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INVESTIGATION INTO PHASE CHANGE IN Al_2O_3 AND SiO_2 EQUIVALENT RATIO VARIATION IN VITREOUS STATE

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ABSTRACT

Phase change phenomena in vitreous state were investigated in a series of glazes composed in accordance with the Zeger formula. The formulated glazes had their bases kept constant while the equivalents of Al_2O_3 and SiO_2, were varied. Examination revealed that development of liquid and crystals from the minerals composing the glazes caused two observed phases of mattness (the result of the development of minute and regularly dispersed crystals of $CaAl_2Si_2O_8$, $ZnAl_2O_4$ and SiO_2) and glossiness (the result of the development of liquid which solidified into glass on cooling.)

Keywords: Crystals, glazes, phase

INTRODUCTION

A glaze, composed of a family of glasses, has special quialities described as transparent, opaque, glossy and matt among others. These qualities attract the ceramist and the user of the ceramic product on which the glaze is applied.

A description of a glaze to the ceramist is made more valuable and practicable if it is accompanied by full details as to the source and analyses of the constituent materials, the details of the preparation, applicastion and firing. Such an information is frequently fragmentary or lacking in published reports.

It is the author's interest to investigate, through careful and critical application of fundamental principles, phases changes in glazes while employing Zeger formula in order to arrive at suitable and reproducible glazes which ceramic industrialists and potters can use. In this attempt the bases, RO, were fixed while equivalents of the amphoteric, R203, and the acidic, R02, in the Zeger formula were varied.

EXPERIMENTAL PROCEDURE

In this work the Zeger formula for a promising glaze arrived at through series of experimentation was employed as:

0.15 KNaO 0.425CaO 0.425ZnO	xAl_2O_3 $ySiO_2$

In the formula the bases were fixed while the equivalents of Al_2O_3 and SiO_2 represented by x, y, were varied. These variable equivalents of oxide ratio of Al_2O_3: SiO_2 are presented in Figure 1 with SiO_2 on the abscissa. In accordance with this figure twenty (20) glaze formulae were obtained for the computation of glaze batches from raw materials which had their ultimate analyses worked into molecular formulae and formula weights as follows:

Raw Material	Formula			Molecular Weight
Hiraku Feldspar	$0.45K_2O$ $0.55Na_2O$	$0.8Al_2O_3$	$5.35SiO_2$	476.0
Limestone	$CaCO_3$			100
Zinc Oxide	ZnO			81.4
Clay	Al_2O_3	$2.33SiO_2$	$2.62H_2O$	289.0
Silica sand	SiO_2			60.1
Alumina	Al_2O_3			102.0

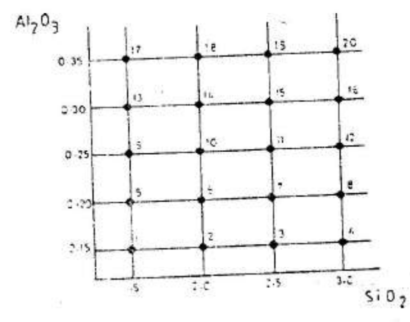

Fig. 1. SiO_2 and Al_2O_3 mole ratio in glaze

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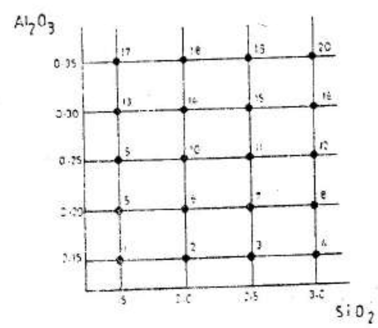


