Corrosion Science 69 (2013) 181–190

Contents lists available at SciVerse ScienceDirect

Corrosion Science

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

Predicting the depletion of chromium in two high temperature Ni alloys

R. Pillai *, H. Ackermann, K. Lucka

Oel Waerme Institut GmbH, Affiliated to RWTH Aachen, Kaiserstrasse 100, 52134 Herzogenrath, Germany

ARTICLE INFO

Article history:
Received 11 June 2012
Accepted 30 November 2012
Available online 10 December 2012

Keywords:
A. Nickel
B. Thermal cycling
C. High temperature corrosion

ABSTRACT

The oxidation resistance of the high temperature Ni-Cr alloys alloy 601 and alloy 602 CA was studied. Based on microanalysis data from cyclic oxidation experiments performed in a burner test rig, the total loss of chromium in the alloy was determined. A numerical analysis using the general diffusion equation was performed to model the mass transport for the observed chromium loss. Chromium depletion profiles were calculated with an effective diffusion coefficient derived from the data of the shortest exposure time. Good agreement was found between the measured and the computed chromium concentration at the alloy-oxide interface for longer exposure.

1. Introduction

High temperature alloys are utilised in the construction of modern oil burners for domestic heating. The so-called low-NOx and blue flame burners are equipped with a flame tube. The fuel is atomised, mixed with air, evaporated and ignited within this tube. The tube also serves for recirculation of exhaust gas into the flame. The static pressure in the fuel–air stream which is flowing at high velocity in the tube is lower than in the combustion chamber. Due to this pressure drop, gas from the combustion chamber flows into the tube through recirculation holes or slits manufactured for that purpose. In this way adding inert exhaust gas to the fuel air mixture lowers the flame temperature which further retards formation of thermal NOx. Present developments of stationary burners for heating oil aim at reducing the dimensions of the heating systems, thereby, raising the thermal stress of the involved materials. Among others austenitic Ni alloys are used for flame tubes. A screening test of selected Ni alloys had been carried out in a burner rig [1–3] some years ago. During these thermal cycling exposure tests, the performance of the materials at a temperature of up to 1000 °C was investigated which is higher than the temperature experienced by flame tubes in the then current burners. The materials' performance was monitored by destructive examination of samples. The selected high temperature Ni alloys form a stable protective chromium oxide scale. The nature and the development of the oxide scale and the inner oxides during exposure have been examined and described by Ackerman et al. [2]. As a result of the measurements the time dependent chromium loss of the chromium oxide forming alloys alloy 601 and alloy 602 has been reported and the relation to failure of the alloys has been pointed out [3]. Chromium is gradually lost during thermal cycling due to the thickening of the oxide scale, the repeated scale spallation and formation as well as the evaporation of volatile reaction products and their removal by the flowing gas atmosphere, especially in wet atmospheres. The already published investigations have been completed by the following experiment. Samples of alloy 602 were exposed in the burner rig and their mass change was measured discontinuously. The present work reports results of this experiment. Additionally a more sophisticated evaluation of the microanalysis data of the previous experiment and based on these reevaluated data, calculations of chromium depletion by a numerical solution of Fick's second law were performed. The aim of this study was to test whether the rather simple calculations of this kind are a proper tool for prediction of the performance of an alloy in the flame tube application.

2. Experimental

2.1. Materials and sample preparation

The alloys of interest here are alloy 601 and alloy 602 CA. In the experiments reported by Teneva et al. [1] segments of a flame tube have been manufactured from sheets of the selected alloys with sheet thickness of 1 mm. The conventionally manufactured sheets were supplied by an industrial project partner. The composition of the alloys is given in Table 1. The complete tube and a tube section from alloy 602 CA after 50 h exposure and after taking sections at two different axial positions are shown in Fig. 1. For the measurement of mass change specimen of alloy 602 CA of rectangular shape 15 × 15 × 1 mm were machined from the sheet material and a hole for suspension was drilled. Prior to exposure the specimens were degreased in acetone and dried in laboratory air.

* Corresponding author. Tel.: +49 2407 9518162; fax: +49 2407 9518262.
E-mail address: R.Pillai@owi-aachen.de (R. Pillai).

0010-938X/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2012.11.040

Table 1
Composition of studied alloys.

Material	Alloy 601[a]	Alloy 602 CA[b]
Nr. according to DIN EN 10 027	2.4851	2.4633
Ni	bal	bal
Cr	23.9	25.1
Fe	14.01	9.25
Al	1.30	2.29
Si	0.24	0.04
Co	0.04	0.02
Ti	0.33	0.15
Mn	0.55	0.08
Y		0.08
Zr	0.018	0.08
Cu	0.06	0.01
C	0.036	0.183
P	0.1	0.008
S	0.003	0.002
B		0.002
Thermal or surface treatment	Bright annealed	Bright annealed

[a] From GDOS analysis.
[b] From batch certificate.

