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X-ray diffraction and Mössbauer studies of the $(Fe_{1-x}Ni_x)_4N$ compounds $(0 \le x \le 0.5)$

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Abstract

X-ray diffraction and Mössbauer spectroscopy studies on the γ -Fe₄N type (Fe_{1-x}Ni_x)₄N compounds ($0 \le x \le 0.5$) were performed. The lattice constants decrease with increasing x. Compared with Fe_{1-x}Ni_x alloys of the same composition, the average relative expansion of the unit cell ($\delta V/V$) is 16.7% after nitriding. The results of the Mössbauer spectra of the (Fe_{1-x}Ni_x)₄N are well in agreement with the structure in which the nickel atoms are prior to locating at the Fe^c sites, and some of the nickel atoms also occupy the face center sites in the meantime. The iron atoms at the Fe^c sites are completely occupied by nickel atoms, when $x \ge 0.5$.

Recently, there has been a great deal of interest in the study of the transitions metal carbides and nitrides. Among them, the nitride γ' -Fe₄N has been the object of intensive experimental [1,2] and theoretical [3-6] studies. Moreover, Fe₄N has long been considered as a potential candidate for high density recording materials due to its higher magnetization than that of iron oxide and its greater stability as compared to that of the metal medial. The γ' -Fe₄N is a nitride with the Perovskite-type structure [7] with two inequivalent iron sites, one occupying the corners (Fe^c) and the other, the face-centered positions (Fe^f) and nitrogen (N) occupying the body center positions. The Fe^c atoms is surrounded by 12 nearest neighbors Fe atoms, while the Fe^f atoms has two nitrogens as the nearest neighbors. According to the

neutron diffraction measurement [8], the magnetic moment on Fe^c and Fe^f sites are 2.98 and $2.01 \mu_{\rm B}$. The (Fe_{1-x}Ni_x)₄N compounds have been studied [9], in which the x is less than 25%. Chen et al. [10] have synthesized (Fe_{1-x}Ni_x)₄N with α -Fe-Ni alloys foils for x < 0.2. Addition of the nickel to Fe₄N has been found to prominently improve the magnetic properties and chemical stability. Recent investigation of thermal expansion and force magnetostriction of Fe₃NiN showed similarities with Fe-Ni Invar alloys [11,12].

In this paper, we report the first results of single phase $(Fe_{1-x}Ni_x)_4N$ compounds with a higher nickel substitution till x = 0.5, and the crystal structure and the occupation priority of the $(Fe_{1-x}Ni_x)_4N$ compounds are given.

We started by preparing the nickel-substituted iron oxalate precursor. The procedure began with coprecipitation of a mixed oxalate of iron and nickel $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ ($0 \le x \le 1.0$), by reaction

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Table 1



Fig. 1. The X-ray diffraction patterns for the $(Fe_{1-x}Ni_x)_4N$ compounds with x = 0.1, 0.2, 0.5.

between aqueous solutions of oxalic acid and divalent sulfates of iron and nickel in appropriate amounts. The precipitate was then filtered, washed and dried. The Fe-Ni nitride particles were prepared by placing the oxalates in a quartz tube furnace in a gaseous flow of an ammonia and hydrogen mixture to assure a simultaneous reducing and nitriding condition with an optimized flow ratio: $H_2/NH_3 = 1:3$. The X-ray diffraction analysis was performed on a D/MAX-RB diffractometer with CuK_{α} radiation. Mössbauer spectra were recorded using a FH1913 conventional constant acceleration spectrometer at room temperature and 77 K. A 10mCi ⁵⁷Co(Rh) source was used. The spectrometer was calibrated with respect to the standard α -Fe at room temperature. The isomer shift is relative to the α -Fe at RT.

The X-ray diffraction patterns for typical samples of the $(Fe_{1-x}Ni_x)_4N$ compounds are shown in Fig. 1. All compounds are the single phase γ' -Fe₄N type structure for $x \le 0.5$. The crystal structure parameters derived from X-ray diffraction are listed in Table 1. It is obvious that the lattice constants decrease with increasing nickel concentration. This also can be seen from the diffraction angle increase from

x	2θ [°]	d [Å]	I/I_0	[h, k, l]
0.2	41.34	2.182	100	111
	48.08	1.891	55	200
	70.30	1.338	25	220
	84.69	1.144	20	311
	89.50	1.095	7	222
0.3	41.32	2.183	100	111
	48.06	1.892	55	200
	70.32	1.338	25	220
	84.86	1.142	20	311
	89.60	1.093	7	222
0.4	41.34	2.182	100	111
	48.10	1.890	61	200
	70.40	1.336	29	220
	85.04	1.140	23	311
	89.82	1.091	8	222
0.5	41.52	2.173	100	111
	48.30	1.883	57	200
	70.60	1.333	27	220
	85.30	1.137	23	311
	90.01	1.089	9	222

The crystal structure parameters for $(Fe_{1-x}Ni_x)_4 N (0.0 \le x \le 0.5)$

x = 0.1 to 0.5 in Fig. 1. This may result from the fact that the Ni atom radius (1.15 Å) is smaller than the Fe atom radius (1.17 Å). The lattice constants of the Fe_{1-x}Ni_x alloys and its nitrides are shown in Fig. 2. One can see that the lattice constants increase after nitrogenation for all Fe_{1-x}Ni_x alloys. The average



Fig. 2. The lattice constants of $\operatorname{Fe}_{1-x}\operatorname{Ni}_x(\Delta)$ alloys and their nitrides (O).

relative volume increase of the unit cell $(\delta V/V)$ is 16.7% for γ -Fe-Ni alloys ($x \ge 0.3$). This may have great effect on the magnetic properties and the chemical stability of $(\text{Fe}_{1-x}\text{Ni}_x)_4\text{N}$ compounds.

