Effects of heat treatment, quartz additions and particle size on the properties of enamel with low-alloy steel substrate

Ibrahim K. Abdulrahman¹, Ibtihal A. Mahmoud² and Adnan S. Jabor³

¹Ministry of Oil, Midland Refinery Company, Karbala Refinery Project, Karbala, Iraq
²University of Technology, Mechanical Engineering Department, Baghdad, Iraq
³University of Basrah, Mechanical Engineering Department, Basrah, Iraq

Abstract. A vitreous enamel coat is a thin layer of glass, typically a few hundred microns in thickness, which is fused onto a metal substrate. The glass used for vitreous enamelling is referred to as the ‘frit’ and is formulated from a wide range of inorganic raw materials including quartz, borax and titania. This research called for the preparation and development of a mixture of ceramic materials, consisting of various metal oxides, for coating low-alloy steel plates with a carbon percentage of 0.18%. A single coating layer was used with a dipping method. Before dipping, the samples were treated with sand blasting. The effects of heat treatment temperature and time, the percentage of quartz additions and coating powder particle sizes were all studied. It was found that crystalline phases (such as (SiO₂), (Na₂O₆SiO₂-TiO₂-SiO₂), (Li₂Al₂O₅SiO₂)) were developed in the structure of the coating after heat treatment processing. The results showed significant improvement in all properties of coating hardness, adhesion, thermal stability and chemical resistance by increase in the heat-treating temperature and time; the best results were obtained in the properties of the coating with the treatment temperature at 650 °C, a time of 120 minutes and 15% quartz addition. The results also showed a clear effect of the particle size of powder coating on the properties of hardness and adhesion. When the particle size decreased, the mechanical properties (hardness, adhesion) and thermal stability improved. The results indicated that the increase in coating particles’ size led to an increase in the coating thickness.

Key words: vitreous enamel, ceramic coating, corrosion resistance, heat treatment, steel enamelling, particle size, crystallization

1. Introduction

Vitreous or porcelain enamel is a thin layer of glass, typically a few hundred microns in thickness, which is fused on the metal substrate. The glass used for vitreous enamelling is referred to as the ‘frit’ and is formulated from a wide range of inorganic raw materials including quartz, borax and titania. Vitreous enamels are complex glasses, which have been formulated to meet their specific in-service requirements. When combined with ceramic colouring agents, vitreous enamels can be obtained in a virtually endless choice of colours[1].

Enamel, applied as a thin coating on steel, is highly suitable for architectural panels, silos and equipment for chemical industries. Vitreous enamel has a hard, abrasion-resistant surface, along with a high resistance to high temperatures and thermal shock. Furthermore, vitreous enamel has a high chemical resistance and a surface that is hygienic due to its ease of cleaning[2].

Thanks to modern technology, a number of surface coating materials for different industrial and engineering applications are now in use. Oxide coatings provide the advantages of chemical inertness, high temperature stability and superior mechanical properties in comparison with other, non-oxide, coatings currently in use e.g. metals, polymers, paints, rubbers, etc. Often, the coating systems are engineered selectively, for very specific end use requirements. Modern engineering technology now demands coatings that should also have a broad spectrum of effectiveness under a range of hostile environments. In recent years, dramatic improvements in property of glass-ceramic coating systems have been achieved, by tailoring the microstructure of the glassy oxide coating matrix either by the addition of secondary phases or by in situ crystallization of glassy oxide coating after application. Besides the functional properties needed to suit particular end use requirements, these coatings in general need to achieve good adherence, a defect-free smooth surface and refractoriness [3].

Several research studies have been performed, giving a reasonably coherent picture of industrial enamelling and the adherence process between ceramic coatings and metals. Most of these studies focus on enhancing the adhesion index of the ceramic coating to the coated substrate by controlling either the chemical composition of coating materials, or other factors like the pre-surface treatment of the metals [4-5]. Other studies have focused of the interface microstructures between the enamel coat and the hot-
rolled steel, pre-treated with and without adhesion agent. Researchers have explored the differences between regular enamelling coating and glass-ceramic coating and shown that the latter has advantages of chemical inertness, high temperature stability and superior mechanical properties such as abrasion, impact, etc. when compared to other coating materials[6].

