

# THE EFFECT OF OPACIFIERS ON SURFACE ROUGHNESS OF CERAMIC GLAZES

R. Sarjahani<sup>1\*</sup>, M. Sheikhattar<sup>2</sup>, S. Javadpour<sup>1</sup> and B. Hashemi<sup>1</sup>

\* sarjahani@bcp.co.ir

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<sup>1</sup> Department of Materials Science and Engineering, Shiraz University, Shiraz, Iran.

<sup>2</sup> Department of Materials Science and Engineering, Shahid Bahonar Kerman University, Kerman, Iran.

**Abstract:** Surface smoothness of ceramic glazes is always an important characteristic of ceramic glazes as a point of surface engineering studies. Surface roughness affects chemical resistivity, glossiness and stainability of glazes. In fact, less surface roughness improves cleanability of the surface by the least usage amount of detergents. In this investigation, surface topography of two common opaque glazes, zirconia and titania-based, has been investigated. Crystallinity of the surface has been studied from SEM images, and comparison of EDS elemental results with phase analysis results of XRD. Surface roughness profile measured by Marsurf M300, shows that titania-based glaze is almost 24% percentage more smooth than zirconia based glaze. Surface smoothness is in relation with crystallinity of glaze surface, crystal type and crystal distribution in amorphous matrix phase.

**Keywords:** Opacifier, Surface roughness, SEM, EDS, XRD

## 1. INTRODUCTION

Proportion of building ceramics in building industry is remarkable. The significance of this subject has been increased these days. According to reliable statistical report of Ceramic World, Iran became the 4th country producing the largest amount of tiles in the world in 2012[1]. Various standard characteristics of these products is always considering, but physical and environmental properties of the glaze as a final coat and the only observable part of the piece, are the main attributes determining the quality of these products. Surface glossiness and smoothness is the significant feature of glaze that affect the appearance quality of building ceramics. Besides, they are the main factors influencing on stain resistivity and sanitization of glaze surface [2, 3]. This investigation focused on zirconia-based opaque glaze, as a common glaze in tile, sanitary ware and tableware industries, and the glaze surface roughness parameter (Ra) has been studied and compared with titania-based opaque glaze. Reasons of surface roughness has been studied from SEM and XRD results.

Crystallization is always an important subject in glazes; because it controls the surface texture of the glaze (glossy, matte, satin...). In addition to crystal formation on glaze surface, other

parameters such as low firing temperature or insufficient firing time to dissolve an excess of refractory batch constituents can affect glaze texture, in this case the glaze is called immature. Glazes and glasses tend to crystallize in temperatures lower than their melting temperature, the very first composition which tends to separate from solution is the composition that has a lower solubility. Therefore, controlling crystals and their solubility in glaze melt is necessary for controlling glaze surface microstructure.

Recent studies of matte glaze surface have been shown that the main reason of surface roughness is the formation of crystals on the surface. Crystals in matte glaze are various in composition, size, morphology and chemical resistivity for different glaze compositions. Morphology of opaque glazes has been less studied and compared so far.

Less solubility of opacifiers such as Zircon, Tin oxide and Titania... in glaze melt leads to precipitation of these crystals on glass phase matrix [5]. Regarding to considerable difference of refractive index between these crystalline and amorphous glass phases, the high percentage of incident beam is specular reflection causing the glaze surface seems high glossy [6]. On the other hand these crystals make surface rough, so the

surface becomes more stainable.

Teixeira et.al have been studied usage of titania in replace of zirconia; their results show that titania is the first oxide system undissolved in glaze melt, and it precipitates in liquid glass; thus it acts as a nucleating agent and it forms rutile, anatase and titanite phases. They also showed that titanite phase makes glaze color a bit yellowish but it improves the glaze glossiness [7].

