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Studying The Effect of Zircon Dioxide on The Corrosion Resistance of Porcelain Enamel

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Abstract

Among various coating systems for industrial and engineering applications, glass–ceramic coatings have advantages of chemical inertness, high temperature stability and superior mechanical properties such as abrasion, impact etc as compared to other coating materials. Besides imparting required functional properties such as heat, abrasion and corrosion resistance to suit particular end use requirements, the glass–ceramic coatings in general also provide good adherence, defect free surface and refractoriness. This research tends to produce a cheep and effective glass- ceramic coating from glass cullet and different percent of crystallization agents ZrO_2, and study the final corrosion resistance properties of them. After several set of acid resistance testing at temperatures range (25, 50, 75,100,125 ^oC) it has been found that porcelain enamel with (4 wt %) ZrO_2 has the best acid corrosion resistance.

Keywords: Glass and glass – ceramic coatings; enameling; coating properties

Introduction

The control of corrosion is based on preventing the reaction between metal surface and its environment One of the methods of preventing corrosion is the protective coatings (surface coatings) [1]. Corrosion resistance coating materials and their application are widely used by different industries. Coating systems are known such as metallic, organic and ceramic coating [2]. A coating is defined as a thin layer of metallic, organic, or ceramic materials which can provide a satisfactory barrier between the metal and its environment [3].

Modern technology uses number of surface coating materials applied using different deposit technologies like physical vapor deposition, and chemical vapor deposition, for different industrial and engineering applications [4]. In recent years, dramatic improvements in property of the glass–ceramic coating systems have been achieved by tailoring the microstructure of the glassy oxide coating matrix either by addition of secondary phases or by in situ crystallization of glassy oxide coating after application [5].

Wear is a gradual digressive process, whereas fracture occurs as a sudden failure. In a study conducted in late eighties, it was reported that cost of wear in 2007 was ~ $ 800 billion/year in USA only [6]. The advantage of a glass–ceramic coating is that it is chemically inert, can withstand high temperature (up to~ 1000°C) and has superior mechanical properties compared to polymer and other non-oxide coatings, paints, metals, rubbers, etc. Polymers can generally withstand a temperature of ~ 250°C and in rare instances; it can go up to 400°C. A glass ceramic coating (table 1) often allows more flexibility in design as it can withstand much wider mechanical and thermal abuses [7].

Crystallization is the method by which a glass can be transformed into a glass–ceramic material. Thus, crystallization is the process by which the regular lattice of the crystal is generated from the less ordered amorphous, super critical liquid structure. In its simplest form, crystallization is observed when a melt of single pure element or compound is cooled; conversion from liquid to solid state occurs at a fixed temperature for a given pressure and is known as the freezing point. Thus, if a glass composition containing suitable nucleating agents is heated from room temperature to the nucleation temperature a large number of nuclei can be generated within the mass of glass. When glass is further heated to the crystallization temperature, crystals will grow on these nuclei leading to the transformation of the glass into a fine grained glass–ceramic material.

The types of crystals that appear and the microstructure of the glass–ceramic depend on the initial glass composition, the nature and amounts of the nucleating agents added and on the heat treatment schedules. The purpose of using a glass–ceramic coating is to prevent abrasion, corrosion, thermal failure and oxidation during different application of metals. These are the primary objectives for choosing a glass–ceramic coating against all other types of available coating materials and its ranges of application [8 – 11].

Experimental Side

The steps of experimental work according to (ASTM 2436/M006 preparation of metal substrate for enameling)

1) Selection of substrate

Substrate is a sheet of low carbon steel with carbon content not more than 0.2% as listed in table (1) illustrates chemical analysis of substrate metal in ministry of science and technology/material science directorate/ceramics material center.