Fig. 1. SiO_2 and Al_2O_3 mole ratio in glaze

Table 1 Glaze batches

Glaze Batch No	Feldspar	Limestone	Zinc Oxide	Clay	Silica	Alumina	Total
1	36.6	21.8	17.7	4.4	19.4	-	99.9
2	31.7	18.9	15.4	3.9	30.2	-	100.1
3	28.0	16.7	13.6	3.4	28.4	-	100.1
4	25.0	14.9	12.1	3.0	44.9	-	99.9
5	35.7	21.2	17.3	4.3	18.9	2.5	99.9
6	31.0	18.5	15.0	3.8	29.5	2.2	100.0
7	27.4	16.3	13.3	3.3	37.6	2.0	99.9
8	24.6	14.6	11.9	3.0	44.1	1.8	100.0
9	34.8	20.7	16.9	4.2	18.5	5.0	100.1
10	30.3	18.1	14.7	3.7	28.5	4.3	100.0
11	26.9	16.0	13.0	3.3	36.9	3.8	99.9
12	24.2	14.4	11.7	2.9	43.3	3.5	100.0
13	33.9	20.2	16.4	4.1	18.0	7.3	99.9
14	29.7	17.7	14.4	3.6	28.2	6.4	100.0
15	26.4	15.7	12.8	3.2	36.2	5.7	100.0
16	23.8	14.1	11.5	2.9	42.6	5.1	100.0
17	33.1	19.7	16.1	4.0	17.6	9.5	100.0
18	29.1	17.3	14.1	3.5	27.7	8.3	100.0
19	25.9	15.4	12.6	3.2.	35.6	7.4	100.1
20	23.4	13.9	11.3	2.8	41.9	6.7	100.0

The Zeger formulae were computed on the basis of the molecular weights and molecular formulae of raw materials as shown above. Accordingly, twenty glaze batches as presented in Table 1 were obtained.

Each batch, multiplied by a factor of 20, was weighed and placed in 2kg milling pot. Into each pot was placed 2kg milling porcelain balls (pebbles). To each of the batch was to be added 1300 ml of water (being 65% total weight of raw materials) but it was noted that not all batches should have the addition of 1300 ml of water needed as some raw material had some amount of water inherent in them. The feldspar, clay and silica sand had, respectively, 20.6%, 11.2% and 22.0% water content. Accordingly, the water addition was made to the batches taking into consideration these values which were deducted from the 1300 ml of water needed for appropriate slurry of each batch. The batches were later milled for twenty hours resulting in an average particle size of 9.4μm for each batch.

Milling of all batches accomplished, each glaze was applied by water fall method on wall tiles. Twenty tiles (each of dimension, 10.0cm x 10.0cm x 1.25cm) were used for each glaze and the amount of glaze on each tile was 8.0g/ 10.0cm². Firing of samples was done with the use of a laboratory roller-hearth kiln for 30 minutes. Two separate firings were undertaken at 1150°C and 1200°C. After firing the tiles were subjected to examination by the use of a glossiness tester and an x-ray diffractometer. Scanning Electron Microscopy was also employed in studying the features of glaze surfaces.

RESULTS AND DISCUSSION

Visual examination of all fired tiles showed three distinct areas of bright, semi-matt and matt qualities respectively. These three phenomena are presented in figures 2 and 3. In order to confirm the visual observations a glossiness meter was employed.

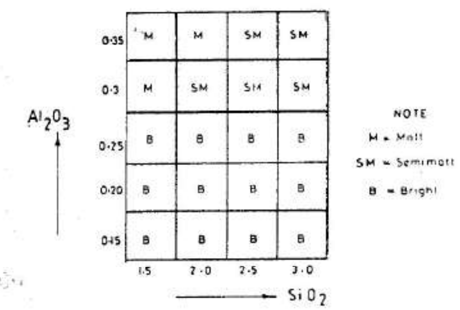


Fig. 2. Glaze appearance on tile at 1150 °C

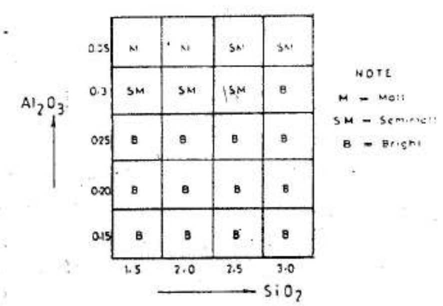


Fig. 3. Glaze appearance on tile at 1200 °C

The use of the glossiness meter underlies the fact that brilliancy or glossiness of a surface relates to the mirror reflection of parallel rays of light which fall on the surface of a material. Hence one can have parallel rays reflected in a certain direction or have them scattered due to the nature of the surface on which the light is directed thereby inducing reduction of glossiness. Glossiness also depends on the angle of incidence of light. These scattering and reflected effects from the use of glossiness meter relate to the glassy and crystalline natures of the glazes studied. Figures 4 and 5 present the results on the use of glossiness tester. Each square box represents a tile and the glaze applied on its surface. The glossiness reading of each tile is the average of the readings of twenty samples.

