OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 8, August 2010, p. 1170 - 1173

Study on the corrosion mechanism of HVOF silicate glass coating in 36% HCl and 10 mol/L NaOH solution

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In the study, on the basis of good anticorrosion capability about silicate glass, silicate glass coating was sprayed by High Velocity Oxygen Fuel(HVOF) and corrosion mechanism in 36% HCl and 10 mol/L NaOH solution were studied. Scanning Electron Microscope(SEM), Energy Dispersive X-Ray analysis(EDX), X-Ray Diffraction(XRD) and corrosion dip experiment were carried out to study coating composition and corrosion process. The result shows that silicate glass coating is entirely noncrystallizable. Silicate glass coating has good anticorrosion capability in the condition of thick hydrochloric acid and strong canstic. The corrosion mechanism of silicate glass coating is similar to glass.

(Received June 23, 2010; accepted August 12, 2010)

Keywords: HVOF, Silicate glass coating, Corrosion, Alkali metals

1. Introduction

Silicate glass has the perfect capability of resisting corrosion and aging, which can be applied to all kinds of corrosion conditions except hydrofluoric acid. Preparation of glass coating on metallic substrate can protect metal against corrosion. But low bond intensity and the relatively large difference in the thermal expansion coefficient between the metallic substrate and the glass coating causes mechanical stress which can contribute to the creation of cracks and potentially separation [1-5].

In recent years, there are few reports about the preparation of anticorrosion silicate glass coating on metal surface. Chen Y. H, Wang Y et al produced the anticorrosion glass coating on oil pipeline by flame cladding technics [6,7]. J. Zhan sprayed the anticorrosion glass coating by high velocity oxygen frame(HVOF) on steel substrate and studied the corrosion mechanism in 5% NaCl solution [8,9]. In this paper, corrosion experiments about the anticorrosion silicate glass coating produced by[8] were carried out in thick hydrochloric acid and strong canstic solutions.

2. Experiment

2.1 Coating preparation

The substrate was 45# steel whose shape was a cylinder of 10cm high and 1cm^2 bottom area. The ingredient of silicate glass powder was(weight): SiO_2: 60~62%, B_2O_3: 10~12%, Na_2O: 8%, Li_2O: 8%, SrO: 3%, CaO: 2%, ZnO: 1%, MgO: 1%, TiO2: 1%, ZrO_2: 1%, SnO_2: 1%, BaO: 1%, Al_2O_3: 1%. Thermal expansion coefficient of above glass powder was 95×10^{-7}/K. Steel substrate was warmed up to about 700 by flame till the surface turned to nacarat before thermal-spraying. In order to decrease the residual stress between glass coating and substrate, the spraying samples were taken to a muffle whose temperature was 500 for 30 minutes after thermal-spraying. Later on, the muffle stopped to heat and spraying samples were naturally cooled in the muffle. Table 1 as follow illustrated the technical parameters [8]. An EDX analysis result for the surface of silicate glass coating is shown in Table 2.

Table1. The technical parameters of thermal spraying.

Techniques	Powder particle diameter /μm	O_2 /$m^3\cdot h^{-1}$	Kerosene /$L\cdot h^{-1}$	Distance spraying /cm
Warm-up	-	28	2	20
Spraying	30 - 50	34 - 36	13 - 14	25

Table 2. EDX analysis results for the surface of silicate glass coating.

Element	Weight/%	Atomic/%	Element	Weight/%	Atomic/%	Element	Weight/%	Atomic/%
O	58.79	73.53	Ca	2.71	1.04	Ba	1.00	1.94
Na	2.30	1.98	Ti	1.54	0.63	B	1.10	2.30
Al	0.58	0.43	Zn	3.22	0.97	Li	1.32	0.28
Si	24.67	16.36	Sn	1.22	0.20	Zr	1.55	0.34

Fig. 1 shows that glass coating was entirely noncrystallizable. The combine intensity about coating and substrate was 8MPa.

