Materials Science & Engineering A 733 (2018) 291–298

Contents lists available at ScienceDirect

Materials Science & Engineering A

journal homepage: www.elsevier.com/locate/msea

Hydrogen embrittlement susceptibility of a Ni-16Mo-7Cr base superalloy

Fenfen Han*, Suixia He, Min Liu*, X.T. Zhou

Thorium Molten Salts Reactor Center, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, China

ARTICLE INFO

Keywords:
Hydrogen embrittlement
Nickel base superalloy
Intergranular cracking
Scanning electron microscopy

ABSTRACT

This study investigated the hydrogen embrittlement sensitivity of a Ni-16Mo-7Cr base superalloy under different hydrogen pre-charging states. Detailed electromicroscopy characterization has been employed on the hydrogen pre-charged alloy after tensile testing to understand the mechanism of hydrogen-assisted cracking. The results show that the tensile strength of the alloy is remarkably decreased with the increasing of hydrogen pre-charging time, whereas the yield strength remains stable all the time. The fractographic study combined with ECCI analysis by Scanning Electron Microscopy demonstrates that the cracks propagated predominantly along the grain boundary in the presence of hydrogen, and a few can propagate along planar dislocation slip bands (DSBs) especially along the intersections between nonparallel DSBs. The proposed hydrogen embrittlement mechanism for the Ni-16Mo-7Cr base superalloy is that the coalescence and widening of the nano-voids, which are resulted from the interaction between the hydrogen and dislocations, cause the crack initiation and propagation along the grain boundary, and further cause the alloy intergranular fracture.

1. Introduction

Structural materials used in molten salt reactor (MSR) face extremely aggressive environments, including high temperature (~ 700 °C), neutron irradiation and molten salt corrosion [1–3]. A Ni-16Mo-7Cr base superalloy, named GH3535, was developed as promising structural materials for application in these challenging conditions in virtue of its superior corrosion resistance and good mechanical properties [4–8]. However, one possible problem should be verified and evaluated urgently. That is the tritium-induced embrittlement of the alloy when exposed to tritium-generating conditions in high-power molten salt reactor.

In the process of MSR operation, tritium is generated by neutron reactions with lithium in molten fluoride salt (46.5LiF-11.5KF-42NaF, mol%) [9,10]. It would exist as molecules of tritium gas (T_2) or tritium fluoride gas (TF) dissolved in the primary salt [11,12]. When tritium gas touches the metal surfaces, it could be dissociated into tritium atoms, which dissolve in the metal and diffuse through the metal walls of the piping and reactor vessel [12]. Tritium is the radioactive isotope of hydrogen and has the similar chemical behavior as hydrogen. Therefore, it can also degrade the alloy as hydrogen embrittlement. That would result in the loss of mechanical properties of the alloy and threaten the component's safety in MSR. Therefore, in order to access the security of this alloy in tritium environment, it is now becoming necessary to evaluate the hydrogen embrittlement susceptibility of GH3535 superalloy.

Numerous mechanisms have been proposed to account for hydrogen embrittlement in various materials. The most recent and common mechanisms in this respect are categorized into hydrogen enhanced decohesion (HEDE) and hydrogen enhanced localized plasticity (HELP) [13]. As to the HEDE mechanism, the hydrogen can reduce the bond strength for atom separation and lower the rupture stress [14–16]. In this framework, grain boundaries and the interfaces between precipitate and matrix are vulnerable to be attacked by hydrogen when the material is stressed. Atomistic simulations have been used to support this mechanism and have proven the reduction of cohesive strength of grain boundary in hydrogen condition [17,18]. According to the HELP mechanism, the presence of hydrogen could enhance the mobility of dislocations [19–23]. It has been verified by in-situ TEM observations in stainless steel, high-purity aluminum and nickel. Extensive dislocation slip activities result in the crack nucleation, propagation and thus promoting the fracture process. To date, for nickel-based superalloys, most studies only focused on a few specific nickel base superalloys used in hydrogen generated environment, i.e., alloy 718 for oil and gas industry application [13,24–26], Inconel 690 for pressurized water reactor (PWR) [27–29]. Their investigations have mainly put emphasis on the role of precipitates, the fracture mode on mechanical properties in hydrogen environment and activity of dislocations for hydrogen embrittlement. It has been concluded that hydrogen promotes increased slip band localization in the Ni matrix, which results in transgranular

