Preparation of the single phase γ'-$(Fe_{1-x}Ni_x)_4N$ compounds $(0 \leq x \leq 0.6)$

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Single phase γ'-Fe_4N type $(Fe_{1-x}Ni_x)_4N$ compounds $(0 \leq x \leq 0.6)$ have been synthesized for the first time by controlled heat treatment of iron–nickel oxalates in a gaseous flow of NH_3 xand H_2. The preparation processes were investigated using differential scanning calorimetry (DSC), X-ray diffraction and Mössbauer spectroscopy. The results confirmed that annealing of oxalates in the NH_3 and H_2 atmosphere included the processes of dehydration, decomposition and reduction, nitrogenation and thermal decomposition of the nitrides. The decomposition and reduction occur simultaneously. The final products depend on the flow rate ratio of $NH_3 : H_2$ and the annealing temperature. The formation conditions for the single phase γ'-Fe_4N type $(Fe_{1-x}Ni_x)_4N$ compounds are related to the nickel concentration, with increasing nickel content, the nitrogenation temperature decreased, in contrast the flow rate ratio of $NH_3 : H_2$ increased.

1. Introduction

The magnetic properties of iron nitrides (γ'-Fe_4N) have been studied in detail [1–3] by virtue of the excellent magnetic properties in combination with significantly improved corrosion and wear resistance compared to pure iron. In order to improve the magnetic properties and the chemical stability, substitution of iron by nickel, tin and manganese has been studied [4–6]. The preparation method for (Fe, Ni)$_4$N compounds reported in the literature [7] is

1. nickel ferrous oxalates are obtained by the chemical coprecipitation method,

2. the oxalates are decomposed and reduced under purified hydrogen, and

3. the finely divided powders are nitrided in a gaseous flow of NH_3 and H_2. The nickel content of the product was not more than 25%, and there are no reports of single phase $(Fe_{1-x}Ni_x)_4N$ compounds with high nickel concentration. Recent investigation [8,9] of thermal expansion and force magnetostriction of Fe_3NiN observed similarities to Fe–Ni Invar alloys. Hence, it is considered worthwhile to prepare $(Fe_{1-x}Ni_x)_4N$ compounds with higher nickel content ($x \geq 30\%$) which is in the range of the Invar alloys.

In this paper, using a modified preparation method, the preparation of single phase $(Fe_{1-x}Ni_x)_4N$ compounds with a higher nickel substitution ($x \leq 0.6$) were first reported. X-ray diffraction, DSC and Mössbauer spectroscopy were used to study the formation processes of the $(Fe_{1-x}Ni_x)_4N$ compounds. The influences of reaction temperature and annealing atmosphere on the formation of the $(Fe_{1-x}Ni_x)_4N$ compounds were examined.

2. Experimental procedure

The ferrous oxalates $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ $(0 \leq x \leq 0.6)$ with different nickel compositions were prepared by the chemical coprecipitation method [10]. The dry powders were obtained by filtering, washing and drying the precipitates at 85 °C for 2 h. DSC measurement of the oxalate powders was carried out in a gaseous flow of NH_3 and H_2. According to the DSC curves, the annealing temperatures were determined at which the powders were heated in a quartz tube furnace. In order to obtain $(Fe_{1-x}Ni_x)_4N$ compounds with a single phase structure and high nickel concentration, a modified reduction and nitrogenation method was used. The oxalates were heated directly in a mixed flow of ammonia and hydrogen. The final products were cooled to room temperature and used as the studied samples. The X-ray diffraction analysis was performed on a D/MAX-RB diffractometer with CuK_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 α-Fe standard at room temperature.

3. Results and discussion
3.1. DSC analysis

The DSC curves of the $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$, for $x = 0.1$, 0.4, 0.5, in a gaseous flow of the NH_3 and H_2 are shown in Fig. 1. The flow rate ratio of $NH_3 : H_2$ is 3. The DSC curves contain three endothermic peaks. Comparing the results of X-ray diffraction after such heat treatment, the three endothermic peaks can be assigned to
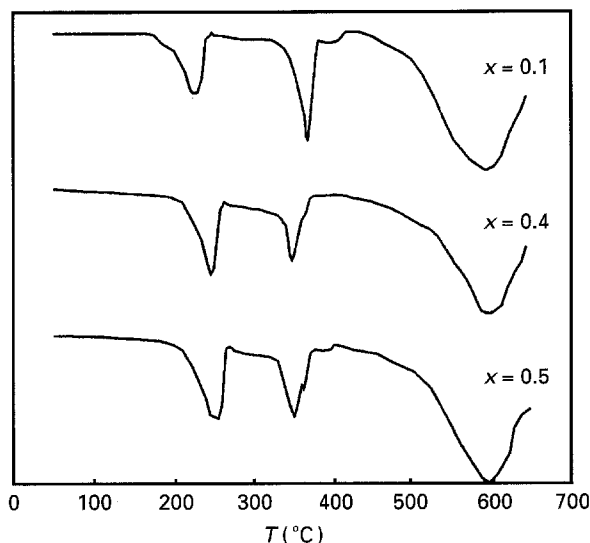
1. peak 1, dehydration of oxalates;

Figure 1 DSC curves of $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ compounds with $x = 0.1$, 0.4 and 0.5 in a gaseous $NH_3 : H_2$ flow.

