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Effects of Nitrogen in the $(Fe_{1-x}Ni_x)_4N$ Compounds $(0 \leq x \leq 0.6)$

By

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Single phase γ'-Fe_4N-type $(Fe_{1-x}Ni_x)_4N$ compounds and $Fe_{1-x}Ni_x$ $(0 \leq x \leq 0.6)$ alloys are synthesized and studied by X-ray diffraction and Mössbauer spectroscopy. The structure changes from b.c.c. to f.c.c. when $Fe_{1-x}Ni_x$ $(x \leq 0.25)$ alloys are nitrided to $(Fe_{1-x}Ni_x)_4N$. The lattice expansion $\Delta a/a$ is 5.3% for f.c.c. $Fe_{1-x}Ni_x$ alloys $(x > 0.25)$ on nitrogenation. The observed decrease in the average iron hyperfine fields with nitrogenation, amounting to 8 to 14 T, is explained by the volume expansion and the chemical bond effects. The chemical bond effect is about three times larger than the volume effect. The increase in the average isomer shift after nitriding is mainly due to the effect of chemical bonds, which changes the electronic configuration of iron.

1. Introduction

Recently iron nitrides γ'-Fe_4N have been the subject of intensive experimental [1, 2] and theoretical [3] studies. The interest in this nitride arises from the high value of its saturation magnetization: 208 emu/g (0 K), which is very close to that of pure α-Fe (218 emu/g). In addition to the magnetic properties, as a fine powder Fe_4N presents a chemical resistance higher than that of metallic alloys in fine powder form. Even further improvement of the corrosion resistance was obtained in the $(Fe_{1-x}Ni_x)_4N$ system [4], which also exhibits better magnetic and electrical properties than pure iron. Recent investigations [5, 6] of the thermal expansion and force magnetostriction of Fe_3NiN observed similarities to the Fe–Ni Invar alloys. It was shown that the thermal expansion coefficient of Fe_3NiN (at room temperature) is relatively small and is significantly smaller than that of Fe_4N, moreover the variation of volume with magnetic field or of magnetization with pressure is rather similar in Fe_3NiN and $Fe_{65}Ni_{35}$. The nitrogen plays an important role in determining the properties of these materials.

In order to distinguish this nitrogen effect in the $(Fe_{1-x}Ni_x)_4N$ compounds, X-ray and Mössbauer spectroscopy studies have been performed on $(Fe_{1-x}Ni_x)_4N$ compounds and $Fe_{1-x}Ni_x$ alloys. The influence of the nitrogen has been related to the structure and the hyperfine parameters.

2. Preparation and Measurements

The initial seed material $(Fe_{1-x}Ni_x) \cdot C_2O_4 \cdot 2\,H_2O$ $(0 \leq x \leq 1.0)$ was obtained by a chemical coprecipitation method [7]; the X-ray diffraction measurement confirmed that the oxa-

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lates are single phase crystals. The dry oxalate powders were obtained by filtering, washing, and drying the precipitates at 85 °C for 2 h. The $Fe_{1-x}Ni_x$ alloys were obtained by heat treatment of the oxalates in pure hydrogen. The oxalates were placed in a quartz furnace to be annealed in an ammonia and hydrogen stream with flow rate ratio $NH_3/H_2 \approx 3:1$ at about 500 °C to prepare the $(Fe_{1-x}Ni_x)_4N$ compounds. The X-ray diffraction analyses were performed on a D/MAX-3X diffractometer with Cu K_α radiation. Mössbauer spectra were recorded at room temperature using a Halder MR-351 type spectrometer. A 10 mCi ^{57}Co(Rh) source was used. The spectrometer was calibrated with respect to the standard α-Fe at room temperature.

3. Results and Discussions

The phase structures of the material are examined with an X-ray diffractometer. Fig. 1 shows the X-ray diffraction patterns for $Fe_{0.5}Ni_{0.5}$ alloy and $(Fe_{0.5}Ni_{0.5})_4N$ compound. The alloys $Fe_{1-x}Ni_x$ exhibit a b.c.c. (α-phase) structure for the $x \leq 0.25$ and an f.c.c. (γ-phase) structure for $x \geq 0.3$. Single phase nitrides $(Fe_{1-x}Ni_x)_4N$ were obtained for $0 \leq x \leq 0.6$. All the nitrides exhibit an f.c.c. γ′-Fe_4N structure. Fig. 2 shows the lattice constants of the $Fe_{1-x}Ni_x$ alloys and $(Fe_{1-x}Ni_x)_4N$ compounds. By comparing the structure and the related crystal parameters of the $Fe_{1-x}Ni_x$ alloys and $(Fe_{1-x}Ni_x)_4N$ compounds, the following statements can be made: a) the b.c.c. structure (α-phase) is being transformed by nitriding into the f.c.c. structure (γ′-phase) for $x \leq 0.25$; b) the f.c.c. structure (γ-phase) is not changed for $x \geq 0.30$, besides the increase of the lattice constant by nitriding. The average relative volume expansion of the unit cell $\Delta V/V$ is 23.6% for the f.c.c. phase structure $Fe_{1-x}Ni_x$ alloys after nitriding. The crystal structure of Fe_4N is similar to the face-centered structure with the nitrogen atom placed at the body-center of the unit cell. Therefore, there are two iron sublattices: one at the corner (Fe^c) and another one at the face-centers (Fe^f). The

