

## Effect of atomic ordering on hydrogen dissociation on Ni<sub>3</sub>Fe surfaces

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The dissociation of molecular to atomic hydrogen on clean surfaces of Ni<sub>3</sub>Fe with either an ordered or disordered structure has been directly investigated by thermal desorption studies. Results show that when exposed to an ordered Ni<sub>3</sub>Fe surface, molecular hydrogen dissociates to produce atomic hydrogen, which desorbs from the surface around 350 K. On the other hand, hydrogen does not dissociate on a disordered Ni<sub>3</sub>Fe surface. These results indicate that atomic ordering has a marked effect on surface chemical reactivity. Furthermore, our study provides a mechanistic basis to explain the hydrogen-induced embrittlement in ordered Ni<sub>3</sub>Fe but not in disordered Ni<sub>3</sub>Fe. © 2009 American Institute of Physics. [DOI: 10.1063/1.3089575]

It is known from previous studies that the hydrogen gas-induced embrittlement of Ni<sub>3</sub>Fe,<sup>1–4</sup> Ni<sub>4</sub>Mo,<sup>5</sup> and (Co,Fe)<sub>3</sub>V (Ref. 6) is much more severe for the ordered structure than the disordered structure with an identical alloy composition. When hydrogen was introduced as atoms (instead of molecules), either by cathodic charging or by turning on the ionization gauge in a hydrogen ambient, severe embrittlement occurred in these same alloys even in the disordered form. These results suggest the importance of atomic hydrogen in the embrittlement process, and the production of atomic hydrogen may depend on atomic ordering in these intermetallics. However, there was lack of a direct evidence to verify the effect of atomic order on dissociation kinetics of hydrogen molecules. This is the reason that prompts us to explore the effect of atomic ordering on hydrogen dissociation in Ni<sub>3</sub>Fe.

A 50 g ingot Ni<sub>3</sub>Fe (the nominal composition is Ni-25at. % Fe) was prepared by arc melting, using raw materials of 99.9 wt % pure Ni and 99.9 wt % pure Fe. The ingot was wrapped in stainless steel and hot rolled at 1223 K to ~2 mm thickness and then cold rolled to ~1 mm thickness. A 10 × 10 × 1 mm<sup>3</sup> sample was disordered at 1073 K for 2 h and then ordered at 743 K for 400 h after being cut from the rolled sheet and sealed in an evacuated quartz tube. The ordered sample was then mechanically polished by standard metallographic methods.

Hydrogen dissociation experiments were carried out in a bakeable stainless steel ultrahigh vacuum (UHV) chamber with a base pressure of 6.9–9.0 × 10<sup>-10</sup> torr equipped with sputtering, gas handling, Auger electron spectroscopy, and residual gas analysis (RGA) (see Fig. 1). Surface cleaning was done with several cycles of Ar-ion bombardment at 3 KeV, followed by annealing at 720 K for 30 min for reordering. Auger electron spectra were acquired using a double-pass cylindrical mirror analyzer with a 3 KeV primary electron beam. The disordered sample was prepared by annealing an ordered sample at 950 K for 2 h under UHV *in situ* after the completion of the experiment with the ordered sample.

Gas exposure was performed by first cooling the sample to a given temperature. To minimize interference from the hydrogen background, we used a 1:1 H<sub>2</sub>/D<sub>2</sub> gas mixture. The exposure was fixed at 900 L, where 1 L = 1 × 10<sup>-6</sup> torr s. Temperature-programmed desorption experiments were then performed by increasing the sample temperature linearly at 1.5 K/s from the initial exposure temperature to 720 K (for ordered Ni<sub>3</sub>Fe) or 950 K (for disordered Ni<sub>3</sub>Fe). Desorption signals due to H<sub>2</sub> (m/e=2), HD (m/e=3), and D<sub>2</sub> (m/e=4) were monitored with the RGA.

X-ray diffraction (XRD) with the Co K $\alpha$  radiation was used to examine the ordering of the Ni<sub>3</sub>Fe before and after the hydrogen dissociation experiment. The exhibition of ordering was indicated by the appearance of (100) and (110) superlattice reflections, and the degree of ordering  $S$  (formally defined by  $S^2 = [I_{100}/I_{200}]/[I_{100}/I_{200}]_{\max}$ , where  $[I_{100}/I_{200}]_{\max}$  is the maximum intensity ratio due to the complete ordering) can be measured by the intensity of (100) to that of the fundamental (200) reflection. For each specimen, the (100) and (110) superlattice reflections were recorded by a cumulative total of ten scans, while each of the fundamental peaks was recorded by a single scan.