TABLE I The temperatures of dehydration, decomposition and reduction, and nitridation for $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ in an $NH_3 : H_2$ gaseous flow

x (at%)	Dehydration (°C)	Decomposition and reduction (°C)	Nitrogenation (°C)
0.1	180–280	300–420	450–750
0.4	190–300	310–430	480–650
0.5	200–300	320–450	520–600

2. peak 2, decomposition of oxalates and reduction of oxide; and

3. peak 3, nitrogenation of the Fe–Ni alloys.

The results show that at higher temperatures the nitrides will decompose. The temperatures of dehydration, decomposition and reduction, and nitrogenation are listed in Table I.

3.2. The effect of annealing temperature, T

According to results of the DSC analysis, the $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ powders were annealed for 30 min at $T = 200$–800 °C, with $NH_3 : H_2 = 3 : 1$. Fig. 2 shows the room temperature Mössbauer spectra of the $x = 0.5$ sample annealed at 250, 325, 400, 500, 585, and 620, Fig. 2b–g, respectively.

Fig. 2a shows the spectrum of $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$; the isomer shift (IS) = 1.37 mm s^{-1}, and quadrupole splitting (QS) = 2.21 mm s^{-1}.

The spectrum recorded for the oxalate annealed at 250 °C consists of two subspectras. The doublet which has an IS = 1.08 mm s^{-1} and QS = 1.06 mm s^{-1}, may be assigned to $Fe_{0.5}Ni_{0.5} \cdot C_2O_4$, which is the product of dehydration of $Fe_{0.5}Ni_{0.5} \cdot C_2O_4 \cdot 2H_2O$. The singlet, which has an IS = − 0.02 mm s^{-1}, is
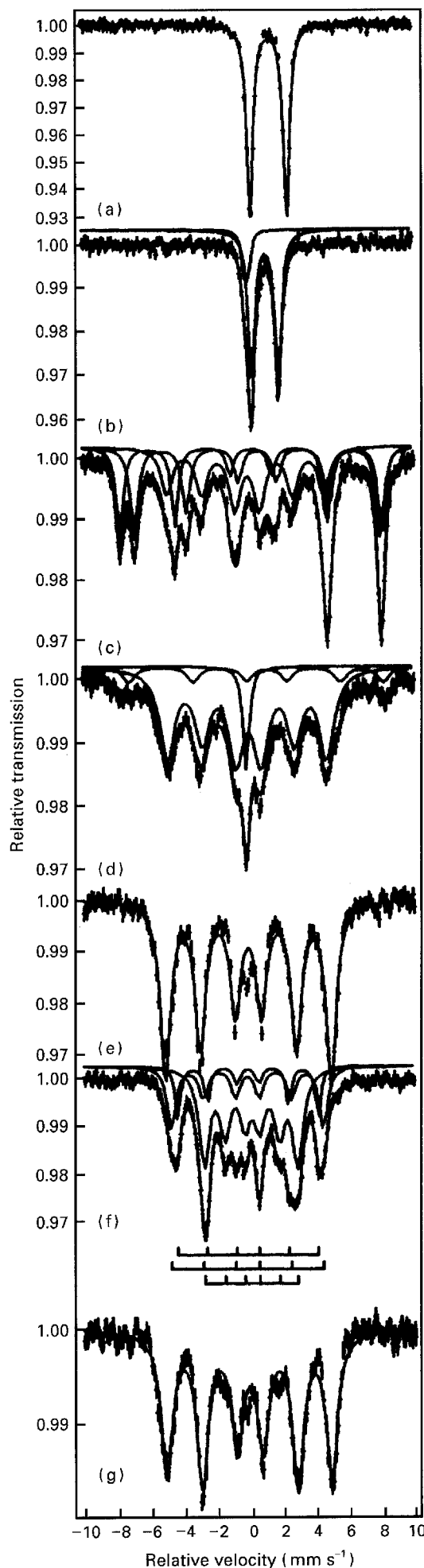
Figure 2 Mössbauer spectra of the products obtained from the $^fFe_{0.5}Ni_{0.5} \cdot C_2O_4 \cdot 2H_2O$ sample annealed at different temperatures.

