Enameling And Study Corrosion Behavior To Low Carbon Steel

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Abstract

This study includes enameling and study corrosion behavior of low carbon steel (carbon continent =0.11%) in different types of corrosive media like the H_2SO_4, HCL and NaOH both acidic solution (H_2SO_4, HCL) has PH= 2 with resistance acid solution enameling and alkaline solution (NaOH) have PH= 12 with resistance alkaline solution enameling. enameling process includes preparing and applying of frit by ground coat method.

The corrosion rate calculated using weight loss method at temperature range (30, 40, 60, 90)^{o}C for acidic and (30, 40, 50, 60) ^{o}C for alkaline solution. The results indicate that corrosion rate increase with time and temperature for both H_2SO_4 and HCL solution, while corrosion rate for NaOH solution decreases with time due to the formation of unsolvable compounds on sample surface. These compounds may caused insulation laminar reduced corrosion rate, while corrosion rate increases with temperature because distortion of this layer.

طلاء ودراسة سلوك التآكل للفولاذ الكاربوني المنخفض

الخلاصه

يتناول هذا البحث طلاء ودراسة تآكل الفولاذ الكربوني المنخفض (بنسبة كـــاربون 0.11%) المطلـــي بطبقة(Ground Coat) باستعمال كل من حامض الكبريتيك (H_2SO_4) وحامض الهيـــدروكلوريك (HCL) بدرجة حامضية مقدارها (PH = 2) مع الطلاء المقاوم للحوامض وهيدروكسيد الصوديوم (NaOH) بدرجة قاعدية مقدارها (PH = 12) مع الطلاء المقوم للقواعد عند درجات حرارة مختلفة تضمنت ^{o}C (30, 40, 60, 90) لكل من حامضي(H_2SO_4) و(HCL). وعند مدى ^{o}C(30, 40, 50, 60) لمحلول NaOH.وقد تبين إن المعدل تآكل يكون منخفض ويزداد بمرور الزمن كما إن معدل التاكل يزداد بزيادة درجة الحرارة في كل من محلول (H_2SO_4) و(HCL).أما معدل التآكل في محلول (NaOH) فانه يقل بمرور الزمن نتيجـــة تكـــوين مركبات غير ذائبة ملتصقة على سطح المعدن المطلي وتؤدي إلى تكوين طبقة عازلة تقلل من معدل التاكـــل وان زيادة درجة الحرارة تؤدي إلى زيادة معدل التاكل نتيجة تكسر تلك الطبقة حيث يتضاعف معدل التاكل. بالرغم من إن معدل التاكل يزداد بزيادة درجة الحرارة إلا انه يبقى منخفض وضمن المدى المســـموح بـــه وبالتالي يمكن استعمال هذا النوع من الطلاء في التطبيقات العديدة للمعادن والتي تحتاج إلى مقاومـــة تآكـــل جيدة.

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Introduction

In modern technology there are many instances where the required bulk and surface properties do not occur in one material. To overcome this problem ,surface coatings are used [1]. Enameling Coating defined as a thin layer of metallic and organic materials can provide a satisfactory barrier between metal and its environment [2].

Oxide and silicate coatings protect the base (metal or ceramics) from the effect of ambient environment at elevated temperatures, and improve the mechanical properties of the surface and appearance of the ware [3].

Enamel

Enamel may be defined in several ways, which are the process of applying a thin coat of finely ground glass melts and fuses to the metal when heated to high temperature [4].Another defined goating of a glassy substance, which has been fused on to the basis metal to give a tightly adherent hard, finish resistant to many abrasive and corrosive materials [5].

Although this term does suggest a glass coating the American expression (porcelain enamel) conveys to the general public a much better concept of this coating system.

Applications of Enamel

Enamel is a protective coating for metal, which is both attractive and permanent, and for these reasons it is widely used both in the home and in industry. [1]

Many of large kitchen appliance such as cookers, clothes washers and dish washers are finished in vitreous enamel, as also are many of the cooking vessels such as pans and casseroles, many smaller appliances, toasters, food mixers and trays are similarly enamel coated. In the bathroom, many baths, sinks, sink units, cabinets and in some countries the not water strong heaters have a coating of vitreous enamel [4].