The aims of this research comprise development of a coating by growing a crystalline phase to produce glass-ceramic using a heat treatment with different conditions, and studying the effect of heat treatments, mill addition and particle size on the hardness, adhesion, thermal stability, chemical resistance and thickness of the enamel coating.

2. Experimental work

2.1. Sample preparation

The substrates used for enamel coating were rectangular plates (20 mm * 30 mm with a thickness of 1.5 mm) of low-alloy steel. Table 1 shows the chemical composition of the low-alloy steel. The metal surface was exposed to a jet of abrasive material (hard sandstone) to remove scale, rust and dirt. The surface became clean and slightly pitted, which helps to promote good bonding. Before sand blasting, oil and organic contaminants were removed by heating the surface to 300°C. In this study, surface treatment by sand blasting of substrates was used. An application significantly reduced the use of acid etching and nickel flashing. Sand blasting only system reduces the costs of in-plant processing for direct-on enamel application to low-alloy steel.

| Table 1. The chemical composition of low-alloy steel |
|-----------------------------------------------|
| Element | C   | Al  | Co  | Cr  | Cu  | Mn  | Mo  | Ni  | Nb  | Pb  | Si  | Ti  | V   | W   | Fe  |
| Weight (100%) | 0.18 | 0.05 | 0.05 | 1.3  | <0.05 | 0.12 | 0.4 | 1.35 | 0.05 | <0.05 | 0.05 | 0.05 | 0.05 | 1 balance |

2.2. Preparation of coating frit

The process of forming one-layer enamels differs from the formation of two-layer enamels because the former fulfil the functions of both ground and cover layers at once. In this study, the possibility of developing a matrix formula for a single-coat glass ceramic with high chemical and mechanical properties was investigated, and then used to coat the steel.

The steps taken to manufacture the frit were:

2.2.1. Weighting raw materials: the weighing more than ten different materials used for preparing the frit was carried out using a digital electrical balance with a sensitivity of 0.0001gm. The weights and compositions of the coat are listed in Table 2.

2.2.2. Smelting: after good mixing, the materials batch was smelted at 1250°C with a 2.5 hour holding time, using an electric furnace. The batch was held at this temperature (1250 °C ) until all the raw materials had reacted and the batch became a homogeneous and a bubble-free liquid.

2.2.3. Quenching and milling: when smelting was complete, the molten material (ceramic oxides) was quenched with a cool water spray that shattered the material into small glass particles called frit. After that, the frit was milled using a ball mill, with alumina balls as grinding media.

| Table 2. The weights and compositions of the coat |
|-----------------------------------------------|
| Compound | SiO₂ | B₂O₃ | Na₂O | TiO₂ | Li₂O | ZnO | CaO | Al₂O₃ | CoO | NiO | CaF₂ |
| Weight (%) | 52  | 10  | 9   | 8   | 7   | 4   | 3   | 3    | 2   | 1   | 1    |

3. Preparation, application and firing of enamel slip

3.1. Sieving: the milled powder was sieved using a mechanical shaker and micro sieves. In this work we used three particle sizes of milled frit (150, 75 and 53 μm) to study their effects on the coating properties.

3.2. Mill addition: Clays and electrolytes were used to control the properties of the slip. Refractory materials and pigments may be added to impart desired properties to the fired coating. All materials
mixed in the mixer for three hours. In this work we added quartz in different amount (5, 10 and 15 %wt) to study their effects on coating properties.

3.3. Weighing a suitable amount of frit, we added to the frit 7% clay, 1% borax [8, 10], (5, 10, 15) % quartz and 50% water to make the coating slip.

3.4. The compositions of the enamel slip were mixed for one hour using a mechanical stirrer, to obtain the required consistency.

3.5. The coating was applied to the specimen by dipping method, and then the coated specimen was dried at 120˚C for 15 minutes [7, 8].

3.6. The coated specimen was fired in a furnace at 860˚C for 4 minutes.

4. Inspections and Testing:

4.1. Coating thickness: Coating thickness was measured with a coating thickness gauge. The instrument was held at right angles to the surface to be measured, the contact pin placed on the surface and the small bottom was pushed down: the thickness of the coating was shown on the digital display.

