Journal of Crystal Growth 312 (2010) 2358–2362

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Crystallization of metal fluoride hydrates from mixed hydrofluoric and nitric acid solutions, part II: Iron (III) and nickel (II)

Kerstin M. Forsberg [a], Åke C. Rasmuson [a,b,*]

[a] Department of Chemical Engineering and Technology, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden
[b] Department of Chemical and Environmental Science, Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

ARTICLE INFO

Keywords:
A1. Supersaturated solutions
A2. Growth from solutions
B1. Acids
B1. Inorganic compounds

ABSTRACT

Crystallization of nickel fluoride hydrate from mixed pickle acid and the influence of Ni(II) on growth rate of β-$FeF_3 \cdot 3H_2O$ have been studied. Iron and nickel crystallize into an unidentified Fe/Ni fluoride hydrate crystal having the overall mol ratio of Ni, Fe, and F equal to 1:2:8, which is in accordance with the number of fluoride ions needed to balance the positive charges of Ni and Fe. The most probable empirical formula of this material is $(FeF_3)_2NiF_2(H_2O)_{6-10}$. By seeded isothermal desupersaturation experiments, growth rate of β-$FeF_3 \cdot 3H_2O$ crystals at 50 °C has been studied in a hydrofluoric acid and nitric acid solution containing Ni(II). It is found that the growth rate of β-$FeF_3 \cdot 3H_2O$ is essentially uninfluenced by the presence of 4 g/kg Ni(II).

1. Introduction

Mixtures of hydrofluoric acid and nitric acid (denoted mixed acid) are used to pickle stainless steels. During pickling the metal ion concentration increases in the mixed acid solutions. Spent stainless steel pickle acid solutions contain high amounts of mainly iron (III) (< 35 g/kg), chromium (III) (1–5 g/kg), and nickel (II) (1–5 g/kg). Different methods have been developed to separate the metals from the mixed acid and the most recent methods are based on precipitation [1–3]. Crystallization of metal fluoride hydrates after concentration by nanofiltration is a straightforward and energy efficient method to separate the metal ions from the mixed acid [3,4]. In this process metal fluorides are separated from the pickle bath solution through crystallization and the solution leaving the crystallizer is then re-circulated back to the pickling bath. This will lead to a gradual accumulation of metal ions like chromium and nickel until a level is reached where these metals may also start to crystallize. Accordingly, in a continuous steady state operation the pickle bath solution will have different compositions at different times, leading the crystallization process to operate at different conditions and other solid phases than just iron(III) fluoride will crystallize.

In the first part of this work crystallization in mixed acid solutions containing iron (III) and chromium (III) was investigated and the influence of chromium on growth rate of β-$FeF_3 \cdot 3H_2O$ was examined [5]. In the second part crystallization in mixed acid supersaturated with Fe(III) and Ni(II) is investigated. Nickel(II) has been found to precipitate as $NiF_2 \cdot 4H_2O$ from mixed acid [6,7]. Iron(III) crystallizes as a fluoride trihydrate ($FeF_3 \cdot 3H_2O$) in HF and HNO_3 pickle liquors [3,7]. The iron fluoride trihydrate has two polymorphic forms, the metastable α-phase and the stable β-phase [8].

2. Experimental work

Crystallization of β-$FeF_3 \cdot 3H_2O$ and crystallization from solutions supersaturated with both iron(III) and nickel(II) have been studied by performing seeded desupersaturation experiments at 50 °C and measuring the desupersaturation curves. The crystals have been investigated by powder XRD and SEM–EDAX. Seed crystals are shown in Fig. 1. The acid and metal concentrations of the prepared supersaturated solutions are presented in Table 1. All concentrations are reported as mol or g per kg solution. The supersaturated solutions were prepared from a 55 g Fe(III)/kg iron nitrate solution ($Fe(NO_3)_3 \cdot 9H_2O$ (s), PA, > 99%), a 113 g Ni/kg iron nitrate solution ($Ni(NO_3)_2 \cdot 6H_2O$ (s), PA, > 99%), de-ionized filtered water, 65.0–69.4 wt% HNO_3 and 40.0–40.5 wt% HF. Supersaturation decay was measured by taking out solution samples every hour and measuring total iron concentration by inductively coupled plasma atomic emission spectroscopy (ICP-AES). In order to

---

* Corresponding author at: Department of Chemical Engineering and Technology, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden.
Tel.: +46 8 790 8227; fax: +46 8 105228.
E-mail address: rasmuson@ket.kth.se (Å.C. Rasmuson).

