

Corrosion Research on Ru Porcelain Glazes Excavated at Qingliangsi, Baofeng, China

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Table S1. The microstructure of Ru porcelain glaze and body under optical microscope.

No.	Bubble diameter in body	Bubble diameter in glaze	Thickness of intermediate layer	Thickness of glaze
R1	ca.50-100μm	ca.50-200μm	ca.250μm. There are a lot of pores between the interlayer and the glaze	The inner glaze thickness is ca.600μm; The outer glaze thickness is ca.200-1000μm.
R2	ca.20-50μm	ca.50-100μm	ca.200μm. The interlayer and glaze are closely connected	The inner glaze thickness is ca.350μm; The outer glaze thickness is ca.600μm

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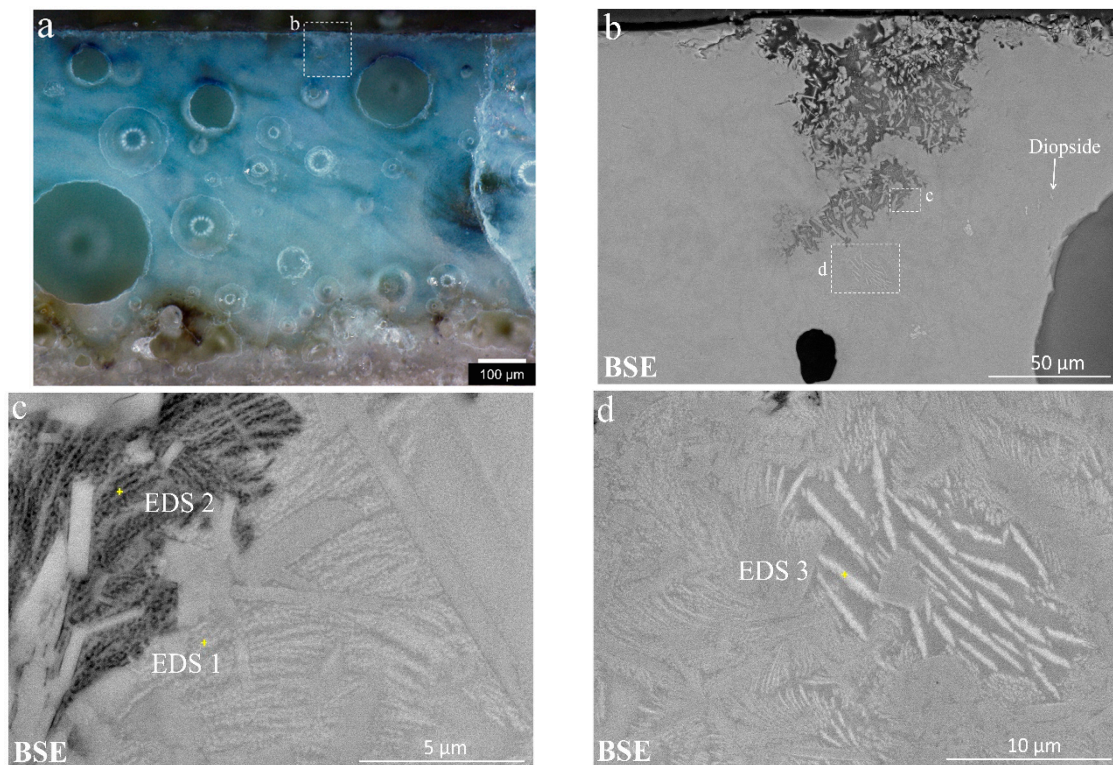


Figure S1. The polished cross-section of R1 glaze. (a) Optical micrograph; (b–d) SEM images.

Calculation process of droplet size with coherent interference:

The phase-separated structure in the R1 glaze has short-range order, which meets the conditions of coherent scattering, and the phase-separation droplet's size can be calculated by Bragg's law. Equations (1) shows the formula to calculate the refractive index, where p is the mole fraction of oxides in the chemical composition, and n_i is the refractive index calculation factor of the oxide composition [1]. The chemical compositions of the Ca-rich phase and Si-rich phase in R1 are shown in Table 2. The calculated refraction index of the Ca-rich phase (n_{Ca}) is 1.511, and the refraction index of the Si-rich phase (n_{Si}) is 1.501. The Maxwell-Garnett equation [2] is then applied to calculate the effective refractive index (n_e), where ϕ is the volume fraction of the microphase, assuming that the volume fraction of the Ca-rich phase is 25% to 50%. According to Equations (2), the effective refractive index n_e is 1.503–1.506.

$$n = n_1 p_1 + n_2 p_2 + \dots + n_i p_i \quad (1)$$

$$n_e = n_{Si} \left(\frac{2n_{Si}^2 + n_{Ca}^2 + 2\phi(n_{Ca}^2 - n_{Si}^2)}{2n_{Si}^2 + n_{Ca}^2 - \phi(n_{Ca}^2 - n_{Si}^2)} \right)^{1/2} \quad (2)$$

