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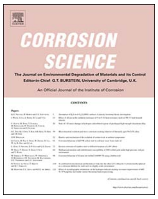

Simulating sulfuric acid dew point corrosion of enamels with different contents of silica

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ABSTRACT

Corrosion of three bulk enamels with different silica contents in sulfuric acid was studied. Catastrophic corrosion happened for enamel with 54.6 wt% silica. Its weight loss reached 36.90 mg/cm^2 after seven-day corrosion. A porous leached layer with tremendous cracks formed at surface during corrosion, which favored acid invading and further corrosion. On the contrary, the durability of enamels with silica content over 60 wt% was guaranteed by their highly connected silicate network and a developed dense gel layer that clogged corrosion pits. Their weight losses were less than 0.2 mg/cm^2 after seven-day corrosion.

1. Introduction

Sulfuric acid dew point corrosion frequently occurs in chemical, power generation industries and marine engine cylinder liners because of condensing gases [1–6]. One of the most serious corrosion components in thermal power plants is the gas–gas heat (GGH) exchanger in desulfurization system (DSS). Burning of the S-containing fuel can produce SO_2 and minor SO_3, which will react with water to form sulfuric acid vapor in GGH [7,8]. At the cold end, its temperature is only 80–100 °C, and such acid vapor begins to condense either as acid droplets or as a thin liquid layer on GGH surface, leading to the sulfuric acid dew point corrosion of the GGH [9,10].

Because GGH is mostly applied in the consideration of environmental protection, taking into account the cost, it is too expensive to prepare it with high alloyed steel [11]. On the other hand, ordinarily, cost effective low alloyed steels cannot resist such harsh corrosion. Thus, applying corrosion resistant coatings on the cheap low-alloyed steel pieces is the ordinary practice in industry, among which borosilicate enamel coating attracts much attention [12–15]. In that case, the life-span of GGH depends mainly on the corrosion resistance and stability of its enamel coating.

However, few researches are available on the corrosion behavior of enamel coating in acid solution, and the only few literatures are mainly focused on the simple comparison of corrosion rate of enamels with different formulations and preparing processes. Rodtsevich et al.[16] compared the weight losses of seven kinds of titanium-boron-silicate enamels in 4% acetic acid solution. It was found that enamels with the ratio B_2O_3: R_2O (R_2O: Li_2O, Na_2O, K_2O) close to 1 had the highest resistance to corrosion in acetic acid solution. Then Tavgen et al. [17] demonstrated that a satisfactory acid resistance of such titanium-boron-silicate enamels can be achieved by adjusting the contents of B_2O_3 and TiO_2 to 8–10% and 20–22%, respectively. Afterwards, the effect of ratio of three alkali oxides on acid resistance was studied. Results indicated that the titanium-containing enamels with 2–4% K_2O, 2–4% Li_2O and 8–12% Na_2O showed the lowest corrosion rate in acetic acid solution. More recently, Goleus et al. [18] found that corrosion rate of enamels could be reduced significantly by reducing the contents of fluorine, anhydrous boron and alkali oxides, as well as introducing zirconium dioxide to its composition simultaneously. In addition to the composition, the preparing process of enamel coatings affects corrosion rate as well. Svetlov [19] enhanced the corrosion resistance of titanium-containing enamels by adding silica and highly siliceous glasses during the powder milling process. Jiang et al. [20,21] conducted a systematic study of milling addition on corrosion of enamel coating, detecting that adding 10–12 wt% $ZrSiO_4$ [20], 5–7 wt% mullite [21] or 2–5 wt% nano-sized SiO_2 [22] can significantly decrease the corrosion rate. However, neither corrosion kinetics nor microstructure evolution of enamel during acid corrosion was carefully studied. Thus a quantitative relationship between the composition and corrosion resistance is still lacking.

Considering the decisive role of silica on the microstructure and acid corrosion resistance of an enamel coating [23–27],we developed our

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Table 1
Nominal composition of enamels (wt%).

	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	CoO	CaF_2
Si54	54.62	12.32	5.96	12.32	5.96	2.46	6.36
Si60	60	10.86	5.25	10.86	5.25	2.18	5.60
Si64	64.62	9.61	4.65	9.61	4.65	1.90	4.96

study that follows: firstly, analyze corrosion kinetics of three enamels with different silica content in sulfuric acid to simulate their sulfuric acid dew point corrosion; secondly, record the microstructure evolutions on the surface of these enamels with prolonging corrosion time, to explore the underlying protection mechanism of enamel coating against acid corrosion and the effect of silica content on corrosion resistance.

2. Experiment

2.1. Preparation of samples

The nominal composition of three enamels is shown in Table 1. Depending on their silica content, the three kinds of enamel were named as Si54, Si60 and Si64, respectively. Corrosion of steel matrix underlying the enamel coating may occur due to some defects introduced by the preparing process of enamel coating, which might affect the evaluation on acid resistance of the enamel itself. For this reason, enamel bulks, instead of enameled steel plates, were used to compare their corrosion resistance in this experiment. The preparation method of enamel powder has been previously described in detail in [28]. Enamel biscuits with diameter of 13.5 mm and height of 6 mm were prepared by tableting enamel powders through a tablet machine (XL140409, Hebi Lixin instrument Co., Hebi, China). Thereafter, the enamel biscuits were sintered for 5 min at proper temperature (Si54: 700 °C; Si60: 720 °C and Si64: 740 °C) in muffle furnace to form regular shape bulks. In order to simulate the firing process of enameled steel plate, the sintered enamel bulks were further heat-treated following the same procedure of enamel coating, i.e. firing at 880 °C for three minutes and then cooling in air.

