

Interaction of H₂O and O₂ with Ni₃Fe and their effects on ductility

J. Wang^{a,*}, W.J. Chia^{a,1}, Y.W. Chung^a, C.T. Liu^b

^aDepartment of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

^bMetals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6115, USA

Received 13 August 1999; accepted 20 September 1999

Abstract

Possible reasons for the high ductility of Ni₃Fe and its insensitivity toward the testing environment have been investigated. Thermal desorption experiments have shown that water dissociates on clean Ni₃Fe surfaces to produce atomic hydrogen. Ductility measurements of cast and cold-rolled polycrystalline Ni₃Fe demonstrated that the reduced ductility was obtained only when the testing was performed with oxygen carefully removed. X-ray photoemission studies indicate that oxygen interacts with water to form hydroxyls, thereby suppressing the production of atomic hydrogen. Hydrogen desorption from the Ni₃Fe surface requires a lower activation energy, resulting in a smaller surface hydrogen concentration at a given temperature. Hence it is possible that there is insufficient hydrogen to cause the nucleation and growth of brittle cracks for severe embrittlement. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Intermetallics, miscellaneous; B. Brittleness and ductility; B. Environmental embrittlement; B. Surface properties

1. Introduction

Recent experimental results have shown that moisture-induced embrittlement is the major cause of the low ductility and grain boundary failure of many L1₂ ordered intermetallic alloys in ambient air [1,2]. The proposed embrittlement mechanism involves chemical reactions between the reactive element in the intermetallic alloy (e.g. Al in Ni₃Al) and water vapor in the atmosphere to produce atomic hydrogen, which embrittles the crack tip during tensile testing. Earlier work by Liu and Takeyama showed that Ni₃Fe (24 at% Fe) achieves over 40% ductility in vacuum, air and water [3]. This high ductility and insensitivity toward the testing environment are unexpected, since water dissociation on iron surfaces to produce atomic hydrogen is well known [4–7]. In addition, it was found that Ni₃Fe shows hydrogen embrittlement at room temperature when there is sufficient hydrogen fugacity [8]. In this article, we will explore the possible reasons why Ni₃Fe is ductile in air or water by (i) examining the surface interactions of H₂O and O₂ with Ni₃Fe and (ii)

performing ductility measurements under well-controlled environments.

2. Experimental procedure

All surface science experiments were performed in an ultrahigh vacuum chamber with a working base pressure of 5×10^{-8} Pa equipped with sputtering, gas handling, Auger and X-ray photoelectron spectroscopy (XPS) capabilities. Photoelectron spectra were collected with a double-pass cylindrical mirror analyzer at a pass energy of 50 eV using the Al K_α radiation at 1486.6 eV. All binding energies were determined using the Ni 2p_{3/2} peak at 852.3 eV as a reference. All gas exposures are expressed in Langmuir units where 1 L = 1.33×10^{-4} Pa·sec (10^{-6} torr·sec). The ionization gauge was turned off during gas exposure to minimize activation of gas species by the hot filament.

Thermal desorption spectroscopy (TDS) experiments were performed at a heating rate of 1–2 K/sec. We used D₂O in water exposures to avoid interference from background H₂O and H₂. H and D are considered to be equivalent in the following discussion. D₂O was purified by multiple freeze-pump-thaw cycles. It was admitted into the chamber through a needle doser placed 1 cm

* Corresponding author.

¹ Now at Western Digital Corporation, USA.

from the sample. Oxygen was introduced from a gas bottle (99.9999% purity) without further treatment. A glass envelope was mounted in front of the ionizer of the mass spectrometer. During thermal desorption, the sample was placed in front of this envelope to minimize detection of background desorption.

The sample can be heated to 1000 K using a tungsten wire radiation heater mounted behind the sample or cooled to ~ 100 K via a copper contact with a liquid-nitrogen reservoir. Temperatures were measured using a K-type (chromel-alumel) thermocouple spot-welded to the sample. Surface cleaning was done with several cycles of Ar-ion bombardment at 2 kV, 45° angle of incidence, followed by annealing at ~ 700 K for 30 min. Auger electron spectroscopy was used to confirm the surface cleanliness. The polycrystalline Ni₃Fe (25 at% Fe) sample of ~ 1 cm² × 1 mm was mechanically polished using standard metallographic techniques, using 0.05 μ m alumina for the final step. An ordering heat treatment was carried out in ultrahigh vacuum at 743 K for 100 h. The average grain size was 300–500 μ m.