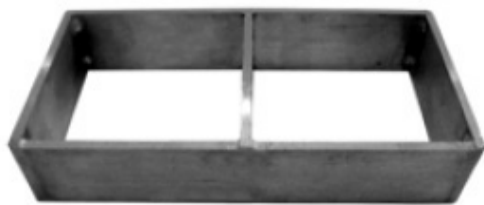


Fig. 1. Glaze applicator (Slash)

## 2. EXPERIMENTS

### 2. 1. Preparation of Glaze

Two commercial opaque boron frits based on zirconia and Titania have been used; two separate small jars was charged with 100 gr; zirconia based, Titania based frits and 5.66 gr kaolin with 40 cc water in each. Crushing has been done in Fast mill MG for 12 minutes. Residue of glaze on 325# sieve (45 micron) was 2.5%, for more accurate particle size measurement, particle size distribution has been measured by particle size analyzer equipped with X-ray counter. Both samples had the same particle size distribution. Rheology condition of samples (Density and viscosity) were measured by pycnometer 100cc and Gallenkamp viscometer. Rheology results have been given in table 1. After setting rheology condition of both glaze slips similar to each other, they applied on the same pressed body with slash method (Fig.1), and left them to become dry. Chemical composition of glazes has been shown

Table1. Rheology condition and sieve analysis of glazes

| Slip density<br>(gr/cm <sup>3</sup> ) | Fordcup viscosity<br>(sec) | Sieve residue<br>(325#) | Milling time<br>(min) |
|---------------------------------------|----------------------------|-------------------------|-----------------------|
| 1.70                                  | 20                         | 2.5                     | 12                    |

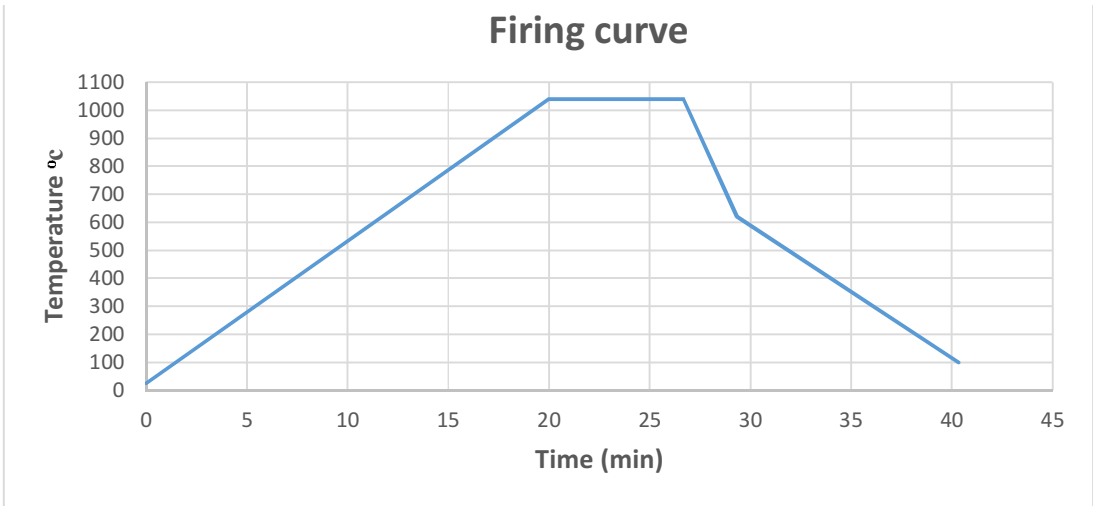


Fig. 2. Common fast firing curve used for samples firing

**Table 2.** Chemical analysis of glazes (wt %)

| Glaze type                         | Na <sub>2</sub> O | K <sub>2</sub> O | ZnO | MgO  | CaO | ZrO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | B <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> |
|------------------------------------|-------------------|------------------|-----|------|-----|------------------|--------------------------------|------------------|-------------------------------|------------------|--------------------------------|
| <b>Zirconia-based opaque glaze</b> | 1.3               | 5.1              | 9.7 | 0.34 | 6.9 | 22.6             | 8.9                            | 0.05             | 8.3                           | 36.7             | 0.16                           |
| <b>Titania-based opaque glaze</b>  | 1.3               | 5.7              | 8.9 | 1.2  | 7   | 1.7              | 6.7                            | 19               | 4.2                           | 44.1             | 0.17                           |

in table 2. Samples fired in fast firing roller kiln (popular in tile industry) at 1040 °C for 40 minutes according to firing curve shown in Fig. 2. Surface morphology of samples were studied from SEM (TESCAN VEGA 2) equipped with EDS, phase analysis was done with XRD (GNR MPT 3000) and surface roughness was measured by MARSURF M300. Chemical analysis of samples has been measured by XRF (ARL 8410).

