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A new high thermal shock resistant one-layer glass–ceramic coating for industrial and engineering applications

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ABSTRACT

Purpose: A new high thermal stability single layer glass–ceramic coating system designing for applied on various grade of steel alloy has been developed in this work.

Design/methodology/approach: The thermal shock resistance, thermal conductivity and thermal expansion of the coating system were evaluated by using suitable standard tests. Some crystalline agents (Lithium oxide Li_2O, Titanium oxide TiO_2, Zircon $ZrSiO_4$ and Feldspar $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) were add at constant ratio 6% to coating system to evaluate their effects on the resultant coatings.

Findings: The results indicate the suitability of these coatings for protection of metal substrate. Also the results show that the properties of resultant coating were hardly affected by composition and concentration of crystalline agent.

Research limitations/implications: Coating with lithium oxide has the lowest thermal expansion, which means the highest thermal shock resistance. While, values of thermal conductivity were too close for all types of coating.

Originality/value: Generally, the resultant coating properties have been enhanced in all cases; this is associated with the introduce the crystalline agent which lead to the formation of a complex network of crystalline phases.

Keywords: Glass-ceramic; Enamel coating; Frit

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PROPERTIES

1. Introduction

For components work at severe temperatures, most deterioration and failures problems of material is due to thermal shock, chemical attack, or extreme differences in thermal expansion coefficients [1]. Nowadays, with the fast progress in technology, the more demand was arising to extend the life or improve the performance of materials and components working at high temperatures. This can be attained by developing a new material, applying coating, or a combination of these [2]. Coating of materials can be achieved using different techniques: thermal spraying, physical or chemical vapour deposition methods, complex multi-step processes. However, the main drawback of these coating methods is the porosity of the coated layer as well as most of them is technically very complex and work for limited geometry [3]. In the other hand, the use of high alloy materials to protect the components at high temperatures has disadvantages lies in the high cost and rare resources for alloy metals like Cr, Ni, Mo and W. Recently, oxide based coatings like glass-ceramic enamel coating has a wide usage in different fields to complement the metal features by adding further refractoriness, erosion resistance, and thermal insulation characteristics. Glass-ceramic enamel coating has additional features of excellent physical and mechanical properties and chemical inertness as well as safe and easy application in addition to quit low cost [4].

Glass-ceramic enamel refers to deposition of a layer of glass on a metal surface and fixed in firing to produce a vitreous coat that protects the metal against the external effects [5]. Often, the coating applied onto metal surface as double layers. In this double coat system there are two steps (layers) of coat: precoat (ground) and top coat (cover). The ground coat which is dried prior to top coating consider as intermediate layer between cover coat and metal substrate and must possess good adherence with surface of metal substrate therefore the composition of the charge for a precoat must include some oxides that promoting the adhesion with substrate such as nickel oxide, cobalt oxide, and manganese oxide [6]. The top coat has to possess excellent chemical resistance and thermal strength and good aesthetic features thus large content of silicon oxide (SiO_2) were often included in the constitution of frit for top coat. The process of forming a single layer enamel differs from the formation of two layer enamels due to the single layer enamel fulfills the functions of both precoat and top coat at once. One-layer enamel allows conserving raw materials and power by decreasing the coats and number of firings. The use of one-layer coatings makes it possible to obtain a higher-quality surface on the metals, since the surfaces become high elastic and shock-resistant when the thickness of resultant coating reduces [7].

In spite of the high performance of enamelled materials but up to now there is still a lack of enamelled materials can be worked at operating temperatures above 500-700°C [8-11]

In this paper, the method of preparation and processing of a new single layer and high thermal stability glass-ceramic coating materials designing for applied on various grade of steel alloy was presented. The process and technique of application, and the effects of crystalline agents on some properties of the resultant coatings were described in this work.

2. Methods

2.1. Preparation of metal substrate

An alloy of low carbon steel with chemical composition shown in table 1 and was used as substrate in current work. All samples were heated at 450°C to remove any organic contaminant. Then samples subjected to grit blasting on two sides to remove the rust and scale. The main purpose of this treatment is to increase the surface roughness of samples that helps promote good adherence.