Two types of Ni₃Fe specimens were prepared for tensile testing. The first was a polycrystalline alloy of Ni-25 at% Fe produced by arc-melting and drop casting, using commercially pure nickel and iron. After an ordering treatment at 743 K for 100 h in vacuum, tensile specimens of the appropriate geometry were fabricated by electric-discharge-machining. The second was cold-rolled Ni₃Fe prepared from an Ni₃Fe ingot containing 24 at% Fe by repeated cold forging and rolling at room temperature, with intermediate anneals at 1273 K in vacuum. Tensile specimens with a gauge section of 12.7 × 3.2 × 0.7 mm were stamped from the sheet stock and then given a duplex heat treatment in vacuum: 2 d at 1273 K for recrystallization and grain growth, and 200 h at 743 K for atomic ordering. The average grain size was about 150 μ m. Tensile tests were performed on an Instron testing machine. In order to remove oxygen in water vapor, a set of specimens were tested in a vacuum (1×10^{-6} torr) system back-filled with a low pressure of pure water (12 torr). The ductility value for cast specimens is the average of 2–3 measurements, while that for cold-rolled specimens is obtained for one single measurement in each environment. Fractured surfaces were examined in a Hitachi S-3500N scanning electron microscope (SEM) operated at 20 kV.

3. Results and discussion

Table 1 shows that water can reduce the ductility of cast Ni₃Fe only when the strain rate is sufficiently small and water is thoroughly purged of dissolved oxygen. Similarly, as shown in Table 2, when dissolved oxygen is removed progressively via purging water or exposure to pure water vapor in a vacuum system, the ductility of

Table 1

Ductility of cast Ni₃Fe measured in different environments and strain rates

Strain rate (/sec)	Environment	Ductility (%) ± 1.5%
1.3×10^{-4}	Air	15.3
1.3×10^{-4}	6.5×10^{-3} Pa	15.0
6.5×10^{-5}	Water, purged with air	14.7
1.3×10^{-3}	Water, purged with He for 1 h	14.2
6.5×10^{-5}	Water, purged with He for 1 h	9.0

Table 2

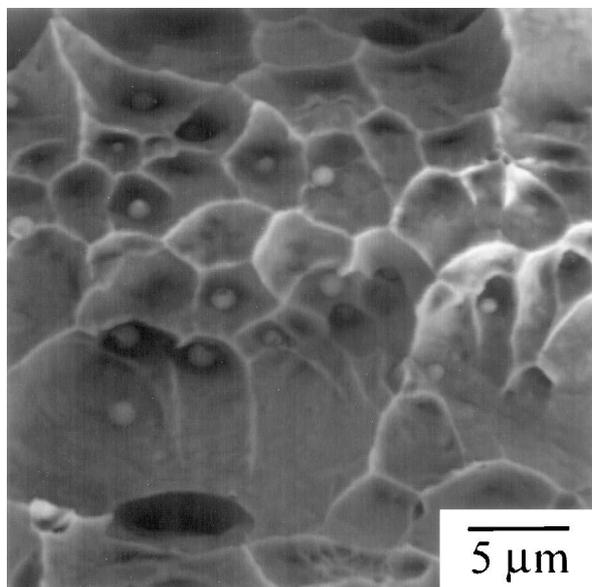
Tensile ductility of cold-rolled Ni₃Fe measured in different environments with strain rate 3.3×10^{-4} /sec

Environment	Ductility (%)
Air	54.8
Water	56.7
Water, purged with He for 2 h	53.6
Water, purged with He for 16 h	52.2
Water vapor (12 torr)	48.1

