Hindawi Publishing Corporation
Advances in Materials Science and Engineering
Volume 2015, Article ID 504207, 6 pages
http://dx.doi.org/10.1155/2015/504207

Research Article

The Effect of Stoichiometry on Hydrogen Embrittlement of Ordered Ni_3Fe Intermetallics

Y. X. Chen,[1,2] Tao Chen,[2] and Haiyan Qian[2]

[1]*Laboratory for Microstructure, Shanghai University, Shanghai 200072, China*
[2]*Institute of Materials Science, Shanghai University, Shanghai 200072, China*

Correspondence should be addressed to Y. X. Chen; yxchen@shu.edu.cn

Received 23 October 2014; Revised 14 January 2015; Accepted 16 January 2015

Academic Editor: Jianfei F. Sun

The effects of Fe stoichiometry on hydrogen embrittlement and hydrogen diffusion in ordered Ni_3Fe intermetallics were investigated. The experimental results show that the ordered Ni_3Fe alloy with the normal stoichiometry has the lowest mechanical property, the highest susceptibility to hydrogen, and the highest ability of catalytic reaction. The mechanical properties, the susceptibility to hydrogen embrittlement, and the amount of adsorbed hydrogen of the ordered Ni_3Fe alloy are dependent of degree of order of the alloy. The apparent hydrogen diffusion coefficient of the ordered Ni_3Fe alloy is independent on degree of order of the alloy but depends on Fe stoichiometry. The activation energy of hydrogen diffusion decreased linearly with Fe stoichiometry for the ordered Ni_3Fe alloy.

1. Introduction

Intermetallics have the good properties of high specific strength, high temperature resistance, and excellent corrosion resistance. But there exists the environmental embrittlement at room temperature for intermetallics [1]. The environmental embrittlement of intermetallics has been proved to be a hydrogen embrittlement process. Among Fe-Ni alloys, Ni_3Fe (permalloy) is known as soft magnetic [2, 3] intermetallic compound that presents a $AuCu_3$ type Pm3m space group face-centered cubic (FCC) structure. Ni_3Fe phase is a solid solution not having a single component. There is a disorder-order transformation in the critical temperature T_c for Ni_3Fe alloy, which is about 500°C. There is no H_2-induced environmental embrittlement for the disordered Ni_3Fe in gaseous hydrogen; however, the H_2-induced embrittlement for the ordered alloy ($L1_2$ crystal structure) having the same chemical composition becomes severer [4]. The susceptibility of the ordered Ni_3Fe alloy to hydrogen embrittlement increases with increasing degree of order [5]. The mechanism of hydrogen embrittlement for Ni_3Fe alloy is that the transitional elements on the surface catalyze H_2 molecule in environment into H atom, and then atomic hydrogen diffuses into materials, segregates at the grain boundaries, and decreases the grain-boundary cohesion [6]. This mechanism has been confirmed by the experimental results of adsorption-desorption of hydrogen on the surface of Ni_3Fe alloy [7, 8]. The effect of B suppressing the environmental embrittlement of ordered Ni_3Al alloy depends on Al stoichiometry of the alloy. It was suggested that alloy stoichiometry strongly influences grain-boundary chemistry which, in turn, affects the grain-boundary cohesion [9]. It was found that the phase composition and the grain size of Ni_3Fe alloy are independent of Fe stoichiometry, and the effect of Fe stoichiometry on the mechanical properties of the ordered alloy is larger than that of disordered alloy [10]. The apparent hydrogen diffusion coefficient decreases with increasing the boron concentration doped in the ordered Ni_3Fe alloy, and the doping boron in the Ni_3Fe alloy is effective in reducing the hydrogen diffusion at the grain boundary [11]. Therefore, Ni_3Fe alloy is an ideal alloy for studying the effect of the stoichiometry on susceptibility to hydrogen embrittlement of ordered intermetallics. The purpose of this paper is to determine the effect of stoichiometry on a mechanism of hydrogen embrittlement and hydrogen diffusion for the ordered Ni_3Fe intermetallics.

