



Models describing the degradation of FeAl and NiAl alloys induced by ZnCl₂–KCl melt at 400–450 °C

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Abstract

In this study, a mechanism to account for the corrosion of Fe–Al and NiAl alloys beneath molten ZnCl₂–KCl at 400–450 °C in air is described. All the examined materials experienced enhanced corrosion, with the formation of porous surface scales or, in some cases, in combination with local attack of the matrix. Comparatively, the corrosion resistance of Fe–Al and NiAl alloys is markedly improved with increased Al contents, whereas different microstructural evolutions are observed for the two systems. For Fe–Al alloys, the outermost layer of corrosion product is a mixed region composed of a large amount of Fe₂O₃, KCl and metallic zinc particles, overlying a mixture of aluminium oxide and KCl that acts as the intermediate layer. Moreover, a multi-layered Fe₂O₃ scale is produced on the surface of the matrix. For Ni–Al alloys, however, the outermost layer is mainly a mixture of KCl, metallic Zn, and some alumina particles in local regions, but no nickel oxide is detected. Beneath this outer layer is an Al-rich oxide layer combined with KCl impurity, and then a metallic nickel bulk containing aluminium oxide precipitation, in contact with the matrix.

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1. Introduction

Boiler superheater tubes used in incinerators for municipal solid waste (MSW) or advanced biomass-fired plants tend to suffer from rapid corrosion when the metal

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temperature is greater than 300 °C. Such corrosion is usually caused by the complicated chemical reactions between the tube materials and the gaseous species (HCl, SO₂, etc.) and, especially, the low melting point eutectic salts of heavy metal (Sn, Pb, Zn) and alkali metal (K, Na) chlorides and sulfates [1–4]. Thus, the corrosion resistance of the materials can be altered by undergoing sulfidation degradation and loss of structural elements as volatile chlorides, which will, in turn, eventually lead to tube thinning and failure [5]. In fact, conventional carbon steels, low alloy steels and stainless steels usually exhibit rapid degradation and there are examples of superheater tubes operating at 484–538 °C in MSW applications that had to be replaced every few months.

In order to reduce the amount of superheater consumption, it is necessary to develop more effective protection coatings for such components in the hostile combustion environments. Normally, Ni-base alloys suffer less corrosion by chlorine but they are susceptible to accelerated corrosion in environments of high sulfur activity, leading to catastrophic liquid phase corrosion. In addition, Ni-based compositions are relatively rather expensive. Moreover, high Cr alloys or chromized coatings seem also to be less effective in chlorine-containing environments. For example, accelerated consumption of Cr may occur due to the formation of volatile Cr-chlorides [6]. Moreover, such materials are prone to preferential attack of the Cr-rich second phases [7–11]. More cost-effective coating materials with improved corrosion resistance are technologically required.

Al-bearing alloys represent good candidate coating materials for such environments considering the reduced costs and useful properties, such as low density, high strength and good wear resistance. It is known that Fe–Al alloys with contents greater than 10 wt%Al possess good oxidation–sulfidation resistance [12]. Further, Fe–Al alloys can also exhibit much better corrosion resistance than chromia-forming coatings in Cl- or Cl–S-environments, especially at temperatures above 600 °C [13–15]. Also, nickel aluminides have considerable potential for hot corrosion environments containing chlorine. At present, these alloys are more likely to make an impact as a corrosion-resistant cladding, through processes such as high velocity oxy-fuel spraying, friction surfacing with powders and plasma transferred arc cladding. However, it is necessary to investigate the feasibility of using iron and nickel aluminides as surfacing media in corresponding hostile environments. In this paper, a ZnCl₂–KCl eutectic salt was selected as the corrodent. One reason was that such a salt has frequently been identified in the ash deposits of waste incinerators and is considered to play an important role in tube thinning [16,17]. Another reason was that more attention has been paid to conventional hot corrosion induced by sulfates, while the aggressiveness of oxyanion-free chloride melts on the corrosion behaviour of Al-bearing materials has not yet been well established.

2. Experimental

The materials used in this study include pure Ni, one NiAl intermetallic compound, and three Fe–Al model alloys. For comparison purposes, an Al-free ferritic

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