Figure 2(a) shows the XRD pattern of the ordered Ni<sub>3</sub>Fe before being introduced into the UHV chamber. Note the (100) and (110) superlattice reflections are for the L1<sub>2</sub> ordered crystal structure. Figure 2(b) shows the XRD pattern of

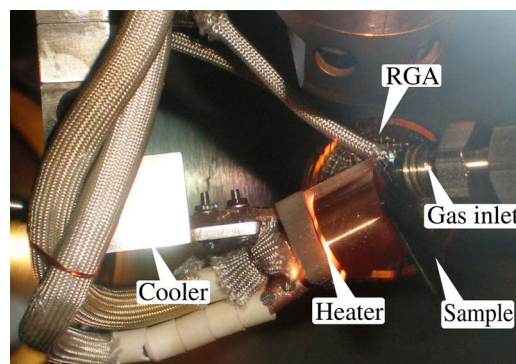


FIG. 1. (Color online) A photo of this equipment.

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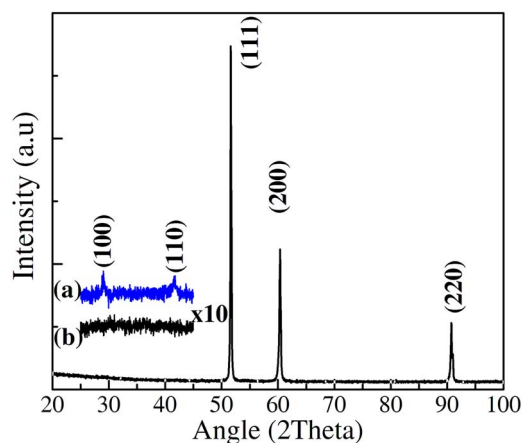


FIG. 2. (Color online) XRD patterns obtained from  $\text{Ni}_3\text{Fe}$  [(a) obtained from the ordered alloy and (b) obtained from the disordered alloy].

$\text{Ni}_3\text{Fe}$  after it has been heated to 950 K for 2 h. Note the disappearance of the superlattice peaks, indicating that the  $\text{Ni}_3\text{Fe}$  was completely disordered due to the heat treatment. Comparing the integrated intensity of the (100) superlattice with the fundamental (200) reflection using the Morris' technique,<sup>7</sup> the degree of order for the ordered  $\text{Ni}_3\text{Fe}$  was measured to be 0.75.

Spectrum (a) in Fig. 3 shows the Auger spectrum of the surface of an ordered  $\text{Ni}_3\text{Fe}$  after sputter cleaning and annealing at 720 K. Spectrum (b) is from the same surface after hydrogen exposure and desorption after heating up to 720 K. Spectrum (c) is from the  $\text{Ni}_3\text{Fe}$  surface after annealing at 950 K for 2 h. This sample was confirmed by XRD to be disordered after annealing at 950 K. According to the peak amplitudes of Ni (848 eV) and Fe (703 eV) and taking into account the atomic sensitivity factors of Ni and Fe, the atomic ratios of Ni to Fe on surface for spectrum (a), (b), and (c) are 3.00, 2.95, and 2.88, respectively. Although some early study suggests that Ni may segregate to the Ni-Fe alloy surface,<sup>8</sup> within experimental uncertainty, there is no evidence that surface concentrations of Ni and Fe were affected by these heat treatments. Our results are consistent with those reported by Chia and Chung,<sup>9</sup> using x-ray photoelectron spectroscopy (XPS).

Figures 4(a)–4(f) show the respective thermal desorption spectra from disordered [Figs. 4(a)–4(c)] and ordered [Figs. 4(d)–4(f)]  $\text{Ni}_3\text{Fe}$  surfaces after 900 L  $\text{H}_2:\text{D}_2=1:1$  mixed gas exposure at different temperatures. Such a high exposure was

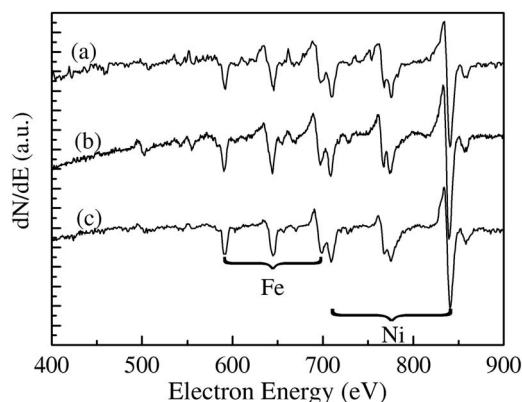


FIG. 3. Auger spectrum from the  $\text{Ni}_3\text{Fe}$  surface [(a) after sputtering and annealing at 720 K, (b) after thermal desorption up to 720 K, and (c) after a disordering treatment (annealing at 950 K for 2 h)].