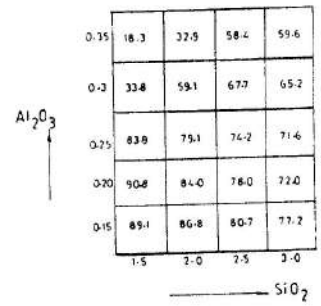


Fig. 4. Glossiness at 1150 °C

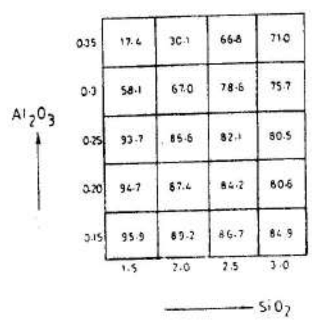


Fig. 5. Glossiness at 1200 °C

Glossiness values of more than 80% show glossy or bright glazes. Values of more than 50% but less than 80% show semi-matt glazes. Below the values of 50% the glazes appear matt. Theoretically, however, areas showing matt appearances scatter and diffuse light thereby exhibiting low values of glossiness [1].

Generally, however, change in glossiness relates to variations in Al_20_3:$Si0_2$ ratio [1-7]. It is noted that when Al_2O_3:SiO_2 ratio is 10 the glossiness increases and the glaze becomes bright. With Al_2O_3:SiO_2 ratio below 10 (about 8-6) the glossiness reduces resulting in semi-matt effect.

It is also observed that temperature also has a considerable effect on the glaze appearance. Notable examples are in areas where Al_2O_3:SiO_2 ratio is 10 and more, resulting in glossy and semi-matt glazes. At 1200°C the glossiness of the glazes is generally higher than that of the glazes fired at 1150°C. The only exceptions observed are in glazes Nos.17 and 18 which contain high Al_2O_3 and low SiO_2 fired at both temperatures.

In order to ascertain the cause of glossiness vis-a-vis mattness x-ray diffraction analysis techniques were resorted to. Figures 6 through 11 present the analytical results. In this exercise glossy, semi-matt, and matt glaze samples were selected. Glazes Nos. 1, 4, 17 and 20 were representative samples for study and comparison. Tile samples having these various glazes were cut to size and placed in an x-ray diffractometer. Cuka radiation was employed.

Figure 6 shows comparison between two bright glazes, Nos. 1 and 4. Figure 7 shows comparison between a bright glaze No.1 and a matt glaze No.17. A bright glaze, No.4, is also compared with a semi-matt glaze No.20 in Figure 8. Figure 9 shows comparison between matt glaze No.17 and semi-matt glaze No.20. Figures 10 and 11 also present comparison between the glossy glaze No.1 and the matt glaze No.17 which were fired at 1150°C and 1200°C for 30 minutes in each temperature.

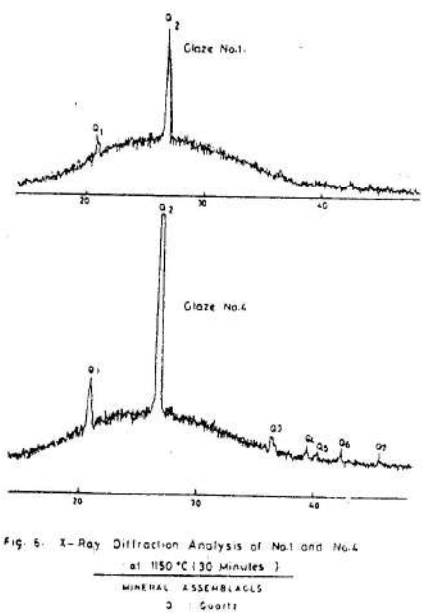


Fig. 6. X-Ray Diffraction Analysis of No.1 and No.4 at 1150 °C (30 Minutes)
MINERAL ASSEMBLAGES
Q : Quartz

