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Technical note

Recovery of a composite powder from NdFeB slurry by co-precipitation

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ABSTRACT

A co-precipitation process was used to recover composite powders from a NdFeB slurry. The most appropriate concentration of HCl and a *v/w* ratio were obtained in the leaching process. The optimum pH range for the co-precipitation process was determined by the log[Me(Nd, Fe, Co, Pr)]–pH curve simulated using a thermodynamics model. Fe_2O_3, $Fe_2O_3 \cdot Nd_2O_3$, and Pr_2CoO_4 phases were detected in the final composite powders after firing the co-precipitated products at 1273 K for 2 h. The content of the valuable metals (Nd, Pr, Co, Fe) in the obtained composite powders was greater than 99.4%, which meets the raw material requirements for preparing recycled NdFeB magnetic powders. The main advantages of the co-precipitation process are that it is efficient, low-cost, and environmentally friendly.

1. Introduction

Increasing attention has been focused on the recycling and recovery of rare earth (RE) elements from NdFeB waste because of the recent shortage of mineral resources and their high prices (China Rare Earth, 2011; Schlummer et al., 2007; Su, 1999; Wang and Shu, 2000). The current methods, such as selective precipitation by oxalic acid (Tang et al., 2009), hydrofluoric acid (Wang et al., 2006), and sodium, or ammonium intermediate double salts (Wei et al., 2010), based aqueous technology that begins with the dissolution of the NdFeB scrap using HNO_3, H_2SO_4 or HCl, and then recover RE elements by selectively interacting with these elements and not with the other elements, which result in secondary environmental pollution. Iron (Fe) and cobalt (Co) were left in the solution without any special treatment and sulfide fumes were generated in the process of ammonium intermediate double salts. At last, a complete separation of RE can be accomplished by using solute/solvent extraction or ion exchange technology (Chen, 2004; Houli, 2005; Vander Hoogerstraete et al., 2013). Furthermore, many of the complicated processes applied to extract high purity RE have significantly increased the recovery cost, which is not suitable for application to industrial production (Chen, 2004).

Considering the environmental impact and high cost, in this study, we substituted a co-precipitation method (Cai et al., 2008; Su et al., 2006; Vives et al., 1999) for the selective precipitation methods, to recover RE from a NdFeB slurry. This method avoids the complicated and high-cost extraction methods, normally consisting of 60–70 extraction cycles (Houli, 2005), which are traditionally used to obtain single, high purity RE. In addition, the amount of extracting agent and back-extractant (e.g. hydrochloric acid, phophorate P507 and di(2-ethylhexly)phosphoric acid) used can be greatly reduced, to make processing more environmentally friendly. Powder metallurgy processing involves the sintering of a powder which is aligned in a magnetic field. This process generates grinding swarf, a mixture of oil, machining chips and other solid residue, in addition to discarded sintered and unsintered magnet pieces (Livingston, 1990). The NdFeB slurry consists of NdFeB waste mixed with the cutting fluid, grinding fluid, oil, machining chips and grind swarf from the production and formation of NdFeB products. In contrast to the selective precipitation methods, the co-precipitation method can simultaneously recover most valuable elements in the NdFeB slurry. A composite powder, containing RE and elemental Fe and Co, can be obtained using this method, which can be directly used as a raw material for preparing all type of recycled NdFeB magnetic powder with controlling to add desirable elements. Moreover, simulations and calculations of the thermodynamics (Haghshenas Fatmehsari et al., 2009; Li et al., 2009; Tang et al., 2004; Valverde et al., 2008) model using MATLAB (Charsooghi et al., 2011) were used to design simple and efficient experiments. In this paper, the simulations and experiments in $H_2C_2O_4$–NH_3 co-precipitation systems are discussed in detail.

2. Simulation

The simulation model for the thermodynamics of the $H_2C_2O_4$–NH_3 system was established using the surplus concentration of each metal ion and the variation in the pH. The metal ions (Nd^{3+}, Pr^{3+}, Co^{2+}, Fe^{3+}, and Fe^{2+}), the complexing agents (OH^-, NH_3, and $C_2O_4^{2-}$),

Abbreviation: RE, rare earth.