used to ensure complete coverage of the surface by adsorbates. If dissociation were to occur with a mixture of hydrogen (H) and deuterium (D) atoms, desorption would result in the formation of  $\text{H}_2$ , HD, and  $\text{D}_2$ . The evolution of HD provides direct evidence for the dissociation of hydrogen. Regardless of the initial exposure temperatures, the disordered  $\text{Ni}_3\text{Fe}$  surface does not dissociate hydrogen, as indicated by the absence of HD desorption signal in Figs. 4(a)–4(c). This observation suggests that hydrogen molecules are physisorbed on disordered  $\text{Ni}_3\text{Fe}$  surfaces. By definition, physisorbed molecules have relatively short residence times on surfaces. They likely all desorb shortly after gas exposure and before initiation of the thermal desorption experiment. On the other hand, a desorption signal of HD appears around 350 K in Figs. 4(d)–4(f), providing a direct evidence for hydrogen dissociation on the ordered  $\text{Ni}_3\text{Fe}$  surface. This desorption signal arises from the recombination of dissociatively chemisorbed atoms that start to diffuse on the surface and recombine at about 350 K. It should be noted that all three hydrogen desorption signals ( $\text{H}_2$ , HD, and  $\text{D}_2$ ) attain maximum intensity at about the same temperature. This is comparable to the results of thermal desorption of  $\text{D}_2$  from ordered  $\text{Ni}_3\text{Fe}$  (maximum at 290 K),<sup>9,10</sup> NiTi alloy (at 400 K)<sup>11,12</sup> or  $\text{Ni}_3(\text{AlTi})$  (100) and (110) surfaces (at  $\sim 350$  and 400 K, respectively)<sup>13,14</sup> after exposure to  $\text{D}_2\text{O}$ . It should be mentioned that because of the high  $\text{H}_2$  background common to most UHV systems, it was difficult to make accurate thermal desorption measurements of  $\text{H}_2$ ,<sup>11</sup> hence a mixture

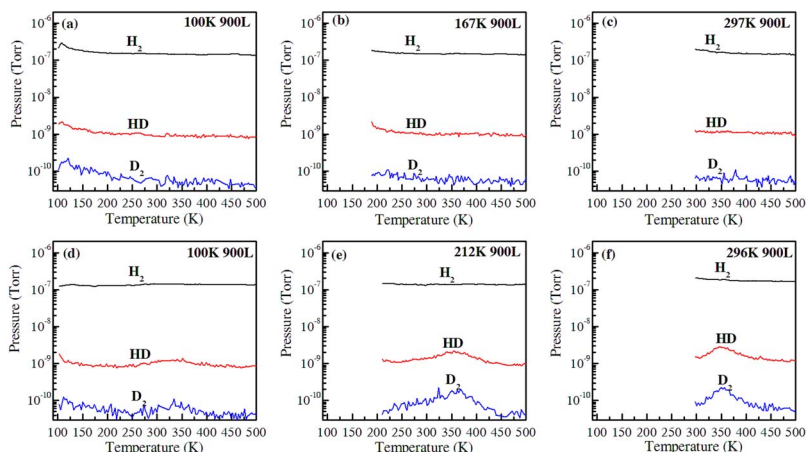


FIG. 4. (Color online) Thermal desorption spectrum of  $\text{H}_2$  ( $m/e=2$ ), HD ( $m/e=3$ ), and  $\text{D}_2$  ( $m/e=4$ ) from the disordered [(a)–(c)] and ordered [(d)–(f)]  $\text{Ni}_3\text{Fe}$  surface after 900 L  $\text{H}_2:\text{D}_2=1:1$  mixed gas exposure at three temperatures.

gas was used in the current study. One should note that when deuterium was introduced into the vacuum system in our experiments, H<sub>2</sub> and D<sub>2</sub> dissociation and scrambling occur within the ionizer of the residual gas analyzer due to the hot tungsten filament that gives rise to a small HD background signal as observed in all thermal desorption experiments.