4.2. X-Ray Diffraction Test: the X-ray diffraction instrument was PANalytical with Cu Kα 1.54060 Å radiation tube and 40Kv - 20mA. To detecting any crystalline zone in the specimen surface, the detector was moved through an angle of 2Ɵ = 2 to 60 degrees. This testing was carried out at the University of Basrah’s science college.

4.3. Micro-hardness measurement: the hardness of the specimens was measured with a Vickers micro-hardness test. The hardness tests were performed under an indentation load of 50 g for 20 s. In order to obtain reliable statistical data, analysis points were spaced so as to eliminate the effect of neighbouring indentations, and the hardness was evaluated by taking three indentations on each specimen and takes the average values.

4.4. Adhesion index tests: all adherence measurements were obtained in accordance with the standard adherence test of the Institute of Vitreous Enamellers T29[9]. The sample enamelled sheet was deformed by a punch with a hemispherical tip, onto which fell 1.5 kg mass dropped onto the enamelled sheets. This test evaluates the degree of adherence of vitreous enamel to metal, in terms of the amount of metal exposed after standard deformation treatment. The indicator of adherence is the adherence index, which is the ratio of the vitreous enamel remaining in the deformed area to that in the same measured area prior to deformation. The enamel adhesion strength can be graded into first, second, third, fourth and fifth grade: the first grade is the best. If most of the enamel layer is removed from the steel sheet, and the surface appears silvery bright after the impact, the adhesion strength is poor and thus fifth grade. If most of enamel layer remains on the steel sheet, the adhesion strength is excellent and first grade. The reference photos of the five adherence levels of each of the three types of enamel – ground coat, cover coat, direct on enamelling – called a ‘visual classification’ are shown in Figure 1.

Figure 1. Visual classification photos[10].
4.5. Acid and alkali resistance: a set of tests for chemical resistance of glass-ceramic coating was conducted. This procedure was used to study several commercial enamels, the acid resistance test complying with ISO 2743 [11]. The sample was exposed to solution of 11% sulphuric acid $\text{H}_2\text{SO}_4$ acting for 2.5 hours at 100°C with a controlled heater. Alkali resistance was made according to ISO 2745 [11]. A sample was exposed to a hot solution of 10% sodium hydroxide $\text{NaOH}$ at 100 °C for 2 hour. The chemical resistance (acid and alkali) of the all specimens was represented in weight loss per unit area.

4.6. Heat treatment: to investigate the effect of crystallization on properties of the vitreous enamel coatings on the steel substrate, the enamelled specimens were held in a furnace at different temperatures (500, 550, 650) °C for one and two hours respectively as shown in Table 3.