Table 1.
Chemical composition of steel

Element	C	Mn	P	S	Si	Cr	V	Cu
wt%	0.09	0.85	0.007	0.005	0.25	0.015	0.003	0.016

2.2. Frit manufacturing and coating application

The inorganic oxides based coating compositions (presented in Table 2) were prepared by the well-known frit manufacturing process and were applied on pre-cleaned cast iron surface by conventional enamelling technique.

Table 2.
Weight percent of four types of frit

Material	Weight percent of frit			
	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	–	–

Various oxides and/or their corresponding nitrates or carbonates along with constant amount 6% of crystalline agents (Lithium oxide Li_2O, Titanium oxide TiO_2, Zircon $ZrSiO_4$, and Feldspar $CaO·Al_2O_3·2SiO_2$) were utilized to make four batches to prepare the coating materials. The required amounts of raw materials of each batches were weighed and thoroughly mixed to ensure even distributed mixture and charged into a ceramic crucible in an electrical furnace and smelted at about 1250°C. The smelted mixture was stirred for homogenization and after soaking for about two hours, the melted mixture was gradually and gently poured into cold water to quench the mixture and produce glassy flakes of the coating material called frit that was then dried by an oven at 125°C for 15 min. Figure 1 illustrate the frit after milling process.

Fig. 1. Milled frit (major constituent in enamel coating)

For applied the coating material, the frit was ground by means a porcelain milling jar along with a number of mill-additives (as detailed in Table 3) to produce a thick slurry called 'slip'. Then, coating slips were applied onto metal surfaces by dipping technique and dried, and then fired at temperature of 780°C for about 10 min to obtain a sample metal enamel. Finally, to obtaining the glass-ceramic

Table 3.
Weight percent composition of slip

Compound	Frit	Clay	Borax	Quartz	Water
Weight part	100	7	1	5	50

structure, the enamelled samples were held in a furnace at temperature 850°C for 120 min. The whole glass-ceramic coating application process is shown in Figure 2.

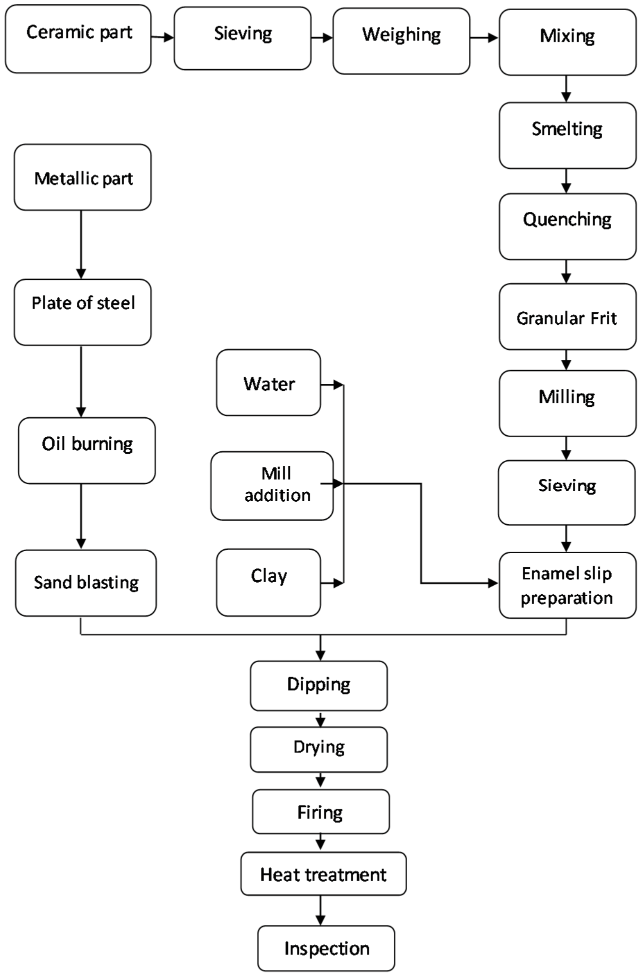

Fig. 2. Flow chart of experimental procedure

3. Inspection and testing

3.1. Visual examination

After applied the coating, all enamelled samples were examined visually to evaluate the coating.

