

A TG/DTA/MS STUDY OF THE OXIDATION OF NICKEL SULPHIDE

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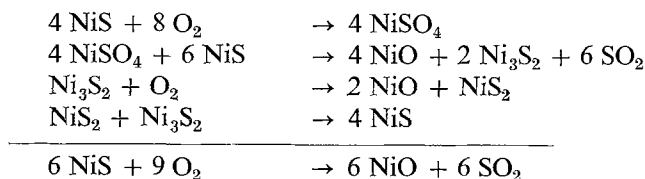
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The oxidative behaviour of synthetic millerite ($\text{Ni}_{0.994}\text{S}$) has been studied by TG and DTA in a dynamic oxygen atmosphere (0.2 l min^{-1}) over the temperature range $20\text{--}1000^\circ$ (heating rate $10^\circ \text{ min}^{-1}$). EGA was carried out by a coupled mass spectrometer. The reaction products at various intermediate temperatures were characterized by X-ray powder diffractometry. A reaction sequence has been deduced, in which in the temperature range $550\text{--}700^\circ$ complete oxidation of $\text{Ni}_{0.994}\text{S}$ had occurred with the formation of NiSO_4 , Ni_3S_2 , NiO and possibly $\alpha\text{-Ni}_7\text{S}_6$. Between $700\text{--}800^\circ$, NiSO_4 continued to be formed, whilst Ni_3S_2 and $\alpha\text{-Ni}_7\text{S}_6$ were oxidised. Above 800° , NiSO_4 decomposed to NiO , the latter being the only species evident above 800° .

The complexity of the nickel-sulphur system is indicated by the published phase diagram [1]. Of the stoichiometries possible, the naturally occurring minerals are heazelwoodite Ni_3S_2 , millerite Ni_{1-x}S , polydimite Ni_3S_4 , vaesite NiS_2 [1] and godlevskite Ni_7S_6 [2].

Several DTA studies have been made of metal sulphides, and these results summarised [3]. Other studies on the oxidative behaviour of nickel sulphides such as millerite, heazelwoodite and vaesite have also been made, utilising TG and DTA techniques. Conflicting statements concerning the mechanism of these oxidative reactions have been made, and some variation occurs in the number of thermal events recorded and the temperatures at which they occurred. Conditions of operation varied considerably, however, and hence comparisons between sets of results may not be strictly valid.

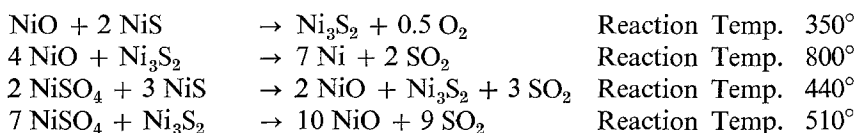
The oxidation of NiS has been studied by TG. One report indicated that between $350\text{--}450^\circ$ under an oxygen atmosphere of 80 mm mercury the products were either NiO or NiSO_4 , depending on the partial pressure of SO_2 above the sample. Other intermediate species detected by XRD were Ni_3S_2 and NiS_2 . The formation of NiSO_4 was assumed to occur by direct combination of O_2 and NiS [4]. A reaction scheme was proposed



Another study carried out with a dynamic oxygen atmosphere of 3 l hr^{-1} again indicated that the major products between $350\text{--}650^\circ$ were NiO and NiSO₄ [5]. The formation of NiSO₄ was assumed to result from the reaction of NiO and SO₃, the latter formed by the catalytic action of NiO. At O₂ flow rates of $300\text{--}500 \text{ l hr}^{-1}$ NiO was the only product. Above 650° , disproportionation of NiS was proposed with subsequent oxidation of sulphur.



The presence of Ni₃S₂ was confirmed by XRD. Above 700° NiSO₄ decomposed. Solid-solid interactions were studied under a dynamic vacuum of 10^{-4} mm Hg, and the following reactions proposed.



The temperatures at which reaction occurred were between $150\text{--}200^\circ$ higher when an inert atmosphere was used. [5–7].

Some DTA studies of the oxidation of NiS have been made, and the results are summarised in Table 1.