Since the forming mechanism of structural colors caused by amorphous photon crystals is also coherent scattering, an approximate expression for the scattering light wavelengths of the amorphous photon crystals is also given by the modified form of Bragg's law:

$$\lambda = 2d\sqrt{n_e^2 - \sin^2 \theta} \quad (3)$$

where λ is the free-space wavelength of light, d is the interplanar spacing, and θ is the angle measured from the normal to the planes [3–5]. In the phase separation glaze, d is approximate to the average diameter of the phase-separation structure. Assuming that the light is shining perpendicularly to the glaze surface, θ is 0 and $\sin\theta$ is also 0. Bragg's law can be expressed as follows:

$$\lambda = 2dn_e \quad (4)$$

The visible blue–violet wavelength λ ranges from 380 to 480 nm; this wavelength is used in Equation (4). If coherent scattering occurs in the visible blue–violet light wavelength range, the calculated phase separation size d ranges from 126 to 160 nm.

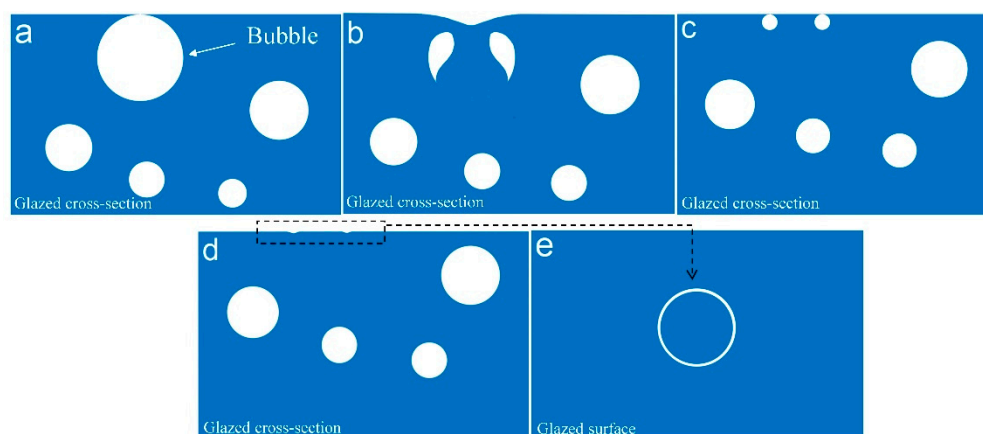


Figure S2. Schematic diagram of formation of annular pits on glaze surface.

Method of calculating the approximate area ratios of pits on a two-dimensional glaze surface

The SEM images of the degradation area on the glaze surface show that the pit and the flat surface have different contrasts. ImageJ software was used to calculate area.

- ① Convert the SEM image into a grayscale image in 8-bit format.
- ② An appropriate "Threshold" was selected.
- ③ The ratio of the selected area to the total area of the image was automatically calculated by the software.

The area ratio of pits of R1 glaze is 65.5%, and of R2 glaze is 13.6%.

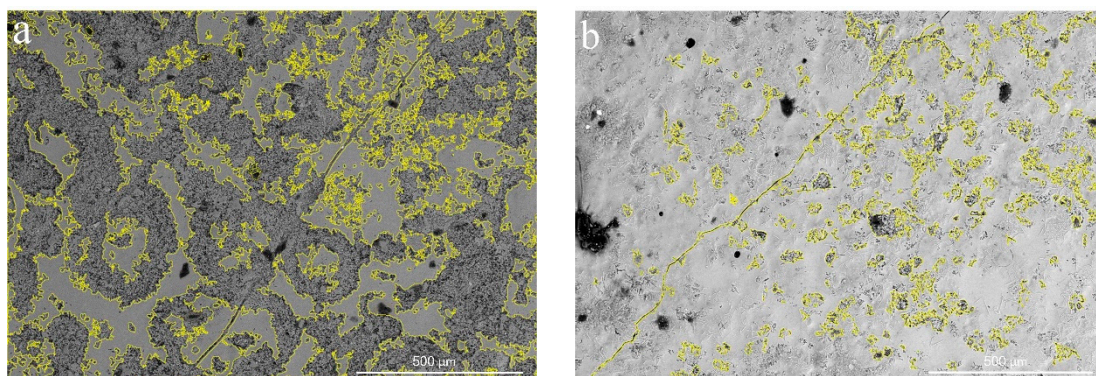


Figure S3. Profile curves of corrosion pits in SEM images at the same magnification (80×). (a) R1 glaze, (b) R2 glaze.

