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# THE MICROSCOPIC CHARACTERIZATION OF CERAMIC / METAL INTERFACE

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## ABSTRACT

An admixture consisting of local silica sand, feldspar and some chemical additives was used to produce varied s of glass by conventional smelting procedures.
These blends of glass with some additives were made into an aqueous slip (slurry) for wet application process. The aqueous slips prepared were applied on OL 140 type of Romanian steel by dipping. The samples were dried and subsequently enameled in an oven maintained at a range of temperatures of 700 - 900 ºC. Double faced enameled surfaces were thus developed.
A microscopic characterization of the formed enamel / steel composite interface was explored with scanning electron microscope and emission dispersive atomic x – ray. The SEM revealed a continuous graded interface which made perfect contact with the glass coating and the steel support. Also dendritic networks were evident. EDAX unmasked the slope of the dissolution and diffusion of the iron into the ceramic phase. The ceramic profile is a mirror image of the iron profile. The emission dispersive atomic x – ray, (EDAX) further monitored the elemental distribution and their quantities at the point of bond formation (ceramic – metal interface). Fe and Si were found to be the major components of the interface.

*Subject Classification: Materials and Engineering*
*Keywords: Characterization, Components, Interface, Glass, Metal*

## 1.0 INTRODUCTION

The growing interest in the production of materials with good surface properties for engineering applications is very desirable. Evidence is the relationship between coating properties and surface functional performance [1]. The huge impact of surface properties is manifested by its pervasive applications in modern industries that produce chemicals, fuels, microelectronics and optical devices, and medical services. The challenges associated by high industrial applications provide a major thrust to the progressive advances in surface chemistry. Surfaces and interfaces define a boundary [2] between a bulk material and its surrounding environment and influence interactions with that environment. The surface atoms, with atomic and electronic structures different from those of the bulk material [3] exhibit varying chemical reactivities. This property makes surfaces and interfaces [4] a favored medium for many important chemical processes and applications in nature and in industrial processes. Quite often, surfaces are modified by various methods including coatings in order to achieve the required functional performance. Coatings applied to materials are an essential part of manufacturing. Without coatings many materials would not have the properties that make them so useful, and many would be impossible to make. Therefore, surface coatings enable development and provision of improved properties to the substrate materials. Thus, a coated surface is an applied superficial region with appropriate depth and with good bonding to function adequately with the bulk material [1]. The coating processes depend on the compositions used in the preparation of the coating material. That consequently determines the method of application of the coating material and subsequent heat - treatments that make a coated surface different from another. In this work SEM and EDAX have been used in investigating the integrity of the ceramic /metal interface and the assessment of the effects of the micro-structure while the surface property remains of particular interest.

## 2.0 EXPERIMENTATION

This work consists of two major procedures. This first step involves glass frit production, preparation of the metal substrate for the coating process and application \ sintering of the coated surfaces, while the second process is the microscopic characterization of the coated surfaces.

### 2.1 Glass Frit Production

Chemical and mineralogical investigations of the silica sand [5] and feldspar established the possibility of using these raw materials for enamel preparation. An OL 140 Romanian steel was chosen to be used as support, with a thermal expansion coefficient of $113.91\times10^{-7}$ ( grd) ,

The composition of the ground coats enamel frits was calculated [6] according to the Appen Formula in order to obtain the theoretical thermal expansion coefficient adequate for a good adherence on the selected steel support.

$$\alpha = 10^{-7} = \sum \gamma i . \alpha'^{i}$$

$$= \frac{\sum \gamma i \,.\, \% \,\alpha' i}{100} = \frac{\sum \gamma_{\,im} .' i}{\gamma\, im}$$

$\gamma 1$ = the content of the oxides expressed in molar fraction

$\gamma i\,\%$ = the content of the oxides expressed in % molar

$\gamma^{\,im}$ = the content of oxides expressed in moles

The composition of the cover coat enamel was calculated to obtain thermal expansion coefficient less than that of the ground coat in order to ensure adhesion of ground coat and cover coat.

The starting compositions of the two enamel frits were selected among those used for obtaining usual enamels without special requirements, except for the black color of the cover enamel. For the oxide compositions presented in (Reference 1), the theoretical expansion coefficients shown in the (Reference 2) were obtained.

Based on the oxide composition of the enamel frits and on the chemical composition of some Nigerian raw materials [5] only sand and feldspar were selected among the analysed local material samples in order to obtain enamel frits.

