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Experimental Study for the Effects of Crystalline Agents on Properties of Glass-Ceramic Coating

Abstract- *In this work, four series of glass-ceramic coatings were developed and applied by using the dipping technique to cast iron sheets. The influence of different types of crystallization agents (Li_2O, TiO_2, $ZrSiO_4$, and $CaO.Al_2O_3.2SiO_2$) was investigated in relation to the mechanical features of the coatings. The resultant coating is characterized using X-ray diffraction analysis. The properties of micro-hardness and adhesion strength are evaluated using suitable standard tests. The X-ray analysis of resultant coatings showed the existence of some of crystalline phases formed depending on the type of the crystallization agent. The results also indicated that the coating properties were strongly dependent on composition and concentration of crystallization agent. Coating with feldspar gives the highest value of hardness and adhesion index. In general, properties of the resultant coatings were improved in all cases; this is related to the formation of a complicated network from crystalline phases.*

Keywords- *Cast iron, Enamel properties, Glass-ceramic.*

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1. Introduction

In spite of there are fast progress was made in the development of new materials, but till now there are no single material that can withstand all the severe working environments in recent technology [1]. Protection of the materials against the hostile environments has consequently become a technical and economic necessity. In many cases, protective coating was needed to reduce such effects as abrasive, erosion, corrosion, high temperature oxidation, and high temperature fusion. From this application, the protective coating is typically chosen to complement of the substrate material, so that the combined properties of the composite system can fulfill a specific set of working conditions [2]. Recent technology uses variety types of surface coating materials, ranging from polymeric or metallic to oxide based ceramic. Among them glass-ceramic or oxide based glassy coating has further features of elevated temperature stability, excellent mechanical properties, and chemical inertness as compared to the other organic or non-oxide coatings (polymers, rubbers, metals, paints, etc. [3,4]. Usually, the coating materials used have certain end use requirements with tight ranges of selectivity. Demands of a new engineering and technology need to coatings which have a broad spectrum of affectivity to satisfy modern industries requirement [5]. For instance, it is important for the high corrosion resistant coating to has a high resistance to abrasive, erosion, and have high thermal stability, and fracture toughness so as to reduce the possibility of failure because of cause other than corrosion [6]. These developed glass-ceramic coatings having improved thermal, chemical, and mechanical features can satisfy the needs of recent industries [2]. Vitreous enamel refers to the application of a thin layer of glass that adheres to material substrate to obtain a protective layer against aggressive media [7,8]. Usually, end use needs have dictated the requirement for particular coating material which have much excellent features as compared with traditional enamels. These coatings give protection of the materials vs. corrosive atmosphere and elevated temperature and are generally named glass ceramic coating. These coatings can be recognized from traditional enameling coatings by the existence of reasonable amounts of regularly distributed and fine crystallites within the resultant coating Figure 1 [9]. These crystalline phases can be formed within the glassy phase coating material by nucleation and crystal growth during a proper thermal treatment process, or by incorporating a suitable crystalline agent in glassy composition. These crystalline phases provide a unique combination of features such as superior resistance against abrasive, wear, erosion, thermal shock, aggressive media and high temperature to avoid the failure of the substrate materials under severe working environments [8]. The

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homogeneity of parent glass alongside the conditions under which the crystals were produced, result in glass–ceramic materials possessing a fine grained and regular structure free from porosity. This aids in growing good electrical insulation properties and high mechanical strength [9]. In present study, a novel single layer glass-ceramic coating material designed for application on various grade of cast iron was obtained and prepared. The process of application, characterization, and evaluation of coatings was described. Also, the effects of four types of crystallization agents (Li_2O, TiO_2, $ZrSiO_4$, and $CaO.Al_2O_3.2SiO_2$) on properties of the resultant coating were studied.

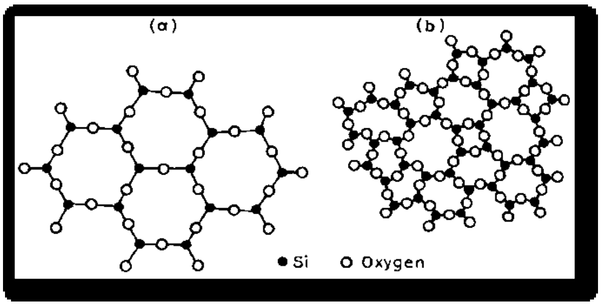

Figure 1: a- Crystalline structure (regular). b- glassy structure (irregular) [9]

2. Experimental work

I. Selection of Substrate

Cast iron alloy with (3.6) %C was selected as substrate metal in current study. The chemical composition of selected cast iron is listed in Table1.