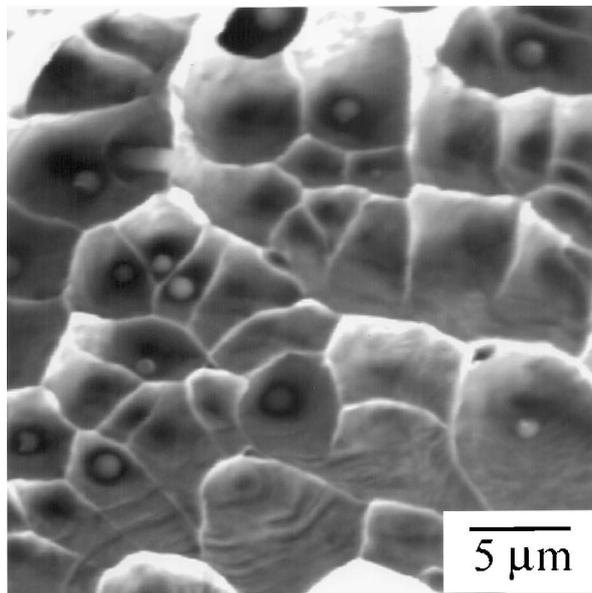
cold-rolled Ni₃Fe is also reduced. Note that the cold-rolled recrystallized samples show higher ductility than the cast samples. There are two possible reasons for this: (a) finer grain size resulting in less stress concentration at grain boundaries; (b) different grain boundary chemistry (such as less segregation of impurities) in these two alloys. It is interesting to note that Takasugi and Hanada [9] also reported high tensile ductility ($\sim 50\%$) for recrystallized Ni₃Fe.

The SEM fractographs of cast Ni₃Fe tested in both 6.5×10^{-3} Pa and water purged with helium show ductile dimple fracture (Fig. 1). The corrosion dots on the fracture surface are believed to result from the exposure to air for an extended period. It has already been reported that cold-rolled Ni₃Fe exhibits ductile dimple fracture in vacuum and water at room temperature [3].

Temperature-programmed-desorption experiments demonstrate that water readily dissociates on clean polycrystalline Ni₃Fe surfaces, resulting in the evolution of hydrogen peaking at 290 K (Fig. 2). Fig. 3 compares the thermal desorption spectra of D₂ from polycrystalline Ni₃Fe after exposure to 45 L of D₂O and 45 L D₂O + 5 L O₂ mixture. Note the strong suppression of D₂ production in the presence of oxygen. This suppression may be partly due to physical site-blocking. That is, adsorbed oxygen blocks some active sites on the Ni₃Fe surface for water adsorption so as to avoid subsequent dissociation. Another possible reason is suggested by the series of O 1s X-ray photoelectron spectra obtained after sequential oxygen and D₂O exposure to the Ni₃Fe surface (Fig. 4). Oxygen exposure at 230 K results in an O 1s peak at 530.8 eV characteristic of atomic oxygen. Subsequent adsorption of D₂O



(a)



(b)

Fig. 1. SEM fractograph of cast Ni₃Fe tested (a) in 6.5×10^{-3} Pa vacuum at strain rate 1.3×10^{-4} /sec, and (b) in water purged with helium for 1 h at strain rate 6.5×10^{-5} /sec.

removes atomic oxygen, and the O 1s peak binding energy shifts to 532.3 eV, which is due to OD formation (Fig. 4c). In light of above X-ray photoemission studies, we believe that adsorbed oxygen promotes the formation of surface hydroxyls, most likely via an abstraction reaction,



Upon further warming, one observes the desorption of water vapor and the formation of atomic oxygen (Fig. 4e), suggesting the following reaction,

