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THE THERMAL DECOMPOSITION OF NICKEL OXALATES DOPED WITH TRACES OF OTHER METAL IONS

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ABSTRACT

The thermal decomposition of nickel oxalate is reported in this study. The samples of nickel oxalates were prepared under various conditions. Thermal analysis studies coupled with other techniques were employed to show the pattern of the decomposition. The nickel oxalate was prepared by reacting equivalent quantities of oxalic acid and nickel nitrate at 25, 50, 75 and 100 ° C. Doped nickel oxalate was prepared by adding lithium and chromium to the lattice structure.

These ions were introduced by adding them as a nickel species in the preparation of the nickel oxalate using the reaction described above. The concentration of nickel species added at this stage was calculated to give an oxide product, nickel oxalate, containing the dopant species in concentrations of 0.5, 1, 5 and 10 atom%.

X-ray powder diffraction analysis showed that the initial sample gave a pattern agreeing with that reported in the A.S.T.M. file. The thermal decomposition was studied in vacuum by mass spectrometry, and in both nitrogen and carbon dioxide atmospheres using DTA units. The main final solid product in both nitrogen and carbon dioxide was nickel metal. A certain quantity of nickel oxide was also obtained. It is possible to calculate the surface area of the nickel metal produced in this manner. In vacuum, the side decomposition reaction also occurred, because carbon monoxide was detected by mass spectrometry, although its quantity was small. A further oxidation stage would be necessary to produce the doped oxide. The kinetics of decomposition were also reported. It was found that the average activation energy of dehydration of the samples under investigation was around 100 kJ mol^{-1} in the TG study, and 80 kJ mol^{-1} in the DTA study, and that of decomposition was around 225 kJ mol^{-1} in TG and 230 kJ mol^{-1} in DTA studies, respectively.

INTRODUCTION

The thermal decomposition of nickel oxalate was previously reported by various other workers [1–9]. Kornienko [2], David [3] and Kadlec and Rosmusova [4] found that the product was a mixture of the metal and its

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oxide. Xin Xinquan et al. [5], Rao and Gandhe [6] and Torov et al. [7] discovered that carbon monoxide was present in the gas phase as a product of the side reaction. Danes and Ponec [8] calculated the Arrhenius activation energy of the decomposition to be 30–93.5 kcal mol^{-1} and that of dehydration to be 10 kcal mol^{-1}, while Kornienko [9] reported the heat of activation for nickel oxalate decomposition to be around 42 kcal mol^{-1}.

The nickel oxalate salt exists as the dihydrate $NiC_2O_4 \cdot 2H_2O$. This makes the compound easy to prepare. On heating, regardless of the atmosphere used, it dehydrates endothermically

$$NiC_2O_4 \cdot 2H_2O \rightarrow NiC_2O_4 + 2H_2O \tag{1}$$

The decomposition of the anhydrous nickel oxalate in an inert atmosphere such as nitrogen or carbon dioxide is also endothermic. The main end product in the solid phase is nickel metal

$$NiC_2O_4 \rightarrow Ni + 2CO_2 \tag{2}$$

The less favourable side reaction also takes place

$$NiC_2O_4 \rightarrow NiO + CO_2 + CO \tag{3}$$

The metal thus produced is readily oxidized on its surface even by the carbon dioxide gas evolved by the reaction, at temperatures higher than 410 °C

$$Ni + CO_2 \rightarrow NiO + CO \tag{4}$$

This is due to the high surface activity of freshly formed powdered nickel. In air, the overall reaction is exothermic. This causes the nickel originally formed to react yielding nickel oxide

$$2Ni + O_2 \rightarrow 2NiO \tag{5}$$

In many catalyst preparations, the oxide catalyst can have its activity controlled by the deliberate introduction of dopant materials, which cause an alteration of its semi-conductor properties. Here, in this study, the dopant is added at the oxysalt preparative stage in order to ensure that the final mixture is very intimately mixed and to give a uniform distribution of the dopant.

