Corrosion Science xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Comparison of the high-temperature chloride-induced corrosion between duplex steel and Ni based alloy in presence of H_2S

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ARTICLE INFO

Keywords:
High temperature corrosion
Steel
Ni based alloy
Hydrogen sulphide
Hydrogen chloride

ABSTRACT

Duplex steel 1.4462 and Ni-based alloy Centralloy ET45 micro were tested in HCl- and H_2S-containing atmospheres at 680 °C for 24, 72 and 240 h. Corroded samples were investigated by metallography, SEM/EDX and XRD. Corrosion products on the surface consisted of Cr_2O_3 and chromium sulfides. Beneath this surface layer, iron and chromium chloride were found. A depletion of iron was observed due to formation of volatile iron chloride. Both materials displayed a selective attack of the existing phases. The ferrite phase of the Duplex steel was attacked, while the Ni-based alloy showed the selective attack of chromium carbides.

1. Introduction

Chlorine-induced high-temperature corrosion is responsible for material failures in coal gasification processing, and in electric power plants based on fossil-fuel firing. Waste-to-energy facilities also suffer from high-temperature corrosion due to HCl gas which is created by thermal decomposition of halogenated plastics [1,2].

In general, the reaction of HCl or Cl_2 with the alloying elements of steel (mainly iron, chromium and nickel) yields the corresponding metal chlorides. Chlorine gas is able to penetrate through the protective oxide layer of the steel. Underneath the oxide layer the partial pressure of oxygen is low, and the metal chlorides become locally stable [3–7].

At 680 °C the Gibbs free energies of formation for the metal chlorides via the reaction

$$Me + 2HCl \rightarrow MeCl_2 + H_2$$

are negative for $CrCl_2$ (−76 KJ/mol) and $FeCl_2$ (−22 kJ/mol) and positive for $NiCl_2$ (38 kJ/mol)*. Thus, chromium and iron form these chlorides in the presence of HCl, while nickel will remain metallic. $FeCl_2$ is volatile and sublimates above 500 °C [8–10] whereas $CrCl_2$ requires higher temperatures of more than 600 °C to sublimate [11]. When the metal chloride reaches the interface between oxide layer and gas atmosphere, it can react with oxygen or an oxygen donor in the gas atmosphere to form corresponding metal oxide(s) and Cl_2 or HCl. This is especially true for chromium, which forms Cr_2O_3 at very low oxygen pressures, and HCl or Cl_2 can enter the reaction cycle again. The continuous evaporation and exchange of metal chlorides with oxygen causes the formation of a thick, but loose oxide layer on the steel surface, which consequently is not protective anymore. This corrosion process is thus called active corrosion. Due to these reactions the corrosion behaviour can be influenced by even small changes of the oxygen/chlorine ratio or temperature [3–7].

Mixed gas atmospheres active during coal gasification processing or in waste-to-energy facilities sometimes contain additional H_2S. Only few studies have dealt with the addition of H_2S in chlorine-induced high-temperature corrosion. For example, Pan et al. reported that an increasing H_2S concentration accelerated the corrosion of Fe-Cr alloys in an H_2-HCl-CO_2 atmosphere [13].

In order to obtain a detailed understanding of high-temperature corrosion in mixed gas atmospheres including H_2S and HCl at low oxygen partial pressures, the Duplex steel 1.4462 and the Ni-based alloy Centralloy ET45 micro were chosen. Duplex steel contains ferrite and austenite in one material, which allows investigation of corrosion behaviours in the two different phases. Nickel based alloy was chosen to analyse the influence of increasing nickel content in this regard. Centralloy ET45 micro is a centrifugal casted alloy of Schmidt + Clemens group and is used in ethylene crackers, where it is known to resist H_2S environments till 900 °C. As the aim of this work was to find a reactor material for a thermal cracking process of anthropogenic resources, which works at 680 °C, this particular nickel based alloy was chosen and used as delivered from Schmidt + Clemens.

*Values are calculated with the software FactSage 7.0

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https://doi.org/10.1016/j.corsci.2018.04.042
Received 31 January 2018; Received in revised form 17 April 2018; Accepted 30 April 2018

Please cite this article as: Schmid, A., Corrosion Science (2018), https://doi.org/10.1016/j.corsci.2018.04.042

Table 1
Chemical composition of the used materials [wt.%] (information from the supplier).

	Fe	Cr	Ni	C	Si	Mo	Nb	Mn
Duplex	67	22	5	0.03	1	3	–	2
Ni based alloy	16	35	44.5	0.45	1.6	–	1	1

2. Experimental methods

Table 1 shows the chemical composition of Duplex steel 1.4462 and Ni-based alloy Centralloy ET45 micro. ET45 was provided by Schmidt + Clemens Group and is also known as GX45NiCrSiNb45-35. Corrosion tests were performed for 24, 72 and 240 h respectively, while new samples were used for each experiment. Microstructures of both alloys prior to corrosion are depicted in Fig. 1 with increasing magnifications. Duplex steel (left) was etched with Beraha 2 and displays the ferrite phase in dark and the austenite phase in bright colours. The ferrite / austenite ratio was about 50:50. Ni-based alloy ET45 (right) was etched with an aqua regia, acetic acid mixture and offers a wide network of carbides (M_7C_3) besides some coarse carbides ($M_{23}C_6$), visible as black dots and titanium nitrides as golden dots. Small, slightly pink precipitations are carbides of niobium.

