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# Non-isothermal decomposition of $NiC_2O_4$ -FeC<sub>2</sub>O<sub>4</sub> mixture aiming at the production of $NiFe_2O_4$

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# Abstract

The non-isothermal decomposition of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O–FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture was studied on heating to the formation of NiO–Fe<sub>2</sub>O<sub>3</sub> mixture at 350 °C in air atmosphere using thermogravimetry. Kinetic analysis of data according to the integral composite method showed that the oxidative decomposition of FeC<sub>2</sub>O<sub>4</sub> and NiC<sub>2</sub>O<sub>4</sub> are best described by the three-dimensional phase boundary model. The activation parameters were calculated and discussed. The solid products at different decomposition stages were identified using XRD, Mössbauer and FT-IR spectroscopic techniques. Some characteristic XRD lines of NiFe<sub>2</sub>O<sub>4</sub> start to appear at 800 °C beside the characteristic lines of NiO and Fe<sub>2</sub>O<sub>3</sub>, whereas at 1000 °C, only the characteristic lines of single phase cubic NiFe<sub>2</sub>O<sub>4</sub> appeared. The Mössbauer spectrum at 1000 °C fitted into two Zeeman sextets characteristic of Fe<sup>3+</sup> on the tetrahedral (A) and octahedral (B) sites of NiFe<sub>2</sub>O<sub>4</sub> inverse spinel. Consistent results were obtained using FT-IR where the absorption bands appeared at 602 and 407 cm<sup>-1</sup> for the mixture calcined at 1000 °C. These can be assigned to the intrinsic vibrations of tetrahedral and octahedral sites of NiFe<sub>2</sub>O<sub>4</sub>, respectively. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Ferrites are a broad class of complex magnetic oxides of considerable technological importance. Their remarkable electrical and magnetic properties depend up on the nature of the ions, their charges and their distribution among tetrahedral (A) and octahedral (B) sites [1].

Nickel ferrite is an inverse spinel in which eight units of NiFe<sub>2</sub>O<sub>4</sub> go into a unit cell of the spinel structure. Half of the ferric ions preferentially fill the tetrahedral sites (A-sites) and the other occupies the octahedral sites (B-sites). Thus, the compound can be represented by the formula  $(Fe_{1,0}^{3+})[Ni_{1,0}^{2+}Fe_{1,0}^{3+}]O_4^{2-}$ , where the round and square brackets represent A and B sites, respectively [1]. Nickel ferrite proved to be a good catalyst for the benzoylation of toluene with benzoyl chloride [2]. Also, it has a peculiar and extraordinary gas sensing capabilities towards low concentrations of chlorine gas in air [3].

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The specific physical behaviour of NiFe<sub>2</sub>O<sub>4</sub> can be considered as a function of its specific chemical and structural properties. For this reason, many researchers have paid attention to the different methods of its synthesis. Music et al. [4] investigated the chemical and structural properties of the system Fe<sub>2</sub>O<sub>3</sub>-NiO prepared by the thermal treatment of co-precipitated hydroxides or the solid-state reaction between NiO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> using X-ray diffraction, FT-IR and <sup>57</sup>Fe Mössbauer spectroscopic techniques. They found that the heating temperature rather than the heating time had the ultimate effect on the microstructure of NiFe2O4. Elmasry et al. [5] prepared nickel ferrite through the thermal decomposition of mixed nickel(II) and iron(III) nitrates at 1500 °C. Nanometre size NiFe<sub>2</sub>O<sub>4</sub> particles were synthesized by the citrate precursors technique. Control of solid-state reactivity yields monophasic ultrafine NiFe<sub>2</sub>O<sub>4</sub>. It was characterized by X-ray diffraction and BET surface area measurements [6]. Sol-gel method [7] using polyacrylic acid as a chelating agent was used to prepare NiFe<sub>2</sub>O<sub>4</sub> nanoparticles by calcining of the gel precursors in air at 300 °C for 2 h. The formation rate of

NiFe<sub>2</sub>O<sub>4</sub> prepared by mechanical alloying process of Fe<sub>2</sub>O<sub>3</sub>/ NiO simple oxide powder system using high energy ball milling has been investigated using X-ray diffraction and Mössbauer spectroscopy [8]. Shock wave treatment of nanosized mixture powders of ferric oxide and nickel oxide prepared by the co-precipitation method yields nanosized nickel ferrite with increased magnetization than that prepared by the conventional calcinations process [9].