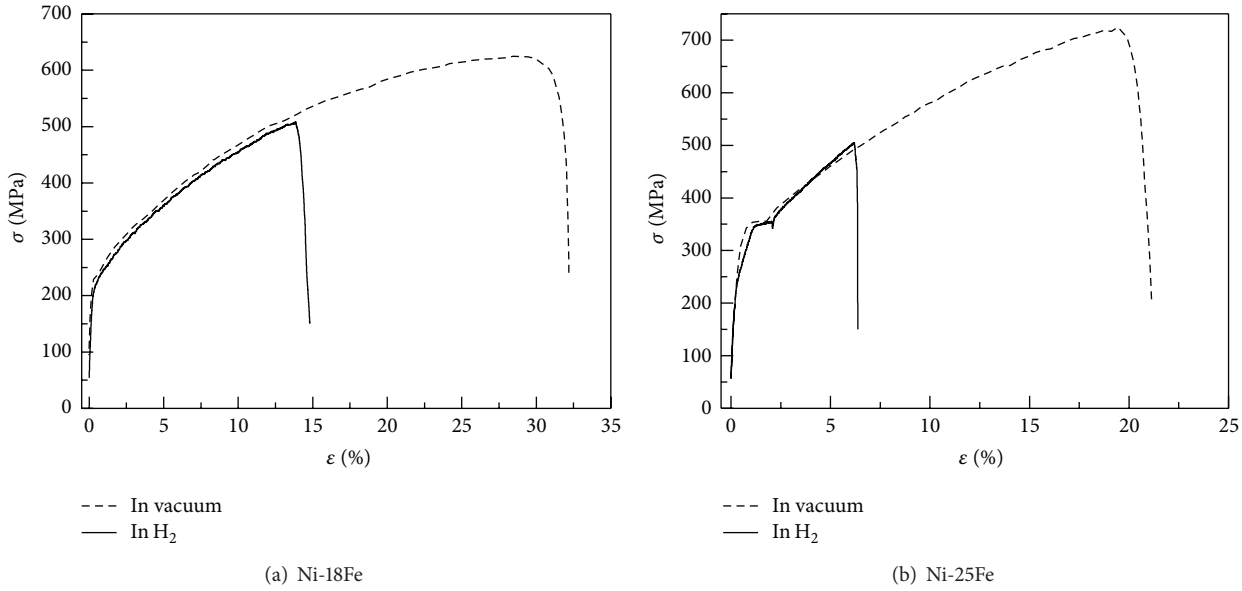


Figure 1: Engineering stress-strain curves for the ordered Ni_3Fe alloys with different stoichiometry when tested in vacuum and H_2.

2. Experimental Procedure

Several Ni_3Fe alloys with different stoichiometry, Ni-18Fe, Ni-22Fe, Ni-25Fe, and Ni-28Fe, (all in at.%) were prepared by arc melting high purity of Ni and Fe. The ingots were hot rolled to sheets of 2 mm at 1050°C. Then the sheets were cold rolled to sheets of about 1 mm thickness after stress relief annealing. Tensile specimens with a gage section of 10 × 2 × 1 mm were electric discharge machined from the sheets and sealed in an evacuated quartz tube. The specimens were disordered by annealing at 800°C for 2 h, and then the capsule was broken under water. For ordering treatment, some disorder treated specimens were sealed also in evacuated quartz tubes and annealed at 470°C for 200 h, followed by furnace cooling. Tensile tests were conducted on an MTS machine equipped with a vacuum chamber. For tensile testing in gaseous hydrogen, the chamber was evacuated twice to a pressure of about 2×10^{-2} Pa and backfilled with pure hydrogen gas released from hydrogen-storage materials (the purity of H_2 is about 99.999%). All tensile tests were carried out at the constant nominal strain rate of 2×10^{-3} s^{-1} and at room temperature. The ductility of the alloys was obtained by comparing the length of gage section before and after fracture. The fracture surface of tested specimens was examined by scanning electron microscopy (SEM). The depth of intergranular (IG) fracture on a fracture surface was also measured in situ by SEM.

The hydrogen adsorption by Ni_3Fe powder with different stoichiometry was conducted on the impulsive adsorption apparatus. The Ni_3Fe powder was made by mechanical alloying using pure Ni and Fe powders. The hydrogen adsorption experiment was performed in a flow system using a thermal conductivity detector (TCD) to monitor the variation of H_2 concentration. The hydrogen adsorption experiment was described detailedly in [7].