It is useful to determine if the HD and D<sub>2</sub> relative desorption signal intensities are quantitatively consistent with hydrogen dissociation. From Figs. 4(d)–4(f), we measured the ratio of integrated intensity under HD to that under the D<sub>2</sub> peak. With experimental error, the measured ratios of 11.9, 10.5, and 11.3 are essentially independent of exposure temperature after exposure at 100, 212, and 296 K, respectively. To convert these quantities into molar ratios, we need to know the relative sensitivity of the RGA toward HD and D<sub>2</sub>. By introducing a 1:1 H<sub>2</sub>/D<sub>2</sub> mixture into the vacuum chamber at various pressures, we measured the average H<sub>2</sub>/D<sub>2</sub> peak intensity ratio to be 11.3. Using a power law to fit this intensity ratio, we interpolated an estimate of HD/D<sub>2</sub> peak intensity ratio of 2.74 for a 1:1 HD/D<sub>2</sub> mixture. From this estimate of the HD/D<sub>2</sub> RGA relative sensitivity and the average experimental HD/D<sub>2</sub> intensity ratio, we determine the HD/D<sub>2</sub> molar desorption ratio to be 4.4, 3.8, and 4.1, or an average of 4.1.

From the kinetic theory of ideal gases, when a surface is exposed to a gas at a given pressure, the arrival rate of gas molecules is proportional to  $M^{-1/2}$ , where  $M$  is the molecular weight of the gas. Therefore, when exposed to a 1:1 H<sub>2</sub>/D<sub>2</sub> gas mixture and assuming 100% dissociation to produce atoms, the expected H/D surface concentration is  $\sqrt{2}:1$ . During the desorption process, atomic scrambling occurs. A simple statistical analysis shows that the HD/D<sub>2</sub> molar desorption ratio should be equal to  $2\sqrt{2}$  or about 2.8, compared with the average experimental ratio of 4.1. Considering the uncertainty in estimating the RGA HD/D<sub>2</sub> sensitivity ratio, this level of agreement is considered to be quite satisfactory. Therefore, based on qualitative observation of the HD signal and quantitative estimate of the HD/D<sub>2</sub> desorption intensity ratio, we conclude that hydrogen dissociates on ordered Ni<sub>3</sub>Fe surfaces, while it does not dissociate on Ni<sub>3</sub>Fe with a disordered structure.

Theoretical studies by Hammer *et al.*<sup>15,16</sup> suggest that the energy difference between the centroid of the  $d$  band of the substrate and the antibonding orbital of the adsorbate plays an important role in determining the likelihood of adsorbate dissociation. Using electron energy loss spectroscopy, Zhong *et al.*<sup>17,18</sup> showed that the 3d occupancies of Ni and Fe atoms in ordered Ni<sub>3</sub>Fe are less than those in disordered Ni<sub>3</sub>Fe, and that the onset energy of the Ni L<sub>2,3</sub> edge in the ordered alloy is 0.3 eV lower than that from disordered phase. These changes in electronic properties due to ordering may explain the marked difference in the alloy reactivity toward hydrogen.

Recently, Wan *et al.*<sup>19</sup> have studied hydrogen gas-induced embrittlement in disordered and ordered Ni-24.5Fe, Ni-25.4Fe, and Ni-26.2Fe alloys. They found that, despite of the difference in alloy stoichiometry and possible surface chemical segregation, all three disordered alloys exhibited no

reduction in tensile ductility, while all three ordered alloys showed severe hydrogen embrittlement when exposed to molecular hydrogen at room temperature. Earlier, Camus *et al.*<sup>3</sup> indicated that both disordered and ordered Ni<sub>3</sub>Fe are susceptible to embrittlement when tested under “dynamic” simultaneous charging conditions where atomic hydrogen is readily available. All the results suggest the possibility that the key factor responsible for the severe hydrogen gas-induced embrittlement resulting is how the atomic hydrogen is produced on alloy surfaces. Our study provides a direct evidence to verify that atomic ordering accelerates dissociation kinetics of hydrogen molecules to produce hydrogen atoms, and thus to explain the hydrogen gas-induced embrittlement in ordered Ni<sub>3</sub>Fe but not in disordered Ni<sub>3</sub>Fe.

In conclusion, based on thermal desorption studies of clean disordered and ordered Ni<sub>3</sub>Fe surfaces after exposure to a hydrogen-deuterium (H<sub>2</sub>–D<sub>2</sub>) mixture, we found that an ordered Ni<sub>3</sub>Fe surface effectively dissociates hydrogen to produce hydrogen atoms. Recombination of these hydrogen atoms occurs with increasing temperature, resulting in evolution of molecular hydrogen around 350 K. On the other hand, a disordered Ni<sub>3</sub>Fe surface does not dissociate hydrogen. Quantitative estimate of the HD/D<sub>2</sub> desorption intensity ratio based on random atomic scrambling on ordered Ni<sub>3</sub>Fe is in a decent agreement with experimental data. Furthermore, our study provides a mechanistic basis to explain the hydrogen-induced embrittlement in ordered Ni<sub>3</sub>Fe but not in disordered Ni<sub>3</sub>Fe.

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