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Corrosion failure analysis of pure nickel thermocouple sheath used in $BaTiO_3$ hydrothermal synthesis reactor

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ABSTRACT

This paper presents corrosion failure analysis on a commercial pure nickel thermocouple sheath used in $BaTiO_3$ hydrothermal synthesis reactor. Detailed investigations of the corrosion products have been performed using stereomicroscope, X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy. It was found that the corrosion failure of the sheath was mainly due to general corrosion and crevice corrosion of pure nickel, and the main corrosion products were $Ni(OH)_2$. Many cracks were observed inside the corrosion products and along the interfaces between the corrosion products and metal matrix. $BaTiO_3$ particles were deposited as parallel white bands along the above cracks inside the corrosion products. Chloride ions also entered the cracks or crevices, resulting in the acidification inside the crevice and aggravated the attack of nickel matrix. Some recommendations to prevent/minimize future similar corrosion failures were proposed.

1. Introduction

Nickel and nickel-based alloys are widely used in chemical process, petrochemical, pulp and paper, energy conversion, power production, supercritical water, waste incineration, pharmaceutical, and many other industries due to their good corrosion resistance in extreme temperature and pressure aqueous environments [1–3]. In chemical industry, nickel and its alloys, such as Nickel 200 and Nickel 201, are the main candidate materials of reactors because of their good resistance to alkaline halogenic environments at elevated temperature. In this paper, corrosion failure of a pure nickel (Nickel 200) thermocouple sheath used in $BaTiO_3$ hydrothermal synthesis reactor was investigated. The reactor is fabricated by stainless steel with a Nickel 200 lining, which has served more than 12 years. Recently, similarly severe corrosion was observed on both inner surfaces of the lining and thermocouple sheath. The reactant solutions mainly contain $Ba(OH)_2$, $TiCl_4$, and $NH_3{\cdot}H_2O$, and the general synthesis reaction is as follows.

$$Ba(OH)_2 + TiCl_4 + 4NH_3{\cdot}H_2O = BaTiO_3 + 4NH_4Cl + 3H_2O \quad (1)$$

The service temperature is 160 °C–240 °C, and the pressure is 6–8 MPa. The reactor is heated to the reaction temperature in 2 h, then held at that temperature for about 4 h to finish the hydrothermal synthesis reaction, and cooled down rapidly by cooling water. Usually there are two working circles every single day. Considering the same material and the very similar corrosion morphology between the thermocouple sheath and the lining of the reactor, the specimen for failure analysis was cut from the sheath (Fig. 1). Table 1 shows the chemical compositions of commercial Nickel 200 [3].

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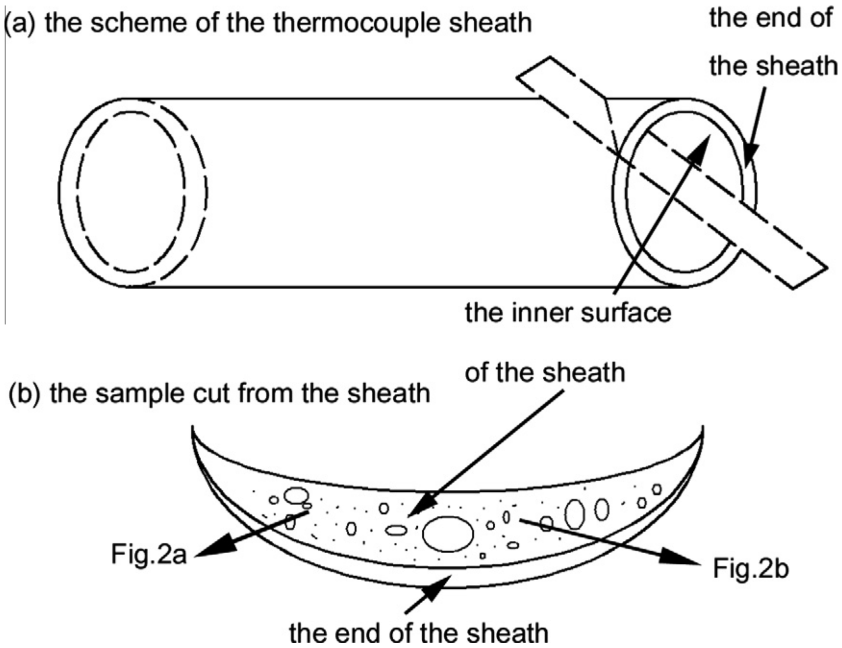

Fig. 1. Scheme illustration of the geometry of the sample: (a) the scheme of the thermocouple sheath, (b) the sample cut from the sheath.

Table 1
The chemical compositions of Nickel 200 [3].

Alloy (UNS No.)	Ni[a]	Cu	Fe	Mn	C	Si	S
Ni 200 (N02200)	99.0 min	0.25	0.40	0.35	0.15	0.35	0.01

[a] Ni + Co. All values max unless noted otherwise.

In the present work, visual inspection, microscopic examinations and X-ray diffraction (XRD) analysis are carried out to evaluate the failure mechanism and its root cause.

2. Characterization of corrosion

2.1. Visual observation

Visual inspection of the as-received specimen was performed using a stereomicroscope (Leica S6D). It was found that severe corrosion took place on inner surface of the thermocouple sheath (Fig. 2). The inner surface of the sheath became rather rough due to extensive general corrosion, where some green scales and white deposition were observed (Fig. 2a and b). Similar corrosion morphology and residual green scales or white deposition were also observed on the end of the sheath (Fig. 2c). However, no obvious corrosive were observed on the outer surface of the sheath except for residual white deposition (Fig. 2d).

2.2. SEM morphological characterization

The inner surface of the thermocouple sheath was investigated using Phillips XL30 scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) (Fig. 3). It was clear that the residual corrosion products were porous with many cracks (Fig. 3a). Fig. 3b and c are the magnification of the corrosion products observed in Fig. 3a. They looked like sheets with disorder orientations. The EDS results are shown in Table 2. The sheet-like products were rich in Ni and O. Fig. 3d is the enlarged morphology of the white particles in area A of Fig. 2a, appearing regular polyhedral crystals with good symmetry, and the EDS analysis showed that particle 3 was rich in Ba, O and Ti.

Figs. 4–8 show the cross-sectional morphologies of the corrosion products in some typical regions with pure nickel matrix. The corrosion products seemed to have a laminar structure, in which many cracks and crevices were observed (Figs. 4–8). Some cracks were parallel with the interface between the corrosion products and metal matrix, and other cracks were vertical to the interface. Frequently a kind of white deposition could be observed along the cracks or crevices inside the corrosion products. As a result, parallel white bands appeared on the cross-sections of the corrosion products (Figs. 5–8). Cracking or