The thermal decomposition of oxalates results in the production of oxides or metal possessing the characteristic necessary for its function as reactive solids. Therefore, much research has been done on their structures, properties and thermal behaviour. Various mechanisms of decomposition have been proposed [10]. A considerable amounts of information on the kinetics of the thermal dehydration and decomposition of the individual as well as mixed metal oxalates have been reported [11]. Diefallah et al. used DTA-TG, XRD and <sup>57</sup>Fe Mössbauer spectroscopy to study the thermal decomposition reactions in air of CdC<sub>2</sub>O<sub>4</sub>–FeC<sub>2</sub>O<sub>4</sub> [12] and MgC<sub>2</sub>O<sub>4</sub>–FeC<sub>2</sub>O<sub>4</sub> [13] mixtures both in with 1:2 mole ratio. They found that the ferrite formation starts to appear at 800 °C.

In the present work, a solid-state mixture of NiC<sub>2</sub>O<sub>4</sub>·2-H<sub>2</sub>O–FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture with the aim of the production of NiFe<sub>2</sub>O<sub>4</sub> spinel was prepared using the impregnation technique. The decomposition products at the different decomposition stages as well as the spinel ferrite formation were characterized using DTA-TG, XRD, FT-IR and <sup>57</sup>Fe Mössbauer spectroscopy. Mössbauer spectroscopy was also used to determine the cation distribution at both A and B sites in the system. The kinetics of the non-isothermal oxalate decomposition processes was studied in air.

The composite method of kinetic integral analysis was used both to identify the mechanistic equation describing the decomposition reaction and to calculate the activation parameters. The results were compared and discussed with respect to other integral methods of analysis of the nonisothermal data.

# 2. Experimental procedure

# 2.1. Materials

Individual metal oxalates, NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O or FeC<sub>2</sub>O<sub>4</sub>·2-H<sub>2</sub>O were prepared by co-precipitation method. Analytically pure reagents of NiCl<sub>2</sub>·6H<sub>2</sub>O of FeSO<sub>4</sub>·7H<sub>2</sub>O were dissolved in bidistilled water, and an equivalent amount of analytical reagent oxalic acid was added till complete precipitation occurred. The fine precipitate obtained in each case was filtered, washed with distilled water and dried.

 $NiC_2O_4 \cdot 2H_2O - FeC_2O_4 \cdot 2H_2O$  (1:2 mole ratio) mixture was prepared by the impregnation technique [18,19] in which few drops of bidistilled water was added to the proper mole ratios of the two metal oxalates with vigorous stirring to assure complete homogeneity. The wetted mixture was then dried at 100 °C for about 2 h.

Samples of the oxalate mixture were inserted into an electrical oven at room temperature, then the temperature was raised to the desired value (obtained from DTA-TG studies) and maintained for specified intervals. Samples were then removed and cooled in a desiccator to room temperature.

#### 2.2. Apparatus

Simultaneous DTA-TG experiments were performed using a Shimadzu DT-40 thermal analyser. The experiments were performed at different specified heating rates of 1, 2, 3 and 5 °C min<sup>-1</sup> in air at a flowing rate of  $3.0 \text{ lh}^{-1}$ . The sample mass in the Pt cell was kept at about 8 mg in all experiments, in order to assure a linear heating rate and accurate temperature measurements.

XRD patterns were obtained at room temperature using a Philips PW 1710 diffractometer which was equipped with Ni-filter and generates a beam of Co K  $_{\alpha}$  radiation ( $\lambda = 1.7889$  Å). The operational setting for the all XRD scans are voltage: 40 kV; current: 30 mA;  $2\theta = \text{range } 20-80^\circ$ ; scanning speed = 5° min<sup>-1</sup> and split width = 0.02°. For identification purposes, the relative intensities (*III*<sub>0</sub>) and the *d*-spacing (Å) were compared with standard diffraction patterns of the ASTM powder diffraction files.

<sup>57</sup>Mössbauer spectra were recorded at room temperature using an Austin Science Mössbauer effect spectrometer. A <sup>57</sup>Co–Rh source (Amersham) was used with an initial activity of 50 mCi. α-Fe spectrum is used for calibration of both observed velocities and hyperfine magnetic fields. The absorber thickness is approximately 10 mg cm<sup>-2</sup> of natural iron. The hyperfine interaction parameters were computed using an interactive least square 'Mos-90' program [14].

FT-IR spectra were obtained at a resolution  $4 \text{ cm}^{-1}$ , between 4000 and 200 cm<sup>-1</sup>, using a model FT-IR 310 Jasco spectrometer (Japan). The specimens were pressed in KBr discs. The spectra were represented as relative transmittance versus wave number (cm<sup>-1</sup>).

# 3. Kinetic consideration

The kinetics of the non-isothermal decomposition is considered here in view of three integral methods: the Ozawa method [15], the Coats–Redfern method [16] and the Diefallah composite method [12,13,17], based either on the modified Coats–Redfern equation [18]; (composite method I) or on Doyle's equation [19]; (composite method II).