2) Chemical cleaning and degreasing

This step is carried out to remove oil, grease and other organic impurities by using organic solvents and alkaline solutions. The first step was cleaning the substrate from the animal and vegetable fats by saponified with alkalis and the soap formed is washed off while mineral oils are removed as emulsion. Mixing/stirring of the solution and heating to 80–100°C to accelerate the process. The pH of the washing solution which contains 35 g/L of Na_2CO_3 and 4g/L of Na OH was 10 depending on the degree of contamination the substrate is rinsed with overflowing water for complete removal of traces of adherent cleaning solution. After this, three important steps are to be followed very cautiously in order to achieve proper coating.

3) Pickling

After chemical or thermal degreasing, the rust and scales are removed from the metal surface by immersing the articles in an acid solution. Pickling in H_2SO_4 improves the quality of the surface. The parameters to be controlled are the acid strength, iron content in solution, sludge and pickling time (which should be minimum to avoid hydrogen absorption).

4) Nickel flushing

After pickling, the metal pieces are immersed in a solution of ($NiSO_4.6H_2O$) in order to deposit a thin layer of metallic nickel on the metal surface which prevents fish scale and copper head formation and promotes adherence.

5) Neutralizing

This process removes the acidic residue adhering on the metal surface in order to prevent rusting on the metal surface during drying. An alkaline solution used for the purpose contains 0.4 wt% Na_2O and is prepared by dissolving Na_2CO_3 and $Na_2B_4O_7.2H_2O$ in the proportion of 2: 1 in water. The operating temperature is maintained at 60–70°C. Two neutralizing baths were used, the first being relatively stronger than the later. After neutralizing, the moisture is removed from the clean metal surface by heating in an oven at 150–200°C for 10 min.

6) Preparation of coating materials

After careful selection of glass cullet which was analysis by chemical and crystallization agent they were weighed according to wt% listed in table (2), mixed, melted and fritted. The frit (glass) is ground in a ball mill type (Retsch. Tech. Germany) in wet condition. During wet milling certain mill additives, clays and electrolytes are incorporated. A thick creamy suspension (slip) is produced for application over clean metal surface. Ceramic coating was applied by spraying and firing at 980?C for two hours.

7) Chemical corrosion tests (ASTM 4562)

A) At room temperature (25 ^oC) and 10% concentration.

I. Weight the specimen before immerse in HCl to find (W_1).
II. Immersed the specimen in the HCl at concentration (10%), after (10hr) we discharged the specimen from the acid & find weight (W_2), then immersed the specimen in fresh solution at the same concentration solution for (15hr) &find weight (W_3), immersed the specimen in fresh solution at the same concentration for (20hr) &find weight (W_4), finely immerse specimen for (25hr) & find weight (W_5).

B) At different temperatures and 10% concentration.

I. Weight the specimen before immerse in HCl to find (W_1).
II. Immerse the specimen in the HCl at concentration (10%) and 50^oC after (10hr) we discharge the specimen from the acid & find weight (W_2), then immerse specimen in the same concentration solution and temperature for (15hr) &find weight (W_3), immerse specimen in the same concentration and temperature for (20 hr) &find weight (W_4), finely immerse specimen for (25 hr) & find weight (W_5).
III. Repeating work of step (II) with different temperatures (75 ^oC, 100 ^oC, 125 ^oC), from citric acid.

8) Microstructure was determined by light microscope testing using a microscope type: Nikon, m773346, Japan (1* 700 X).

Although weight loss method considers an old method but we use it instead of the polarization method because the ceramic enamel is an insulator material. The expression mil per year is the most desirable way of expressing corrosion rates and will be used throughout this text. This expression is readily calculated from the weight loss of the metal specimen during the corrosion test by the formula given below [1]. The set of instrument and devices which have been used for testing are illustrate in figure (1).

$$mpy = 534W/DAt$$

Where:
W= weight loss in (mg).
D= density of specimen in g/cm^3
A= area of the specimen in (sq. in.).
t= exposure time in hr.

Table (1) Chemical Composition of metal substrate.

Element	Low Carbon Steel (wt. %)
C	0.12
Cr	0.021
Cu	0.061
Mn	1.29
Ni	0.37
P	0.010
S	0.022
Si	1.21
Ti	0.069
Fe	96.827

Table: (2) Composition of enamel frits.

