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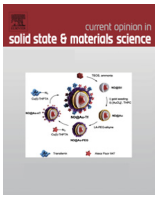

Hydrogen embrittlement in compositionally complex FeNiCoCrMn FCC solid solution alloy

K.E. Nygren [a], K.M. Bertsch [b,c], S. Wang [a], H. Bei [d], A. Nagao [c,e], I.M. Robertson [a,c,f,*]

[a] Department of Engineering Physics, University of Wisconsin-Madison, Madison, WI 53706, USA
[b] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[c] International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Fukuoka 819-0395, Japan
[d] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
[e] Material Surface & Interface Science Research Department, Steel Research Laboratory, JFE Steel Corporation, 1-1 Minamiwatarida-cho, Kawasaki-ku, Kawaksai, Kanagawa 210-0855, Japan
[f] Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

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ABSTRACT

The influence of internal hydrogen on the tensile properties of an equi-molar FeNiCoCrMn alloy results in a significant reduction of ductility, which is accompanied by a change in the fracture mode from ductile microvoid coalescence to intergranular failure. The introduction of 146.9 mass ppm of hydrogen reduced the plastic strain to failure from 0.67 in the uncharged case to 0.34 and 0.51 in hydrogen-charged specimens. The reduction in ductility and the transition in failure mode are clear indications that this alloy exhibits the classic signs of being susceptible to hydrogen embrittlement. The results are discussed in terms of the hydrogen-enhanced plasticity mechanism and its influence on hydrogen-induced intergranular failure. Furthermore, a new additional constraint that further promotes intergranular failure is introduced for the first time.

1. Introduction

Equi-molar and multi-element alloys, including the group of five-element alloys referred to as high-entropy alloys, provide the opportunity to tailor the properties of the system; see reviews by Miracle and Senkov [1], Zhang et al. [2] and Diao et al. [3]. Single-phase FCC high-entropy alloys exhibit high thermal stability [4], high malleability [5], slow diffusion [6], low yield strength, high ductility [7], and high fracture toughness at cryogenic temperatures [8]. The electronic, thermal and magnetic properties are also modified by increasing the number of elements [9,10]. It was predicted theoretically and shown experimentally that the electrical and thermal conductivity is reduced significantly in high-entropy alloys compared to other alloys, as is the electron mean free path. These changes result in slower heat dissipation from displacement cascades created by heavy-ion irradiation, which results in a greater tolerance for the accumulation of radiation damage [9–11]. However, it was found that the number of elements was not the dominating factor, as specific elements had a different influence on the accumulation of the damage under both ion [12] and electron irradiation [13]. These properties have been explained by the combined influences of the high entropy (thermodynamics), low diffusivity (kinetics), and lattice distortion (structure) of these alloys as well as the sensitivity of the properties to alloy composition [14].

Recently, it has been reported that the five-element high-entropy alloy FeNiCoCrMn was not susceptible to hydrogen embrittlement, which would place it in a unique class of metals and alloys [15,16]. Zhao et al. reported that the tensile properties were similar in the uncharged and hydrogen-charged alloys, with the hydrogen-charged alloy showing only a 5% decrease in ductility [15]. The fracture surfaces of the uncharged and hydrogen-charged specimens of the FeNiCoCrMn alloy were similar and consisted of microvoids, which indicate a ductile failure mode in both cases. Based on these observations, Zhao et al. concluded that this alloy was not embrittled by hydrogen. However, hydrogen-induced ductile failure by microvoid coalescence is common, although it is often accompanied by a change in the characteristics of the dimples in terms of size and depth [17]. Luo et al. used electrochemical charging to introduce hydrogen into an alloy of the same composition and concluded that hydrogen, rather than being detrimental to the mechanical properties as it is in most other alloys, was beneficial [16]. Hydrogen was reported to enhance strengthening and

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[*] Corresponding author.
E-mail address: irobertson@wisc.edu (I.M. Robertson).

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toughening mechanisms. This was attributed to hydrogen reducing the stacking-fault energy and therefore the phase stability of the alloy.

In this paper, the tensile behavior of the five-element alloy FeNiCoCrMn was studied in the absence and presence of hydrogen. Gas-phase hydrogen charging at elevated temperature was used to introduce hydrogen uniformly throughout the sample. It will be demonstrated unequivocally that this alloy is susceptible to hydrogen embrittlement. It undergoes a significant decrease in the strain to failure in the presence of hydrogen, which is accompanied by a transition in the fracture mode from ductile microvoid coalescence to a mixed failure mode that includes intergranular failure. This reduction in ductility coupled with the transition in fracture mode are classic characteristics of hydrogen embrittlement and are explained in terms of the hydrogen enhanced localized plasticity mechanism [18,19]. In addition, it will be proposed that the inability of the grain boundaries to realign towards the tensile axis during uniaxial loading in the hydrogen-charged alloy provides an additional driving force for the hydrogen-induced transition in the failure mode.

2. Experimental procedure

The near-equi-molar FeNiCoCrMn alloy was produced by arc melting, rolling, and annealing. Electrical discharge machining was used to cut flat dog-bone-type specimens with a gauge length of 10 mm and cross-sectional dimensions of approximately 2 mm × 2 mm from the cold-rolled sheets. The specimens were cut such that the longitudinal axis was perpendicular to the rolling direction. The specimens were annealed at 1200 °C for 24 h. The resulting microstructure consisted of approximately equiaxed grains with a mean grain size of ~70 μm; annealing twin boundaries were frequently observed making the effective grain size ~50 μm.