According to the composite method I, when use was made of the modified Coats-Redfern equation [18]

$$\frac{g(\alpha)}{T^2} = \frac{AR}{\beta E} e^{-E/RT},\tag{1}$$

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(2)

the equation was rewritten in the form

 $\ln\left[\frac{\beta g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT},$ 

where  $g(\alpha)$  is the kinetic model function calculated for the fraction reacted  $\alpha$  at temperature *T* and heating rate  $\beta$ , and is given by the equation

$$\frac{g(\alpha)}{T^2} = \frac{A}{R} \int_0^T \exp(-E/RT) dT,$$
(3)

where A is the frequency factor and E is the activation energy. The dependence of  $\ln[\beta g(\alpha)/T^2]$ , which was calculated for different  $\alpha$ -values at their respective  $\beta$ values, on 1/T must give rise to a single master straight line for the correct form of  $g(\alpha)$ , and hence a single activation energy and frequency factor can be calculated readily. In a similar way, according to composite method II, the Doyle's equation has been rewritten in the form:

$$\log(\beta g(\alpha)) = \left[\log\frac{AE}{R} - 2.315\right] - 0.4567\frac{E}{RT}.$$
(4)

Again, the dependence of  $\log g(\alpha)\beta$ , calculated for the different  $\alpha$ -values at their respective  $\beta$ -values on 1/T must give rise to a single master straight line for the correct form of  $g(\alpha)$ . A computer program [20] has been written to perform the data analysis using the different models of heterogeneous solid-state reactions [17] listed in Table 1. The results of the calculation allow choosing the kinetic mechanism which best fit the data and give the highest correlation coefficient and the lowest standard deviation. The program also calculates the activation energy (*E*) and the frequency factor (*A*) from the slope and intercept of the linear fit line.

In the Ozawa method [15] the activation energy is calculated from the thermogravimetric data obtained at different heating rates using the equation

$$-\log(\beta) = 0.4567(E/RT) + \text{constant}$$
(5)

Table 1

Kinetic equations examined in this work

and the frequency factor is calculated from the equation

$$\log A = \log g(\alpha) - \log \left[ \frac{E}{\beta R} p\left(\frac{E}{RT}\right) \right].$$
(6)

In the Coats–Redfern method [16], the function  $g(\alpha)$  is approximated to the form:

$$g(\alpha) = \frac{ART^2}{\beta E} \left[ 1 - \frac{2RT}{E} \right] e^{-E/RT}.$$
(7)

This equation has been written in the form:

$$-\ln\left[\frac{g(\alpha)}{T^2}\right] = -\ln\frac{AR}{\beta E}\left[1 - \frac{2RT}{E}\right] + \frac{E}{RT}.$$
(8)

The quantity  $\ln(AR/\beta E)(1 - 2RT/E)$  is reasonably constant for most values of *E* and in the temperature range over which most reactions occur.

# 4. Results and discussion

#### 4.1. DTA-TG studies

Thermal decomposition studies of NiC2O4·2H2O-FeC2-O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture show that the mixture dehydrate and decompose through three well defined steps in the temperature range from 140 to 350 °C. A typical DTA-TG thermogram measured at 5 °C min<sup>-1</sup> is shown in Fig. 1. The thermogravimetry (TG) curve implies the dehydration of the mixture at 140-190 °C with a mass loss of 19.0% compared with expected mass loss of 19.9% corresponding to the complete dehydration of the mixture with the formation of anhydrous oxalate mixture, NiC<sub>2</sub>O<sub>4</sub>-FeC<sub>2</sub>O<sub>4</sub>. This was followed immediately by a mass loss of 24.5% up to about 250 °C attributed to the oxidative decomposition of FeC<sub>2</sub>O<sub>4</sub> in the mixture with the formation of NiC<sub>2</sub>O<sub>4</sub>-Fe<sub>2</sub>O<sub>3</sub> mixture (theoretical mass loss, 23.6%). The mixture is thermally stable up to a temperature of 290 °C after which the nickel oxalate content starts to decompose giving a mass loss of 13.5% at 330 °C. This

Reaction model	$g(\alpha)$	Symbol
One-dimensional diffusion	$\alpha^2$	$D_1$
Two-dimensional diffusion	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	$D_1$ $D_2$
Jander equation, three-dimensional diffusion	$[1 - (1 - \alpha)^{1/3}]^2$	$D_3^2$
Ginsling-Braunshtein equation, three-dimensional diffusion	$(1-2/3\alpha) - (1-\alpha)^{2/3}$	$D_4$
Two-dimensional phase boundary reaction	$[1 - (1 - \alpha)^{1/2}]$	$R_2$
Three-dimensional phase boundary reaction	$[1 - (1 - \alpha)^{1/3}]$	R <sub>3</sub>
First order kinetic, Mampel unimolecular law	$\left[-\ln(1-\alpha)\right]$	F <sub>1</sub>
Random nucleation: Avrami equation	$[-\ln(1-\alpha)]^{1/2}$	$A_2$
Random nucleation: Erofeev equation	$[-\ln(1-\alpha)]^{1/3}$	A <sub>3</sub>
Exponential law	$\ln \alpha$	$E_1$



