The Performance of Ceramic Enamels Containing CoO-Additives

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Abstract

Ceramic coatings (enamels) are normally to protect and isolate metallic surfaces against aggressive environments. In the present work, a set of low alloy steel plates are coated with a special ceramic – glass layer. The stability of which is investigate in terms of its nature adhesion, and the nature of the protected metal surface. These are considered to control the final performance of the laminated composite. Factors which are investigated are those related to the mechanical integrity of ceramic coat, like the porosity, hardness, glossiness, and thermal resistance. And those related to the state of bonding between the metal surface and the protective coating like adhesion index, coat thickness, and the percentage of carbon present in the low alloy steel surface. Moreover, the corrosion behavior of the coated metal surface was studied to investigate the performance of this protective barrier. During this work some measures were taken in an attempt to modify and develop this protective barrier by adding of various amounts of CoO to the basic ceramic mix of coat.

It is notice that the overall coat thickness would progressively reduce stability and encourage the pore formation. However the addition of CoO to a certain limit of concentration has progressively enhanced the adhesion with metal surface, the glossiness of the ceramic barrier, its thermal resistance.

Key words: Enamel, adhesion, ground coat, covers coat, corrosion resistances, and cobalt oxide**.**

أداء طبقة طلاء آلمينا السيراميكي بإضافات نسب من أوكسيد الكوبالت (CoO)

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الخلاصة

يستخدم طلاء السيراميك (آلمينا) عادة لحماية وعزل سطح المعدن ضد أوساط التآكل. وفي هذا البحث تم اختيار مجموعة من صفائح الحديد قليل الكربون (law alloy steel) وطلائها بطبقات من الزجاج- سيراميك ، والتحقق من إستقرارية الالتصاق الطبيعي وطبيعة حماية سطح المعدن من خلال السيطرة على المنتج النهائي للمركبات الصفائحية (طبقات الطلاء) . تم دراسة العوامل التي تحقق السلامة الميكانيكية لخواص الطلاء السيراميكي مثل المسامية ، الصلادة ، اللمعان والمقاومة الحرارية. وهذه العوامل لها علاقة بحالة التلاصق بين سطح المعدن وطبقة الطلاء من خلال مؤشر التلاصق (adhesion index)، سمك الطلاء ، ونسب الكربون في سطح المعدن. علاوة على ذلك تم دراسة تصرف التآكل للتحقق من إمكانية صمود طبقة الطلاء. وفي هذه الدراسة تم إجراء بعض القياسات لأجل تطوير إمكانية الحماية من خلال إضافة نسب مختلفة من أوكسيد الكوبالت (CoO).

وجد أن ازدياد سمك طبقة الطلاء يقلل من استقرارية الالتصاق ويشجع في تكوين الفقاعات. في حين لغاية نسب معينة من أوكسيد الكوبالت يزيد من التصاق طبقة الطلاء بالمعدن ، واللمعان ، ومقاومة التآكل والمقاومة الحرارية.

الكلمات المفتاحية: طلاء المينا ، التلاصق ،طبقة الأساس ، طبقة الغطاء ، مقاومة التآكل ، اوكسيد الكوبالت

Introduction

Virtuous enamels are classified as a ceramics which possess many desirable properties [1]. The ceramic family is always associated with some excellent like chemical inert, heat resistance high surface hardness, and resistance to degradation by ultraviolet light. Modern engineering and technology demands such a corrosion resistance coat or barrier, which has a broad spectrum of affectively under a wide range of hostile environment [2-4]. It is also essential that these protective barriers should have high resistance to thermal shock and mechanical impact, to reduce the chances of failure for reasons other than corrosion. It might be of real interest to developed ceramic / glassy barriers which fulfill the above mentioned specifications.

Ceramics highly have a drawback with its poor impact toughness, but when composited with a metallic back plate toughness is improved specially when the larger of structure is well bonded [5,6]. Much of the work in this field since the thickness have concentrated on the adherence and bonding among the ceramic and metallic layers. One of the major achievements is when the metal surface is saturated with a layer of its oxide such that this oxide must be soluble in the glassy barrier and not possible to be reduced by metal [7-9]. Marcus [10] and Lelia [11] investigated the adherence of glassy coatings on steel as function of the presence of adherence promoters by testing their impact resistance. They reported enhanced adherence strength with increasing content of Co_3O_4 Up to a limit of 1.5 %. References [12,13] of methods were used for the evaluation of the chemical resistance of porcelain enamels under various conditions of pH, time and temperature.