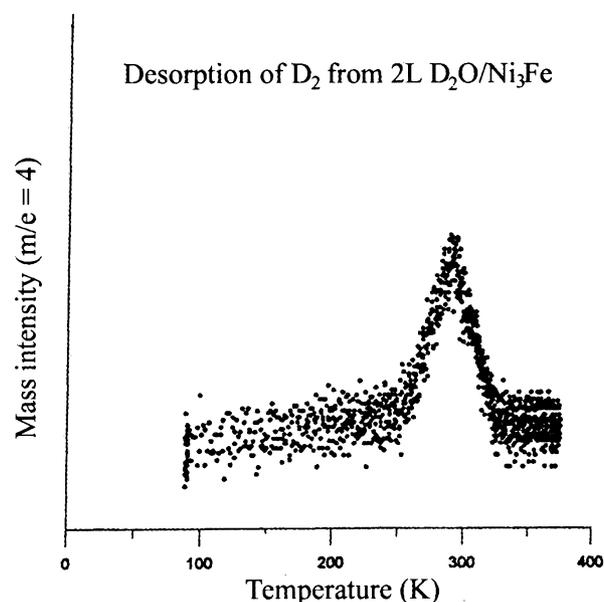


Fig. 2. Thermal desorption spectrum of D₂ (m/e=4) from polycrystalline Ni₃Fe after 2 L D₂O exposure at 77 K.

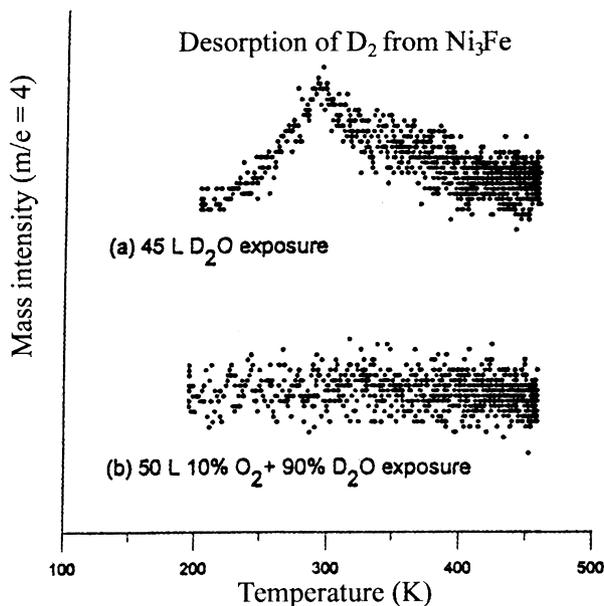


Fig. 3. Thermal desorption spectra of D₂ (m/e=4) from polycrystalline Ni₃Fe after exposure to (a) 45 L D₂O, and (b) 45 L D₂O + 5 L O₂ at 180 K.



An isotope scavenging experiment was carried out to confirm the occurrence of reaction (2). We repeated the above thermal desorption experiments by first exposing the clean Ni₃Fe surface to the oxygen-18 isotope, followed by D₂O¹⁶. Thermal desorption was then performed, with the mass spectrometer monitoring the

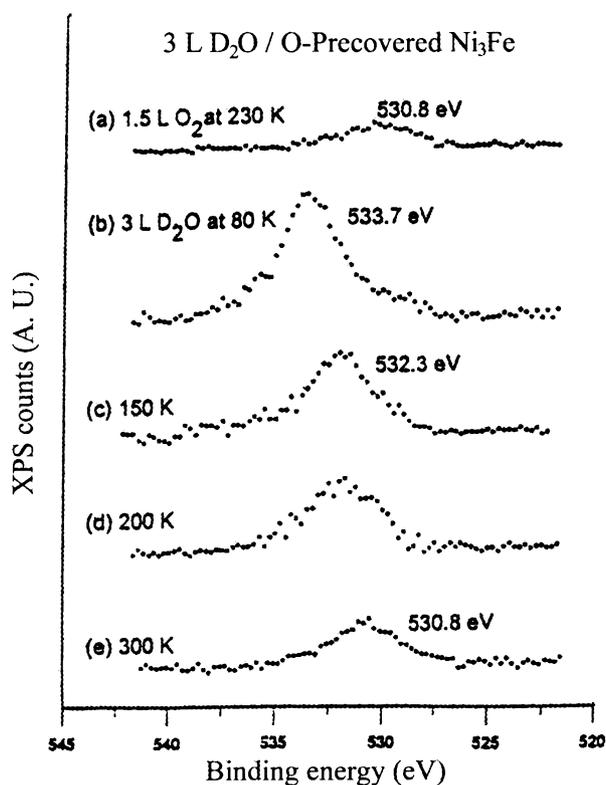


Fig. 4. O 1s spectra from Ni₃Fe taken at different temperatures after exposure to 1.5 L oxygen at 230 K, followed by 3 L D₂O at 80 K and then warming to 300 K.

signal of D₂O¹⁸ (*m/e*=22). Fig. 5 shows clearly the evolution of D₂O¹⁸, which verifies reactions (1) and (2).