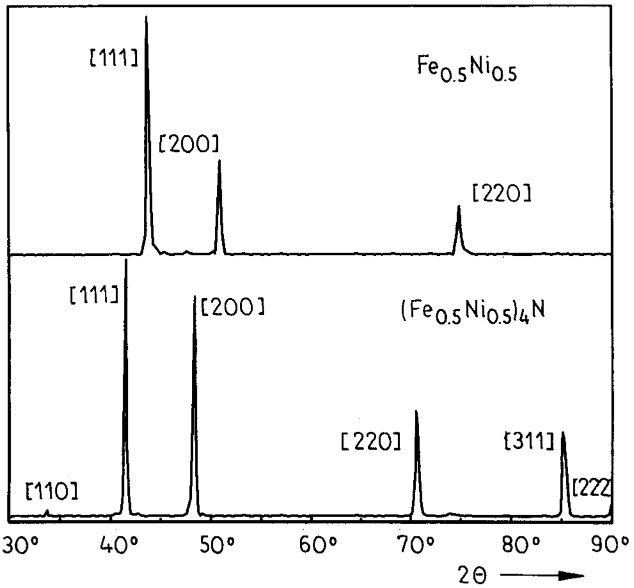

Fig. 1. The X-ray diffraction patterns of $(Fe_{1-x}Ni_x)_4N$ and $Fe_{1-x}Ni_x$ with $x = 0.5$

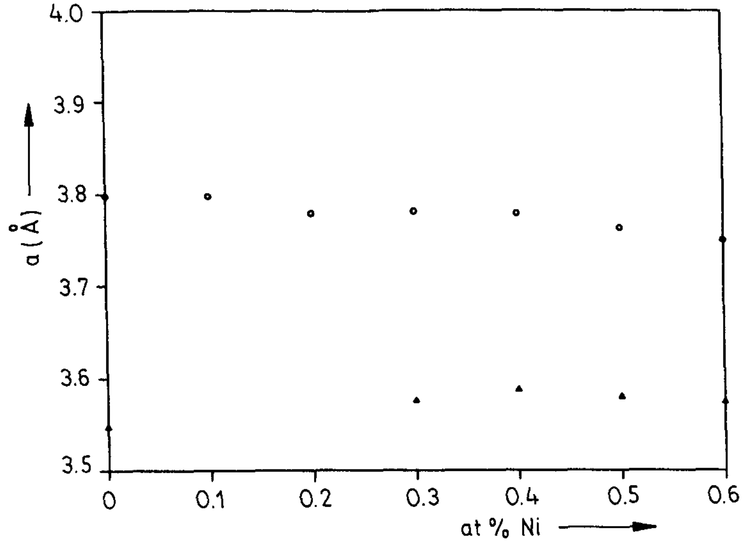

Fig. 2. The lattice constants of the $(Fe_{1-x}Ni_x)_4N$ compounds (○) $(0 \leq x \leq 0.6)$ and $Fe_{1-x}Ni_x$ alloys (△) $(0.3 \leq x \leq 0.6$ and $x = 0)$

Fe–Ni alloys tend to adopt the f.c.c. structure after nitriding. According to the results of [8], there is a direct bond interaction between N and the face-center Fe. One can assume the bond between nitrogen and the face-center Fe atoms to be stronger than the bonds between nitrogen and the corner Fe atom. This may be the reason that the structure of $(Fe_{1-x}Ni_x)_4N$ is the γ'-phase.