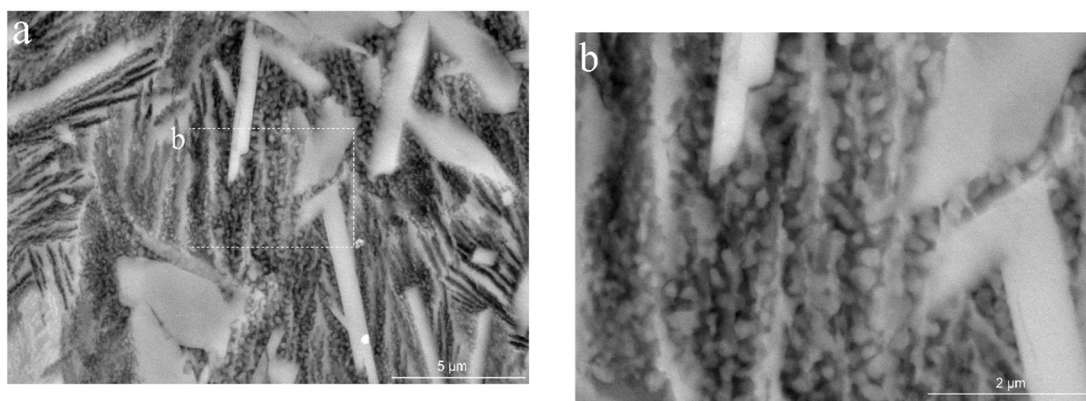


Figure S4. SEM images of the polished cross-section of R2 glaze.

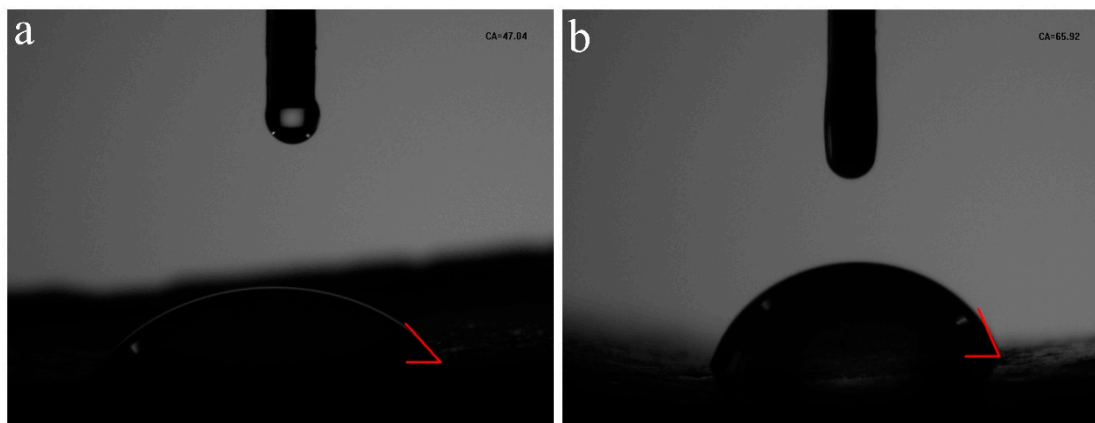


Figure S5. Contact angle of R2 glaze surface. (a) Obvious corrosion area; (b) No obvious corrosion region.

References

- 1 Gan, F. Optical glass. Science Press: Beijing, China, 1964. (In Chinese)
- 2 Forster, J.D.; Noh, H.; Liew, S.F.; Saranathan, V.; Schreck, C.F.; Yang, L.; Park, J.-G.; Prum, R.O.; Mochrie, S.G.J.; O'Hern, C.S.; et al. Biomimetic Isotropic Nanostructures for Structural Coloration. *Adv. Mater.* **2010**, *22*, 2939–2944. <https://doi.org/10.1002/adma.200903693>.
- 3 Dong, B.Q.; Zhan, T.R.; Liu, X.H.; Jiang, L.P.; Liu, F.; Hu, X.H.; Zi, J. Optical response of a disordered bicontinuous macroporous structure in the longhorn beetle *Sphingnotus mirabilis*. *Phys. Rev. E.* **2011**, *84*, 011915. <https://doi.org/10.1103/PhysRevE.84.011915>.
- 4 Parker, A.R. 515 million years of structural colour. *J. Opt. A: Pure Appl. Opt.* **2000**, *2*, R15. <https://doi.org/10.1088/1464-4258/2/6/201>.
- 5 Romanov, S.G.; Maka, T.; Sotomayor Torres, C.M.; Müller, M.; Zentel, R.; Cassagne, D.; Manzanares-Martinez, J.; Jouanin, C. Diffraction of light from thin-film polymethylmethacrylate opaline photonic crystals. *Phys. Rev. E.* **2001**, *63*, 056603. <https://doi.org/10.1103/PhysRevE.63.056603>.

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