

Some aspects of thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$

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Abstract

$\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposition in air and in helium was studied using TG, DTA and MS and FTIR analyses. It was found that the dehydration phase of reaction is not complete. Remaining water occluded in the pores of nickel oxalate is not liberated until the decomposition of oxalate ions starts. The residual water takes part in reaction of the basic nickel carbonate formation. The basic nickel carbonate decomposition is a source of traces of nickel oxide stated in the final product of decomposition along with metallic nickel. It was found that the double peak endothermic DTA signal which accompanies decomposition of nickel oxalate results from changing of the microscopic mechanism of reaction.

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1. Introduction

Thermal decomposition $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ has been studied for many years. In the extensive reports on thermal decomposition of oxalates [1,2] the number of references concerning this process are cited. Despite the numerous works and publications on thermal decomposition of nickel oxalate dihydrate this reaction still remains the subject of investigations.

There are several effects that accompany this reaction which still have no clear explanation and give rise to many controversies. One of them is incomplete dehydration process and an inability to obtain anhydrous compound. The possibility of obtaining anhydrous nickel oxalate was discussed in several works. In paper [3] Authors stated that dried nickel oxalate can take up to 15% of original water on storing on air and that this water can be completely removed about 250 °C. Authors of Ref. [4] stored dehydrated nickel oxalate at 200 °C in the desiccator over P_2O_5 for 2 years to remove residual water. After this time nickel oxalate re-absorbed 15% of water. Dehydration of nickel oxalate dihydrate in the dynamic vacuum led to the compound

of composition 99.2% NiC_2O_4 and 0.8% H_2O [5]. The residual water was considered as the occluded water [6,7]. All the results quoted indicate that complete dehydration of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ to obtain anhydrous nickel oxalate cannot be achieved. However, in other papers full dehydration of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was stated and the kinetics of decomposition of anhydrous nickel oxalate was determined [8].

The second unexplained effect related to nickel oxalate decomposition in inert atmosphere is the complex DTA/DSC peak corresponding to oxalate ions degradation. The complexity of DTA or DSC curve, manifested by a shoulder on the peak, was pointed out in many works [2,5–7,9–11]. The same shape shows the DTG curve [9]. The different explanations of this effect were given. It was supposed to be connected with the phase transition of nickel at Curie point [7,9] or with the formation of solid intermediate [8]. The secondary reaction of nickel with residual water was indicated as the cause of complex DTA signal in Ref. [5]. In Ref. [12] three stage mechanism of decomposition of NiC_2O_4 was proposed and the differences in the particular reactions rate were assumed to be responsible for the complex DTA curve.

And finally there are still controversies concerning the primary and secondary reactions occurring during $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposition. In most experiments performed in air NiO was

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claimed to be the primary product of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposition. However, Authors of Refs. [10,13] suggest that the primary product of decomposition is Ni and NiO forms in result of secondary oxidation of nickel by oxygen. Almost everybody agrees that decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in inert atmosphere leads to the formation of Ni and CO_2 , however some Authors suggest that Ni forms due to the reduction of the primary product NiO by CO in secondary reaction [14]. During decomposition in the atmosphere of CO_2 metallic Ni was found as the product of NiC_2O_4 decomposition by Authors of Ref. [10] whereas in paper [15] the final product of decomposition was NiO.

The objective of this work is to present new results concerning mentioned effects which shall throw some light on these controversial points in thermal decomposition of nickel oxalate dihydrate.

2. Experimental

2.1. Preparation of nickel oxalate

Nickel oxalate dihydrate was prepared by the reaction of nickel nitrate(V) with oxalic acid in aqueous solution at about 65°C for 4 h (all chemicals were of analytical grade Polskie Odczynniki Chemiczne S.A.). pH 4.0 of the mixture was maintained with ammonia and hydrochloric acid to avoid precipitation of nickel hydroxide. Next, crystalline precipitate was filtered, washed with dilute oxalic acid and finally with an absolute alcohol. The product obtained was dried at 50°C on air.