Because the easy magnetization axis of the γ' -Fe₄N has been found to be parallel to the $\langle 100 \rangle$ direction, the group of Fe^f atoms is split into two sub-groups with a ratio of 2:1. The Mössbauer spectra of the γ' -Fe₄N were fitted to three sextets with line intensity Fe^c : Fe^f₁₁ : Fe^f₁ = 1 : 2 : 1 [13]. The component having the largest hyperfine field and zero quadruple interaction is assigned to the Fe^c atoms, while other components are assigned to the Fe^f atoms. Because of substitution of the iron by nickel in the (Fe_{1-x}Ni_x)₄N compounds ($x \neq 0$), the neighbor environment of the iron should be split



Fig. 3. The Mössbauer spectra for the $(Fe_{1-x}Ni_x)_4N$ compounds with x = 0.0, 0.2, 0.3, 0.5 at 77 K.

into subspectra. Five sextets are used to give the best results in the fitting procedure.

The 77 K Mössbauer spectra of the $(Fe_{1-x}Ni_x)_4N$ ($0 \le x \le 0.5$) compounds were shown in Fig. 3. From Fig. 3 one can see that the outer sextet is related to the Fe^c and the other six lines related to the face center Fe atoms, Fe^f₁ and Fe^f₁₁ atoms. The relative intensities of the peaks assigned to the Fe^c atoms decrease with increasing Ni content and disappear at x = 0.5. This indicates that the Fe^c sites have been completely replaced by the nickel. The relative intensities of the other peaks changed slightly, which results from some Ni atoms also replacing the Fe^f atoms.

According to Ref. [14], the Fe₃NiN structure was orderly, namely the nickel atoms located at Fe^c sites. So one can deduce that when x = 0.25, and the compound is an orderly structure, the subspectrum of the corner iron will disappear completely. Our experiments have confirmed that the subspectrum of the corner iron exists until x = 0.5. This shows that the substitution of the iron by nickel may has some disorderly characteristics within the results of our experiments.

The occupation preference of the nickel in the $(Fe_{1-x}Ni_x)_4N$ can be discussed by the high nickel substitution. Supposing the recoil-free fraction f is the same for the Fe atoms at different crystallographic sites, we have the formula

$$\frac{A_{\rm c}}{A_{\rm f}} = \frac{N_{\rm Fe}^{\rm c}}{N_{\rm Fe}^{\rm f}} = \frac{1 - N_{\rm Ni}^{\rm c}}{3 - N_{\rm Ni}^{\rm f}},\tag{1}$$

where A_c and A_f are the peak areas of the Mössbauer spectrum for Fe^c atoms and the Fe^f atoms, respectively. N_{Fe}^c and N_{Fe}^f are the fractional number of the Fe atoms located at the Fe^c sites and Fe^f sites, respectively. N_{Ni}^c is the number of the nickel atoms replacing the Fe^c atoms, and the N_{Ni}^f is the number of the nickel atoms replacing the Fe^f atoms.

The values A_c and A_f can be obtained from the Mössbauer spectra. Combining the relationship N_{Ni}^c + N_{Ni}^f = 4x, for x = 0.0, 0.1, ..., 0.5, with the Eq. (1), we evaluate the values of N_{Ni}^c and N_{Ni}^f . The percentage of the Fe replaced by Ni in the different crystallographic sites can be calculated also, as listed in Table 2. From Table 2, one can see that the Fe^c sites are preferentially replaced by Ni atoms, and

0.4

0.5

Table 2 The percentage of Fe atoms replaced by Ni at the different sites in $(Fe_{1-x}Ni_x)_4N$ compounds. P^c is the percentage of corner Fe

88.6

100.0

atoms replaced by Ni atoms. P ^f is the percentage of face cente Fe atoms replaced by Ni atoms				
x	P ^c [%]	P ^f [%]		
0.0	0.0	0.0		
0.1	16.6	7.8		
0.2	45.2	11.6		
0.3	72.9	15.7		

23.8

33.3

completely replaced by nickel atoms for x = 0.5, and only some of Fe^f atoms are replaced by nickels atoms. The replaced percentage slowly increases with increasing x. The data in Table 2 indicate that during the process of the substitution, which has a priority to occupying the Fe^c sites, but some of the nickel atoms are still located at the face center sites.

From our X-ray diffraction and Mössbauer spectral measurements in the $(Fe_{1-x}Ni_x)_4N$ compounds, we can conclude:

- Lattice constants of the $(Fe_{1-x}Ni_x)_4N$ compounds decrease with increasing nickel content.

- The unit cell volume of the Fe-Ni alloys increases after nitrogenation.

- The substitution of the nickel atoms for the iron

atoms has a preference to replacing the Fe^{c} sites, but some of the nickel atoms still occupy the Fe^{f} sites.

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