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H₂ Evolution Reactivity of Carbon-Bearing Ni(II) Ferrite (CBNF)

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Abstract: Two-step water-splitting with a carbon-bearing Ni(II) ferrite (CBNF) at 300°C has been studied. The chemical analysis of the solid phase showed that the CBNF was gradually oxidized during repeated water splitting, but the evolved H₂ amount is 1.5-2 times larger than that expected from the oxidation of the CBNF. Following two types of hydrogen evolution reactions are considered to be participated: Type I is the water splitting by the activated form of CIO layer(α_n), where the activated form changes to the original form (β_n), Type II is hydrogen evolution by the oxidation of CIO layer, where the original CIO layer form(β_n) changes to an oxidized form (β_{n+1}). The amount of released oxygen was about 40-80% of the amount estimated from the amount of hydrogen gas evolved by the Type I reaction. Thus, the stoichiometry of the above two steps has been demonstrated.

1. Introduction

We have found that a carbon-bearing Ni(II) ferrite (CBNF) is composed of bulk Ni(II) ferrite and carbon iron oxide layer (CIO layer) on the surface [1,2], so a CBNF is referred to as CIO-layered Ni(II) ferrite (CIO-NF). The CIO layer is activated in O₂-free inert gas at 300°C (activation step), and the activated form react with steam to form H₂ (H₂ evolution step). The carbon content of the CIO layer did not change during water-splitting cycles, indicating that any carbon compounds were not released. The evolved H₂ amount is 1.5-2 times higher than the oxidation of the solid phase. We have considered that there are two types of the H₂ evolution; 1) the oxide ion in the CIO-layer(β_n)(n = repetition number) is released as O₂ gas in the activation step, and the CIO layer changes to a more reduced form (CIO-layer(α_n)), and decompose H₂O to generates H₂ gas, 2) H₂ is generated by the oxidation of the CIO layer to a slightly oxidized form of CIO-layer(β_{n+1}) without O₂ releasing step.

The purpose of this paper is to prove the Eqs. 1 - 3 by measuring the O₂ amount released in the activation step (Eq. 1) and the stoichiometry of the H₂ evolution in the 2-step water splitting will be discussed in relation to a reaction mechanism of the oxygen releasing in Eq. 1.

2. Experimental

A CIO-NF was synthesized by repeated CO₂ decomposition on H₂-reduced Ni(II) ferrite according to the previous paper [1]. The 0.5g of sample was placed in the reaction cell, and Ar gas was passed through the sample at 300°C (activation step). The oxygen gas, which was released from the CIO layer during activation step, was trapped with Cu powder at 400°C and the trapped oxygen amount was determined with mass spectroscopy as H₂O by passing H₂ gas through the Cu powder at 400°C. Then, 25 μ l of water was injected into the steam generator, and the sample was allowed to react with steam. The evolved gases were monitored with mass spectroscopy.

3. Results and discussion

A typical H₂ evolution profile by the reaction of the CIO-NF with H₂O at 300°C is shown in Fig. 1. When the steam (H₂O) was passed through the sample at a first time, a larger peak (Peak a) appeared, then the smaller Peaks b and c appeared successively by passing the steam every after 5 min. The areas of Peaks b and c were nearly equal, but smaller than that of