In order to study the effect of Fe stoichiometry on diffusion coefficient of hydrogen, the sheet specimens were cathodically precharged with hydrogen at 25°C, 35°C, or 45°C for 5 h, respectively. A charging current density of 45 mA/cm^2 was applied to the unmasked gage length area. The electrolyte was 0.5 mol/l H_2SO_4 solution poisoned with 50 mg/l $NaAsO_2$. After charging, the specimens were quickly rinsed first in distilled water and then in acetone and alcohol, respectively. After being dried by blowing air at room temperature, the specimens were immersed in liquid nitrogen to limit the redistribution of charging hydrogen. Tensile test of the charging specimens was conducted on an MTS machine in vacuum condition at room temperature and at the nominal strain rate of 2×10^{-3} s^{-1}. A diffusion coefficient of hydrogen of the ordered Ni_3Fe with different stoichiometry was calculated by time lag method, which was described in [11].

3. Results and Discussion

It was found that there is only single phase in the disordered Ni_3Fe alloys with different stoichiometry, which means that the stoichiometry of Ni_3Fe alloy with the studied composition does not change the phase composition of the alloy [10]. Figure 1 illustrates the engineering stress-strain curves of the ordered Ni-18Fe and Ni-25Fe alloy when tensile tested in vacuum and gaseous hydrogen. The stress-strain curves of the ordered Ni-22Fe and Ni-28Fe are similar to that of Ni-25Fe. The mechanical properties of the ordered Ni_3Fe with different stoichiometry when tested in vacuum and in H_2 are listed in Table 1. Figure 2 shows the relation curve between the maximum tensile strength (σ_{max}) and Fe stoichiometry for the ordered Ni_3Fe alloy in vacuum and H_2. It can be seen from Figure 2 that σ_{max} increases firstly and decreases and then increases again when Fe stoichiometry changes from

Table 1: The mechanical properties of the ordered Ni_3Fe alloy with different stoichiometry when tested in vacuum and H_2.

Alloy	In vacuum		In H_2		I_{H_2}, %
	σ_{max}, MPa	δ, %	σ_{max}, MPa	δ, %	
Ni-18Fe	627.7	32.5	509.3	15.6	51.9
Ni-22Fe	762.3	28.2	616.8	11.9	57.7
Ni-25Fe	725.9	23.4	505.7	6.9	70.7
Ni-28Fe	958.3	30.8	681.1	10.4	66.2

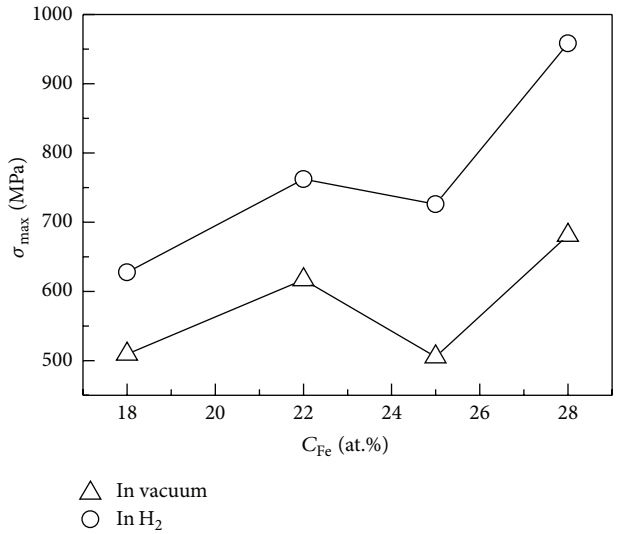


Figure 2: Relationship between the maximum tensile strength and Fe stoichiometry.

18 at.% to 28 at.%. The change of the stoichiometry of alloy alters contents and kinds of point defect and degree of order of the alloy, which affects the mechanical properties of the ordered Ni_3Fe alloy [10]. The change range of tensile strength of the ordered Ni_3Fe when tested in vacuum is larger than that when tested in H_2.

It can be seen from Figure 2 that σ_{max} when tested in vacuum is all higher than that when tested in H_2 for the ordered Ni_3Fe alloy with the same stoichiometry because of the effect of hydrogen embrittlement. The effect of the hydrogen embrittlement varies with Fe stoichiometry of Ni_3Fe alloy. We define a parameter $\Delta\sigma_{max}$ to describe the effect of the hydrogen embrittlement on σ_{max}; $\Delta\sigma_{max}$ is defined as follows:

$$\Delta\sigma_{max} = \sigma_{max}^{\text{in } H_2} - \sigma_{max}^{\text{in vacuum}}, \quad (1)$$

where $\sigma_{max}^{\text{in vacuum}}$ and $\sigma_{max}^{\text{in } H_2}$ are the maximum tensile strength of the ordered alloy when tested in vacuum and in H_2, respectively. According to the data of Figure 2, we can plot the curve of $\Delta\sigma_{max}$ versus C_{Fe} (Figure 3). It is showed in Figure 3 that $\Delta\sigma_{max}$ value induced by the hydrogen embrittlement decreases with the increase of Fe stoichiometry of the ordered Ni_3Fe alloy. The higher the maximum tensile strength of the ordered alloy in vacuum, the larger the effect of the hydrogen embrittlement on σ_{max}.