II. Sample Preparation

For preparing the surface samples to be coat, all samples were heated to about 450˚C to remove all organic contaminants (oil and drawing compounds) then the samples were blasted by exposing the sample surface to a jet of an abrasive material (quartz) shots to eliminate rust, scale, and dirt. The surface of samples become clean and pitted which helps promote good adherence.

III. Frit Manufacturing

Different crystallization agents (Li_2O, TiO_2, $ZrSiO_4$, and $CaO.Al_2O_3.2SiO_2$) have been used in this study to prepare four types of coating materials (frit) (C1, C2, C3, and C4). These crystallization agents were added for each type of coating material to study their effects on properties and performance of resultant oxide based coatings. The four types of frit were prepared from reagent grade chemicals: SiO_2, $CaO.Al_2O_3.2SiO_2$, $BaCO_3$, Co_3O_4, $Na_2O.2B_2O_3.2SiO_2$, ZnO, MnO, KNO_3 TiO_2, Li_2CO_3, NiO and $ZrSiO_4$. The batch was mixed and melted in a crucible in electrical furnace at 1250˚C, the batch held at this temperature till the all of raw materials have reacted and the batch became homogeneous, and bubble-free liquid. After that a stream of the refined molten batch is poured from the crucible and quenched into water in order to yield frit with coarse granular. The coarse frit was milled by a ball mill and screened with a mesh size of 200 μ mesh (≤ 75μm), heated in an oven at 125˚C to avoid moisture problems. The chemical composition of the four types of frit are presented in Table 2.

IV. Preparation of Enamel Slip

To prepare the enamel slip, the frit has to further process by mixing it with mill-additive. In this work borax, Kaolinite, bentonite, were used as mill-additive. In addition to quartz was added to batch of enamel slip to impart the desired properties of the fired coating. The specific gravity of the enamel slip was controlled between (1.7-1.8) by adjusting the water content. Finally, before enameling the slip was aged for 24 hrs. at room temperature to increase its fluidity. Table 3 presents the slip composition.

Table 1: chemical composition of base metal (cast iron)

Element	C	Mn	P	S	Si	Fe
Measured Cast Iron wt.%	3.6	0.5	0.65	0.85	2.25	92.15
Standard (DIN-GG 15)	3.6	0.5-0.9	0.20-0.30	0.10-0.30	2,3	balanced

Table 2: Weight percent of four types of frit

Material	C1	C2	C3	C4
$BaCO_3$	11	11	11	11
Co_3O_4	1	1	1	1
$Na_2O.2B_2O_3.2SiO_2$	18	18	18	18
$CaO.Al_2O_3.2SiO_2$	14	14	14	20
K_2NO_3	7	7	7	7
Li_2O	6	---	---	---
MnO	1.5	1.5	1.5	1.5
NiO	1.5	1.5	1.5	1.5
SiO_2	37	37	37	37
TiO_2	---	---	6	---
ZnO	3	3	3	3
$ZrSiO_4$	---	6	---	---

Table 3: Slip composition

Material	Weight (%)	Material	Weight (%)
Frit	100	Quartz	5

Clay	7	Water	50	Borax	1

V. Coating Application

The coating material was applied on the surface of metal substrate by dipping technique. Dipping technique is a quick and simple method which is not required to special plant. In this study, the sample was immersed in enamel slip for 30 s, then withdrawn, and allowed to drain for 30 s (by hold the sample vertically and allowed for excessive slip to flow down).

After the application of the coating slip on surfaces of sample, the coated sample was dried at 125˚C for 15 min in an oven to eliminate the moisture. Then, the dried sample was fired in an electrical furnace at 870˚C for tin minutes; the coating material then reacts and fuses with the surface of metal substrate to form a firmly adherent coating. Finally, the enameled sample was held in a furnace at (850)˚C for 15 min., to obtain the glass-ceramic coating, and left to cool slowly in the furnace. Figure 2 presents the coated samples, while the summarizing of whole glass-ceramic coating process is present in Figure 3.