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and the precipitants (OH^- and $C_2O_4^{2-}$) were chosen to form the complexation–precipitation system of $H_2C_2O_4$–NH_3 based on the mass balance principle and the simultaneous equilibrium principle. Using the chemical reactions and the chemical equilibrium parameters, balanced Eqs. (1-1) to (1-15) were established:

$$\left[H^+\right] = 10^{-pH} \tag{1-1}$$

$$[OH^-] = K_w * 10^{pH} \tag{1-2}$$

$$\left[Nd^{3+}\right] = \min\left\{\left(K_{spnac}/\left[C_2O_4^{2-}\right]^3\right)^{1/2}, K_{spnh}/[OH^-]^3\right\} \tag{1-3}$$

$$\left[Pr^{3+}\right] = \min\left\{\left(K_{sppac}/\left[C_2O_4^{2-}\right]^3\right)^{1/2}, K_{sppH}/[OH^-]^3\right\} \tag{1-4}$$

$$\left[Fe^{3+}\right] = K_{spf3h}/[OH^-]^3 \tag{1-5}$$

$$\left[Fe^{2+}\right] = \min\left\{K_{spf2ac}/\left[C_2O_4^{2-}\right], K_{spf3h}/[OH^-]^2\right\} \tag{1-6}$$

$$\left[Co^{2+}\right] = K_{spch}/[OH^-]^2 \tag{1-7}$$

$$\begin{aligned}[H_2C_2O_4] &= \left[C_2O_4^{2-}\right] + [H\,C_2O_4^-] + [C_2H_2O_4] \\ &= \left[C_2O_4^{2-}\right]\left\{1 + 10^{-pH}/K_{aac2} + 10^{-2pH}/(K_{aac2} * K_{aac1})\right\}\end{aligned} \tag{1-8}$$

$$\begin{aligned}[Nd] &= \left[Nd^{3+}\right] + \left[Nd(OH)^{2+}\right] + \left[Nd(C_2O_4)^+\right] + \left[Nd(C_2O_4)_2^-\right] \\ &+ \left[Nd(C_2O_4)_3^{3-}\right] = \left[Nd^{3+}\right] + K_{nh} * \left[Nd^{3+}\right] * [OH^-] \\ &+ K_{nac11} * \left[Nd^{3+}\right] * \left[C_2O_4^{2-}\right] + K_{nac12} * \left[Nd^{3+}\right] * \left[C_2O_4^{2-}\right]^2 \\ &+ K_{nac13} * \left[Nd^{3+}\right] * \left[C_2O_4^{2-}\right]^3\end{aligned} \tag{1-9}$$

$$\begin{aligned}[Pr] &= \left[Pr^{3+}\right] + \left[Pr(OH)^{2+}\right] + \left[Pr(C_2O_4)^+\right] + \left[Pr(C_2O_4)_2^-\right] \\ &+ \left[Pr(C_2O_4)_3^{3-}\right] = \left[Pr^{3+}\right] + K_{ph} * \left[Pr^{3+}\right] * [OH^-] \\ &+ K_{pac11} * \left[Pr^{3+}\right] * \left[C_2O_4^{2-}\right] + K_{pac12} * \left[Pr^{3+}\right] * \left[C_2O_4^{2-}\right]^2 \\ &+ K_{pac13} * \left[Pr^{3+}\right] * \left[C_2O_4^{2-}\right]^3\end{aligned} \tag{1-10}$$

$$\begin{aligned}[Fe2] &= \left[Fe^{2+}\right] + \left[Fe(OH)^+\right] + \left[Fe(OH)_2^0\right] + \left[Fe(OH)_3^-\right] \\ &+ \left[Fe(OH)_4^{2-}\right] + \left[Fe(C_2O_4)^0\right] + \left[Fe(C_2O_4)_2^{2-}\right] \\ &+ \left[Fe(C_2O_4)_3^{4-}\right] + \left[Fe(NH_3)^{2+}\right] + \left[Fe(NH_3)_2^{2+}\right] \\ &+ \left[Fe(NH_3)_4^{2+}\right] = \left[Fe^{2+}\right]\left\{1 + K_{f2h1} * [OH^-]\right. \\ &+ K_{f2h2} * [OH^-]^2 + K_{f2h3} * [OH]^3 + K_{f2h4} * [OH^-]^4 \\ &+ K_{f2ac11} * \left[C_2O_4^{2-}\right] + K_{f2ac12} * \left[C_2O_4^{2-}\right]^2 \\ &+ K_{f2ac13} * \left[C_2O_4^{2-}\right]^3 + K_{f2am11} * [NH_3] \\ &\left. + K_{f2am12} * [NH_3]^2 + K_{f2am14} * [NH_3]^4\right\}\end{aligned} \tag{1-11}$$

