STUDYING THE EFFECT OF HEAT TREATMENT ON THE CHEMICAL RESISTANCE OF PORCELAIN ENAMEL IN DIFFERENT ACIDIC MEDIAS [+]

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Abstract:

This research aims to study the effect of heat treatment especially the crystallization, on the chemical resistance of porcelain enamel sample. For a crystallization to occur half of the amount of frit was reheated up to (850 C°) for a period of (90 min) and left to cool at a rate of (10C°/min) in the furnace. The two specimens were tested by X-ray diffraction to ensure the difference between them. The first specimen show a glassy material or amorphous phase, while the treated sample has the beaks of a crystalline material. By testing the chemical resistance of the two samples to (10%) concentration of hydrochloric, sulphuric, citric, and CH_3COOH it is obviously appeared that the crystallization enamel has a much better chemical resistance than the amorphous one.
Key words - :porcelain enamel, crystallization, chemical resistance.

دراسة تأثير المعاملة الحرارية على المقاومة الكيمائية لطلاء البورسلين في اوساط حامضية مختلفة

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المستخلص:

يهدف هذا البحث إلى دراسة تأثير المعاملة الحرارية وخاصة البلوَرة على المقاومة الكيميائية لعينة من الطلاء البورسليني. لضمان حدوث البلوَرة تم إعادة تسخين نصف كمية الطلاء (الوجبة) المحضرة إلى (850°C) ولمدة (90 min) ثم بردت تدريجيا في جو الفرن وبمعدل (10°C/min) , وبعدها خضعت كلتا العينتين للفحص بالأشعة السينية للتأكد من حصول التبلور وتأكيد الاختلاف بينهما, وقد أظهرت العينة الأولى نمط المادة الزجاجية أي الطور العشوائي , فيما أظهرت العينة المعامّلة حراريا الطور البلوري واضحا من خلال القمم التي ظهرت عند الفحص. باختبار المقاومة الكيميائية للعينتين وفي تركيز (10%) من حوامض الهيدروكلوريك, الكبريتيك, ستيارك والخليك اتضح أن المقاومة الكيميائية للطلاء قد زادت بصورة ملحوظة بعد المعاملة الحرارية.

Aim of this search:

The major interest of this research was how the crystallization process affects the chemical resistance of porcelain enamel against acidic medias.

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Introduction:

The industrial civilization depends in a crucial way upon the stability of metals in their moist atmospheres which can be achieved if their surfaces are isolated from the normal terrestrial environment, if not they develop cracks and break upon strain with catastrophic suddenness[1]. A number of coating systems are known such as metallic, organic and ceramic coating [2]. Enamels or ceramic coatings are glass like coatings that are fused to base metals giving a tightly adhering, hard, and durable finish. They are composed of a glassy matrix in which crystalline opacifiers and pigment are suspended [3]. The matrix is usually borosilicate, and the opacifiers are oxides of titanium, antimony, zirconium, lead, and tin. The basic material from which vitreous enamel is made is referred to as a frit [2]. Porcelain enamel is distinguished from other ceramic coating by their predominantly vitreous nature and the types of application for which they are employed, and from paint by their inorganic composition and the fusion of the coating matrix to the substrate metal [3].

An enamel system consists of one or more layers. The first coat is called the ground coat, usually contains cobalt oxide, and often oxides of nickel and manganese to promote good adhesion [4,]. One or two cover coats are normally applied over the ground coat in porcelain enamel systems. There are hundreds of different cover coat formulations to meet various decorative and protective requirements [6].

Porcelain enamel is best appreciated when the glass- ceramic structure is understood. Glass compositions those are prone to devitrification but otherwise have suitable enameling characteristics have been developed to permit their application to metals coatings by conventional enameling techniques. Subsequent heat treatment of an essentially glassy coating several hundred degrees below the firing temperature causes precipitation and growth of the stable crystalline phases from solution to form a crystal- glass composite fused to the metal substrate. The type, size and distribution of the crystalline phases within the glass are determined by, the original glass composition, the process variable such as frit particle size, firing cycles, and nucleating agents, and the final heat treatment. Whatever the final product is technical glass- ceramic enamels which represent the crystallized silicate coatings, which with suitable composition and after suitable thermal treatment, contain a significant concentration of finely dispersed and uniformly distributed crystalline phases. These very special enamels possess much better (thermo- mechanical- chemical) properties relative to conventional enamel coatings. Glass- ceramic enamel is characterized by high thermal stability, working ability at considerable higher temperatures, depending on their structure composition, and some of their properties are strongly dependent on the perfect crystallinity of the system [7, 8].

