Formation of oxide phases in the system Fe$_2$O$_3$-NiO

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Mixed metal oxides in the system Fe$_2$O$_3$-NiO were prepared by coprecipitation of Fe(OH)$_3$/Ni(OH)$_2$ and the thermal treatment of hydroxide coprecipitates up to 800 or 1100 °C. X-ray diffraction showed the presence of α-Fe$_2$O$_3$, NiO and NiFe$_2$O$_4$ in samples prepared at 800 °C. The oxide phases α-Fe$_2$O$_3$, NiO, NiFe$_2$O$_4$ and a phase with structure similar to NiFe$_2$O$_4$ were found in samples prepared at 1100 °C. Fourier transform–infrared spectra of oxide phases formed in the system Fe$_2$O$_3$-NiO are discussed. Two very strong infrared bands at 553 and 475 cm^{-1}, a weak intensity infrared band at 383 cm^{-1} and two shoulders at 626 and 441 cm^{-1} were observed for α-Fe$_2$O$_3$ prepared at 1100 °C. NiFe$_2$O$_4$, prepared at the same temperature, showed two broad and very strong infrared bands at 602 and 411 cm^{-1}, while NiO showed a broad infrared band at 466 cm^{-1}. Fourier transform–infrared spectroscopic results were in agreement with X-ray diffraction.

1. Introduction

Mixed metal oxides, prepared in the system Fe$_2$O$_3$-NiO, have been investigated from different points of view.

Sitakara Rao et al. [1] investigated transformations of iron(III)-nickel(II) mixed oxide gels. The experimental results indicated that addition of Ni^{2+} ions to Fe^{3+} solution created unfavourable conditions for the formation of α-FeOOH. The mixed oxide gels containing more than 2 mol % NiO did not show the presence of α-FeOOH. Differential thermal analysis (DTA) results suggested the formation of a solid solution between Fe$_2$O$_3$ and NiO up to 2 mol % NiO, and of nickel ferrite, NiFe$_2$O$_4$, at a higher concentration of NiO. At the stoichiometric ratio for NiFe$_2$O$_4$ formation, a nickel ferrite precursor was formed at $\sim$ 185 °C, which further transformed to amorphous ferrite at $\sim$ 275 °C and above 400 °C to crystalline nickel ferrite.

Tamaura et al. [2] investigated the formation of Fe$_3$O$_4$ and NiFe$_2$O$_4$ films in aqueous solutions at 100–200 °C. In solutions containing FeCl$_2$ and NaNO$_2$, two phases, Fe$_3$O$_4$ and α-Fe$_2$O$_3$, were formed. Addition of Ni^{2+} ions to FeCl$_2$ + NaNO$_2$ solution created conditions for the formation of nickel ferrite. The Ni^{2+} content in nickel ferrite was dependent on starting concentration of NiCl$_2$ and the temperature of ferrite formation.

Spherical and hollow NiFe$_2$O$_4$ particles were prepared using the aerosol technique [3]. A dilute aqueous solution of Ni(NO$_3$)$_2$ + Fe(NO$_3$)$_3$, with stoichiometric ratio for NiFe$_2$O$_4$ formation, was used for the production of aerosols. The aerosol droplets were thermally treated at 450–810 °C. Particle-size distribution, degree of crystallinity of NiFe$_2$O$_4$ particles and

their magnetic behaviour, were dependent on the temperature of pyrolysis.

Ibrahim and El-Shobaky [4] investigated the effects of Li$_2$O doping on the interaction between α-Fe$_2$O$_3$ and basic nickel carbonate. Doping with Li$_2$O enhanced the formation of NiFe$_2$O$_4$ to an extent proportional to the amount of Li$_2$O added. These authors [4] concluded that Li$_2$O doping stimulated the formation of NiFe$_2$O$_4$, due to an increase in the mobility of the reacting cations.