**TABLE 1: OXIDE COMPOSITIONS OF THE ENAMEL**

| | **CHEMICAL COMPOSITIONS** | | | |
|---|---|---|---|---|
| **OXIDES** | Enamel frits obtained from chemical oxides | | Enamel frits obtained from Nigerian raw materials | |
| | Ground Enamel | Cover Enamel | Ground enamel | Cover enamel |
| $SiO_2$ | 39.35 | 46.17 | Sand | 47.35 |
| $Al_2O_3$ | 39.19 | 3.82 | 14.60 | 3.86 |
| $B_2O_3$ | 27.83 | 18.16 | 35.60 | 18.24 |
| $Na_2O$ | 18.57 | 15.72 | Feldspar | 15.78 |
| $K_2O$ | 4.17 | 5.04 | 36.30 | 5.06 |
| $CaF_2$ | 5.30 | 6.52 | 05.30 | 5.47 |
| CoO | 1.59 | 1.96 | 00.20 | 0.97 |
| $MnO_2$ | - | 2.61- | 00.60 | 2.50 |
| CaO | - | | | 0.77 |

**TABLE2 : VALUES OF THEORETICAL EXPANSION COEFFICIENTS**

| Sample | | The expansion coefficient (grd -) |
|---|---|---|
| Enamel frits obtained from Chemical Oxides | Ground enamel | $114.3 \text{ X } 10^{-7}$ |
| | Cover enamel | $104 \text{ X } 10^{-7}$ |
| Enamel frits obtained from local raw materials | Ground | $116.2 \text{ X } 10^{-7}$ |
| | Cover | $109 \text{ X } 10^{-7}$ |
| OL140 type steel | | $113.91 \text{ X } 10^{-7}$ |

The silica sand, feldspar and some chemical additives were used to produce varied blends of glass by conventional smelting procedures. These compositions were melted in an electrical laboratory furnace at temperatures above 1000 $^{o}$C. The melts were quenched in cold water and the frits produced milled to fine powder.

**2.2 Metal Preparation**

The OL 140 type steel with thermal expansion 113.91×10$^{-7}$ (grd$^{-1}$) was used as the metal support. The steel was made into coupons of dimension 60mm X 20mm X 1.5mm. The traditional procedure [7] was used for degreasing and etching.

**2.3 Slip Preparation and Application**

The different glass formulations were processed into slips as shown in the table below and applied on the steel samples.

TABLE 3: MILL ADDITIVES

| Composition of slip | % |
|---|---|
| Frits | 100 |
| Clay | 6 |
| Water | 50 |
| Sodium nitrite | 0.5 |

The additives were added largely for the purpose of controlling the rheology of the aqueous slip. The selection of the clay is an important consideration. Clays for enamel mill batches should be fine grained and highly plastic [8]. The slips prepared were applied on the steel piece by dipping .

**2.4 Sintering of the Enamel**

The samples were sintered in the furnace. The enamels obtained from commercial oxides and that from local raw materials were realized at 750 $^{o}$C and 780 $^{o}$C respectively.

**2.5 Visual Inspection**

The coated surfaces were monitored and observed every week for over a period of six months. The stability of the color and the appearance of lines and cracks were of paramount interest.

**2.6 Atomic Force Electron Microscopic (AFM) Study**

Microstructural changes / transformations that occurred during the baking of the frits were examined, using AFM. e figure 1 is the 3-dimensional micrograph at 20µ of enameled samples of one of the oxide compositions obtained from the sand and feldspar.

**2.6 Characterization of the Interface**

The interface was examined using SEM and EDAX.

**2.6.1 Scanning Electron Microscopic (SEM) Investigations**

The enameled samples were cut transversely using a diamond blade. The samples were polished and etched with Nital 2% special solution [9], and prepared for examination. Scanning of the samples was achieved with optical microscope Reichert Unvier at a magnification of 10×. Further investigations of the samples were achieved with Electron dispersive atomic x-rays (EDAX).

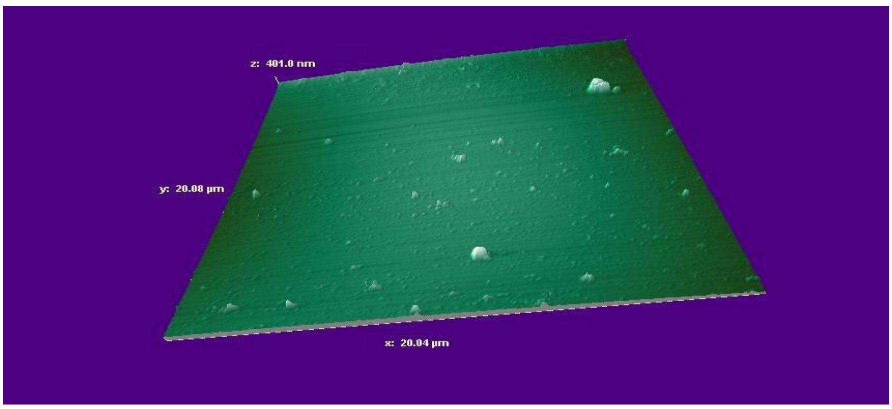


*Figure 1: Three Dimensional Micrograph (at 20µ) of Enamelled sample obtained from sand and feldspar*