2.2. Corrosion test

In actual working condition, the temperature of cold end of heat exchanger is about 80 °C. In order to simulate the hot-cold and wet-dry cyclic working environment, the following steps of cyclic corrosion test were carried out: (1) Enamel bulk was rinsed in ethanol for 2 min, dried at 120 °C and weighed; (2) Enamel bulks were immersed in 10 ml 30% (vol.) H_2SO_4 solution in a Teflon container with condensing device; (3) The container was then fixed in water bath that has already been heated to 80 °C; (4) Bulks were taken out from the container after 24 h corrosion, flushed by deionized water for 2 min (83.3 ml/s of the flow rate) at room temperature to remove the residual solution on their surface; (5) After rinsing in ethanol for 2 min, all the corroded enamel bulks were dried for 1 h in the hot-air oven at 120 ± 5 °C. After a further two-hour holding in the desiccator, they were cooled down to room temperature and their masses were recorded. The above five steps constitute a cycle of acid corrosion. Before the next cycle proceeds, the acid solution used in the former cycle was replaced by a fresh one. According to their corrosion kinetics, enamels with higher silica content enter into a steady stage of corrosion after 4 ~ 7 days soak, so a total of seven cycles was carried out. Each group of enamel contained three parallel bulks.

2.3. Characterization

Surface and cross section of the samples were analyzed by SEM (Inspect F 50, FEI Co., Hillsboro, OR) and EDS (X-Max, Oxford instruments Co., Oxford, U.K.). Test condition is set as: Gun pressure: 1.90 e^{-7} Pa; Emission current: 162 μA; HV: 25 KV; WD: 10 mm. Electron probe microanalysis (EPMA-1610, Shimadzu, Kyoto, Japan) technique was employed to study the details of the leached layer. Test condition is set as: Acc.V: 15.0KV; Beam Size: 1 μm; B.C.: 20 nA. Phase constituent was characterized by using XRD (X'PertPRO, PANalytical Co., Almelo, Holland, Cu Ka radiation at 40 kV). To in situ observe the corrosion process of enamel bulk, a mark was made at the middle of sample surface by Vickers impresser. This mark is very small, and should not have a significant impact on corrosion behavior of the bulk. Due to the low conductivity of enamel, a thin carbon layer was always deposited on it before SEM observation, which will affect more or less its further corrosion. In order to avoid such an influence during the cyclic corrosion test, surface morphologies of enamel bulks were observed by a laser scanning confocal microscopy (LEXT-OLS4, Olympus Co., Tokyo, Japan) after each cycle of corrosion, instead of SEM. Raman spectra of pristine samples were obtained by LabRAM HR Evolution Raman spectrometer. Test condition is set as: YAG laser: 532 nm; laser power: 10% of 100 mW; exposure time: 10 s; scan rounds: 6 and scanning range: 300–1300 cm^{-1}.

3. Result

3.1. Macro morphology

Fig. 1 shows macro morphologies of the three kinds of enamel bulks after acid corrosion for different times. Before corrosion (0 d), all the enamel bulks were blue. Their surface was smooth and glossy. However, for Si54, it lost luster and the color faded from blue into white after only one day of corrosion. Differing from Si54, Si60 lost its luster gradually within the first three days of corrosion, and the color transformed to brown. However, with the corrosion continuing to seven days, its surface, incredibly, turned blue and luminous back again. Si64 maintained its gloss and color for the entire corrosion duration.

3.2. Corrosion kinetics

Fig. 2 shows corrosion kinetics of the three kinds of enamel bulks at 80 °C in 30% H_2SO_4 solution. The weight loss of Si54 is catastrophic (36.90 mg/cm^2 at seventh day), and far higher than that of Si60 and Si64 (0.1950 mg/cm^2 and 0.093 mg/cm^2 at seventh day, respectively). For Si54, its weight loss shows nearly a linear relationship with the slope $k_{Si54} = -3.72\ mg/(cm^2\ d)$. For Si60, its weight loss is small, but is still twice as that of Si64 after seven days of corrosion. At the first three days, its rate of weight loss is relatively high, which slows down thereafter and follows a nearly linear relationship with the slope $k_{Si60} = -0.0102\ mg/(cm^2\ d)$. For Si64, it is found that the stage of high corrosion rate occurs only within the initial one day, follows by the linear section with the slope $k_{Si64} = -\ 0.0097\ mg/(cm^2\ d)$.

3.3. Changes of the chemical composition at surfaces

Elemental analysis at surface of the corroded enamel bulks after different corrosion times was carried out by EDS, shown in Fig. 3. For Si54, the elements of Na, K and Co were hardly detected by EDS on surface after one day of corrosion. However, their contents slightly increase thereafter. The contents of Al and Ca also slump rapidly after one day of corrosion. After three days of corrosion, the content of Al improves, following the footsteps of Na, K and Co, but that of Ca decreases continuously with prolonging corrosion time. Anyway, the content variations of Na, K, Co, Al and Ca during the corrosion stage of 2 ~ 7 days were very small and totally in the scope of measuring error. After the initial one day of corrosion, the percentage of Si goes up from 19.7 to 23.1, and is basically unchanged thereafter. In conclusion, the element content changed substantially during the initial one day of corrosion, and was almost unchanged thereafter.