Evaluation of Enamel Coatings General Corrosion in Sulphuric Acid Solution at Different Temperatures

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Abstract

The aim of this study is to evaluate the general corrosion resistance for different ground and cover enamel coated specimen in 20% (by volume) of sulphuric acid solution for 48 hrs. duration time.

Groups of enameled specimen were tested, was of low carbon steel base metal(0.14%C) that was covered two layer coating and the outer layer having different wt% of titanium oxide TiO_2 content (15.5,20, and 24.5%) each tested at solution temperature (65°C, 96°C, 150°C, and 200°C) separately in apparatus specified by DIN 51.157.

General corrosion rate is calculated for each specimen in mil per year MPY.Results revealed that as the TiO_2 content increased in the outer ground coated cover, MPY values also increased (higher corrosion and for all the test temperatures. The highest MPY value was recorded at 200 °C, at 24.5% of TiO_2 content (MPY= 0.59).

This result was attributed to the formation of the Ti-ion bonding in the glassy network of the enamel this bond enhance the chemical resistance.

Glossiness test and restitution hardness tests were performed to investigate the results obtained previously for the enameled tested specimens.

Both tests confirms the results showing that higher TiO_2 cover content yields higher glossiness percent (low corrosion).

Also restitution hardness tests show an increase in the hardness values recorded as the weight content of TiO_2 in the cover coat increases, whatever the solution temperature was.

Keywords: General corrosion, enamel, corrosion resistance.

تقييم مقاومة طلاءات المينا للتاكل العام في محلول حامض الكبريتيك وبدرجات حرارية مختلفة

الخلاصة

تم في هذا البحث تقييم مقاومة التاكل العام لطلاءات المينا بـالنوعين (ground, and cover) لسبيكة ذات أساس من الفولاذ الكربوني المنخفض (0.14C%) وفي محلول مـن حـامض الكبريتيك بتركيز 20% حجما.

مجاميع العينات تم طلائها بطبقتين من طلاء المينا الطبقة الاساس (Ground Coat) والنـوع الاخر من العينات طليت بطبقتين من الطلاء. الطبقـة الاســاس (Ground Coat) والطبقـة الخارجية (Cover Coat) مع تغيير النسبة المئوية الوزنية لاوكسيد التيتـانيوم فـي الطبقـة الخارجية (15.5% و 20% و24.5%) وزنا على التوالي وفـي درجـات حراريـة مختلفة للمحلول هي (65 °C و 96 °C، 150 °C و 200 °C) وبصورة منفصلة لكل عينـة

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ولمدة 48 ساعة غمر مستمرة. تم حساب معدل التآكل العام بـ(MPY (Mil/ Year حيث تبين بان زيادة نسبة اوكسيد التيتانيوم في طبقة الطلاء الخارجية تؤدي إلى زيادة مقاومة التآكل العام للعينات وعند مختلف الدرجات الحرارية المذكورة أن وقد كانت أقصى قيمة لـ MPY=0.88 وذلك عندما كانت نسبة اوكسيد التيتانيوم في طبقة الطلاء الخارجية تساوي Ground cover coat%24.5 ويمكن أن يعزى ذلك إلى تكون آصرة التيتانيوم في الشبكة الزجاجية للطلاء حيث تعمل هذه الاصرة على تحسين المقاومة الكيماوية.

تم أيضا في هذا البحث دراسة اختبار اللمعان وكذلك قياس صلادة الارتداد للعينات التي تم إجراء اختبار التآكل عليها (اى بعد الغمر في محلول الفحص) وقد أكدت هذه الاختبارات ان زيادة نسبة اوكسيد التيتانيوم تؤدي إلى انخفاض اللمعان و تقلل من معدل التآكل أي زيادة في مقاومة العينات للتآكل في محلول حامض الكبريتيك بتركيز 20%حجما.

Introduction

Vitreous or Porcelain enaml is a thin layer of glass, typically of few hundered microns in thickness it is fused into the metal substrate.

The glass used for enamilling is referred to as **"frit"** and is formulated from a wide range of inorganic raw materails including quartz, borax and titanium[1].

Vitreous enamels are complex glasses formulated to meet specific insrevice requirments. They offer endless choice of colours, when combined with ceramic coloring agents [1].

Vitreous enamels form inseprable bond at the interface with steel due to the chemical reactions that occur between the molten emamel and the heated steel surface[1,2] .

The integrity of the bond between the vitreous enamel coating and the steel substrate is such that interlayer or "under corrosion" of the substrate cannot occurs [3].

