

A NOVEL PRODUCTION PROCESS OF COMPOSITE POWDERS USING SOLVENT EXTRACTION

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ABSTRACT

Some fundamental studies were carried out in order to produce composite powders comprising of two or three metal oxides by using liquid-liquid extraction and to develop the control technology of the particle size. The combination of samarium and cobalt was selected as the two component composite powders. Both stripping and crystallization occurred at the same time by emulsifying the organic phase loading the two metals extracted with Versatic Acid 10 and the aqueous solution containing oxalic acid. The effect of aqueous pH, oxalic acid concentration and agitation speed was examined on some properties such as crystallization percent, particle size and shape of each metal oxide powders obtained in this process. The analysis by using EDX showed that the two metal oxides were distributed uniformly.

INTRODUCTION

Composite metal and metal oxide powders with high purity are indispensable as industrial materials in the fields of electrical engineering, electronics and metallurgy. It is difficult to mix metal powders or metal oxide powders uniformly for the production of alloy powders.

If insoluble metal salts are allowed to collect as crystallization products in the crystallization-stripping process, the conventional melting and crushing process can be avoided¹⁾⁻⁴⁾. After mixing of the organic phase containing metals in fixed composition, fine metal and metal oxide powders of alloy composition are produced by using a crystallization-stripping method⁵⁾⁻⁷⁾. Versatic Acid 10 and D2EHPA, both acidic extractants, were chosen in this experiment, and the metal oxide powders were produced by using oxalic acid as a crystallization reagent. Mixed metal oxalates containing samarium and cobalt were precipitated from the mixed organic phase containing these metals. Furthermore, the physical properties of the powders, such as particle

size, shape and thermal decomposition, were measured in order to evaluate them for industrial purposes.

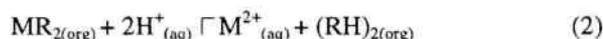
SOLVENT EXTRACTION-CRYSTALLIZATION STRIPPING PROCESS

Solvent extraction is mainly constructed by three processes, namely extraction, scrubbing and stripping. Extraction is the operation in which an objective component is separated from the aqueous phase into the organic phase using an extraction reagent. Scrubbing is the operation in which undesirable components in the organic phase are removed to the aqueous phase. Stripping is the operation where the objective component is returned from the organic phase to the aqueous phase again. Our process is a modification of the conventional method by adding a crystallization operation, in which the metal salts of low solubility are precipitated in the aqueous phase. The crystallization operation means the collection of stripped metal ions as insoluble salts in the aqueous phase. The reaction mechanism in this process is shown by the following equations.

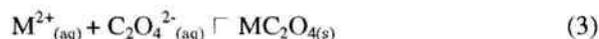
Extraction



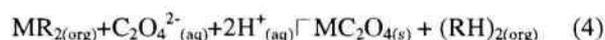
Stripping



Crystallization of oxalate



The overall crystallization-stripping reaction is shown as,



where subscripts, aq, org and s, mean aqueous, organic and solid phases, respectively.

EXPERIMENTAL METHOD

Versatic acid 10 and D2EHPA diluted in kerosene were used in the concentration range of 0.5 ~ 1.0 mol/dm³. Aqueous solutions containing Sm(Γ) and Co(Γ) were prepared at a fixed concentration as aqueous feed. Crystallization-stripping experiments were carried out as follows. Fifty cm³ of the organic phase containing metal and the same volume of oxalic acid solution were placed in a 4-necked flask and agitated with an impeller. One hundred cm³ of the solvent mixture was separated in the separation funnel into organic-aqueous-solid phases. Metal in the organic phase was stripped using 2 mol/dm³ HCl. Metal concentrations were determined by using an atomic absorption spectrometer(Z-6000 Hitachi Ltd.). The crystallization products were washed several times with acetone, and the composition was identified by X-ray diffraction analysis (JDX-3530 JOEL Ltd.). The size and shape of crystallization products were monitored by SEM (JSM-5410 JOEL Ltd.). Thermal decomposition analysis of the crystallization products was carried out in order to confirm the temperatures at which metal oxalates were converted to oxides.

