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SOME ADDITIONAL RESULTS CONCERNING THE THERMAL BEHAVIOUR OF THE β-$Ni(OH)_2$/β-NiOOH SYSTEM

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ABSTRACT

Thermoanalytical measurements were performed on samples obtained by chemical and electrochemical oxidation of β-$Ni(OH)_2$ in order to reinvestigate the thermal behaviour of the β-$Ni(OH)_2$/β-NiOOH system.

The variation of the peak temperature of the DTG curve was studied as a function of oxidation state.

The results of this study furnished further evidence proving that partly charged nickel hydroxide is either a homogeneous or a heterogeneous system.

The comparison of thermoanalytical data obtained in the presence of air and nitrogen revealed an almost completely neglected aspect of the heat treatment of the system.

INTRODUCTION

In recent studies [1,2], the possible paths of the decomposition reaction of the β-$Ni(OH)_2$/β-NiOOH system when subjected to heat treatment have been discussed. It has been found that the transformation of partly charged nickel hydroxide to nickel oxide is a fairly complex process in which at least three different types of chemical reaction should be taken into consideration

$$Ni(OH)_2 \rightarrow NiO + H_2O \tag{1}$$

$$NiOOH \rightarrow NiO + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \tag{2}$$

$$NiO + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \rightarrow NiOOH \tag{3}$$

Although the formation of Ni^{3+} ions in the course of the dehydration of nickel hydroxide has been reported in the literature [3–6], in most cases [7–12] reaction (3) was not even mentioned as a factor to be considered. An aim of this study is to demonstrate that reaction (3) cannot be neglected. In fact, the rates of reactions (3) and (2) may be commensurable at a given temperature range.

On the other hand, Barnard et al. have established from their reversible potential measurements [13] that the partly charged nickel hydroxide is either a homogeneous or a heterogeneous system, depending on its oxidation state. This was also confirmed by positron lifetime spectroscopy [14].

In this paper, it is shown that the change of the phase characteristics of the system is revealed in the thermal behaviour of the partly charged nickel hydroxide. However, as has occurred in other attempts [15], β-type samples of oxidation state below 2.23 could not be prepared by discharging the formed and charged oxyhydroxide, because of the low conductivity of discharged material. To avoid this difficulty, the thermal analysis was extended to include samples prepared by chemical oxidation, because any oxidation state between 2 and 3 could be easily attained using chemical methods. The results (related to the product of chemical oxidation) proved to be necessary in order to give a complete picture of the characteristics of the β-Ni(OH)$_2$/β-NiOOH system.

EXPERIMENTAL

The preparation of the starting material, β-Ni(OH)$_2$, and the subsequent electrochemical oxidation have been described in the previous study [1]. The chemical oxidation of the nickel hydroxide was carried out at 80 °C in 0.1 mol dm^{-3} NaOH solution using sodium hypochlorite [16], which was prepared by the saturation of 2.5 mol dm^{-3} NaOH solution with Cl_2 gas. The oxidized samples were washed free of oxidizing agent and dried in a desiccator over P_2O_5 in vacuum. The usual analytical methods were applied for the determination of the oxidation state of the oxyhydroxide.

Thermal analyses were performed both in air (static) and in N_2 atmosphere (flow rate of 5 l h^{-1}). Experiments were run (25–600 °C) at a linear heating rate of 6 °C min^{-1} and, in many cases, at various constant temperatures.

RESULTS AND DISCUSSION

The thermogravimetric curves and the derivative curves (DTG curves) for electrochemically and chemically oxidized nickel hydroxides were evaluated in order to determine the temperature of the maximum decomposition rate (temperature of the DTG peak). These data are represented in Fig. 1 as a function of oxidation state. As expected from the difference in the oxidation technique, curves 1 and 2 are not entirely identical. In the case of chemically treated samples, the peak temperature versus oxidation state curve (curve 2) is shifted in the direction of higher temperatures. One possible explanation for this shift ($<$ 15 °C) is that the relatively high rate of chemical oxidation may result in some departure from a uniform composition, i.e. the appearance of under- and overoxidized regions [17]. Despite the different