Similar tendency was reported for use NiO of up to 2.5% with a difference in the process of introducing these oxide agents. However, it seemed that technology of adding the NiO has some reflection on the final behaviors of the protective glass barrier [14,15] .This work aims to studying the effects of CoO Concentration in the ceramic glass enamel layer coating low alloy steel surface , which is commonly used in various industrial applications .

Experimental Procedure

Low carbon steel substrates (20mm × 20mm) with (3mm) thickness whose chemical composition is measured by spectrometer instrument (Bergenalmer-W.G. in Materials Engineering Department – Technology University) as shown in table (**1**), are enameled with a glass – ceramic coat after being subjected to mechanical and chemical cleaning. The later process leaves the surface with remnant roughness which promotes adhesion.

The mechanical cleaning includes sand plats by a silicon carbide as a first stage to have a rough surface. The chemical cleaning includes many steps:

1- Alkaline cleaner.
2- Warm rinse.

3- Cold rinse.
4- Pickling.
5- Cold rinse.
6- Nickel deposition.
7- Cold rinse.
8- Neutralization

These steps with details as shown in table (2) [16].

The required glass ceramic frit was prepared from the oxides constituents listed in table (3), which were mixed properly and after that melted in a ceramic crucible in a furnace for 2 hrs at 1300°C. The molten glass is quenched in cold water fragmenting into cores grained granules (frit). After milling the cores frit some additives were added as shown-in table (4) to make a suspension (slurry) called the slip, suitable for application to metal surfaces by spraying with gun.

The sprayed surface is then left to dry in air, then fired at temperature ranging between (820°C and 840°C) per four minutes in order to enable the glass particles to melt and flow over the surface forming a thin glassy film adhered to the surface the test made throughout this work included the coefficient of thermal expansion of the glass- ceramic coat which was measured by dilatometer in accordance to ASTM slandered (C539) [17].The thickness of the coat were measured using special device made by elcometer Instruments Ltd.

All adherence measurements were obtain in accordance to standard adherence tests issued by the Institute of Vitreous Enamels T 29 [18], the thickness of coat about 0.6– 3 mm.

Thermal shock resistance test were made in accordance to ASTM 385.58 standard methods [19]. Moreover acid resistance tests were made according to DIN 51 157 standard [20], which is normally used in cases of enamel coatings. In this case the coating is exposal to solution of 20% concentrated sulfuric acid for 48hrs at 96 °C.

The porosity of the fired enamels (both open and closed) was established by using the following formula [21]:-

$$P\% = [\frac{W - D}{W - A} \times 100]$$

Where P is the percentage porosity %, W is the weight of saturated specimen in air, D is the weight of dry specimen in air and A is the weight of saturated specimen in water.

Table (1) Chemical composition of the metal substrate

Composition	Wt%
C	0.12
Si	1.21
Mn	1.29
P	0.010
S	0.022
Cr	0.021
Ni	0.37
Mo	0.019
Cu	0.061
Al	0.055
Ti	0.069
V	0. 12
Nb	0.085
Co	0.068
W	0.017
Pb	0.007
Fe	96.456

Table (2) Showing the chemical process for cleaning surface metal [16]

No.	Solution	Composition	Temp.(°C)	Time(min)
1	Alkaline cleaner	34 g/l Na_2CO_3 + 4 g/ l NaOH	100	10
2	Warm rinse	Water	60	4
3	Cold rinse	Water	room	4
4	Pickle	H_2SO_4 7%	70	10
5	Cold rinse	Water H_2SO_4 2%	room	4
6	Nickel deposition	$NiSO_4 .6H_2O$ 7% g/ l	70	10
7	Cold rinse	Water, H_2SO_4 2%	room	4
8	neutralize	Na_2CO_3 1.2 g/ l + $Na_2B_4O_7$ 0.375 g/l	70	5

Table (3): Chemical composition of ground coat

Formula	Ground coat Wt%
SiO_2	50
B_2O_3	19.5
Na_2O	18
F_2	1.63
K_2O	1
Li_2O	1.5
CaO	2.5
TiO_2	5
CuO	0.5
MnO	0.6
CoO	1