The numbers on the abscissa of figures 6 through 11 are diffraction angles. Quartz peaks numbered Q_1 through Q_7 correspond to (100), (101), (110), (102), (111), (200), and (201) faces respectively. Anorthite peaks indicated as A_1 through A_{13} correspond to $(\bar{2}02)$, $(1\bar{3}0)$, (200), $(\bar{1}\bar{3}1)$, (100), $(1\bar{3}2)$, $(0\bar{4}2)$, (132), $(\bar{1}34)$, $(2\bar{2}2)$, $(\bar{2}\bar{4}5)$, (006), (152) faces and gahnite peaks indicated as G_1 through G_3 correspond to (220), (311), and (400) faces respectively.

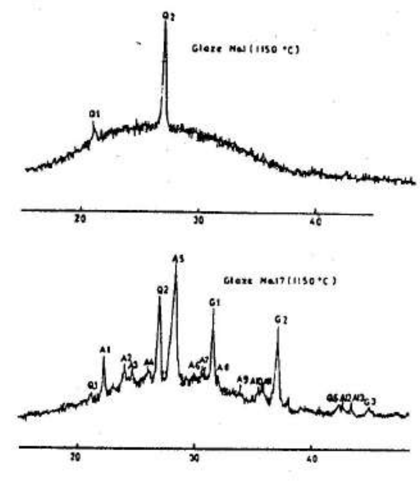
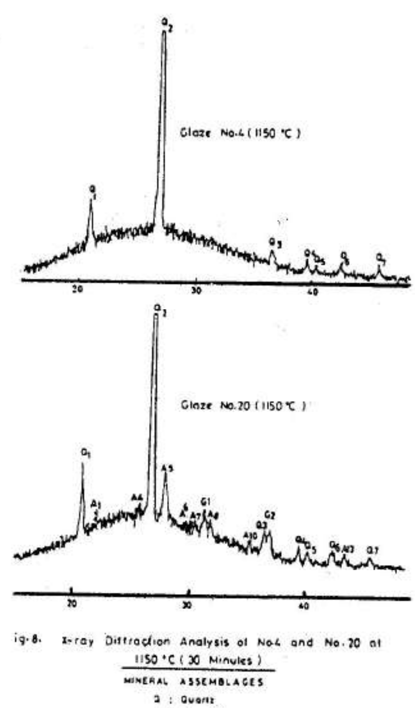


Fig. 7. X-Ray Diffraction Analysis of No.1 and No.17 at 1150 °C (30 Minutes)
MINERAL ASSEMBLAGES
Q : Quartz
A : Anorthite
G : Gahnite



ig. 8. X-ray Diffraction Analysis of No.4 and No.20 at 1150 °C (30 Minutes)
MINERAL ASSEMBLAGES
Q : Quartz
A : Anorthite
G : Gahnite

In glazes Nos. 1 and 4 the Al_2O_3 content is the same but both of them have different SiO_2 content. Comparing the x-ray diffraction results in figure 6, one finds that there are only two crystal peaks of quartz. The crystals in this glaze No.4 render its appearance near semi-matt. The glaze No.1 is a brighter glaze, resulting from less crystal formation in the glassy matrix at 1150°C.