Most of heating systems, including gas fires, central heating boilers, space heaters and water heaters are also in vitreous [6].

There are, in addition, other articles scattered throughout most homes. Which are partly decorative in nature, such as lampstands and ashtrays, which are finished in enamel this decorative aspect is further emphasized in small trinkets, jewellery and snuffboxes where the ornamental considerations are even more important enamel panels are used architecturally in both internal and external surfaces. They may be used externally to give an attractive appearance to the building concerned internally to provide protection for surface subjected to wear such as a escalator side panels or turnel walls.

Ground Coat

This enamel coat was applied directly to the bas metal as an intermediate layer between the metal and cover coat, in must serve to produce a film and lasting bond with the metal a characteristic of most ground coats enamels is their content of transition metal oxides, in particular cobalt, nickel, manganese and copper oxide, know as adhesion oxides[7]. Their addition in enamel glass was to promote adherence of porcelain n enamels to iron metal. If used a lone the cobalt oxides is most effective in a mounts of about 0.5 weight percent of enamel [8].

Although the adhesion oxides are used in small amounts, they gave rise to dark colored layer, so that if a lighter color is required a second or "cover coat" is required a single coat chemical resisting enamels applied direct to steel, as a one-coat finish.

Miscellaneous Properties

Chemical Resistance

Since Porcelain Enamels Posses excellent corrosion resistance in a variety of corrosive environments, the enameling process is considered one of several methods of surfaces protection against corrosion [9].

Theories of Enamel Adhesion

The primary aim of all enameling is to achieve a good bond between the enamel and the steel. Many of the complexities of the process are related to this requirement, and an understanding of the mechanisms involved will facilitate the establishment of conditions favorable for the formation of a good bond. It has been assumed that a good bond is one, which fails cohesively. i.e. the fracture surface does not coincide with the enamel / steel surface. Adhesive failure is said to occur when the steel and enamel separate cleanly with no particles of enamel left adhering to the steel or vice versa. Although mainly concerned with the modern techniques for enameling steel, any general account of adhesion should explain all the various enameling systems, which are known to work successfully.

These include the use of cast iron and enamels without adhesion oxides, enameling steels and ground coats, low carbon steels and copper with jewellery enamels [10].

Mechanical Adhesion Theory

Interatomic bonding suggested for situations which are athick and amonomolecular oxide layer in "A" and "B" respectively as shown in figure (1) [12], originally it was believed that the enamel / metal bond was entirely mechanical in nature and that dovetails or (anchor points) could be recognized and counted under the optical microscope. In work on the ground coat system it was suggested that the adhesion oxides were reduced to metal, which subsequently plated out on to surface of the steel. This promoted the formation of an electro chemical cell, with the cobalt-cated area being protected from oxidation and the uncoated areas oxidized. It was thought that this mechanism led to undercutting of the protected area the formation anchor points[10, 11].

Chemical Adhesion Theory

Chemical adhesion theory that a ferrous phase was present at the interface and this was responsible for bond formation figure (1) [15].

This ferrous phase has usually been taken to be the layer of enamel adjacent to the interface into which the iron oxide has diffused.

Most subsequent theories have been on this concept of a bond between the steel and enamel layer contain substantial amounts of iron oxide.

Later modifications have been concerned with chemical or thermodynamic criteria which must be met either in the enamel or at the interface. Most authors have suggested with the oxide of the substrate metal it is then believed that a type of thermodynamics equilibrium exists a cross the interface, thus giving a strong bond [13, 14].

Experimental Part

Metal composition

As shown the samples carbon continent less than (0.15%). The composition of sample determine by using spectrometer. Table (1) shows the chemical continent of sheet low carbon steel with sample dimension (1x1x1) cm3.

Metal Surface Preparation

Enameling process cannot be successful unless the metal is thoroughly cleaned and kept until a final coat is fired. Simply touching the surface by hand may cause defects.