In addition the electrical insulating properties of vitrous enamel ensures the galvanic corrosion of the substrate of any other environment in contact with the coating, does not occur [2].

Vitreous enamels are classified as ceramic materials that have many desirable properties associated with ceramics as excellent chemical, high surface hardness, high resistance to heat and degradeation by ultraviolet light [2,5] as well as other glassy properties like excellent ease of cleaning, and aesthetically pleasing appearance[1].

But ceramics are known to have poor impact toughness, but when fused to steel the impact toughness of vitreous enamel is improved. The impact load that is sufficient to cause deformation of steel substrate is usually required to cause chipping or spelling the enamel coat [6].

Corrosion is a destructive attack of metal (alloy)by chemical or electrochemical reaction with its environments, and one of the major roles of the enamel that is expected to play is protection of the metal corrosion[2,3]. Thus the aim of this study is to evaluate the corrosion resistance of ground enamel low carbon steel coated sheet in strong oxidizing acid (H_2SO_4) to investigate the coating resistance as there is still lack of such studies in our country.

Experimentations:-

Low carbon steel alloy is used as a metal substrate of a chemical composition that is shown in Table[1], these results were obtained using spectrometric method.

1.Enamling:-

Two (2 mm) thickness steel sheets were blasted using silicon carbide blasting to overcome excessive loss of metal and excessive wrapping).

The commercial treatments of metal preparation process may be carried out using continuous cleaning, preparation process may be carried out with continuous cleaning and pickling equipment. The specimens subsequently are subjected to pickling acids[6] .

The solutions that are used for enameling are specified briefly in Table 2 in the stages with their relevant conditions {as process time, temperature, solution content, and concentrations[6].

Glass frit is the major consistuent in bisque (unfired) enamel coating. Frit is a homogenous melted mixture of inorganic materails that are used in anameling steel process [1,2,3,].

Fig.(1) shows the flow diagram of frit preparation.

The constituent of the change for a ground coat include the same compounds plus smaller amount of metal oxides such as Cobalt oxide, Nickle oxide, and Magnesium Oxide [4,6].

Porcelain enamel frit compositions are designed to meet a variety of parameters as shown in Table 3, including appropriate match to the thermal expansion, or/and properties of the metal substrate as abrasion and corrosion resistance when demanded[3 ,6]

Varying amounts of Titanium Oxide {20%-24.5%} were added to the cover coat frit in order to study the maximum acid corrosion resistance of this type of enamel at different times and temperature.

II. General Corrosion Test:-

In order to evaluate the general corrosion of porcelain enamel {ground coat, and cover coat} in sulphuric acid tests were performed at different solution temperatures and different weight percents of TiO_2 added. These tests conformed to **DIN 51.157** that is commonly used for porcelain enamels[7].

In these tests porcelain enamel sample exposed to constant acid concentration{ 20% (by volume)} of boiling sulphuric acid for 48hr duration time for different solution temperature (65 °C,96 °C, 150 °C, and 200 °C). The corrosion rate is expressed in MPY according to the equation:[8]:-

MPY = 534 Wt./AT D ....[8].

where MPY=Mil Per Year (general corrosion rate).

Wt = weight loss during test duration in mg .

A= Surface area of the tested specimen in square dc.

T= test duration in hrs.

And D= density of the gm/ Cm.

III. Shorsclorscope Hardness:

In this test a steel falling ball with diamond-pointed hammer weighting 5gms which is allowed to fall from a standard light of 50 Cm inside a graduated glass-tube where the height of rebound is calculated directly as hardness index [9].

This hardness is usually determined from the degree in rebound of the falling steel ball that is totally dependent on the integrity of the bulk strength and continuity i.e. {the presence of crack, pores, or erosion would rebound due to the energy absorption, or spelling of the surface[6].

The hardness test was performed for each specimen separately after it was exposed to the corrosion test.

IV. Glossiness Measurements:

The glossiness of all the samples was measured by using Gloss meter. This instrument contains black color stage, where the samples are applied.

After calibration {using control sample of glossiness= 90}, the samples are detected in 45 degree angle. Then the reflection in the device is taken directly as a percentage.

Each specimen glossiness is measured after it was subjected to the corrosion test, in order to calculate its glossiness degree.

Results and Discussion:-

Fig.2 shows the general corrosion rate in MPY of the sets of specimens having double layer of enamel and ground coat at various test temperatures {65°C, 96°C, 150°C, and 200°C} respectively.

In this Fig MPY values are inversely proportional to weight percent of TiO_2 up to 24.5% regardless of the test temperatures maximum MPY value = 0.88 at 23.5% of titania at 200 °C.