2.2. Experimental techniques

Thermal decomposition measurements were performed with an apparatus that enabled simultaneous recording of TG and DTA signals (SDT 2960 TA INSTRUMENTS). The samples of mass from the range 6 to 20 mg were heated in a standard platinum sample pan. The experiments were carried out in dynamic flow of helium (99.999%) or synthetic air (<15 ppm H_2O). The gas flow rate was $0.1 \text{ dm}^3 \text{ min}^{-1}$ and the volume of thermoanalyzer was 0.06 dm^3 .

The analysis of gaseous products of decomposition was carried out using a quadrupole mass spectrometer (QMD 300 THERMOSTAR BALZERS) connected on-line with SDT 2960 apparatus by the heated quartz capillary. The mass spectrometer was operated with an electron impact ionizer with energy 0.112 aJ (70 eV). Mass spectra were recorded for m/z equal to 18, 28, 32 and 44 which correspond to ions: H_2O^+ , CO^+ , O_2^+ and CO_2^+ , respectively.

CRTA (Constant Rate Thermal Analysis) measurements [16] were performed on an apparatus designed and built in MADIREL Laboratory. This apparatus controls the vacuum pressure signal above the sample at a predetermined constant value. The PID type regulation uses the pressure gauge input to regulate the heating of sample such that the pre-set pressure value, a resultant of vapour from the reaction, is obtained and remains constant until the end of the experiment where there is no more vapour produced by the thermolysis. In experiment the pre-set pressure value was 2 Pa.

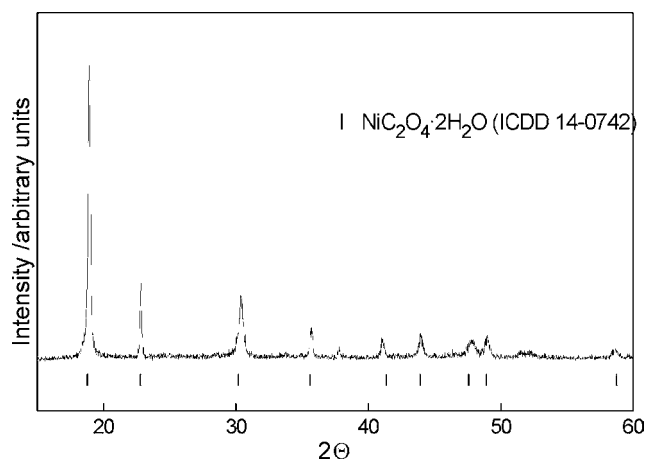


Fig. 1. XRD pattern of the initial sample of nickel oxalate dihydrate.

X-ray diffraction analyses were carried out on Philips X-ray diffractometer using $\text{Cu K}\alpha$ radiation.

FTIR and HT-DRIFT (High Temperature Diffuse Reflexion Infrared Fourier Transform) spectroscopy measurements were performed on an Equinox 55.

3. Results and discussion

The initial sample was analysed for the oxalate ions content by wet analysis and for the nickel content by gravimetric analysis with dimethylglyoxime. Analysis showed that the molar ratio $\text{Ni}^{2+}/\text{C}_2\text{O}_4^{2-}$ was 0.97 ± 0.03 . X-ray powder diffraction analysis confirmed that the only component of initial sample was $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (ICDD 14-0742) (Fig. 1).

Figs. 2 and 3 show TG/DTA and MS (MS, mass spectrometry) results of thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ obtained in

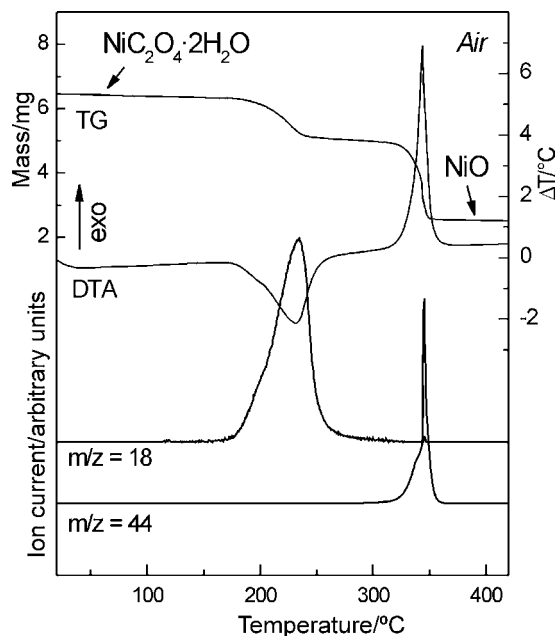


Fig. 2. Thermogravimetric and mass spectrometry results of decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air (heating rate $\beta = 5^\circ\text{C min}^{-1}$).