Glass ceramic, demonstrating such as favorable properties , can be developed with a variety of microstructures by carefully varying the base glass composition and heat treatment conditions [9].

Controlled growth of crystals in glass coating on ferrous metal increases the resistance of such coatings to mechanical and thermal shock than would be predicted from consideration of the residual compressive stresses developed by differences in expansion between coating and base metal [7].

Experimental set up:

1- Materials:

i. Metal Substrate: - the metal substrate is cast iron with the compositions shown in Table (1) which is used for food cans. Cast iron is prepared by blasting to remove adhering mold sand and thin surface layer of chilled iron. Silicon carbide grains propelled by compressed air, was used for blasting cast iron. After being blasted the surface is aspect for cracks, sand holes and slag holes by microscope type: NYKON, Japan (1*400), in the Light Industries Co. S.A.

Table (1) Chemical Composition of Cast Iron Suitable for food Cans [10].

Element	C	Mn	P	Si	S	Fe
Weight (%)	3.6	0.6	0.8	3	0.12	91.88

ii. Ceramic Enamel: - ten different materials were used for the preparation of the frit. Cast iron enamel weighing was done by using an electrical balance type: (SEGAM, CS2, 0.001, England) the sensitivity of the balance was 0.001gm. The weights and the compositions of the frit are listed in Table (2).

Table (2) weight Percent of frit of Cast Iron Food Cans.

Material	$BaCO_3$	K_2NO_3	Co_3O_4	$Na_2O.2B_2O_3.10H_2O$ (Borax)	$CaO.Al_2O_3.2SiO_2$ (Feldspar (anorthite)
Weight (%)	9.24	8.48	1.43	20.16	16.74
Material	Li_2O	MnO	NiO	Si_2O	ZnO
Weight (%)	4.9□	1.2□	2.32	33.74	1.69

After thoroughly mixing, the patch was put in graphite crucibles and fired at 1200C° for 3hours using furnace type: CARBOLITE, England in the Company of Geological Survey and Mineralizing.

After firing the raw materials becomes a homogeneous molten liquid, a stream of the fired molten was drawn from the crucible directly into a stainless tank immersed in cold water producing coarse granular quenched frit, which was then milled using a ball mill type: LOGAN 301, England with porcelain balls the grinding media in the Technical College/ Baghdad. Fig 1 shows the X-Ray diffraction of amorphous frit which was examined in the Company of Geological Survey and Mineralizing. For crystallization to occur (□0%) of the frit was reheated in an electrical furnace type: NABERTHERM, Germany, in the Technical College/Baghdad up to 8□0C° for a period of (90min) and left to cool at a rate of (10 C°/min) in the furnace. Fig. 2 Shows the X-Ray diffraction of reheated frit with crystallization beaks, which was examined in the Company of Geological Survey and Mineralizing.

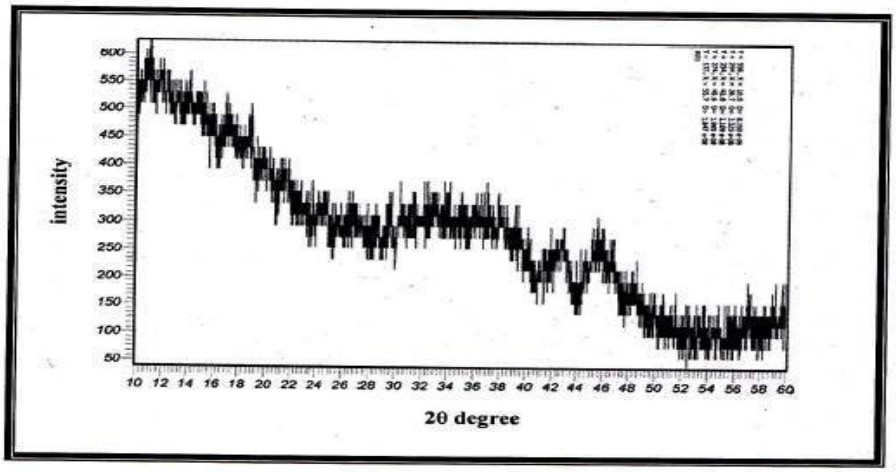

Fig. (1) X-Ray Diffraction of Amorphous Frit.