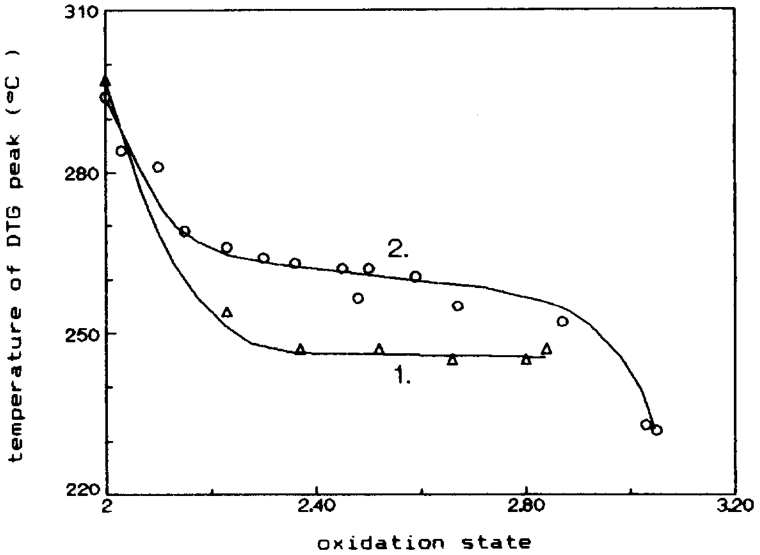

Fig. 1. Dependence of the temperature of the DTG peak on the oxidation state: 1, electrochemically; and 2 , chemically oxidized nickel hydroxide.

position of curves 1 and 2 on the temperature axis, the main characteristics of these curves are very similar. Thus, the peak temperature continuously decreases below the oxidation state of 2.3 and above 2.8 (curve 2), but remains practically constant in the range 2.3–2.8. It is worth mentioning that in this latter case the deviation of the points of curve 2 from a constant temperature value can also be explained by the effect of non-uniformity. The interpretation of these results does not involve any difficulties if we rely on the findings of Barnard et al. [13]. Accordingly, the first decreasing part of the curves (Fig. 1) can be related to the continuous change in composition of a single homogeneous phase. The decreasing trend, however, indicates that the higher the oxidation state of the system the lower the temperature needed for the dehydration of the oxyhydroxide. In the intermediate region (oxidation state of 2.3–2.8), the constancy of the peak temperature is a typical feature of a heterogeneous system and this is in excellent agreement with the assumption that above oxidation state 2.25 the partly charged nickel hydroxide is a mixture of two solid solutions [13]. Considering that no pure β phase material exists at higher oxidation states [15], the third descending part of curve 2 denotes the formation of a γ-type nickel oxyhydroxide.

On the basis of earlier experimental results [1–6], it is not to be questioned that the thermal dehydration of nickel hydroxide in air always leads to nickel oxide with an oxidation state above 2. Nevertheless, this deviation from the stoichiometric composition is fairly small and thus in many cases no apparent sign of this feature could be observed. In the contrast, the

TABLE 1

The development of the dehydration reaction in air and in nitrogen

Material	Temperature (°C)	Oxidation state after heat-treatment in air	Relative amount of material transformed in 120 minutes (wt. %) in air	in N_2
β-$Ni(OH)_2$	200	< 2.005	3.5 ± 2	9 ± 2
	250	2.035 ± 0.005	81 ± 2	87 ± 2
	300	2.025 ± 0.005	90 ± 2	95 ± 2
	500	2.010 ± 0.005	99 ± 2	100 ± 2
β-$Ni(OH)_2$/β-NiOOH oxidation state of 2.66	150	2.51 ± 0.02	8.5 ± 2	18 ± 2
	200	2.24 ± 0.02	49 ± 2	70 ± 2
	250	2.060 ± 0.005	73 ± 2	82 ± 2
	300	2.040 ± 0.005	77 ± 2	83 ± 2
	500	2.010 ± 0.005	101 ± 2	98 ± 2

dehydration process of partly charged nickel hydroxide is radically influenced by this factor and it is clear that the rate of the oxidation reaction (eqn. (3)) was high enough to bring the system to a steady state [1,2], in spite of the fact that the decomposition process was still not complete. In order to confirm that the appearance of this steady state entirely depends on the occurrence of reaction (3), the extent of the dehydration reaction in nitrogen atmosphere was determined using the same approximation as in ref. 1. Table 1 shows a comparison of the results obtained by thermal analysis in air and in nitrogen. The relative amount of material transformed in 120 min in nitrogen was always found to be larger than that in air. (Except at 500 °C where the extent of transformation in air and in nitrogen is equal within experimental error). In the range 200–500 °C, the excess amount of material transformed in nitrogen approximately corresponds to the active oxygen content of the system remaining after a heat treatment in air. This finding is in accordance with the evident assumption that reaction (3) does not occur without atmospheric oxygen and water. At 150 °C, however, the rate of the decomposition reaction was so low that the complete decomposition of the sample (in N_2) would have required more than 24 h. Therefore, the amount of material transformed in 120 min does not relate to a final state of the system.

It is very important to mention that the temperature of the DTG peak of the β-$Ni(OH)_2$/β-NiOOH system (independent of the oxidation state) does not depend on the atmosphere used for the measurement. Accordingly, the increase in the rate of the dehydration reaction in nitrogen is still not high enough to alter the thermogravimetric curve recorded at the linear heating rate of 6 °C min^{-1}. This means that the occurrence of reaction (3) in the presence of air is not reflected in the conventional thermoanalytical curves, and presumably this is the reason why the change in the dehydration kinetics has not been recognized in previous studies.

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