Fig. 1. DTA-TG curves of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O –FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture in air at heating rate of 5 °C min<sup>-1</sup>.

makes the total mass loss to 57.0%, which is close to that expected (56.8%) for the over all conversion of NiC<sub>2</sub>O<sub>4</sub>·2-H<sub>2</sub>O-FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture to NiO-Fe<sub>2</sub>O<sub>3</sub> mixture.

DTA curve shows peaks that closely correspond to the mass loss observed on the TG trace. The two broad overlapped endothermic peaks in the temperature range 150-190 °C with peak's temperature at 170 and 183 °C are attributed to the successive dehydration of NiC2O4.2H2O and FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in the mixture. These dehydration temperatures suggest that the water molecules present in the crystalline hydrate as co-ordinately linked as well as a crystal water [17]. The two broad overlapped exothermic DTA peaks in the temperature range of 200-240 °C (at 213 and 220 °C) accompanied the FeC<sub>2</sub>O<sub>4</sub> decomposition step, which suggests that the decomposition is through two steps. Macklen [21] proposed that the oxidation of ferrous ion was the first step in the decomposition of ferrous oxalate in an oxidizing atmosphere, and this was immediately followed by bond rupture of the relatively unstable oxidation product to evolve CO<sub>2</sub>. The broad exothermic peak in the temperature range 305-324 °C with the peak temperature at 318 °C characterizes the thermal decomposition step of NiC<sub>2</sub>O<sub>4</sub>. The exothermic nature of the decomposition is attributed to the oxidation of CO evolved on decomposition to  $CO_2$  [10].

From the above results it was obvious that the decomposition behaviour of  $NiC_2O_4$ · $2H_2O$  or  $FeC_2O_4$ · $2H_2O$  in their mixture is similar to that of the individual metal oxalates [10,21] which indicate that each metal oxalate behaves as it was present alone in the mixture, and that no chemical reactions can takes place between the two metal oxalates. Also, DTA-TG curves gives information about the minimum temperatures needed for the calcination processes. Consequently, samples of the mixture were calcined to characterize the decomposition products at different

stages and following the ferrite formation at 30 min at 250 °C, 30 min at 350 °C, 2 h at 600 °C, 2 h at 800 °C and 2 h at 1000 °C. For simplicity, these different calcined mixtures are denoted in the text by NiFe, followed by the calcination temperature. Thus NiFe-250 indicates a mixture calcined at 250 °C.

#### 4.2. X-ray diffraction

The characteristic parts of the X-ray powder diffraction patterns of (NiFe) mixture annealed at various temperatures are shown in Fig. 2. The parent mixture, NiFe gave the individual characteristic lines of both NiC2O4·2H2O (JCPDS file No. 25-582) and FeC2O4·2H2O (JCPDS file No. 23-293). A nearly amorphous pattern was obtained for the NiFe-250 mixture (Fig. 2(b)). This behaviour is attributed to the formation of fine grained (or possibly even amorphous) iron(III) oxide. For the NiFe-350 mixture (Fig. 2(c)), the obvious broadening of the all diffraction peaks suggests that the size of iron(III) oxide particles is still relatively small. The increase in the annealing temperature yields an increased sharpness of the major peaks, that is, the growth of the grain size of iron(III) oxide. This behaviour is clear in the XRD of NiFe-600 mixture (Fig. 2(d)) which shows the characteristic XRD lines of Fe<sub>2</sub>O<sub>3</sub> with larger grain size (JCPDS file No. 13-534) and NiO (JCPDS file No. 4-835). The unit cell parameters [22] of NiFe<sub>2</sub>O<sub>4</sub> is very close to twice as large as that of NiO. Both compounds posses the fcc crystal structure and for this reason, NiO does not exhibit independent diffraction lines. No separation between overlapped diffraction lines of these two compounds was detected for sample where both compounds were present even at high Bragg angles. For such samples the changes in the fraction of NiO and NiFe<sub>2</sub>O<sub>4</sub> can be followed by comparison of the intensities of overlapped



Fig. 2. Characteristic parts of XRD patterns of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O–FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture calcined at different temperatures. (a) parent mixture, (b) mixture calcined at 250 °C, (c) mixture calcined at 350 °C, (d) mixture calcined at 600 °C, (e) mixture calcined at 800 °C and (f) mixture calcined at 1000 °C. Phases: ( $\Delta$ ) NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, (+) FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, ( $\bigcirc$ ) Fe<sub>2</sub>O<sub>3</sub>, (×) NiO and ( $\bigcirc$ ) NiFe<sub>2</sub>O<sub>4</sub>.