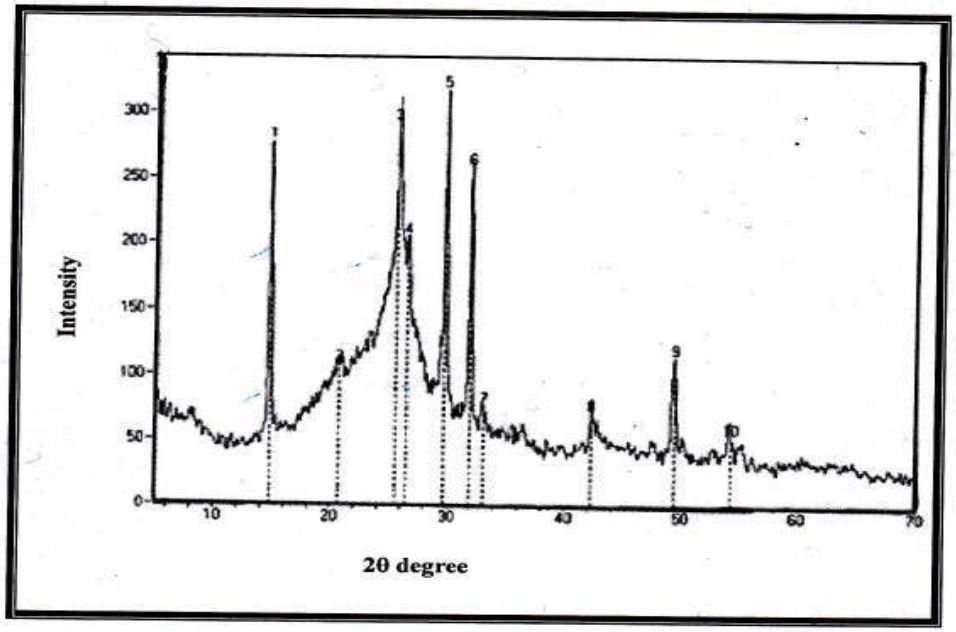

Fig. (2) X-Ray of Reheated Frit Shows the Crystallization Beaks

The frit powder was first sieved by shaken using a mechanical shaker type: RETCH, Germany and micro sieves type: E 11 BODY 316, Germany of 200 mesh and (30 μm) diameter according to Retsch Standard in the University of Technology. A (□0gm) of water was added to each batch and mixed for half an hour using a mechanical stirrer type: BADFORD, USA 303 to obtain the required homogeneity. Then the viscosity of the slurry was measured using BAYER ENAMEL SLIP GAUGE in the University of Technology . Bayer gauge is a blade of stainless steel with holes of steadily increasing diameters and a

handle. The gauge is straightly immersed in the slip and lifted out vertically, a greater or lesser number of holes opens up depending on the viscosity.

Chemical testing:

A set of tests for acid resistance of the amorphous and crystalline coats were made. Special attention was given to time. The acids used are HCL, H_2SO_4, $C_2H_8O_7$, and CH_3COOH, with PH= 4 end the source is (BHD- GERMANY).

Tests were carried out at fixed temperature of 2□C° with time intervals from (30-240) day with an increasing rate of 30 day for each cycle. This is according to the ASTM C346, and ASTM C□38,[11].

In every case the corrosion rate (C.R) was determined by weight loss and calculated using equations below [12]:-

$$C..R = \Delta W / A.t.....(mdd) .. (1)$$

Where:

ΔW : Weight loss in (mg).

A : Area of the specimen in (dcm^2)

t : Time in day.

mdd : Mill decimal per day

In mill per year mpy corrosion rate is calculated from the equation below (11):

$$C..R = 1..44.mdd / S.G.....(mpy) \ldots (2)$$

Where:

$S.G$: The specific gravity.

Results and Discussion:

Chemical durability (corrosion resistance) has long been one of the major properties of interest when considering the selection of porcelain enamel as a coating for metals. Many researchers have tried to correlate data on the chemical attack of enamel surfaces. These studied divide chemical resistance into two parts acid, and alkali resistance, normally enamel is formulated to withstand one of the corrosive agents more than the other, although porcelain enamel as a general finish has good (all around) resistance.

With the growing acceptance of surface coating technologies there is a real need to understand the inter-relationship between the properties of a coating-substrate system chemical, and the coating microstructure.

Crystallization process largely affect the particle size of the ceramic grains in the frit, and pore size and distribution, this is can be seen in Fig. (3).