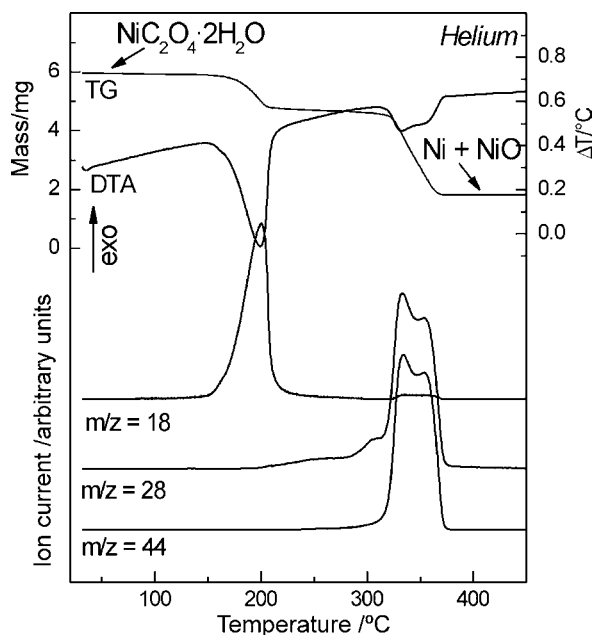


Fig. 3. Thermogravimetric and mass spectrometry results of decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in helium (heating rate $\beta = 5^\circ\text{C min}^{-1}$).

helium and in air. The decomposition proceeds generally in two steps, dehydration and decomposition of the anhydrous oxalate. XRD analysis confirmed that the final product of decomposition in air is NiO and in helium–Ni. In the residue after decomposition in helium, beside Ni, the traces of NiO have been stated on the basis of measurements of reduction of the residue in hydrogen. It was found that residue contains about 2 mol% of NiO.

3.1. Dehydration

$\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ loses the main part of hydration water on heating up to the temperature at which decomposition of the oxalate ions starts. The remaining, small amount of water broke free of the nickel oxalate structure together with decomposition of the compound. This is confirmed by the raise of line $m/z = 18$ during decomposition above 300°C (particularly evident in helium). To find out what is the character of the residual water remaining after dehydration the series of XRD, FTIR and HT-DRIFT analysis were performed. The samples of nickel oxalate dihydrate were dried at 200 and 250°C in static air and at 150°C in dynamic vacuum for several hours. After this treatment the colour of the samples changed: from blue-green to yellow-green, which means that the crystallization water was removed. After taking samples out of the dryer their weight systematically raised due to adsorption of water vapour. The final mass gain was about $9.5 \pm 0.5\%$, which corresponds 8.3% of crystallization water in nickel oxalate dihydrate. XRD diffraction patterns of the sample dehydrated in air and for the sample dehydrated in vacuum are similar to each other, but both are different from the pattern in ASTM file. The X-ray diffraction patterns obtained are close to the one published in Ref. [17] (Fig. 4). Stability of this phase in the range of temperature 200 – 290°C was confirmed by high-temperature XRD.

