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Effects of bubbles on high-temperature corrosion of helium ion-irradiated Ni-based alloy in fluoride molten salt

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ABSTRACT

Samples of a Ni-Mo-Cr-Fe-Si alloy subject to helium ion irradiation damage were corroded in a eutectic mixture of FLiNaK at 750 °C. It was found that the helium bubbles that formed increased the number of surface defects so greatly increasing the physical contact area between the alloy and the molten salt, resulting in acceleration of corrosion damage. Segregation and depletion of chemical elements at bubble surfaces were also identified, and became more severe with increasing bubble size. Significant segregation of Si resulted in the formation of Ni-Si precipitates at large bubbles. This segregation enhanced the chemical corrosion damage to the alloy.

1. Introduction

An important challenge for Ni-based alloys used in extreme nuclear environments is the formation of helium and helium bubbles that result from neutron irradiation. This formation of helium and bubbles can lead to enhanced swelling, embrittlement, surface roughening and surface blistering [1,2]. Hence, nucleation and growth of helium bubbles have been widely investigated within the nuclear materials literature [1–5]. During irradiation, helium atoms interact with vacancies induced by irradiation to form helium and vacancy (He-V) clusters which can act as nucleation sites for the promotion of the formation of bubbles [1,3,4,6,7]. Initially, small bubbles then grow by various mechanisms [3]. Thus, the nucleation and growth of He-V clusters and helium bubbles often results in the development of cavities within the microstructure [4,8]. The corrosion behaviour of Ni-based alloys in molten salt environments has been previously studied [9–11], and in an initial study of the GH3535 the present authors have shown that formation and growth of helium bubbles can greatly enhance corrosion damage of the helium-ion irradiated Ni-based alloys in high-temperature fluoride molten salts [12]. This paper presents a detailed mechanistic study of the influence of helium bubbles on corrosion damage of a Ni-based GH3535 alloy in a FLiNaK fluoride molten salt.

Another important radiation challenge for metallic materials used in extreme nuclear environments is radiation-induced segregation (RIS), which occurs during high-temperature irradiation of metals due to the segregation of solute and impurity elements at defect sinks such as dislocation loops, internal interfaces, and external surfaces [6,13]. When the local solute concentration (due to segregation) exceeds the solubility limit of the solute in the matrix, new phases can precipitate. The newly formed precipitates, particularly when formed at grain boundaries, can cause embrittlement [13]. Hence, the investigation of RIS is a significant aspect of reactor performance [6,14] and RIS at grain boundaries has been widely investigated and reported [13,15]. However, solute segregation at helium bubbles and consequent effects on corrosion do not appear to be studied.

In the present paper, samples of GH3535 with and without helium ion irradiation were exposed to a eutectic mixture of FLiNaK at 750 °C for different durations. The physical and chemical characteristics of the helium bubbles and their evolution were examined using advanced analytical transmission electron microscopy (TEM). This enabled the mechanistic details of the physical and chemical effects of the helium bubbles on corrosion of the Ni-based alloy in high temperature molten salt environments to be identified.

2. Material and methods

The material used in this study was GH3535, a Ni-Mo-Cr-Fe-Si alloy similar to Hastelloy-N. Samples were initially prepared using electrical discharge machining. One surface was then polished using 50 nm colloidal silica to prepare a surface with minimal surface deformation. To investigate the influence of helium bubbles on high-temperature corrosion of GH3535, one set of samples were exposed to helium ion

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irradiation. Both the irradiated and unirradiated samples were exposed to molten salt at 750 °C. To investigate the kinetic effect of salt exposure time on corrosion, corrosion durations of 10, 100 and 200 h were used. Detailed procedures and parameters used for irradiation and corrosion were described in a previous publication [12].

TEM samples containing cross sections of the corroded samples were prepared using a Zeiss Auriga 60 FIB. A layer of protective platinum was deposited on the surface of the sample for protection from the ion beam. Coarse milling was performed to prepare a trench and create a lamella. Subsequent lamella lift out and TEM grid attachment was performed in-situ with the sample polished using a series of steps to achieve a uniform thickness of electron transparent sample. TEM, high resolution TEM (HREM), scanning TEM (STEM) and STEM-energy-dispersive X-ray spectroscopy (EDS) analyses were carried out using a JEM 2200FS TEM device operating at 200 kV. Scanning electron microscopy (SEM) examination was performed in a Jeol 6300 SEM.

3. Results

3.1. Physical morphologies of helium bubbles

Helium ion irradiation at energies of up to 30 KeV introduces helium into the microstructure to approximately 210 nm from the ion implanted surface [12]. Above a critical helium concentration, bubbles nucleate and form [6,12,16], and previous work [12] showed that the thickness of the bubble layer is approximately 120 nm in the as-irradiated sample. During subsequent corrosion at 750 °C, the bubbles change their morphology. Fig. 1 presents TEM images of cross sections of the irradiated samples after corrosion for 10, 100 and 200 h. The images for the samples corroded for 10 and 100 h were taken from areas near the corrosion surface whilst the image for the sample corroded for 200 h was obtained from the bulk.

