

Structure and Aging of Ni(OH)₂ Precipitated from Sulfate and Chloride Solutions

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Kinetics of aging of Ni(OH)₂ particles precipitated from (NiSO₄)_n + (NiCl₂)_{1-n} parent solutions by NaOH solutions are studied by means of X-ray diffraction. Three stoichiometric ratios, *R*, are used. The growth of primary Ni(OH)₂ particles is found to be strongly dependent on *R*. From sulphate solutions a smaller size and a relatively long incubation time for the growth of fresh nuclei are generally found in the understoichiometric case, *R* = 0.8. For *R* ≥ 1.0, the crystal growth is prevented because of free OH⁻ ions in solution. These observations are explained on the basis of the nature and behavior of the double layer formed at the [001] surfaces of the primary particles.

The precipitation of nickel(II) hydroxide from an aqueous solution has been the subject of numerous studies.¹ In particular, the size and shape of the primary particles of the precipitate have been studied by X-ray diffraction.²⁻⁸ The sorption processes on the [001] faces of the platelike, thin crystals of hexagonal Ni(OH)₂ have been shown to control the aging processes in the precipitate. The [001] faces of the crystals are first covered with Ni²⁺ ions, which accounts for the fact that the amount of hydroxide ions needed for a superficially complete precipitation of nickel is less than stoichiometric.⁹ The adsorbed nickel ions attract anions from the solution, thus forming an electric double layer on the surface of the crystals. The aging of the precipitates is caused by the desorption of the anions from the double layer, followed either by their substitution with hydroxide ions, or by a subsequent desorption of the Ni²⁺ ions as well.

Since the type of anion is obviously important in the desorption process, a comparison of the aging of precipitates aged in solutions containing different anions is interesting. The drastic slowing-down of the aging caused by the presence of carbonate ions is already well established.^{4,6} Furthermore, dependence of the strength of the double-layer formation on the nature of the

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ions is revealed by the differing behavior of the pH of the solution during the precipitation: the sulfate ions seem to produce a considerably stronger deviation from stoichiometry in the precipitate than do the chloride or nitrate ions.⁹ However, most studies of the aging process seem to be limited to precipitates obtained from pure chloride or nitrate solutions. In the present work, the aging process of nickel hydroxide, precipitated from $(\text{NiSO}_4)_n + (\text{NiCl}_2)_{1-n}$ solutions, was studied by using X-ray diffraction.

EXPERIMENTAL

The samples were prepared by slowly adding NaOH solutions with various OH^- concentrations (see below) to a $(\text{NiSO}_4)_n + (\text{NiCl}_2)_{1-n}$ solution at 24°C with constant stirring. The values of n used were 0, 0.1, 0.9, and 1.0. The values 0.8, 1.0, and 1.2 were used for the stoichiometric ratio, R ; the value 1.0 corresponding to the amount needed for stoichiometric precipitation of Ni^{2+} . The Ni^{2+} concentration of all solutions was 10 g/l. In this way twelve different solutions were obtained, the volume of each was 1 l after 0.55 N, 0.69 N, and 0.83 N NaOH had been added to set $R=0.8$, 1.0, and 1.2, respectively.

The precipitates were aged at 24°C in the mother liquor until investigated. They were then filtered and placed into a Philips wide angle X-ray goniometer (PW 1380).