Table 3. Heat treatment at different temperatures and times

| Alloy        | Particle size of milled frit (µm) | Quartz addition %wt | Heat treatment                              | Symbol |
|--------------|----------------------------------|---------------------|---------------------------------------------|--------|
| Low- alloy steel | ≤ 53                             | 0                   | As-fired                                    | A      |
|              |                                  |                     | Heating to 500°C and holding for 1hr         | $A_{11}$ |
|              |                                  |                     | Heating to 500°C and holding for 2hr         | $A_{12}$ |
|              |                                  |                     | Heating to 550°C and holding for 1hr         | $A_{21}$ |
|              |                                  |                     | Heating to 550°C and holding for 2hr         | $A_{22}$ |
|              |                                  |                     | Heating to 650°C and holding for 1hr         | $A_{31}$ |
|              |                                  |                     | Heating to 650°C and holding for 2hr         | $A_{32}$ |
|              |                                  | 5                   | As-fired                                    | B      |
|              |                                  |                     | Heating to 500°C and holding for 1hr         | $B_{11}$ |
|              |                                  |                     | Heating to 500°C and holding for 2hr         | $B_{12}$ |
|              |                                  |                     | Heating to 550°C and holding for 1hr         | $B_{21}$ |
|              |                                  |                     | Heating to 550°C and holding for 2hr         | $B_{22}$ |
|              |                                  |                     | Heating to 650°C and holding for 1hr         | $B_{31}$ |
|              |                                  |                     | Heating to 650°C and holding for 2hr         | $B_{32}$ |
|              |                                  | 10                  | As-fired                                    | C      |
|              |                                  |                     | Heating to 500°C and holding for 1hr         | $C_{11}$ |
|              |                                  |                     | Heating to 500°C and holding for 2hr         | $C_{12}$ |
|              |                                  |                     | Heating to 550°C and holding for 1hr         | $C_{21}$ |
|              |                                  |                     | Heating to 550°C and holding for 2hr         | $C_{22}$ |
|              |                                  |                     | Heating to 650°C and holding for 1hr         | $C_{31}$ |
|              |                                  |                     | Heating to 650°C and holding for 2hr         | $C_{32}$ |
|              |                                  | 15                  | As-fired                                    | D      |
|              |                                  |                     | Heating to 500°C and holding for 1hr         | $D_{11}$ |
|              |                                  |                     | Heating to 500°C and holding for 2hr         | $D_{12}$ |
|              |                                  |                     | Heating to 550°C and holding for 1hr         | $D_{21}$ |
|              |                                  |                     | Heating to 550°C and holding for 2hr         | $D_{22}$ |
|              |                                  |                     | Heating to 650°C and holding for 1hr         | $D_{31}$ |
|              |                                  |                     | Heating to 650°C and holding for 2hr         | $D_{32}$ |
| 53> and ≤ 75 | 0                                | As-fired            | E                                            |
| 75> and ≤ 150| 0                                | As-fired            | F                                            |
5. Results and discussion
5.1. The effect of heat treatment, quartz addition and particle size on the coating thickness
The thickness of as-fired and crystalline coating was nearly unchanged and fell in the range (220 – 416 μm); the heat treatment and mill addition had no significant effect on coating thickness. The particle size variation made a change in coating thickness and this is shown in Figure 2. It is clear that the increasing particle size of the coating led to increase in its thickness, and this is due to the size of particles when they accumulated on the metal surface for the same coating technique.

5.2. The effect of heat treatment, quartz addition and particle size on the phase structure
The coating having been characterized by x-ray diffraction, that x-ray diffraction analysis indicated the presence of two types of crystalline phase, quartz and rutile, in both as-fired and heat treated coatings. Figure 3 illustrates.

The x-ray diffraction charts of the heat-treated coatings showed four types of crystalline phase: (Q)quartz (SiO2), network of sodium-aluminium-titanium-silicate (B) (Na2O-Al2O3-TiO2-SiO2), lithium-aluminium-silicate (C) (Li5AlSi2O8) and rutile (R) (TiO2), as is shown in Figure 4 (a, b and c). It is clear that the heat treatment process promoted the transformation from amorphous glassy matrix coating to the crystalline (glass–ceramic) coating. The x-ray diffraction shows that increase in the heat treatment temperature led to the growth of the crystalline phases when the heat treatment time was kept constant. The same action occurred when the heat treatment time increased and the temperature was constant. The result also indicates that the quartz addition had no significant effect on the development and growth of the crystalline phases, only on its intensity peaks.
Figure 4. (a) X-ray diffraction charts of coating heat treatment at 500 °C, (b) x-ray diffraction charts of coating heat treatment at 550 °C, (c) x-ray diffraction charts of coating heat treatment at 650°C.
5.3. The effect of heat treatment, quartz addition and particle size on the mechanical properties

5.3.1 Hardness: figure 5 shows the effect of the heat treatment temperature and time on the coating hardness, with different amount of quartz addition. It is clear that the increase in the heat treatment temperatures led to increasing hardness values in both heating times, and that improved coating hardness came from development and growth of the hard crystalline phases, especially quartz (SiO_2) and rutile (TiO_2).

Figure 5. The effects of the heat treatment temperatures on coating hardness with different amounts of quartz addition, (a) for 1hour and (b) for 2hours.