Due to the XRF limitation to measure B<sub>2</sub>O<sub>3</sub>, wet chemical analysis has been used for the measurement.

## 2. 2. Sample Preparation and Settings

- SEM: samples of 1×1×1 cm has been provided and they were cross sectioned, mounted and polished. Due to non-conductivity of samples, 10 nm gold layer coating was deposited using a sputter coater prior to SEM-EDX analysis. Voltage was set to 20KV.
- XRD: phase analysis of crystals, formed on glass matrix, has been done with X-ray diffraction. Samples are in bulk form and their glazed surface were exposed to X-ray. For this analysis cathode lamp were used. Voltage and Amperage were set to 40KV and 30mA. Since glazes have different types of crystals, samples rotation angle rate was set to 0.02 degree/s. The initiation angle selected 4 and the ending was 70.
- Surface roughness analysis: the mechanism of this machine is based on the mechanical movement of a probe on the surface. To measure surface roughness of glazes, sample of 3×3×3 cm were provided; the

probe was located on their glazed surface, speed of probe movement on the surface set to 0.5 mm/s and it was set to move for 5.6 mm. The reference standard of this machine is BS EN ISO 4287(2000).

## 3. RESULT AND DISCUSSION

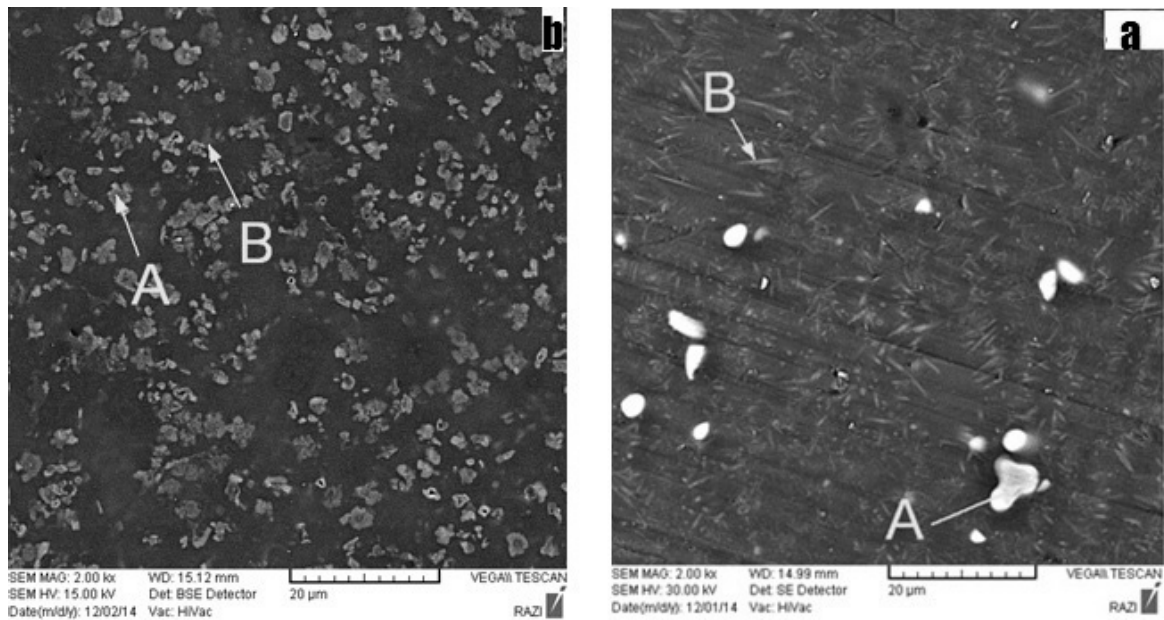
Fig. 3 has been shown SEM images of surface morphology of glazes in BSE mode. Presence of crystals on glass matrix is completely obvious in both pictures.