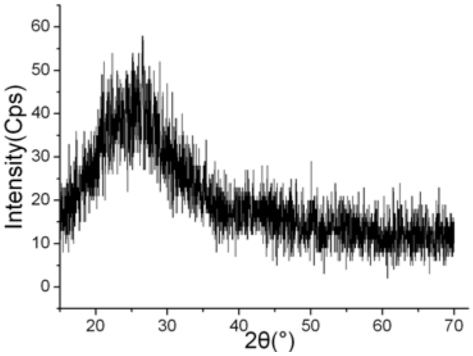


Fig. 1. XRD pattern of silicate glass coating.

2.2 Dip corrosion experiment

The samples of dip experiment encapsulated with epoxy colophony were dipped into 36%HCl solution and 10mol/L NaOH solution for 30 days.

3. Results and discussion

3.1 Dip experiment in 36% HCL solution

In this experiment, because 36%HCL solution is of strong corrosive and could permeate the protection layer of epoxy colophony, the whole substrate of 45# steel was entirely corroded after 7 days and only the coating left in HCL solution. The total experiment time was 30 days. Fig. 2 illustrates that the coating had little changes which had strong capability of resisting corrosion of thick HCL solution.

Fig. 2. The photograph of glass coating corroded in 36%HCL solution for 30 days.

Analyzed the surface and the insides section of the coating with EDX. In order to analyze the insides section of the coating with EDX, the glass coating was broke. Fig. 3 shows the sketch map of analyzed region. Table 3 illustrates the content of main elements.

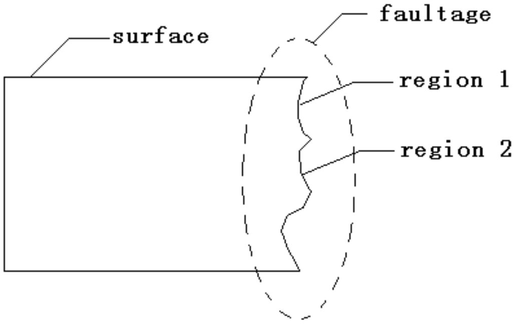


Fig. 3. The sketch map of glass coating analyzed region with EDX.

Table 3. EDX analysis results for silicate glass coating corroded in 36%HCL solution for 30 days.

region element	surface	1	2
C	19.23	0	2.60
O	40.07	56.63	54.02
Na	0.45	2.63	2.59
Si	20.74	30.13	29.64
Cl	2.03	0	0

There are four characters of elements changes from the above table.

(□) There are more C element on the surface apparently than in region 1 and 2, up to about 20% .

(□) Alkaline metals (element Na) on the surface is less than in region 1 and 2.

(□) Element Si and O on the surface are less than in region 1 and 2.

(□) There is no element Cl in region 1 and 2.

As we know, these chemical reactivities as follow would happen if the silicate glass is put into HCl solution or put in the atmosphere [10-13].

$$\equiv\text{Si-OR} + H^+ \Leftrightarrow \equiv\text{Si-OH} + R^+ \text{ (R equaled to alkali metals)} \quad (1)$$

$$\text{Si-O-Si}+H_2O \rightarrow \text{Si-OH}+ \text{OH- Si} \quad (2)$$

$$R+ + OH- \Leftrightarrow ROH \quad (3)$$

$$ROH + HCl \Leftrightarrow RCl + H_2O \quad (4)$$

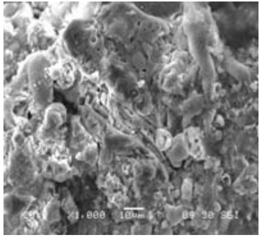
$$2ROH+CO_2 \rightarrow R_2CO_3+ H_2O \quad (5)$$