EXPERIMENTAL AND RESULTS

Materials

Nickel oxalate was prepared at room temperature by adding 100 ml of 0.375 M oxalic acid to 100 ml of 0.375 M nickel nitrate. The resulting solution was stirred for one hour and then filtered. The precipitate was then stored in a desiccator. Nickel oxalate was also formed by this method in a steam bath at 50, 75 and 100 °C. Doped nickel oxalates were prepared by adding lithium and chromium nitrate at the preparative stage, such that the total nitrate concentration, including the nickel, remained at 0.375 M. When doping with lithium, for example, the lithium nitrate solution was added to the nitrate solution, stirred, and then mixed with the oxalic acid. The introduction of chromium as dopant was achieved in the same manner. Four samples of lithium-doped nickel oxalate and four samples of chromium-doped nickel oxalate at dopant levels of 0.5, 1, 5 and 10 atom% were prepared.

Instrumentation

Thermal analysis equipment

Thermogravimetric runs on various samples weighing about 10 mg were performed on a Du Pont TG unit in an atmosphere of nitrogen. Rising temperatures with heating rates of 2, 4, 6, 8 and 10 °C per minute, temperature-jump and isotherm methods were used for the sample prepared at 50 °C. Then kinetic parameters were calculated and the results using the above different methods were compared. The activation energies of dehydration and decomposition of nickel oxalate by the isotherm method were 74.826 kJ mol^{-1} and 158.326 kJ mol^{-1}, respectively. These were nearer to those obtained using the rising temperature method with a heating rate of 10 °C per minute (see Table 1). Therefore, a heating rate of 10 °C per minute, in addition to the temperature-jump technique, was chosen for the investigation of the remainder of the samples and the activation energies and pre-exponential factors for the dehydration and decomposition are listed in Table 2. A typical TG plot is shown in Fig. 1.

DTA experiments were carried out for all samples in both nitrogen and carbon dioxide atmospheres using a Stony DTA unit controlled by an omnitherm work station. In these experiments, samples weighing 90 mg were used. Each DTA plot showed an endothermic dehydration peak followed by an endothermic decomposition one. The temperature at which these peaks

TABLE 1

Rising temperature experiment for the sample prepared at 50 °C

Heating rate (°C min^{-1})	Dehydration		Decomposition	
	E (kJ mol^{-1})	A (min^{-1})	E (kJ mol^{-1})	A (min^{-1})
2	110.853	3.03×10^{10}	277.108	1.36×10^{22}
4	62.355	9.87×10^{4}	259.813	2.28×10^{20}
6	66.518	5.40×10^{5}	267.263	1.26×10^{21}
8	93.533	3.73×10^{8}	294.673	1.22×10^{23}
10	69.283	1.00×10^{6}	241.862	5.13×10^{18}

TABLE 2

Rising temperature experiment with heating rate of 10 °C min^{-1}

Sample name	Dehydration		Decomposition	
	E (kJ mol^{-1})	A (min^{-1})	E (kJ mol^{-1})	A (min^{-1})
25 °C	96.997	1.25×10^{9}	277.133	4.11×10^{21}
50 °C	69.283	1.00×10^{6}	241.862	5.13×10^{18}
75 °C	108.082	1.50×10^{10}	199.536	2.02×10^{15}
100 °C	103.925	6.87×10^{9}	249.42	2.02×10^{19}
0.5% Li	113.070	8.42×10^{10}	207.85	2.08×10^{16}
1% Li	75.582	1.12×10^{7}	221.707	2.52×10^{17}
5% Li	96.997	2.14×10^{9}	180.137	1.50×10^{14}
10% Li	91.454	5.47×10^{8}	285.051	3.23×10^{22}
0.5% Cr	95.931	1.60×10^{9}	232.792	1.81×10^{18}
1% Cr	92.378	5.86×10^{8}	203.231	7.35×10^{15}
5% Cr	95.931	1.71×10^{9}	190.034	6.93×10^{14}
10% Cr	95.931	1.71×10^{9}	249.42	3.01×10^{19}

occurred varies with the method of sample preparation, the heating rate and the amount and type of dopant. These are summarized in Table 3. Plots for samples doped with lithium and chromium are given in Fig. 2.

