Effect of CeO₂ on Enamel Coatings on the Surface of Corten Steel

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Abstract. Different amounts of CeO₂ were added to the basic enamel formula, and preparation of enamel samples by two-burning method, the enamel coatings with different contents of CeO₂ were characterized by acid resistance, IR, SEM and DSC. The results show that introduced CeO₂, B-O-B vibration in [BO₄] enhanced, acid resistance of ceramic layer increased. The introduction of CeO₂ reduces the glass transition temperature of the enamel, while the high temperature viscosity of the porcelain glaze decreases, the surface of the porcelain layer becomes smoother, and the structure becomes denser after enamel sintered.

1. Introduction

Enamel is a composite material composed of metal matrix and inorganic porcelain layer. The commonly used metal matrix materials include low carbon steel, cast iron, aluminum and titanium alloy, etc. The composition and dosage of enamel glaze can be adjusted according to different uses. The raw materials of enamel can be divided into matrix agent, flux, densifier, coloring agent and so on [1, 2, 3]. The original formula material determines the physical and chemical properties of enamel, such as high temperature resistance and acid corrosion resistance [4, 5]. Therefore, adjusting the formulation to obtain better acid resistance enamel coating is the key to this study.

Enamel, as a composite material, exhibit significantly higher performance advantages than a single inorganic material or metal material [6], so it is widely used in petrochemical industry, traditional daily necessities, construction industry and other fields [7,8]. Corten steel such as Q355 serial is a kind of low alloy steel between ordinary steel and stainless steel. This kind of steel is generally suitable for harsh working environment, such as high temperature and acid gas corrosion in air preheater for heat exchanger. With good high temperature resistance and chemical stability, enamel coating is applied on the surface of weatherproof steel to improve its performance.

CeO₂ can eliminate bubbles and trace colored elements, and reduce the viscosity of glass melt at high temperature. Zhang Chunhua etc. [9], showed that the structure of ceria-added enamel was more delicate, the hard particles were dispersed, and the frictional resistance of enamel was significantly improved. Lu Jing etc. [10]. introduced cerium oxide with different content into enamel glaze, and found that doping CeO₂ improved the oxidation resistance and heat resistance of enamel layer. Cheng Jun etc. [11]. found that the addition of a small amount of cerium oxide to Ca-Al₂O₃-SiO₂ series microcrystalline glass can promote the sintering densification of powder and reduce the glass transition temperature.

In this study, enamel was prepared by using basic formula glaze and glaze with different content of
The acid resistance of the coating was compared. The influence of CeO$_2$ on the acid resistance of enamel coating was analyzed by experiments including acid resistance, IR, SEM and DSC.

2. Experimental Procedures

2.1. Preparation of Enamel Glaze
The chemical composition of the oxide of the base glass glaze was shown in Figure 1, 0.00%, 0.40%, 0.80%, 1.20% and 1.60% CeO$_2$ were added into the base formula glaze respectively, and then weighed the raw materials according to the formula and mixed them evenly with mechanical stirring. The mixture was melted at 1550°C for 2.5 hours, poured into a graphite module and then moved into the muffle furnace immediately at 600°C, cooled with the furnace after two hours of heat preservation. The rest of the mixture was poured into the cold water for water quenching, and dried the obtained glass slag for use. The enamel glaze component is shown in Table 1.

Table 1. Compositions (wt%) of foundational glass

| Component | SiO$_2$ | Na$_2$O+K$_2$O+Li$_2$O | CaO+MgO | Al$_2$O$_3$ | B$_2$O$_3$ | Other |
|-----------|--------|------------------------|---------|-------------|------------|-------|
| Mass Fraction | 58.00 | 18.3 | 6 | 3 | 4 | 10.7 |

2.2. Surface Pretreatment of Cowden Steel
The enamel steel plate is made of Q355NH steel plate. The steel plate was kept in a high temperature furnace at 980 °C for 30 minutes, and subjected to high temperature annealing and degreasing to remove the oxide layer and rust on the surface of the steel sheet. In order to remove the rust of the iron billet completely, it was pickled with an 8% sulfuric acid solution, and then the steel sheet was washed with water and then neutralized with a 0.5% caustic soda solution. On the one hand, the lye can neutralize the residual acid, on the other hand, it can form an alkaline film on the surface of the steel plate, which can play a role of rust prevention in a short period of time. Table 2 shows the impurity components of the steel sheet.

