

Solubility of Metal Oxides under Control of Basicity by Electrolysis in Fused Na₂SO₄

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The dissolution behavior of NiO, Co₃O₄, Fe₂O₃, Fe₃O₄, SiO₂, Al₂O₃ and Cr₂O₃ powders under the control of the O²⁻ activity of fused Na₂SO₄ by electrochemical polarization was investigated. As a result, the increase in the quantity of electricity for the anodic reaction with increasing polarization potential for the platinum electrode caused an increase in the basicity ($-\log a_{\text{Na}_2\text{O}}$) of the fused Na₂SO₄, while the increase in the quantity of electricity for cathodic reaction with decreasing polarization potential caused a decrease in basicity of the fused Na₂SO₄. The solubility of NiO and Co₃O₄ in fused Na₂SO₄ increased in the anodic potential region. However, their solubility did not increase in the cathodic potential region. The solubility of Fe₂O₃ and Fe₃O₄ slightly increased in the anodic potential region. The solubility of SiO₂ did not increase in the anodic potential region, whereas the solubility of SiO₂ increased with a decrease in the polarization potential in the cathodic potential region. The solubility of Al₂O₃ and Cr₂O₃ increased in the cathodic and anodic potential regions. The solubility of Al₂O₃ was larger than that of Cr₂O₃. We found that the resistance of acid and basic dissolution for oxides could be estimated by the electrochemical polarization method.

(Received May 26, 2004; Accepted August 18, 2004)

Keywords: basicity, fused sodium sulfate, electrolysis, polarization, solubility, metal oxides

1. Introduction

The boiler tubes for thermal power generation or the gas turbine blades for power generation and airplanes corrode aggressively when fused salt, consisting mainly of sulfate, adheres to these surfaces. This corrosion is called hot corrosion and is associated with the dissolution of the protective oxide scale formed on the metal surface in the fused salt. A fluxing model has been proposed as a mechanism of this dissolution. For this model, the basic dissolution of an oxide occurs when the O²⁻ activity at an oxide/molten salt interface increases, while the acid dissolution of an oxide occurs when the O²⁻ activity decreases. Thus, the O²⁻ activity in molten salt is the dominant factor in the dissolution reaction of an oxide. To clarify such a dissolution behavior of an oxide, the solubility of metal oxides such as Fe,^{1,2)} Al,³⁾ Ni,⁴⁾ Co⁵⁾ and Cr⁶⁾ in fused Na₂SO₄ was investigated through the influence of the O²⁻ activity in the molten salt; it has been reported that each metal oxide is subjected to acid and basic dissolution.

For the investigations¹⁻⁶⁾ of the solubility of metal oxides conducted so far, the O²⁻ activity in molten salt has been controlled by the addition of Na₂O. On the other hand, we have investigated the anodic and cathodic polarization behavior of a Pt electrode in fused Na₂SO₄. As a result, we found that SO₃ gas evolution occurs by the oxidation reaction of SO₄²⁻ under anodic polarization,⁷⁾ and then SO₃ reacts with O²⁻ in the fused Na₂SO₄ to decrease the O²⁻ activity of the fused Na₂SO₄, while the O²⁻ ions, generated by the

reduction reaction of SO₄²⁻ under cathodic polarization,⁸⁾ increase the O²⁻ activity. This result shows that the control of the O²⁻ activity of fused Na₂SO₄ by electrochemical polarization is possible. Such a research in which the basicity of the molten Na₂SO₄ was controlled by electrolysis of the molten Na₂SO₄ has been not performed, and the measurement of the solubility of the oxide under the basicity control by electrolysis has been not done.

In the present work, we attempted to change the O²⁻ activity of fused Na₂SO₄ by the electrochemical polarization of the Pt electrode. Furthermore, the dissolution behavior of the metal oxides, such as Fe₂O₃, Fe₃O₄, NiO, Cr₂O₃, Al₂O₃, Co₃O₄ and SiO₂, was investigated under electrochemical polarization. The acid and basic dissolution of these oxides under electrochemical polarization is discussed.

2. Experimental

Figure 1 shows the electrochemical set-up used for the solubility measurement of a metal oxide powder during the polarization of the platinum electrode. An alumina crucible of 44 mm inside diameter and 155 mm height was used for the electrolytic cell. This cell was placed into a quartz tube of 63 mm outside diameter and 332 mm height. The quartz tube was inserted into the length-type electric furnace. The working and counter electrodes were separated by a mullite crucible of 20 mm inside diameter and 120 mm height. A platinum sheet of 1 mm thickness with an area of about 10 mm × 10 mm was used for the working and counter electrodes. The surface of both electrodes was polished with #800 SiC paper and then washed ultrasonically in acetone. The reference electrode was a Ag wire immersed in a Na₂SO₄-Ag₂SO₄ (90:10 mol%) salt mixture, which was placed into a mullite tube of 6 mm outside diameter and 500 mm length.