The glazes Nos. 1 and 17 have the same SiO_2 content but differs in Al_2O_3 content. On comparing the two glazes in figure 7 one finds

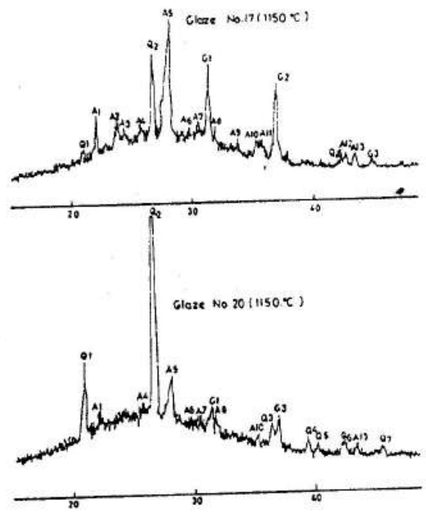


Fig. 9. X-ray Diffraction Analysis of No.17 and No.20 at 1150°C (30 Minutes)

MINERAL ASSEMBLAGES
Q : Quartz
A : Anorthite
G : Gahnite

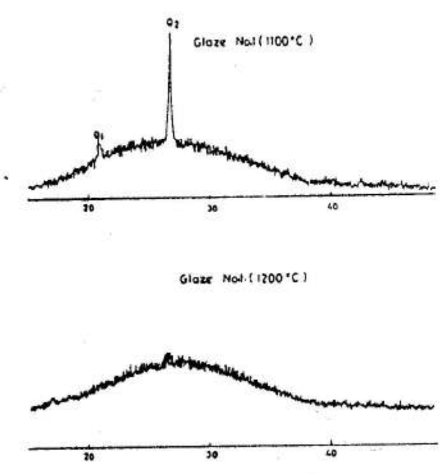


Fig.10. X-ray Diffraction Analysis of No.1 at 1150°C (30 minutes) and 1200°C (30 minutes)

MINERAL ASSEMBLAGES
Q : Quartz

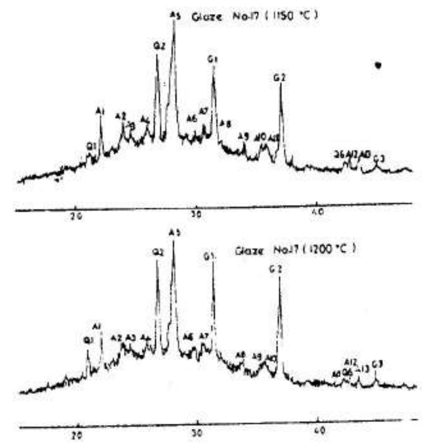


Fig. 11. X-ray Diffraction Analysis of No.17 at 1150 °C (30 Minutes) And 1200 °C (30 Minutes)

MINERAL ASSEMBLAGES
Q : Quartz
A : Anorthite
G : Gahnite

that the glaze No.17 exhibits much more crystals of anorthite ($CaAl_2Si_2O_8$) gahnite ($ZnAl_2O_4$) and quartz (SiO_2) with anorthite predominating. Examination shows that the glaze No.17 has very little glass phase. The glaze appears completely matt. This matt effect is attributable to the presence of the crystals developed.

The glazes Nos.4 and 20 also have the same equivalent ratio of SiO_2 but differ in Al_2O_3 equivalent ratio. Examination of figure 8 shows that the glaze No.20 has developed crystals of anorthite, gahnite and quartz. This glaze contains a proportion of glass which renders it semi-matt. The proportion of glass to crystal phase in glaze No.4 is more than observed in glaze No.20. This condition renders the glaze No.4 bright but with nearness to semi-matt effect.

Examining glaze No.17 (matt) and glaze No.20 (semi-matt) one finds in figure 9 that both glazes show a considerable development of anorthite, gahnite and quartz crystals but these crystals are more pronounced and prominent in the glassy matrix of glaze No.17 than of glaze No.20. This phenomena accounts for mattness in the glaze No.17 and semi-mattness in the glaze No.20.

At 1200°C glaze No.1 shows no crystal development. The x-ray diffraction analysis as presented in figure 10 shows only glass phase due to the dissolution of the quartz crystals earlier observed at 1150°C. It is observed that glossiness increases in this glaze due to the glass phase formed.

It is surprising to note that there is no significant change in glaze No.17 fired at 1200°C. Figure 11 shows that crystal peaks produced at

1150°C have the same intensity as those produced at 1200°C. This glaze No.17 remains essentially matt at the two temperatures.