Table (4): Enamel composition for ground coat suspensioin

Component	part
Ground frit	100
Kaolin	6
Borax	1
Water	50

Results and discussion

Metal surfaces have to be engineered prior to their use or operation in the various non-friendly environments. Various coating may be designed to perform affectively as a barrier isolating the metallic surface from these environments .The mechanical integrity of this barrier is of prime important to its operational effectiveness and life time. on the other hand, porosities remnant in the bulk of the ceramic barrier in another very important factor .They may undermine the mechanical integrity since they pose as point, it may be noticed that this addition of CoO has exponentially reduce the percentage porosity in the ceramic barrier. An addition of about 2wt% CoO has eliminated about 75% of the remnant porosity .Such a value may be considered as a sizable improvement in the quality of the ceramic barrier. It has may be improved the consol suggested that the introduction of the Co^{+2} ion has progressively action process of the ceramic- glasses barrier a glassy phase formation may have encourages the fusion of the ceramic particles ,and filled most of the pores such as possibility may be confirmed by the behavior shown in Fig(1).

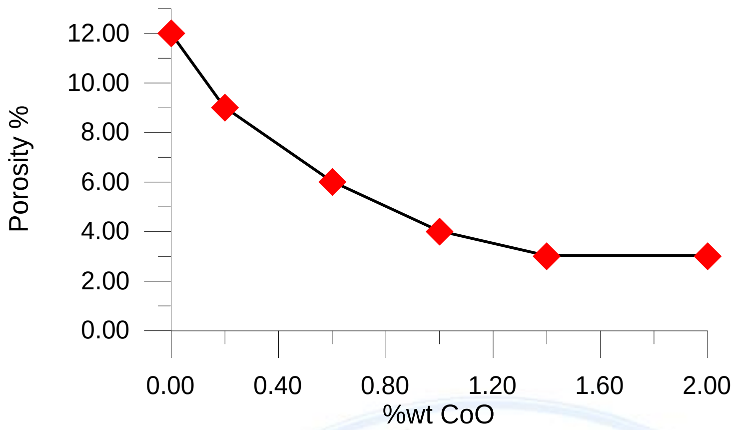


Fig (1): Relation between porosity and wt % CoO for ground coat.

The hardness of the ceramic is plotted as a function of CoO percentage in the ceramic mix as shown in Fig (2). It is exhibited that this addition enhanced the hardness value, when the presence of about 1%wt CoO has enhanced the hardness by about 75% of its original value. This improvement in hardness, due to pore elimination process mansion above.

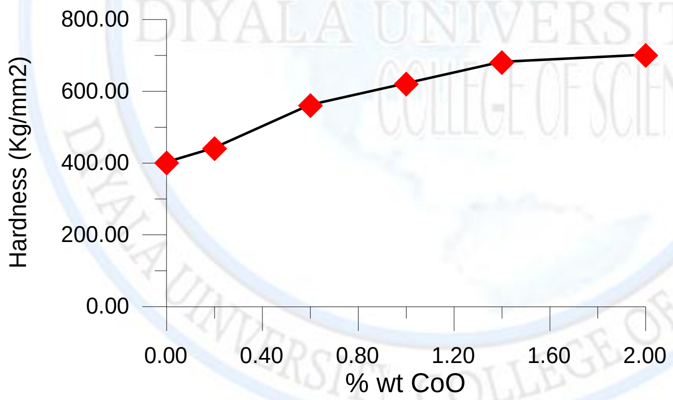
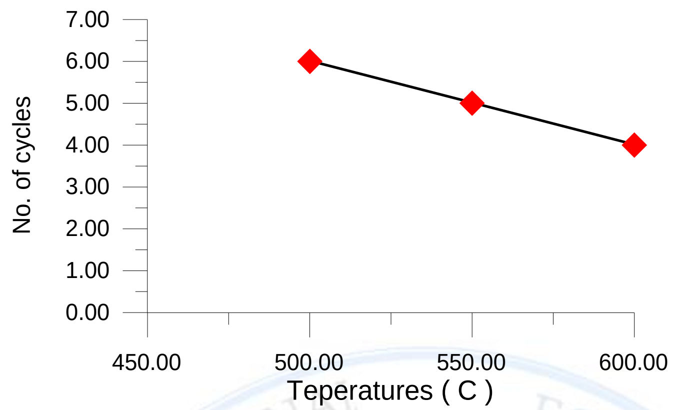


Fig (2): Relation between hardness and wt% CoO for ground coat

Another factors which relates the mechanically stability of the ceramic barrier is its thermal resistance to thermal shocks. Fig (3) show the number of cycles at varies temperature drops progressively as the test temperature with 1%wt CoO.



Fig(3) Relation between thermal shock resistance and temperature.

