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Failure analysis of 316L stainless steel crucible by molten fluoride salt interaction with clay bonded silicon carbide

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ABSTRACT

Detailed investigation of a recently failed static corrosion test involving molten eutectic LiF–NaF–KF salt at 850 °C contained in 316L stainless steel crucibles shows that a single sealed crucible leaked molten salt into the electric furnace due to mechanical failure, causing a chemical reaction between the molten salt and the clay bonded silicon carbide insulation used in the furnace. As a result, corrosive vapors of Na_2SiF_6, K_2SiF_6, SiF_3, and F_2, were formed. These vapors reacted with the stainless steel crucibles and lead to the formation of a porous corrosion crust and the eventual catastrophic structural failure of all nine sealed 316L stainless steel crucibles.

1. Introduction

Fluoride salt mixtures are used in industry as high temperature heat transfer fluids, heat treatment baths and media for electroplating [1]. Recently, research has been directed towards using eutectic fluorides as potential primary and secondary reactor coolants for Generation IV nuclear power plants [1–11]. One mixture, 46.5%LiF–11.5%NaF–42%KF (mol%), commonly referred to as FLiNaK, has generated interest due to its advantageous thermo physical properties including relatively low melting point, high thermal conductivity, high specific heat, low viscosity and high boiling point [1,10].

Structural material compatibility is a concern when using fluoride salts at high temperatures. Typically, stainless steels derive their passive nature from a thin oxide film formation at the surface. However, in the presence of FLiNaK, these oxide films are unstable due to the reduction-oxidation (redox) reaction of fluorine ions with oxide scales of Cr, Al or Si [12]. Traditional fluoride salt corrosion of structural materials involves the depletion of chromium at the surface of the exposed material [13–16].

High temperature systems containing fluoride salts commonly require substantial insulation to prevent accidental freezing and to minimize trace heat. However, little effort has been directed towards studying the interaction between fluoride salts and common insulation materials, which can occur in the event of a leak or failure. Therefore, very little is known how insulation introduced to a fluoride salt environment will impact the corrosion of structural materials.

In the present study, the failure of a 316L stainless steel crucible containing FLiNaK molten salt and subsequent interaction with furnace materials will be examined. Visual inspection, scanning electron microscopy techniques (SEM–EDS), and X-ray diffraction (XRD) analysis are carried out to identify the root cause of the system failure and understand the molten salt interactions with the furnace insulation material. However, it bears emphasizing that this study is a retroactive failure

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investigation in a test environment where some details are unknown. As such, the best is made of the limited quantitative information available combined with relevant literature.

2. Experimental

The original purpose of the experiment was to create a controlled test environment to study the static corrosion characteristics of clean molten FLiNaK on structural materials. The test consisted of nine crucibles constructed of 316L stainless steel tube with wall thickness approximately 3 mm, welded shut on both ends and containing 512g FLiNaK. Installed in each crucible were several alloy test coupons upon which analysis would be performed at the conclusion of the test.

Salt preparation, crucible filling and final welding was performed in a dry argon atmosphere glove box. At the testing temperature of 850 °C, each sealed crucible would become pressurized to an extent corresponding to the initial quantity of argon contained in each crucible. Previous static corrosion tests have been fabricated and tested in the same manner with a successful outcome [14,16].

3. Corrosion characterization and discussion

3.1. Visual observation

Fig. 1 shows visual characteristics of the crucibles and the high temperature electric box furnace after the termination of the test. A close up comparison of a corroded crucible and a crucible prior to testing is shown in Fig. 2. The scale formation is porous and brittle with shiny metallic sections and areas of green, white, purple, and red residue. The crucible interiors show relatively thin predominately red scale formations. Two steel sheathed type K thermocouples were used to monitor the internal temperature. Both were nonoperational due to heavy corrosion at the conclusions of the 1000 h test. The alumina sheathed type S control thermocouple remained operational the entire time and appeared unaffected. Throughout the duration of the test, the furnace was held at slight positive pressure with nitrogen cover gas making oxygen ingress unlikely.

The furnace base plate, constructed of 1 mm sized particles of silicon carbide held in a clay matrix, showed extensive attack. The clay matrix is composed of minerals containing O, Si and Al. A cross section of the base plate can be seen in Fig. 3 where affected areas are discolored black. The black damaged region is accompanied by light swelling, indicative of vapor formation.

Upon inspection, it appears that the set of nine static test crucibles failed by several different mechanisms. Some crucibles exhibit circumferential cracking, shown in Fig. 4. Localized outward plastic deformation near the cracks indicates that they are stress induced. These stress ruptures are likely created by lowered crucible structural integrity caused by outward corrosion combined with internal pressurization of the argon cover gas contained within the sealed crucible. It has been shown that a structurally sound crucible is able to contain this minor pressurization, therefore this failure mode depends on the presence of corrosive vapor so stress induced cracking cannot be the method by which FLiNaK was first released into the furnace [16]. One crucible shown in Fig. 5 has a prominent failure point located at a weld joint. All failure modes considered, a faulty weld with a pinhole leak is likely the reason why FLiNaK initially escaped into the furnace.

3.2. SEM/EDS and XRD characterization

To understand the nature of the test failure, samples of corrosion crust from the top of a crucible were investigated using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Pieces taken from the top of the corroded crucibles display a variety of morphologies. Fig. 6 shows jagged, rough sections identified in Table 1 to be rich in O, Si, K and Fe dispersed among smoother sections composed primarily of O, K and Cr. Mixed within the jagged sections are

Fig. 1. Photograph of crucibles at the conclusion of the 1000 h static test.