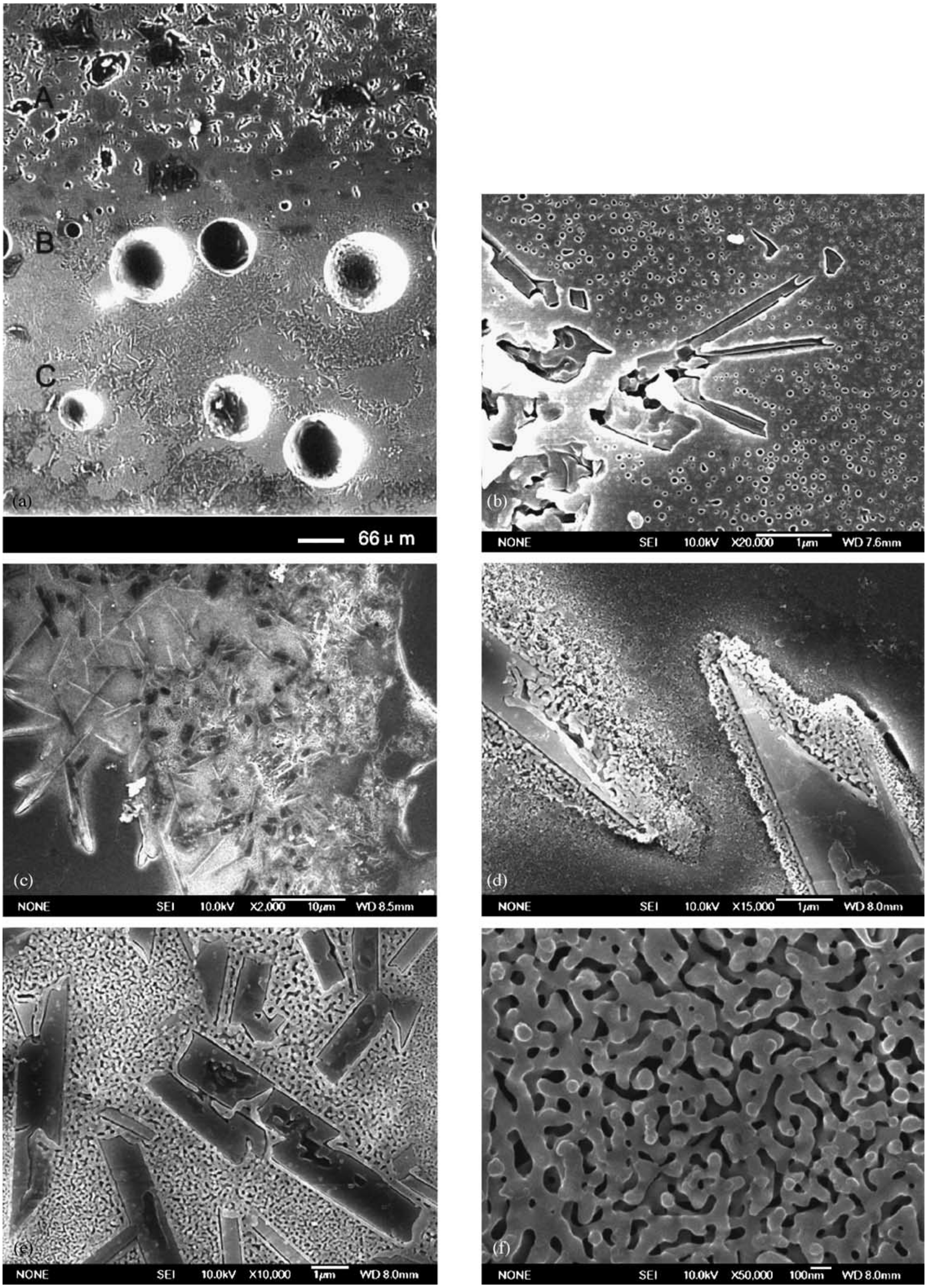

Fig. 5. SEM images of the etched cross section of N1 sample (a) loose body, an interaction layer with dense anorthite crystallization at the glaze–body interface, and extensive anorthite dispersion within the glaze: (A) body, (B) interaction layer, (C) glaze; (b) discrete SiO_2-rich droplet phase separation between anorthite crystals; (c) rough texture of nano-sized liquid–liquid phase separation within the interspaces of anorthite clusters or around the brims of anorthite needles or columns resulting from local chemical variation caused by anorthite crystallization; (d) interconnected