3.2. Thermal shock resistance

A simple method was employed to determine the thermal shock resistance property [12]. The test includes exposed the coated specimens to cyclic heating up to a specified temperature in an electrical furnace, maintain the temperature for 30 min to attain the thermal equilibrium, and then taken out and instantly quenched in distilled water at room temperature. The process heating and cooling is repeated several times, beginning from 200°C, whereby the enamelled specimens were heated each time to a temperature 50°C higher than the previous one.

The specimen surface is examined and evaluated visually until the occurrence of visible surface damage. The difference of temperature ΔT (°C) was calculated between the maximal heating temperature, at which, after cooling with distilled water, the destruction of the enamel coating occurred, and water temperature (20°C).

3.3. Thermal expansion coefficient

According to the (ISO 17562:2001E), a rod of enamelled specimens was prepared by semidry pressing them to dimensions 5x30 mm using hydraulic press and fired at 780°C for 7 min. Next the enamel rod specimen heat treated at 850°C for 2 h to obtained the crystallization structure. Coefficient of thermal expansion was determined by using equation:

$$\alpha = \frac{\Delta L}{L\,\Delta T}, \quad (1)$$

where: ΔL is the change in length, L is the original length, ΔT is the temperature difference.

3.4. Thermal conductivity

The conduction of heat through solids occurs as a result of temperature gradients. In analogy to Fick's law, the relationship between the heat flux and temperature gradients ($\Delta T/\Delta X$) is given by:

$$\frac{\Delta Q}{\Delta t} = K_{th}\frac{A*\Delta T}{\Delta X} \quad (2)$$

where: $\frac{\Delta Q}{\Delta t}$ is the heat transferred per unit time across a plain, A is the area of the plane normal to the flow of the thermal energy, K_{th} is a material property that describes the ability of a material to transport heat (Eq. (3)).

For enamel coating the test of thermal conductivity is carried out by using Lee's disk [13]. Specimens are disks of 50x3 mm dimensions prepared by semidry pressing using hydraulic press heating up to 750°C in electric furnace. Figure 3 is showing the Lee's disk device. Specimen was putting between two disks (A, B), H is an electric heater connected to an electrical source, C is a brass disk. Temperature of disks A, B, and C were measured by thermometers. Electric current used was 4.5 Am and voltage 6 V.

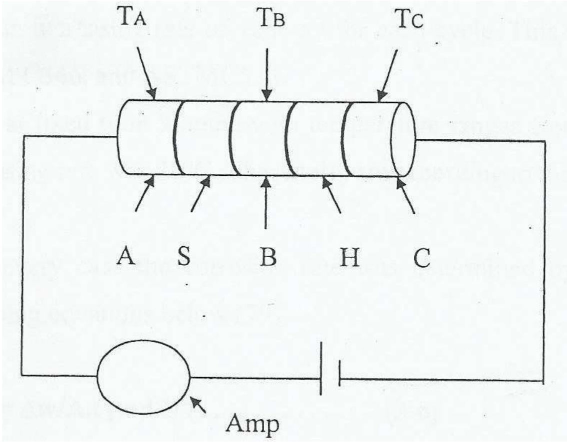

Fig. 3. Lee's disk, A, B, C are brass disks, H is an electrical heater, S is the sample

Thermal conductivity is calculated by using the following equations:

$$K_{th} = \frac{T_A - T_B}{ds} = E_{th}\left[T_A + \tfrac{2}{r}\left(d_A + \tfrac{1}{4}ds\right)T_A + \tfrac{1}{2r}(dsT_B)\right] \quad (3)$$

$$H = V \cdot I = \pi r^2 \cdot E_{th}(T_A + T_B)2\pi \cdot E_{th}(d_A T_A + + \tfrac{ds}{2}(T_A + T_B) + d_B T_B + d_C T_C \quad (4)$$

where: E_{th}: thermal energy (W/m^2·K), r: radius of disks = 20 mm, d_A: thickness of cupper disks $=d_B=d_C=$ 10 mm, ds: specimen thickness = 3 mm, H: thermal energy per unit time, I: current= 4.5 Am, V: voltage= 6 volt.