For the 10 h corroded sample, a large number of white dot defects are observed in the under-focus TEM condition (Fig. 1(a)), and as black dot defects in the over-focus TEM condition (Fig. 1(b)). This indicates that these dot defects are helium bubbles [12,17]. These bubbles are small having a radius of ~1.2 nm and are distributed in the near-surface layer approximate 190 nm thickness. This is greater than the bubble layer seen in the as-irradiated sample. For the 100 h corroded sample, as shown in the under-focus images of Fig. 1(c), the bubbles that exhibit white and round defects become larger and migrate toward the bulk of the sample. The radius of the bubbles in the sample corroded for 100 h range from ≈4–12 nm and the thickness of the bubble layer is greater than that in the 10 h corroded sample. In the 200 h corroded sample, it was observed that both the radius of the bubbles and the thickness of the bubble layer increase further, to ≈4.8 μm. These results indicate that with increasing corrosion duration, helium bubbles grow and spread towards the bulk of the irradiated sample. The growth and migration of the helium bubbles is caused by diffusion of the helium atoms and various defects in the matrix which was exposed to elevated temperature (750 °C) [12].

During the formation and growth of the helium bubbles, both micro- and nano-scale defects can form at the bubble surfaces due to the introduction of the helium atoms and the breakdown of the continuity of

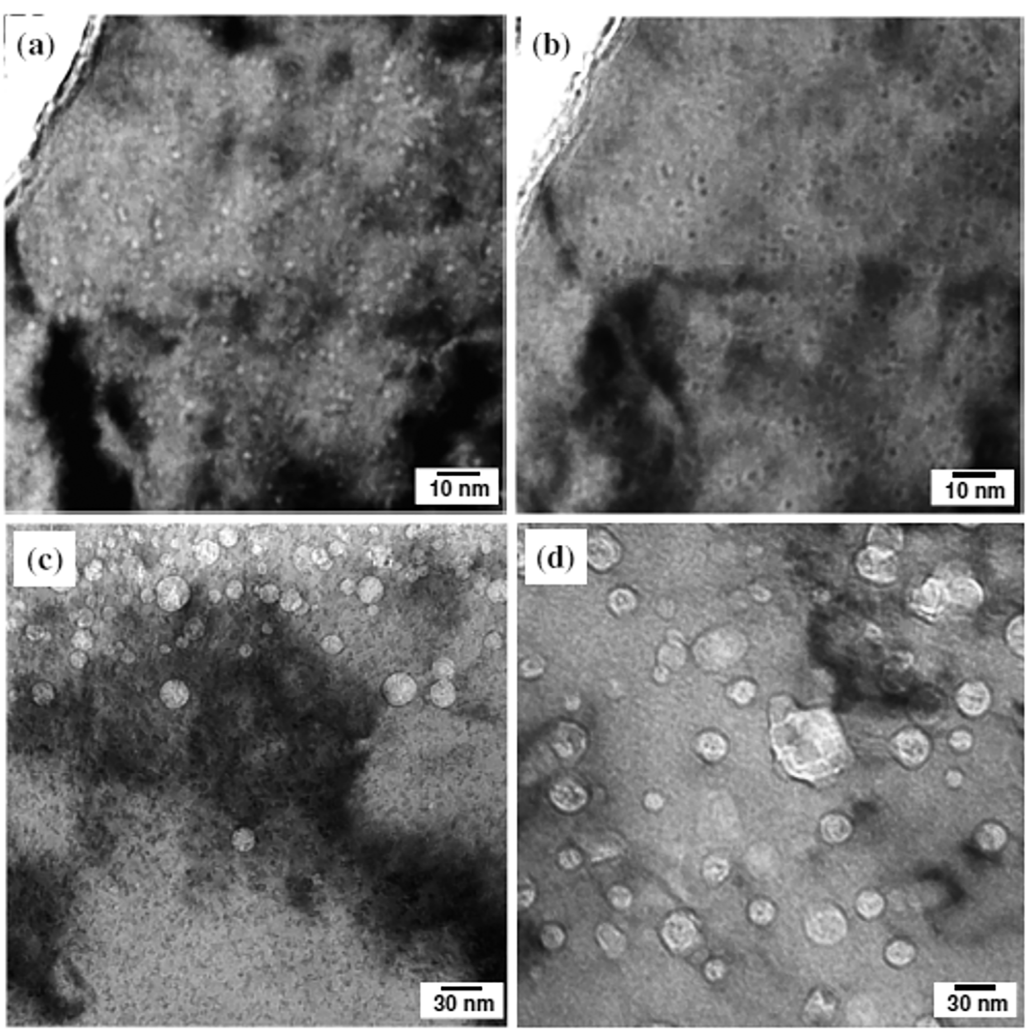

Fig. 1. TEM images of irradiated Ni-based alloy samples after corrosion in 750 °C molten fluoride salt for (a) 10 h, under-focus, (b) 10 h, over-focus, (c) 100 h, under-focus, and (d) 200 h, under-focus.