Table 1
Peak temperatures recorded by DTA in the oxidation of NiS

Temperature, °C			Assigned reaction
Ref. [8]	Ref. [9, 10]	Ref. [11]	
390 endo	400 endo	120 endo	$\beta\text{NiS} \rightarrow \alpha\text{NiS}$
		385 exo	$\text{NiS} + 2 \text{ O}_2 \rightarrow \text{NiSO}_4$
680 exo	610 exo	480 endo	$\beta\text{NiS} \rightarrow \alpha\text{NiS}$
		556 exo	$\text{NiS} + \text{NiSO}_4 + \text{O}_2 \rightarrow 2\text{NiO} + 2\text{SO}_2$
750 exo	730 exo		$\text{NiS} + 2\text{O}_2 \rightarrow \text{NiSO}_4$
			$10\text{NiS} + 2\text{O}_2 \rightarrow \text{Ni}_7\text{S}_6 + \text{Ni}_3\text{S}_2 + 2\text{SO}_2$
800 exo	787 endo		$\text{Ni}_3\text{S}_{2(s)} \rightarrow \text{Ni}_3\text{S}_{2(l)}$
		816 endo	$\text{NiSO}_4 \rightarrow \text{NiO} + \text{SO}_2 + 0.5\text{O}_2$
	840 exo		

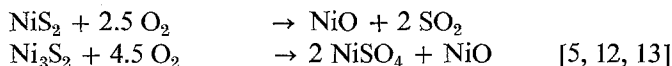
The DTA curves have been used to calculate heats of oxidation of NiS between $600\text{--}860^\circ$ [8]. The exotherm at 840° was claimed to result from the further oxidation of a nickel sulphide phase [9, 10].

Since the formation of Ni_3S_2 and NiS_2 has been reported during the oxidation of NiS , a brief review of the oxidation studies of these compounds is considered pertinent.

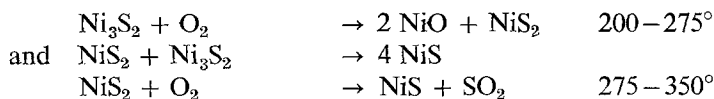
A TG study of the oxidation of Ni_3S_2 at various isothermal temperatures between $250-350^\circ$ suggested the following reaction.



Between $450-750^\circ$, the following reactions were reported



At low pressure and slow heating rate the reaction scheme was different [14].



A DTA study on the oxidation of Ni_3S_2 indicated that below 650° NiSO_4 was formed. At 690° an exotherm was found, which was attributed to the reaction:

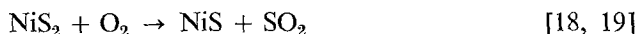


Above 760° another exotherm was observed, and assigned to the decomposition reaction of NiSO_4 . Other endotherms at 513° and 557° were not assigned [15, 16].

A study of the decomposition of NiS_2 in vacuo, using TG and XRD indicated that at 400° the following reaction took place [17].



An oxidative study on NiS_2 at low O_2 pressures (12–80 mm Hg) between $280-370^\circ$ gave rise to the simple reaction.



We have studied the oxidation of synthetic millerite, using TG–MS and DTA–MS systems. An attempt has been made to deduce a comprehensive reaction scheme, which may help to clarify some of the previously proposed reaction schemes.

Experimental

Oxidation runs were followed on a Stanton Redcroft TR-1 thermobalance modified to receive upflowing gas. Temperature control was achieved using a Stanton Redcroft Linear Temperature Variable Rate Programmer, Model LVP CT/10R. Heating rates of 600°hr^{-1} were used, with a gas flow rate of 0.2 l min^{-1} . For TG sample sizes of 250 mg were used. Weight changes were expressed as percentage starting weight. TG profiles are presented as recorded, but calculations of weight

changes include correction for buoyancy effects. Samples were contained in silica dishes (internal diameter 19 mm, depth 11 mm) and were distributed in thin layers to ensure maximum exposure to the atmosphere.

DTA runs were carried out using a Stanton Redcroft DTA attachment. Sample sizes ranged from 6–42 mg, and were contained in platinum cups (internal diameter 5.5 mm, depth 8.5 mm). An equal weight of calcined alumina was used in the reference crucible.

Qualitative XRD results were obtained with a Siemens Type F Diffractometer (Goniometer). An EAI Quad 160 Quadrupole Mass Spectrometer was used for EGA.