VI. Testing and Inspections

Coatings Characterization

The thickness measurements of the resultant coatings were made by the eddy current devise with ND-2 type probe.

X-Ray diffraction measurements for as coated and heat treated coated samples was done by diffractometer instrument model (Philips PLO1840 X-ray diffractometer). The conditions of measurements were as follow:

- Monochromatic X-ray {Cu Kα, 1.54 A^{o}, 40.0 KV,30.0 mA}
- Measure {(Axis: θ-2θ), (Scan Mode: Continuous Scan), (Range: 10-60 deg.), (Step :0.05deg), (Speed:5 (deg./min), (Preset time:0.60 sec)}.
- Slit {(Divergence: 1 deg.), (Scatter: 1 deg.), (Receiving: 0.15mm)}.

Microhardness Measurement

The microhardness measurements of the samples were done by using a Vickers micro-hardness model (HVS-1000). The micro-hardness tests were carried out under an indentation load of 50 (g) for 20 s. In order to obtain reliable values, the microhardness test was performing by taking three indentations on each sample and averaging of three values.

Adherence Strength Test

The enameling sample was tested accordance to Europe standard of enamel adherence strength, EN10209, this test includes impact enameling specimen by a steel ball. Following the destruction, the adherence strength is judged according the relics of enamel on the destroyed surface. The enamel adherence strength could be graded into five grade (1st, 2nd, 3rd, 4th and 5th) and the 1st grade is the best. If the most of the enamel layer was removed from the steel sample, and the appearance of the surface was silvery bright after the impact, the adherence strength considered as a poor and 5th grade. On the other hand, if the most of enamel layer remains on the steel sample, the adherence strength is 1st and excellent.

Figure 2 : Coated samples

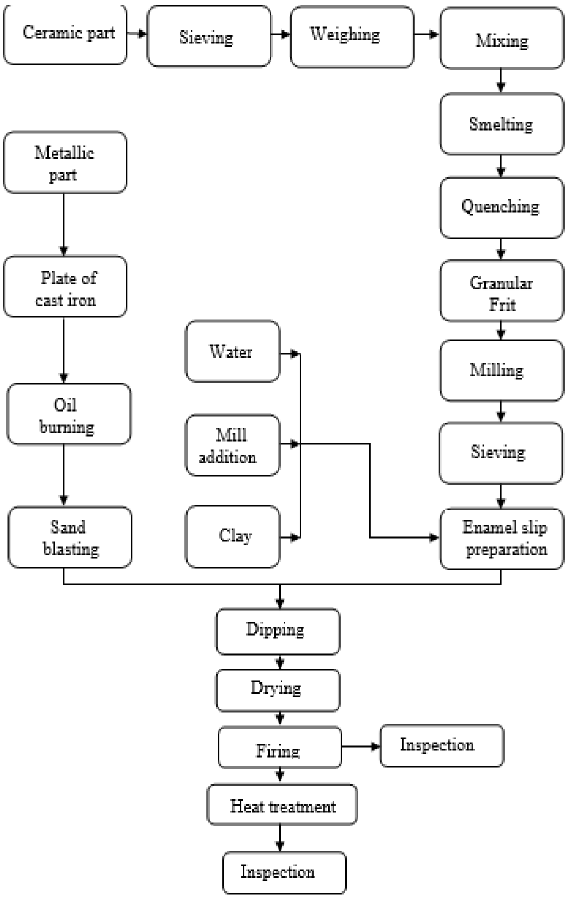

Figure 3: Experimental program flow chart

3. Results and Discussion

I. X-ray Diffraction (XRD) Analysis

Phase analysis of the resultant coatings have been performed by X-ray diffraction analysis. The X-ray diffraction patterns of different coating were present in Figure 4. X-ray diffraction analysis indicates presence of several types of crystalline phases (Quartz, Nepheline, Mullite, Mica, β-Spodumene, β-Eucryptite, Rutile, Zircon sand, and Celsiane) depending on the type of added crystallization agent. XRD samples (type C1) indicate that the β-Spodumene phases is most predominated in coating, while the Zircon crystallizes as the major phase were observed in samples type C2 as illustrated in Figure 4-a, b. In other hand the results indicate that the higher amounts of the crystallization phases were observed in XRD samples (type C3, and C4). It can be seen the longer crystalline phases peak in these samples especially for phases of Rutile, Quartz, Mullite, and Mica as shown in Figure 4-c, d. Generally, the results of XRD analysis reveals that the crystalline transformation was induced by crystalline agent in all cases.