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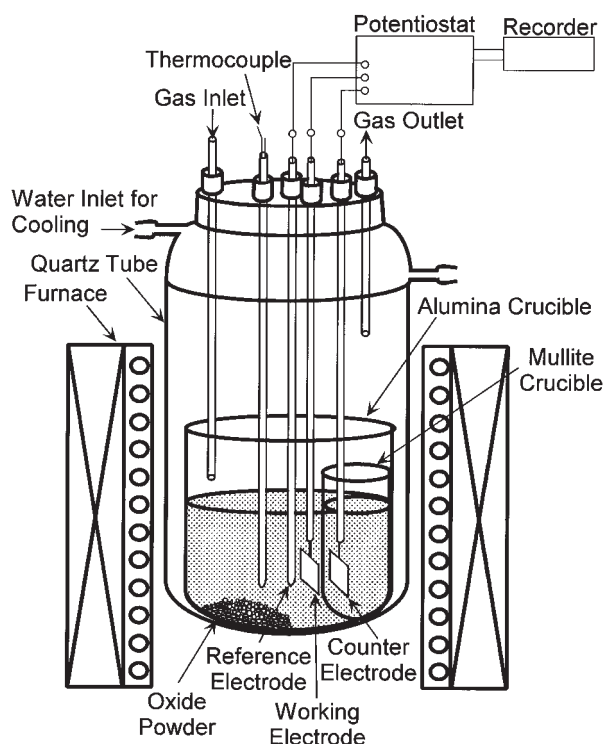


Fig. 1 Electrochemical set-up used for solubility measurements of a metal oxide.

Measurement of the anodic and cathodic polarization curves was carried out by the potential sweep method with $1.6 \times 10^{-3} \text{ V} \cdot \text{s}^{-1}$ in fused Na₂SO₄ at 1173 K, using the platinum sheets (1 mm × 10 mm × 10 mm) as the working and counter electrodes.

For solubility measurements of the oxides, three grams of the oxide powder were used. The used oxide specimens were commercial nickel oxide (NiO), cobalt oxide (Co₃O₄), iron oxides (Fe₂O₃, Fe₃O₄), silicon dioxide (SiO₂), aluminum oxide (α -Al₂O₃) and chromium oxide (Cr₂O₃) powder reagents. Solubility measurements of the oxides were carried out as follows: the oxide powder was put into the compartment, in which the working electrode was placed. The working electrode was potentiostatically polarized at various potentials in the fused Na₂SO₄ at 1173 K. The mass of Na₂SO₄ placed in the compartment, in which the working electrode was set, was 50 g. The change in current density with the polarization time was measured, and the amount of charge in the electrochemical reaction was also measured. The potentiostatic polarization was carried out at potentials from -2.5 to 1.2 V and polarization time was set to 3.6 ks. For the electrochemical measurement, high-purity Ar gas was introduced into the cell before the temperature of the salt rose. During the potentiostatic polarization, Ar gas was introduced into the cell with a flow rate of $1.7 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$. After the polarization, the salt placed in the working electrode compartment was solidified and then dissolved in $5 \times 10^{-4} \text{ m}^3$ of de-ionized water. The concentration of the metal ion in the solution was measured using ICP analysis (SII SPS3000).

Measurement of O²⁻ activity in fused Na₂SO₄ was carried out using the oxide ion probe shown in Fig. 2(a), which

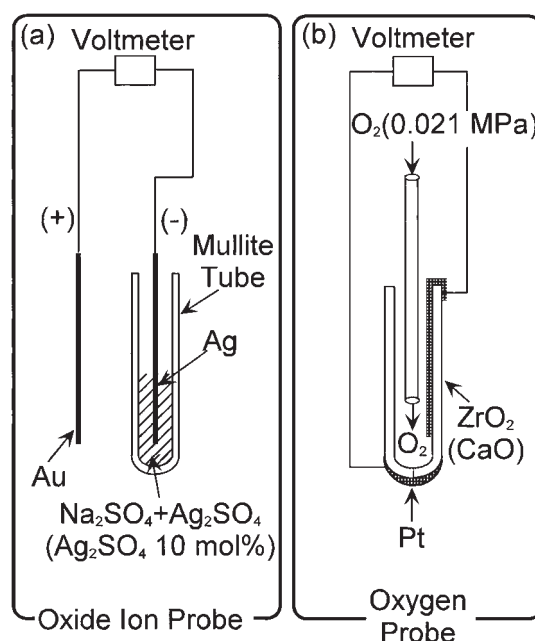
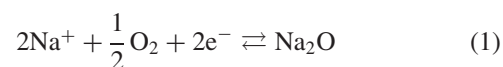