0022-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2010.05.017

measure iron and nickel concentration in the solution in equilibrium with the crystals the suspensions were left in a water bath (stirred at 50 °C) and a solution sample was taken 1 week and sometimes also 2 weeks after the beginning of the growth experiment (i.e. after the addition of seed crystals). The experimental procedure is explained in more detail in part I [5].

The growth kinetics of β-$FeF_3 \cdot 3H_2O$ were evaluated from the experiment where β-$FeF_3 \cdot 3H_2O$ only crystallized in the presence of lower concentrations of Ni(II). The method of evaluation is presented in part I of this work [5].

3. Results

3.1. *Crystallization from solutions of Fe(III) and Ni(II)*

Fig. 2 shows concentration versus time curves for experiments A–C (as squares, diamonds, and triangles, respectively), where the initial nickel concentration is 4 g/kg (A), 40 g/kg (B) and 55 g/kg (C), respectively. The measured nickel concentration after 15 days in experiments A and C and after 8 days in experiment B is also shown as horizontal lines in the figure for comparison. At the higher level, concentration is shown to increase as a result of the removal of water as hydrate during crystallization of β-$FeF_3 \cdot 3H_2O$. From Fig. 2 it is evident that in these experiments there is no precipitation of Ni(II) during the first 600 min. However, after a longer period of time there is a decrease in Ni(II) concentration in the experiments having a higher Ni(II) concentration (B and C), as shown in Fig. 2 by the straight horizontal lines and as presented in Table 2. Obviously, there is crystallization of nickel in experiment B and C but not in experiment A.

The iron concentration in sample A after 15 days (8.8 g/kg) is close to the solubility of β-$FeF_3 \cdot 3H_2O$ in solutions of 3.5 mol/kg HF_{total} and 3.2 mol/kg HNO_3 at 50 °C (9 g $(Fe(III)_{tot})$/kg; [9]). However, the iron concentrations after 8 days in experiment B (5.8 g/kg) and after 15 days in experiment C (6.2 g/kg) are lower than the solubility of β-$FeF_3 \cdot 3H_2O$ in 3.4 mol/kg HF_{total} and 3.2 mol/kg HNO_3 (9 g/kg) and in 2.4 mol/kg HF_{total} and 4.2 mol/kg HNO_3 (9 g/kg) at 50 °C [9].

After the first 10 h and after 15 days of the experiment, the crystals from experiment A were white to pink and the crystals from experiment C were green. Crystals of β-$FeF_3 \cdot 3H_2O$ are pink. The crystals from experiments B and C were investigated by powder-XRD but the resulting diffractogram could not be found in the powder data file (International Centre for Diffraction Data). The diffractogram of the crystals from experiment B is shown in Fig. 3. An attempt was made to determine the structure by single crystal XRD but the crystals were too small. The crystals were investigated by SEM-EDAX, and the results are shown in Figs. 4a and b. The crystals from experiment A are shown in Fig. 4c and are of about the same size (about 5 μm) as the seed crystals. The samples from experiments B and C contains crystals in two size ranges, where the larger crystals are as much as 5 times larger (25 μm) than the largest crystals seen in the sample from experiment A. The SEM-EDAX analysis showed that both large and small crystals in samples B and C had the same composition of Fe, Ni, F, and O, down to a depth of 0.5 μm into the crystals, see Table 3.