The pretreatment line of metal consists of various processes as follows:

Degreasing

Preservative oil, drawing grease and pressing lubricants, these materials can cause problems if carried to the next process, therefore the degreasing process is used to process the dirt, dust, oil and grease.

Pickling

The purpose of pickling process is to remove rust and scales from the degreased surface, which is simultaneously roughened, roughening is most important for ground coat enameling. The composition of acids are used for pickling sheet steel in project is hydrochloric acid with (20%) concentration. By immersion it in solution for 10 minutes.

Rinsing

Effective rinsing after each stage of the enamel cleaning process is essential to ensure that no carry-over of liquid can transfer from one stage to another.

Drying

After removed from the rinsing of acid etch, the component is dried at temperature of about (110 - 120)^{o}C this ensure quick and complete application of the enamel slip.

Preparation Frits

Frit is a water-quenched glass; it is a brittle and friable material. The purpose of fritting is to render water soluble glass formers insoluble, and to convert highly refractory material into more fusible form. Volatile products of decomposition removed during process.

The frits making process is similar to glass melting. The furnace is scaled down for the smaller amounts of materials melted and requirements for product homogeneity are not sodemonding the raw materials are also similar to those used in the glass industry, but mostly with lower purity requirements in comparison with glasses.

Enamel frits are containing larger amounts of B2O3, alkalis, fluorides and frequently also TiO2 Table (2) shows the composition of tow type frit is prepared.

Ground coat for steel contain as significant ingredients adhesion premoting oxides (NiO or CoO).Opacity of white enamels is attained mostly by means of fluorides, phosphates, ZrO2, which are constituents of the melted frits. the melt process occur at temperature about (1000 – 1400) ^{o}C.

In this project melted frits at 1300 ^{o}C at rate 6 ^{o}C/min percent in electrical furnace and stabled to (10 min) then the melt frits is quenched in water to cause granulation which is then crushed into partical size less than 0.01 mm by mill grinding.

Preparation of Enamel Slip

The conventional enameling process involving milling of the frit particles and the suitable additives in the presence of water to form a stable suspension which has a consistency similar to that of a thick coffee cream. The ingredients of the mill batch are carefully controlled. The amount and parity of all materials in the mill affect the properties of the amount and parity of all materials in fired enamel. Ground-coat enamels are ball milled to a degree of fineness of 95% solid particles smaller than (74μm).The composition of slip is shown in table(3).

Applications and Fusing of Enamel

Application of Enamel Slip

The application method refers to the technique employed. In coating the metal substrate with a uniform coating of ground frit, applied by wet or dry systems. The methods used to coat the component will be dependent on many factors, including shape, size and finish required. The wet method is used as shown below.

Wet Application

This established method of powder application, most enamel is milled and applied using water as the suspending medium. Although there are two basic means of application, dipping and spraying wet method by dipping is used in project because it applied without any change in phase. Since slip fired at (750 - 850) oC while the dry method would to change of phase because it transformation occurs[10].

Firing **Process**

Firing process represents the last step in application of enamel on metal sheet. When heating to the firing temperature at (850) oC and within the firing time, strongly adhering smother and hard enamel coat in its final state is formed[8].

Corrosion Resistance

Tests for corrosion resistance of porcelain enamel was made by using wet loss method (complying with Din 51 157), which is commonly used, for porcelain enamels in chemical media.

A porcelain enamel sample has dimension (1×1×1) cm was exposed to acidic solution of H2SO4, HCl (purchased from Fluka) PH = 2 for 2.5 hrs at temperature range (30 - 90) oC and alkaline solution NaOH (purchased from BDH) PH = 12 for 2.5 hrs at temperature range (30 - 60) ^{o}C. [7, 8]

The corrosion rates were estimated according to the equation.

$$CorrosionRate(mdd) = \frac{Weightloss(mg)}{Area(dm^2).Time(day)}$$

Results and Discussion

Acidic Solution

In general strong mineral acids are more severe in their attack on enamel, figures (2), (3) show the corrosion rate for acidic solution at vary temperatures of acidic resistance sample using H2SO4 & HCl acids.

