

Effect of Varying H₂S Content on High Temperature Corrosion of Austenitic Alloys in a Pyrolysis Process of Post-Consumer Plastics

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ABSTRACT

Several austenitic alloys were tested under conditions simulating a pyrolysis process of post-consumer plastics. Impurities in the plastic feedstock like chlorine containing materials or organic components yield HCl and H₂S, respectively, during the cracking process. The reactor material must be able to withstand these harsh corrosive conditions.

To evaluate the applicability of commonly used construction materials, high-temperature corrosion experiments were performed in lab-scale test equipment at 580 °C for 240 hours. The gas atmosphere consisted of either 0.02 vol% or 2 vol% H₂S and 3.8 vol% HCl, 1.9 vol% CO₂, 0.3 vol% CO, 2.8 vol% H₂, balance N₂, denoted as low-H₂S and high-H₂S mixture, respectively. After the corrosion experiments the samples were analyzed by metallography, SEM/EDX and XRD. Additionally, the corrosion rates were evaluated.

Results showed that the corrosion rates of the materials increased with rising H₂S content in the gas atmosphere. Additionally, the corrosion behavior of the materials changed when going from the low-H₂S mixture to the high-H₂S mixture. In the low-H₂S mixture the alloying element nickel was identified to be helpful for corrosion protection. In the high-H₂S mixture chromium was beneficial alloying element against corrosive attack at the given conditions.

Key words: High temperature corrosion; complex atmosphere; hydrogen chloride; hydrogen sulfide; austenitic stainless steel

INTRODUCTION

Pyrolysis processes of post-consumer plastics are a promising chemical recycling route and a good alternative to disposal. Nevertheless, these processes are challenging for metallic materials since chlorine containing materials or biological components inside the feedstock can yield HCl and H₂S, respectively, during cracking. In combination with high temperatures of the reactor zone metallic construction materials can be attacked by high-temperature corrosion. [1-4]

Most of the commonly used high-temperature alloys rely on the formation of oxide scales to resist high-temperature corrosion, but these materials are often not able to do so in atmospheres that contain chlorine. Chlorine-induced high temperature corrosion of alloys is strongly correlated with the formation of volatile metal chlorides beneath the initial passive layer of the materials and their subsequent outward diffusion and conversion to other corrosion products, e.g. to the corresponding oxides or sulfides. The result is the formation of non-protective oxide or sulfide scales. [1, 5-12] Haanappel et al. [13] exposed various steels to an atmosphere simulating coal gasification processes with and without the addition of 500 ppm HCl. The results showed that the addition of 500 ppm HCl to the oxidizing–sulfidizing environment increased the corrosion rate significantly and yielded a thick, porous and non-protective sulfide scales.

In pyrolysis processes the conditions are reducing and partial pressures of oxygen are extremely low. If chlorine is present in reducing atmospheres, the corrosion rate increases. [6, 14] High chromium containing materials that can form passive oxide layers even in atmospheres with low partial pressure of oxygen are rapidly attacked in the presence of chlorine. Bakker et al. [6] found that this accelerated corrosion in reducing atmospheres is also caused by the formation of porous and non-protective scales. At reducing conditions, HCl may act synergistically with both CO and H₂ to break down the otherwise protective oxide layer by forming voids and cracks. [15] Thereby, the access of other corrosive species to the base material is favored, including H₂S, which tends to yield metal sulfidation.

In addition, in reducing atmospheres sulfur from biological components or fuels is released as H₂S gas, which is known to be very corrosive compared to SO₂ that is released in oxidizing atmospheres. [16] It is well known that corrosion is more severe in reducing sulfur-containing combustion atmospheres than in oxidizing environments since cation diffusion is much faster in sulfides than in corresponding oxides. Due to a higher lattice disorder, sulfide scales grow more rapidly and spall more easily than oxide scales. [17-20]

However, investigations about the effect of sulfur on the high-temperature corrosion behavior of alloys in chlorine containing and reducing atmospheres has not yet been well clarified due to a lack of a precise and systematic analysis of the actual reactions in these complex multi-reactant environments. Only a few authors dealt with this topic and even found differing results in some cases. [2, 21] Pan et al. [22] reported that an increase in H₂S level in a mixed H₂S-H₂-HCl-CO₂ atmosphere accelerated the corrosion of Fe-Cr alloys. Bakker and Perkins [23, 24] reported an increase of corrosion rates of iron in H₂S-HCl mixtures above 400 °C, but a decrease in sulfidation below 399 °C. Other authors [11] found the reduction of corrosion rates by the addition of H₂S in chlorine containing atmospheres. Thus, the corrosion behavior of metallic materials in reducing atmospheres that contain HCl as well as H₂S needs to be further investigated.