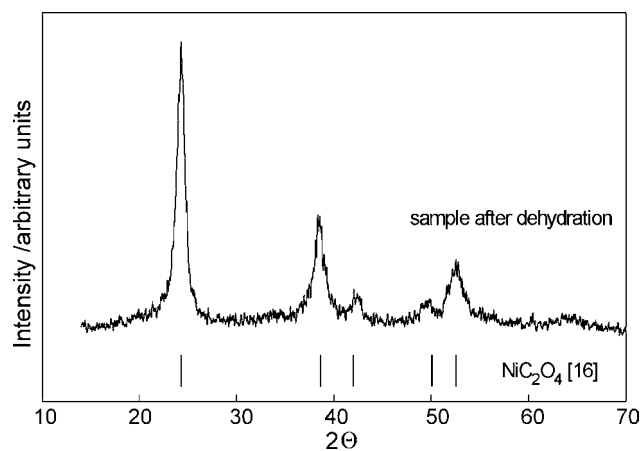


Fig. 4. XRD pattern of the sample after dehydration.

Fig. 5 presents the FTIR spectra of the initial sample and of the sample after dehydration at heating rate 2°C min^{-1} until 300°C . After this treatment, the bands at 617 and 758 cm^{-1} , present in the initial sample and corresponding to Ni–O–H and water of crystallization vibration modes, respectively, have vanished. The band at 3400 cm^{-1} , corresponding to OH stretching vibration mode, is still present, but results from the presence of the adsorbed H_2O (not water of crystallization). This is the consequence of the preparation of sample for the FTIR measurement: during grinding the sample with KBr powder the water is adsorbed very quickly.

A study of specific area of the sample after dehydration made with the BET method with N_2 revealed a value of $12.4\text{ m}^2\text{ g}^{-1}$. The method t showed an external surface of $3.9\text{ m}^2\text{ g}^{-1}$ and a microporosity of $8.5\text{ m}^2\text{ g}^{-1}$. This microporosity explains adsorption of water in the product after crystallographic dehydration (increase of weight and intense band in the FTIR spectra relative to adsorbed water at 3400 and 1650 cm^{-1}).

HT-DRIFT experiment has confirmed the total or quasi-total departure of water at 250°C at which the band at 3400 cm^{-1} vanished (Fig. 6).

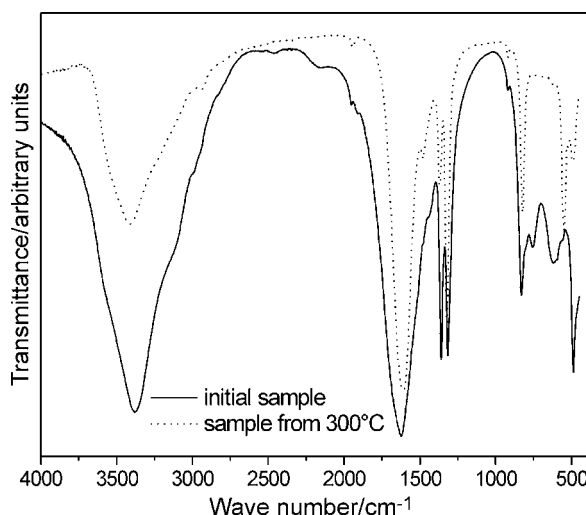


Fig. 5. FTIR spectra of initial nickel oxalate dihydrate sample and sample after dehydration at temperature raising with rate $\beta = 2^\circ\text{C min}^{-1}$ up to 300°C .

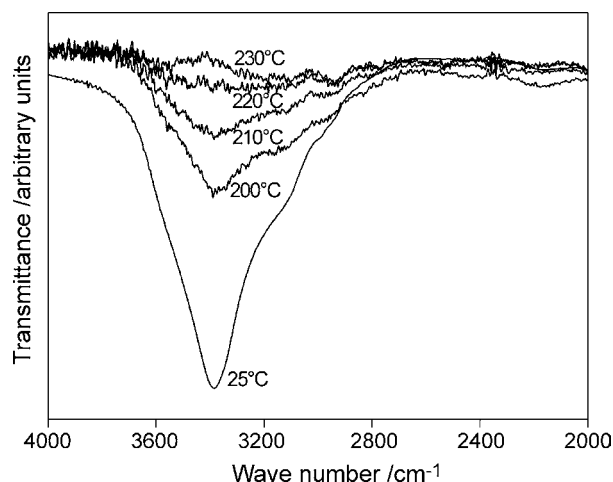


Fig. 6. HT-DRIFT spectra of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ samples dehydrated at temperature raising with rate $\beta = 2^\circ\text{C min}^{-1}$ up to different temperatures.