Fig. 2 Schematic representation of the oxygen probe and oxide ion probe apparatus.

consists of a Au electrode(+) and a reference electrode(-). It was assumed that in the fused Na₂SO₄ the reversible equilibrium reaction shown by eq. (1) occurred.



The electromotive power V of this probe is expressed by eq. (2).

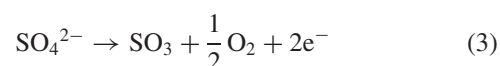
$$V = -1.448 - 0.116 \log(a_{\text{Na}_2\text{O}}/P_{\text{O}_2}^{1/2}) \quad \text{at } 1173 \text{ K} \quad (2)$$

where the value of -1.448 was calculated using the Gibbs energy⁹⁾ of formation of Na₂SO₄, Na₂O, and Ag₂SO₄ at 1173 K. When V and P_{O_2} were measured, the basicity $a_{\text{Na}_2\text{O}}$ was determined. As Na₂O dissociates into Na⁺ and O²⁻, $a_{\text{Na}_2\text{O}}$ corresponds to the O²⁻ activity, $a_{\text{O}^{2-}}$ in the molten salt. The P_{O_2} was measured using the oxygen probe shown in Fig. 2(b). Dry air ($P_{\text{O}_2} = 0.021 \text{ MPa}$) was used as the standard gas for the oxygen probe.

3. Results

3.1 Anodic and cathodic polarization curves

Figure 3 shows the anodic and cathodic polarization curves of the platinum electrode in fused Na₂SO₄ at 1173 K under an Ar atmosphere. The anodic and cathodic polarization curves are represented by the dashed line and the solid line, respectively. The anodic current density increases in the potential region higher than about 0.5 V. Such an increase in anodic current density corresponds to that for the rate of the oxidation reaction of SO₄²⁻ ions shown in eq. (3).⁷⁾



The SO₃ gas evolved by eq. (3) reacts with the O²⁻ generated

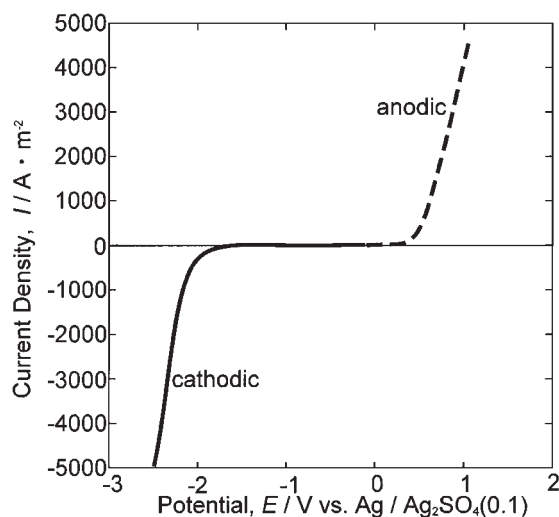
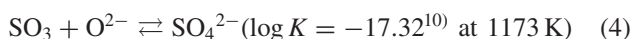
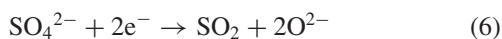
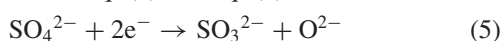


Fig. 3 Anodic and cathodic polarization curves of platinum in fused Na_2SO_4 at 1173 K.

by the acid-base equilibrium of SO_4^{2-} shown in eq. (4).



Therefore, it is assumed that the basicity ($-\log a_{\text{O}^{2-}}$) of fused Na_2SO_4 increases with increasing anodic current density. On the other hand, the cathodic current density increases in the potential region lower than about -1.8 V . The authors reported that the increase in the cathodic current density corresponds to that for the rate of the reduction reaction of SO_4^{2-} ions shown in eq. (5) and eq. (6).⁽⁸⁾



Therefore, it is assumed that the increase in the cathodic current density induces a decrease in the basicity of the fused Na_2SO_4 .