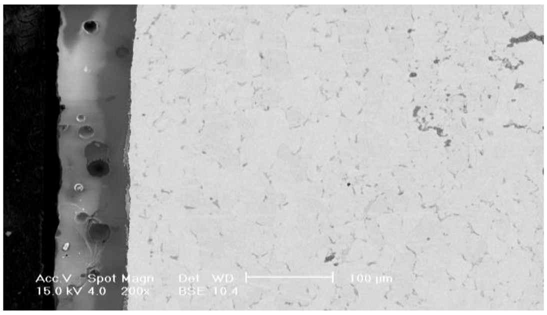


*Figure 2: Cross-Section of enamelled sample showing continuous graded interface*

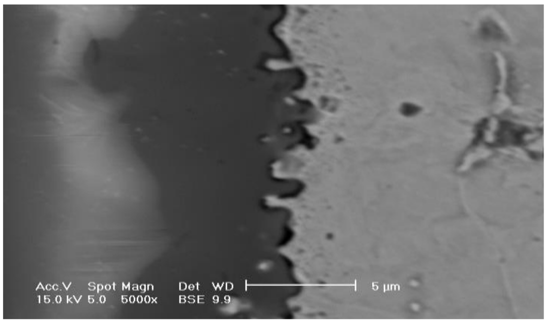


*Figure 3: Cross-Section of enamelled sample showing dendrite formation*

The bonding between the enamel coating and the steel was evident on SEM micrographs as shown in Figure 2 and 3

### 2.6.2 Emission Dispersive Atomic X rays (EDAX) Analysis

Element distribution at the point of bond formation (ceramic /metal interface) was elucidated using EDAX. The different colors represent the following elements;
Red -- Iron; Blue -- Oxygen; Yellow -- Silica; Green --Aluminum Light Green -- Sodium /Potassium; Purple --- Calcium

## 3.0 RESULTS

Visual observation of the coated samples showed that the enamels presented good adhesion to the OL 140 steel type substrate as smooth, hard, black glossy colored surfaces were observed with the cover coat enamels. The surfaces were void of discoloration and impervious to water.
The Atomic Force Microscopy result (Figure 1) confirmed the visual observation. The coatings appeared consistent without blisters or any known morphological defect or surface flaws. The coatings attained some degree of uniformity. The SEM (Figs.2 and 3) presented the surface preview of the sample interface layer, revealing a continuous graded layer of the interface that made perfect contact with both the coating material and the metal substrate.