They suggestion that the coefficient of thermal expansion might have been enhanced by the Co $^{+2}$ ion which quite logical since this ion is considered as modifying ion when taking part in forming a glass structure. The other factor which affects the service life of the ceramic protective barrier is the state of its bonding with surface of the metal to be protected. An essential condition for the success of such protective measure is the adherence between the metal surface and the ceramic barrier, which is related to the nature of both materials .In the present work the metallic surface is sensitized mechanically (sand blasting) or chemically (flashing) .

The adherence index for this metal ceramic system is evaluated as histogram in Fig(4). Comparing varies ceramic enamel containing different oxide additions (CoO, NiO, Sb_2O_3, MnO_2, CuO, CdO).The ceramic barriers Containing seem to exhibitive the higher adhesion index among the set ,covering both sensitization.

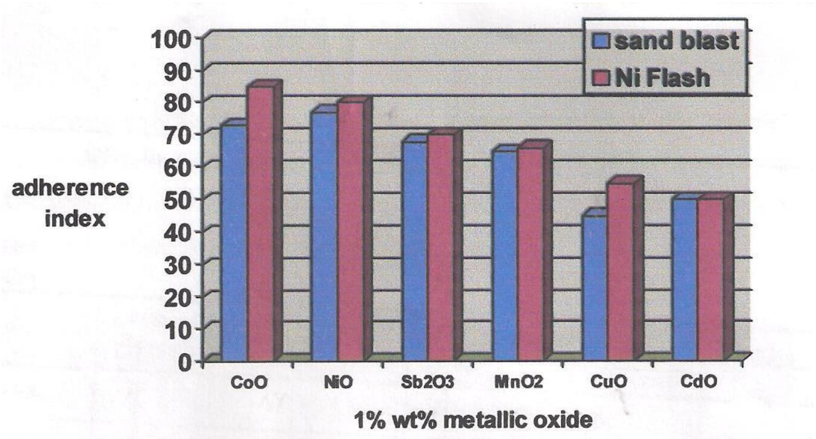
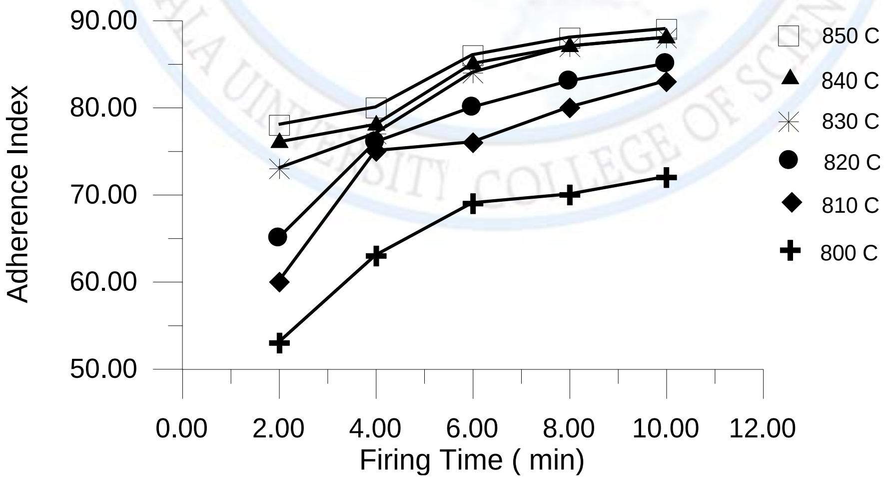


Fig (4): Adherence index as a function of 1% metallic oxide smelted into a porcelain-Enamel ground coat showing the effects of metal reparation.

Techniques mention above, longs firing periods and higher firing temperatures for metal - ceramic system seem to promote the adhesion of the ceramic barrier to the metal surface with 1%wt CoO as shown in Fig(5). By progressively improving the mechanical interlocking mechanism between them, via a further ceramic surfaces compaction which would enhance the inter phase contact area when 75% of the porosity is eliminated. Because exhibited a lower index, such an increase in the thickness of about 300%reduced.



Fig(5): Relation between firing time and adherence index at different temp.

Relation between adherence index and thickness for ground coat as shown in Fig (6), seem to affect on stats of adhesion here thicker ceramic the adherence index less by about 30%. Suggesting that thicker barriers might induce the possibility of mismatch between the two surfaces (metal and ceramic), because the increased rigidity of the ceramic barrier.