TABLE II The products of heat treatment for the $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ with $x = 0.1, 0.5$ and $NH_3:H_2 = 3$ (the relative intensity of the phase in Mössbauer spectrum is given in brackets)

T (°C)	$x = 0.1$	$x = 0.5$
85	$Fe_{0.9}Ni_{0.1} \cdot C_2O_4 \cdot 2H_2O$	$Fe_{0.5}Ni_{0.5} \cdot C_2O_4 \cdot 2H_2O$
325	$Fe_{0.9}Ni_{0.1} \cdot C_2O_4 + $ Fe-Ni oxide	$Fe_{0.5}Ni_{0.5} \cdot C_2O_4 + $ Fe-Ni oxide
350	$(Fe_{0.9}Ni_{0.1})_3O_4 + Fe_{0.9}Ni_{0.1}$	$(Fe_{0.5}Ni_{0.5})_3O_4 + Fe_{0.5}Ni_{0.5}$
440	$(Fe_{0.9}Ni_{0.1})_3O_4 + Fe_{0.9}Ni_{0.1}$	$(Fe_{0.5}Ni_{0.5})_3O_4 + Fe_{0.5}Ni_{0.5}$
500	$Fe_{0.9}Ni_{0.1} + (Fe_{0.9}Ni_{0.1})_4N(90\%)$	$Fe_{0.5}Ni_{0.5}$
585	$(Fe_{0.9}Ni_{0.1})_4N(100\%)$	$(Fe_{0.5}Ni_{0.5})_4N(56.2\%) + Fe_{0.5}Ni_{0.5}$
620	$(Fe_{0.9}Ni_{0.1})_4N(100\%)$	$Fe_{0.5}Ni_{0.5}(100\%)$
650	$(Fe_{0.9}Ni_{0.1})_4N(100\%)$	$Fe_{0.5}Ni_{0.5}(100\%)$
700	$Fe_{0.9}Ni_{0.1}(100\%)$	$Fe_{0.5}Ni_{0.5}(100\%)$

TABLE III The products of heat treatment with different flow rate ratios of $NH_3:H_2$ for $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$, with $x = 0.5$ at $T = 585\,°C$ for 30 min (the relative intensity of the phase in Mössbauer spectrum is given in brackets)

$NH_3:H_2$	Products
1:1	$\gamma - Fe_{0.5}Ni_{0.5}(100\%)$
3:1	$Fe_{0.5}Ni_{0.5} + (Fe_{0.5}Ni_{0.5})_4N(56.2\%)$
5:1	$Fe_{0.5}Ni_{0.5} + (Fe_{0.5}Ni_{0.5})_4N(85.0\%)$
10:1	$Fe_{0.5}Ni_{0.5} + (Fe_{0.5}Ni_{0.5})_4N(95.3\%)$
12:1	$(Fe_{0.5}Ni_{0.5})_4N(100\%)$
15:1	$(Fe_{0.5}Ni_{0.5})_4N + (Fe, Ni)_3N(85\%) + Fe_{0.5}Ni_{0.5}$

Figure 3 X-ray diffraction patterns of $Fe_{0.5}Ni_{0.5}$ $(Fe_{0.5}Ni_{0.5})_4N$ compounds of $x = 0.4$ and 0.6.

associated with the Fe–Ni oxide originating from the decomposition of $Fe_{0.5}Ni_{0.5} \cdot C_2O_4$.

The ^{57}Fe Mössbauer spectrum for the sample annealed at 350 °C was consistent with the presence of two hyperfine fields ($\bar{H}\bar{F}$) of 47.73 and 29.59 T, and which can be associated with the presence of $(Fe_{0.5}Ni_{0.5})_3O_4$ ferrite and $Fe_{0.5}Ni_{0.5}$ alloy.

Treatment of the material at 400 and 500 °C, was accompanied by reduction of the $(Fe_{0.5}Ni_{0.5})_3O_4$ ferrite to $Fe_{0.5}Ni_{0.5}$ alloy. A paramagnetic phase with a single line ($IS = -0.15 \, mm\,s^{-1}$) was observed at 400 °C, and a small amount of this phase also was detected in Fig. 2e, g. The X-ray diffraction pattern indicated that only the peaks of the Fe–Ni alloy phase were identified. It may be safe to assume that it is the Fe–Ni alloy that shows paramagnetism.

When the sample was annealed at 585 °C, the corresponding Mössbauer spectrum (Fig. 2f) could be fitted to an $(Fe_{0.5}Ni_{0.5})_4N$ phase with $\bar{H}\bar{F} = 17.61$ T and to an Fe–Ni alloy phase with $\bar{H}\bar{F} = 27.86$ T. Annealing above 585 °C, the percentage of $(Fe_{0.5}Ni_{0.5})_4N$ began to decrease, which means the nitrides decomposed. At 650 °C (Fig. 2g), the nitrides have decomposed to $Fe_{0.5}Ni_{0.5}$ alloy with one sextet.