This trend is expected since TiO_2 does net works formely due to the strong interionic bonding that enhances both the chemical resistance and the mechanical resistance [4,6].

Also an increase in titania content acts as silica in enhancing acid resistance with added advantage. The coefficient of expansion is also raised slightly and the glass viscosity does not increase as much as by the equivalent amount of silica increment[4].

The coefficient of thermal expansion measurements are listed below:-[9].

Thermal Expansion Coefficient in **Cm/Cm C**

Low carbon Steel	$12.5*10^{-6}$
Ground Coat	$10.5*10^{-6}$
Cover Coat	$9.5*10^{-6}$

These results confirms the compatibility induced by CO-ion in the ground cover and Ti-ion in the cover coat.

The specific concentrations of Co and Ti ions are chosen because they mark points at which the observed was stabilized. The closeness of the thermal coefficient expansion values explains the observed thermal shock resistance and confirms the mechanism by which Co-ions and Ti-ions act in consolidating the glass network of the enamel [5,7].

In Fig.3 comparison of the general corrosion rates in MPY is performed for ground and cover coats. In these specimens three cover coated specimens have different wt content of TiO_2.

This Fig.3 shows that as the solution temperature increases the corrosion rate in MPY increases with in increase in TiO_2 wt content, and the MPY values tend to be stable regardless of the test temperature. This indicates that solution temperature increase causes the stability of high protection of the enameled metal [10].

Glossiness tests for the above mentioned enamels were determined after the corrosion test for these specimens were performed, the glossiness test results are shown in Fig.4, in this figure it could be noticed that higher TiO_2 specimens yield higher glossiness percent (70% -80%) i.e. of less corrosion rates. This glossiness percent is proportional to the increase in solution tested temperatures, which in turn confirms the corrosion test results and the decisive role played by the network formers in supporting the chemical resistance of glassy enameled steel.

Fig.5. shows a set of curves exhibiting the variation in the restitution hardness of the corrosion tested specimens, these specimen were covered with enamels that contained different TiO_2 wt content. In this figure the overall behavior indicates that higher temperature would result in lower rebounding heights or lower restitution hardness. This may be attributed to degree of erosion inflicted on the ceramic surfaces, which is inversely related to the restitution hardness[5] .

Moreover the increase in wt percent of TiO_2 exhibits direct variance with the restitution hardness, as explained above, since higher TiO_2 wt percent has reflected quite positive properties on the cover coat .

Conclusions

1. The ground coat layer has performed quite successful intermediate layer binding both the enameled and the metal substrate, preventing strong acid corrosion in range between 65 C_200 C.
2. Ti_ion bonding in the cover coat enamel plays direct and explicit role in enhancing acid resistance, metal glossiness and hardness.
3. Inexpensive low carbon steel could be successfully used in application in low concentration of sulphuric acid, if coated by ground cover enamel up to 200°C temperature.

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Table 1. Chemical Composition of Low Carbon Steel Substrate Alloy

Metal	C	Si	Mn	S	P	Fe
Wt %	0.14	1.2	<0.010	0.021	<0.01	Remained

Table 2. Solutions used for different enameling stages, and concentrations[2].

No.	Solution	Composition	Temperature °C	Cycle Time Dipping(min)
1.	Alkaline cleaner	34g/l Na_2Co_3 NaOH 4g/l	100	10
2.	Warm Rinse	Water	60	5
3.	Cold rinse-1-	Water	---	5
4.	Pickling	7% H_2SO_4	70	10
5.	Cold rinse-2	Water and 2% H_2SO_4	---	5
6.	Nickel Deposition	7% $NiSO_4 .6H_2O_4$	70	5
7.	Cold Rinse-3-	Water and 2% H_2SO_4	---	5
8.	Neutralizing	1.2g/l Na_2CO_3 0.37g/l NaB_4O_7	70	5

Table 3. Chemical Composition Of ground Coat

and Cover Coat .