RESULTS AND DISCUSSION

The aim of this study is to clarify the phenomena and mechanisms of the crystallization-stripping of metals from the organic phase containing Sm(Γ) and Co(Γ). Extraction curves of Sm(Γ) and Co(Γ) with Versatic Acid 10 and D2EHPA are shown in Figure 1. The figure shows that the metals can be extracted at different pH values with Versatic Acid 10 and D2EHPA. Sm(Γ) is extracted at the lowest pH levels (pH 0-1) with D2EHPA, while Co(Γ) is extracted at pH 2-3.5 with D2EHPA. It is found that the separation of Sm(Γ) from Co(Γ) is carried out easily by extraction with D2EHPA. On the other hand, Sm(Γ) and Co(Γ) are extracted at a higher pH with Versatic Acid 10 than they are with D2EHPA. The difference in extraction behavior is based on the value of dissociation constants of the two extractants.

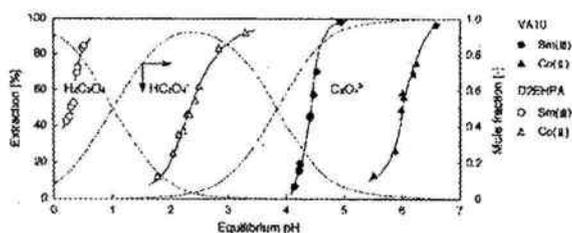


Figure 1: Mole fraction of oxalic acid in aqueous solution and extraction curves with various extractants

Figure 1 also shows a distribution diagram for oxalic acid in an aqueous solution. Oxalate ion (C₂O₄²⁻), which contributes to the formation of insoluble oxalates, exists in the condition of pHΓ 4.0. As the extraction is a reversible reaction, an aqueous solution with a lower pH than equilibrium pH of the extraction is required in order to strip the metals from Versatic acid 10. The extraction curves of Sm and Co with Versatic acid 10 locate in the pH region, 4-5 and 5.5-6.5, respectively, while the extraction of Sm and Co with D2EHPA takes place in the pH region, 0-1 and 1.5-3, respectively. It is considered that the Versatic acid 10 is favorable for crystallization- stripping from the viewpoint of the distribution of oxalate ion (C₂O₄²⁻) and the position of the extraction curve.

The crystallization-stripping was carried out at a concentration of 0.1mol/dm³ oxalic acid. Versatic acid 10 organic phases of 0.1mol/dm³ containing 0.01mol/dm³ Sm(Γ) or 0.085mol/dm³ Co(Γ) were stripped by oxalic acid. Stripping and crystallization approach almost 100% within 300s for Sm(Γ) and 1200s for Co(Γ). Figure 2 shows the relationship between pH and stripping, and pH and crystallization. The crystallization of Sm(Γ) takes place in aqueous solution prior to Co(Γ) crystallization because of the low solubility of Sm(Γ) oxalate. The crystallization of Sm(Γ) oxalate takes place in the wide pH range of 0.5 to 6, while Co(Γ) oxalate is quantitatively produced in the pH range of 2 to 6. The decrease in crystallization of Sm(Γ) in the higher pH is explained by the fact that the stripping does not proceed in the pH region, whereas the decrease in Co(Γ) crystallization is due to the high solubility of Co(Γ) oxalate in the pH region.

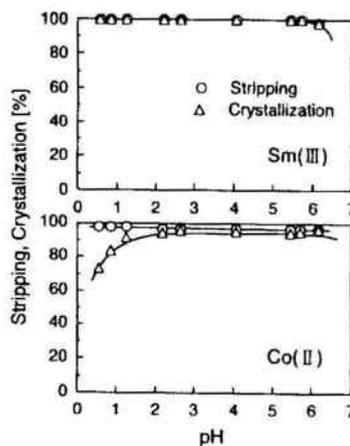


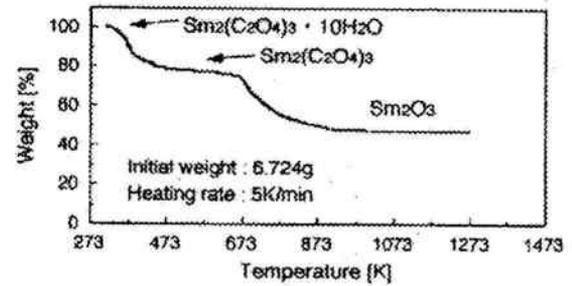
Figure 2 : Stripping and crystallization of Sm(III) and Co(II) as a function of pH