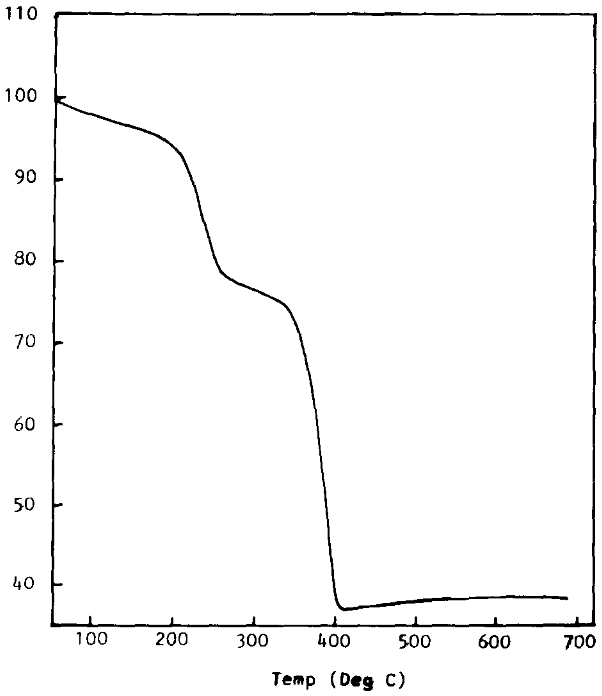

Fig. 1. TG plot of nickel oxalate in a nitrogen atmosphere.

TABLE 3

DTA results in a nitrogen atmosphere with heating rate of 10 ° C min^{-1}

Sample name [a]	First peak (° C)		Second peak (° C)		
	Onset [b]	Main [c]	Onset	Main	2nd [d]
25 ° C	217	273.1	334.7	362.8	380
50 ° C	219.8	273.1	334.5	360	386.5
75 ° C	219.2	274.3	338.3	367.1	390.3
100 ° C	219.2	276.9	338.7	371.6	392
0.5% Li	220.6	272.1	340.1	252.3	375.5
1% Li	217	272.6	331.2	353.1	372.6
5% Li	213.6	269.5	326.8	347	369.2
10% Li	215.5	271.1	316.3	352	375
0.5% Cr	213.9	269.2	331.9	355.2	379.1
1% Cr	214.6	269.5	333	356.5	380.1
5% Cr	212.7	266.8	331.7	355.2	377.8
10% Cr	216.8	271.8	334.5	354.8	378

[a] Refers to the sample prepared at different temperatures or doped with other elements.

[b] Temperature at which peak began to develop.

[c] Temperature at which the first peak occurred.

[d] Temperature at which the second peak occurred.

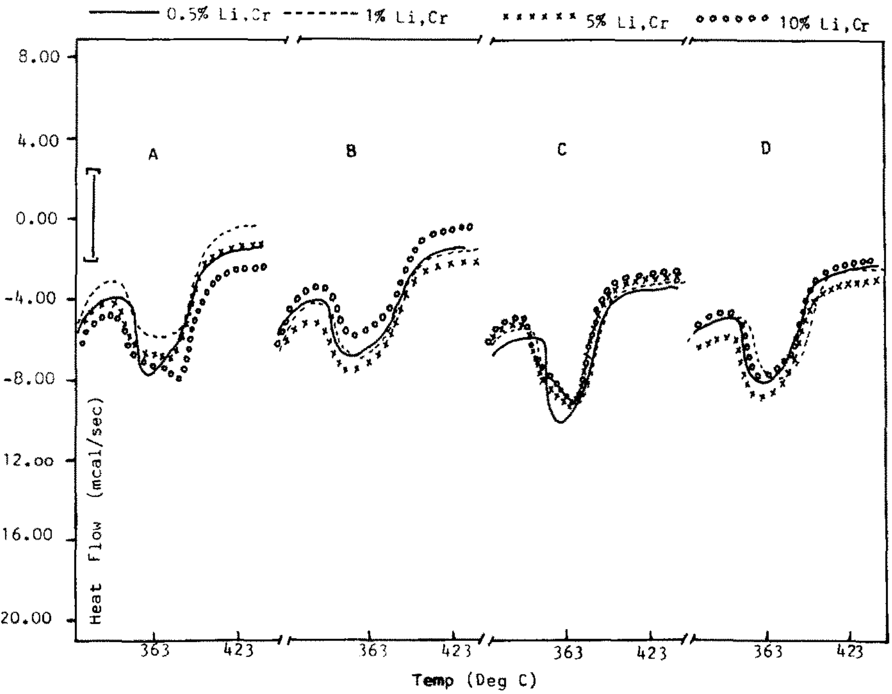

Fig. 2. DTA plots of nickel oxalate doped with Li (A and C) and Cr (B and D). A and B, nitrogen atmosphere; C and D, carbon dioxide atmosphere.