liquid–liquid phase separation around the brims of anorthite columns; (e) interconnected liquid–liquid phase separation between anorthite crystals; (f) close-up of (d) showing interconnected liquid–liquid phase separation structure; (g) discrete CaO (MgO, Fe_2O_3)-rich droplet phase separation between anorthite crystals; (h) close-up of (f) showing discrete droplet liquid–liquid phase separation structure; (i) multi-level phase separation structure: (A) CaO (MgO, Fe_2O_3)-rich discrete droplet, (B) semi-interconnected worm, (C) interconnected structure.

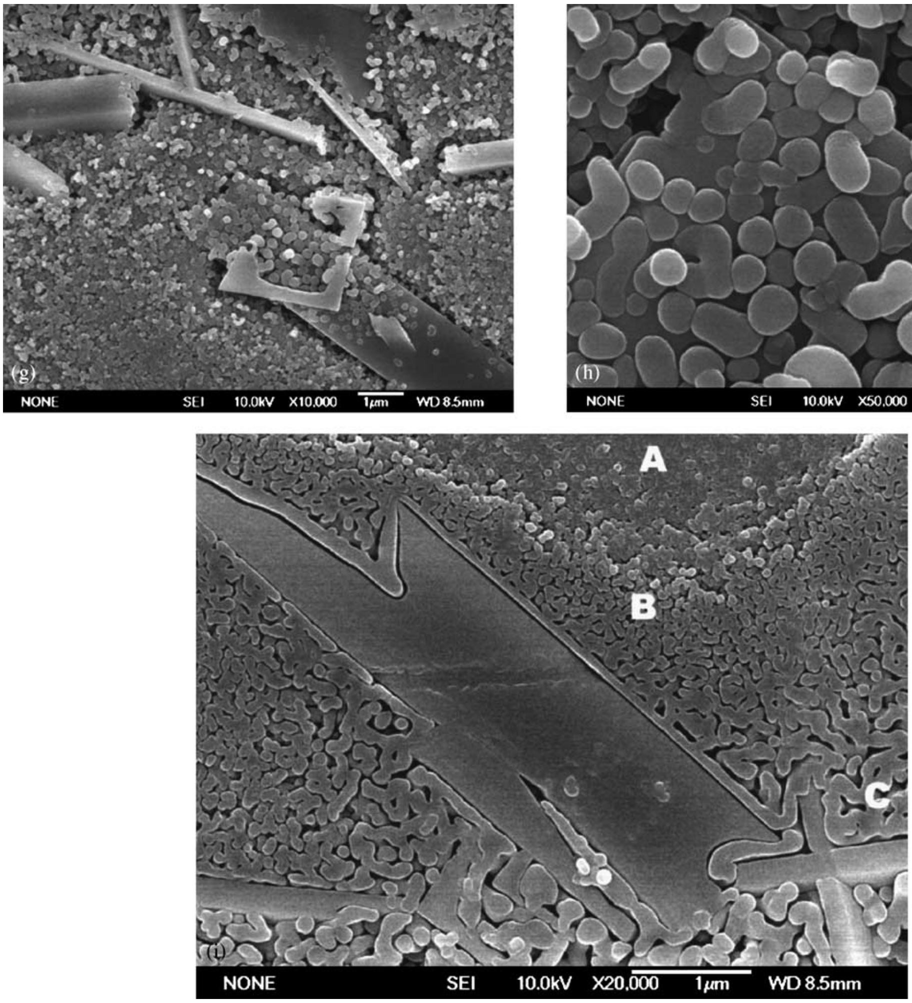

Fig. 5. (*Continued*).