Synthetic millerite was prepared by reaction of high purity nickel and sulphur (the latter purified by distillation [20]) according to the method of Kullerud [1]. The reactants were weighed under N_2 into Vycor tubes, evacuated, sealed and heated to allow reaction. The product was removed under N_2 and ground to -90μ . XRD and chemical analysis characterized the sample as millerite of formula $Ni_{0.994}S$.

Results and discussion

Typical TG–DTA–MS profiles for the oxidation in O_2 of $Ni_{0.994}S$ over the temperature range $20-1000^\circ$ are shown in Figures 1a and 1b. (In the rest of the text, the starting material will be referred to simply as NiS).

Because of the different sample holder configurations correlations between DTA and TG results were in some cases difficult to make. The TG sample holder, being wide and shallow, allowed evolved gases to be swept away readily, and also allowed good contact between the dynamic reactive gas atmosphere and the solid. In the DTA sample holder, these processes were accomplished less efficiently. This resulted in broad endo- and exo-therms in the DTA profiles compared to quite sharp weight changes in the TG. In some cases well defined reactions in the TG sample holder occurred to almost negligible extent in the DTA sample holder.

Table 2

XRD analysis of rapidly quenched samples from oxidative TG runs of $Ni_{0.994}S$

Temperature °	Phases present	
	major	minor
535	NiS	NiO, NiSO ₄
560	NiS	NiO, NiSO ₄
660	NiS	NiO, NiSO ₄
700	NiO	NiSO ₄ , Ni ₃ S ₂ , α -Ni ₇ S ₆
740	NiO	NiSO ₄ , Ni ₃ S ₂ , α -Ni ₇ S ₆
780	NiO	Ni ₃ S ₂ , NiSO ₄
850	NiO	—

The weight gain shown by the TG (Figure 1a) between 400–535° was due to the formation of NiSO_4 . (The apparent weight gain up to 400° was due to buoyancy effects). An XRD of a sample quenched rapidly from 535° (see Table 2)

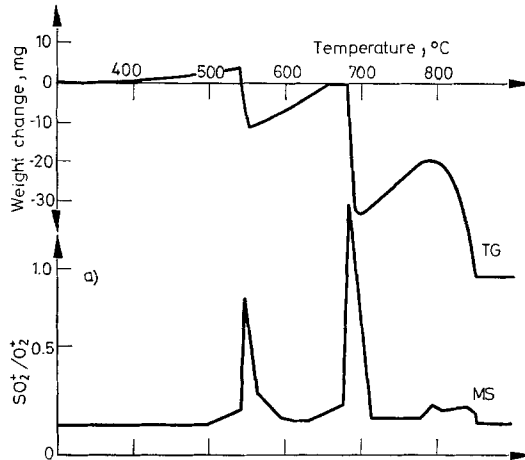


Fig. 1a. TG and MS of 250 mg $\text{Ni}_{0.994}\text{S}$ heated in oxygen.

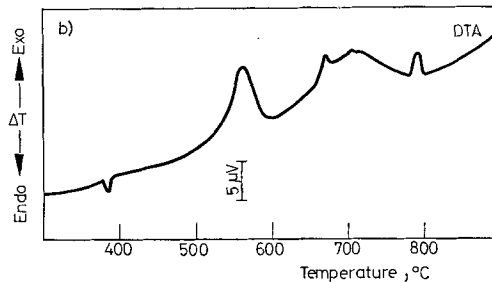
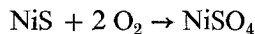


Fig. 1b. DTA of 6 mg $\text{Ni}_{0.994}\text{S}$ heated in oxygen.

indicated that NiS was still the major phase, with small concentrations of NiO and NiSO_4 also present. Since no SO_2 was detectable by the mass spectrometer below 490°, it was likely that the formation of NiSO_4 occurred by a simple combination reaction, as previously proposed [4].



Above 500°, however, the formation of NiSO_4 by the reaction of SO_3 on NiO was also possible [5]. The formation of NiSO_4 occurred over such a wide temperature range that no thermal event was apparent on the DTA graph.

Contrary to a previous publication [11], the first discernible DTA peak was found at 385°, and was attributed to the $\beta \rightarrow \alpha$ NiS phase change. This value is in good agreement with previously reported DTA values. [8–10].