TABLE 4

Thermal decomposition of nickel oxalate in vacuum

T (°C)	P (mmHg$\times 10^{-7}$)	N_2+CO	O_2	CO_2	CO	CO_2/CO
52	4	352.5	87.5	20	–	–
95	4.2	200	25	–	–	0
130	4	175	15	–	–	0
135	3.9	146	42	32	–	–
170	3.9	170	40	110	10	11
195	4	182.4	38	226	30.4	7.4
230	4.4	224	44	356	48	7.4
263	5.5	130	25	855	30	28.5
280	4.6	97.5	23	85	5.5	15.5
315	5	104	26	69	–	–
320	5.15	111	26	84.5	7	12

Note: Numbers listed (excluding those in column 1 and 2) are the relative intensities from MS patterns.

In both TG and DTA experiments, the inert gas used purged the system for 2 hours before the run was started.

Mass spectrometer

A Nuclide mass spectrometer was used for the same prepared at room temperature. Some relevant results are listed in Table 4.

Diffractometer

A Philips diffractometer with Cu $K\alpha$ (1.54178 Å) radiation was employed for X-ray powder diffraction of both the initial samples and of samples in gram quantity heated to 550 °C and then carefully cooled to room temperature, both in a nitrogen atmosphere. Some diffraction patterns of initial samples are shown in Fig. 3.

Analysis of the dehydration and decomposition peaks was attempted. The theory concerning this analysis was explained by Dollimore et al. [10]. The rate of the reaction can be written as

$$\frac{d\alpha}{dt} = K f(\alpha) \qquad (6)$$

where $d\alpha/dt$ is the rate, α is the fraction decomposed, t is the time and K is the specific reaction constant.

The variation of the specific reaction constant K with temperature is given by the Arrhenius equation

$$K = A \exp(-E/RT) \qquad (7)$$

where A is the pre-exponential factor, E is the energy of activation and T is the temperature on the Kelvin scale. We also have

$$T = T_o + \beta t \qquad (8)$$

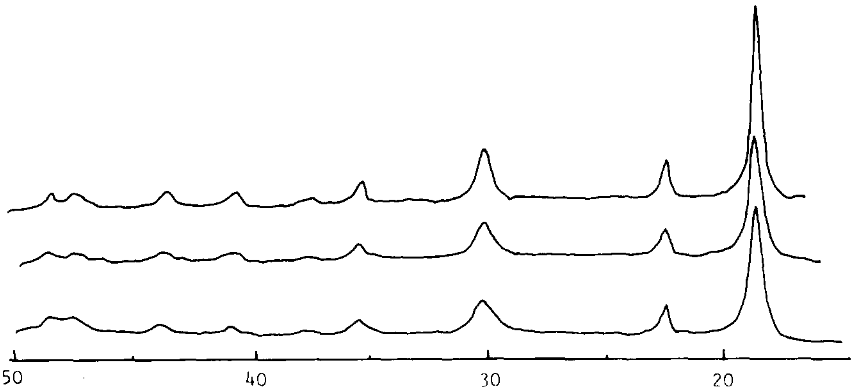

Fig. 3. X-ray powder diffraction patterns of some samples. Top curve, pure nickel oxalate; middle curve, nickel oxalate doped with 5% Cr; bottom curve, nickel oxalate doped with 5% Li.

to describe the linear temperature rise where T_o is the starting temperature and β is the heating rate.

A combination of the above equations results in

$$K=\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}t}}{\mathrm{f}(\alpha)}=\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}t}}{\mathrm{f}(\alpha)}=\frac{\frac{\mathrm{d}\alpha}{\mathrm{d}T}}{\mathrm{f}(\alpha)}\beta \tag{9}$$

where β is a known constant and T can be obtained from a TG plot.

