



Inhibitors and coatings against vanadate-containing oil ash corrosion of boilers



X. Montero ^{*}, M.C. Galetz

DEHEMA-Forschungsinstitut, Theodor-Heuss-Allee 25, Frankfurt am Main 60486, Germany

ARTICLE INFO

Article history:

Received 29 April 2016

Revised 8 July 2016

Accepted in revised form 11 July 2016

Available online xxx

ABSTRACT

Corrosion in oil-fired boilers is accelerated in the presence of vanadium, sodium, and sulfur from low grade fuels. In order to avoid vanadate-induced corrosion several ceramic inhibitors and intermetallic coatings and their interaction were studied. Inhibitor ceramics such as CaO and MgO tend to react strongly with vanadium oxides forming vanadates with higher melting temperatures whereas Cr₂O₃, Al₂O₃, and SiO₂ are the most protective oxides for alloys at high temperatures even in the presence of vanadium pentoxide.

Three potential inhibitors were tested on uncoated as well as on Cr, Al, and AlSi diffusion coated 10CrMo9-10 steel by immersion in 60 mol% V₂O₅–40 mol% Na₂SO₄ salt at 650 °C. Materials performance was analyzed by calculating substrate recession rates and by metallographic characterization of the corrosion scales and of the metal subsurface zones so that the mechanism and extent of corrosion could be characterized.

In the end different materials combinations (coatings and inhibitors) could be ranked with regard to the detrimental or beneficial role of the different approaches. The present results thus provide a much deeper insight into materials resistance in vanadium-containing environments at boiler simulating conditions than previous studies.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A number of industrial high temperature processes, e.g. boilers in chemical or energy production and marine and aircraft turbines, operate on low grade fuel oils that induce accelerated corrosion rates and premature material failure [1–6]. The reason for this severe type of high temperature corrosion is the presence of ash deposits containing vanadium oxides and sodium sulfate which prevent the formation of protective oxide scales on the metallic materials. Concerning hot corrosion, vanadates are among the most corrosive components in fused salts. While part of their effect lies within lowering the viscosity of the melt, another issue is introduced by the strong acidity of their complex oxide ions and their ability to dissolve the otherwise protective oxide scales formed on structural alloys [7].

The combined effect of sodium sulfates–vanadates has been reported in several works [6,8,9]. In general it has been established that, under normal operating conditions in combustion engines and for vanadate deposits with Na/V ratios smaller than one, the SO₃ pressure is usually not enough to convert sodium vanadates to sodium sulfate. However at boiler conditions (below 700 °C) both salts can be present, and the corrosion caused by sodium sulfate/sodium vanadate mixtures is a complex mechanism.

In order to prevent or reduce metal wastages and maintain the operational efficiency of the processes two approaches are possible: the use of inhibitors that increase the melting temperature of the corrosive slags or the use of coatings that are inert against the attack by the slags.

1.1. Inhibitors

Early in the study of vanadate corrosion it was recognized that the accelerated oxidation associated with the presence of liquid V₂O₅ could be attenuated if the melting point of the reaction products could be raised above the operating temperature or if the oxidation state of the vanadium oxide could be reduced [10]. The metal oxides of Group II of the periodic table were initially identified as prime candidates for attenuating the corrosion associated with V₂O₅ because they could form refractory vanadates [4].

Numerous additives have been evaluated: Mn, Ca, Mg, Si, Zn, Be, Sr, Ba, Al, Ce, and Cr oxides. Patents have been filed [4,11,12]. Among those, the most effective addition used to control vanadium corrosion is based on the formation of the refractory orthovanadate Mg₃(VO₄)₂ [11]. Nevertheless, as noted by many investigators, the inhibition of vanadate corrosion by magnesium compounds can be impeded if high sulfur species are present [1,13]. The reduction in the ability of MgO to inhibit vanadic corrosion is attributed to the sulfation of MgO to MgSO₄ which causes a change in the MgO:V₂O₅ molecular ratio and subsequent formation of corrosive molten vanadates.

^{*} Corresponding author.

E-mail address: montero@dechema.de (X. Montero).

Table 1
Composition of tested steel (wt.%).

	Fe	Ni	Cr	Si	Mn	V	Mo
10CrMo9-10	95.710	0.086	2.253	0.225	0.487	0.005	0.973

1.2. Coatings

In the presence of vanadates, most alloys form rather non-protective and porous oxide scales which do not act as an effective diffusion barrier [14]. In order to **reduce** corrosion, inert materials that do not react with sulfur or vanadium have to be coated onto the substrate tubes. According to the Lewis acid-base theory, vanadate salts can vary in acidity from the most acidic V_2O_5 to the most basic Na_3VO_4 . As shown before, acidic vanadates such as bronzes ($Na_2V_{12}O_{31}$ and NaV_3O_8) or sodium metavanadate ($NaVO_3$) can hardly react with acidic oxides such as SiO_2 , Al_2O_3 , or Cr_2O_3 [15–18].

In the design of alloys to resist hot corrosion, chromium is known to be the most effective alloying element. Since Cr_2O_3 is such an acidic oxide, the formation of basic chromate ions is generally driven by a dissolution mechanism. However because of the positive power law dependence of chromate solubility on oxygen activity, the solubility of chromate increases in the direction of the salt-gas interface, so that the requirement of a negative solubility gradient is not fulfilled. Different MCrAlY ($M = Fe, Ni, \text{ or } Co$) have been tested against sulfate/vanadate deposits. At temperatures around 650 °C it was found that FeCrAlYs behave better because of the better resistance of the coating against sulfate-induced corrosion. At higher temperatures protective scales of Cr_2O_3 - Al_2O_3 fail to develop in the presence of vanadate salts [19–21].