Oxide	Frit (1) (wt. %)	Frit (2) (wt. %)	Frit (3) (wt. %)
SiO_2	69.05	٦٧.٠٥	٦٥.٠٥
$Al_2 O_3$	١٢	١٢	١٢
Mg O	٥	٥	٥
$Na_2 O$	٨	٨	٨
CaO	٤	٤	٤
PbO	١.٢	١.٢	١.٢
ZnO	٠.٥	٠.٥	٠.٥
$Zr O_2$	-	٢	٤
K_2O	٠.٢٥	٠.٢٥	٠.٢٥

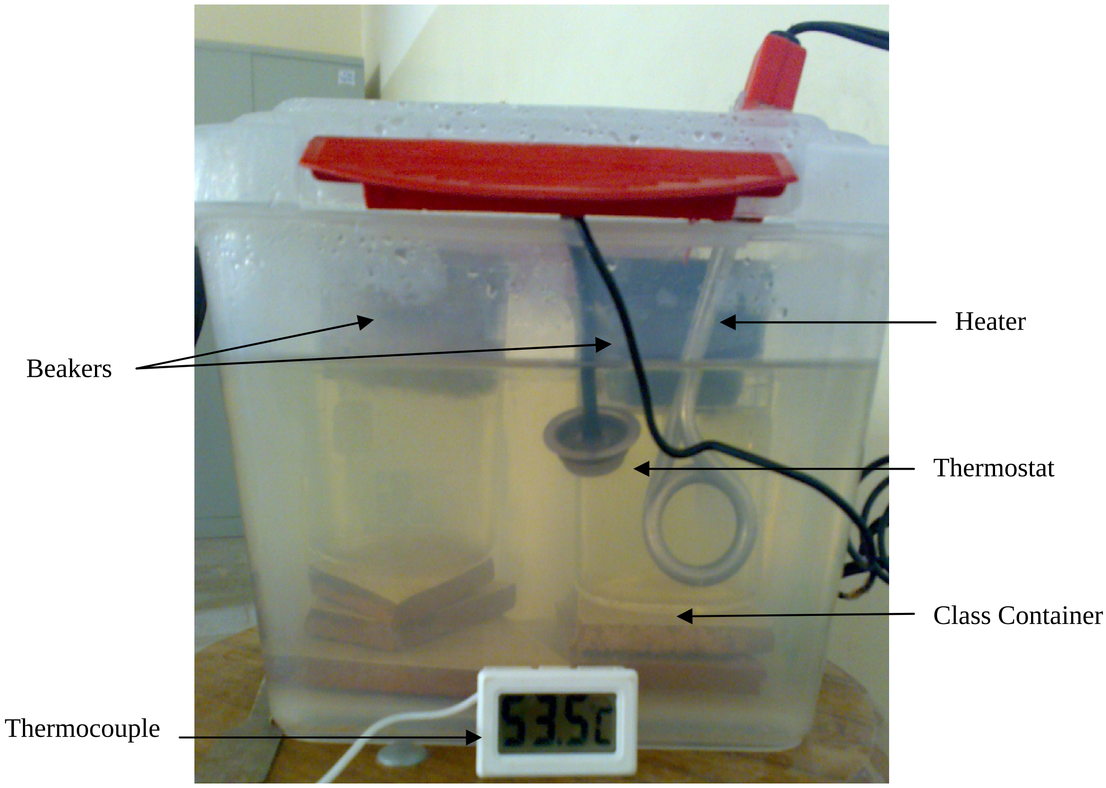

Figure: (1) The set of devices using for corrosion resistance test.