MacKenzie and Cardile [5] investigated the formation of NiFe$_2$O$_4$ from haematite, magnetite or spinel ironsand which was found on the West coast of the North Island of New Zealand. All three starting materials reacted with NiO producing NiFe$_2$O$_4$. The spinels formed from haematite, magnetite or ironsand and NiO in an inert atmosphere had larger lattice parameters than the corresponding air-reacted samples indicating the presence of Fe^{2+} in ferrite structure. Mössbauer spectroscopy suggested that the Fe^{2+} in the ferrite structure is located preferentially in the octahedral sites. It was also concluded that the NiFe$_2$O$_4$ formed in air was not fully inverse as is usually assumed, and that it contained varying amounts of tetrahedral Ni^{2+}.

Mixed metal oxides, Fe$_2$O$_3$-NiO, containing up to 5 mol % NiO, were prepared by sintering the corresponding oxides at 1050–1300 °C [6]. It was concluded that the addition of NiO changed the majority of charge carriers in the Fe$_2$O$_3$ from n to p-type. In samples containing more than 0.5 mol % NiO, the electrical conductivity was strongly influenced by the formation of nickel ferrite.

Mössbauer spectroscopy was used to study magnetic properties of small NiFe$_2$O$_4$ particles [7, 8].

[57]Fe Mössbauer spectra of $NiFe_2O_4$ were recorded, when a longitudinal magnetic field was applied. The spectra indicated a non-collinear magnetic structure of small $NiFe_2O_4$ particles. The experimental results also indicated the importance of the particle morphology which must be taken into account in any detailed analysis of the surface magnetism. The authors of these papers [7, 8] proposed the model in which the $NiFe_2O_4$ particles consisted of a core with the usual spin arrangement and a surface layer with atomic moments inclined to the direction of the net magnetization. Similar results were obtained for γ-Fe_2O_3 and [57]Fe–CrO_2 particles [9].

Allen et al. [10] investigated structural properties of spinels containing nickel, chromium and iron, which were prepared by the solid state reactions of the corresponding metal oxides in an atmosphere of CO_2 or $CO_2/2$ % CO at 950 °C.

Oxidation products formed on stainless steel 18Cr–10Ni–2Mn at 900–1100 °C were studied using X-ray diffraction, conversion electron Mössbauer spectroscopy (CEMS) and Fourier transform–infrared spectroscopy (FT–IR) [11]. The oxidation products on the steel surface, Cr_2O_3, $MnCr_2O_4$ and α-Fe_2O_3, were detected. However, $NiFe_2O_4$, NiO or $NiCr_2O_4$ were not detected in oxide layers.

The aim of the present work was to obtain further information about chemical and structural properties of oxide phases formed in the system Fe_2O_3–NiO. The samples were prepared by gradually changing the molar contents of Fe_2O_3 and NiO components over the whole concentration range. X-ray diffraction and FT–IR spectroscopy were used as experimental techniques. In our previous works [12, 13] it was proved that vibrational spectroscopy was a very useful technique for detection of chemical and structural changes in mixed metal oxides.

2. Experimental procedure
Analar reagent grade chemicals and doubly distilled water were used for the preparation of samples. Mixed metal hydroxides were obtained by addition of NaOH solution to $Fe(NO_3)_3$ + $Ni(NO_3)_2$ solution. $Fe(OH)_3/Ni(OH)_2$ coprecipitates were carefully washed using a Sorvall RC2-B ultra-speed centrifuge (20 000 r.p.m.). After drying, the hydroxide coprecipitates were heated as follows: 1 h at 200 °C, 1 h at 300 °C, 1 h at 400 °C and 5 h at 800 °C ("step-by-step" heating). These samples were additionally heated for 1 h at 1100 °C in a high-temperature furnace LKO II with Kanthal heaters. The samples heated at 1100 °C are labelled with an asterisk. The chemical composition of 26 samples, S-1 to S-13 and S-1* to S-13*, is given in Table I.

X-ray diffraction powder patterns were taken at room temperature using a counter diffractometer with monochromatized CuK_α radiation (Philips diffractometer, proportional counter and graphite monochromator).

