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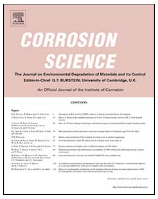

Studies on the corrosion behavior of Fe-20Cr alloy in NaCl solution spray at 600 °C

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ABSTRACT

The corrosion behavior of Fe-20Cr in NaCl solution spray at 600 °C, compared with that under solid NaCl deposit in water vapor, has been studied by mass-gain measurements, scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, secondary ion mass spectrometry and transmission electron microscopy methods The results demonstrated that Fe-20Cr undergoes serious corrosion in NaCl solution spray. Significantly different corrosion products with outer Fe_2O_3 and inner $FeCr_2O_4$ layers were formed. Meanwhile, a small amount of Cl was found in the corrosion scale, which was thought to have an important effect on corrosion. The corrosion behavior of Fe-20Cr in NaCl solution spray at 600 °C has been discussed in detail.

1. Introduction

The marine environment is a highly humid and saline atmosphere, especially in that there are large amounts of NaCl particles and water vapor in the marine air. Research results in the past decade revealed that the corrosion behavior of turbine blade materials of airplanes and ships working in the marine environment had been accelerated by the synergistic effect of solid NaCl deposits and water vapor at intermediate temperatures [1–5].

The corrosion behavior of metals/alloys, not only pure Fe [3], pure Cr [4] and Fe-Cr alloys with different Cr contents [5] but also applied metals, such as 1Cr-11N-2W-2Mo-V [1], high-temperature titanium-base alloy Ti60 [2], 304 stainless steel [6], K38G alloy [7] and MgGdYZr alloy [8], have been studied under this solid NaCl deposit in water vapor environment at 500–700 °C. These research results showed that different metals had different susceptibilities to this special corrosive environment. For pure Cr [4], Fe-Cr alloys [5] and stainless steel [6], the synergistic effect of NaCl and water vapor could destroy the protective oxide scale (Cr_2O_3) and form non-protective scales that consisted of loose oxides and metal sodium salts (such as Na_2FeO_4 and Na_2CrO_4). Meanwhile, some researchers speculated that volatile products (such as HCl and MCl_x) also formed during corrosion; in fact, which volatile products form have never been testified in experiments. In the corrosion study of K38G alloy [7] in this special environment, the protective Cr_2O_3 scale also did not form, and corrosion was serious. For pure Fe, corrosion was accelerated compared with the environment without NaCl. However, Mg alloy [8] was not sensitive to the synergistic effect of NaCl and H_2O at middle-high temperature and almost did not corrode in this environment. Meanwhile, according to possible corrosion reactors and products, a series of possible chemical reactions of dissimilar metals with NaCl and H_2O at 500–700 °C have been deduced and calculated.

Moreover, some studies showed that KCl(s) was equally corrosive as NaCl for 304L stainless steel, Fe-2.25Cr-1Mo steel and FeCrAl alloy in water vapor in a middle-high temperature environment [9–13]. The background of these studies focused on the corrosion behavior of steam superheaters in waste-fired power plants. The protective Cr-rich oxide that formed in the absence of KCl was replaced by a rapidly growing oxide scale (K_2FeO_4 and K_2CrO_4) in the presence of KCl [14–20]. Considering the similar effects of NaCl and KCl on the corrosion behavior of Fe-Cr alloys, it might be expected that the corrosion reactions between both salts and metals are analogous. Meanwhile, it was interesting that both NaCl and KCl could react with the Cr-rich oxides at middle-high temperature. Considering the similar chemical characteristics of K and Na (the same main group elements), most people thought that Cl in NaCl or KaCl played a leading role in the corrosion of metals/alloys [1–5,9–13]. Most people believed that Cl might promote the generation of gaseous products such as Cl_2 or HCl. Gases might

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penetrate the corrosion scale and form volatile metal chlorides at the scale/metal interface, which would greatly accelerate the corrosion rate [10]. In addition, extensive results regarding how alkali chlorides accelerated the corrosion rate of several metals or alloys have been obtained [21–24]. The synergistic effect of alkali chlorides and wet O_2 on stainless steel has been attributed to an “active corrosion” (Cl cycle) mechanism [2,11,23–28]. According to this published mechanism, Cl^- acted as a catalyst for corrosion in this special environment. In addition, HCl and Cl_2 gases produced by the chemical reactions between metal and alkali chlorides could multiply the corrosion rate of Fe alloy, Fe-Cr alloy and Ni-Cr alloy [29–31]. In conclusion, the effect of alkali chlorides on the corrosion of many metals was impressive and serious in the environment with or without H_2O at 500–700 °C.

However, in fact, not only for the turbine blades of airplanes or ships in marine air but also for the steam superheaters in waste-fired power plants, it was very difficult to form a thick solid NaCl or KCl deposit layer on the metal surface during their service life in reality. Therefore, the previous experimental method for this corrosion was a type of acceleration experimental method that imposed more salt. However, in reality, the existing state of salt was not a thick solid deposit layer but instead a NaCl or KCl solution vapor. The corrosive atmosphere consisted of small NaCl particles and water vapor in the air; thus, the simulated environment, to be closer to the real one, should consist of NaCl solution sprayed at a sufficiently high temperature. However, relative investigations in this simulation corrosive environment have been neglected in previous studies. We did not know if the real corrosion behavior of metals on turbine plates in service or the initial real corrosion behavior of metals was similar to the previous study results, which were obtained under an accelerated environment with a thick solid NaCl deposit layer. Therefore, the corrosion behavior of metals under NaCl solution spray at middle-high temperature should be studied in detail.