In summary it may be seen that annealing of oxalates in NH_3 and H_2 includes the processes of dehydration, decomposition and reduction, nitrogenation and thermal decomposition of the nitrides. The processes of decomposition and reduction occur in the meantime.

Mössbauer study was used as a complementary method in addition to X-ray diffraction to identify the phase after heat treatment. The annealing products at different temperatures for $x = 0.1$ and 0.5 are given in Table II. Under the same annealing conditions, the percentage of the (Fe, Ni)$_4$N phase in the final

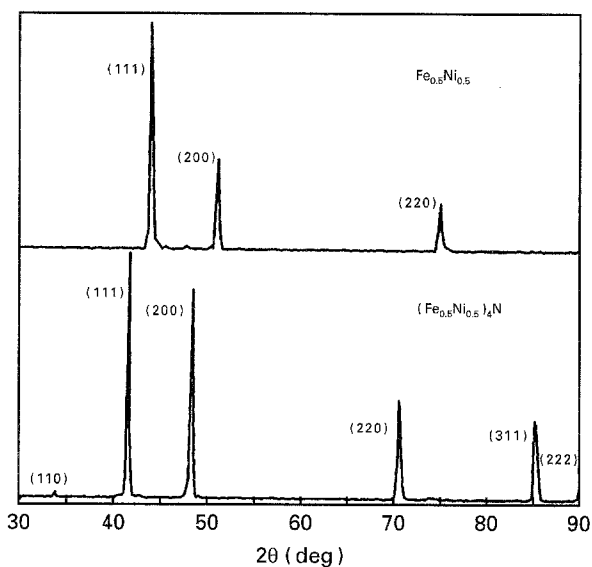products is different for $x = 0.1$ and 0.5. For example, the single phase $(Fe_{0.9}Ni_{0.1})_4N$ compound can be obtained in the temperature range 510–700 °C for the $x = 0.1$ sample, but for the $x = 0.5$ sample only 56.24% of the single phase $(Fe_{0.5}Ni_{0.5})_4N$ is obtained at 585 °C, and the nitride $(Fe_{0.5}Ni_{0.5})_4N$ decomposes when the temperature is higher than 600 °C.

For $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ $(0 \le x \le 0.6)$, the results of the annealing showed that the decomposition temperature of the nitrides decreased with increasing nickel content.

3.3. The effect of the $NH_3:H_2$ flow rate ratio

$T = 585\,°C$ and the flow rate ratios of $NH_3:H_2$ equal to 1:1, 3:1, 5:1, 10:1, 12:1 and 15:1 have been selected to treat the $Fe_{0.5}Ni_{0.5} \cdot C_2O_4 \cdot 2H_2O$ samples. Table III summarizes the phase composition of the final products. It can be seen from Table III that a large amount of the alloy phase appears when the flow rate ratio is less than 5:1. When the flow rate ratio is higher than 12:1, some other nitrides richer in nitrogen content, such as (Fe, Ni)$_3$N, are observed. So one is not able to obtain the single phase (Fe, Ni)$_4$N compounds. Investigation of the heat treatments for $Fe_{1-x}Ni_x \cdot C_2O_4 \cdot 2H_2O$ samples indicated that with increasing nickel content the ammonia concentration should be increased to obtain single phase (Fe, Ni)$_4$N.

Studies of Mössbauer spectra and X-ray diffraction for different nickel content samples have shown that temperature has no influence on the final products when the heat treatment time is more than 30 min.

Considering the points of view discussed above, and choosing the best heat treatment conditions, single phase $(Fe_{1-x}Ni_x)_4N$ $(0 \leq x \leq 0.6)$ compounds have been synthesized. In Fig. 3, the X-ray diffraction patterns for $Fe_{0.5}Ni_{0.5}$ alloy and $(Fe_{0.5}Ni_{0.5})_4N$ compound samples are given. The diffraction analysis confirms the products are single phase γ'-Fe_4N type $(Fe_{1-x}Ni_x)_4N$ compounds.

4. Conclusions

The preparation of single phase $(Fe_{1-x}Ni_x)_4N$ compounds with higher nickel substitution $(x \leq 0.6)$ are reported. Studies of the formation conditions show that the final products are dependent on the flow rate ratio of $NH_3:H_2$ and on the annealing temperature. The annealing conditions for the single phase γ'-Fe_4N type $(Fe_{1-x}Ni_x)_4N$ compounds depend on the nickel concentration. With increasing content of nickel, the temperatures of dehydration, and decomposition and reduction change little. The decomposition temperature of the nitrides decreases with increasing nickel content, and the formation temperature range of $(Fe_{1-x}Ni_x)_4N$ contracts. In order to obtain single phase $(Fe_{1-x}Ni_x)_4N$ compounds, the heat treatment temperature should be decreased, in contrast to the flow rate ratio of $NH_3:H_2$ which increases with increasing x.

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