The α and T data can also be obtained from a DTA plot. To collect a single point i.e. the extent of reaction at temperature T, we measure the area

TABLE 5

TG: temperature jump experiment

Sample name	Dehydration		Decomposition	
	E (kJ mol^{-1})	A (min^{-1})	E (kJ mol^{-1})	A (min^{-1})
25 °C	83.14	4.19×10^{7}	216.164	2.77×10^{16}
50 °C	124.71	1.95×10^{12}	232.792	5.78×10^{17}
75 °C	133.024	1.13×10^{13}	152.423	2.73×10^{11}
100 °C	155.888	4.05×10^{15}	207.85	2.04×10^{15}
0.5% Li	114.318	1.17×10^{11}	227.781	3.70×10^{17}
1% Li	79.181	2.20×10^{7}	228.635	4.51×10^{17}
5% Li	106.894	3.06×10^{10}	228.635	6.16×10^{17}
10% Li	96.997	2.03×10^{9}	178.03	2.07×10^{13}
0.5% Cr	101.616	5.98×10^{10}	191.682	2.25×10^{14}
1% Cr	106.894	2.05×10^{10}	187.065	8.30×10^{13}
5% Cr	96.997	2.00×10^{9}	228.635	3.39×10^{17}
10% Cr	99.768	3.58×10^{9}	193.993	3.20×10^{14}

TABLE 6

DTA, heating rate 10 °C min^{-1}

Sample name	Dehydration		Decomposition	
	E (kJ mol^{-1})	A (min^{-1})	E (kJ mol^{-1})	A (min^{-1})
25 °C	62.355	1.15×10^{5}	213.789	1.15×10^{17}
50 °C	74.862	1.51×10^{6}	221.707	4.29×10^{17}
75 °C	77.944	2.98×10^{6}	211.048	6.32×10^{16}
100 °C	80.981	5.64×10^{6}	193.993	1.59×10^{15}
0.5% Li	95.017	2.74×10^{8}	266.048	1.65×10^{22}
1% Li	73.902	1.36×10^{6}	346.417	2.11×10^{27}
5% Li	81.510	7.84×10^{6}	277.133	2.93×10^{22}
10% Li	62.355	1.40×10^{5}	237.543	1.48×10^{19}
0.5% Cr	81.34	1.33×10^{7}	197.458	8.57×10^{15}
1% Cr	77.944	3.66×10^{6}	217.443	3.41×10^{17}
5% Cr	78.834	4.80×10^{6}	201.911	1.85×10^{16}
10% Cr	95.017	1.97×10^{8}	199.536	1.17×10^{16}

marked T when

$$\alpha_i = \text{Area}(T_i)/\text{Total area of peak} \qquad (10)$$

Once a series of α and corresponding T values are obtained, they are put into a computer program and $d\alpha/dT$ is calculated.

Before log K can be plotted against $1/T$, $f(\alpha)$ must be known. This can be determined using reduced time plots [11]. In this study none of the functions listed in reference 11 fits the kinetics for the thermal decomposition of nickel oxalate. However, it was found that for the dehydration process, $f(\alpha) = 3\,(1-\alpha)^{2/3}/2$, and for the decomposition process, $f(\alpha) = 1-\alpha$, although there was some discrepancy between E, the activation energy for both processes, based on the above functions' calculation and that obtained from isotherm experiments. Values of E and A for TG and DTA studies are shown in Tables 5 and 6, respectively.

DISCUSSION

From Fig. 1, one can see that each TG plot shows two weight losses, corresponding to a two-stage decomposition process.

The first stage with weight loss of 19.57% (theoretical value 19.71%) was attributed to the dehydration. The temperature range for this stage is from 150 to 300 °C. The calculated dehydration energy value E in both TG (Table 5) and DTA (Table 6) studies for the samples prepared at different temperatures, increased with temperature. It appears that dehydration becomes difficult as the sample preparation temperature is increased. For the samples doped with lithium and chromium, E varied depending on the amount and type of dopant, but no regular pattern was found. The E value for this stage ranges from 62.355–155.888 kJ mol^{-1}, with an average value of around 100 kJ mol^{-1} for TG and 80 kJ mol^{-1} for DTA studies.