The presence of undissolved crystals diffused and refracted reflected incident light rays [1,2] from the surfaces of the tiles on which the glazes were applied causing gradation in mattness. A notable feature of glazes No.17 and 18 was their characteristic velvety to the touch which was the result of the development of the minute and regularly dispersed crystals of $CaAl_2Si_2O_8$, $ZnAl_2O_4$, and SiO_2. The development of anorthite and gahnite, no doubt, resulted from the reaction between the bases and the variable equivalents of Al_2O_3 and SiO_2. All other glazes without any crystals particularly at 1200°C remained glossy and bright due to the liquid or glass phase formed.

In order to study the surface feature of the matt, semi-matt and bright glazes, scanning electron microscopy was employed. In this exercise small test pieces were cut from the glazed titles of glazes Nos.17 (matt), 14 (semi-matt) and 11 (bright). On each of these test pieces was deposited Au layer of 30nm thickness by iron spattering. Later each test piece was placed in the SEM. The results are photomicrographs presented in figure 12. The photomicrographs in Figs. 12a through 12c show secondary electron image (SEI) of the glazes Nos.17, 14 and 11 respectively. Photomicrographs as shown in Figs. 12d through 12f are composition based scattering image (COMPO) of same glazes.

The image of SEI exhibits unevenness of the surfaces caused by the development of crystals in the vitreous phase. This feature is observed to be much more distinct in the matt glaze No.17 than in the two other glazes. In the case of the composition based scattered electron image (COMPO) the brighter sections of the glaze exhibit the image of heavier elements composing the glaze. Generally, however, the photomicrographs show not much contrast between bright glaze No.11 and semi-matt glaze No.14, but contrast between the semi-matt glaze No.14 and the matt glaze No.17 is quite prominent.

CONCLUSION

A successive change in the oxide equivalents of Al_2O_3 and SiO_2 effectively gave matt and bright glazes. Generally, however, the range of glossy glazes was quite large with 0.15 to 3.0 equivalents of SiO_2 and 0.15 to 0.25 equivalents of Al_2O_3. Increase in Al_2O_3 and reduction in SiO_2 impaired gloss.

Increase in temperature from 1100°C to 1200°C has no appreciable effect on the matt glaze as observed in the x-ray diffraction peaks of gahnite, anorthite, and quartz crystals in figure 11. The most affected crystal by temperature increase is quartz which dissolves partially or completely in accordance with equivalent ratio variation of SiO_2, and Al_2O_3 in the glaze at 1200°C and in combination with the bases. The phenomenon of partial or complete dissolution of quartz increases glass phase and produces gradation of gloss or brightness in the glaze. Glossiness increases with increase in temperature for the glossy and semi-matt glaze. But mattness rather increases with increase in temperature for the matt glaze. This claim is within the range of experimental temperatures only as established by figure 4 and 5.

The qualities of glazes arrived at in this exercise are promising white glazes for the whiteware industry.