Figure 4 shows the quantity of electricity passed during the potentiostatic polarization for 3.6 ks at various potentials

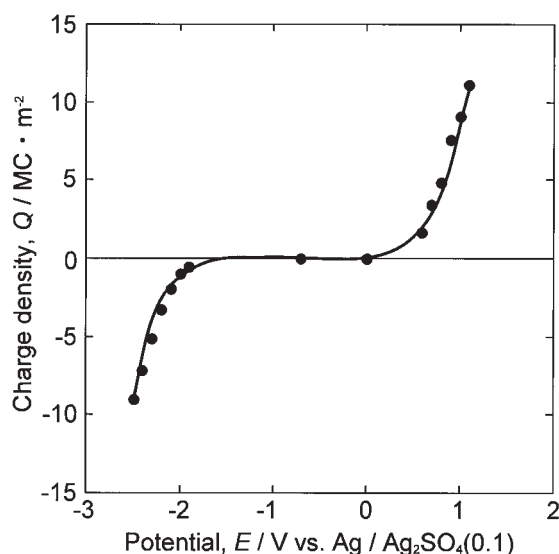


Fig. 4 Quantity of charge density passed during potentiostatic polarization of platinum for 3.6 ks, as a function of polarization potential.

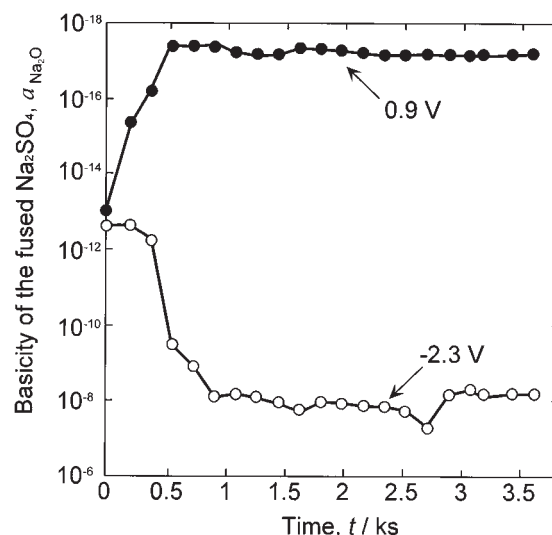


Fig. 5 Change in basicity of the molten Na_2SO_4 with time during potentiostatic polarization of platinum at 0.9 and -2.3 V .

as a function of the polarization potential. The quantity of the electricity-potential curve corresponds to the anodic and cathodic polarization curves shown in Fig. 3. Thus, the quantity of electricity for the anodic reaction increases with increasing polarization potential in the potential region higher than about 0.5 V , whereas the quantity of electricity for the cathodic reaction increases with decreasing polarization potential in the potential region lower than about -2 V .

3.2 Polarization potential dependence of basicity

The basicity ($-\log a_{\text{Na}_2\text{O}}$) in fused Na_2SO_4 after the potentiostatic polarization of the Pt electrode for 3.6 ks at each potential was measured using the O^{2-} probe (Fig. 2). Figure 5 shows examples of the change in basicity with time during potentiostatic polarization. In the potential regions below -2 V and more than 0.5 V , the basicity changed with time after the start of polarization. As shown in Fig. 5, it decreased at the potentials below -1.7 V , and it increased at the potentials more than 0.5 V .

Figure 6 shows the basicity of fused Na_2SO_4 measured after potentiostatic polarization for 3.6 ks at various potentials as a function of the polarization potential. Since the value of basicity did not change after polarization was carried out for 1 ks, as shown in Fig. 5. Polarization was performed to 3.6 ks in order to get a full equilibrium condition. And the value of basicity after polarization of 3.6 ks was shown in Fig. 6. As shown in Fig. 1, the counter electrode and the working electrode were isolated by mullite crucible. The mullite is Na^+ conducting material, but O^{2-} is not penetrated through the mullite. Therefore, the basicity in the molten salt, in which the working electrode was set, was not influenced by the basicity in the molten salt, in which the counter electrode was set. When the Fig. 6 data were compared with the data shown in Fig. 4, it was found that the basicity increases with an increase in the quantity of anodic electricity, while the basicity decreases with an increase in the quantity of cathodic electricity. That is, the O^{2-} activity decreases when the amount of anodic reaction increases, while O^{2-} activity increases when the amount of cathodic reaction increases.