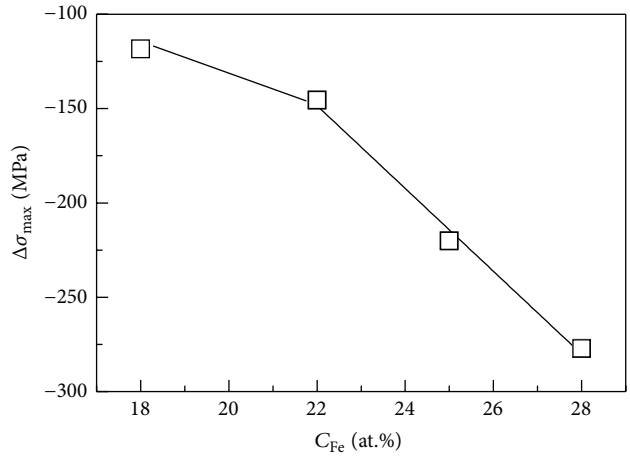


Figure 3: The curve of $\Delta\sigma_{max}$ versus C_{Fe}.

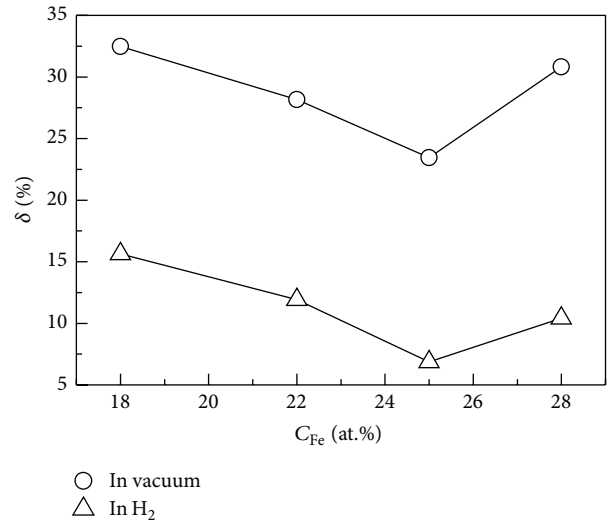


Figure 4: The change of elongation of the ordered Ni_3Fe with Fe stoichiometry when testing in vacuum and in H_2.

Figure 4 illustrates the changes of elongation of the ordered Ni_3Fe alloy when tested in vacuum and in H_2 with Fe stoichiometry. Different from the change of the tensile strength with Fe stoichiometry, the elongation of alloy increases linearly with increasing the extent of deviating the normal stoichiometry, and the elongation of the normal stoichiometric ordered Ni_3Fe alloy is the lowest in the studied alloy. The elongations of the alloy when tested in H_2 are all lower than that when tested in vacuum for the ordered Ni_3Fe having the same stoichiometry because of the effect of hydrogen embrittlement.

Generally, the susceptibility to hydrogen embrittlement of a material is characterized by a factor of hydrogen embrittlement (I_{H_2}). The factor of hydrogen embrittlement is defined as

$$I_{H_2} = \frac{\delta_{\text{vacuum}} - \delta_{H_2}}{\delta_{\text{vacuum}}} \times 100\%, \quad (2)$$

Table 2: The value of x and D_A of the ordered Ni_3Fe alloy with different stoichiometry precharged hydrogen at various conditions.