* Corresponding authors.
E-mail addresses: hanfenfen@sinap.ac.cn (F. Han), liumin@sinap.ac.cn (M. Liu).

https://doi.org/10.1016/j.msea.2018.07.077
Received 18 May 2018; Received in revised form 20 July 2018; Accepted 21 July 2018
Available online 23 July 2018
0921-5093/

slip band cracking or intergranular decohesion for the alloy. However, there is still no work carried out to clarify the hydrogen embrittlement susceptibility and mechanism in Ni-16Mo-7Cr base superalloy for MSR application.

In this work, we investigated the hydrogen embrittlement of alloy GH3535 by tensile testing, with focus on the underlying hydrogen-related deformation and cracking. Scanning electron microscopy (SEM), electron channeling contrast imaging (ECCI), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM) were used to analyze the deformation microstructure, to establish correlations between the microstructure, crack initiation sites and crack propagation pathways of the alloy in the hydrogen environment.

2. Experiment

The nominal chemical composition (wt%) of the investigated alloy in this study is: Mo, 16; Cr, 7; Fe, 4; Mn, 0.5; Si, 0.5; C, 0.05; Ni, balance. The hot forged rods in the annealed condition were prepared by vacuum induction melt-furnace (VIM). Then hot forging and rolling were conducted in the temperature range of 1150–1200 °C. The solution annealing for the rods was conducted at 1177 °C for 40 min, followed by water quenching (WQ).

Tensile specimens with gauge dimensions of 3 mm in width, 18 mm in length and 1 mm in thickness were cut by electrospark wire-electrode cutting from the as heat-treated rods. Cylindrical specimens with the length of 5 mm and diameter of 3 mm were also machined from the as heat-treated rods for measuring the content of hydrogen in the hydrogen-charged alloy. All these specimens were mechanically grinded on metallographic SiC papers to #1500 and ultrasonically cleaned in acetone before hydrogen charging. Hydrogen charging was conducted electrochemically at a cathodic current density of 160 mA cm^{-2} in a 5% H_2SO_4 aqueous solution containing 200 mg of As_2O_3 as a hydrogen recombination poison. A platinum foil was used as the counter electrode. Only the gauge portion of each tensile specimen together with one cylindrical specimen was immersed in the electrolyte solution for hydrogen charging. The charging times were 24 h, 48 h, 96 h, and 144 h respectively. After hydrogen charging, the tensile specimens were tested to failure by using a universal tensile testing machine (Zwick/Roell, Z100) operated at a constant strain rate of 8.33×10^{-5} s^{-1} (0.005/min) and at room temperature. The content of hydrogen in the cylindrical specimen was measured by high performance oxygen, nitrogen and hydrogen analyzer (Bruker, G8 GALILEO).

The detailed microstructure analysis was conducted by SEM and TEM. A Zeiss Merlin Compact SEM equipped with an EBSD was used to observe the fracture morphology and deformation microstructure. The Kernel average misorientation (KAM) values were obtained by EBSD analysis to qualitatively assess the local plastic strain related to deformation gradients. ECCI analyses were also conducted using the Zeiss Merlin Compact SEM at a 15 kV acceleration voltage and a working distance of approx. 3 mm in Backscatter Electron imaging mode. The lattice defects, such as dislocations, stacking faults as well as slip lines, twins and grain boundaries in materials could be observed at a wider field of view using ECCI. The samples with thickness of 83 nm for TEM observation were prepared by a focus ion beam (FIB) machine in this study.