Formula	Ground Coat	Cover Coat
SiO_2	48.0	47.5
B_2O	20.0	13.9
Na_2O	18.5	8.5
F_2	1.4	3.5
K_2O	0.51	5.5
Li_2O	0.7	1.5
CoO	2.5	---
TiO_2	6.0	15.5
P_2O_5	---	2.5
ZnO		1.6
CuO	0.3	---
MnO_2	0.5	---
NiO	0.5	---
C_oO		
Total	100%	100%

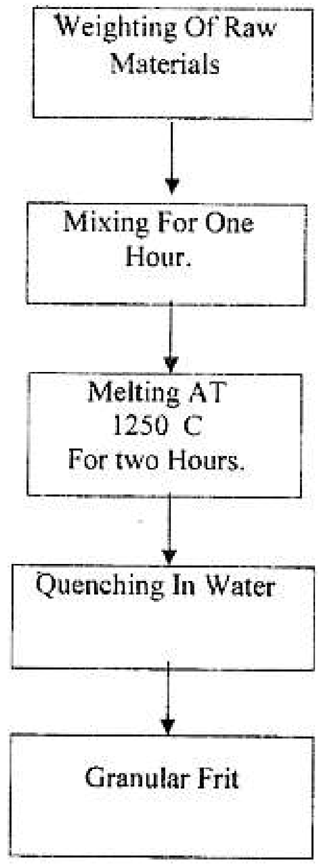
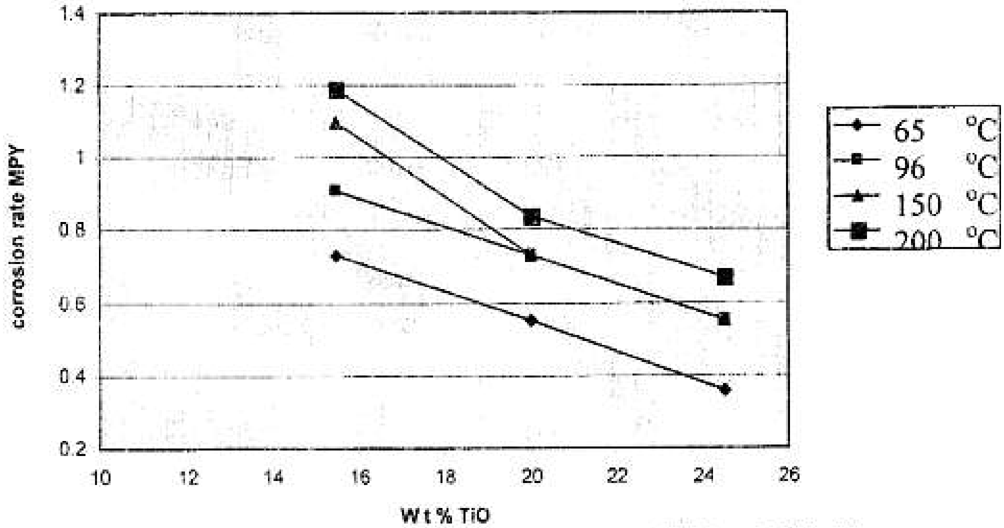
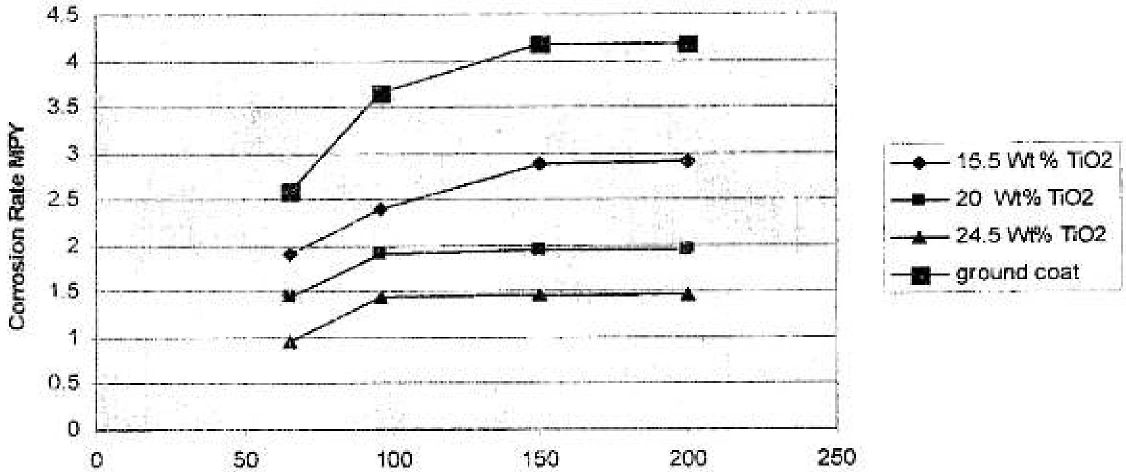


Fig.1. Flow Diagram of Porcelain Enameling Showing Frit preparation.