In conclusion the water present in the sample at the temperature of decomposition in experiments performed at raising temperature is the water occluded in highly porous product obtained after dehydration process.

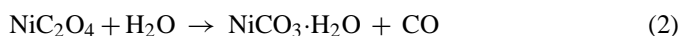
3.2. Decomposition

The TG line between the end of first step (dehydration) and the beginning of decomposition reveals the distinct slope connected with about 3.5% loss of mass (in respect to the initial mass). This change of mass is connected with evolution of CO_2 and H_2O . The value of ion current for $m/z = 44$ in this range is raising and the value of ion current for $m/z = 18$ is continuously approaching the baseline. This means that CO_2 and H_2O evolve from the sample. For the measurement in helium it was possible to make comparison of ion current $m/z = 28$ to this being the result of fragmentation of CO_2 and calculated from ion current $m/z = 44$ with fragmentation factor 0.0658 [18]. MS signal for $m/z = 28$ can be a sum of CO^+ ion current and ion current resulting from fragmentation of CO_2 (mass spectrum of CO_2 consists of m/z : 44, 28, 22, 16, 12). If CO_2 is present in a gas mixture and CO is absent, signal $m/z = 28$ has to be the same as ion current from fragmentation of CO_2 . If gas mixture contains both CO_2 and CO , $m/z = 28$ signal should have the value higher than ion current from fragmentation of CO_2 . The comparison showed (Fig. 7) that two lines do not overlap which means that a small amount of CO evolves. Thus, 3.5% loss of mass results from the evolution of H_2O , CO_2 and CO .

There are two ways of explaining the presence of carbon monoxide in the gas evolved at the beginning of decomposition by assuming the following reactions:



or



Both proposed reactions have to occur in a very little scale.

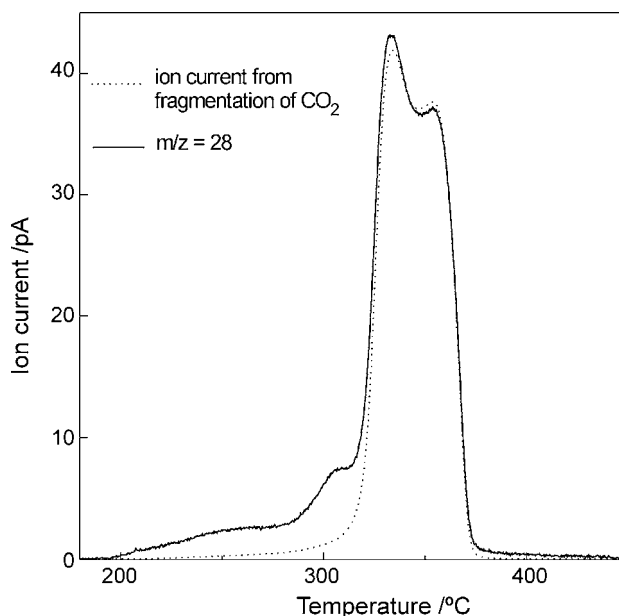


Fig. 7. Ion current of $m/z = 28$ measured and calculated from experimental signal of $m/z = 44$ (helium, $\beta = 5^\circ\text{C min}^{-1}$).

Let us consider if reaction (1) takes place. In that case the amount of CO_2 and CO has to be the same and the signals from $m/z = 28$ and $m/z = 44$ should have the same shape, because both gases evolve with equal amount and with identical rate. The results obtained do not confirm the behaviour of MS signals described above which means that first reaction does not happen. In conclusion evolution of CO at the beginning of nickel oxalate decomposition can be the consequence of reaction (2) with basic nickel carbonate and carbon monoxide as the products.