Results And Discussions

This research tends to study the effect of zirconium dioxide (ZrO_2) on the corrosion resistance of porcelain enamel. Zirconium dioxide has a high tendency to react with (SiO_2) at elevated temperature (nearly 1200C^o) to form ($ZrSiO_4$) zircon sand. Zircon sand has a very high corrosion resistance against chemical abrasives including (HCl) acid even at high temperatures [12]. Nearly (125C^o) for prolonged times (25hr) as it clearly obvious from figures (5-8) which display the result of the research. Where corrosion resistance largely increased by increasing (ZrO_2) from (0%, 2%, and 4%). Beside zircon sand there are several phases that may form like mullite (Al_2O_3-SiO_2) and mica (K_2O-Na_2O-Al_2O_3-SiO_2) which have a high chemical resistance that contribute in the total corrosion resistance of porcelain enamel but yet Zircon sand has the major role because its chemical resistance is largely more than mullite and mica (Grossman, 1972). Thus we may conclude that corrosion resistance of porcelain enamel increases with an increase in (ZrO_2) content [13].

It is obviously shown from figures (5 to 8) that a slight increase in corrosion resistance at first stages when temperature lower than 100 ^{o}C is observed, but when temperature exceed 100 ^{o}C a large and sudden increase in corrosion resistance is revealed.

Indeed the very effectiveness of ZrO_2 in increasing the chemical durability of glass can be seen from results of tables (3 to 6) and figures (5 to 8).

The mechanical interlock between porcelain enamel is the major responsible from the good adheres between enamel and substrate metal [14].

Conclusions

1- Several places are formed during firing like mullite, mica and $ZrSiO_4$.
2- Some of these phases have high chemical resistance like mullite and mica but phases like $ZrSiO_4$ has the highest chemical resistance.

3- The corrosion resistance increases with an increase in ZrO_2 content.
4-Corrosion resistance increase with increasing in temperature especially at regions when temperatures exceed (100 ^oC).

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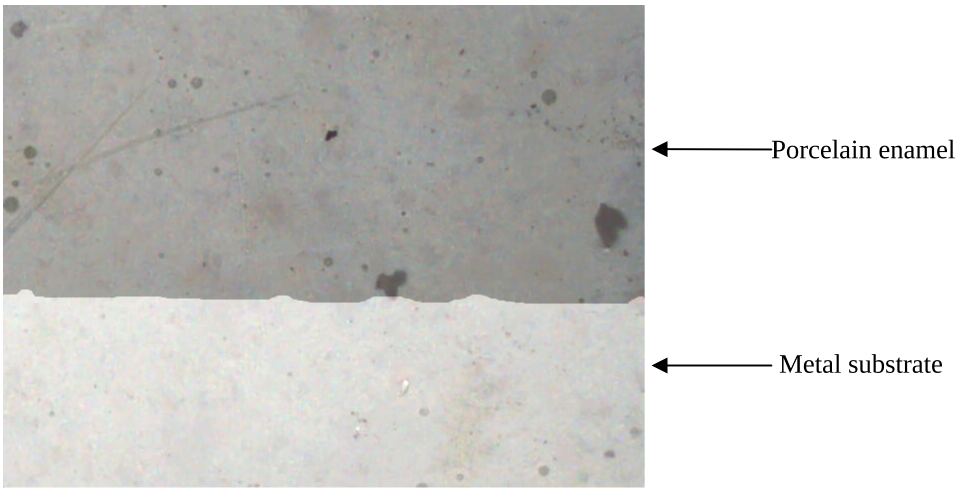