All FT–IR spectra were recorded using a Fourier transform–IR spectrometer, model 1720–x (Perkin–Elmer). The specimens were pressed in KBr discs. In this paper, the FT–IR spectra are presented as relative transmittance versus the wave number (cm^{-1}).

3. Results and discussion
The crystalline phases found in the system Fe_2O_3–NiO were identified according to the data given in the literature [14]. Crystallographic data for α-Fe_2O_3, NiO, $NiFe_2O_4$ and (Ni, Fe)Fe_2O_4 are summarized in Table II.

The unit-cell parameter of $NiFe_2O_4$ is very close to twice as large as that of NiO. Both compounds possess the f c c crystal structure and for this reason, NiO does not exhibit independent diffraction lines of $NiFe_2O_4$. $NiFe_2O_4$ by itself exhibits some independent diffraction lines. No separation between overlapped diffraction lines of these two compounds was detected for samples where both compounds were present, even at high Bragg angles. For such samples the changes in fractions of NiO and $NiFe_2O_4$ can be followed by comparison of the intensities of overlapped diffraction lines belonging to both compounds with the intensities of diffraction lines belonging only to $NiFe_2O_4$.

TABLE I Chemical composition of the samples prepared in the system Fe_2O_3–NiO

Sample	Molar fraction	
	Fe_2O_3	NiO
S-1, S-1*	1	
S-2, S-2*	0.99	0.01
S-3, S-3*	0.975	0.025
S-4, S-4*	0.95	0.05
S-5, S-5*	0.90	0.10
S-6, S-6*	0.80	0.20
S-7, S-7*	0.50	0.50
S-8, S-8*	0.20	0.80
S-9, S-9*	0.10	0.90
S-10, S-10*	0.05	0.95
S-11, S-11*	0.025	0.975
S-12, S-12*	0.01	0.99
S-13, S-13*		1

TABLE II Crystallographic data for α-Fe_2O_3, NiO, $NiFe_2O_4$ and (Ni, Fe)Fe_2O_4 [14] at room temperature

JCPDS-PDF card no.	Compound	Space group	Unit-cell parameters at 25 °C (nm)
13–534	α-Fe_2O_3	$R\bar{3}c$ (no. 167)	Hexagonal axes: $a = 0.5034$ $c = 1.3752$
10–325	$NiFe_2O_4$ (synthetic sample)	$Fd3m$ (2 2 7)	$a = 0.8339$
23–1119	(Ni, Fe)Fe_2O_4 (mineral trevorite)	$Fd3m$ (2 2 7)	$a = 0.8367$
4–835	NiO	$Fm3m$ (2 2 5)	$a = 0.41769$

TABLE III X-ray diffraction phase analysis of samples in the system Fe_2O_3–NiO heated at a maximum temperature of 800 °C

Sample	Molar fraction of NiO	Phase composition (approximate molar fraction)
S-1	0	α-Fe_2O_3
S-2	0.01	α-Fe_2O_3
S-3	0.025	α-Fe_2O_3 + $NiFe_2O_5$ (< 0.01)
S-4	0.05	α-Fe_2O_3 + $NiFe_2O_4$ (0.01)
S-5	0.10	α-Fe_2O_3 + $NiFe_2O_4$ (0.02)
S-6	0.20	α-Fe_2O_3 + $NiFe_2O_4$ (0.25)
S-7	0.50	$NiFe_2O_4$ + α-Fe_2O_3 (0.02)
S-8	0.80	$NiFe_2O_4$ + NiO (0.20)
S-9	0.90	$NiFe_2O_4$ + NiO (0.35)
S-10	0.95	NiO + $NiFe_2O_4$[a] (0.15)
S-11	0.975	NiO
S-12	0.99	NiO
S-13	1	NiO

[a] Broadened diffraction lines.