4. Results and discussion

Visual examination revealed the success of coating process and obtained free defect enamelled samples (Fig. 4). Also, the examination of enamelled samples revealed that most have thin thickness layer coating which adhered tightly to steel surface and have a glossy touching. The low fired temperature mainly contributed in reduce the chance of formation of well-known defect fish scale which related with hydrogen dissolve in austenite [9].

Thermal expansion coefficient is considered as the most important parameter for ensure the strong bond between coating and metal substrate. If the enamel coatings have thermal expansion coefficient lower as compared to that of the metal, it contracts less quickly and will be in compression at room temperature and in the reverse case the enamel coating will be in tension [11]. As well known a glass is strong in compression and weak in tension thus it is preferred to design the enamel coating to have a smaller

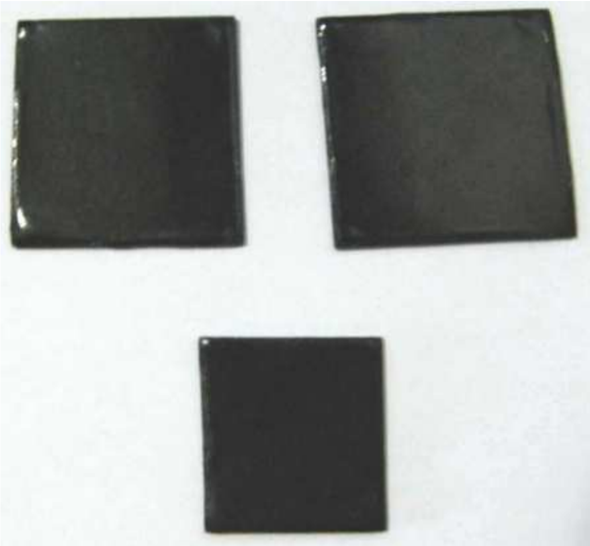

Fig. 4. Enamelled samples

thermal expansion coefficient than that of the metal in order to keep the coating in compression. Thermal expansion coefficient for the four types of low carbon steel frits were measured by heating rods that have been formed by pressing the frit powders up to 650°C and T.E.C. calculated from Equation (1), results for thermal expansion coefficient are shown in Figure 5. According to the effect on thermal expansion coefficient, crystallization agent can be arranged as follow; lithium oxide, zircon sand, titanium oxide, and feldspar. Compressive stresses in enamel coating have additional benefit of increasing the resistance to chipping and fish scaling. In other hand, the excessive compressive stresses in enamel coating will lead to warping of enamelled samples and produce micro cracks at coating-metal interface. Therefore, it is necessary to control the thermal expansion coefficient enamel coating to be approximately half of that of the substrate. From results it is clear that the coating with lithium oxide has the lowest thermal expansion which means the highest resistance to enamel defects (chipping and fish scaling).

Thermal expansion coefficient is usually taken as a guide to the thermal shock resistance [14]. The general plan classification of thermal shock resistance enamels involves three levels of thermal expansion, the high, the intermediate, and the low thermal expansion. The classification might be justified by the facts that most of the analytical expression for the thermal shock resistance contain (α) in the denominator. Indicating that as (α) approaches zero, the shock resistance would theoretically reach infinity. It is well known historical and experimental fact that the dense, low porosity materials with extremely