Very careful analysis of FTIR spectra of the decomposition product of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ obtained during isothermal heating at 200, 260 and 300 °C for 10 h in air showed the formation of nickel carbonate. In the spectrum of sample from 260 °C the band at 1375 cm^{-1} appears which corresponds to the C–O vibration in CO_3^{2-} group [19]. It is partially masked by the band at 1360 cm^{-1} of the C–O stretching mode of the oxalate ion, but in the sample from 300 °C the band at 1375 cm^{-1} is clearly seen (Fig. 8). The same result was obtained for samples heated in air with the rate 2°C min^{-1} until 300 and 325 °C (Fig. 9). At 300 °C we can see the band at 1360 cm^{-1} characteristic for oxalate ion. At 325 °C this band has decreased that enabled to spot the band at 1375 cm^{-1} of carbonate group. The vibration band at 500 cm^{-1} originates from Ni–O bond. However, the XRD analysis of product obtained at studied temperatures did not confirm the presence of nickel carbonate, which allows stating that carbonate phase forms in small amount and/or in amorphous form.

In conclusion, during decomposition of nickel oxalate dihydrate small amount of basic nickel carbonate forms. This reaction is possible because reaction of dehydration of nickel oxalate is not complete. $\text{NiCO}_3 \cdot \text{H}_2\text{O}$ decomposes with formation of NiO . This explains the presence of traces of nickel oxide in the final product of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposition in helium.

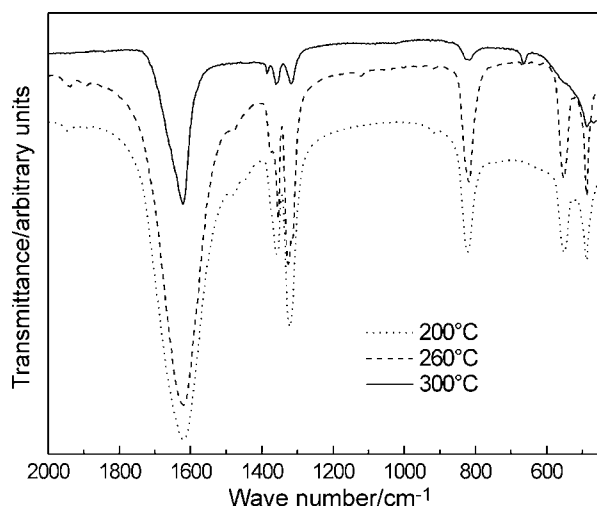


Fig. 8. FTIR spectra of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ heated isothermally at different temperatures for 10 h in air.

The main step of decomposition of nickel oxalate corresponds to the reaction:



Reaction (3) starts just after dehydration step and develops very slowly until the temperature reaches about 310°C and next accelerates. The final solid product of nickel oxalate decomposition in helium and in vacuum is nickel. The way of decomposition in air is the same but metallic nickel is oxidized by oxygen from air giving NiO as a final product of reaction. It is worth to notice that onset temperatures of DTA peaks of decomposition are close to 310°C , both in helium and in air.

The dihydrate of cobalt oxalate, $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, metal very similar to nickel, decomposes in a different way [20]. Decomposition of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ proceeds through two parallel reactions: one leading to metallic cobalt, and second to cobalt oxide. The amount of cobalt oxide in the residue was significant and dependent on the heating rate.

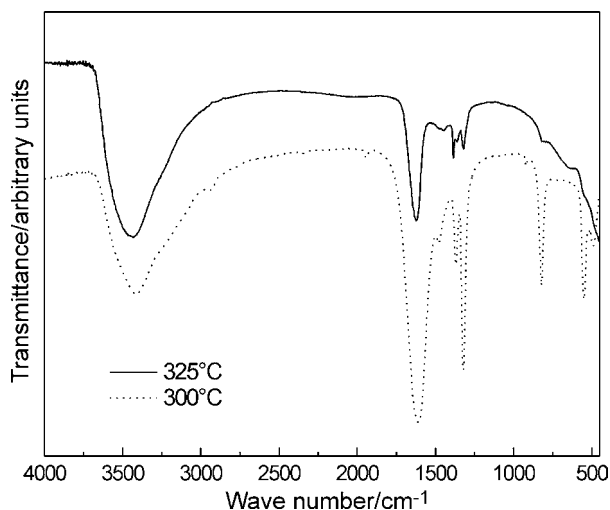


Fig. 9. FTIR spectra of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ heated with rate 2°C min^{-1} until 300°C and 325°C .