TABLE IV X-ray diffraction phase analysis of samples in the system Fe_2O_3–NiO heated at maximum temperature of 1100 °C

Sample	Molar fraction of NiO	Phase composition (approximate molar fraction)
S-1*	0	α-Fe_2O_3
S-2*	0.01	α-Fe_2O_3 + "$NiFe_2O_4$"[a] (0.01)
S-3*	0.025	α-Fe_2O_3 + "$NiFe_2O_4$" (0.03)
S-4*	0.05	α-Fe_2O_3 + "$NiFe_2O_4$" (0.10)
S-5*	0.10	α-Fe_2O_3 + "$NiFe_2O_4$" (0.20)
S-6*	0.20	α-Fe_2O_3 + "$NiFe_2O_4$" (0.25)
S-7*	0.50	$NiFe_2O_4$
S-8*	0.80	$NiFe_2O_4$ + NiO (0.15)
S-9*	0.90	$NiFe_2O_4$ + NiO (0.35)
S-10*	0.95	NiO + $NiFe_2O_4$ (0.35)
S-11*	0.975	NiO + $NiFe_2O_4$ (0.15)
S-12*	0.99	NiO + $NiFe_2O_4$ (0.05)
S-13*	1	NiO

[a] "$NiFe_2O_4$" represents a phase having a structure similar to that of $NiFe_2O_4$.

The unit-cell parameters of α-Fe_2O_3 (samples S-1 and S-1*) and NiO (samples S-13 and S-13*) measured in this work were practically equal to the literature data given in Table II. For this reason, the literature data were used for calibration of the angular scale of the diffractometer.

The results of X-ray diffraction phase analysis are summarized in Tables III and IV. It can be seen that the structural characteristics of the samples depended on the maximum heating temperature. For samples prepared at 800 °C the fraction of α-Fe_2O_3 decreased from sample S-1 to sample S-7. In sample S-6, α-Fe_2O_3 was dominant, while in sample S-7, α-Fe_2O_3 was present only with a few per cent. In samples S-8 to S-12, α-Fe_2O_3 was not detected. α-Fe_2O_3 exhibited sharp diffraction lines, which did not change their angular positions, over the whole interval, from sample S-1 to sample S-7.

The phase $NiFe_2O_4$ appeared in sample S-3 and its fraction increased up to sample S-7, where it was dominant. Then $NiFe_2O_4$ fraction decreased up to

sample S-10. In samples S-8 and S-9, $NiFe_2O_4$ was also dominant, while in sample S-10 it exhibited rather broad diffraction lines. $NiFe_2O_4$ was not detected in samples S-11 and S-12. Diffraction lines of $NiFe_2O_4$ practically did not change their positions in the interval from sample S-6 to sample S-10. The same might also be concluded for the interval from sample S-3 to sample S-5, although diffraction lines of $NiFe_2O_4$ in these samples were rather faint.

NiO appeared in sample S-8, its fraction increased to sample S-13, and it was already a dominant component in sample S-10. NiO exhibited sharp diffraction lines, which did not move over the whole interval from sample S-8 to sample S-13.

For samples prepared at 1100 °C, the fraction of α-Fe_2O_3 decreased from sample S-1* to sample S-6* in which α-Fe_2O_3 was still dominant. Over the whole concentration region, α-Fe_2O_3 exhibited sharp diffraction lines, which did not change their angular positions with change of composition, as was also found for samples heated at a maximum temperature of 800 °C. α-Fe_2O_3 was not detected in sample S-7* and in all samples up to S-12*. Faint diffraction lines of an fcc phase, "$NiFe_2O_4$", similar to the spinel structure of $NiFe_2O_4$, appeared in sample S-2*. This phase exhibited the unit cell parameter larger by $\sim 1.0\%$ than that of $NiFe_2O_4$. The fraction of "$NiFe_2O_4$" increased from sample S-2* to sample S-7*. The important experimental fact is that diffraction lines of this phase moved towards higher Bragg angles, as the molar fraction of NiO increased from sample S-2* to sample S-7*. This shift corresponded to a decrease of the lattice parameter towards the value of $NiFe_2O_4$. For sample S-7* the positions of diffraction lines corresponded to $NiFe_2O_4$ and were practically equal to those obtained for sample S-7. The fraction of $NiFe_2O_4$ decreased from sample S-7* to sample S-12*. This phase was also dominant in samples S-8* and S-9*. Diffraction lines of $NiFe_2O_4$ did not move in the interval from samples S-7* to S-12*.