The next significant event was found to be a rapid weight loss of 5.1% between 540–552°. This had a corresponding DTA exotherm with a peak temperature of 562°, and a strong emission of SO₂ as indicated by the MS results. XRD results obtained on a TG sample rapidly quenched from 560° showed that NiS was still the predominant phase, with a significant increase in the NiO concentration and NiSO₄ as a minor phase. The exotherm and weight loss are considered to be the result of the oxidation of NiS.

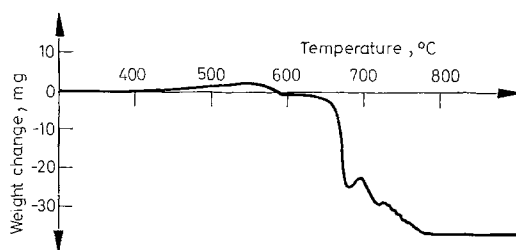
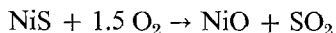


Fig. 2. TG of Ni_{0.994}S in air.

This reaction occurred to a limited extent, which may be due to the presence of a protective coating of NiSO₄. The ability of surface coatings of sulphates to inhibit diffusion controlled gaseous-solid reactions has been previously noted. [21] The reaction was also significantly dependent on the oxygen availability to the sample. This was demonstrated by using air as the dynamic atmosphere and covering the TG sample holder with a perforated lid. The results are given in Figure 2. The weight loss now occurred between 560–594°, a temperature range of 34° compared to 12° under O₂, and the weight loss was also significantly less, 1.4% compared to 5.1%.

When the DTA was carried out on a 42 mg sample (see Figure 3), then no appreciable exotherm or SO₂ emission was noted at 562°. The increased depth of sample may have limited the O₂ availability to the extent that no appreciable reaction occurred. A new exotherm at 635° was evident. An endotherm peaking at 852° was also evident, and not detectable in Figure 1b. The peak at 671° in Figure 1b appeared as a shoulder in Figure 3, and the broad exotherm centred at 707° (Figure 1b) now showed as a multi-peaked exotherm. This effect is probably due to oxidation occurring at separate reactive sites rather than individual chemical reactions. This effect has been reported for other sulphides [3]. Similar profiles to Figure 3 were also obtained with 25-mg samples, except that the 707° peak was rounded. In some cases the shoulder at 671° was resolved into a separate peak. The MS profile also indicated two peaks, at 671° and 710°, respectively.

Returning to Figure 1, between 552–670° there was a further weight gain of 3.2%. This was through the formation of more NiSO₄, as indicated by qualitative XRD analysis of a sample quenched from 660°. This weight gain did not reflect the amount of NiSO₄ actually formed, since a simultaneous weight loss was occurring through the formation of NiO from NiS. Isothermal runs carried out at temperatures between 550–670° produced samples which contained up to 22% NiSO₄, as determined by chemical analysis. The NiO content had also increased.

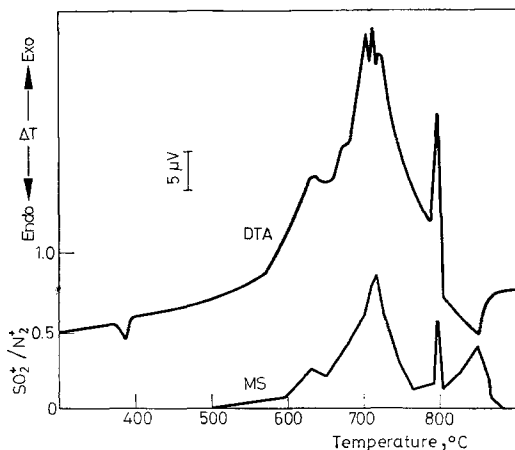
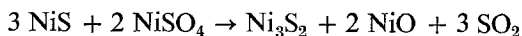
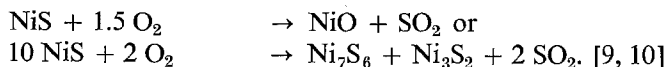


Fig. 3. DTA and MS of 42 mg Ni_{0.994}S heated in oxygen.