Also, the quartz acted as the nucleation agent in coating materials and that helped to develop a new network of crystalline phases, which had significant effects on the hardness values of the coating, and that is obvious when the hardness values reach the strongest peak (819 Hv) at 15% quart addition at 650 °C for 2h. The results also indicated the quartz addition increased the hardness value. This improvement in hardness of the coating was due to incorporating a percentage of a hard component (quartz) into the coating materials, as shown in Figure 6.
5.3.2 Adhesion testing: the heat treatment process in both treating times (1 hour and 2 hours) had a significant effect on the adhesion strength, as is shown in Figure 7. The metal surface was pre-treated by sand blasting, and that led to a roughened surface and made mechanical anchor points (catch points) which increased the mechanical interlocking (contact area) between the coating and metal interface. But the improvement in adherence strength, which is clear from the figure, also arose from the contribution of other methods (chemical, galvanic theory) that increased its action, with an increase in temperature and time of heat treatment on the coating / metal interface morphology, and finally on the adhesion strength. This is shown in the strongest peak at 650 °C and 2 hour heat treatment stage in Figure 9. The results agree with the research [14].
There are further factors that affect the adhesion strength; one of these is the particle size of the coating material. Figure 8 shows the relationship between the adherence strength and the coating particle size, and it is obvious from the figure that the adhesion strength decreased with increasing particle size. This can be attributed to the bad mechanical interlocking between the coarse particles and metal interface, which caused partial filling of pitting on the metal surface after firing.

![Graph showing adherence index vs. particle size](image1)

Figure 8. The effect of particle size on adherence index for as-fired coating and pictures of the deformed as-fired samples as a particle size effect on the deformation morphology.

5.3.3 The effects of heat treatment, quartz addition and particle size on thermal stability

The results indicate that crystallization treatment had a significant effect on thermal stability (thermal shock resistance) as shown in Figure 9 (a and b). The results show that an increase in thermal stability was realized in all of the crystallization treatments and times, and there was no difference in results when the amount of added quartz fell in the range 0–5 %. The coating, which was treated at 550 °C for 1 hour) and at 650 °C for 1 and 2 hours, and quartz addition in the range 10–15% had maximum thermal stability values (resisting up to ΔT=875°C without any damage). That improvement came from the crystalline transformation, which occurred in the coating and led to developed phases that had a low thermal expansion coefficient, especially the quartz (SiO₂) phase, and that led to increased thermal stability (thermal shock resistance).

![Graph showing stability temperature vs. heat treatment temperature](image2)

(a)
Thermal shock resistance is a direct function of enamel coating thickness. The greater the residual compressive stress in the vitreous enamel, the greater is the resistance to thermal shock failures. Thin coatings (with their greater residual compressive stress), such as one-coat enamels or the two-coat enamel with a low expansion cover coat, provide excellent thermal shock resistance[8]. So, it was known previously that the increase in particle size of the coating material would increase the thickness of the coat. This leads to decreased thermal shock resistance, as shown in Figure 10.

5.3.4 The effects of heat treatment, mill addition and particle size on chemical resistance properties

Figure 11 shows how acid resistance was greatly affected by heat treatment temperature and time with different amount of quartz addition, as given in Figure 10. The acid resistance (11% H2SO4 at 100 °C) was enhanced by increased treating temperature in both treating time with different amounts of quartz addition (5%, 10%, 15%), and that may be due to the crystallization process that occurred in the coating, leading to the development of complex and strong crystalline phases with quartz (SiO2), network of sodium-aluminum-titanium-silicate (Na2O-Al2O3-TiO2-SiO2), lithium-aluminium-silicate (Li5AlSi2O8) and rutile (TiO2)).
The result also indicated that alkali resistance was affected by the heat treatment conditions, and quartz addition in all cases as seen in Figure 12. It is clear that the alkali resistance improved when crystallization temperature and time were increased. This improvement is associated with the presence of crystalline phases (network of sodium-aluminium-titanium-silicate (Na₂O-Al₂O₃-TiO₂-SiO₂), lithium-aluminium-silicate (Li₅AlSi₂O₈) and rutile (TiO₂)), which as previously mentioned also may improve the resistance to attack by alkali solutions. Also, it is obvious from the figure that alkali resistance slightly decreased when the quartz addition was in the range 10–15%. This is explained by the fact that the kinetics of failure of the coating in alkaline solutions have a different mechanism to that seen in acids. Accordingly, the hot alkaline solution reacted with the acidic oxide (silica SiO₂) which was present in the coating and the added oxide (quartz SiO₂), leading to a decrease in alkali resistance. These results agree with the research (12–14) and indicate that particle size had no effect upon acid and alkali resistance.
6. Conclusions
The present work has generated following conclusions:

