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ERDA, RBS, TEM and SEM characterization of microstructural evolution in helium-implanted Hastelloy N alloy

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ABSTRACT

Hastelloy N alloy was implanted with 30 keV, 5×10^{16} ions/cm^2 helium ions at room temperature, and subsequent annealed at 600 °C for 1 h and further annealed at 850 °C for 5 h in vacuum. Using elastic recoil detection analysis (ERDA) and transmission electron microscopy (TEM), the depth profiles of helium concentration and helium bubbles in helium-implanted Hastelloy N alloy were investigated, respectively. The diffusion of helium and molybdenum elements to surface occurred during the vacuum annealing at 850 °C (5 h). It was also observed that bubbles in molybdenum-enriched region were much larger in size than those in deeper region. In addition, it is worth noting that plenty of nano-holes can be observed on the surface of helium-implanted sample after high temperature annealing by scanning electron microscope (SEM). This observation provides the evidence for the occurrence of helium release, which can be also inferred from the results of ERDA and TEM analysis.

1. Introduction

As one of the most promising generation IV nuclear reactor systems, the molten salt reactor (MSR) has been attracting increasing attention, due to its inherent safety and high efficiency, etc. However, the corrosive molten fluoride salts and the high temperature [1,2] pose significant challenges for MSR structural materials. Due to the excellent high temperature mechanical properties and compatibility with the molten salts, the nickel-base Hastelloy N alloy has been considered as the most promising candidate structural material for MSR. However, the dimensional instability due to irradiation-induced helium embrittlement or swelling in nickel-based alloys, particularly from helium bubbles formed directly from nickel by transmutation reaction (n, α) during neutron production, has been a cause of much concern in terms of safety and structural integrity [3–7]. In the Molten Salt Reactor Experiment (MSRE) (which went critical on June 1, 1965), the fluences of thermal neutrons (<0.876 eV) and epithermal neutrons (>0.876 eV) in the core were respectively about 1.04×10^{21} and 3.05×10^{21} n/cm^2 per year for a full-power operation at 8 MW [8]. This introduced a helium concentration of 30 appm in the alloy. The results of tensile tests on the neutron exposed Hastelloy N alloy showed that the fracture strain decreased abruptly with helium concentration of only 1 appm [8].

The evolution of helium in various nuclear structural materials has been extensively investigated in the last thirty years [5–17]. However, experimental studies related to the nickel-based alloys, especially for helium diffusion and release, have been rarely reported. In view of the fact that helium embrittlement is one of the main reasons for the degradation of the nickel-base Hastelloy N alloy, it is particular important to clarify the helium behavior in such alloy at high temperatures. In this work, the diffusion and release of helium atoms (bubbles) in Hastelloy N alloy on post-implant annealing conditions have been investigated. Elastic recoil detection analysis (ERDA) technique was used to detect the diffusion of helium atoms under different annealing conditions. In addition, the helium bubble evolution and implanted surface morphology were characterized using transmission electron microscopy (TEM) and scanning electron microscopy (SEM), respectively.

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2. Experimental procedures

2.1. Sample preparation

Hastelloy N alloy in this work was provided by Haynes International Company. The chemical composition is Ni (bal.), 17.1 wt.% Mo, 7.1 wt.% Cr and 4.2 wt.% Fe (Mn, Si, C, Al, Cu, total <1.5 wt.%). The alloy was firstly cut into sheets (6×8 mm^2) with a thickness of 1 mm. The sheets were mechanically polished with silicon carbide paper and diamond polishing paste. After the vibratory polishing, these sheets were ultrasonically cleaned with a solution of 50% acetone and 50% ethyl alcohol. Finally, the samples were irradiated with 30 keV He^+ ions at room temperature using a 400 kV ion implanter located at Beijing normal university, to a dose of 5×10^{16} ions/cm^2. The implanted samples were firstly annealed at 600 °C for 1 h, and then some of them were further annealed at 850 °C for 5 h in a vacuum (below 10^{-4} Pa).

Cross-sectional TEM samples were prepared using ion milling. The samples were cut into strips with a section of 2×10 mm^2 using a low speed diamond saw. The irradiated surface of two strips was glued to each other. Then, the glued cuboid was polished at four edges to be inserted into a brass tube of 3 mm outer diameter along with the glue to fill as much of the tube volume as possible. Afterwards, the tube was heated on a hot plate at 100 °C for 45 min to solidify the filled glue. After the curing process, the tube was sectioned into cylinders of 3 mm in diameter and ~0.25 mm in thickness. Two sides of these cylinders were mechanically ground and polished to a sample thickness of less than 50 μm. Then these disks were dimpled to thickness of approximate 20 μm. Finally, the disks were thinned using a low angle (from 6° to 4°) and low energy (from 4.2 keV to 4 keV) Ar ion milling in a Gatan PIPS. The samples were investigated using a FEI Tecnai G2 F20 TEM operated at 200 kV.