This was followed by a rapid weight loss of 10.9% between 682–692°. A corresponding broad exotherm was found in the DTA, and a rapid emission of SO₂ in the MS results. XRD analysis of a TG sample quenched from 700° showed that there had been a significant decrease in the NiSO₄ content and that NiS was no longer detectable. NiO was now the major phase. Ni₃S₂ was present as a minor component, and α-Ni₇S₆ was tentatively identified. Several reactions are required to explain these results. The partial disappearance of NiSO₄ may be due to a solid state reaction, as previously proposed [4].



The disappearance of NiS may have been due to the simple oxidation of unreacted NiS.



The latter reaction could explain the appearance of Ni₇S₆. The validity of the solid state reaction was tested by mixing correct proportions of the reactants and obtaining a TG profile under N₂. (See Figure 4).

The rapid weight loss commenced at 670°, 12° lower than observed under O₂. The weight loss was also lower, 6.0% compared to 10.9% under O₂. The second weight loss in Figure 4, commencing at 736°, was assumed to be due to the decomposition of unreacted NiSO₄.

The presence of two DTA peaks (Fig. 1b) supports the suggestion that at least two reactions have occurred within the temperature range 670–710° (see also Fig. 3).

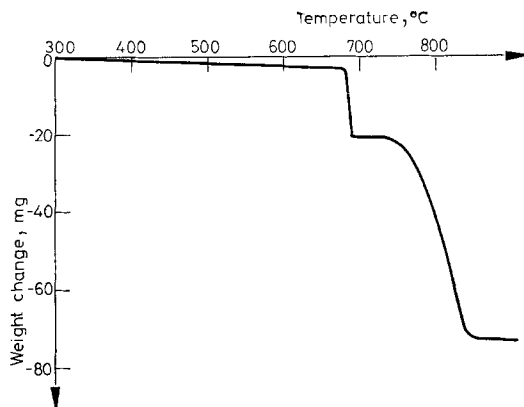


Fig. 4. TG of a mixture of 155 mg NiSO₄ and 136 mg of Ni_{0.994}S heated under nitrogen.

It is further suggested that the solid state reaction gives rise to the low temperature peak (671°) with either or both of the other reactions occurring subsequently.

At 740°, XRD analysis indicated that the NiSO₄ content had increased, as shown by a weight gain of 4.2% in the TG between 690–785°. This may be formed by the oxidation of Ni₃S₂ or Ni₇S₆, or alternatively by the sulphation of NiO. Ni₃S₂ and α-Ni₇S₆ were still present at 740°, but only NiO, Ni₃S₂ and NiSO₄ were evident at 780°.

Between 790 and 848° a weight loss of 9.3% was observed. This resulted from two reactions. At 793° a peak was observed in the DTA, and a corresponding SO₂ emission observed. This was probably due to the reaction of Ni₃S₂ with O₂.



Ni₃S₂ is reported to have a melting temperature range of 789–793° [1]. Hence the formation of liquid Ni₃S₂ could result in its rapid oxidation at this temperature. The other reaction causing weight loss would be decomposition of NiSO₄ to NiO and SO₂. This gives rise to a broad SO₂ evolution, over a wide temperature range. In the DTA of small samples, less than 6 mg, it was difficult to observe this thermal effect. It would in fact be easy to interpret the decomposition as exothermic by reference to Figure 1b. For larger sample sizes, however, the endothermic nature of this decomposition was readily observed (see Figure 3) as a peak at

852°. This agrees with results obtained for the decomposition of NiSO₄ under N₂, and as previously reported [11]. XRD analysis of samples quenched from 840° indicated that NiO was the only phase present.

From these results, it is possible to suggest a reaction scheme for the oxidation of NiS, under the dynamic conditions outlined previously. The temperature ranges quoted are based on TG results.

- | | |
|--|----------------------|
| 1. NiS + 2 O ₂ → NiSO ₄ | 400–785 (°C) |
| 2. NiO + SO ₂ + 0.5O ₂ → NiSO ₄ | 500–785 |
| 3. NiS + 1.5 O ₂ → NiO + SO ₂ | 540–552 and 682–692; |
| 4. 3 NiS + 2 NiSO ₄ → Ni ₃ S ₂ + 2 NiO + 3 SO ₂ | 682–692 and possibly |
| 5. 10 NiS + 2 O ₂ → Ni ₇ S ₆ + Ni ₃ S ₂ + 2 SO ₂ | 682–692 |
| 6. Ni ₇ S ₆ + 9.5 O ₂ → 7 NiO + 6 SO ₂ | 682–780 and/or |
| Ni ₇ S ₆ + 12.5 O ₂ → 6 NiSO ₄ + NiO | |
| 7. Ni ₃ S _{2(s)} → Ni ₃ S _{2(l)} | 793 |
| 8. Ni ₃ S _{2(l)} + 3.5 O ₂ → 3 NiO + 2 SO ₂ | 793 |
| 9. NiSO ₄ → NiO + SO ₂ + 1/2 O ₂ | >800 |