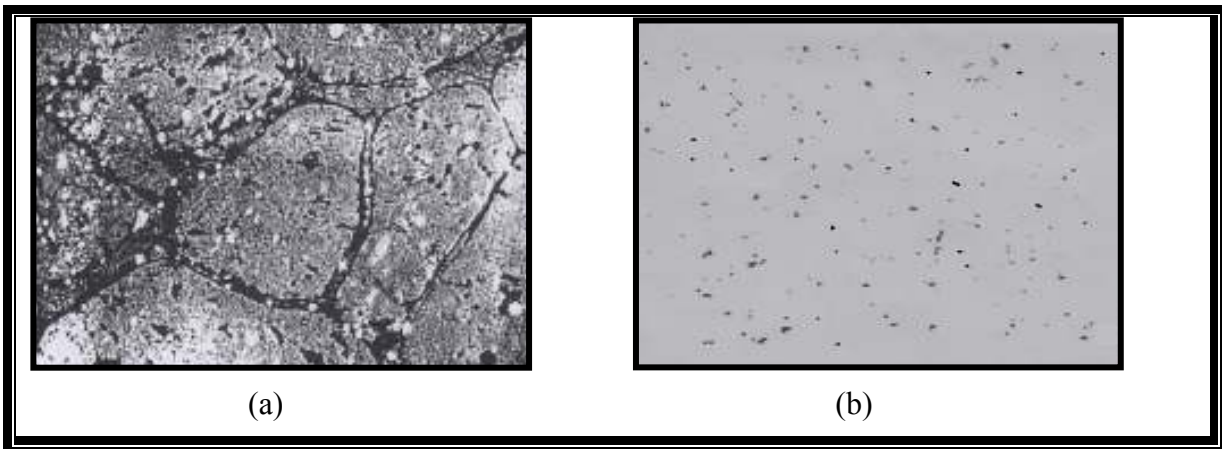

Fig. (3) (a) The microstructure of crystalline enamel, using optical microscope and (b) The microstructure of amorphous enamel, using optical microscope for the research specimens.

It is a microscopic photograph for both the surface of amorphous and crystalline enamel the amount and distribution of pores were contaminated by the crystallization process. This contamination leads to decrease in the ability of acidic media to penetrate inside the enamel.

Chemical properties including corrosion resistance are largely affected by microstructure. Phase alignment (anisotropy) can be used by proper design of components, an inhomogeneous dispersion of the reinforcement leads to undesirable local variations in properties.

Nucleation and forming of clusters of particles may result in high chemical resistance due to phases like mullite ($3AL_2\ O_3\ 2SiO_2$), mica ($K_2AL_6Si_6O_{20}(OH)_4$) and quartz (SiO_2), which are formed during crystallization process, and all of these phases have high chemical durability which consolidate chemical resistance of coating[4].

Grain sizes of the formed ceramic phases usually increases with increasing in time of treatment thus lead to a high decrease in grain boundaries which are the most favorable at taking areas leading to a high increase in chemical corrosion resistance as clearly shown from fig.(4 to 7).

Fig.(4) shows that ceramic enamel have remarked corrosion resistance up to (7□) days at ($10\%H_2SO_4$) ,while the corrosion of the same enamel at (10%HCl) is very low comparing with other chemical solutions (fig.□). Although citric and Acetic acids have very close corrosion resistance values and they are the lowest corroded media.(fig.6 and 7).

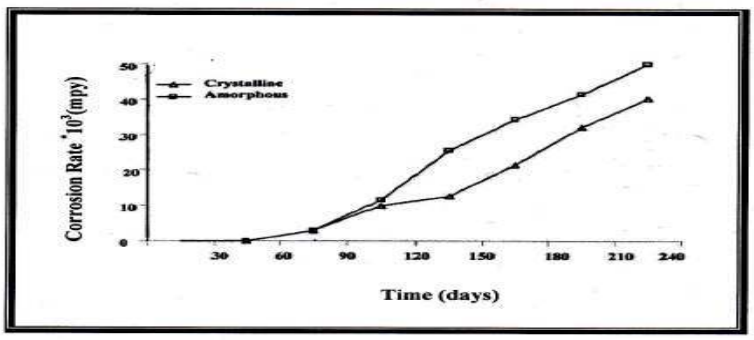

Fig. (4) The Corrosion Rate Vs Time Enameled Cast Iron in 10% H_2SO_4 Solution.