FeAl intermetallics showed high corrosion rates at temperatures around 700 °C, but at higher temperatures around 900 °C their protection behavior improved because they were capable to develop a stable protective alumina scale. This behavior suggests that at this temperature the dissolution of the oxides due to vanadate compounds can be neglected compared to the high oxidation kinetics of FeAl alloys. However, the increase in temperature also modified the composition of the salt. V_2O_5 seems to evaporate at such high temperatures, and less acidic vanadate salts are left as main corrosive components [9].

Ni-base alloys with high Si content maintained a protective silica layer at temperatures around 700 °C whereas similar alloys without Si were not protective. The protective silicon dioxide scale could be dissolved by a basic fluxing reaction that yields sodium silicate, however the protection can be maintained due to an extremely low solubility of sodium silicate in the deposits (no negative solubility gradient) [22].

In this study two inhibitors and three coatings were considered to be used in oil-fired power stations where typical sodium- and vanadium containing molten salts are present. Their corrosion resistance was investigated by short term exposure tests combined with statistical metal wastage measurements. The corrosion products were determined in order to investigate the protection method and to understand the corrosion mechanism. The main aim of these investigations was to clarify the role of different inhibitors and their interaction with coating elements with regard to corrosion performance. Finally the goal is to allow the design of an optimum combination for high resistance in high temperature sulfate/vanadate-containing environments.

2. Experimental procedure

Low-chromium (10CrMo9-10) steel was selected as substrate for the experiments. The chemical composition is listed in Table 1. Planar samples with dimensions of $20 \times 10 \times 2 \text{ mm}^3$ were cut and ground with SiC120 abrasive paper. Prior to exposure or coating, these samples were cleaned in an ultrasonic bath with acetone and measured with a TESA-Micromaster model micrometer (resolution 1 μm ; accuracy 1.6 μm).

The salt mixture between Na_2SO_4 (40% mol) and V_2O_5 (60% mol) was chosen because it has the lowest melting temperature in the sodium vanadate system [23,24]. Several salt compositions were examined after exposure as published in a previous article [18], where NaV bronzes and $NaVO_3$ were the main vanadate forms.

CaO and MgO (Alfa Aesar) powders were added at 10 wt.% to the vanadate salt in order to examine the effectivity of the pre-selected inhibitors. Pack cemented Cr diffusion coatings were manufactured as described in detail in [25] during a heat treatment of 2 h at 1050 °C in Ar/5% H_2 atmosphere. The resulting coating consists mainly of a $Cr_{23}C_6$ layer of 3–5 μm (see Fig. 1a). Al and AlSi slurry diffusion coatings were

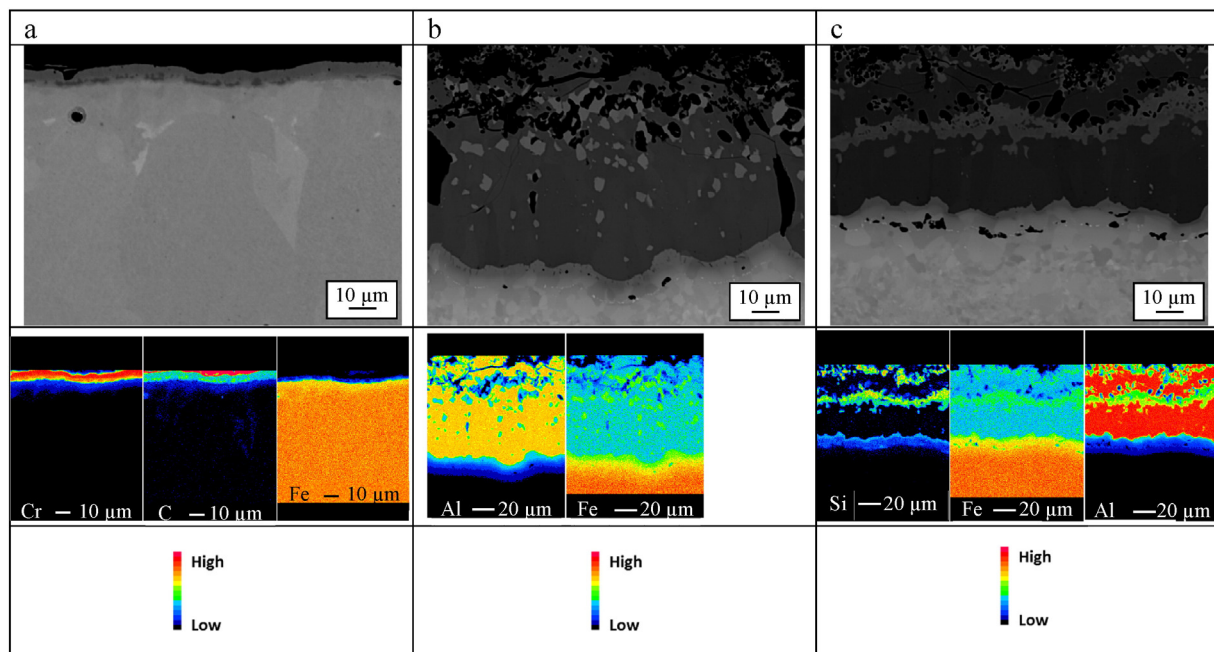


Fig. 1. Cr pack cemented (a), Al slurry (b) and AlSi slurry (c) coated 10CrMo9-10.

Download English Version:

<https://daneshyari.com/en/article/8024934>

Download Persian Version:

<https://daneshyari.com/article/8024934>

[Daneshyari.com](https://daneshyari.com)