Alloy	25°C		35°C		45°C		Q, kJ/mol
	x, μm	D_A, cm^2/s	x, μm	D_A, cm^2/s	x, μm	D_A, cm^2/s	
Ni-22Fe	44.86	1.86×10^{-10}	58.15	3.13×10^{-10}	72.29	4.84×10^{-10}	37.64
Ni-25Fe	27.69	7.10×10^{-11}	34.73	1.12×10^{-10}	41.83	1.62×10^{-10}	32.54
Ni-28Fe	22.50	4.69×10^{-11}	27.03	6.77×10^{-11}	31.55	9.22×10^{-11}	26.65

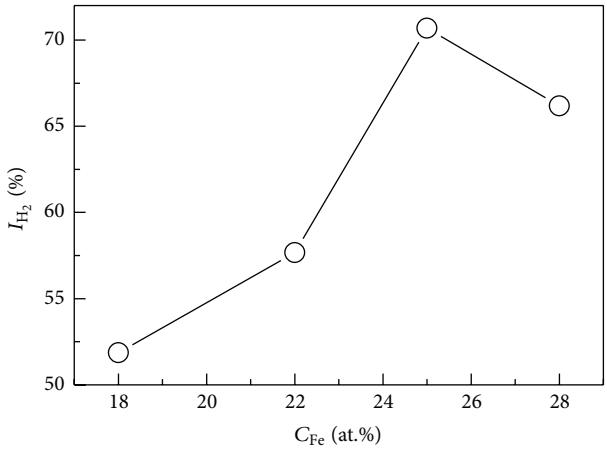


Figure 5: The factor of hydrogen embrittlement of the ordered Ni_3Fe versus Fe stoichiometry.

where δ_{vacuum} is the elongation of the material when tensile tested in vacuum and δ_{H_2} is the elongation of the material when tensile tested in H_2.

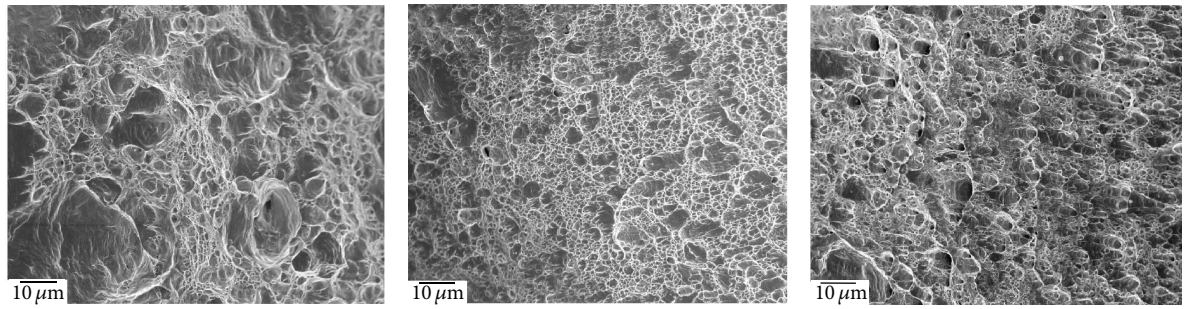
I_{H_2} of the ordered Ni_3Fe alloy with different stoichiometry is listed also in Table 1. Figure 5 shows that I_{H_2} of the ordered Ni_3Fe alloy changes with Fe stoichiometry. It can be seen from Table 1 and Figure 5 that I_{H_2} of the ordered Ni_3Fe alloy increases firstly and then decreases with the increase of Fe stoichiometry. I_{H_2} of the ordered Ni_3Fe alloy with the normal stoichiometry is the largest in the studied alloy. This means that the susceptibility of the ordered Ni_3Fe alloy with the normal stoichiometry to hydrogen embrittlement is the largest in the ordered Ni_3Fe.

Fractographs of the ordered Ni_3Fe with different stoichiometry when tested in vacuum are showed in Figure 6. It can been seen from Figure 6 that the fracture surfaces of the ordered Ni_3Fe with different stoichiometry when tensile tested in vacuum present all 100% transgranular fracture. But examination of the fracture surface failing in gaseous H_2 reveals that the ordered Ni-18Fe and Ni-28Fe failed by a mixed transgranular-intergranular rupture as shown in Figures 7(a) and 7(c) whereas the ordered Ni-25Fe (normal stoichiometry) exhibited very brittle fracture, that is, with 100% intergranular fracture (Figure 7(b)). Thus, the observed fractographs are quite consistent with the elongation and ultimate tensile strength listed in Table 1.