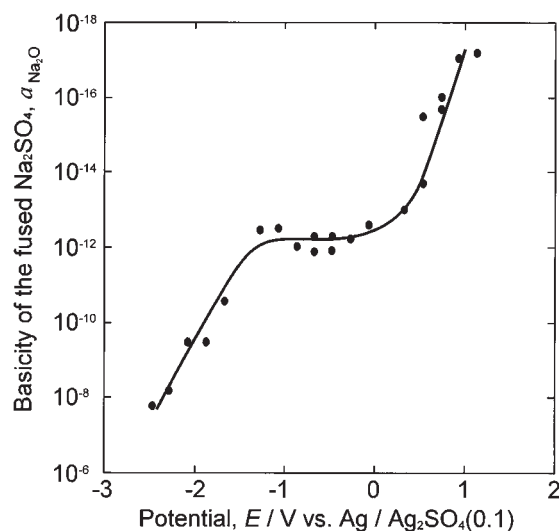


Fig. 6 Basicity of fused Na₂SO₄ measured after potentiostatic polarization of platinum for 3.6 ks, as a function of polarization potential.

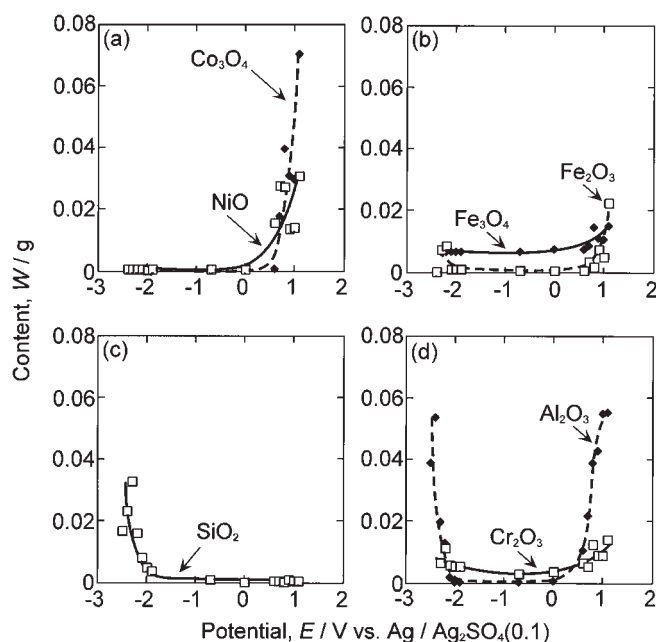


Fig. 7 Solubility of oxides measured after potentiostatic polarization for 3.6 ks as a function of polarization potential. (a) NiO and Co₃O₄, (b) Fe₂O₃ and Fe₃O₄, (c) SiO₂ and (d) Cr₂O₃ and Al₂O₃

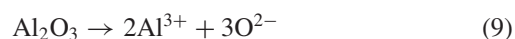
3.3 Polarization potential dependence of solubility

Figures 7(a)–(d) show the solubility of various oxides in molten Na₂SO₄ after potentiostatic polarization using Pt electrode for 3.6 ks as a function of polarization potential. In the potential region higher than about 0 V, the solubility of NiO and Co₃O₄ [Fig. 7(a)] increased with an increase in the polarization potential. However, in the potential region lower than about −2 V, the solubility was independent of the increase in the quantity of electricity for the cathodic reaction. The solubility of Fe₃O₄ [Fig. 7(b)], similarly to NiO and Co₃O₄, did not increase in the cathodic potential region lower than about −2 V. The solubility of Fe₂O₃ [Fig. 7(b)] slightly increased in the cathodic potential region lower than about −2 V. The solubility of Fe₂O₃ and Fe₃O₄

slightly increased in the anodic potential region higher than 0 V, in which the quantity of electricity for anodic reaction increased. However, the solubility of these Fe oxides was smaller than that of NiO and Co₃O₄. On the other hand, the solubility of SiO₂ [Fig. 7(c)] did not increase with an increase in the quantity of electricity for the anodic reaction in the potential region above 0.5 V. However, in the potential region lower than about −1.8 V, in which the quantity of electricity for the cathodic reaction increased, the solubility of SiO₂ increased with a decrease in the polarization potential. The solubility of Al₂O₃ and Cr₂O₃ [Fig. 7(d)] increased in the potential region above 0 V and the potential region lower than about −2 V. The solubility of Cr₂O₃ under both anodic and cathodic polarizations was smaller than that of Al₂O₃.