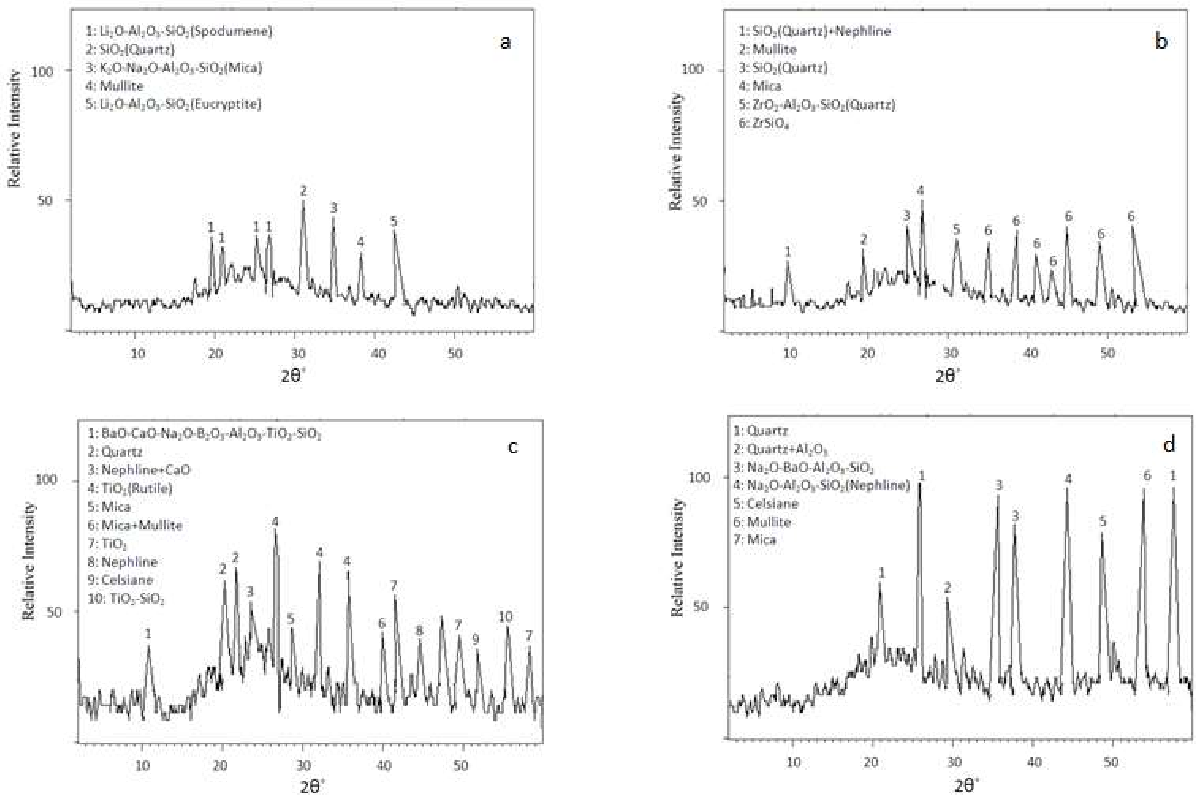

Figure 4: X-ray diffraction of cast iron enamel (a) enamel containing Li_2O (b) enamel containing ZrO_2 (c) enamel containing TiO_2 (d) enamel containing $CaO.Al_2O_3.2SiO_2$

II. Microhardness

Figure 5 shows the values of micro-hardness of four types of coating. It is clear from the figure that the feldspar containing enamel (C4) has the highest hardness value. Then, the hardness of enamel with lithium oxide (C1), while the hardness value of the zircon sand, and titania containing enamels (C2, and C3) were too close. The results show that the hardness of resultant coating is strongly related to the properties of its constituents, and it can be affected by modifying the microstructure, and chemical composition of the enamel coating. The excellent micro-hardness value of (C4) coating is attributed to the presence of higher amounts of crystallites in resultant coating. The hard, unique and complex microstructure of the formed crystalline phases, especially (Nepheline and Celsiane) gives a rise to increase the micro-hardness value of the resultant coatings.