diffraction lines belonging to both compounds with the intensities of diffraction lines belonging only to NiO. Thus, comparing the XRD patterns of NiFe-600 and NiFe-800 mixtures (Fig. 2(d) and (e), respectively) it is clear that, the new two peaks appear in the pattern of NiFe-800 together

with  $Fe_2O_3$  and NiO peaks are attributed to the formation of spinel ferrite,  $NiFe_2O_4$  (JCPDS file No. 10-325). Also, the overlapping of  $NiFe_2O_4$  peaks with NiO peaks leads to an increase in the peak's intensities compared to NiFe-600 pattern. X-ray diffraction pattern of NiFe-1000 mixture

(Fig. 2(f)) shows only the characteristic peaks of the singlephase ferrite,  $NiFe_2O_4$ , crystallized in the cubic system. At the same time, no peaks attributed to  $Fe_2O_3$  and/or NiO were detected.



Fig. 3. The Mössbauer spectra of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O–FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture calcined at different temperatures: (a) parent mixture, (b) mixture calcined at 250 °C, (c) mixture calcined at 350 °C, (d) mixture calcined at 600 °C, (e) mixture calcined at 800 °C and (f) mixture calcined at 1000 °C.

# 4.3. Mössbauer spectroscopy

The room temperature Mössbauer spectra of NiFe mixture annealed at different temperatures are shown in Fig. 3. The spectral parameters such as isomer shift ( $\delta$ ), quadrupole splitting ( $\Delta E_{\rm O}$ ) and hyperfine magnetic splitting (H) are computed and summarized in Table 2. Spectrum of NiFe mixture (Fig. 3(a)) is fitted with a doublet that is assigned to divalent iron in FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2-</sub> O. The obtained Mössbauer parameters are in good agreements with the values reported by Brady and Duncan [23]. Spectrum of Nife-250 and NiFe-350 mixtures (Fig. 3(b) and (c), respectively) are fitted with a doublet with a very small magnetically split pattern and a sextet subspectra, which are characteristic of iron(III) oxide having two different magnetic states. The doublet is owing to the paramagnetic finely divided (nearly amorphous) iron(III) oxide, while the sextet is attributed to magnetically oriented iron(III) oxide. Diefallah et al. [17] have defined a similar paramagnetic behaviour in ultrafine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles prepared by calcination of CdC<sub>2</sub>O<sub>4</sub>-FeC<sub>2</sub>O<sub>4</sub> mixture at 250 °C. The ratio of the different magnetic phases is based on the calculated absorption ratio of the two subspectra. In agreement with the previous XRD results, which show an evolution in the crystallinity of Fe<sub>2</sub>O<sub>3</sub> as the temperature increased, the ratio of the paramagnetic phase (Table 2) was observed to decrease with rising the annealing temperature. The hyperfine magnetic splitting obtained at 350 °C (497 kOe) is significantly less than the reported value [24], for iron(III) oxide with a larger particle size, of 515 kOe. The paramagnetic component disappears completely by raising the annealing temperature to 600 °C (Fig. 3(d)). The hyperfine magnetic splitting of the obtained sextet (510 kOe) is very close to the normal value of iron(III) oxide. The Mössbauer spectrum of NiFe-800 mixture

Table 2

Mössbauer parameters for  $NiC_2O_4$ :2H<sub>2</sub>O-FeC<sub>2</sub>O<sub>4</sub>:2H<sub>2</sub>O (1:2 mole ratio) mixture calcined at different temperatures

Mixture	Sub- spectra	Area (%)	Isomer shift ( $\delta$ ) ( $\pm 0.02$ mm s <sup>-1</sup> )	Quadrupole splitting $(\Delta E_Q)$ $(\pm 0.02$ mm s <sup>-1</sup> )	Hyperfine filed ( <i>H</i> ) (±5 kOe)
NiFe	Doublet	100	1.26	1.70	_
NiFe-250	Doublet	23	0.41	-0.68	_
	Sextet	77	0.51	0.49	546
NiFe-350	Doublet	6	0.40	-0.45	_
	Sextet	94	0.44	-0.20	497
NiFe-600	Sextet	100	0.44	-0.21	510
NiFe-800	Sextet	85	0.44	-0.19	512
	(A) site	15	0.27	0.06	486
NiFe-1000	(A) site	49	0.44	0.01	488
	(B) site	51	0.32	0.01	518