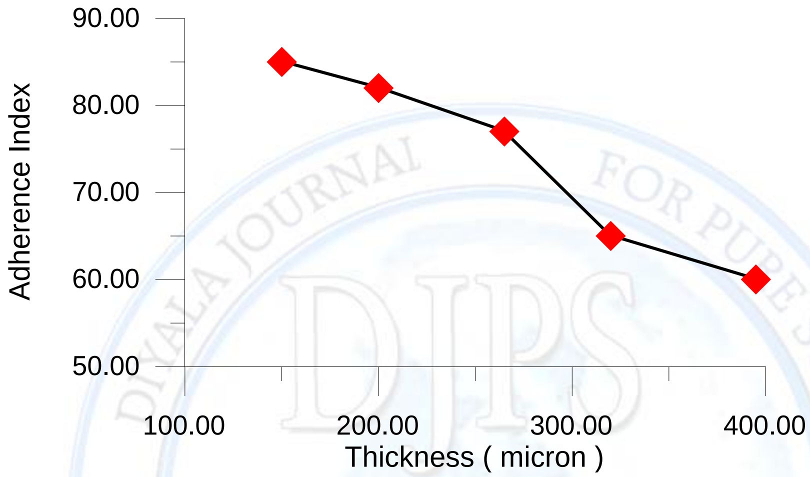


Fig (6): Relation between adherence index and thickness for ground coat.

On the other hands the increased carbon contain of the low alloy steel plate has also affected negatively on the adhesion index as shown in Fig(7). Since an increase of carbon by ten times reducing the adherence index by about 35% which might be due to un enhanced state of mismatch between the two materials.

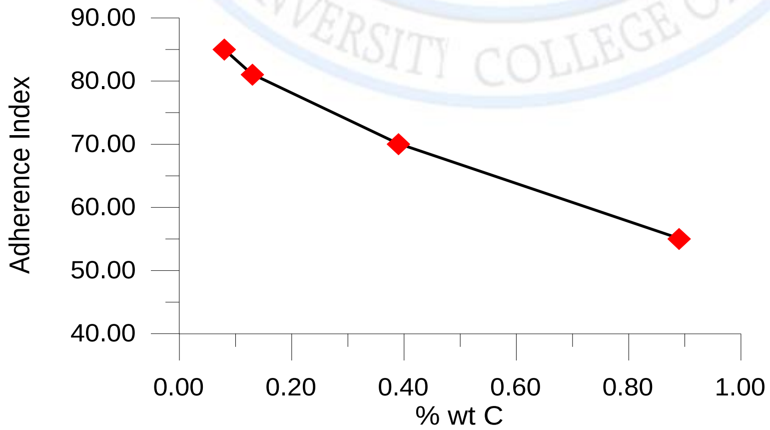


Fig (7): The Effects of wt% of carbon on the adherence index for ground coat.

Finally, the performances of the protection barrier is also depended on the operation environment, since higher temperatures from (65 ºC–to 200ºC) enhance the corrosion rate of metal by factor of 13% suggestion that the different thermal expansion and the possible crack initiation higher have pricing role in this observation, since a saturation behavior is clearly absorbed in Fig (8).

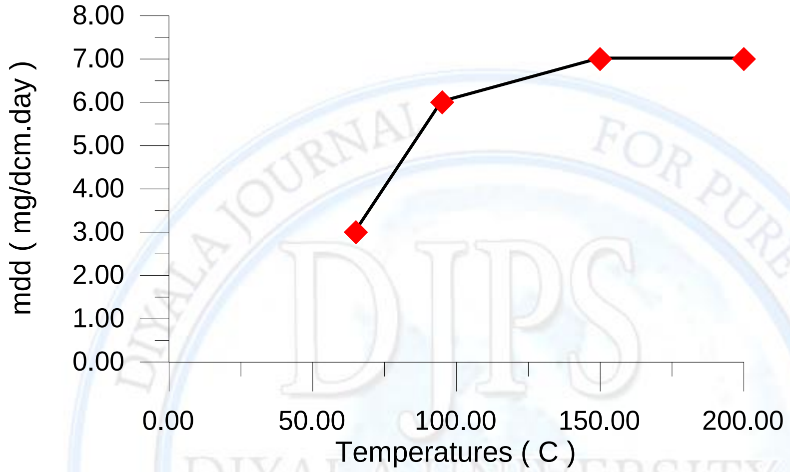


Fig (8) Relation between corrosion rate (mdd) and temperatures for ground coat.

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