NiO appeared in sample S-8* and its behaviour was similar to that in samples heated up to 800 °C. The fraction of NiO gradually increased up to sample S-13*.

In previous papers [12, 13] we used vibrational spectroscopy to follow the chemical and structural changes in mixed metal oxides, Fe_2O_3–In_2O_3 and Fe_2O_3–Cr_2O_3, which formed solid solutions. In these papers the infrared spectrum of haematite was discussed in detail.

Vibrational spectroscopy was also used in the study of spinel oxides. For instance, cobalt-substituted magnetites, $(Fe^{3+})_A(Co_x^{2+} Fe_{1-x}^{2+} Fe^{3+})_B O_4^{2-}$, were oxidized under controlled conditions, and the transformation of γ-phase to α-Fe_2O_3 was followed by infrared spectroscopy [15]. It was found that the defect spinels with $x < 0.30$ showed a partial vacancy ordering at octahedral sites. On the basis of the disappearance of the infrared band at $720\ cm^{-1}$ of the defect γ-phase or the appearance of the infrared band at $470\ cm^{-1}$ of α-Fe_2O_3, it was shown that the transition temperature $\gamma \rightarrow \alpha$ increased with cobalt substitution. The effect of divalent cations on the formation

of α-Fe_2O_3 from the defect γ-phase was most pronounced in case of Zn^{2+}. Magnetite, $FeFe_2O_4$, was characterized by two infrared bands at 570 and 370 cm^{-1}. For $CoFe_2O_4$, two characteristic infrared bands at 590 and 383 cm^{-1} were found.

Ishii *et al.* [16] calculated optically active lattice vibrations of magnetite. The infrared band at 570 cm^{-1} was assigned to Fe–O stretching mode, $v_1(T_{1u})$, of the tetrahedral and octahedral sites. The infrared band at 370 cm^{-1} was assigned to Fe–O stretching mode, $v_2(T_{1u})$, of the octahedral sites.

In their book, Nyquist and Kagel [17] reported two characteristic infrared bands for magnetite at 570 and 410 cm^{-1}.

The Raman spectra of single crystal of $NiFe_2O_4$ and of polycrystalline Fe_3O_4, $NiFe_2O_4$ and $MnFe_2O_4$, were recorded at room temperature or at 4.2 K [18]. For polycrystalline $FeFe_2O_4$ the following Raman bands (cm^{-1}) were observed at room temperature: 706 and 570 (A_{1g} vibrational modes), 666 and 336 (E_g), and 490 and 226 (T_{2g}). For polycrystalline $NiFe_2O_4$ the following Raman bands (cm^{-1}) were observed at room temperature: 700 and 579 (A_{1g}), 666 and 339 (E_g) and 490 (T_{2g}).

Zanzucchi and Yim [19] investigated infrared emission for oxides formed on iron, nickel or Invar (36 % Ni–Fe alloy). The infrared spectra of oxidized iron and 36 % Ni–Fe alloy were similar. Nickel ions were not

Figure 2 Fourier transform infrared spectra of samples S-6, S-7, S-8 and S-9 recorded at room temperature.