Chromium is considered to be the most beneficial alloying element against sulfidation. [16-18, 25] Pan et al. [22] reported that an increase in chromium content, especially in the range of 8-12 wt% Cr, reduced the corrosion rate in HCl-H₂S containing atmospheres due to a larger volume fraction of Cr₂O₃ in the scale. This paper examines the corrosion behavior at 580 °C of several austenitic materials with different Cr contents (16.8 wt% - 25 wt%) in two gaseous H₂-HCl-H₂S-CO-CO₂-N₂ mixtures containing either 0.02 vol% or 2 vol% H₂S, denoted as low-H₂S and high-H₂S mixture, respectively, producing similar chlorine

and oxygen pressures, but different sulfur pressures. These gas mixtures were selected to simulate the conditions in a pyrolysis reactor of post-consumer plastics, in an attempt to clarify the possible role of H_2S on the corrosion of commonly used austenitic materials in reducing atmospheres in the presence of HCl .

EXPERIMENTAL PROCEDURE

The corrosion behavior of several austenitic steels was evaluated under conditions simulating a pyrolysis process of post-consumer plastics. The corrosion experiments were performed at laboratory scale in a heated silica glass tube at 580 °C for 240 hours. The corrosive test gas atmosphere consisted of either 0.02 vol% or 2 vol% H_2S and 3.8 vol% HCl , 1.9 vol% CO_2 , 0.3 vol% CO , 2.8 vol% H_2 , bal. N_2 , denoted as low- H_2S and high- H_2S mixture, respectively. These atmospheres represented the partial pressures of sulfur, chlorine and oxygen, which can be present in the reactor zone of the pyrolysis process and were calculated by the software FactSage 8 and PetroSIM. Partial pressures of sulfur, chlorine and oxygen for the initial test gas atmospheres at 580 °C are given in Table 1. The selection of the testing temperature as well as the gas composition was based on the knowledge achieved from a pilot plant and previous experiments. [2, 21, 26]

Figure 1 shows a scheme of the testing equipment. The gas mixture was provided in two separated bottles by Linde Gas (Eggendorf, AUT) as HCl cannot be stored together with H_2S . Stainless steel tubes were used to transport the gas from the bottles to the silica tube. During heating and cooling the chamber was flushed with nitrogen. The test gas leaving the test chamber was neutralized in 10% KOH and 10% NaOH solution. A detailed experimental procedure can be found elsewhere. [26]

Table 1: Partial pressures of sulfur, chlorine and oxygen of the given atmospheres at 580 °C (in bar)

Species	low- H_2S	high- H_2S
S_2	8.2E-08	2.2E-04
Cl_2	2.3E-12	1.1E-12
O_2	1.3E-24	1.3E-24

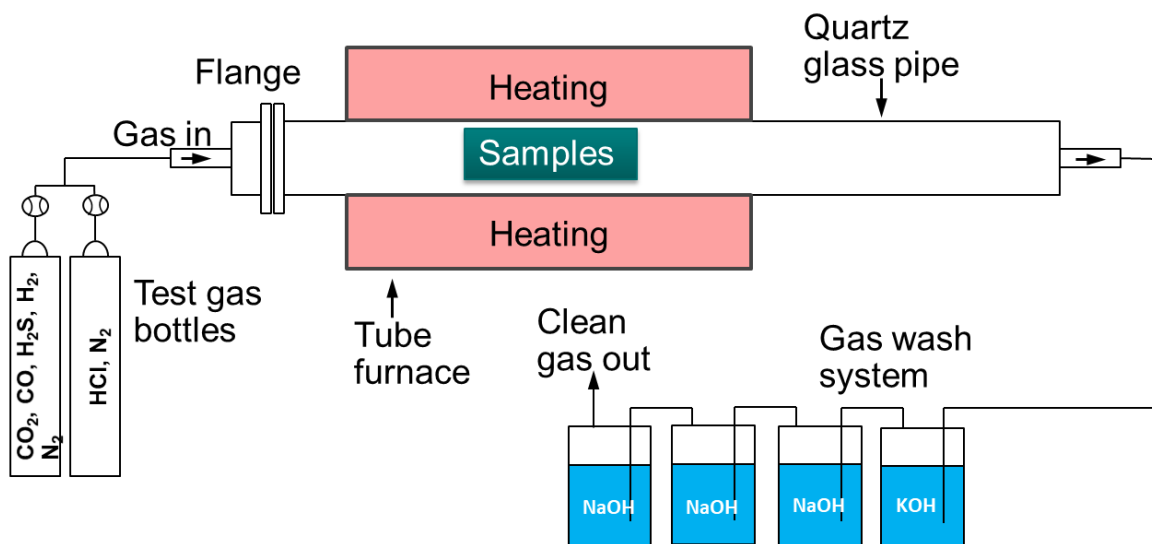


Figure 1: Scheme of the testing equipment [26]

Table 2 shows the chemical composition of the tested austenitic steel alloys. Before the corrosion tests were performed, all test specimens, which had a rectangular shape with dimensions of 25 x 10 x 2 mm, were polished up to 1000 grit SiC paper in order to achieve a uniform surface, cleaned with acetone, degreased and gauged. For corrosion experiments four specimens of one material were placed simultaneously in the silica tube by using a silica glass holder. While three samples were used for the mass loss determination, one was cold mounted in epoxy resin for metallographic and SEM/EDX investigation.