Fig. 4 clearly shows the variation in scale of the interconnected phase separation structure located in different sized interstice regions framed by anorthite. Confirmed by EDS, the dark phase in Fig. 4b is rich in CaO, MgO and Fe_2O_3, the light phase is rich in SiO_2. The white belt along the crystal border in Fig. 4a is rich in SiO_2 with Al_2O_3 depletion. It is worth mentioning that in this study, Al_2O_3 is the most sensitive constituent for phase separation. The tendency towards phase separation or the immiscibility temperature Tb increases with the rise of SiO_2/Al_2O_3 ratio caused by anorthite crystallization. A higher Tb corresponds to a lower viscosity at Tb, which bears a bigger temperature range for the development of phase separation structure. So smaller interstice between denser crystals with more Al_2O_3 consumption and hence stronger tendency towards phase separation is always associated with larger scale liquid–liquid phase separation.

In areas with sparsely dispersed crystals, most anorthite columns do not border on each other, a clear verge of the rough texture of nano-sized liquid–liquid phase separation can be observed along the crystal border, showing a legible boundary between liquid–liquid immiscible glass and homogeneous glass. Al_2O_3 supply for the crystallization of small amount of anorthite can be satisfied by the narrow region of glass around the crystals. Then phase separation is suppressed in the area at a distance from anorthite due to the rise of Al_2O_3 content (Figs. 5c, d and 6b, e, f).

A kind of multi-level phase separation structure appears in the relatively large interstices framed by anorthite columns, where gradient compositional variation is reflected by the variation in the relative amounts of the two liquid phases over a few micron distance, which can vary from an interconnected structure of both phases to discrete particles of a minor amount of one of the phases. The discrete CaO (MgO, Fe_2O_3)-rich droplets seem to stack in a “pit” since the SiO_2-rich continuous phase has been etched out by HF solution. (Fig. 5i)

3.5. *Correlation of microstructure and chemical composition with visual appearance of Ru glaze*

Ru ware is famous primarily for the subtle beauty of its neat and simple glaze, presenting the soft and aesthetically pleasing colors described as celeste blue, pale green, sky blue, moon white and bean green etc. Generally, the