6.1. The heat treatment processes led to development of crystalline phases such as quartz (SiO2), network of sodium-aluminium-titanium-silicate (Na2O-Al2O3-TiO2-SiO2), lithium-aluminium-silicate (Li5AlSi2O8) and rutile (TiO2) whereby glass-ceramic enamels were obtained.

6.2. The heat treatment processes improved and increased the hardness, adhesion, thermal stability and chemical resistance properties (acid and alkali resistances) of the resultant coatings, in all cases.

6.3. An increase in the quartz addition (5–15%) to the coating material improved the hardness and adhesion properties and acid resistance, but it also led to a decrease in the alkali resistance when a high addition percentage (15% quartz) was reached.

6.4. Increase in the size of particles size (53–150) μm of the coating material (frit), led to increase in the coating thickness, and deterioration in the mechanical properties (hardness and adhesion strength). It had no effect on the chemical properties (acid and alkali resistances).
References

[1] F. Singer and S. Singer, *Industrial Ceramics*, Chapman and Hall Ltd., London, 1971.

[2] D. Verboom, Trends and developments in the enamelling industry, *The Vitreous Enameller*, Vol. 46, No. 2, pp. 28, 1995.

[3] A. Majumdar, S. Jana, Glass and glass–ceramic coatings, versatile materials for industrial and engineering applications, *Bull. Mater. Sci.*, Vol. 24, No. 1, p. 69–77, 2001.

[4] F. S. Shieu, Effect of surface pre-treatments on the adherence of porcelain enamel to a type 316L stainless steel, *Journal Material Science*, vol. 34, pp. 5265–5272, 1999.

[5] Dr. Ali H. Ataiwi, Dr. Ibtihal A. Mahmoud, Jabbar H. Mohmmed. Studying and modelling the effects of quartz addition and heat treatment on mechanical properties of glass-ceramic coating, *Eng. & Tech. Journal*, Vol. 32, Part (A), No. 7, 2014.

[6] F. Dana, L. Chuck, Optimizing enamel adhesion, *Bull. Mater. Sci.*, Vol. 25, No. 1, 2002.

[7] X. Yang, A. Jha, An analysis of the microstructure and interfacial chemistry steel–enamel interface”, *Science Direct*, Vol. 443, pp. 33, 2003.

[8] Md. Abul Hossain, Aninda Nafis Ahmed and Md. Anwar Arfien Khan Vitreous enamel coating on mild steel substrate: characterization and evaluation. *International Journal of Scientific & Engineering Research*, Volume 5, Issue 2, February 2014.

[9] M. R. Pérez García et al., Corrosion resistance of enamel vitreous coating obtained by electrophoretic deposition, *Key Engineering Materials*, Vol. 654, pp. 127-131, 2015.

[10] D. Someswar, Studies on broad spectrum corrosion resistant oxide coatings, *Bull. Mater. Sci.*, Vol. 24, No. 6, pp. 569–577, 2001.

[11] Dragica, Nikola, Gruj. Modeling glass-ceramic enamel properties *JS.C.S*, vol. 67, No. 2, pp. 135–142, 2002.

[12] Ibtihal A., Mahmoo Ahmad A., Zainulabdeen, Jabbar A. Mohmmed Experimental study for the effects of crystalline agents on properties of glass ceramic coating *Engineering and Technology Journal* Vol. 36, Part A, No. 2, 2018.

[13] D. Someswar, Studies on broad spectrum corrosion resistant oxide coatings, *Bull. Mater. Sci.*, Vol. 24, No. 6, pp. 569–577, 2001.

[14] I.G. Berdzenishvili. Functional corrosion-resistant enamel coatings and their adherence strength *Acta Physica Polonica* No. 1, Vol. 121 (2012).