Peak a. However, a larger Peak d appeared again, when the steam was passed after allowing the sample to stand in Ar stream for 1.5 h. Thus, there were two kinds of the H_2 generation peaks: 1) small peaks by successively passing H_2O every after 5 min, and 2) a larger peak (Peak d) by passing H_2O after 1.5 h of the activation. Since, Peaks b and c appeared by passing H_2O successively every after 5 min, the O_2 gas evolved from CIO layer is very small, indicating that Peaks b and c appeared without the O_2 gas releasing from CIO layer. Thus, the H_2 evolution for Peaks b and c (smaller peaks) mainly comes from the Type II (Eq. 3) reaction, where the CIO layer reacts with H_2O without O_2 releasing step. This means that the CIO layer is more oxidized by the amount equivalent to the evolved H_2 gas amount, and CIO-layer(β_n) is oxidized to CIO-layer(β_{n+1}). However, if the CIO layer is subjected to the O_2 releasing step of Eq. 1 every time after the H_2 evolution, we can obtain the H_2 gas by 2 step water splitting of Eqs. 1 and 2 with a minimal oxidation of the CIO layer. A larger Peak d may be come from O_2 releasing from CIO layer described as Eq. 1. Being thus activated CIO layer reacted with H_2O , it is oxidized to generate the H_2 gas by the reactions of Eqs. 2 and 3, although the reactions 2 and 3 practically take place at the same time and can not be distinguished. Thus, the evolved H_2 amount of Peak d is the sum of the H_2 volume evolved by Eqs. 2 and 3. In the present study, the H_2 (Eq. 3) in Peak d is assumed to be equal to the H_2 amount of Peak c, since they are mainly due to Eq. 3. The H_2 of (Peak d - Peak c) is considered to correspond to the H_2 (Eq. 2). A ratio of oxygen amount detected during an activation step to the amount expected from H_2 (Peak d - Peak c) ranges 40-80%. This suggests that the 2-step water splitting of Eqs. 1 and 2 proceeds stoichiometrically. The ratio of H_2 (Eq. 2) to H_2 (Eq. 3) is calculated to be 0.67-1.0.

Figure 1: H_2 evolution profile by the reaction of CIO-NF and H_2O at 300°C

Figure 2: Oxygen release mechanism from CIO layer

The release of oxide ion in the CIO layer as O_2 gas in a low-oxygen content gas only at 300°C seems to come from the specific structure of the CIO layer. The CIO-NF is represented by $(Ni_{0.30}Fe_{2.70}O_4)_{1-x}(Ni^{2+}_{0.63}Fe^{2+}_{2.37}O^{2-}_3)_xC$, where $x=0.249$; mol fraction of CIO layer, $\tau=0.280$; carbon content [1]. Thus, the general formula of the CIO layer is represented by the -wüstite structure (MO), and that of the bulk by spinel structure (M_3O_4). The Fe^{2+} ion in the MO structure (FeO) is unstable below 600°C, and can decompose H_2O to form H_2 and Fe_3O_4 . However, Fe_3O_4 is too stable to released oxide ions in O_2 -free Ar gas at 300°C. Therefore, the Fe^{2+} ions in the CIO layer are not in the pure form of MO structure. Considering the chemical composition of the CIO layer, some metallic Ni or Fe should be formed in the CIO layer in the activation step, since the Fe^{2+} or Ni^{2+} ions in the CIO layer should be reduced by releasing O^{2-} ions as O_2 gas. To confirm the existence of the metallic component, the surface of the activated CIO layer was treated with a nitric acid solution, which can dissolve metallic Ni to form NO. The NO was determined by colorimetry as NO^{2-} ion. This indicates that some Ni^{2+} ions would be reduced to metallic Ni in the activation step. That is, the CIO-layer(α_n) is considered to consist of metallic Ni along with Ni^{2+} , Fe^{2+} , C and O^{2-} . Since nickel oxide powder itself did not release O^{2-} in a flow of Ar gas at 300°C, the reduction of Ni^{2+} ion would not be attributed to the reduction of nickel oxide. Rather, the specific chemical structure of the CIO layer would facilitate the release of the O^{2-} ions to reduce the Ni^{2+} ions. Especially, the coexistence with carbon would take an important role for the release of the O^{2-} ion. The driving force will be considered as follows: some of carbon of graphite will be bonded weakly to Ni^{2+} , which would be similar to Ni-C carbide bond. When the CIO layer was heated over 350°C, some weak carbide peak appeared in XRD pattern, while no such peak appeared at 300°C. This suggests that this weakly bonding $Ni^{2+}-C$ (X in Fig. 2) become stronger in an O_2 -free atmosphere at 300°C and that O_2 gas can be released to from the CIO layer at 300°C.

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