Figure 1 Fourier transform infrared spectra of samples S-2, S-3, S-4 and S-5 recorded at room temperature.
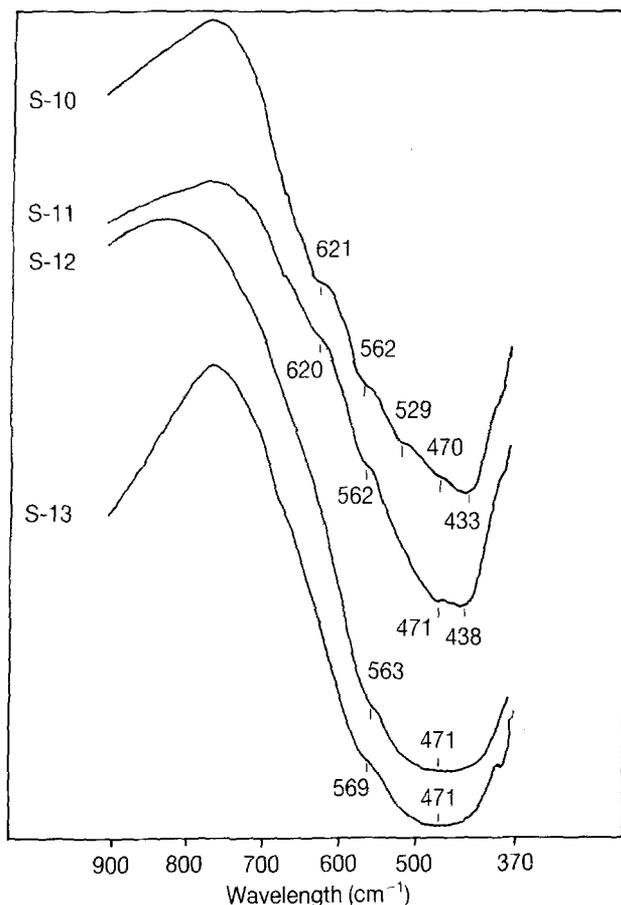
Figure 3 Fourier transform infrared spectra of samples S-10, S-11, S-12 and S-13 recorded at room temperature.
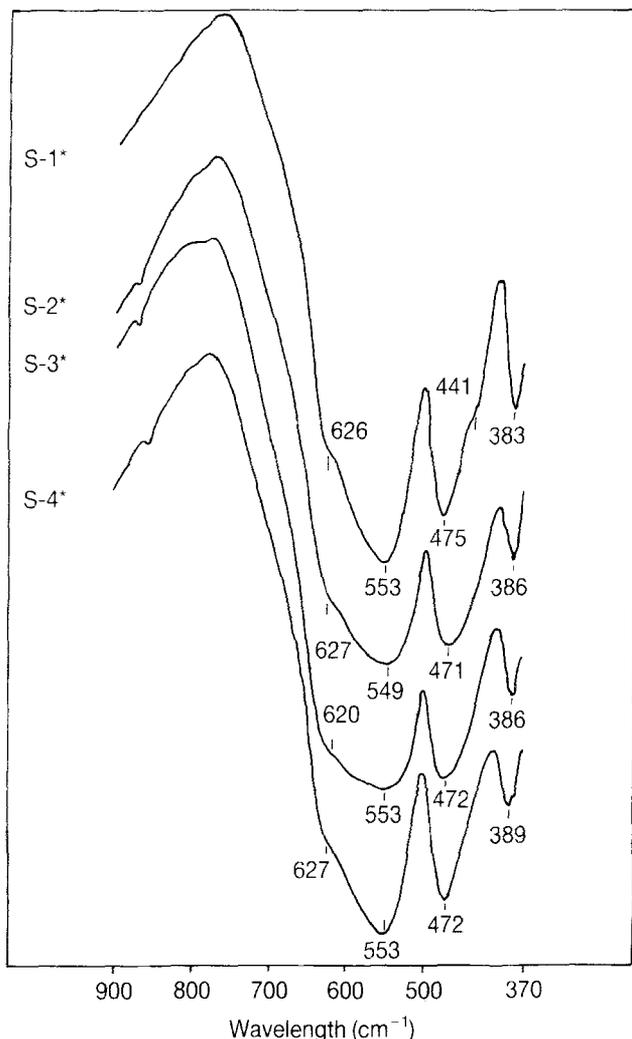
Figure 4 Fourier transform infrared spectra of samples S-1*, S-2*, S-3* and S-4* recorded at room temperature.
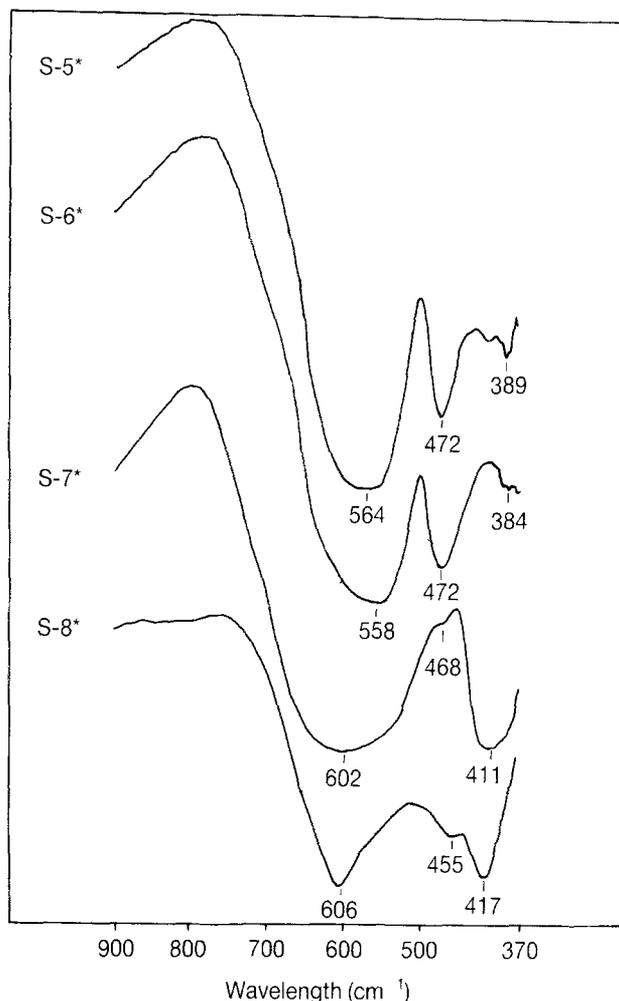
Figure 5 Fourier transform infrared spectra of samples S-5*, S-6*, S-7* and S-8* recorded at room temperature.