Figure: (2) Coated specimen with frit free of ZrO_2 before testing

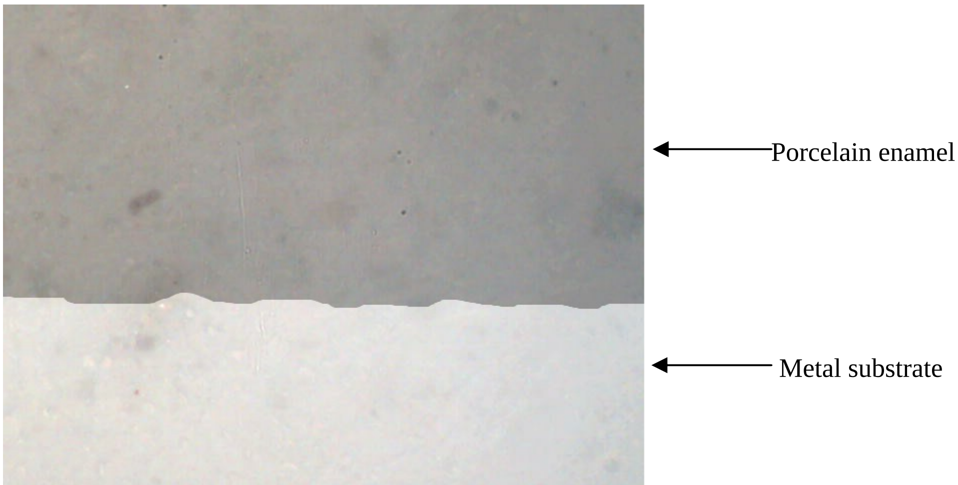

Figure: (3) Coated specimen with 2% ZrO_2 enamel before testing

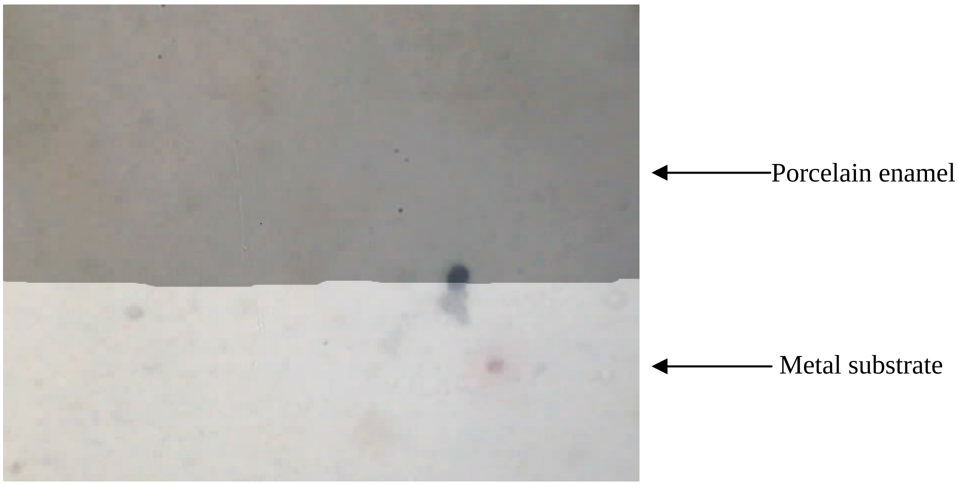

Figure: (4) Coated specimen with ٤% ZrO_2 enamel before testing

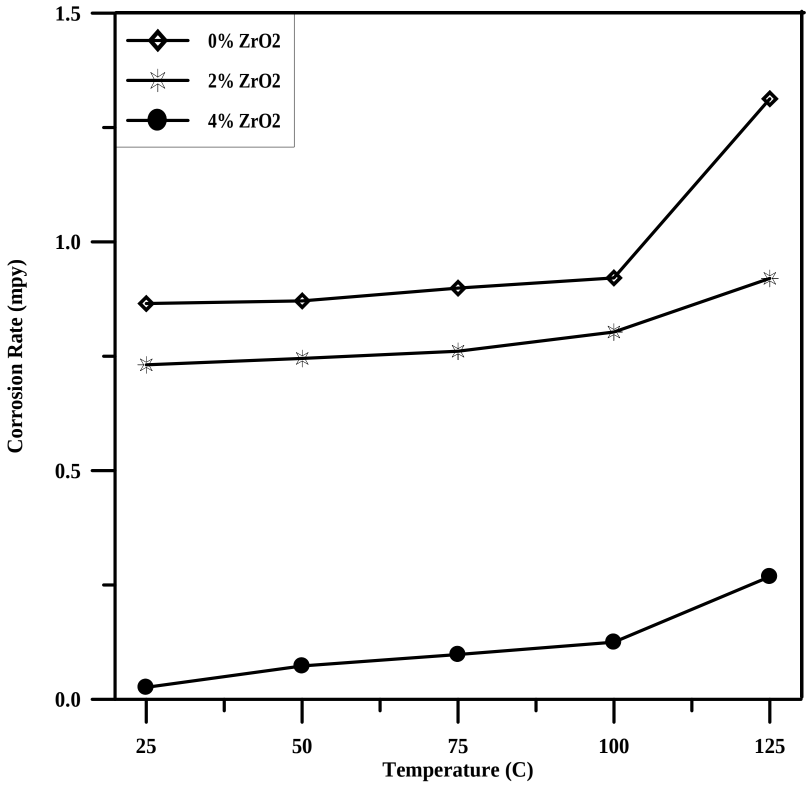