Table 2. Impurities (wt%) of Enamel Steel

| Component | C | Si | Mn | P | S | Cr | Ni | Cu |
|-----------|---|----|----|---|---|----|----|----|
| Content /wt% | 0.14 | 0.22 | 0.72 | 0.016 | 0.01 | 0.18 | 0.17 | 0.15 |

2.3. Preparation of Enamel Plate
The enamel glaze blocks prepared in Table 3 were ground dryly for 1 hour with the ball-to-material mass ratio of 3:1. Table 3 was the amount of grinding additives.

Table 3. The amount of grinding material

| Frit | Clay | Sodium nitrite | Borax |
|------|------|----------------|-------|
| 100  | 5    | 0.35           | 0.35  |

2.4. Performance Characterization
The sulfuric acid vapor corrosion test of enamel steel plate was carried out by GB/T 7938-2013 [12]. The glass blocks were cut into 5mm *5mm *25 mm blocks and put into 30 wt.% H$_2$SO$_4$ at 80 °C for 50 H. The surface corrosion of the samples was analyzed by Quanta250 Environmental Scanning Electron Microscopy. The samples were ground into 100 - 200 mesh powders. The X-ray diffraction
3. Analysis and Discussion

3.1. Effect of CeO$_2$ on Section Morphology and Porcelain Layer Structure

3.1.1. Profile characterization
The microstructure of samples in Figure 1 shown that the enamel coatings with or without the CeO$_2$ in the frit. It could be seen from Figure 1 that under the same firing process, porosity existed in the original enamel coating (Figure 1a). The reason is that a large amount of gas is produced in the coating during the firing process. These gases cannot spill over and remain in the ceramic layer to form structural defects. The pore number of enamel coatings containing CeO$_2$ decreases obviously (Figure 1b), the structure is more compact, and smoother surface of ceramic layer. The reason is that cerium ion has two valence states in ceramic layer. Ce$^{2+}$ and Ce$^{4+}$ have strong oxidation and thermal sensitivity. It is easy to obtain electrons during enameling, which reduces the activation energy of crystallization and nucleates spontaneously, thus making the structure of ceramic layer more compact.

![Figure 1. SEM microstructure of the cross section of common and CeO$_2$-containing enamel coatings. (a) Ordinary; (b) With 0.8% CeO$_2$.](image)

3.1.2. Surface profile characterization
Figure 2 shown the surface profile of the ceramic layer. The smoothness of the enamel layer is closely related to the high temperature fluidity of the enamel. Usually, the better the high temperature fluidity of the enamel, the easier the gas in the enamel layer escapes, the better the compactness of the enamel layer and the smoother the surface. The data shown that [13] CeO$_2$, as a network modifier, existed in the network skeleton when there was less CeO$_2$, which played the role of breaking the network and reduced the high temperature viscosity and glass transition temperature of the glaze.

![Figure 2. Surface topography of common and CeO$_2$-containing enamel coatings. (a) Ordinary; (b) With 0.8% CeO$_2$.](image)
3.1.3. The Influence on The Structure of Enamel

Results shown in Figure 3 indicated that the IR spectra of different CeO$_2$ ceramic layers. It could be seen from the figure that there are four obvious absorption peaks near 1450 cm$^{-1}$ wave number, 1080 cm$^{-1}$ wave number, 798 cm$^{-1}$ wave number and 482 cm$^{-1}$ wave number, which correspond to the absorption bands caused by O-B-O antisymmetric stretching vibration. The stretching vibration of Si-O in [SiO$_4$], the anti-stretching vibration of Si-O-Si, and the B-O-B vibration in [BO$_4$], The flexural vibration of O-Si-O; the flexural vibration of Si-O-Si. The results showed that when the content of CeO$_2$ was between 0% and 1.20%, the stretching vibration of Si-O in [SiO$_4$], the back-stretching vibration of Si-O-Si and the B-O-B vibration in [BO$_4$] are enhanced, which was beneficial to improving the continuity of the network structure of the ceramic layer, while increasing the content of CeO$_2$ would reduce the stability of the structure.