3. Results

3.1. The tensile property of the hydrogen-attacked alloy

The microstructure of the alloy after heat treatment has been investigated in previous research [30]. As shown in Fig. 1, it contains equiaxed grains with the average grain size of about 70 μm, accompanied by secondary phase of M_6C carbide distributed across the grains in a chain-like manner along the roll direction (M represents metal elements such as Ni, Mo, and Cr).

The stress-strain curves of the samples with and without hydrogen pre-charging are shown in Fig. 2. It can be seen that the yield strength of the alloy is not obviously influenced by hydrogen pre-charging, whereas the ultimate tensile strength and the total elongation decrease dramatically with the increase of charging time.

3.2. The fracture morphology and microstructure analysis

SEM analysis using secondary electron mode was carried out to observe the fracture morphology at a voltage of 15 kV and a working distance of 9 mm. Fig. 3 shows the fracture morphologies of samples with and without the presence of hydrogen. For the alloy without hydrogen pre-charging, the fracture mode is ductile. Many dimples and voids are observed on the fracture surface (as shown in Fig. 3a). However, a different morphology of the fracture is observed in the samples with hydrogen pre-charging: brittle fracture features close to the sample surface and ductile fracture features in the interior of the alloy. The surface of brittle fracture is typically fairly flat, in which some voids and granular carbides can be clearly seen. With the increasing charging time, the depth of brittle fracture is gradually increased to 143 μm, as shown in Fig. 3b-e. The diffusion depth of the hydrogen into the alloy is limited. It can be explained by diffusion theory according to the diffusion equation: $X = \sqrt{2Dt}$, where X is the diffusion depth, t is the hydrogen charging time, and D is the diffusion coefficient of hydrogen in Alloy GH3535. In this study, the only variable is the charging time t. The penetration depth of hydrogen is increased with the increasing charging time. However, in this paper, the thickness of the sample is 1 mm and the charging time is limited up to 144 h. Therefore, hydrogen has no enough time to diffuse into the center region where the ductile fracture mode is still maintained as that in Fig. 3a. From the Fig. 3b-e, it can be seen that the intergranular fracture is the main fracture mode in the regions with the presence of hydrogen.

Higher magnification of secondary electron images using SEM at voltage of 15 kV were obtained from the hydrogen charged specimens in order to understand the material failure mechanism in hydrogen environment. As hydrogen only diffuses into the outer rim of the sample, the regions with hydrogen presence in the sample are observed and shown in Fig. 4. It can be seen that although the intergranular cracking mode is dominated in this zone, some transgranular cracking features are also presented on the fracture surfaces (the areas as shown in Fig. 4 delimited in dash lines). The tear ridge can be clearly observed in transgranular fracture zone. The size of transgranular cracking region increases gradually with the increasing of hydrogen pre-charging time. Those areas evolve from a small fraction in a grain to the whole grain when the alloy subjected long time hydrogen pre-charging. For the alloy with hydrogen pre-charge for 144 h, the transgranular cracking is easy to be found near the surface in the whole brittle fracture zone, as shown in Fig. 4d.

More detailed analysis on the fracture surface was conducted to reveal the cracking behavior of GH3535 caused by hydrogen adsorption. Typical high-resolution secondary electron images obtained by InLens detector equipped in SEM (voltage: 10 kV, work distance: ~ 5 mm) were used to shown the morphologies of the brittle failure region in which close to the sample outer surface, as shown in Fig. 5. It is evident that two or three sets of parallel linear features are formed on the fracture surface in the sample with hydrogen pre-charging. The lines are highly analogous to the dislocation slip bands. Cracks, micro- and nano-voids can be observed along the traces, especially at the intersections of nonparallel traces, as shown in Fig. 5a-c. Potential linkage of the voids on the traces can lead to the crack initiation and promote the crack propagation. Fig. 5d shows the crack propagation features formed along the traces. These features do not appear in the region where hydrogen is absent (See the ductile fracture area in Fig. 3).

The ECCI images show the cross-section morphologies of the deformed alloy near the outer surface, as exhibited in Fig. 6. The cracks