Fig. 3 shows some typical Mössbauer spectra of the $Fe_{1-x}Ni_x$ alloys and $(Fe_{1-x}Ni_x)_4N$ compounds at room temperature. Table 1 lists their hyperfine interaction parameters. The Mössbauer spectra of the $Fe_{1-x}Ni_x$ alloys were fitted with two subsextets [9]. The Mössbauer spectra of the Fe_4N compounds were resolved into three subsextets with relative intensities $1(Fe^c):2(Fe^f\text{-}A):1(Fe^f\text{-}B)$ [10]. The Mössbauer spectra of the $(Fe_{1-x}Ni_x)_4N$ compounds were fitted to five subsextets considering the substitution of iron by nickel. For all samples, the average hyperfine fields decrease after nitriding. The largest decrease of the hyperfine field is 14 T for the $x = 0.6$ sample, and the minimum decrease is 8.3 T for the $x = 0$ sample. It can be assumed that the decrease of the hyperfine field is the result of the nitrogenation. The effects mainly originate in two ways: 1. expansion of the lattice or phase change after nitriding; 2. chemical bonds formed between iron and nitrogen, as well as between nickel and nitrogen. The expansion of the lattice causes the neighbor distance of iron to increase which may decrease the hyperfine fields of iron. The bonds of iron and nitrogen which have covalent character [5] will decrease the hyperfine field of iron also. Taking these two effects into account, one can describe the effects of volume expansion and chemical bonds in the $(Fe_{1-x}Ni_x)_4N$ compounds by the following equation:

$$\frac{\Delta H}{H} = A\frac{\Delta V}{V} + B - X\,, \tag{1}$$

where H is the average hyperfine field of iron in the $Fe_{1-x}Ni_x$ alloys, ΔH the increase of the hyperfine fields after nitriding, V the volume of the Wigner-Seitz unit cell of the $Fe_{1-x}Ni_x$

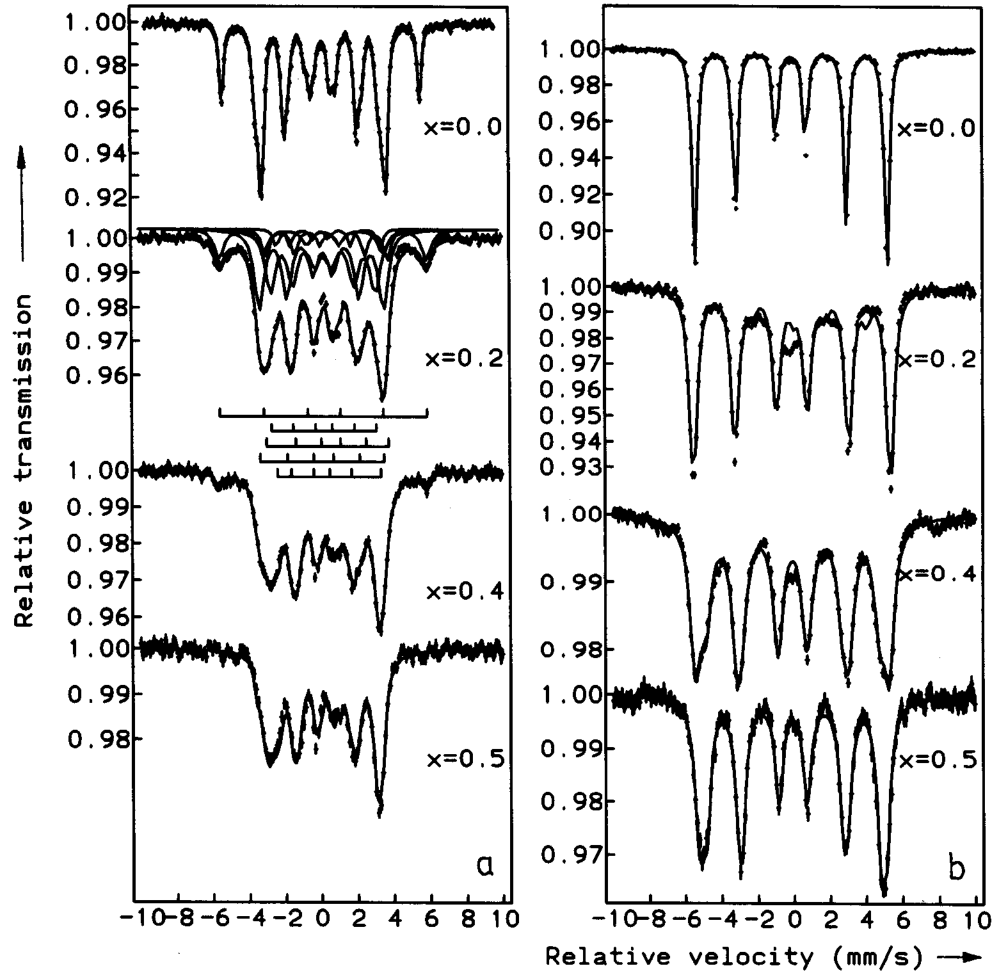

Fig. 3. The Mössbauer spectra of a) $(Fe_{1-x}Ni_x)_4N$ compounds and b) $Fe_{1-x}Ni_x$ alloys with $x = 0$, 0.2, 0.4, 0.5