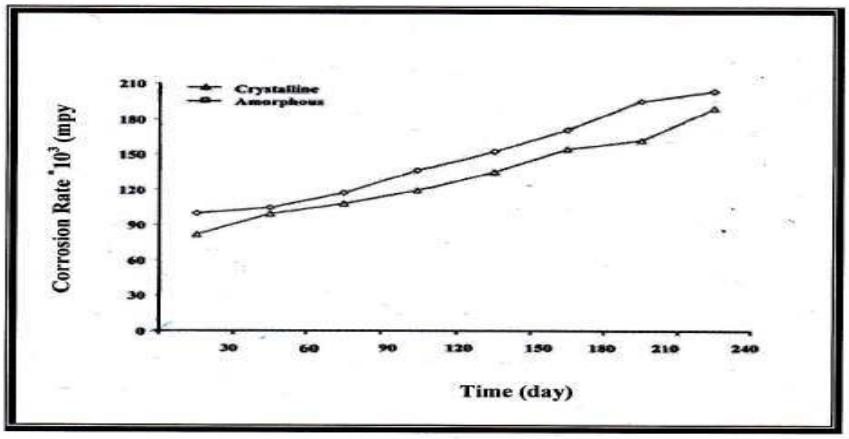

Fig. (5) The Corrosion Rate Vs Time of Enameled Cast Iron in 10% HCl Solution

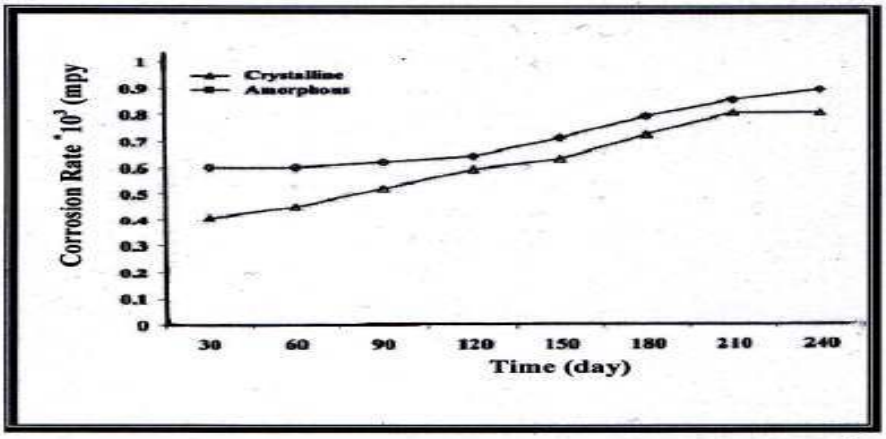

Fig. (6) The Corrosion Rate Vs Time of Enameled Cast Iron in (10%) CH_3COOH Solution.

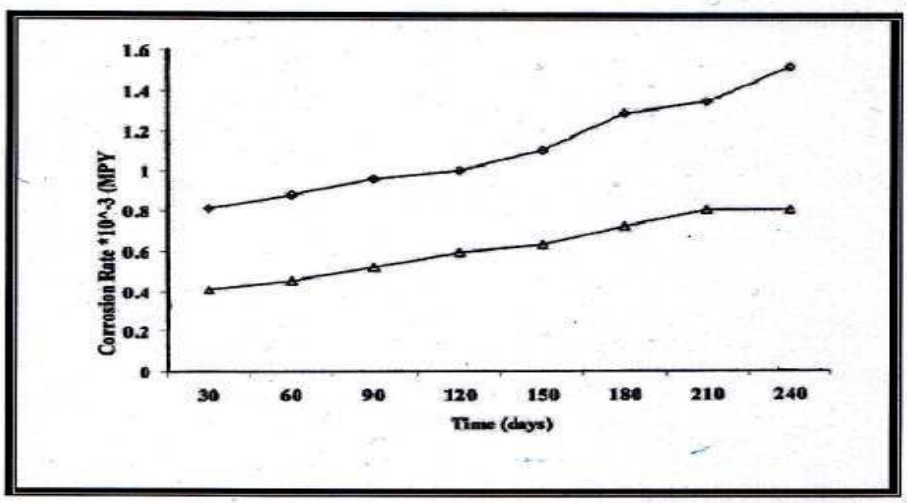

Fig. (7) The Corrosion Rate Vs Time of Enameled Cast Iron in (10%) $C_2H_8O_7$ Solution.

Figures (4-7) shows the corrosion rate (mpy) of both types of enamel coatings (crystalline and amorphous) as a function of immersing time (day) in 10% (H_2SO_4, HCl, CH_3COOH, $C_2H_8O_7$) acids respectively. These figures clearly show that crystalline enamel has remarked higher corrosion resistance in all acids, and even at prolonged time, than amorphous enamel. This is due to the presence of phases mentioned above (mullite, mica, and quartz) which have a very high chemical inertness in all medias, and not found in amorphous enamel. Comparing between figures shows that H_2SO_4 is the most aggressive media among the four acids used in research, while CH_3COOH, $C_2H_8O_7$ acids have close corrosion resistance and they are much lower aggressive than H_2SO_4, HCl.

Conclusions:

1- Crystallization processes largely enhance corrosion resistance of enamel.
2-Sulpheric and hydroloric acids are more aggressive than citric and acetic acids.

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