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RÉSUMÉ — On a étudié l'oxydation de la millérite synthétique ($\text{Ni}_{0.994}\text{S}$) par TG et ATD en atmosphère dynamique d'oxygène ($0,2 \text{ l} \cdot \text{min}^{-1}$) et dans l'intervalle de températures allant de 20 à 1000° (vitesse de chauffage $10^\circ \cdot \text{min}^{-1}$). L'analyse des gaz émis s'est effectuée avec un spectromètre de masse couplé. Les produits de réaction ont été caractérisés à diverses températures intermédiaires par diffractométrie de poudre aux rayons X. On a déduit une séquence de réactions, selon laquelle, dans l'intervalle compris entre 550 et 700°, l'oxydation complète de $\text{Ni}_{0.994}\text{S}$ a lieu avec formation de NiSO_4 , Ni_3S_2 , NiO et probablement $\alpha\text{-Ni}_7\text{S}_6$. Entre 700 et 800°, la formation de NiSO_4 se poursuit tandis que Ni_3S_2 et $\alpha\text{-Ni}_7\text{S}_6$ sont oxydés. Au-dessus de 800°, NiSO_4 se décompose en NiO qui constitue l'unique composé qui puisse être décelé au-dessus de 800°.

ZUSAMMENFASSUNG — Das oxidative Verhalten von synthetischem Millerit ($\text{Ni}_{0.994}\text{S}$) wurde mittels TG und DTA in einer dynamischen Sauerstoffatmosphäre ($0,2 \text{ l min}^{-1}$) im Temperaturbereich von 20 bis 1000° (Aufheizgeschwindigkeit $10^\circ \text{ min}^{-1}$) untersucht. EGA wurde mit einem gekoppelten Massenspektrometer durchgeführt. Die Reaktionsprodukte bei verschiedenen Zwischentemperaturen wurden mittels Röntgen-Pulver-Diffraktometrie charakterisiert. Eine Reaktionssequenz wurde abgeleitet, nach welcher im Temperaturbereich von 550 bis 700° die vollständige Oxidierung von $\text{Ni}_{0.994}\text{S}$ unter Bildung von NiSO_4 , Ni_3S_2 , NiO und wahrscheinlich $\alpha\text{-Ni}_7\text{S}_6$ vor sich geht. Zwischen 700 und 800° wird NiSO_4 auch weiterhin gebildet, während Ni_3S_2 und $\alpha\text{-Ni}_7\text{S}_6$ oxidiert wurden. Oberhalb von 800° wurde NiSO_4 zu NiO zersetzt, das einzig nachweisbare Produkt oberhalb von 800°.

Резюме — Было изучено окислительное поведение синтетического миллерита ($\text{Ni}_{0.994}\text{S}$) с помощью ТГ и ДТА в динамической кислородной атмосфере ($0,2 \text{ л} \cdot \text{мин}^{-1}$) в области температур 20—1000° при скорости нагревания $10^\circ \text{ мин}^{-1}$. ЕГА было выполнено с помощью соединенного масс-спектрометра. Продукты реакции при различных промежуточных температурах были охарактеризованы с помощью порошковой рентгеновской диффрактометрии. Выведена последовательность реакций при которой в области температур 550—700° протекает полное окисление $\text{Ni}_{0.994}\text{S}$ с образованием NiSO_4 , Ni_3S_2 , NiO и возможно $\alpha\text{-Ni}_7\text{S}_6$. Между 700—800° сульфат никеля остается неизменным, в то время как Ni_3S_2 и $\alpha\text{-Ni}_7\text{S}_6$ уже окисляются. Выше 800° сульфат никеля разлагается до NiO, который появляется как очевидные частицы выше 800°.