found in the surface layers of oxidized Invar alloy. Infrared bands of oxides of iron and nickel, from different literature sources, were summarized [19].

Infrared spectroscopy was also used to characterize nickel(II) hydroxide [20–23]. The infrared band observed in the range 450–475 cm^{-1} was interpreted as the nickel–oxygen stretching vibration.

The present FT–IR spectroscopic results, obtained for samples prepared in the system Fe_2O_3–NiO, can be summarized as follows. Figs 1 and 2 show FT–IR spectra of samples S-2 to S-9. The FT–IR spectrum of sample S-2 is characterized by two dominant infrared bands at 557 and 476 cm^{-1} and a weak intensity infrared band at 390 cm^{-1}. Two shoulders at 626 and 440 cm^{-1} are also visible. These infrared bands are typical for α-Fe_2O_3. FT–IR spectra of samples S-3 and S-4 are very similar to the spectrum of sample S-2. In the FT–IR spectra of samples S-5 and S-6 the shoulders at 436 and 438 cm^{-1} are pronounced, while the relative intensity of the infrared band at 384 cm^{-1} is decreased in relation to the infrared band at 390 cm^{-1}, recorded for sample S-2. The FT–IR spectrum of sample S-6 is also characterized by a broad infrared band with a transmission minimum at 600–564 cm^{-1}. Two dominant infrared bands at 602 and 407 cm^{-1} are observed in the FT–IR spectrum of

sample S-7, due to the presence of $NiFe_2O_4$. Changes in the FT–IR spectra of samples S-8 and S-9 can be ascribed to the appearance of NiO, characterized by an infrared band at 470 cm^{-1}.

Fig. 3 shows FT–IR spectra of samples S-10 to S-13. The FT–IR spectrum of sample S-10 is characterized by a very broad infrared band with a transmission minimum at 470–433 cm^{-1}. This spectrum indicates the transition from a two-phase system to a single-phase system. For the same sample, S-10, X-ray diffraction showed a broadening of diffraction lines corresponding to $NiFe_2O_4$. The shape of the FT–IR spectrum of sample S-11 is very similar to the previous spectrum. X-ray diffraction showed only the presence of NiO in sample S-11. On the basis of the similarity of the FT–IR spectra of samples S-10 and S-11, it can be supposed that in sample S-11, besides NiO, there is also "amorphous" $NiFe_2O_4$. FT–IR spectra of samples S-12 and S-13 can be ascribed to NiO. These spectra are characterized by a broad infrared band with a transmission minimum at 471 cm^{-1}.