In the present work, a new simulation device was built to simulate the marine atmospheric environment, which is close to the real service environment of an aircraft engine fan blade material. The corrosion behavior of Fe-20Cr under NaCl solution spray at 600 °C has been studied compared with that of Fe-20Cr alloy studied in the previous way under solid NaCl deposit in water vapor at the same temperature. The effect of Cl on the corrosion behavior of Fe-20Cr in NaCl solution spray has been discussed based on experimental results.

2. Experimental procedures

The studied metal in this paper was Fe-20Cr alloy, which could be a representative material model for stainless steel. The material was cut into coupons with dimensions of 10 mm × 15 mm × 2 mm, and a hole (Ø = 1.5 mm) was drilled at the top for hanging. Before the corrosion experiments, the samples were ground with 800 grit SiC paper. They were degreased and cleaned with acetone and ethanol, separately, in an ultrasonic bath and then dried with flowing cool air.

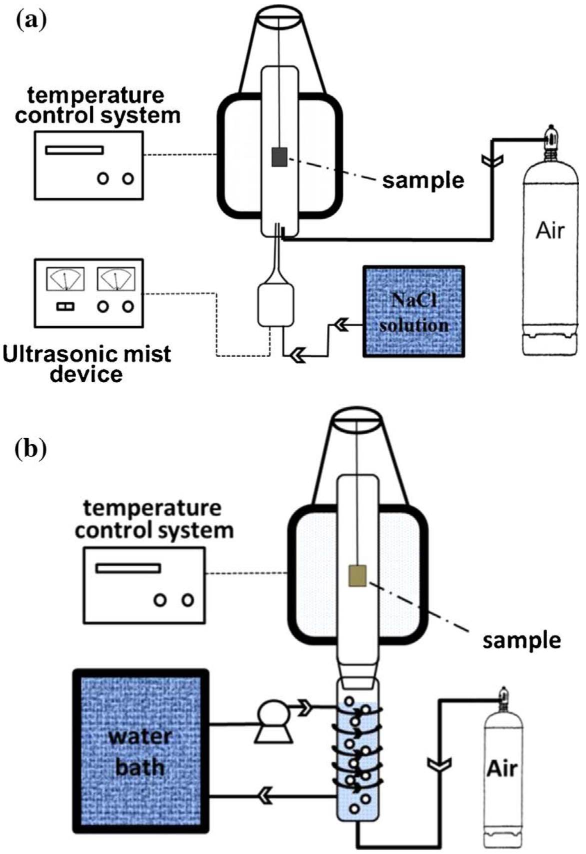

Fig. 1. Schematic of the furnace system with the NaCl solution spray environment **(a)** and traditional solid NaCl deposit in water vapor environment **(b)**.

Both corrosion experiments, in NaCl solution spray and under solid NaCl deposit in water vapor, were performed in a tube furnace fitted with a 35 mm i.d. silica-glass tube. The testing temperature was held isothermally at 600 ± 3 °C. Experiments of samples in the NaCl solution spray were carried out in the simulated system shown in Fig. 1(a). This simulated system consisted of a temperature control system, an ultrasonic mist device, a NaCl solution container and a gas cylinder. Samples were hung in the constant temperature zone of the furnace chamber. At the end of the furnace tube, the ultrasonic mist device atomized the 3.5% NaCl solution into small particles of NaCl spray. The NaCl solution container was connected with the ultrasonic mist device to maintain a sufficient solution supply. The volume fraction of the water vapor was controlled by the temperature of the 3.5% NaCl spray at the location of the ultrasonic atomization nozzle, which had a temperature of 75 °C. In this work, there is the assumption that through the effect of carrier air flow, the NaCl solution spray becoming gaseous can bring all of the NaCl into the furnace chamber, which is a maximum calculated value. According to Raoult's law, NaCl dissolved in solution could reduce the vapor pressure of the solution: $P_b = P_b{}^* \times \chi$. P_b is the saturated vapor pressure of the NaCl solution; $P_b{}^*$ is the saturated vapor pressure of deionized water; and χ is the mole fraction of the solvent. Then, the P_b value of the 3.5% NaCl solution at 75 °C was calculated to be 38.11 kPa. Therefore, the volume fraction of the water vapor in the furnace was calculated to be 37.7 vol.%, which was near the true marine air value. The air in the gas cylinder carried the NaCl solution spray into the furnace chamber at a constant flow rate of 310 mL/min. According to the testing temperature (600 ± 3 °C), we used Formula (1) [32] to calculate the amount of NaCl on the samples:

$$d_v = \left({}^{P_b}\!/_{760}\right)*\left({}^{1000}\!/_{22.4}\right)*\left({}^{273}\!/_{273 + t}\right)*18 \tag{1}$$

In this formula, d_v is the water content of saturated steam in a cubic meter at different temperatures (g). P_b is the saturated vapor pressure of the NaCl solution at different temperatures (mmHg), and t is the temperature (°C). According to this formula, the value of d_v was 237.3 g/m^3. In this test, the solution we used was 3.5% NaCl solution, and then, we calculated the amount of NaCl in the furnace chamber to be 0.0083 mg/cm^3. Suppose that NaCl in the occupied space of the sample could adhere to the entire sample surface (sample area: 3.6 cm^2, sample volume: 3 cm^3). The vapor flow rate in the furnace chamber was 310 mL/min (the chamber diameter was 35 mm i.d.), so transient NaCl deposited on the sample can be calculated as 0.0037 mg/(cm^2·min).

The previous experimental method included exposing samples to solid NaCl deposit in water vapor at 600 °C, which was carried out in the furnace system shown in Fig. 1(b). A thick solid NaCl deposit membrane was applied to the preheated specimen surface by repeatedly brushing it with a saturated NaCl solution. The solid NaCl amounts of the membrane were approximately 4 ± 0.2 mg/cm^2 [1,2]. The