Fig. 3a) shows needle-shape of the most crystalline phase, according to their shape they might be zircon crystals [20]. The EDS and XRD results revealed that crystalline phases presented in glass matrix are zircon crystals. These crystal sizes range from 3 to 5 micron. Fig. 3b) shows small plate-like crystals in 2-4 micron size. Crystal size and distribution of titania-based glaze seems to be less than Zirconia-based glaze.

Detection of crystalline phases on glaze surface is not just possible with XRD because of X-ray penetration into glaze thickness. However, comparison of EDS and XRD results determine crystals on the surface of glaze samples. Table 3 shows elemental analysis of crystalline phases pointed in Fig. 2, and table 4 shows XRD results.

Point A in Fig. 3a) shows zirconia crystals; comparison of XRD and EDS results show that the only phases made up of zirconium element are zircon and zirconia, on the other hand, since the amount of Si atom is trivial in EDS analysis of this point, so the crystalline phase is zirconia. The main reason of some differences in atomic percentage of phases and EDS results is due to the inaccuracy of EDS in point analysis.

Point B in Fig 3b) shows zircon crystals,



**Fig. 3.** SEM images of samples in BSE mode and points of EDS analysis a) Zirconia based opaque glaze b) Titania opaque glaze

**Table 3.** Result of EDS analysis of pointed crystals in Fig. 2.

| Point details                  | Elemental analysis (%at) | O     | Si    | Al   | Na   | K    | Ca    | Zn   | Ti   | Zr    |
|--------------------------------|--------------------------|-------|-------|------|------|------|-------|------|------|-------|
| Point A- Zirconia opaque glaze |                          | 83.61 | 1.24  | 0    | 0    | 0.51 | 0.69  | 0.49 | 0    | 13.22 |
| Point B-Zirconia opaque glaze  |                          | 74.82 | 9.85  | 1.95 | 2.17 | 2.21 | 3.84  | 2.12 | 0    | 3.04  |
| Point A- Titania opaque glaze  |                          | 55.84 | 21.75 | 2.68 | 0    | 2.45 | 10.69 | 4.27 | 1.40 | 0     |
| Point B- Titania opaque glaze  |                          | 62.38 | 20.79 | 3.39 | 0    | 2.66 | 5.28  | 0.42 | 4.22 | 0     |

**Table 4.** Phases detected by XRD analysis of glaze bulk samples.

| Sample type           | Phases detected by XRD analysis                                                                                                                                                                                                                                                                                          |
|-----------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Zirconia opaque glaze | Zircon( $\text{ZrSiO}_4$ ), Potassium Boron Silicate( $\text{KBSi}_3\text{O}_8$ ), Zinc Silicate( $\text{Zn}_2\text{SiO}_4$ ), Potassium Zinc Silicate( $\text{K}_{1.10}\text{Zn}_{0.55}\text{Si}_{1.45}\text{O}_4$ ), Zirconia( $\text{ZrO}_2$ ), Calcium Zinc Silicate( $\text{CaZnSi}_2\text{O}_6$ ), Amorphous phase |
| Titania opaque glaze  | Hardystonite( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ ), Titanite( $\text{CaTi}(\text{SiO}_4)\text{O}$ ), Albite(Feldspar( $\text{Ca, Na}$ )), Amorphous phase                                                                                                                                                              |

detection of zircon is obvious from comparison of XRD and EDS results, because the only phases have Zr element are zirconia and zircon phases,