The FT–IR spectra of samples S-1* to S-13* are shown in Figs 4–7. The FT–IR spectrum of sample S-1* is characterized by two dominant infrared bands at 553 and 475 cm^{-1}, a weak intensity infrared band at 383 cm^{-1} and two shoulders at 626 and

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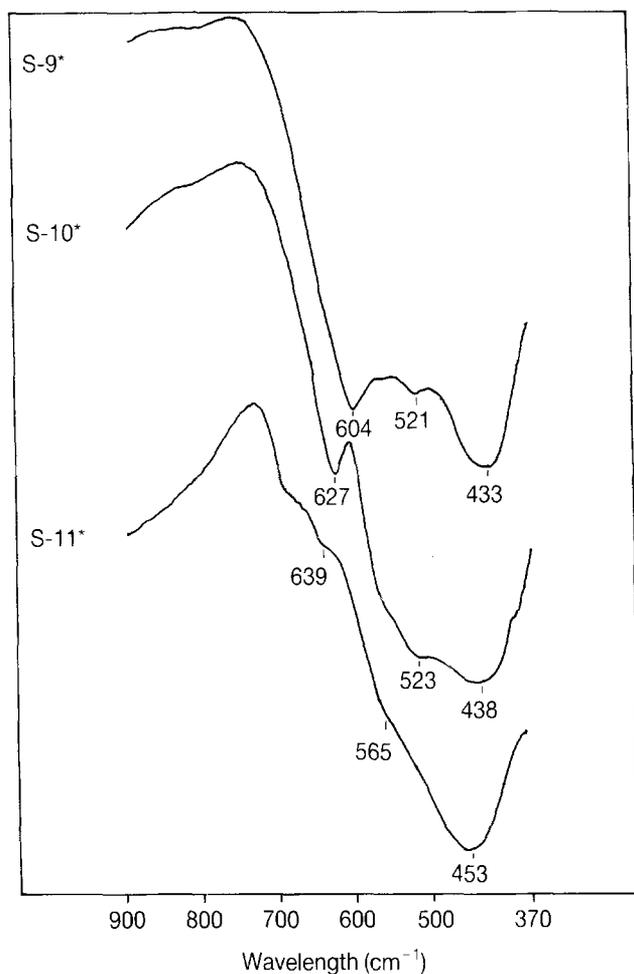
Figure 6 Fourier transform infrared spectra of samples S-9*, S-10* and S-11* recorded at room temperature.

Figure 7 Fourier transform infrared spectra of samples S-12* and S-13* recorded at room temperature.

441 cm^{-1}. These infrared band positions correspond to α-Fe$_2$O$_3$. As the content of α-Fe$_2$O$_3$ decreases, there is a corresponding decrease of the relative intensity of the infrared band at 383–389 cm^{-1}, and a disappearance of the shoulder at 441 cm^{-1}. Sample S-7* shows two very strong and broad infrared bands at 602 and 411 cm^{-1}, due to the presence of NiFe$_2$O$_4$. A further increase of the molar fraction of NiO introduces changes in the corresponding spectra. In the FT–IR spectrum of sample S-8*, the infrared bands corresponding to NiFe$_2$O$_4$, are shifted to 606 and 417 cm^{-1}. The infrared band appearing originally at 602 cm^{-1} for sample S-7* becomes a shoulder at 639 cm^{-1} for sample S-11*, while the infrared band originally at 411 cm^{-1} for sample S-7* overlaps the infrared band which corresponds to NiO. FT–IR spectrum of pure NiO prepared at 1100 °C (sample S-13*) is characterized by a broad infrared band with a transmission minimum at 466 cm^{-1}.

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