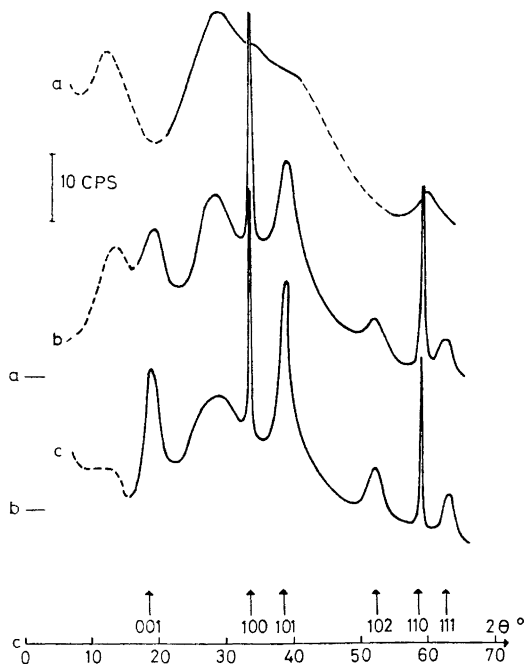


Fig. 1. Diffraction spectra of $\text{Ni}(\text{OH})_2$ samples precipitated stoichiometrically from a NiSO_4 solution at 24°C . Aged in the parent solution (a) 6 h, (b) 8 days, (c) 90 days. The zero level of the curves is indicated in the left margin. Curve for the case (a) was not run between $42^\circ \leq 2\theta \leq 54^\circ$. The dashed parts in the low 2θ region indicate interference caused by the specimen holder.

A CuK α diffraction tube (Ni filter) with the power of 45 kV \times 30 mA was used. The divergence of the beam was 1°.

Samples of the precipitates were examined at times up to three months from precipitation. A diffraction spectrum was run at $2\theta = 30^\circ \dots 36^\circ$ and $56^\circ \dots 62^\circ$. The form of the diffraction peaks was carefully recorded by running the spectrometer at a sufficiently slow speed ($0.5^\circ 2\theta/\text{min}$) in these regions. In order to permit an analysis of the intensity along [001], as made in Ref. 7, an attempt was made to prepare oriented samples with the [001] direction parallel to the diffraction vector. To this end, a diffraction spectrum on a sample precipitated from NiSO₄ was run up to $2\theta = 65^\circ$. This spectrum is shown in Fig. 1. It proved very difficult to obtain a sufficiently strong [001] orientation of the sample, particularly at the start of aging. Samples prepared from chloride solutions were clearly different in this respect. Nevertheless, the [001] reflection of all samples was found to be too weak for quantitative measurements. Furthermore, the masking effect of the adjacent diffuse peak at $2\theta \approx 13^\circ$, caused by the plastic sample holder, proved disturbing (Fig. 1). Hence, only the crystallization in the $[hkl]$ directions (hexagonal plane) of Ni(OH)₂ has been studied here.

Fig. 1. also shows another diffuse peak at $2\theta \approx 28^\circ$. It is caused by water remaining in the sample. This peak is, within the resolution of our measurement, identical to the diffuse peak obtained from a pure water sample. This does not, of course, prove that all water in the precipitates is similarly bonded; *cf.* Refs. 10, 11. The remaining peaks in Fig. 1 can be attributed to different $[hkl]$ reflections of Ni(OH)₂, as indicated by vertical arrows.

The full widths at half maximum of the [100] and [110] peaks were measured for each run from recordings similar to the ones shown in Fig. 2. These widths were then corrected for instrumental broadening by a graphical method.¹² The average diameter of the primary disc-shaped particles in the precipitate was determined as an arithmetic mean of the sizes in the [100] and [110] directions from the corrected half widths, β , by using the Scherrer formula¹⁰

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Here, D is the average diameter of the particles in the direction of the hexagonal base plane, $K = 0.9$ and $\lambda = 1.541 \text{ \AA}$.

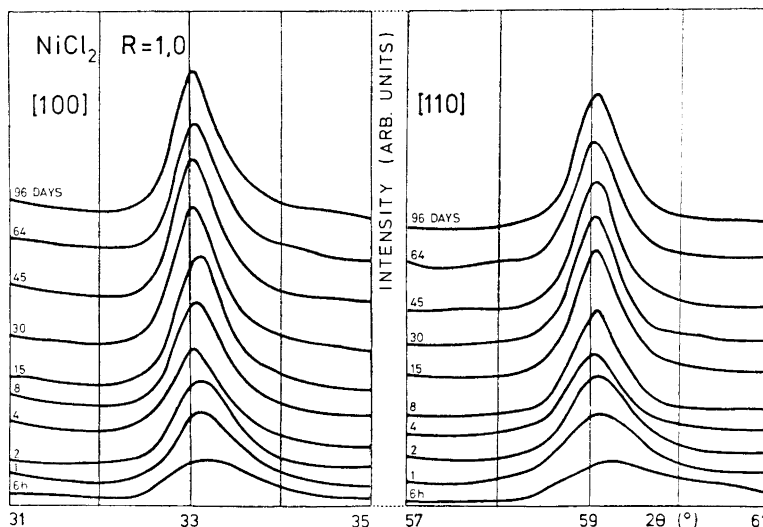


Fig. 2. Effect of aging on the primary particle size of Ni(OH)₂ precipitated from NiCl₂ solution. $R = 1.0$. Directions are [100] and [110].