2.2. Burner rig

A detailed description of the used burner rig has been given by Teneva et al. [1] and Ackermann et al. [3]. A commercial low-NOx burner for heating oil was arranged in a water cooled boiler. Instead of the standard flame tube the combined tube described above, which had the same dimensions as the standard tube, was attached to the burner. A cylindrical chamber was installed in the boiler so that more than half of the flame tube was within that chamber. Hence the burner was operating in a hot combustion chamber. Prior to the exposure test the temperature of the tube was measured with thermocouples pressed into grooves on its exterior surface. Along a distance of 40 mm at the tube outlet a temperature of 995(±15 °C) was measured during stationary operation of the burner with a burner power of 13 kW. In the experiment for measurement of mass change the standard flame tube was attached to the burner and three rectangular specimens were suspended in the hot combustion chamber on a ceramic rod directly at the end of the flame tube. The plane surface of the samples was oriented parallel to the tube axis. The temperature of the specimens measured with thermocouples was 996, 988 and 977 °C (reproducible within ±3 °C) during stationary operation of the burner.

2.3. Burner operation and test procedure

During the exposure experiments the burner operated in the burner rig intermittently. A 15 min operational period was followed by a 5 min shut-down before the restart. The tube cooled down to 200 °C during the break. Ackerman et al. [3] showed from measured gas concentrations, that at the outlet of the flame tube the oxygen concentration in the wet gas near the tube wall was between 0.5 and 1.8 vol.% in the stationary state. For the fuel to air ratio given in the experiment the oxygen concentration of the exhaust gas after complete combustion of the fuel is 2.55 vol.%. The volume concentration of CO_2 and H_2O are 11.7 and 12 vol.%, respectively with the volume fraction of SO_2/SO_3 being 102 ppm. The liquid fuel used was heating oil with sulphur content up to 2000 mg/kg. Segments of the flame tube were removed and replaced by a new one of the same material for alloy 601 after 500, 1000 and 2000 h and for alloy 602 CA after 50, 500, 2000 and 3000 h exposure at dwell temperature. In one experiment with the suspended rectangular specimen three specimens from alloy 602 were exposed and their mass was measured discontinuously every 2 h up to 16 h and subsequently every 3 h up to 34 h. In a second experiment three other specimens of the same material were discontinuously exposed in two intervals of 24 h, and two intervals of 48 h for a total of 144 h. After each exposure interval the specimens were removed from the suspension and weighed with an accuracy of 4×10^{-5} g using a microbalance.

2.4. Post-exposure examination

The alloy samples with dimensions $15 \times 10 \times 1$ mm for the metallographic and microanalytical investigations were cut from the segments at the tube outlet at the position where a temperature of 995(±15) °C was measured. After vapour deposition of a thin gold layer and electro-deposition of nickel onto the sample surface the specimens were carefully aligned normal to the section thickness and metallographic cross-sections were prepared. The metallographic investigations were carried out at the Central Facility for Electron Microscopy of the University of Technology in Aachen. Quantitative concentration profiles were measured perpendicular to the alloy surface and elemental mapping was done with an electron microprobe. The operating conditions: 15 keV electron beam energy and 20 nA beam current resulted in an effective spot diameter of about 0.5 μm. Secondary (SE) and back scattered electron (BSE) pictures of each analysed area were taken. The cross-sections of some samples were etched and observed by light microscopy.

3. Experimental results and discussion

3.1. Metallographic analysis and chromium depletion

As an example Fig. 2 shows micrographs of the metallographic cross-section of the sample of alloy 601 after 1000 h exposure.

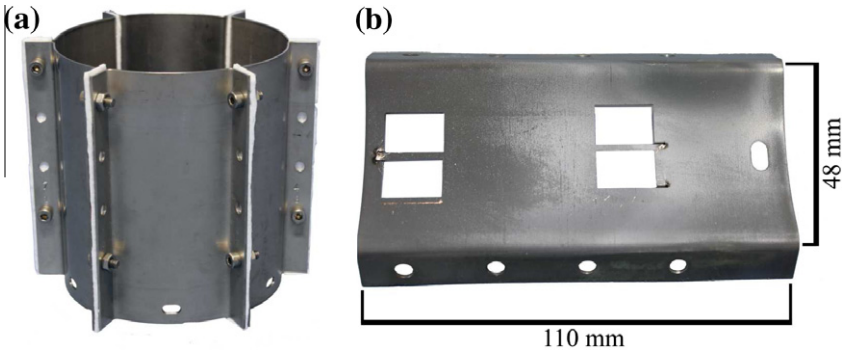

Fig. 1. Flame tube combined from six segments, single segment of alloy 602 CA after 50 h cyclic oxidation in the burner rig and after laser cutting of two samples at two axial positions.