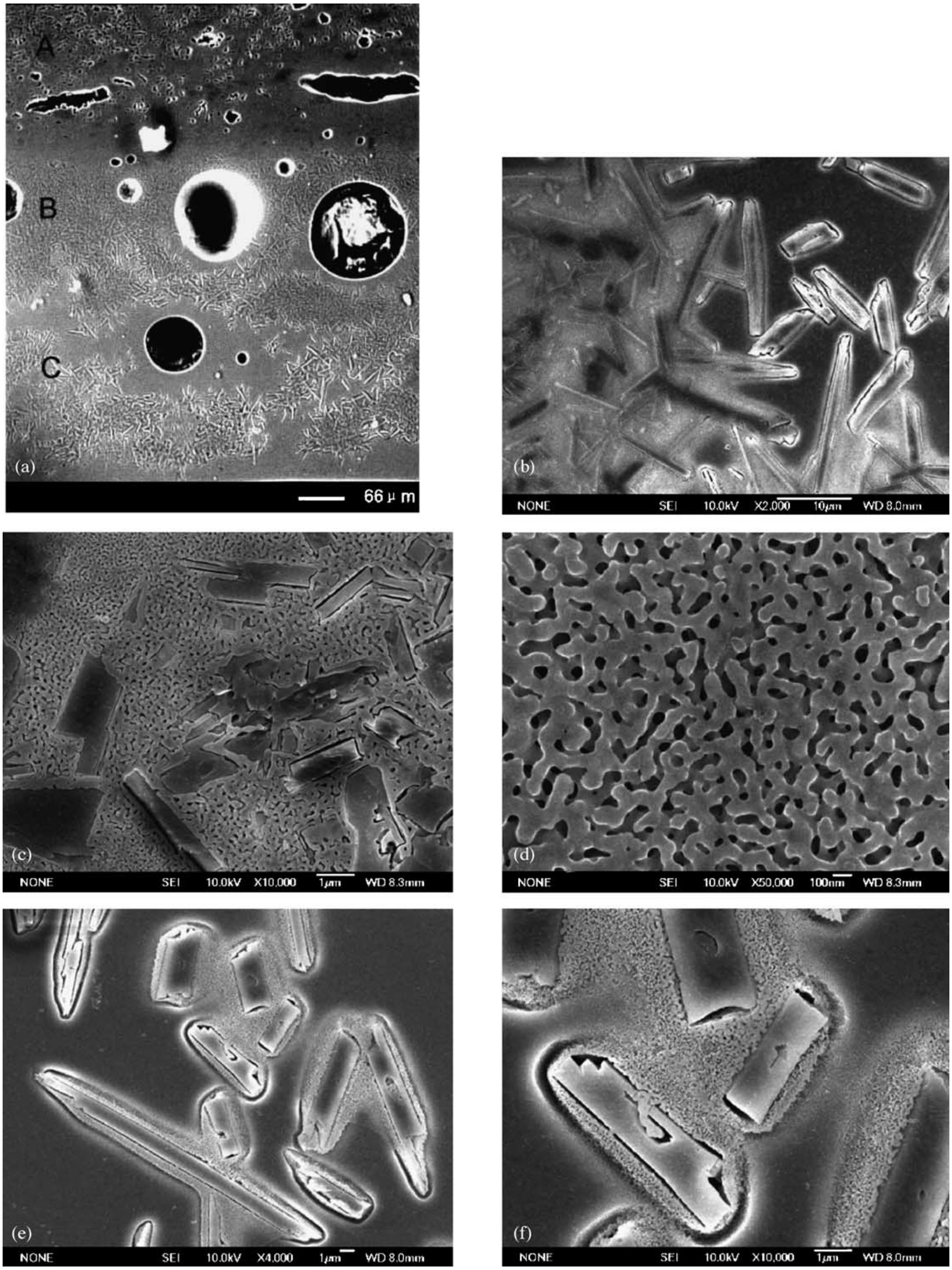

Fig. 6. SEM images of the etched cross section of N2 sample (a) loose body, an interaction layer with dense anorthite crystallization at the glaze–body interface, and extensive anorthite dispersion within the glaze: (A) body, (B) interaction layer, (C) glaze; (b) rough texture of nano-sized liquid–liquid phase separation within the interspaces of anorthite clusters or around the brims of anorthite needles or columns resulting from local chemical variation caused by anorthite crystallization; (c) interconnected liquid–liquid phase separation between anorthite crystals; (d) close-up of (c) showing interconnected liquid–liquid phase separation structure; (e) phase separation around the brims of anorthite needles or columns; (f) close-up of (e) showing interconnected liquid–liquid phase separation around the brims of anorthite columns.

variations in hue, saturation of color, translucency, and opalescence are based on iron as the primary coloring constituent, and also based on the diffuse reflection and refraction caused by optical inhomogeneities within glaze layers.

Transition metal iron ion is the principal coloring constituent in Ru glazes. The mechanism of such absorption of light energy, and hence the production of chemico-compositional coloring, may be explained on the basis of electron displacement or excitation in the absorbing material. Thus part of the energy in the incident radiation is utilized in producing excitation and light of certain wave lengths which falls upon the surface tends to be reflected selectively. The state of oxidation or mode of combination or coordination of the iron ions is highly significant. In the glaze there exists a reduction–oxidation equilibrium for Fe^{2+} and Fe^{3+} determined by glaze melt status, temperature and kiln atmosphere. The ratio of ferrous to ferric iron consequently has an important bearing on the color exhibited, which could be measured using Mössbauer spectra.