Figure: (5) Corrosion Rate (mpy) Versus Temperature of coated specimen at 10hr

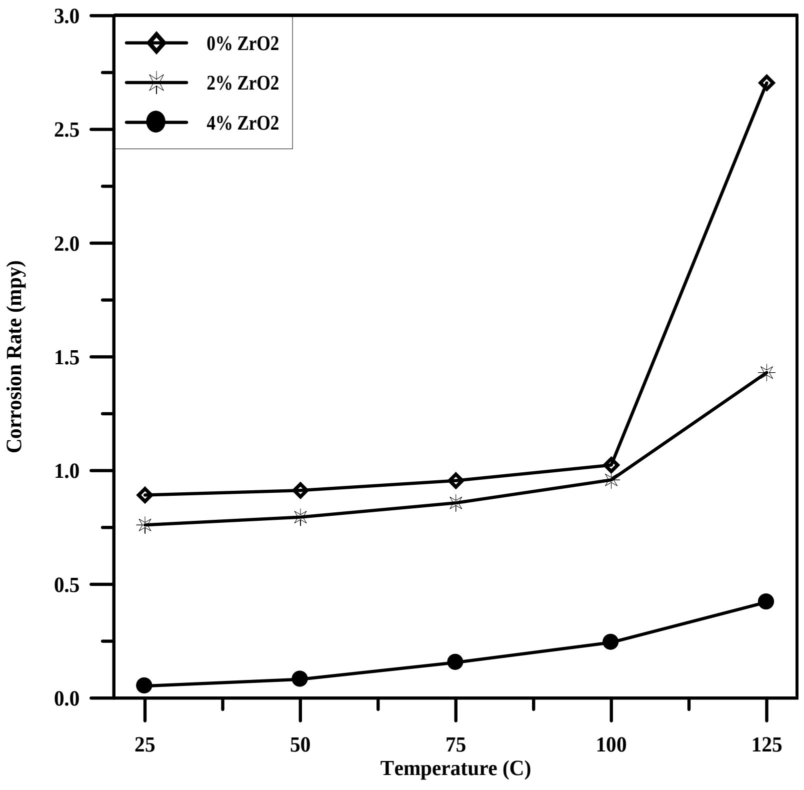

Figure: (6) Corrosion Rate (mpy) Versus Temperature of coated specimen at 15hr

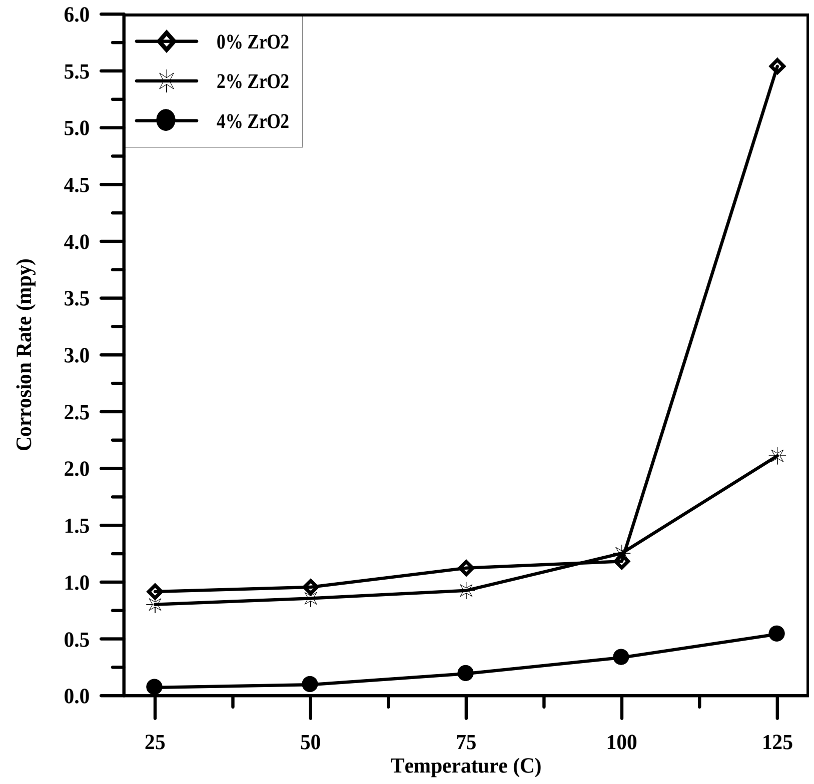

Figure: (7) Corrosion Rate (mpy) Versus Temperature of coated specimen at 20hr

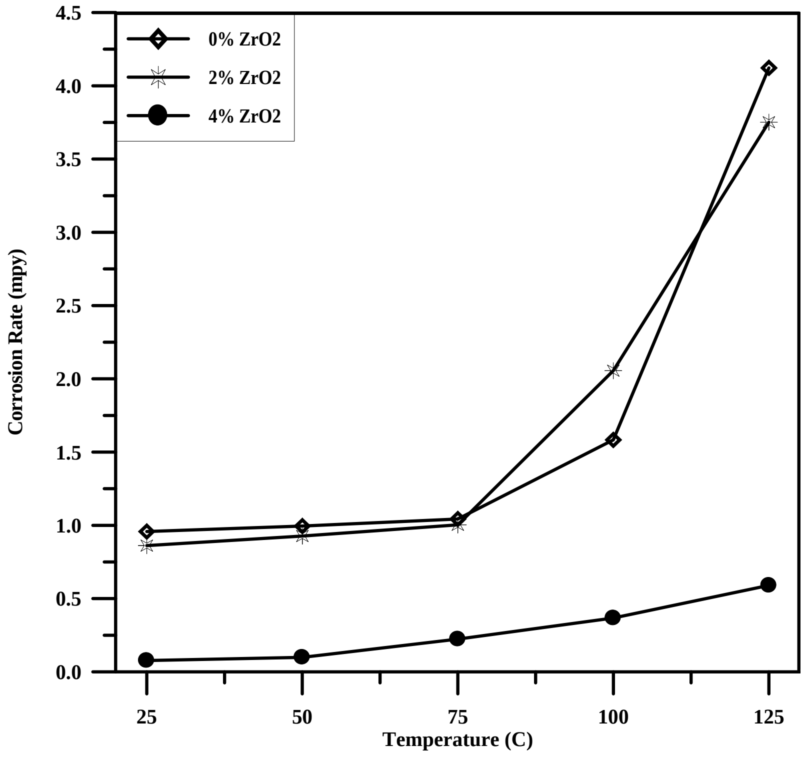

Figure: (8) Corrosion Rate (mpy) Versus Temperature of coated specimen at 25hr

Table (3): Corrosion Rate (mpy) Versus Temperature of coated specimen at 10hr			
C.R. (mpy) of enamel free of ZrO_2	C.R. (mpy) of enamel with 2%ZrO_2	C.R. (mpy) of enamel with ٤%ZrO_2	Temperature (^oC)
٠.٨٦٥	٠.٧٣١	٠.٠٢٦	٢٥
٠.٨٧١	٠.٧٤٥	٠.٠٧٣	٥٠
٠.٨٩٩	٠.٧٦١	٠.٠٩٨	٧٥
٠.٩٢١	٠.٨٠٣	٠.١٢٥	١٠٠
١.٣١٣	٠.٩٢٠	٠.٢٦٨	١٢٥