(Fig. 3(e)) is fitted into two six-line patterns. The first sextet is assigned to iron(III) oxide as revealed from XRD, and the other one is attributed to  $Fe^{3+}$  ions at one of the two distinct crystallographic sites of NiFe<sub>2</sub>O<sub>4</sub>. It can be assigned to the tetrahedral (A) site on the bases of the isomer shift and the hyperfine magnetic splitting values obtained (Table 2). In most magnetically ordered spinel ferrites the hyperfine magnetic splitting due to  $Fe^{3+}$  ions at A sites is usually smaller than that of  $Fe^{3+}$  ions at B sites [25]. The spectrum of

NiFe-1000 mixture (Fig. 3(f)) exhibits the normal two clearly split Zeeman sextets. One is due to Fe<sup>3</sup> ions at the tetrahedral (A) sites, and the other is due to Fe<sup>3+</sup> ions at the octahedral (B) sites. The relative number of Fe<sup>3+</sup> ions on A and B sites is determined by knowing the area under the resonance lines due to these ions. Since the spectrum is well resolved into two Zeeman sextets with nearly equal areas of A and B subspectra (Table 2), then the cation distribution may be described by the chemical formula:  $(Fe_{1.0}^{3+})[Ni_{1.0}^{2+}Fe_{1.0}^{3+}]O_{2}^{2-}$ .



Fig. 4. FT-IR spectra of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O–FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture calcined at different temperatures: (a) parent mixture, (b) mixture calcined at 250 °C, (c) mixture calcined at 350 °C, (d) mixture calcined at 600 °C, (e) mixture calcined at 800 °C and (f) mixture calcined at 1000 °C.

#### 4.4. FT-IR spectral studies

The present FT-IR spectroscopic results obtained for NiFe mixture calcined at different temperatures were summarized in Fig. 4. Consistent with the presence of the oxalate moiety in the parent mixture; NiFe (Fig. 4(a)), the bands appeared (at 1317 and 1362  $\text{cm}^{-1}$ ) and (at  $1632 \text{ cm}^{-1}$ ) are assigned to O-C-O symmetric and asymmetric stretches, respectively. The bands obtained at 812 and 493 cm<sup>-1</sup> are assigned to C=C-O and O-C-O bending vibration, respectively [26]. The broad band at  $3385 \text{ cm}^{-1}$  is assigned to the water of hydration in the mixture. FT-IR spectrum of NiFe-250 mixture (Fig. 4(b)) shows the same bands as those appear in the parent mixture, which are assigned to the presence of nickel oxalate. Schwertmann and Taylor [27] suggested that the characteristic IR bands at 540, 470 and 345  $\text{cm}^{-1}$  could be used as fingerprints in the identification of hematite. The presence of the foreign ions as well as the degree of crystallinity strongly affects the location of these bands. Yariv and Mendelovici [28] showed that three strong absorption bands characterize the poorly crystalline hematite at 530, 445 and  $308 \text{ cm}^{-1}$ , which were assigned to  $O^{2-}$  displacement. Thus, the FT-IR bands that appear at 550, 450 and 325 cm<sup>-1</sup> in the spectrum of NiFe-250 mixture (Fig. 4(b)) are assigned to poorly crystalline iron(III) oxide. The band at  $3400 \text{ cm}^{-1}$  is assigned to the stretching O-H band which is attributed to the absorption of moisture from the air by the fine granules of iron(III) oxide [29]. The FT-IR spectrum of NiFe-350 and NiFe-600 mixtures (Fig. 4(c) and (d), respectively) are characterized by two dominant bands at 540 and 470 cm<sup>-1</sup> and a weak intensity band at  $390 \text{ cm}^{-1}$ . Two shoulders at 626 and 430 cm<sup>-1</sup> are also visible. These bands are typical for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [22]. Also, the band observed in the range 450-475 cm<sup>-1</sup> was interpreted as the nickel-oxygen stretching vibration. In the FT-IR spectrum of NiFe-800 mixture (Fig. 4(e)), the bands appear at 530, 460, 430 and  $390 \text{ cm}^{-1}$  are assigned to Fe<sub>2</sub>O<sub>3</sub>. The appearance of the new band 596 cm<sup>-1</sup> is attributed to the presence of NiFe<sub>2</sub>O<sub>4</sub>.

Waldron [30] attributed the band  $\nu_1$  at around 600 cm<sup>-1</sup> to the intrinsic vibration of tetrahedral metal oxygen complexes and the band  $\nu_2$  at around 400 cm<sup>-1</sup> to the intrinsic vibration of octahedral metal oxygen complexes. Thus, the band appears at 596 cm<sup>-1</sup> is assigned to the intrinsic vibration of the tetrahedral complex in agreement with the Mössbauer results previously reported. Two dominant bands at 602 and 407 cm<sup>-1</sup> are observed in the FT-IR spectrum of NiFe-1000 mixture (Fig. 4(f)), due to the presence of NiFe<sub>2</sub>O<sub>4</sub> [22].