Being scatterers in the submicron and micron size range, bubbles, residual quartz grains, undissolved batch material and anorthite microcrystals create full-waveband reflection and refraction opon the incident light, responsible for the opacification of the glaze layer. In this case, structural coloring is prominent, the size of the scattering particles exceeds the wavelength of visible light, the Mie scattering theory applies. The opacity is increased by increasing both the number and the fineness of the scatterers, which is influenced by the firing conditions.

Another essential contribution to coloring of the glaze is made by the nano-sized inter-crystal phase separation structure, a kind of optical nonhomogeneity which is smaller than the wave-length of the visible light. The significant factor in this case is the repeated, abrupt change in refractive index between particle or structure and the contacting or embedding medium. The intensity of the scattered light, varies inversely with the fourth power of the wavelength, a relation known as the Rayleigh law. Hence, for liquid–liquid immiscibility structure within the Rayleigh limit, blue light is scattered in all directions much more than red light, contributing to coloring of the glaze in addition to the chemico-compositional coloring of iron ion. The intensity of the scattered light is dependent on the area and scale of the phase separation structure, the difference in refractive index, and the angle of observation. A more intense scattering of blue light can be obtained, for example, from the glaze containing larger areas of such immiscibility structure.

Color of Ru glaze due to chemico-compositional and structural coloring mechanisms is quite sensitive to firing conditions, may undergo marked changes in both hue and saturation on the variation of temperature and atmosphere. The variations in color from moon white to pale green to celeste blue is not related to the variation of chemical composition within the limited compositional region we have established. Instead, the color variability is related to the relative amounts of the above mentioned structural inhomogeneities and the Fe^{2+}/Fe^{3+} ratio of glass resulting from the differences in firing temperature and atmosphere at the different positions of the chamber kiln.

4. Conclusion

For the first time, Ru glaze has been revealed as a crystalline-phase separated glaze. The physio-chemical foundation of Ru glazes can be supposed within the confines of the phase equilibrium relationships and the metastable liquid–liquid immiscibility region above 950 °C in $CaO–Al_2O_3–SiO_2$ system. In all areas of anorthite crystallization, especially the interspaces of crystal clusters or the peripheral regions around crystals, crystallization is always accompanied by the general occurrence of the rough texture of nano-sized liquid–liquid phase separation. Liquid–liquid phase separation turns out diversiform variations in shape, scale and distribution, closely associated with the size and crowding level of crystal crystallization, which on one hand shows local chemical heterogeneity of glaze, on the other hand demonstrates the essential impact of the un-equilibrium thermodynamic firing process on the formation of the glaze microstructure. A dual coloring mechanism is in effect for Ru glazes, covering chemico-compositional coloring by iron ion chromophore and structural coloring by structural inhomogeneities including nano-sized phase separation and micron-sized crystals, bubbles and inclusions.

Acknowledgments

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References

[1] J.-Z. Li. (Ed.), Science and Technology History of China, Vol. Ceramics, Science Publishing Company, Beijing, 1998.

[2] J.R. Charleston (Ed.), World Ceramics, Crown Publishers, New York, 1990.

[3] Z.-G. Zhang, Y.-Y. Guo, X.-L. Zhou, M.-L. Ruan, Microstructure Characteristics of Ru-Guan Ware. ’02 Science and Technology of Ancient Ceramics 5 Proceedings of the International Symposium, Shanghai Science and Technology Literature Publishing Company, Shanghai, 2002, pp. 206–210.

[4] F.-K. Zhang, G.-Y. Tao, M.-L. Ruan, H.-Q. Yuan, Scientific Study on Glaze Colours, Surface Textures, Fish-Scale Crackles and Etching Spots of Ru Guan Ware. ’02 Science and Technology of Ancient Ceramics 5 Proceedings of the International Symposium, Shanghai Science and Technology Literature Publishing Company, Shanghai, 2002, pp. 194–200.

[5] H. Rawson, Inorganic Glass-Forming Systems, New York Academic Press, London, 1967.

[6] O.V. Mazurin, E.A. Porai-Koshits, Phase Separation in Glass, North-Holland Physics Publishing, Netherlands, 1984.