Table (4): Corrosion Rate (mpy) Versus Temperature of coated specimen at 15hr			
C.R. (mpy) of enamel free of ZrO_2	C.R. (mpy) of enamel with 2%ZrO_2	C.R. (mpy) of enamel with ٤%ZrO_2	Temperature (^oC)
٠.٨٩٢	٠.٧٦١	٠.٠٥٣	٢٥
٠.٩١٣	٠.٧٩٥	٠.٠٨٢	٥٠
٠.٩٥٦	٠.٨٥٨	٠.١٥٦	٧٥
١.٠٢٤	٠.٩٥٩	٠.٢٤٤	١٠٠
٢.٧٠٥	١.٤٣١	٠.٤٢٢	١٢٥

Table (5): Corrosion Rate (mpy) Versus Temperature of coated specimen at 20hr			
C.R. (mpy) of enamel free of ZrO_2	C.R. (mpy) of enamel with 2%ZrO_2	C.R. (mpy) of enamel with ٤%ZrO_2	Temperature (^oC)
٠.٩١٥	٠.٨٠٣	٠.٠٧١	٢٥
٠.٩٥٦	٠.٨٥٦	٠.٠٩٦	٥٠
١.١٢٤	٠.٩٢٦	٠.١٩٣	٧٥
١.١٨٣	١.٢٥٤	٠.٣٣٦	١٠٠
٢.٥٤٢	٢.١١٢	٠.٥٤١	١٢٥

Table (6): Corrosion Rate (mpy) Versus Temperature of coated specimen 25hr			
C.R. (mpy) of enamel free of ZrO_2	C.R. (mpy) of enamel with 2%ZrO_2	C.R. (mpy) of enamel with ٤%ZrO_2	Temperature (^oC)
٠.٩٥٧	٠.٨٦١	٠.٠٧٧	٢٥
٠.٩٩٥	٠.٩٢٧	٠.٠٩٩	٥٠
١.٠٤٣	١.٠٠٣	٠.٢٢٣	٧٥
١.٥٨٣	٢.٠٥٥	٠.٣٦٧	١٠٠
٤.١٢٢	٣.٧٥٢	٠.٥٩٠	١٢٥

دراسة تأثير أوكسيد الزركونيوم على مقاومة تأكل الطلاء البورسليني

نغم سلمان حسن
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الكلية التقنية / بغداد

الخلاصة

من ضمن انظمة الطلاء المختلفة للتطبيقات الهندسية والصناعية، طلاءات الزجاج السيراميكي لها ميزة المقاومة الكيميائية، والاستقرارية في درجات الحرارة العالية والخواص الكيميائية المدهشة مثل القشط، والصدمة الى اخره مقارنة مع مواد الطلاء الاخرى. اضافة الى باقي الخواص الضرورية للاغراض التطبيقية مثل الحرارة ، مقاومة القشط ، والتاكل لتلائم متطلبات التطبيق النهائية، طلاءات الزجاج السيراميكي بصورة عامة توفر التصاقية جيدة وسطح خالي من العيوب وعازل حراريا. هذا البحث يهدف الى انتاج طلاء من الزجاج السيراميكي يكون فعالا ومنتج من مخلفات الزجاج ونسب مختلفة من عامل التبلور ZrO_2، ودراسة خواص مقاومة التاكل النهائية. بعد سلسلة متعددة من اختبارات مقاومة الحامض في درجات حرارية تتراوح بين ($25, 50, 75,100,125\ ^oC$) وجد ان الطلاء ذو (٤% نسبة وزنية) من ZrO_2 له احسن مقاومة تاكل.