Fig(2) Relation Between Corrosion Rate MPYand Wt % of TiO_2 at Different Temperatures



Temperature

Fig(3)Relation Between Corrosion Rate MPY and Temperatures For Different Enamel Coating

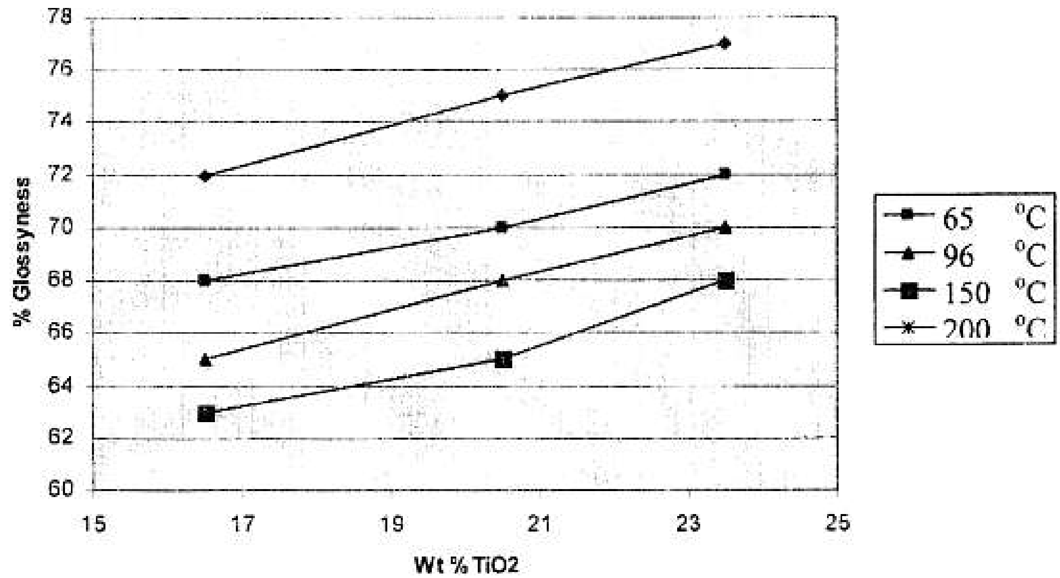


Fig (4) Loss of Glossness at Different Corrosion Temperatures

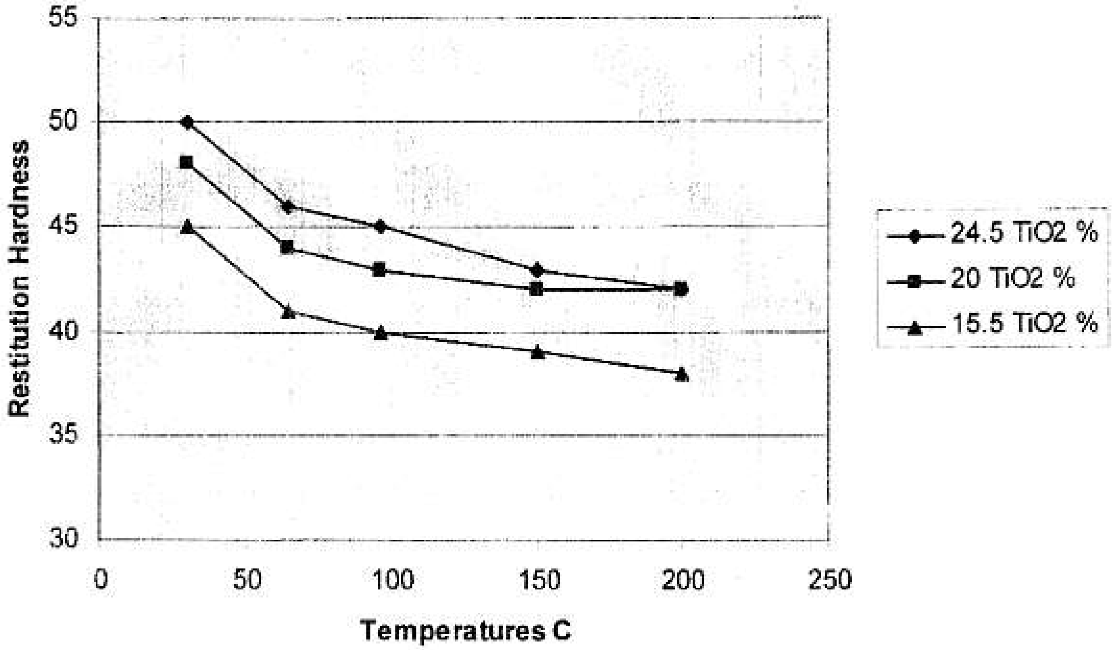


Fig (5) the Variation of Restitution Hardness of Corroded Surfaces with Corrosion Ambient Temperatures