The experimental results approved that the higher sensitivity to H_2-induced environmental embrittlement of the ordered Ni_3Fe in gaseous H_2 was attributed to the enhancement of the catalytic reaction on the surfaces to produce more atomic hydrogen [7]. The effect of Fe stoichiometry on ability of catalysis has been studied by the impulsive adsorption apparatus. Figure 8 illustrates that the specific capacity of adsorbed hydrogen by the ordered Ni_3Fe powder varies with Fe stoichiometry of the alloy. It can be seen from Figure 8 that the amount of adsorbed hydrogen by the normal stoichiometric Ni_3Fe alloy is the largest in all studied Ni_3Fe powder. This means that there is an effect of the Fe stoichiometry on the ability of catalytic reaction to produce atomic hydrogen. Because of the relation between the Fe stoichiometry and degree of order in the ordered Ni_3Fe alloy [10], it is suggested that the ability of catalytic reaction of the ordered Ni_3Fe alloy depends on degree of order of the alloy.

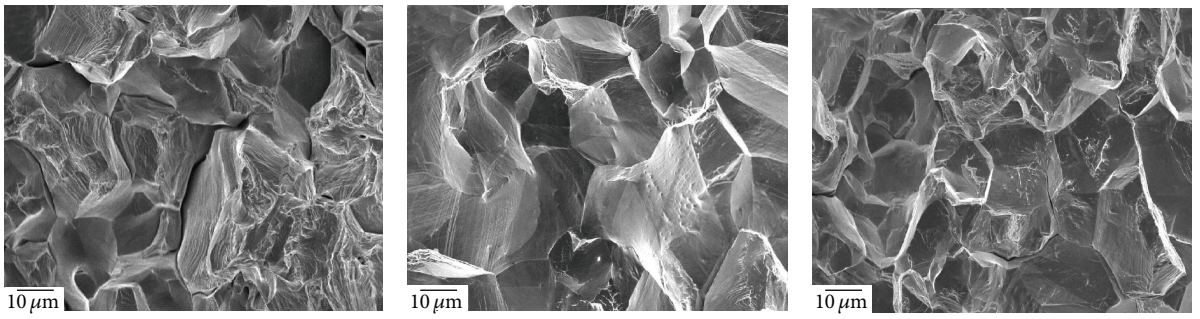
It was found that the factor of hydrogen embrittlement of the ordered Ni_3Fe alloy increases linearly with increasing degree of order of alloy [5]. According to results of Figure 5, the ordered Ni_3Fe alloy with the normal stoichiometry should have the highest degree of order in four Ni_3Fe alloys studied in this experiment. The experimental results approved that the change of the stoichiometry of Ni_3Fe alloy altered degree of order of the alloy, which affected the mechanical properties of the ordered Ni_3Fe alloy [10]. Similarly, it is also confirmed in this paper that the Fe stoichiometry alters degree of order of the ordered Ni_3Fe, which changes the susceptibility of the ordered Ni_3Fe to hydrogen embrittlement.

The hydrogen embrittlement contains generation of the atomic hydrogen and hydrogen atom diffusion in the alloy. Thus, the diffusion of hydrogen is an important step of the hydrogen embrittlement. After precharged with hydrogen at various temperatures for 5 h, the mechanical properties of the sheet specimens of Ni-22Fe, Ni-25Fe, and Ni-28Fe were investigated by tensile test in vacuum at room temperature. The average depth of IG fracture (x) was measured in situ by SEM and a value of x is obtained by averaging twenty measurement data from both sides of each specimen after rupture. Table 2 shows x value measured for the ordered Ni_3Fe alloy with various stoichiometric ratios charging hydrogen at different temperatures. It can be seen from this table that the depth of IG fracture of the ordered Ni_3Fe alloys decreases with the increment of Fe stoichiometry at the same precharging temperature. The apparent hydrogen diffusion coefficient (D_A) of the ordered Ni_3Fe alloy may be calculated by the depth of IG fracture and the time lag method [11]. The calculated apparent hydrogen diffusion coefficient of the ordered Ni_3Fe alloy with various stoichiometries is also listed in Table 2. It can be seen from Table 2 that the change of the apparent hydrogen diffusion coefficient of the ordered Ni_3Fe alloy is consistent with change of the depth of IG fracture when changing the precharging temperature or Fe



(a) Ni-18Fe (b) Ni-25Fe (c) Ni-28Fe

Figure 6: SEM fractographs of the ordered Ni_3Fe with different stoichiometry when tested in vacuum.



(a) Ni-18Fe (b) Ni-25Fe (c) Ni-28Fe

Figure 7: SEM fractographs of the ordered Ni_3Fe with different stoichiometry when tested in H_2.