alloys, and ΔV the increase of the unit cell volume after nitriding, X the ratio of the nitrogen atoms to the iron atoms in the nitrides. For the f.c.c. $Fe_{1-x}Ni_x$ ($x > 0.25$), the values of H, ΔH, V, ΔV, and X have been obtained from the Mössbauer spectra and the X-ray diffraction analysis. Fitting these data with (1), we have obtained the values $A = -1.31$ and $B = -0.38$. The negative sign of A and B means that these two effects decrease the hyperfine fields. The effect of chemical bonds is about three times as large as the volume effect. It should be pointed out that this is the first time the effects of the volume expansion and the chemical bond on the hyperfine field of the $(Fe_{1-x}Ni_x)_4N$ compounds are calculated.

The average isomer shifts of the $Fe_{1-x}Ni_x$ alloys are increased after nitriding, which means that the electronic configuration of the iron atoms has changed. The electronic configuration is $3d^7 4s^1$ and $3d^8 4s^1$ for the corner Fe atoms and the face-center Fe atoms, respectively [11]. This configuration is different from the configuration $3d^7 4s^1$ in the $Fe_{1-x}Ni_x$

Table 1
Mössbauer parameters of ^{57}Fe nuclei for $(Fe_{1-x}Ni_x)_4N$ and $Fe_{1-x}Ni_x$ $(0 \leq x \leq 0.6)$

	$(Fe_{1-x}Ni_x)_4N$				$Fe_{1-x}Ni_x$	
x	$\overline{H_{Fe}}$	$\overline{IS_{Fe^c}}$	IS_{Fe^f}	$\overline{IS}$	$\overline{H_{Fe}}$	$\overline{IS}$
0.0	24.77	0.24	0.18	0.22	33.08	0.00
0.1	23.75	0.26	0.30	0.29	33.81	0.11
0.2	21.81	0.28	0.30	0.30	33.74	0.07
0.3	21.01	0.32	0.32	0.32	32.78	0.02
0.4	19.98	0.13	0.26	0.25	32.04	0.02
0.5	18.72	–	0.18	0.18	31.27	0.04
0.6	16.91	–	0.28	0.28	30.95	0.03

alloys, which will increase the isomer shift, however, decrease the hyperfine fields of the iron atoms. This is in good agreement with our experimental results.

We have used the chart of Walker et al. [12] to determine the electronic configuration of iron in the corner and face-center sites by combination of the observed isomer shifts. The configurations of iron in the $(Fe_{1-x}Ni_x)_4N$ compounds were listed in Table 2. The number of the 4s electron is less than 1.0, and the configuration of the corner iron is similar to $3d^7 4s^{1-x}$ $(0 \leq x \leq 1.0)$. But the configuration of the face-center iron is approximately $3d^{8-x}4s^x$ $(0 \leq x \leq 1.0)$, which is not consistent with the configuration $3d^8 4s^1$ of the face-center iron atom in Fe_4N. This result is more interesting and worthy to be further studied.

4. Conclusions

The nitrogen effects in the $(Fe_{1-x}Ni_x)_4N$ compounds were discussed by comparing $(Fe_{1-x}Ni_x)_4N$ compounds and $Fe_{1-x}Ni_x$ alloys. The effects of volume expansion and chemical bonds have been estimated. These two effects will decrease the hyperfine field, and the effect of the chemical bond is about three times larger than the volume expansion effect. The electronic configuration of the $Fe_{1-x}Ni_x$ alloys is changed by the formation of the iron–nitrogen bond after nitriding. The increase of the average isomer shifts after nitriding is mainly the result of the decrease of the number of 4s electrons. For the $(Fe_{1-x}Ni_x)_4N$ compounds, the observed isomer shift corresponds to the electronic configurations $3d^7 4s^{1-x}$ and $3d^{8-x}4s^x$ for the corner and the face-center iron atoms, respectively.

Table 2
The electronic configuration of ^{57}Fe nuclei for $(Fe_{1-x}Ni_x)_4N$ in different sites $(0 \leq x \leq 0.6)$

x	Fe^c	Fe^f
0.0	$3d^{7.08}4s^{0.92}$	$3d^7 4s^{0.84}$
0.1	$3d^{7.15}4s^{0.85}$	$3d^7 4s^{0.79}$
0.2	$3d^{7.16}4s^{0.84}$	$3d^7 4s^{0.77}$
0.3	$3d^{7.17}4s^{0.83}$	$3d^7 4s^{0.75}$
0.4	$3d^{7.13}4s^{0.87}$	$3d^7 4s^{0.88}$
0.5	$3d^{7.10}4s^{0.90}$	–
0.6	$3d^{7.14}4s^{0.86}$	–

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