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THERMAL ANALYSIS OF COBALT SULFATE IN SO_2-O_2-SO_3 ATMOSPHERES

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ABSTRACT

The SO_3 pressure for dissociation of $CoSO_4$ to Co_3O_4 is measured at temperatures of 700-1070 K by means of the emf method using an SO_2-O_2-SO_3 concentration cell. The temperature dependence of the emf shows an anomalous change below 900 K, suggesting the formation of a higher sulfate or an intermediate oxide sulfate. Powdered anhydrous $CoSO_4$ is heated at 820 K in the SO_2-O_2-SO_3 atmosphere and quenched. The TG of the resulting powder detects a small mass gain at 675 K, which is absent in the TG curve of anhydrous $CoSO_4$. This fact indicates that a new phase is formed during the heat treatment in the SO_2-O_2-SO_3 atmosphere. The decomposition of the new phase is susceptible to the presence of water.

INTRODUCTION

The present authors [1] have been developing a potentiometric solid electrolyte sensor for gaseous sulfur oxides (SO_2 or SO_3). Metal sulfate-oxide mixtures are potentially applicable to the solid reference electrode for the sensor because the mixture provides the equilibrium partial pressure of SO_3. Equilibrium partial pressures of SO_3 for several kinds of sulfate-oxide mixtures have been measured by the electromotive force (emf) method with an SO_2-O_2-SO_3 concentration cell using NASICON ($Na_3Zr_2Si_2PO_{12}$) as a solid electrolyte [2]. The emf obtained for the mixture of $CoSO_4$ and Co_3O_4 has shown an anomalous change below 900 K suggesting the formation of another phase. Therefore, thermogravimetry and differential thermal analysis were carried out on cobalt sulfate in oxygen or SO_2-O_2-SO_3 atmospheres.

EXPERIMENTAL

Figure 1 shows the SO_2-O_2-SO_3 concentration cell. A solid electrolyte of NASICON separates the two compartment for electrodes. The preparation of the NASICON electrolyte has been

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described in the previous paper [1]. The reference electrode (I) is a gaseous electrode into which the standard gas of O_2-SO_2 (5 Pa) is introduced. For the measuring electrode (II), the mixture of $CoSO_4$ and Co_3O_4 is placed in an alumina crucible on which a hole is drilled. Then the oxygen partial pressure on the mixture is fixed at 2.1×10^4 Pa (air). Emf of the cell is expressed as:

$$E=(RT/2F)\ln(P^{\mathrm{I}}_{SO_3}P^{\mathrm{I}}_{O_2}{}^{1/2}/P^{\mathrm{II}}_{SO_3}P^{\mathrm{II}}_{O_2}{}^{1/2}) \qquad (1)$$

where R is the gas constant, T the absolute temperature, F the Faraday constant and P_i the partial pressure of a species i. The value of $P^{\mathrm{II}}_{SO_3}$ can be calculated from the emf because other factors are known when the temperature is fixed.

Anhydrous $CoSO_4$ was heated at 820 K for 20 ks in the SO_2 (9.3×10^1 Pa)-O_2 (9.9×10^4 Pa)-SO_3 (2.1×10^3 Pa) atmosphere and quenched to room temperature. This sample is referred to as "$CoSO_4$". Cobalt (III) sulfate hydrate, $Co_2(SO_4)_3\cdot18H_2O$ was prepared by the anodic oxidation of sulfuric acid solution of $CoSO_4$ and stored in a desiccator with concentrated sulfuric acid, which was kept in a refrigerator.

Thermogravimetry (TG) and differential thermal analysis (DTA) were simultaneously carried out in oxygen by an apparatus (SSC/560GH, Seiko Instruments and Electronics Ltd.), and TG in the SO_2-O_2-SO_3 atmosphere was performed by the laboratory-built thermobalance using a quartz spring. The heating rate employed was 1.6×10^{-1} Ks^{-1}.

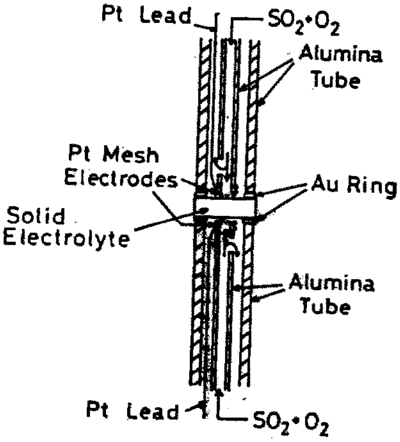

Fig. 1 The SO_2-O_2-SO_3 concentration cell.