The samples were charged with hydrogen in an autoclave at a hydrogen gas pressure of 120 MPa at 200 °C for 160 h. The total time the samples were at room temperature was between 8 and 10 days for transportation to and from the hydrogen-charging facility. At all other times they were stored in liquid nitrogen. Uniaxial tensile tests were conducted at a constant displacement rate of 1.7×10^{-5} mm s^{-1} (an initial strain rate of approximately 1.7×10^{-6} s^{-1}) using a MTS QTest/5 tensile machine with a 5 kN load cell. Two hydrogen-charged samples were tested and are referred to as HC1 and HC2. HC1 was tested shortly after it was removed from the liquid nitrogen storage vessel and brought to room temperature, whereas HC2 was mechanically polished for initial electron backscattering diffraction (EBSD) analysis before testing. The polishing and EBSD analysis took approximately 10 h.

The hydrogen content of the uncharged and hydrogen-charged samples was measured using gas chromatograph thermal desorption analysis after the tensile tests were complete. This ensured that the 8 and 10 days the samples were at room temperature did not result in loss of hydrogen. A ramp rate of 200 °C h^{-1} was used in the thermal desorption test from room temperature to 800 °C.

The fracture surfaces and external surfaces were investigated using scanning electron microcopy (SEM) with either a LEO 1530–1 FESEM or an FEI Helios G4 PFIB CXe with an Elstar^{TM} SEM column being used. Electron dispersive spectroscopy (EDS) and EBSD measurements were performed using EDA TEAM^{TM} EDS software and instrumentation attached to the FEI Helios G4 PFIB. The EDS measurements were performed using an Octane Elite silicon drift detector. EBSD measurements were performed using an Hikari EBSD camera using a step size of 0.5 μm, accelerating voltage of 30 kV, and current of 26 nA.

Samples for examination in a scanning/transmission electron microscope were prepared by focused ion beam machining using an FEI Helios G4 PFIB CXe. The electron microscopy was performed in a Tecnai TF-30 S/TEM, which was operated at 300 keV.

3. Results

The thermal desorption analysis spectra for the uncharged and hydrogen-charged alloy following the completion of the mechanical property tests are shown in Fig. 1. The hydrogen concentration of the uncharged sample is defined to be the total hydrogen desorbed from room temperature to 643 °C, and that of the HC1 sample from room temperature to 660 °C, which corresponds to the first desorption peak. From Fig. 1, the hydrogen concentration remaining in the uncharged (open circles) and HC1 samples (filled circles) was 1.4 mass ppm (76 at. ppm) and 146.9 mass ppm (8239 at. ppm), respectively. For comparison, the thermal desorption analysis spectra for a 2.0 mm thick Ni sample (filled squares) following charging at 200 °C for a duration of 160 h under a gas pressure of 120 MPa, and for 4.0 mm thick SUS316L austenitic stainless steel (filled triangles) charged with hydrogen in a 120 MPa hydrogen gas environment at 280 °C for 400 h are included in Fig. 1. The peak 1 hydrogen concentration in Ni and SUS316L were 42.5 mass ppm (2492 at. ppm) and 104.2 mass ppm (5812 at. ppm), respectively. The rate-determining step for the thermal desorption process of these three materials is diffusion due to the low hydrogen diffusivity [20]. The observation that the maximum in the desorption peak for the FeNiCoCrMn alloy and Ni occurs at 409 °C suggests that the hydrogen diffusivity is similar in both materials and lower than in stainless steels. The calculated initial hydrogen concentration for the charging conditions used for Ni is 41.3 mass ppm (2423 at. ppm) [21] and the thermal desorption analysis of Ni presented in Fig. 1 was conducted after 11 days of storage at room temperature. This result suggests that the outgassing of hydrogen from Ni was negligible after 11 days at room temperature. The hydrogen concentration in the FeNiCoCrMn alloy was measured following a total time at room temperature of between 8 – 10 days, by comparison with the Ni result it is reasonable to conclude that the change in the hydrogen concentration due to the time at room temperature was negligible. In comparing this hydrogen

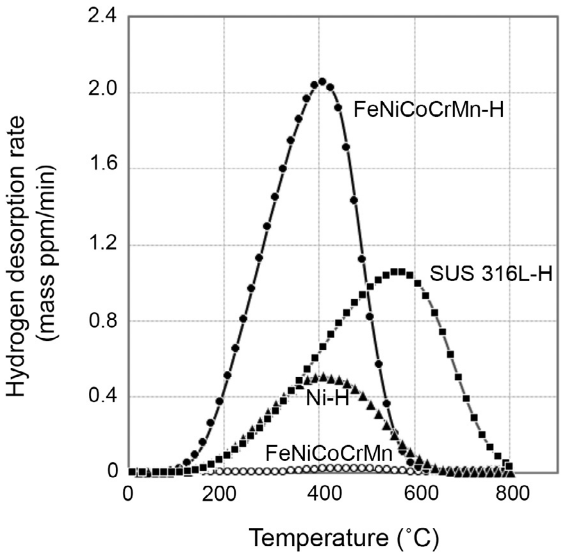

Fig. 1. Thermal desorption analysis spectra of the uncharged and hydrogen-charged FeNiCoCrMn alloy; heating rate = 200 °C/h. Data for Ni and SUS316L austenitic stainless steel (heating rate = 200 °C/h) are included for comparison. ● HC1; ○ uncharged; ▲ Ni; ■ SUS 316 L austenitic stainless steel.

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