2.2. ERDA experiments

The quantitative helium concentration depth profiles in samples were obtained using ^{4}He (^{12}C, ^{4}He) ^{12}C reaction by employing two detectors simultaneously. The experimental setup is shown in Fig. 1. In this configuration, the grazing incidence of 9 MeV $^{12}C^{3+}$ beam is at 20° to achieve proper detecting depth. The ERD detector detects the helium recoils at recoil angle of 30° after filtering the forward-scattered incident ^{12}C particles by a 10 μm-thick Mylar foil. It should be pointed out that the yields of helium recoils were limited by the low $^{12}C^{3+}$ ion beam current of 0.3 μA and the measurement time. Higher beam current and longer measurement time can result in additional radiation damage and sample heating [18]. The RBS (Rutherford backscattering spectrometry) detector measures the backscattering yields of the incident ^{12}C particles at a scattering angle of 165° to calculate the amount of the incident ^{12}C ions. The main purpose of RBS experiments is to reduce the uncertainty of the number of incident ions hitting the target. In other words, the RBS spectrum permits to assess the exact quantity of the incident C ions, which is needed in the ERD spectrum deconvolution to obtain the quantitative helium concentration depth profiles [19]. The ERD and RBS measurements were performed at the NEC 9SDH-2 tandem accelerator [20] in the Institute of Modern Physics of Fudan University, China.

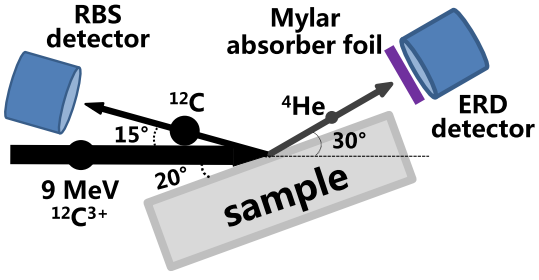

Fig. 1. Schematic drawing of the experimental setup of ERD.

All ERD spectra were converted to helium concentration profiles using the Alegria 1.2 code [21]. The stopping power of incident ^{12}C and recoiled ^{4}He particles in Hastelloy N alloy and Mylar foil (Fig. 3(a)), used for the spectra analysis in Alegria 1.2 code, were calculated using SRIM code [22]. It should be noticed that the stopping powers of "C → He" and "He → He" were used to correct respectively the stopping powers of incident C ions and He recoils in the helium-contained alloy during the iterative calculation of concentration depth profile (more details see [21]). It means that the presence of helium atoms actually influences the calculation of the depth profile, by affecting the stopping power data of incident C and He recoils. In addition, the depth profile was obtained by calculating the helium concentration in each depth slice of ~22 nm in thickness. Therefore, the presence of helium bubbles was assumed to have no difference from dispersed helium atoms in the correction to stopping powers when they have the same content of helium atoms. In practical calculations, the number of iterations was set to be three since more iteration brings little change to the final depth profile.

The cross section of the ^{4}He (^{12}C, ^{4}He) ^{12}C reaction at a scattering angle of 30° was converted from that of ^{12}C (^{4}He, ^{4}He) ^{12}C reaction (Fig. 3(b)), which was calculated from SigmaCalc 2.0 [23]. The depth resolution of concentration-depth profiles was calculated considering the following contributions of experimental system: energy and angular spread of the beam, geometric spread caused by finite beam size and detector's solid angle, energy straggling and multiple scattering in the sample, effect of the absorber foil and the energy resolution of the detector. Based on all these affecting parameters, the depth resolution of experimental concentration-depth profiles was calculated to be 20 nm at the sample surface, and it increases to 32 nm at a depth of 175 nm, according to the calculations using the program MDEPTH [24]. The reduction in depth resolution along sample depth direction was mainly caused by the energy loss of C ions in each depth slice of the sample. The systemic error on the amounts of helium determined from the ERDA experiments was estimated to be within 5%, which was calculated using the error transfer formula.

3. Results and discussion

3.1. Diffusion behaviors of molybdenum and helium

Fig. 2 shows typical RBS and corresponding ERD spectra. The RBS spectra were perfectly fitted by the SIMNRA program [25]. In these fitted RBS spectra, only contributions from Mo, Cr, Ni and Fe elements are showed. Fig. 2(a) and (b) show distinct difference in spectrum shape from backscattered energy of 5620 to 4740 keV. The backscattered C atoms within this energy range correspond to the backscattering reactions with molybdenum elements from the sample surface to depth of about 95 nm. It can be deduced that the diffusion of molybdenum elements to the surface occurred during the annealing at 850 °C (5 h). In view of the fact that the molybdenum enrichment in this 95 nm thick region was attributed to the diffusion of molybdenum atoms from a far larger region, the depletion of molybdenum was too small to be detected by RBS.

Fig. 2(c) and (d) show the corresponding ERD spectra. It should be noted that both helium and hydrogen contributed to the recoil spectra when the recoil energy was were lower than ~2030 keV.