From the figure the corrosion rate increase with the time because of the corrosion product soluble. Increase of temperature plays a major part in acid resistance, with increase of temperature will increase of corrosion rate.At high temperature nearer the boiling point the greater the rate of attack where are almost doubled. But it is recognised that vitreous enamel processes good acid resistance.

Alkaline solution

Figure (4) shows the corrosion rate for alkaline solution at vary temperatures of sample (2) by using NaOH solution. It seen from that figure basic attack is accompanied by a deposit on the enamel this deposit decreases the corrosion rate with the time (this contrasts with acid attack)because that deposit behave as insulator layer between the sample and corrosive media.

The rate of corrosion is very dependent upon temperature. Corrosion rate increase with temperature increase.That increase at boiling temperature being several times greater than that at room temperature.

Figures (5), (6), (7) where shows corrosion rate at different temperature at 2 hours where the corrosion rate increases with temperature increase in very type of acidic basic solution that figure shows although the corrosion rate increases with temperature but stay tower and within the permissible range.

Conclusions

1. Vitreous enamel processes good acid and basic resistance.
2. Corrosion rate of acid solution increases with time.
3. Corrosion rate of basic solution decreases with time.
4. Corrosion rate for both acidic and basic solution increase with temperature increases.
5. Increase of corrosion rate within stay permissible range.

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Table (1) chemical composition of Used sample

Metal	C	Si	P	S	Cr	Mn
Low carbon steel	**0.11**	**0.08**	**0.022**	**0.99**	**0.05**	**0.59**

Table (2) shown the composition of tow type frit is prepared [14]:

Factors	Mass concentration %								
	Na_2O	K_2O	CaO	B_2O_3	ZrO_2	Li_2O	SrO	CoO	SiO_2
Acids resistance	12.0	2.0	3.0	2.0	9.0	6.0	4.0	1.0	61.0
Basic resistance	15.0	3.0	4.5	3.0	12.0	3.0	6.0	1.0	47.5

Table (3) shows the compassion of enamel slip.