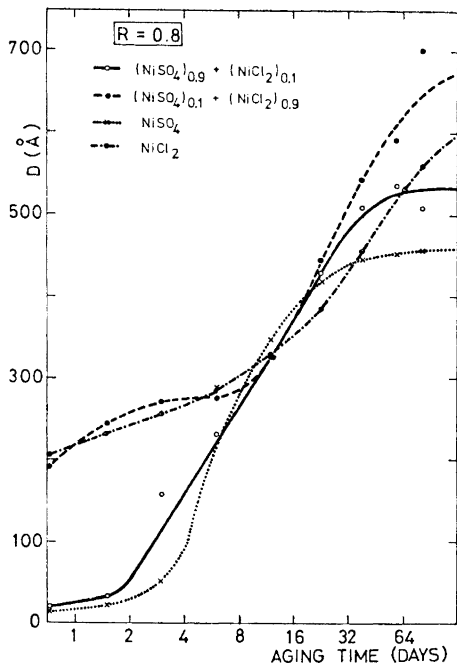


Fig. 3. The average particle size, D , in the hexagonal plane [100] and [110] as a function of the aging time for an under-stoichiometric amount of NaOH ($R=0.8$).

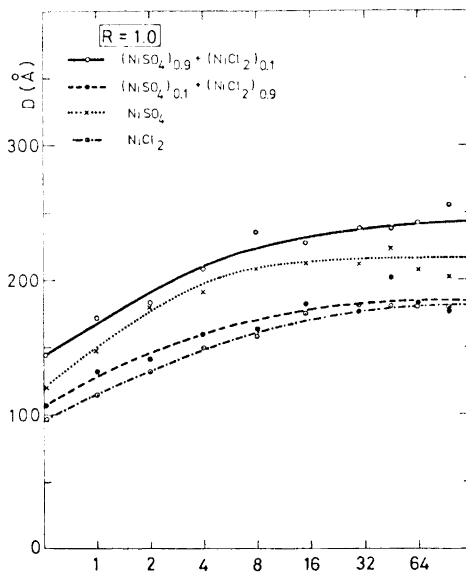


Fig. 4. The data corresponding to Fig. 3 for $R=1.0$.

Figs. 3 to 5 shows the effect of the aging time on the particle size of $\text{Ni}(\text{OH})_2$ precipitated from the above mentioned solutions for the three values of the stoichiometric ratio, R .

DISCUSSION

A comparison of a part of the present work with the results previously obtained for precipitates prepared from a pure chloride solution under similar conditions¹¹ shows that the structure and the aging mechanism of the precipitates are basically the same in both cases. It has been found, however, that the quantitative values of D may show quite a considerable amount of variance because of certain difficulties in the sample preparation. The anomalous behavior of the growth rate of the primary particles precipitated from the $(\text{NiSO}_4)_{0.9} + (\text{NiCl}_2)_{0.1}$ solution at $R=1.2$ (Fig. 5) remains unexplained, but is probably associated with the preparation conditions which could have changed drastically during precipitation (impurities likely to be present). This curve has been disregarded in the following considerations.

A qualitative comparison of Figs. 3 to 5 is interesting. For the under-stoichiometric case, $R=0.8$ (Fig. 3), a clearly distinguishable initiation of the growth after an incubation time (about 3 days) is found for the growth of the

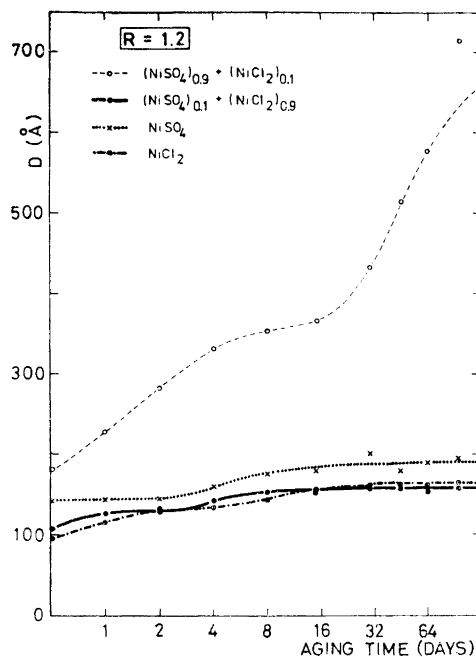


Fig. 5. The data corresponding to Fig. 3 for $R=1.2$.