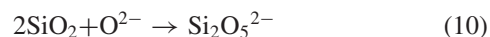
4. Discussion

The basicity of the fused Na₂SO₄ was changed by the anodic and cathodic polarization using platinum electrode. The solubility of the various oxides with the change in the basicity was investigated. The solubility of Co₃O₄, NiO, Fe₂O₃, Fe₃O₄, Al₂O₃ and Cr₂O₃ increased in the anodic polarization region. Especially, the solubility of Co₃O₄, NiO and Al₂O₃ was large. As shown in Fig. 6, the basicity (−log *a*_{Na₂O}) increased with increasing the polarization potential in the anodic potential region higher than about 0 V. This corresponds to the decrease in O^{2−} activity by the reactions given eqs. (3) and (4). Therefore, we believe that NiO, Co₃O₄ and Al₂O₃ were much more subject to acid dissolution. These dissolution reactions are shown in eqs. (7), (8) and eq. (9).



We found that the resistance of acid dissolution for SiO₂ was very high. It was reported that the corrosion resistance of a high Si content alloy, which forms SiO₂ scale, was very high under a coating of molten salt, which corresponds to a waste incineration environment.¹¹⁾ The basicity of molten salt in a waste incineration environment was estimated to be more than 17.¹²⁾ Figure 6 showed that the basicity of Na₂SO₄ became about 17 by the polarization at 1 V. However, SiO₂ was not dissolved under polarization at 1 V [Fig. 7(c)]. This result proves that the corrosion resistance of high Si content alloy is very high under a coating of molten salt, which corresponds to a waste incineration environment.

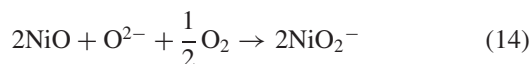
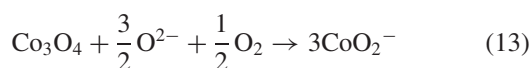
In the cathodic potential region lower than about −2.0 V, on the other hand, the solubility of SiO₂ and Al₂O₃ increased. Figure 6 showed that in the potential region, decrease in basicity, that is, an increase in O^{2−} activity, was observed. As shown in eqs. (10) and (11), we believe that when SiO₂ reacts with O^{2−}, Si₂O₅^{2−} and SiO₃^{2−} are formed. As a result, the basic dissolution of SiO₂ proceeded.



We also think that for Al_2O_3 the solubility increased by the reaction of Al_2O_3 with O^{2-} to form AlO_2^- .



We found that for Co_3O_4 and NiO the resistance against basic dissolution was high. On the other hand, D. K. Gupta *et al.*⁴⁾ reported that Co_3O_4 and NiO in fused Na_2SO_4 (1200 K) under an oxygen partial pressures of 1 atm caused basic dissolution. In this case, eqs. (13) and (14) were presumed as a reaction.



As this experiment was carried out under cathodic polarization in an argon atmosphere, the oxygen partial pressure was very low. Therefore, the reaction shown in eqs. (13) and (14) did not proceed. Consequently, Co_3O_4 and NiO were not dissolved even if the O^{2-} activity increased.

5. Conclusions

The dissolution behavior of NiO , Co_3O_4 , Fe_2O_3 , Fe_3O_4 , SiO_2 , Al_2O_3 and Cr_2O_3 powders in fused Na_2SO_4 under the control of the O^{2-} activity by electrolysis was investigated. The results are summarized as follows:

- (1) The increase in the quantity of electricity for the anodic reaction with increasing polarization potential for the platinum electrode caused an increase in the basicity of the fused Na_2SO_4 , and the increase in the quantity of electricity for the cathodic reaction with decreasing polarization potential caused a decrease in the basicity of the fused Na_2SO_4 .
- (2) The solubility of NiO and Co_3O_4 in fused Na_2SO_4 increased with the increase in the quantity of electricity

for the anodic reaction in the anodic potential region. On the contrary, in the cathodic potential region, their solubility was independent of the increase in the quantity of electricity for the cathodic reaction.

- (3) The solubility of Fe_2O_3 and Fe_3O_4 slightly increased in the anodic potential region.
- (4) The solubility of SiO_2 did not increase in the anodic potential region even if the quantity of electricity for the anodic reaction increased. However, the solubility of SiO_2 increased with an increase in the quantity of electricity for the cathodic reaction in the cathodic potential region.
- (5) The solubility of Al_2O_3 and Cr_2O_3 increased in the cathodic and anodic potential regions with an increase in the quantity of electricity for anodic and cathodic reactions. The solubility of Al_2O_3 was larger than that of Cr_2O_3 .

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