Materials	Weight (gm)
Frit	100
Clay	4
Borax	1
Water	50

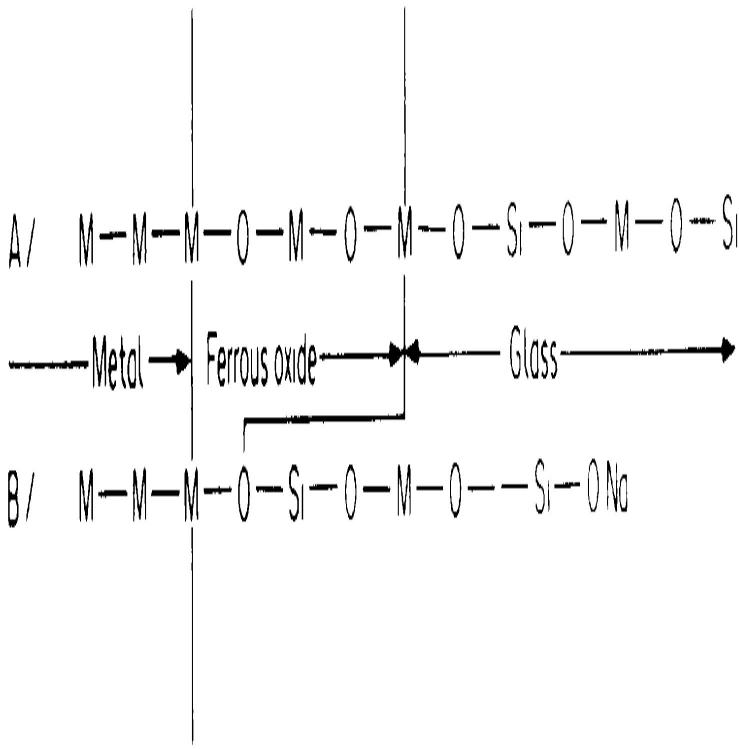
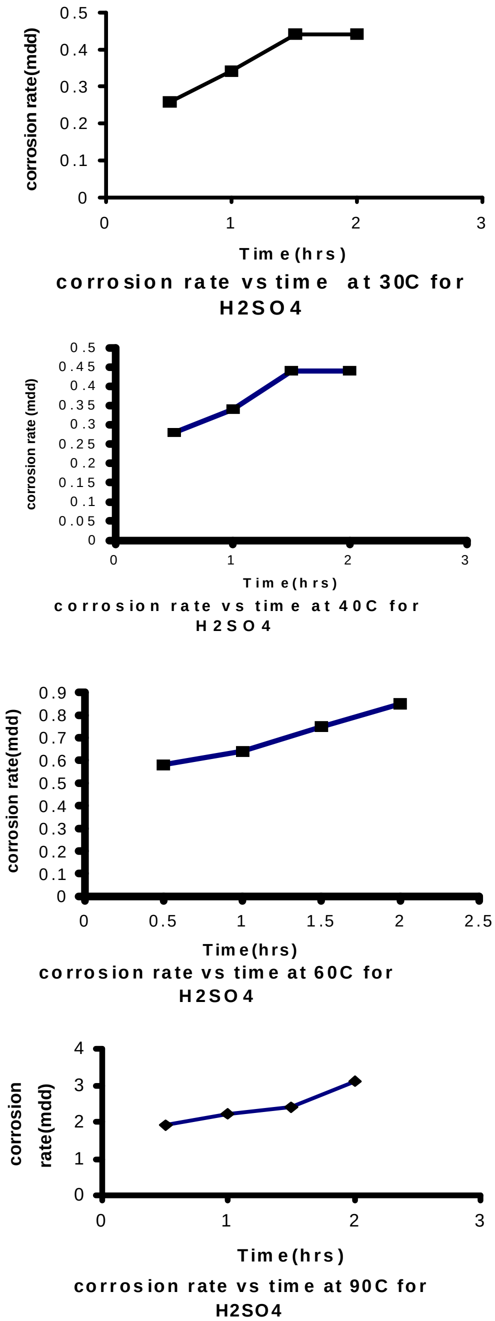


Figure (1) Shows interatomic bonding suggested for situations in which there is thick and a monomolecular oxide layer in A and B respectively. [15]