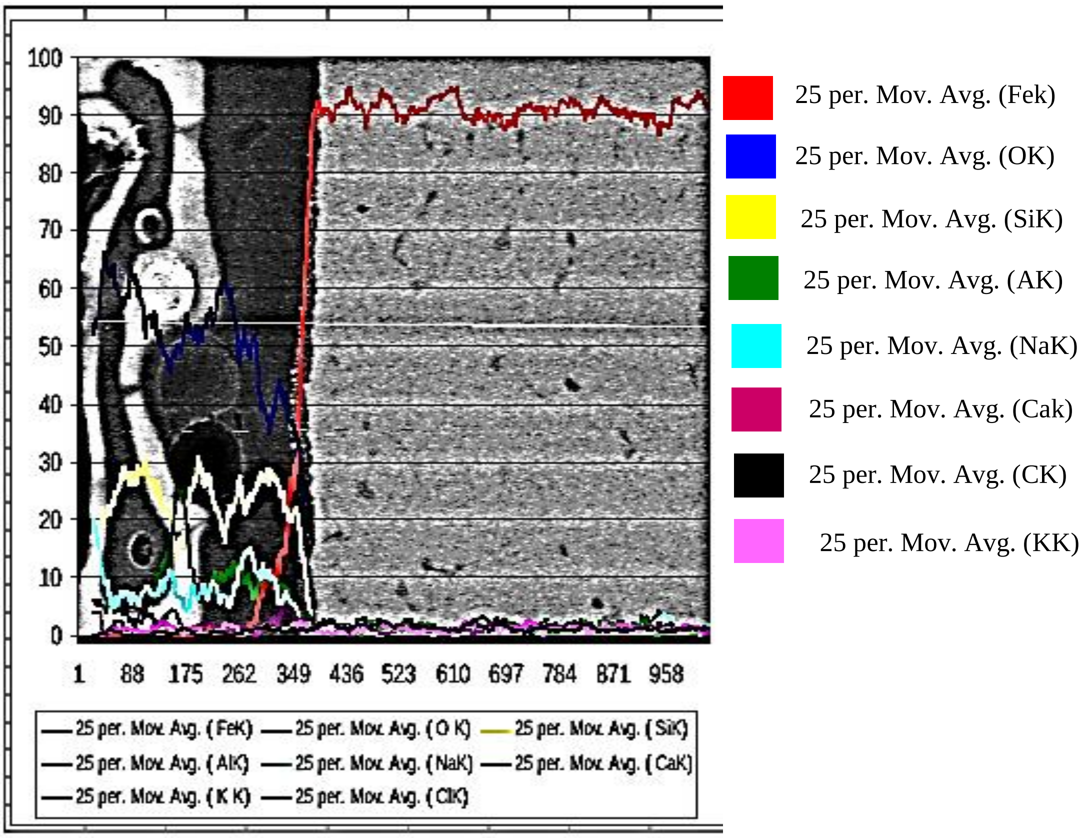


*Figure 4: EDAX Micrograph of Enamelled sample Elemental Composition*

This depiets a rigid chemical bond with excellent adherence of the coating material on the metal substrate (Figs. 2 and 3). The presence of peaks and sharp drops as seen in (Fig. 3) demonstrated points of anchor as explained by the mechanical interlocking theory of adhesion [6]. EDAX analysis gave the picture of chemical interaction in the ceramic – metal matrix. It revealed a high concentration of iron in the metal matrix which decreased drastically at the point of contact with the ceramic matrix (Fig. 4). This reflected the dissolution of the metal in the ceramic matrix which is evidence of good chemical interaction. Similarly, the silica profile is approximately the mirror image of the iron profile. It is constant over the coating matrix and decreases at the point of interface with a slope similar to that of iron (Figure 4).

## 4.0 DISCUSSION

The multicomponent glass coatings obtained with both the commercial oxides and the local silica sand and feldspar on application on the OL 140 steel support adhered perfectly well producing double faced enameled samples. This is direct experimental evidence that the local sand and feldspar can serve as raw materials for glass ceramic coatings. From the calculated coefficient of expansion, the coefficients of expansion of the glasses are greater than that of the steel (Table 2), that is $\alpha_{glass} > \sigma_{steel}$, but they are within the same range. This satisfies Appen theory [3], thus ensuring compactibility of the glass coat with the steel.

The Atomic Force Microscopy result confirmed the visual observation. The coatings attained some degree of uniformity and smoothness [Fig 1]. However, few clusters of white fragments (unmelted quartz particles) within the coated surface were very distinct and varied with the different formulations. The controlled batch formulation gave more orderly surfaces

The metallographic study of the interface boundary established that during firing a heterogenuos interaction occured on the steel – ceramic contact surface followed by diffusion. The SEM depicted rigid chemical bond with excellent adherence of the coating material on the metal substrate. The presence of peaks and sharp drops as seen in (Figure 3) demonstrated points of anchor as explained by the mechanical interlocking theory of adhesion [10]. These are Fe-Ni-Co alloy precipitates [10] at the enamel steel inteface that are responsible for the adhesion in enamel steel. Therefore, these dendritic formations confirm the presence of mechanical bond.

EDAX analysis gave the picture of chemical interaction of the ceramic–metal matrix. It revealed a high concentration of iron in the metal matrix which decreased drastically at the point of contact with the ceramic matrix from about 90% to 0% at the interface region (Figure 4). This revealed absolute dissolution of the metal into the ceramic matrix which shows evidence of good chemical reaction. The silica profile is approximately the mirror image of the iron profile. It is constant over the coating matrix with a concentration of about 30% and decreases at the point of contact with the metal matrix to zero percent, with a slope similar to that of the iron profile (Figure 4). Both elements have the highest concentration in their various matrices and were completely assimilated at the interface region. Therefore, they are the major constituents of the interface micro-structure. Other significant elements present at the interface are sodium and potassium with a concentration of above 15% in the ceramic matrix but reduced to 0% at the interface. The concentration of aluminum, calcium and oxygen remained constant at 0% both in the ceramic matrix and at the interface region.

## CONCLUSION

This study has proved that enamel coatings produced with the local sand and feldspar adhered strongly forming chemical and mechanical bonds with the metal substrate. This result confirms that the enamel produced can be applied to metals. Hence, there is the need to standardize Silica sands and Feldspar deposits in the country. The result further showed that the contribution of aluminum and calcium at the interface is insignificant as deduced from their low levels of concentration which were constant before and during the interface reaction. The concentrations of Si and Fe at the interface region decreased, as both elements dissolved and were completely diffused into the interface layer. Consequently, Fe and Si are the major constituents of the interface layer.

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