Table 2: Chemical composition of the tested materials in wt% (balance Fe)

Material	C	Si	Mn	Cr	Mo	Ni
UNS S30403 (1.4306)	0.01	0.4	1.2	18.3	0.3	10
UNS S31603 (1.4404)	0.01	0.3	1.8	16.8	2	10.2
UNS S30815 (1.4835)	< 0.08	1.5	0.8	21	-	11
UNS S31008 (1.4845)	0.03	1.5	2	25	-	21
UNS N08811 (1.4959)	0.07	-	0.6	20.5	-	30.4

For the evaluation of the corrosion rate, the samples were cleaned with 5% hydrochloric acid and a wire brush. The additional mass loss of the materials due to the attack of the hydrochloric acid and the wired brush was determined in prior experiments and was considered to be negligible. [27] The loose corrosion products were characterized by XRD. Additionally, uncleaned samples were cold mounted in epoxy resin and polished up to 4000 μm SiC paper. Metallographic preparation of the corroded samples happened water-free to preserve water-soluble corrosion products for visualization of unaltered cross sections. The samples were investigated by means of light optical microscopy and SEM/EDX. SEM/EDX measurements were performed after 15 s gold sputtering, using a SEM by Zeiss (EVO MA 25 ®). The electron source was a LaB₆ cathode. Thermodynamic calculations were performed with the software Fact Sage 8.

RESULTS

Figure 2 shows the general appearance of the samples and the silica glass tube after the corrosion experiments. In both gas atmospheres the materials were uniformly attacked and the scales showed a poor adherence to the substrate and easily spalled off. The formed corrosion products were black with metallically shining dots. Colorless crystals were detected at the colder parts of the silica glass tube after the corrosion experiments. XRD identified these crystals as FeCl₂, which formed at the samples, evaporated, was carried away with the gas flow and crystallized outside at the colder parts of the furnace. The amount of FeCl₂ varied depending on the H₂S content in the atmosphere. The amount of detected FeCl₂ decreased with increasing H₂S content in the gas mixture. In the high-H₂S mixture almost no FeCl₂ could be detected after the corrosion experiments.

Silica glass tube after corrosion experiments



Samples after corrosion experiments

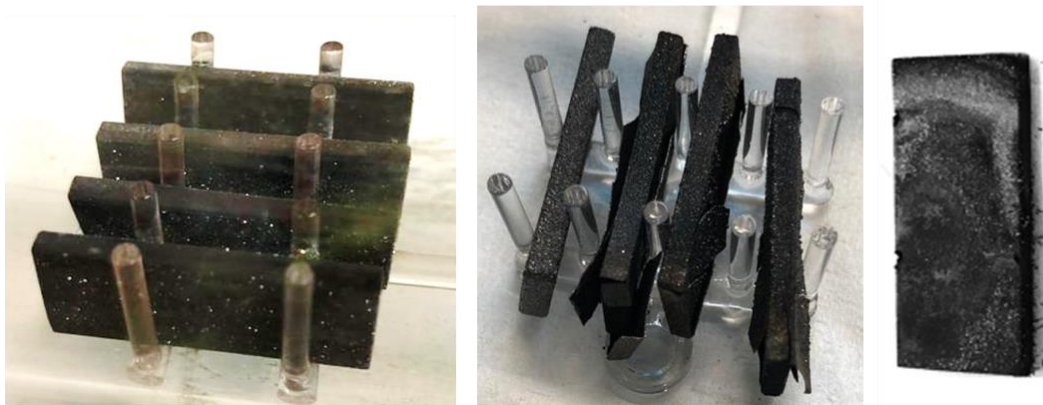


Figure 2: General appearance of the samples after corrosion experiments

Corrosion rates

Figure 3 shows the corrosion rates of the tested materials versus the H_2S content in the atmosphere after 240 hours at 580 °C.

- In the low- H_2S mixture, N08811 showed the best performance with a corrosion rate of around 0.42 mm y^{-1} , while S31603 showed the worst performance with a corrosion rate of around 0.81 mm y^{-1} . In general, the corrosion rates of the materials decreased with increasing nickel content in the alloys.
- In the high- H_2S mixture, S30815 showed the best performance with a corrosion rate of around 0.93 mm y^{-1} , while S30403 showed the poorest performance with a corrosion rate of around 1.32 mm y^{-1} . In general, the corrosion rates of the materials decreased with increasing chromium content in the alloys.
- Generally, the corrosion rates of all materials increased with rising H_2S content.