The crystallization product was separated by filtration and washed with acetone several times. Undesirable components were removed from the surface of the crystallization products. Then, the

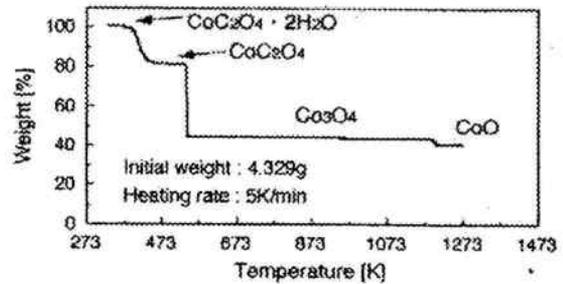
products were dried in a vacuum dryer at room temperature.

Photo.1(a)–(d) shows the complex oxalates of $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$. The size and shape of crystallization products for $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ depend on the conditions, such as pH and mixing speed where crystallization are carried out. Mixed organic solutions were prepared by mixing each organic phase containing $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ for the production of composite metal oxide and metal powders with the interest composition. The composition ratio of $\text{Sm}(\Gamma):\text{Co}(\Gamma) = 2:17$ is required in the filed of magnet industry. Though the size and shape of crystallization products depend on the conditions such as pH and mixing speed, $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ oxalates in the crystallization product are both angular crystal as small as $1\mu\text{m}$ in the condition of pH 7 and 600rpm. It is found from the EDX analysis that $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ are uniformly distributed in the product crystallized in the above condition. In the condition such as pH 0.6 and 400rpm, $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ oxalates in the crystallization product are the angular crystal of $1\mu\text{m}$ and the needle-like crystal of $1 \times 7\mu\text{m}$, respectively.

X-ray analysis showed the crystallization products to be $\text{Sm}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ and $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The temperature at which metal oxalates are converted to metal oxides should be lower for practical use. The results of thermal decomposition analysis for each metal oxalate are shown in Figure 3(a)–(b). $\text{Sm}(\Gamma)$ oxalate is decomposed to become the oxide in air at temperature of 913K, while the decomposition of $\text{Co}(\Gamma)$ oxalate to the oxide takes place in air at temperature of 553K.



(a) $\text{Sm}(\text{III})$ oxalate



(b) $\text{Co}(\text{II})$ oxalate

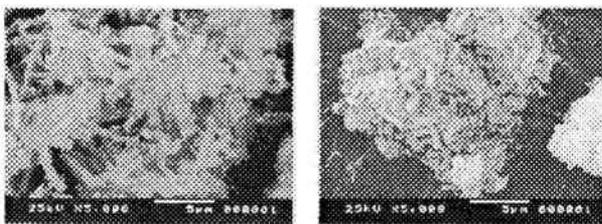
Figure 3: Thermodynamic analysis of metal oxalates

CONCLUSION

The studies of a production process for metal oxide and metal powders were carried out using a solvent extraction method. The crystallization-stripping is a suitable method to produce the composite powders comprising of two or three metals. Though the size and shape of crystallization products depend on the conditions such as pH and mixing speed, $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ oxalates in the crystallization product are both angular particle as small as $1\mu\text{m}$ in the condition of pH 7 and 600rpm. $\text{Sm}(\Gamma)$ and $\text{Co}(\Gamma)$ are uniformly distributed in the product crystallized in the above condition.

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(a) pH0.57, 400rpm

(c) pH7.04, 600rpm



(b) pH7.04, 400rpm

(d) pH7.04, 600rpm

Photo. 1: SEM analysis of $\text{Sm}(\text{III})$ - $\text{Co}(\text{II})$ oxalate powders prepared at different conditions

Vol. 51(1990),831-843

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