$$\begin{aligned}[Fe3] &= \left[Fe^{3+}\right] + \left[Fe(OH)^{2+}\right] + \left[Fe(OH)_2^+\right] + \left[Fe(OH)_3^0\right] \\ &+ \left[Fe(C_2O_4)^+\right] + \left[Fe(C_2O_4)_2^-\right] + \left[Fe(C_2O_4)_3^{2-}\right] \\ &= \left[Fe^{3+}\right]\left\{1 + K_{f3h1} * [OH^-] + K_{f3h2} * [OH^-]^2 + K_{f3h3} * [OH^-]^3\right. \\ &\left. + K_{f3ac11} * \left[C_2O_4^{2-}\right] + K_{f3ac12} * \left[C_2O_4^{2-}\right]^2 + K_{f3ac13} * \left[C_2O_4^{2-}\right]^3\right\}\end{aligned} \tag{1-12}$$

$$\begin{aligned}[Co] &= \left[Co^{2+}\right] + \left[Co(OH)^+\right] + \left[Co(OH)_2^0\right] + \left[Co(OH)_3^-\right] \\ &+ \left[Co(OH)_4^{2-}\right] + 2 * \left[Co_2(OH)_3^{3-}\right] + 4 * \left[Co_4(OH)_4^{4-}\right] \\ &+ [Co(NH_3)] + \left[Co(NH_3)^{2+}\right] + \left[Co(NH_3)_2^{2+}\right] + \left[Co(NH_3)_3^{2+}\right] \\ &+ \left[Co(NH_3)_4^{2+}\right] + \left[Co(NH_3)_5^{2+}\right] + \left[Co(NH_3)_6^{2+}\right] \\ &+ \left[Co(C_2O_4)^0\right] + \left[Co(C_2O_4)_2^{2-}\right] + \left[Co(C_2O_4)_3^{4-}\right] \\ &= \left[Co^{2+}\right]\left\{1 + K_{ch1} * [OH^-] + K_{ch2} * [OH^-]^2 + K_{ch3} * [OH^-]^3\right. \\ &+ K_{ch4} * [OH^-]^4 + 2 * K_{ch21} * \left[Co^{2+}\right] * [OH^-] \\ &+ 4 * K_{ch44} * \left[Co^{2+}\right]^3 * [OH^-]^4 + K_{cam11} * [NH_3] + K_{cam12} * [NH_3]^2 \\ &+ K_{cam13} * [NH_3]^3 + K_{cam14} * [NH_3]^4 + K_{cam15} * [NH_3]^5 \\ &+ K_{cam16} * [NH_3]^6 + K_{cac11} * [C_2O_4]^{2-} + K_{cac12} * \left[C_2O_4^{2-}\right]^2 \\ &\left. + K_{cac13} * \left[C_2O_4^{2-}\right]^3\right\}\end{aligned} \tag{1-13}$$

$$\left[NH_4^+\right] = K_{am} * [NH_3] * \left[H^+\right] \tag{1-14}$$

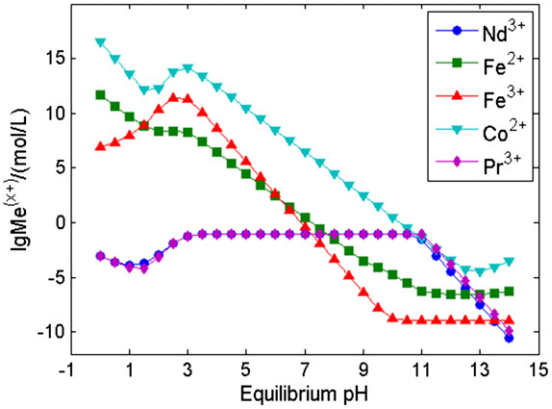

Fig. 1. Theoretical log [Me^{x+}]–pH curve in the $H_2C_2O_4$–NH_3 system.