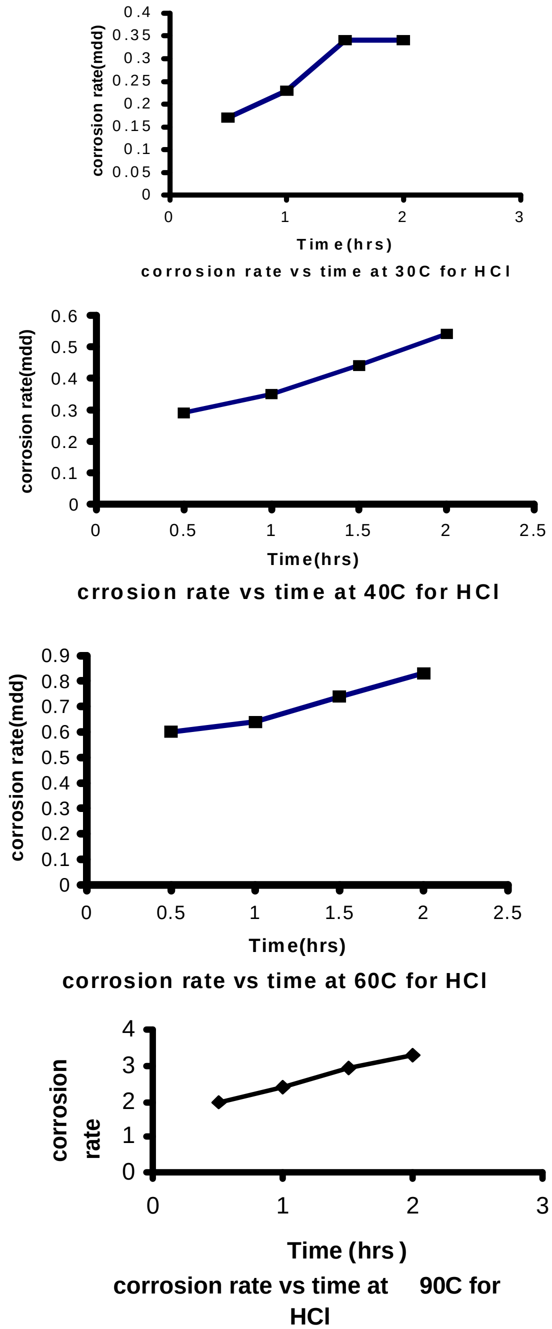


Figure (2) Shows corrosion rate for H_2SO_4 acid solution at different temperature.

Figure (3) Shows corrosion rate for HCL acid solution at different temperature

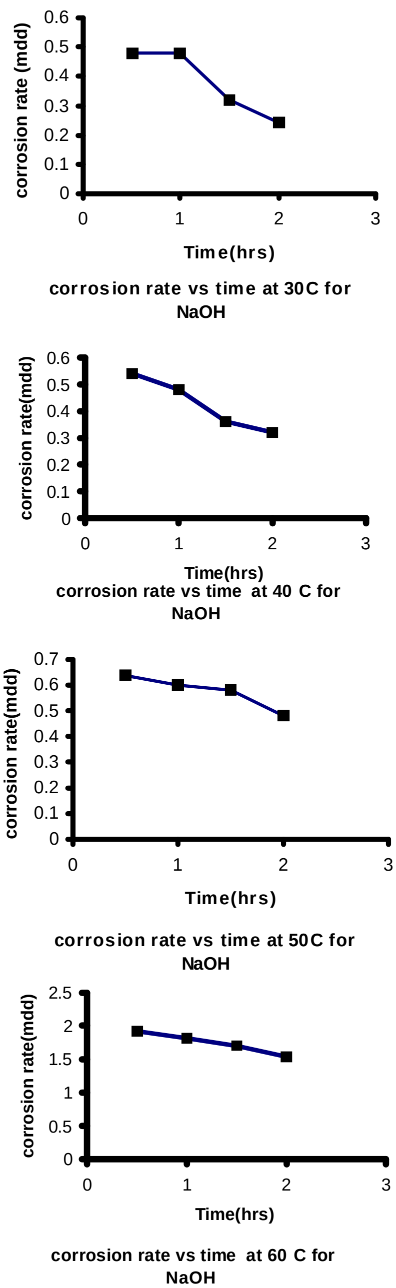


Figure (4) Shows corrosion rate for NaOH acid solution at vary temperature

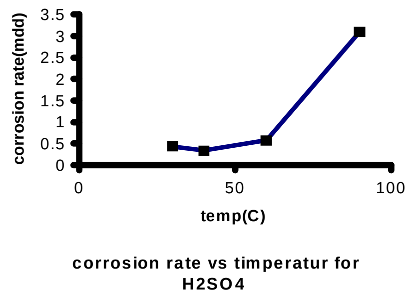


Figure (5) Shows corrosion rate for acidic solution at vary temperature for H_2SO_4

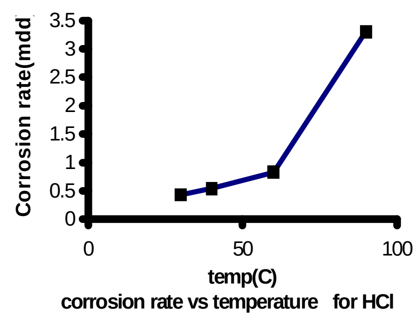


Figure (6) Shows corrosion rate for acidic solution at vary temperature for HCL.

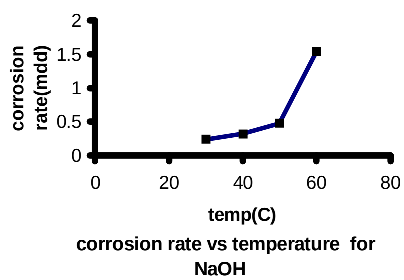


Figure (7) Shows corrosion rate for alkaline solution at vary t emperature for NaOH solution.