particles prepared from solutions with sulfate predominating ($n=0.9, 1$), whereas the particles prepared from solutions with large amounts of chloride ions ($n=0.1, 0$) begin to grow without a clearly distinguishable incubation time. Furthermore, the size of fresh nuclei is considerably smaller in sulfate dominated solutions (about 20 Å) than in predominantly chloride solutions

Table 1. Parent solutions from which the Ni(OH)₂ particles were precipitated, the average sizes of fresh nuclei (1 day) and aged particles (90 days) with estimated error limits (possible systematic errors neglected) for different stoichiometric ratios R .

Parent solution	D (1 day), Å	D (90 days), Å	R
NiSO ₄	15 ± 5	460 ± 120	0.8
(NiSO ₄) _{0.9} + (NiCl ₂) _{0.1}	25 ± 5	530 ± 170	0.8
(NiSO ₄) _{0.1} + (NiCl ₂) _{0.9}	220 ± 45	650 ± 200	0.8
NiCl ₂	220 ± 45	570 ± 190	0.8
NiSO ₄	150 ± 25	215 ± 45	1.0
(NiSO ₄) _{0.9} + (NiCl ₂) _{0.1}	165 ± 30	240 ± 55	1.0
(NiSO ₄) _{0.1} + (NiCl ₂) _{0.9}	125 ± 20	185 ± 35	1.0
NiCl ₂	115 ± 20	180 ± 35	1.0
NiSO ₄	145 ± 25	190 ± 35	1.2
(NiSO ₄) _{0.9} + (NiCl ₂) _{0.1}	—	—	—
(NiSO ₄) _{0.1} + (NiCl ₂) _{0.9}	130 ± 20	165 ± 30	1.2
NiCl ₂	115 ± 20	160 ± 30	1.2

(about 200 Å). On the other hand, the size of fresh nuclei are rather similar (about 100 Å) for all solutions when $R=1.0$, see also Table 1.

Widely varying, but systematic, behavior of the crystal growth is found when R and the anion composition are changed. Where a clearly distinguishable incubation time is found, the growth, once started, progresses rapidly and is almost complete in two months. In the other cases, the growth is more gradual and seems to continue later. An overstoichiometric amount of NaOH always yields very low growth rates, indicating an efficient inhibition process in the presence of free hydroxyde ions in all solutions (Fig. 5).

The above observations show that the attachment of the sulfate ions to the double layer is obviously stronger than that of the chloride ions. A likely bonding mechanism for sulfate ions is the formation of a complex involving the top layer atoms of the hydroxide precipitate. Such a mechanism is not likely in the case of chloride ions. This explains the incubation time needed for the growth in understoichiometric, sulfate-dominated solutions. It seems likely, however, that sulfate ions are not adsorbed into the double layer in preference to chloride ions, despite the stronger bonding of the former. This is shown by the behavior of the solution with $n=0.1$, which closely resembles the behavior of a pure chloride solution. Hence, the kind of anions initially attached to the double layer is determined by statistics rather than by the strength of the bonding (the number of Cl^- is twice the amount of SO_4^{2-}).

The growth behavior in the overstoichiometric region suggests a virtually permanent double layer inhibiting growth, irrespective of the kind of anions in the solution. The natural explanation is that the anion attached to the double layer is in this case the OH^- ion, which is now abundant in the solution.

Finally, it should be noted that the above description in terms of simple free ions in the solution is, of course, an over-simplification of the real situation, in which solvated complexes, including the above ions, in fact exist. This does not, however, alter the conclusion concerning the effect of the relative abundances of the simple ions on the growth mechanism.

The aging structures produced here resemble the "turbostratic" structure obtained by pressure washing precipitates from nitrate solutions.^{8,13} Unfortunately, no data for the aging kinetics of these precipitates have so far been published.

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