All specimens were polished with 1000 grit SiC paper, washed, degreased, weighed and gauged in order to reach a well-defined surface. All experiments were performed in a silica glass tube which was heated in a tube furnace. The silica glass tube was connected with gas wash bottles filled with sodium hydroxide solution in order to neutralize excessive HCl and H_2S gas (scheme in Fig. 2, temperature profile of the furnace and sample position Fig. 3).

The gas mixture for the tests consisted of 3.8 vol.% HCl, 1.9 vol.% CO_2, 0.3 vol.% CO, 2.8 vol.% H_2, 0.02 vol.% H_2S, bal. N_2. It was provided by Linde gas (Eggendorf, AUT) in two separated bottles in order to be able to modify the gas composition for further investigations.

Thermodynamic calculations were performed with the software Fact Sage 7.0 It evaluates the equilibrium concentrations of all species at 680 °C, based on the composition of the gas mixture mentioned above. Calculations determined that the oxygen partial pressure in the gas atmosphere is high enough (10^{-25} bar) to oxidize chromium, but not iron and nickel. The partial pressure of chlorine was calculated to be 10^{-13} bar.

Four specimens (25 × 10 × 2 mm) of the same material were accommodated simultaneously in the silica tube by using a silica glass holder, whereby the largest surfaces of each sample were aligned parallel to the gas flow (see Fig. 5). While three samples were used for the mass loss determination, one was cold mounted for metallographic and SEM/EDX investigation. After the samples were placed in the glass tube, the system was purged with nitrogen for 30 min and during the initial heating process. Once the furnace reached a temperature of 680 °C, the reaction gas mixture was added with a flow of 120 ml/min. After the experiment was completed, the system was again purged with nitrogen gas to replace the reaction gas before the furnace was turned off. The samples were removed after the equipment reached room temperature.

Uncleaned samples were cold mounted in epoxy resin and polished under the exclusion of water to 3 µm diamond grit before they were investigated by light microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX). This was necessary to

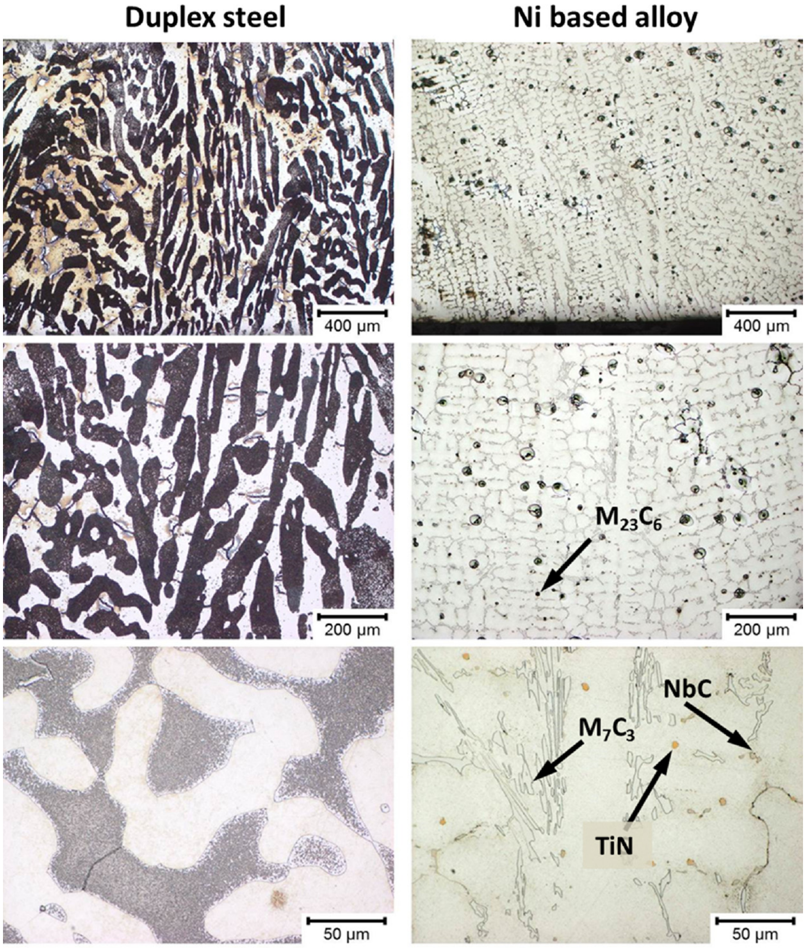

Fig. 1. Microstructures of tested alloys in different magnifications.