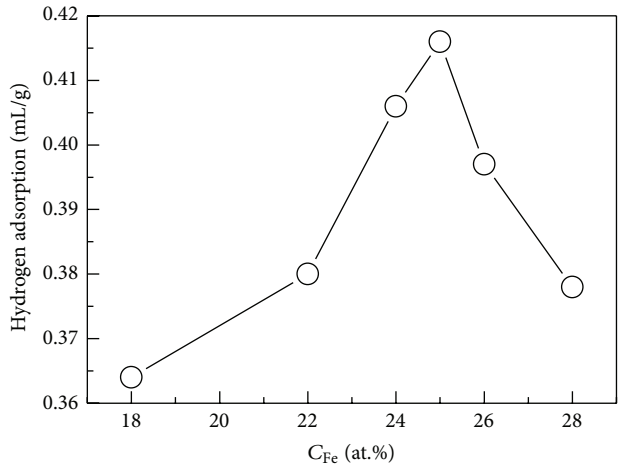


Figure 8: The curves of the quantity of hydrogen adsorption per gram for the ordered Ni_3Fe powder versus Fe stoichiometry.

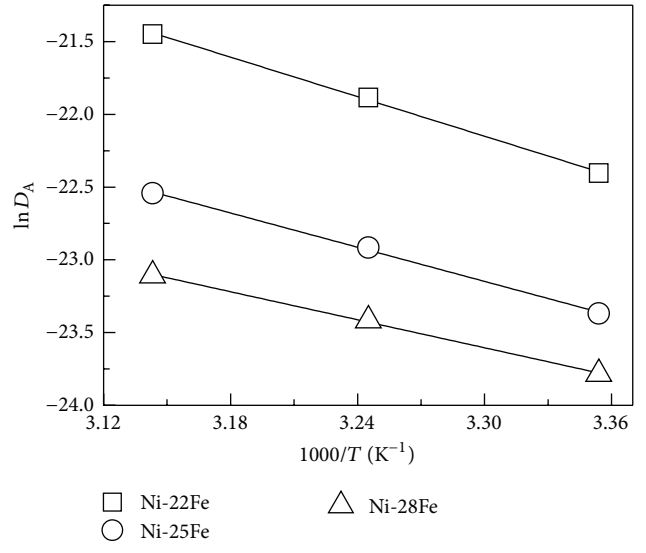


Figure 9: $\ln D_A$ versus $1/T$ for the ordered Ni_3Fe alloys with various stoichiometry.

stoichiometry. At the same precharging temperature, D_A of the ordered Ni_3Fe decreases with increasing Fe stoichiometry. The data of Table 2 demonstrate that Fe stoichiometry of the ordered Ni_3Fe alloy has a strong effect of reducing the hydrogen diffusion along the grain boundaries.

The relationship between the apparent hydrogen diffusion coefficient (D_A) of the ordered Ni_3Fe alloy with various Fe stoichiometries and reciprocal absolution temperature is shown in Figure 9. There is a good linear relationship between $\ln D_A$ and T^{-1} for the ordered Ni_3Fe alloy. From Figure 9, the activation energy of hydrogen diffusion (Q) can be estimated for the ordered Ni_3Fe alloys and is also listed in Table 2. Figure 10 shows that there is a linear relation between the activation energy of hydrogen diffusion and Fe

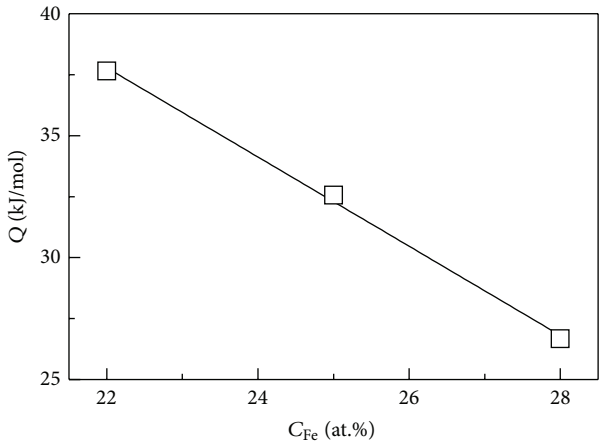


FIGURE 10: Relationship between the diffusion activation energy and Fe stoichiometry.

stoichiometry. Because the normal stoichiometric alloy has the highest degree of order in the ordered Ni_3Fe alloy, it can be deduced by the above experimental results that the diffusion coefficient and the activation energy of hydrogen diffusion are independent of degree of order of the alloy. This result means that the effect of Fe stoichiometry in the ordered Ni_3Fe alloy may influence grain-boundary chemistry which, in turn, affects hydrogen diffusion along the grain boundary.