The second stage was attributed to the decomposition of the anhydrous salt. The temperature range was 320–410 °C. If the salt decomposed to an oxide, the theoretical weight loss is 40.84%. If it decomposed to the metal the theoretical weight loss is 48.16%. But the observed weight loss for the decomposition was 46.40%, a value somewhat in between 48.16 and 40.84%, nearer to the former than to the latter. This implied that reaction (2) was predominant. The E value for the decomposition showed a wide range from 152.423 to 346.714 kJ mol^{-1}. For the TG study, it was 225 kJ mol^{-1} and for the DTA study 230 kJ mol^{-1}, on average.

Mass spectrometric analysis supported the above argument. Table 2 shows that carbon monoxide was evolved along with carbon dioxide at temperatures higher than 170 °C. The ratio of carbon dioxide to carbon monoxide varied with temperature and pressure, but was found to be larger than that reported by Xin Xinquan et al. [5].

DTA experiments provided further evidence that reactions (2) and (3) took place at the same time during the thermal decomposition of nickel oxalate. From Fig. 2 it is clear that in nitrogen the second stage was composed of two peaks, which overlapped in most cases, whereas in carbon dioxide the shoulder peak was retarded. At first, it was assumed that the shoulder peak was due to a phase change from one allotropic modification of nickel metal to another, but this was not supported by the evidence shown in the cooling curve of a DSC experiment (see Fig. 4). The fact that the dopants, especially lithium, do accelerate one of the reactions was certain because the intensity of the shoulder peak increased with the amount of dopant.

From the TG plot in Fig. 1 shows that each curve reaches a minimum in weight percentage before it goes up and levels out. This is due to the high surface activity of the finely divided nickel and reaction (4) takes place ($\text{Ni} + \text{CO}_2 \rightarrow \text{NiO} + \text{CO}$). On average, around 2.5% weight increase was observed. This weight increase must be due to the addition of oxygen. We assume that oxidation takes place on the surface of the metal, and the nickel oxide thus formed is hemispherical in shape. Assuming that 1 g of sample has decomposed, the surface area of nickel metal can be calculated

$$\begin{aligned}\text{Surface area} &= \tfrac{1}{16} \times 2.5\% \times 6.023 \times 10^{23} \times 4\pi r^2/2 \\ &= 115.9\ \text{m}^2\ \text{g}^{-1}\end{aligned}$$

where r is the radius of NiO, which is equal to 1.4×10^{-10} m.

X-ray diffraction patterns of initial doped samples (two of them were chosen at random) showed little difference from that of the pure nickel oxalate, except the bands became broadened when 2θ was greater than 40

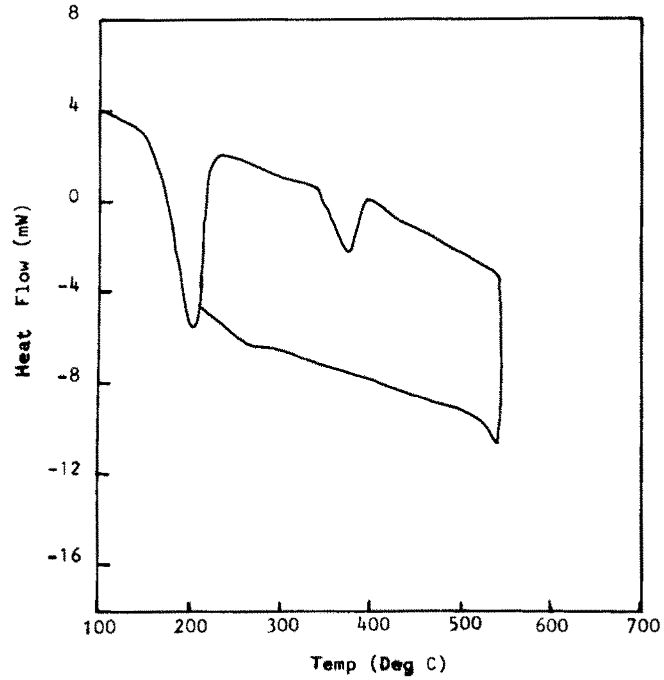

Fig. 4. DSC plot of nickel oxalate in a nitrogen atmosphere.

deg (see Fig. 3), suggesting that all the dopants were incorporated into the nickel oxalate lattice. The only final decomposition solid product detected was nickel metal. This is probably due to the fact that the oxide formed was in an amorphous form.

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