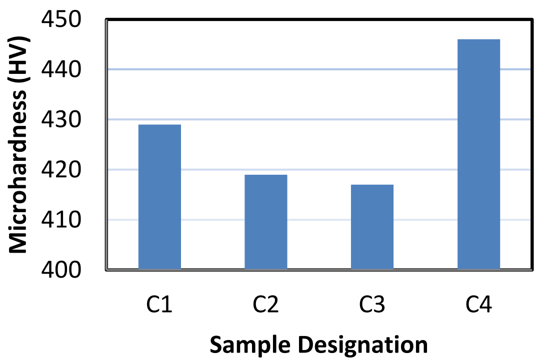

Figure 5: Microhardness of enameled cast iron

III. Adhesion Strength

The adhesion strength is strongly associated with the micro-structure and morphology of the intermediate boundary between metal substrate and enamel coat. Considering that the addition of crystallization agent and heat treatment may exert a great influence on the micro-structure of intermediate bonding layer, and as result on the strength of adhesion. Figure 6 shows the values of adhesion index of four types of coatings. It can be seen that the adhesion index of feldspar containing enamel is the greatest (92.2%) followed by the lithium (90%), zircon sand (88%), and at last titania containing enamel (83.1%), it is obvious that this result is similar to that indicated by hardness test is because both of the testes are based on mechanical concept. The enamel –metal bond is the most related factor to the real application and it is governed by the wettability between the two materials and the mechanical interlocking between the two surfaces which in turn is related to the contact area. The electrolytic theory of ceramic-metal bonding may explain the enhanced adhesion by the currents flowing between the molten glass and the metal surface causing some kind of pitting.

This in turn will sensitize the surface and-enhance greatly the mechanical gripping. Considering that, the increasing in crystallization agent concentration into coating material (frit) and heat treatment process for enamel coating have significant effect on the microstructure of intermediate bonding layer, and as result on adhesion strength. As we explained previously, the metal surface was pretreated by sand blasting method, and that leading to roughen surface and made mechanical anchor points (catch points) which are increasing the mechanical interlocking (contact area) between coating / metal interface, but the improving in adherence strength which is clear from the figure not come only from the mechanical interlocking (mechanical theory) , it also came from contribution of another methods (chemical, galvanic theory), which are increase its action, and effect with carried out the heat treatment on the coating/metal interface morphology, and as a result on adhesion strength. The photograph and microstructure of the peeled surface after adhesive test for coated sample is present in Figure 7 (a, and b), the white area refers to the peeled surface without enamel coating, and the darken area represents the unpeeled surface with adhesive coating layer.

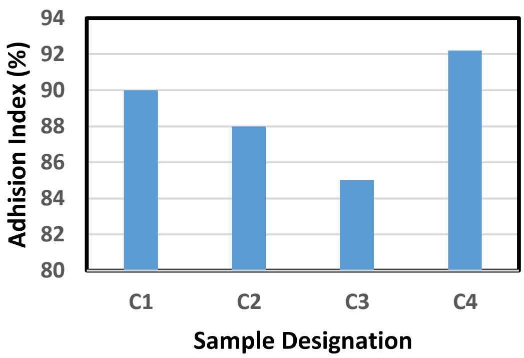

Figure 6: Adhesion index (%) of enameled cast iron

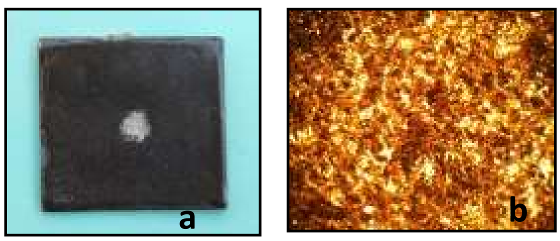

Figure 7: Photograph and microstructure of the peeled surface of coating by the adhesion test

4. Conclusion

It can be concluding the following from the results obtained in this study:

- The enamel coatings successfully applied as a single layer by simple enameling processes on cast iron alloys.

- Generally, crystallization agents improve the mechanical properties.
- The proposed coating material have a reasonable low melting (1250˚C) and processing 870˚C temperature, that lead to reduce the cost and energy consumption during enameling processes.
- The crystalline phases formed in resultant coatings depend on initial composition, type and concentration of crystallization agent.

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