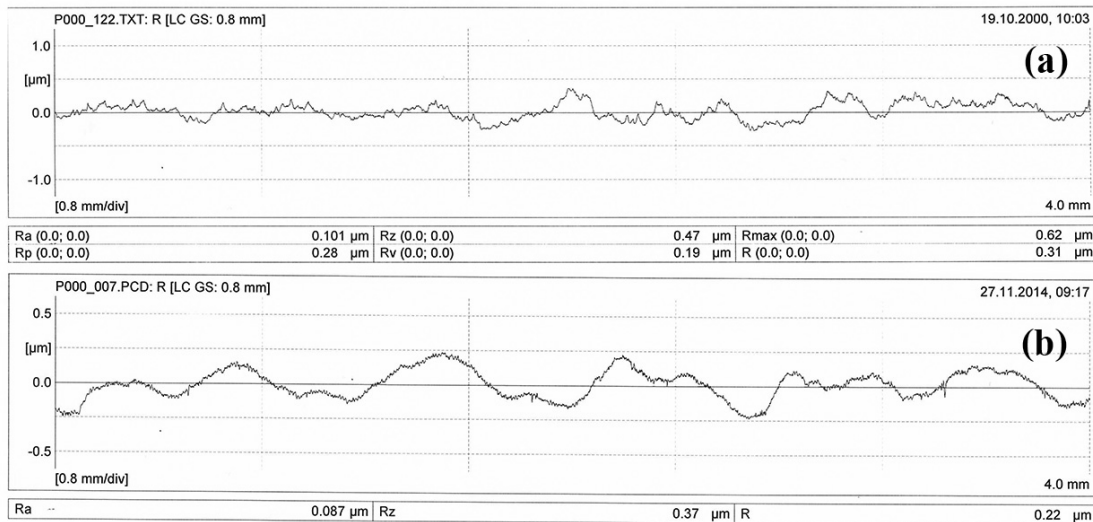
on the other hand since silicon element is present in a large quantity, so the crystalline needle-like phase in SEM images of zirconia based glaze is

**Table 5.** Results of surface roughness for samples

| Glaze Type            | Ra ( $\mu\text{m}$ ) | Rz ( $\mu\text{m}$ ) | R( $\mu\text{m}$ ) |
|-----------------------|----------------------|----------------------|--------------------|
| Opaque- Zirconia base | 0.101                | 0.47                 | 0.31               |
| Opaque- Titania       | 0.087                | 0.37                 | 0.22               |

**Table 6.** Result of glossiness measurement

| Glaze type           | Glossiness(gu) |
|----------------------|----------------|
| Opaque-Zirconia base | 80.1           |
| Opaque-Titania base  | 85.3           |



**Fig. 4.** Surface roughness profile a) Zirconia-based glaze b) Titania-based glaze

zircon phase in tetragonal structure.

Point A in Fig. 3b, shows hardystonite crystals, comparison of XRD and EDS results candidate hardystonite and titanite as two possible phases, but as atomic percentage of hardystonite is more likely regarding to EDS results, so the phase is hardystonite.

Point B in Fig. 3b is titanite phase, in fact the main difference of titanite and hardystonite is in presence of 12.5%wt Ti element in titanite, meanwhile EDS analysis shows 4.22%wt Ti, moreover there is no Zn in titanite, EDS results confirmed the trivial amount of Zn (0.42%wt).

Replacing zirconia with titania in glaze as opacifiers shows a tangible change in crystal shape, size and distribution on the surface. Results have been revealed that titanite crystal is

smaller and their distribution on glass matrix is less dense apparently. Results of surface roughness measurements (Table 5) for the samples shows that replacing zirconia with Titania improves surface roughness about 24%.

Surface roughness profile of the samples is also depicted in Fig. 4. As it is seen average surface roughness parameter (Ra) is a proper parameter to compare surface roughness.

Glossiness measurement with an incident beam angle of 60 shows that glossiness of titania-based glaze is more than zirconia-based, this improvement is the result of smoothness improvement of titania-based glaze, because both titanite and zircon crystals have the same refractive index.

#### 4. CONCLUSION

This investigation has been focused on advantage of replacing zirconia with titania, to avoid other effects, firing curve, particle size and sample preparation have been fixed. SEM images, XRD analysis and surface roughness measurements prove that:

1. The most dominant crystal phase in titania-based glaze is titanite, these crystals are smaller in size and their distribution on glaze surface is less dense than zircon crystals in zirconia-based glaze apparently.
2. Due to the smaller titanite crystals, its less dense distribution on glass matrix and plate like morphology of the crystal, the surface roughness of titania-based glaze has been reduced 24% comparing to zirconia-based glaze; therefore cleanability of titania-based glaze must be better.
3. Regarding to the surface roughness improvement owing to replacement of zirconia with titania, glossiness of glaze has been increased. Since titanite and zirconia phase both have the same refractive index, it seems that increase of glossiness is just due to the surface roughness improvement.

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