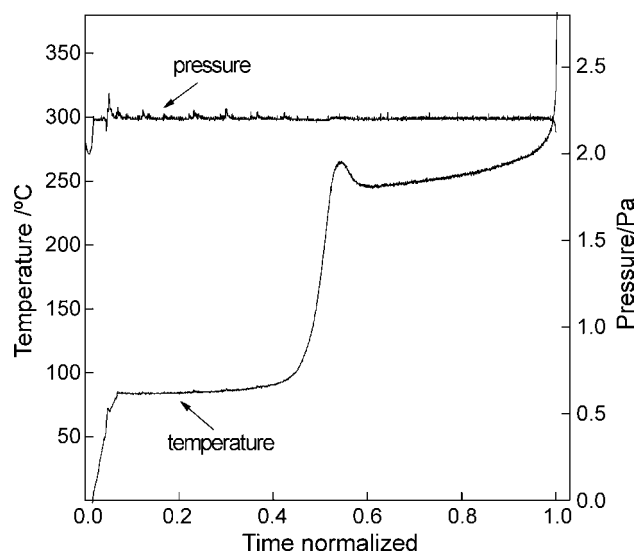


Fig. 10. CRTA result of decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at pressure 2 Pa.

DTA line of NiC_2O_4 decomposition in helium shows double peak. The shape of DTG and CO_2^+ ion current signal $m/z = 44$ (MS analysis) copies DTA shape. This shape could be the evidence that the process is complex. However, the double DTA and DTG signal cannot be explained by occurring of parallel reactions since this is the single step reaction with no intermediates and Ni as a final product.

One of the possible explanations of this unusual shape of DTA line can be the change in the microscopic mechanism of decomposition, for instance: in the beginning the rate of decomposition is controlled by the process of decomposition of oxalate ions with activation energy E_1 . This process is very fast. Next rate of the whole reaction slows down and is controlled by the nickel nuclei growth according to the diffusion mechanism with activation energy E_2 . The results of CRTA experiment seem in good agreement with this explanation (Fig. 10). If we consider the part of temperature line in Fig. 10 related to decomposition of nickel oxalate, i.e. above 250°C , we can notice that in order to keep constant all at once pressure and rate, it is necessary to increase then decrease temperature. This is typical of a nucleation process. Then the temperature of the reaction has to be continuously increased to maintain the constant pressure which could correspond to a diffusion mechanism of nickel nuclei growth. In paper [21], where mechanism of decomposition of nickel oxalate at high temperatures in $\text{Ar}/5\%\text{H}_2$ atmosphere was examined, Authors stated that nanosized nickel grains form in result of homogeneous nucleation. Taking these considerations into account we believe that the double DTA signal seems to be the consequence of not the chemical changes but of changes of the kinetics of reaction.

DTA signal obtained for decomposition of nickel oxalate in air has the shape different from this characteristic for decomposition in helium. The main reason of this is that in air the process is exothermic as a whole. The growth of nickel nuclei does not occur because nickel is at once oxidized. Additionally relatively strong exothermic effect being

the result of metallic nickel oxidation increases the rate of decomposition.

3.3. Summary

Thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ proceeds in two main stages: one is dehydration and second is decomposition. Dehydration is never complete and water remains in the product of dehydration as occlusion in highly porous structure. The product after dehydration is very hygroscopic. At the beginning of decomposition the presence of residual water enables formation of small amount of basic nickel carbonate. The products of decomposition of NiC_2O_4 are nickel and carbon dioxide, but in oxidizing atmosphere nickel is instantly oxidized giving NiO. In the product of decomposition in helium, beside nickel, a little amount of NiO is always present. NiO is a product of nickel carbonate decomposition. The decomposition of NiC_2O_4 in inert atmosphere proceeds by two consecutive reactions: the very fast reaction of homogeneous nucleation of metallic nickel throughout the grain following by distinctly slower reaction of nickel nuclei growth most probably with diffusion mechanism.

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