Based on the above experimental results and discussions, we deduce that the effect of Fe stoichiometry on the susceptibility to hydrogen embrittlement is achieved by altering degree of order of the ordered Ni_3Fe alloy. The normal stoichiometric Ni_3Fe alloy has the highest degree of order; thus it has the highest ability of catalytic reaction and the highest susceptibility to hydrogen embrittlement. But Fe stoichiometry affects the behavior of hydrogen diffusion by influencing grain-boundary chemistry of the ordered Ni_3Fe alloy.

4. Conclusion

(1) The mechanical properties and the susceptibility to hydrogen embrittlement of the ordered Ni_3Fe alloy vary with the Fe stoichiometry.

(2) The normal stoichiometric Ni_3Fe alloy has the lowest mechanical properties, the highest susceptibility to hydrogen embrittlement, and the highest ability of catalytic reaction.

(3) Degree of order is a key factor to influence susceptibility to hydrogen embrittlement of the ordered Ni_3Fe alloy.

(4) The apparent hydrogen diffusion coefficient and the activation energy of hydrogen diffusion of the ordered Ni_3Fe alloy decrease with the increase of Fe stoichiometry.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under Contract nos. 51271102 and 50671057. The authors also thank Instrumental Analysis and Research Center of Shanghai University for the help and support in the experiment and analysis of SEM.

References

[1] T. L. Lin, "Recent advances in high-temperature ordered intermetallics," *Journal of Shanghai Jiaotong University*, vol. 32, no. 2, pp. 95–108, 1998.

[2] P. Villars and L. D. Calvert, *Person's Handbook of Crystallographic Data for Intermetallic Phases*, vol. 3, ASM International, Materials Park, Ohio, USA, 1991.

[3] I. Chicinas, V. Pop, and O. Isnard, "Magnetic properties of Ni_3Fe intermetallic compound obtained by mechanical alloying," *Journal of Magnetism and Magnetic Materials*, vol. 242–245, part 2, pp. 885–887, 2002.

[4] G. M. Camus, N. S. Stoloff, and D. J. Duquette, "The effect of order on hydrogen embrittlement of Ni_3Fe," *Acta Metallurgica*, vol. 37, no. 5, pp. 1497–1501, 1989.

[5] Y. X. Chen, A. P. Chen, X. J. Wan, and S. R. Yan, "Ordering process and effect of ordering on the environmental embrittlement for Ni_3Fe alloy," in *The New Progress on Material Science and Engineering' 2004*, pp. 758–764, Chinese Materials Research Society, Metallurgical Industry Press, Beijing, China, 1st edition, 2004.

[6] J. L. Wright and J. H. Zhu, "Environmental embrittlement of an ordered Ni-Mo alloy," *Scripta Materialia*, vol. 38, no. 2, pp. 253–257, 1997.

[7] X. J. Wan, Y. X. Chen, A. P. Chen, and S. R. Yan, "The influence of atomic order on H_2-induced environmental embrittlement of Ni_3Fe intermetallics," *Intermetallics*, vol. 13, no. 5, pp. 454–459, 2005.

[8] Y. Liu, C. T. Liu, L. Heatherly, and E. P. George, "Effect of boron on the fracture behavior and grain boundary chemistry of Ni_3Fe," *Scripta Materialia*, vol. 64, no. 3, pp. 303–306, 2011.

[9] C. T. Liu, C. L. White, and J. A. Horton, "Effect of boron on grain-boundaries in Ni_3Al," *Acta Metallurgica*, vol. 33, no. 2, pp. 213–229, 1985.

[10] Y. Chen, H. Y. Qian, and T. Chen, "The effect of stoichiometry and degree of order on mechanical properties of Ni_3Fe intermetallics," *Materials Science Forum*, vol. 747-748, pp. 19–24, 2013.

[11] Y. X. Chen, J. Ma, and C. T. Liu, "Hydrogen diffusivity in B-doped and B-free ordered Ni_3Fe alloys," *Intermetallics*, vol. 19, no. 1, pp. 105–108, 2011.