3.2. *Crystal growth rate of β-$FeF_3 \cdot 3H_2O$*

The linear growth rate of the crystals was determined by the same methodology as described in part I of this work [5]. Growth rate of β-$FeF_3 \cdot 3H_2O$ was evaluated from the experiments where only iron in the form of β-$FeF_3 \cdot 3H_2O$ (A) precipitated in the presence of Ni(II). Growth rate of β-$FeF_3 \cdot 3H_2O$ was not evaluated from experiments B and C although nickel was not precipitated

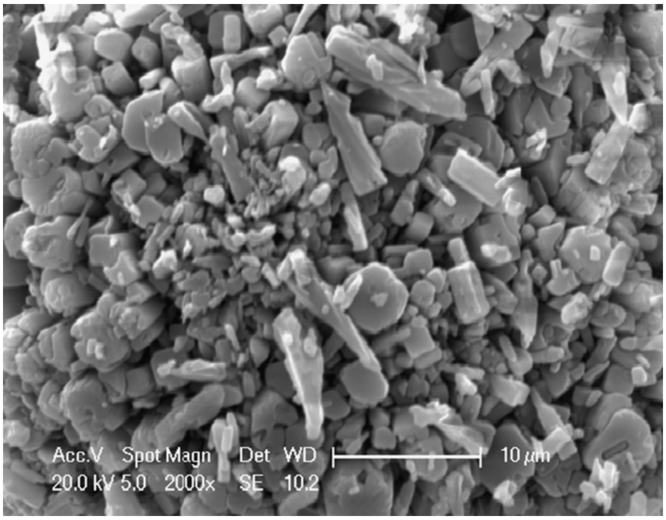

Fig. 1. β-$FeF_3 \cdot 3H_2O$ seed crystals.

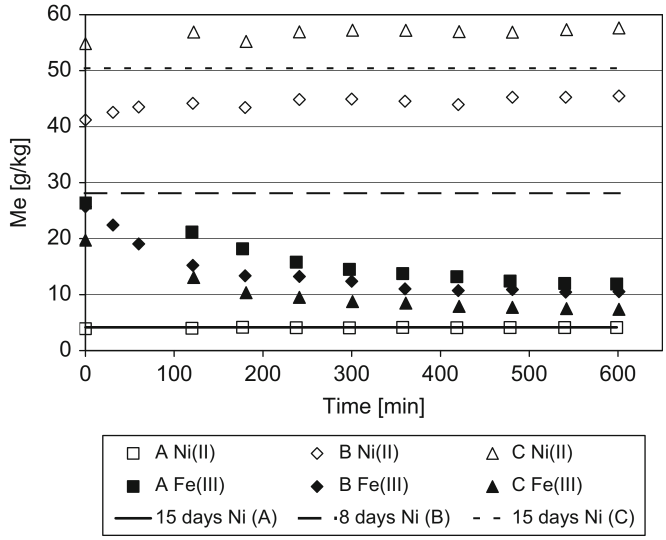

Fig. 2. Desupersaturation curves in experiments with solutions initially containing 4 mol/kg HF_{total} and 3 mol/kg HNO_3 (A, B) or 3 mol/kg HF_{total} and 4 mol/kg HNO_3 (C) and Fe(III) and Ni(II) (A)–(C) at 50 °C.

Table 1
Supersaturated solutions prepared for the growth rate experiments.

Experiment	HF_{total} (HF_{free})[a] (mol/kg)	HNO_3 (mol/kg)	Fe(III) (g/kg)	Cr(III) (g/kg)	Ni(II) (g/kg)	Seed crystals
A	4.3 (3.3)	3.0	26.3	–	3.9	β-$FeF_3 \cdot 3H_2O$
B	4.3	3.0	25.7	–	41.2	β-$FeF_3 \cdot 3H_2O$
C	3.0	4.0	19.7	–	54.8	β-$FeF_3 \cdot 3H_2O$

[b] Calculated from solution preparation.

[a] Calculated by SSPEC.