Even when oxygen is eliminated, Ni₃Fe exhibits high ductility in water vapor (Tables 1 and 2). One possible reason is insufficient hydrogen concentration to nucleate and propagate brittle cracks for severe embrittlement. This low hydrogen concentration is due to rapid hydrogen desorption. Our previous studies indicate that water dissociates on clean Ni₃(Al, Ti) (100) surface to produce atomic hydrogen [10]. In this case, hydrogen evolution peaks at about 330 K. Fig. 2 shows that the peak hydrogen desorption temperature is only 290 K for Ni₃Fe (actually, the desorption starts at ~250 K). This implies that less thermal energy is needed for hydrogen desorption from Ni₃Fe surfaces, resulting in a smaller surface concentration of hydrogen at a given temperature. Therefore, there may be insufficient hydrogen available for brittle crack nucleation and growth.

It is also possible that grain boundaries of Ni₃Fe are stronger than those of other ordered intermetallic compounds which suffer severe environmental embrittlement. If grain boundaries remain intact during tensile testing, fresh exposed surfaces (cracks) will partly or mostly be transgranular (depends on the grain size), as shown in Fig. 1 and previous report [3]. In this case, the atomic hydrogen concentration at crack tips (produced

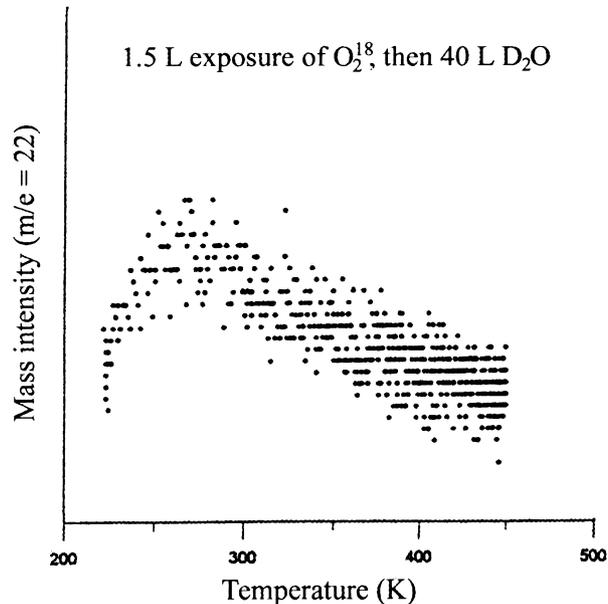


Fig. 5. Thermal desorption spectrum of D₂O¹⁸ (*m/e*=22) from polycrystalline Ni₃Fe after 1.5 L O₂¹⁸ exposure at 250 K, followed by 40 L D₂O¹⁶ at 200 K.

via interaction of water with clean Ni₃Fe surfaces) is controlled mainly by the much slower bulk diffusion (cf. grain boundary diffusion) and is likely insufficient to cause embrittlement.

4. Conclusions

Careful ductility measurements performed on polycrystalline Ni₃Fe under different environments and strain rates reveal a subtle environmental effect: one obtains reduced ductility only when oxygen is carefully removed from the testing environment. Thermal desorption experiments clearly indicate that water does dissociate on clean polycrystalline Ni₃Fe surfaces. X-ray photoemission studies demonstrate that adsorbed oxygen interacts with water to form hydroxyls on Ni₃Fe surface, thus suppressing the formation of atomic hydrogen. Compared with Ni₃Al, Ni₃Fe has a lower activation energy for hydrogen desorption, resulting in lower surface hydrogen concentration. This provides a natural explanation for the high tensile ductility of Ni₃Fe under pure water vapor environments.

Acknowledgements

This work is jointly supported by the National Science Foundation, grant No. DMR-9713052, and the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Research Corporation.

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