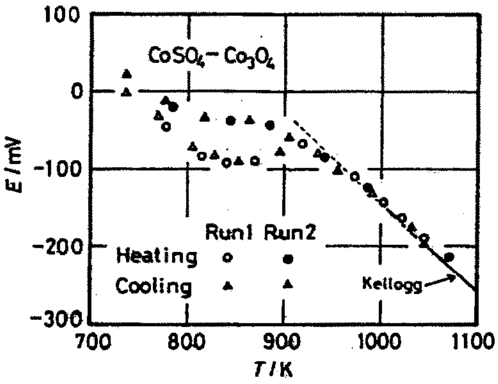

Fig. 2 Emf of the SO_2-O_2-SO_3 concentration cell.

RESULTS AND DISCUSSION

Figure 2 presents the emf of the cell shown in Fig. 1. The solid line is the calculated value from the data compiled by Kellogg [3]. The calculated value is based on the following two reactions:

$$CoSO_4 \rightarrow CoO + SO_2 + 1/2O_2$$
$$3CoO + 1/2O_2 \rightarrow Co_3O_4$$

The observed emf is consistent with the calculated value above 900 K. However, the emf deviates from the calculated emf in an anomalous manner below 900 K. Because a decrease in emf corresponds to an increase in $P^{II}_{SO_3}$, this fact suggests the formation of a higher sulfate or an intermediate oxide sulfate below 900 K.

In order to confirm the formation of a new phase, TG measurements were conducted on the "$CoSO_4$" in oxygen. Figure 3 shows TG curves. The solid line is of the "$CoSO_4$" immediately after quenched from the heat treatment with platinum as a catalyst. It took about 600 s to insert the sample into the thermobalance. The mass loss of about 1 % is observed between 320 and 440 K accompanying an endothermic peak in DTA, and then the mass of the sample becomes constant. This mass loss is due to the release of water which has been absorbed during the period for inserting the sample into the thermobalance. A small mass gain is recognized at 675 K, whereas it has not been observed in $CoSO_4$. No DTA peak was detected around 675 K probably because the mass gain was too small. On the other hand, the TG curve of the sample which has been stored in a desiccator with silica gel for 54 ks is shown by the dash-dotted line. The mass loss of about 5.5 % is recognized for dehydration, suggesting that the sulfate is more hygroscopic than silica gel. And the mass gain at 675 K is diminished. These results indicate that phases other than $CoSO_4$ or Co_3O_4 are formed during the heat treatment in the SO_2-O_2-SO_3 atmosphere and that the stability of the phase is sensitively affected by the presense of water. The "$CoSO_4$" prepared without platinum gives a TG curve similar to that for "$CoSO_4$" with platinum, although the mass gain at 675 K is smaller (broken line).

Figure 4 shows TG curves of $Co_2(SO_4)_3 \cdot 18H_2O$. The solid line presents the TG curve in the gas mixture of SO_2 (2.2×10^3 Pa)-O_2 (9.88×10^4 Pa), and the broken line illustrates that in oxygen. No significant difference is recognized between the two curves. The mass of the sample decreases in three steps, and finally

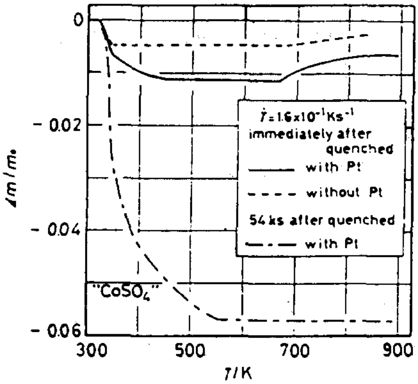

Fig. 3 TG curves of "$CoSO_4$" in oxygen.

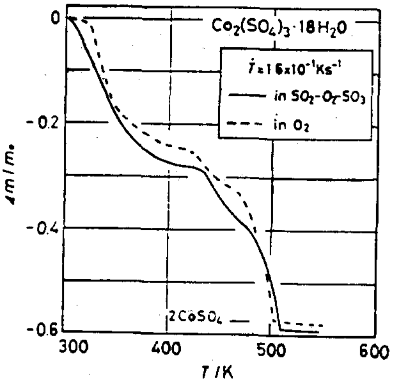

Fig. 4 TG curves of $Co_2(SO_4)_3 \cdot 18H_2O$.

reaches the value corresponding to $CoSO_4$ around 500 K. The subsequent heating up to 800 K did not give the mass gain at 675 K. The observation of the first plateau of TG curves around 430 K revealed that the color had already changed from green to pale violet. This fact suggests that Co (III) has been reduced to Co (II) by H_2O forming sulfuric acid and oxygen before the first plateau.

In conclusion, the heat treatment of $CoSO_4$ in the SO_2-O_2-SO_3 atmosphere at 820 K gives a new phase, whereas it has not been identified yet. The new phase is supposed to be higher sulfate and to decompose easily to $CoSO_4$. The decomposition is susceptible to the presence of water.

REFERENCES

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