## 4.5. Kinetic studies

Analysis of dynamic data for the oxalate decomposition steps in NiFe mixture (viz. the second and the third decomposition steps) were carried out at heating rates of 1, 2, 3 and 5 °C min<sup>-1</sup>. The fractional reaction remaining as a function of temperature for the oxalate decomposition reactions are shown in Fig. 5. The composite method of analysis performed a complete analysis of all nonisothermal curves into a single master curve. A deviations from the straight-line relationship are interpreted in the terms of multi-step reaction mechanisms [15,17]. The method allows us to choose the kinetic model which best fits the data, and gives the highest correlation coefficient and the lowest standard deviation. The results always show that [13,17] both composite methods equivalent curves and nearly identical values for the activation parameters. The values of the activation parameters for the non-isothermal decomposition of  $FeC_2O_4$  and  $NiC_2O_4$  in their mixture that were calculated according to the composite method II, assuming the different kinetic models are reported in Table 3. From the table, it is clear that, the oxalate decomposition reactions are best described by the two- and three-dimensional phase boundary and random nucleation models. The exponential low and the other models gave less satisfactory fit of data. Fig. 6 shows the results of the kinetic data analysis for the oxalate decomposition reactions calculated using the three-dimensional phase boundary



Fig. 5. Dynamic measurements for the thermal decomposition of  $NiC_2O_4$ :  $2H_2O-FeC_2O_4$ :  $2H_2O$  (1:2 mole ratio) mixture in air, (a) decomposition of  $FeC_2O_4$  to  $Fe_2O_3$  and (b) decomposition of  $NiC_2O_4$  to NiO. Heating rate: curve A, 1 °C min<sup>-1</sup>; curve B, 2 °C min<sup>-1</sup>; curve C, 3 °C min<sup>-1</sup> and curve D, 5 °C min<sup>-1</sup>.

Table 3

 $Activation\ parameters\ of\ the\ non-isothermal\ decomposition\ in\ air\ of\ FeC_2O_4\ and\ NiC_2O_4\ in\ their\ mixture,\ calculated\ according\ to\ the\ composite\ method\ II,\ assuming\ different\ kinetic\ models$ 

Model	Decomposition of FeC <sub>2</sub> O <sub>4</sub> (step II)			Decomposition of NiC <sub>2</sub> O <sub>4</sub> (step III)		
	$E (\mathrm{kJ}\mathrm{mol}^{-1})$	$\log A \ (\min^{-1})$	<i>r</i> *	$E (\mathrm{kJ}\mathrm{mol}^{-1})$	$\log A \ (\min^{-1})$	$r^*$
D <sub>1</sub>	$223 \pm 12$	$23.0 \pm 1.4$	0.879	357 ± 22	$30.5 \pm 2.1$	0.862
$D_2$	$245 \pm 13$	$24.9 \pm 1.5$	0.891	$370 \pm 24$	$32.2 \pm 2.3$	0.849
$D_3$	$264 \pm 14$	$27.0 \pm 1.5$	0.905	$407 \pm 29$	$34.1 \pm 2.6$	0.832
$D_4$	$253 \pm 13$	$25.1 \pm 1.5$	0.896	$388 \pm 26$	$32.4 \pm 2.4$	0.843
R <sub>2</sub>	$134 \pm 5$	$13.3 \pm 0.6$	0.935	$221 \pm 8$	$18.7 \pm 0.8$	0.940
R <sub>3</sub>	$140 \pm 5$	$13.8 \pm 0.6$	0.972	$227 \pm 9$	$19.1 \pm 0.9$	0.970
$F_1$	$153 \pm 7$	$15.8 \pm 0.6$	0.956	$244 \pm 12$	$21.0 \pm 1.1$	0.914
A <sub>2</sub>	$81 \pm 1$	$8.3 \pm 0.4$	0.920	$150 \pm 8$	$12.7 \pm 0.5$	0.957
A <sub>3</sub>	$57 \pm 1$	$5.9 \pm 0.5$	0.818	$120 \pm 6$	$9.9 \pm 0.6$	0.898
$E_1$	$94 \pm 30$	$11.0 \pm 3.6$	0.625	$98 \pm 29$	$9.3 \pm 2.8$	0.285

 $(R_3)$  model according to the composite method based on Doyle's equation. Analysis of the dynamic data was also carried out using the Ozawa and Coats–Redfern methods, assuming also the  $R_3$  model, and the results were compared with those obtained using the composite method of analysis. The results of the different methods are shown in Table 4. The three methods of calculation show similar activation parameters for the thermal decomposition of  $FeC_2O_4$ . The values calculated by the Coats–Redfern method for the decomposition of NiC<sub>2</sub>O<sub>4</sub> within experimental errors agree with that calculated by the composite method. However, these results do not show agreement with values calculated by the Ozawa method. In many cases [13,29], the activation energies estimated by the composite method are, within



Fig. 6. Composite analysis of TG data for the non-isothermal decomposition of NiC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O–FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O (1:2 mole ratio) mixture in air based on Doyle's equation assuming: (1)  $R_3$  model and (2)  $E_1$  model. (A) Decomposition of FeC<sub>2</sub>O<sub>4</sub> and (C) decomposition of NiC<sub>2</sub>O<sub>4</sub>.