![Figure 3. IR pattern of enamel with different CeO$_2$ contents](image)

3.2. Effect of CeO$_2$ on Mechanical Properties of Enamels

3.2.1. Thermal expansion performance test

As shown in Figure 4, the variation of linear expansion coefficient of ceramic glaze with the addition of CeO$_2$. It could be seen from the figure that with the increase of CeO$_2$ content, the linear coefficient of expansion of the enamel fluctuates. According to the theory of "microcrystalline" glass, the macro thermal expansion coefficient of glass was the sum of its internal crystalline phase and amorphous phase [14]. CeO$_2$ could reduce the activation energy of crystallization of glaze, but because there were many crystalline phases in the ceramic layer, the nucleation temperatures of different crystalline phases were different, and they inhibited each other to form fine grains, which was the reason for the fluctuation of linear expansion coefficient of glaze.

![Figure 4. Linear expansion coefficient of enamel with different CeO$_2$ contents](image)
3.2.2. **DSC performance test**

The curves in Figure 5 showed the DSC curve of the enamel. It could be seen from the figure that the glass transition temperature of the glaze decreases with the addition of CeO$_2$. The main reason was that a small amount of CeO$_2$ acts as a network modifier in the glaze, which broke the network structure of the glaze, made the structure of the glaze loose and reduced the glass transition temperature. When the content of cerium oxide increased to 2.0wt.%, the glass transition temperature of the glaze decreased to 495.2°C.

![DSC curve of enamel with different CeO$_2$ contents](image)

**Figure 5.** DSC curve of enamel with different CeO$_2$ contents

3.3. **Test of Acid Resistance of CeO$_2$ to Enamel**

Figure 6 showed the acid resistance of enamel coatings with different concentrations of CeO$_2$. It could be seen that when the content of CeO$_2$ was less than 0.8wt.%, the acid resistance of the enamel layer increased with the CeO$_2$ content. The reasons may be as follows: Firstly, the addition of CeO$_2$ reduced the activation energy of crystallization and spontaneous nucleation. According to the characterization of cross section and surface morphology, it is also confirmed that the structure of the ceramic layer is more compact and the acid resistance is improved [15]. Secondly, according to DSC curves and experimental phenomena, cerium oxide decreased the high temperature viscosity of the enamel just shown in figure 5, which resulted in the surface of the enamel layer smooth and less internal defects just shown in Figure 1 and Figure 2. These would improve the acid resistance of the enamel layer. In addition, because of the high field strength and coordination of rare earth ions, CeO$_2$ played a role of "charge compensation" and it would further improve acid resistance.

![Acid resistance of enamel coatings with different CeO$_2$ contents](image)

**Figure 6.** Acid resistance of enamel coatings with different CeO$_2$ contents

4. **Conclusion**

In this paper, the enamel coatings containing CeO$_2$ were coated on the surface of Corten Steel. The results showed that: (1) CeO$_2$ reduced the glass transition temperature of the enamel glaze, and made
the surface of the enamel layer smoother; (2) CeO₂ played a role in the formation of [BO₄] tetrahedron and the acid resistance. When the content of CeO₂ was between 0.8% and 1.2%, the acid resistance of the ceramic layer was the best. (3) The addition of CeO₂ reduced the viscosity of enamel melt, and enhanced the mutual diffusion ability between enamel layer and substrate.

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6. Reference
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