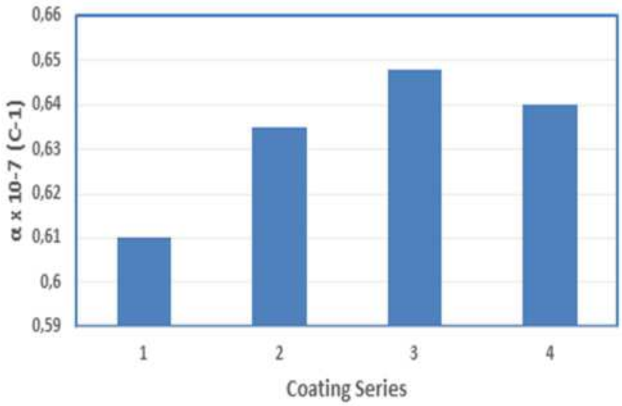

Fig. 5. Thermal expansion coefficient of enamelled steel

low coefficient of expansion have the best resistance to thermal shock. The greater the residual compressive stress in the enamel, the greater in the resistance to thermal shock failures. Also, thermal shock resistance is a direct function of coating thickness. Thin coatings (with their greater residual compressive stress), such as one-coat enamels, provide excellent thermal shock resistance. The results for thermal shock resistance are shown in Figure 6. It can be observed that the addition of crystallization agent has a significant effect on thermal shock resistance of coatings. As mention above the thermal shock resistance increased with decreasing of thermal expansion coefficient where the coating with lithium oxide has the highest thermal shock resistance as compared to other types of coating.

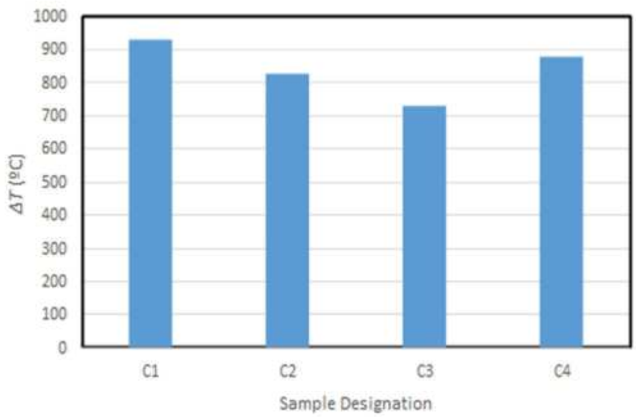

Fig. 6. Thermal shock resistance of enamelled steel

Thermal conductivity is an important factor in detecting the refractoriness of enamel. It is measured using Lee's disk and calculated by Equation (3). The results of thermal conductivity of enamelled samples are present in Figure 7.

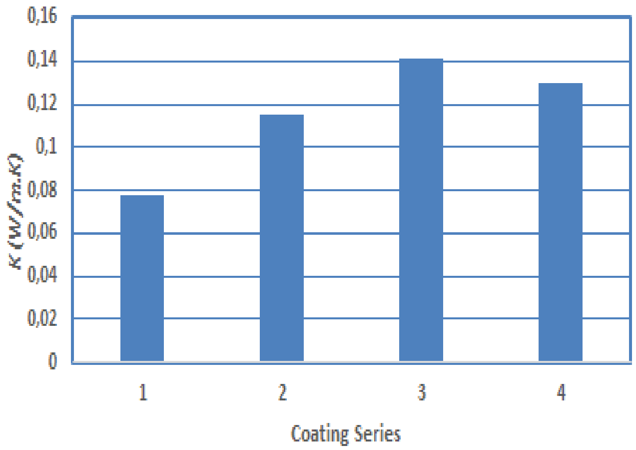

Fig. 7. Thermal conductivity of enamelled steel

Enamel with lithium oxide has the lowest thermal conductivity and this is because of the developed system has a very low coefficient of thermal expansion as compared to those for other coatings. The very low expansion coefficient in this system, which is in some cases are appreciably lower than that of fused silica, are associated with the presence of crystalline phases which have a low expansion coefficient. Other values are so close but we may see that thermal conductivity of zircon sand enamel is lower than that of titanium enamel.

5. Conclusions

The following conclusions may be drawn from the results obtained in this work:

- The new glass-ceramic coating system can be applied successfully as a single coat by using a simple vitreous enamelling technique onto low carbon steel sheets.
- Coating with lithium oxide has the lowest thermal expansion and subsequently the lowest thermal conductivity as compared to other types of coating which means the highest resistance to enamel defects (chipping and fish scaling).
- Coating with lithium oxide has the highest thermal shock resistance as compared to other types of coating.
- Generally, crystallization agents enhance the thermal properties of resultant coating in all cases.
- The proposed coating system has approximately low smelting point (1200°C) and processing 780°C temperature, which lead to reduce the cost and energy consumption during preparation and application process.

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