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Local structure study of tellurium corrosion of nickel alloy by X-ray absorption spectroscopy

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ABSTRACT

Clarifying the atomic structure of tellurium corrosion product in nickel alloy will help understand the mechanism of Tellurium corrosion in Molten-salt reactor (MSR). Extended X-ray absorption fine structure (EXAFS) complemented by first-principles density functional theory (DFT) calculations was used to characterize the atomic local structure of tellurium in nickel at operando temperature of 1000 °C. The investigation indicated that Te atoms diffuse into the Ni substrate to form Ni-Te solid solution with outward relaxation of the neighboring Ni atoms around Te in both grain lattice and grain boundaries (GBs). Furthermore, we propose a process of tellurium diffusing into nickel at high temperature.

1. Introduction

Nuclear energy will be one of the best candidates to meet the future demand for clean and high effective energy [1,2]. Specifically, molten-salt reactor (MSR) [3,4], the only liquid-fuel reactor of generation IV, has many special advantages compared with other solid-fuel reactor systems, such as recycling of fission fuel within reactor, producing less long-lived wastes and so on [1,3,5]. However, liquid fuel means direct contact between the reactor components and the molten salt with dissolved fuel and fission products, which challenges the performance of the structural material, the nickel alloys. In 1960s, Oak Ridge National Laboratory (ORNL, USA) performed a Molten Salt Reactor Experiment (MSRE) and found that the surface of Hastelloy N exhibited apparent intergranular embrittlement after exposed to the fuel salt for 4 years [5]. These cracks would propagate inward after long-time service, which seriously threaten the safety of MSR. Early study of ORNL revealed that the cracks result from the inward diffusion of the fission-product tellurium (Te) along nickel grain boundaries (GBs) and thus it was defined as "Tellurium corrosion" [6].

However, the corrosion effect is not fully understood in terms of the underlying mechanism, and efforts have been made to correlate it to the structural and electronic features of the Ni-Te system. Ignatiev et al. [7] found Tellurium corrosion exists in different nickel alloys. Jia et al. [8] confirmed ORNL's finding that high-temperature and long-time service will aggravate alloy's Tellurium corrosion and the surface reaction products are $NiTe_{0.67}$ (Ni_3Te_2) or a mixture of $NiTe_{0.67}$ and a spot of $NiTe_{0.69}$. They also proposed that Te diffuses into pure nickel predominantly along the GBs at low temperature (below 900 °C), while the diffusion mechanism of Te turns to be lattice diffusion above 1000 °C. Chen et al. [9,10] found that CrTe was formed as the Te corrosion product in the GBs and surface of Ni-16Mo-7Cr alloy. Liu et al. [11] and Vsianskaet al. [12] presented first-principles calculations to investigate the effect of Te on the Nickel GBs and indicated that Te favored substituting Ni and forming substitutional solid solution which would induce intergranular corrosion. Nevertheless, the mechanism of Tellurium corrosion is still unclear, due to the fact that the above mentioned works mainly focus on the GB but haven't figured out the GB diffusion product. On the other hand, the mechanical property of nickel alloys is influenced not only by GB but also by grain lattice [13–16]. Therefore, clarifying the atomic structure of tellurium corrosion product in nickel lattice at high temperature, where lattice diffusion is predominant [8], is of great help for deeply understanding Tellurium corrosion.

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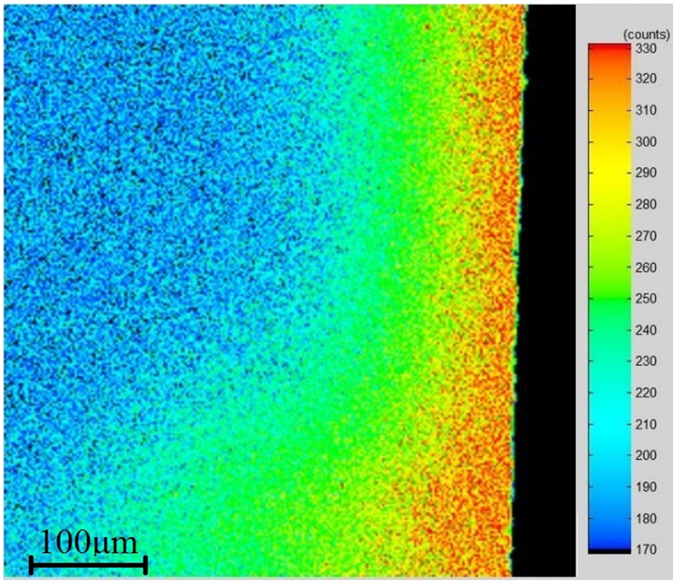

Fig. 1. The element distribution (500 μm × 500 μm) of Te for the annealed sample. The surface is on the right side. The color bar from blue to red shows the increment of Te counts. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

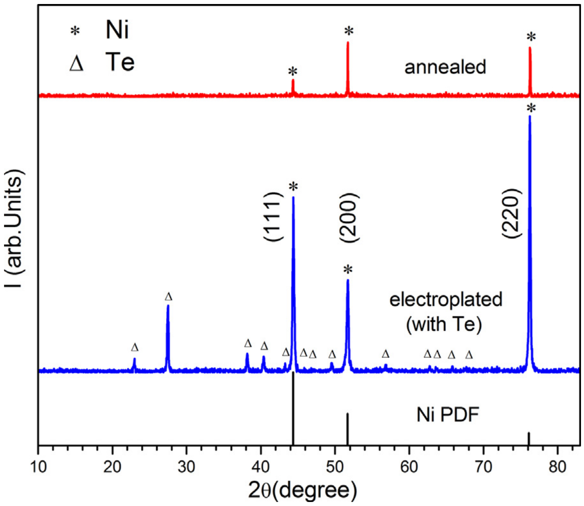

Fig. 2. XRD patterns of sample electroplated with Te, annealed sample and Ni PDF#65-0380.