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Table 4

 $Activation \ parameters \ of \ the \ non-isothermal \ decomposition \ in \ air \ of \ FeC_2O_4 \ and \ NiC_2O_4 \ in \ their \ mixture \ calculated \ according \ to \ R_3 \ model$ 

Method of analysis	Decomposition of FeC <sub>2</sub> O <sub>4</sub> (step II)		Decomposition of NiC <sub>2</sub> O <sub>4</sub> (step III)	
	E (kJ mol <sup>-1</sup> )	$\log A \; (\min^{-1})$	E (kJ mol <sup>-1</sup> )	$\log A \ (\min^{-1})$
Composite method II	$140 \pm 5$	$13.8 \pm 0.6$	$227 \pm 9$	$19.1 \pm 0.9$
Coats-Redfern	$140 \pm 7$	$10.9 \pm 0.6$	$250 \pm 20$	$13.9 \pm 0.8$
Ozawa	$140 \pm 10$	$14.0 \pm 1.4$	$157 \pm 14$	$17.2\pm0.9$

experimental errors, in good agreement with the values estimated using the model-free method of Ozawa.

Dollimore [10] has been discussed the different decomposition mechanisms for the metal oxalates and found that for the oxalates of divalent metals, the extent to which the metal–O bond is covalent depends on the electronegativity of the metal. Decomposition will occur when a temperature is reached at which rupture of the M–O link is possible, or at which rupture of the C–O bond occurs. For the oxalates which produce the metal in nitrogen atmosphere, the decomposition temperature represents the temperature at which the M–O bond is ruptured and will depend critically on the size and charge of the metal ion. The decomposition of NiC<sub>2</sub>O<sub>4</sub> in nitrogen atmosphere gives Ni metal, and the decomposition of FeC<sub>2</sub>O<sub>4</sub> gives Fe, Fe<sub>3</sub>O<sub>4</sub> and a trace of FeO. In air, the metal formed in the decomposition is oxidized to metal oxide [11].

Since the composite method of analysis gives the least calculated standard deviation for the activation parameters than the other methods (Table 4), then the data will be discussed according to this method. The reported activation energy for the thermal decomposition of  $FeC_2O_4$  (Table 4) is in agreement with that present in the literature [11-13]. The activation energy obtained (163 kJ mol<sup>-1</sup>) from the non-isothermal kinetic of the thermal decomposition of NiC<sub>2</sub>O<sub>4</sub> found by Palanismy et al. [31] using the Coats-Redfern method is very small compared with that reported in Table 4. This is due to the presence of Fe<sub>2</sub>O<sub>3</sub> (produced from the thermal decomposition of FeC<sub>2</sub>O<sub>4</sub>) in the vicinity of NiC<sub>2</sub>O<sub>4</sub>. The electronegativity of  $Fe^{3+}$  (1.9) is higher than that of Ni<sup>2+</sup> (1.8) [32] so that the presence of  $Fe^{3+}$ ions with NiC<sub>2</sub>O<sub>4</sub> results in an increased negative on the nickel ion. Thus a more covalent type of bond thus occurs in the mixed oxalate than in pure NiC<sub>2</sub>O<sub>4</sub>. This results in strengthening of Ni-O bond and an increase in the activation energy of NiC2O4 decomposition. The electronegativity of Ni<sup>2+</sup> has no effect on the decomposition of  $FeC_2O_4$  since both Ni<sup>2+</sup> and Fe<sup>2+</sup> has the same electronegativity [32].

Generally, in NiC<sub>2</sub>O<sub>4</sub>–FeC<sub>2</sub>O<sub>4</sub> mixture, the activation energy for the thermal decomposition of NiC<sub>2</sub>O<sub>4</sub> is higher than that of FeC<sub>2</sub>O<sub>4</sub> (Table 4). The radius of Ni<sup>2+</sup> (0.72 Å) is smaller than that of Fe<sup>2+</sup> (0.76 Å), so that Ni<sup>2+</sup> would have a stronger metal-oxygen bond than Fe<sup>2+</sup>.

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