Analyzed the result of x-ray diffraction experiment, the coating were uncrystalline on the whole, it is likely to be similar to glass about the process of corroding. The chemical reactivity (1) is often diffusion controlling process which is proportionable to $T^{-1/2}$. This reactivity resulted in increasing the PH value of solution and R ion in the solution. At the same time, SiO_2 on the surface also increased correspondingly and formed the loose structures and the surface full of SiO_2. In the chemical reactivity (2), the coating whose surface full of SiO_2 was corroded by water in HCl solution and made the Si-O-Si chemical bond destroyed and formed a great of Si-OH radicals on surface. Parts of SiO_2 on the surface where full of SiO_2 were dissolved in HCl solution in the form of $Si(OH)_4$ which is dissoluble, it led element Si and O on the surface to reduce, and formed many corrosive defects on surface. This process was controlled by interface reactivity and was direct ratio to the reactivity time. With the leaving of R^+ on the surface of coating continually, the surface full of SiO_2 would shrink and aggregate again. There were element Cl in the surface coating which indicated that the chemical reactivity (3) and (4) might have happened. There was no element Cl in region 1 and 2 which included that the reactivity (1), (2) and (3) were only happened on the surface of coating. These changes indicated that the glass coating had very low incidence of hole. The reactivity (5) might happen when the coating was took out from HCl solution, and resulted in increasing element C on the surface of coating.

3.2 Dip-experiment in 10mol/L NaOH solution

Take from the photograph of corrosive coating and SEM (seen Fig. 4 (a) and (b)), the coating was in good condition on the whole, and there were some corroded notches partly. The coating figurations of corrosion areas were influenced. The shape of lots of half-molten and compressed particles had changed and whose boundary became to be illegible.

(a)



(b)

Fig. 4. The photograph of (a)corrosive coating(b)SEM(×1000).

Table 4. EDX analysis results for silicate glass coating corroded in 10mol/L NaOH solution for 30 days.

Element	Weight %	Atomic %	Element	Weight %	Atomic %
C	12.42	19.23	Cl	1.22	0.64
O	52.24	60.71	Ca	1.94	0.90
Na	2.32	1.88	Ti	0.66	0.25
Al	0.60	0.41	Fe	6.80	2.26
Si	19.88	13.16	Zn	1.92	0.55

In the condition of PH>9, the silicate glass is easy to be corroded by alkali solution. Taking from the elements of the corroded area, the content of Si was less than the uncorroded coating and the content of alkali metals was also decreased, but not conspicuous. After analyzing element, it is included that the corrosion mechanism in NaOH solution was similar to glass. It was as follows:

The alkali liquid cut the Si-O-Si bond firstly, and made the number of Si-O increased, the SiO_2 destroyed dissolved into the solution, it was expressed as reactivity (6). At the same time, reactivity (7) happened, and prevented the glass from forming gel film in the corrosion of alkali condition. As a result, the content of element Si reduced.

$$\equiv SiOR + H_2O \Leftrightarrow Si\text{-}OH + ROH \tag{6}$$

$$Si\text{-}OH + NaOH \rightarrow [Si(OH)_3O]\,Na + H_2O \tag{7}$$

Parts of Si-OH were ionized into SiO^- and H^+, and there were double ionization layer formed between glass coating and solution. There were negative charges on the surface of coating and magnetized the alkali metals ion [9]. At the same time, the more PH value, the more active of Si-OH when PH>9, and the active of H+ drops, active of alkali ion improves and holds the surface of coating. It made alkali metals difficult to leave coating. As a result that there is almost no change of the content of alkali metals on the surface of coating.

4. Conclusions

In the study, on the basis of good anticorrosion capability about silicate glass, silicate glass coating was sprayed by High Velocity Oxygen Fuel(HVOF) and corrosion mechanism in 36% HCl and 10mol/L NaOH solution were studied. Scanning Electron Microscope(SEM), Energy Dispersive X-Ray analysis(EDX), X-Ray Diffraction(XRD) and corrosion dip experiment were carried out to study coating composition and corrosion process. The result shows that silicate glass coating is entirely noncrystallizable. Silicate glass coating has good anticorrosion capability in the condition of thick hydrochloric acid and strong canstic. The corrosion mechanism of silicate glass coating is similar to glass.

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