In this work, the atomic structure of tellurium corrosion product in nickel lattice at 1000 °C is studied by Extended X-ray absorption fine structure (EXAFS) and first-principles density functional theory (DFT) calculations. Based on the analysis of the corrosion product, we further propose the process of interaction between Te and Ni at high temperature.

2. Experimental method

The sample was prepared from commercial Ni (99.9 wt%) with a size of 20 mm × 10 mm × 2 mm. By electroplating in 40 °C thermostatic telluric oxide-potassium hydroxide electrolyte, the surface of Ni substrate was coated with Te equably to a content about 0.5 mg/cm^2. The concentrations of TeO_2 and KOH used in the electroplating bath are 0.08 mol/L and 1.0 mol/L, respectively. The platinum foil was used as anode and the electroplated sample as cathode. The plating potential was 15 V DC and the current 10 mA. Then the sample was sealed in a vacuum quartz tube and subsequently annealed at 1000 °C for 100 h in a muffle furnace as detailed elsewhere [8]. Cross-sectional mapping of Te were performed by a SHIMADZU EPMA-1720H electron probe microanalyzer (EPMA) with step size 2 μm × 2 μm. X-ray diffraction (XRD) was conducted to investigate the phase in surface layer. K-edge EXAFS spectra of the annealed sample, the pure Te and Ni as reference were measured at the BL14W1 beamline at Shanghai Synchrotron Radiation Facility [17] (SSRF). All data were processed using ATHENA and ARTEMIS [18]. Scattering amplitude and phases were calculated using FEFF6 [19,20]. DFT calculations were implemented in the Vienna *ab initio* simulation package (VASP) [21,22] to further study the atomic distribution of tellurium in nickel lattice.

3. Results

The cross-sectional element distributions of Te for the annealed sample were measured with EPMA as shown in Fig. 1. It is obvious that the concentration of Te is decreased from surface to bulk, and Te is homogeneously distributed along the surface plane direction.

The phase investigation of the surface layer by XRD was performed as well for the samples, as displayed in Fig. 2. As can be seen, there only exists diffraction peaks attributed to pure Ni and pure Te for the electroplated sample. After annealed at 1000 °C, the peaks from Te (according to PDF#36-1452) disappeared with the peaks corresponding to Ni remaining and no new peaks from Ni-Te intermetallic compound were discovered. And the peak position of Ni for annealed sample did not shift either compared with that of fcc-structure Ni according to PDF. These observations indicate that at high annealing temperature Ni-Te solid solution was formed without changing the Ni substrate lattice parameters, or that the grain sizes of the new Ni-Te intermetallic phase are too small to be detected by XRD. Therefore, the local structure of Te need to be further explored to assess whether the Ni-Te intermetallic phase exists or not.

EXAFS technique, because of its sensitivity to the short range order and atomic species, was used to probe the local geometry around Te atoms in Ni substrate. The radial distribution functions (RDF) of the annealed sample and the Ni and Te reference, obtained from their k^2-weighted EXAFS by Fourier transform, are displayed in Fig. 3. It is easily noted that the annealed sample exhibits an fcc-structure feature similar to that of the reference Ni but not Te, which implies that the local structure around Te atoms in the annealed sample is similar to that of the fcc Ni. The prominent peak of Te at 2.6 Å does not show in the RDF of the annealed sample. This indicates that there were no Te clusters in the annealed sample. Therefore, we consider the corrosion product as substitutional Ni-Te solid solution (Fig. 3a).

To extract quantitative structural parameters for the atoms surrounding the central Te atoms, we have fitted the FT main peaks from 1.3 to 4.3 Å for the annealed sample. The coordination numbers N of all the paths were fixed to their corresponding values in the fcc-structure Ni substrate, assuming the local environment is substitutional. This model produced a satisfactory fit to the data (Fig. 3b) with the percentage misfit (R-factor) being only 0.6%, and the sound structural parameters are summarized in Table 1. However, the fitting deteriorated dramatically when Te—Te bonding was attached to each shell, which suggested no Te clusters or Ni-Te intermetallic phase but only fcc-structure Ni-Te solid solution exists. Moreover, Table 1 revealed an overall increasement of the bond length of 0.07 Å, 0.01 Å and 0.04 Å for the nearest three shells, respectively. Generally, EXAFS provide the direct evidence that Te substitutes Ni atoms to form Ni-Te solid solution resulting in lattice relaxation of the Ni substrate.

Further supporting to the conclusion about the lattice corrosion products drawn above can also be contributed by DFT calculations.