ACKNOWLEDGEMENT

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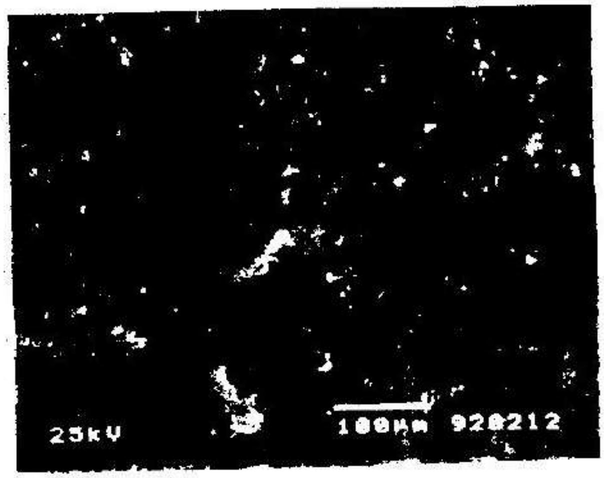
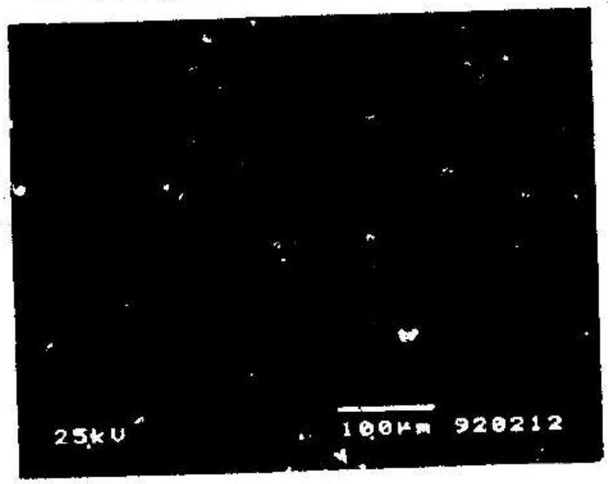
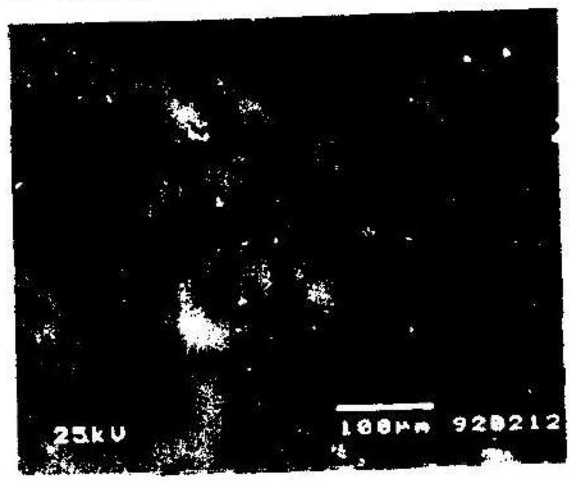


a. Matt glaze No.17 (SEI)

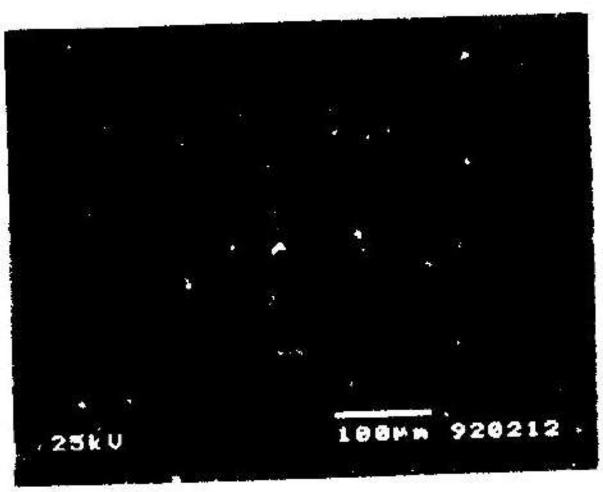
d. Matt glaze No.17 (COMPO)



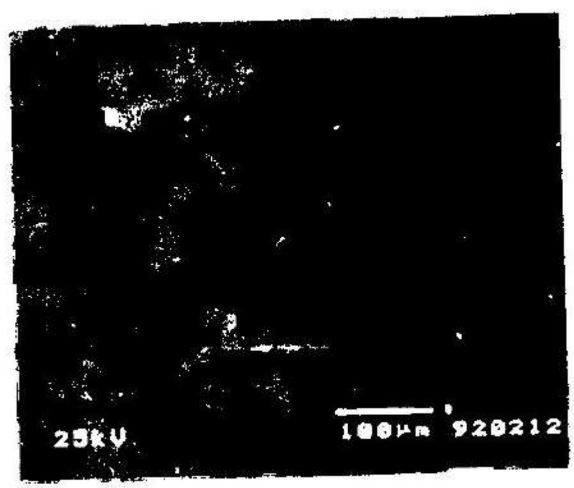
b. Semi-matt glaze No.14 (SEI)



e. Semi-matt glaze No.14 (COMPO)



c. Bright glaze No.11 (SEI)



f. Bright glaze No.11 (COMPO)

Fig.12. Scanning Electron Migrographs of matt, semi-matt and bright glazes.