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Synthesis and Characterization of Carbon-Bearing Ni(II) Ferrite (CBNF)

T. Sano, H. Hasegawa, M. Kojima, M. Tsuji and Y. Tamaura

Research Center for Carbon Recycling & Utilization, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

Abstract: Carbon-bearing Ni(II)-ferrite (CBNF) was prepared by repeated decomposition of CO₂ on H₂-reduced Ni(II)-ferrite. The material was also characterized by Mössbauer spectra, XRD and chemical analysis. A peculiar amorphous surface layer composed of carbon, divalent transition metals and oxide ions (CIO layer) was found to be synthesized on the surface of the CBNF. Deposited carbon on the CBNF was characterized using X-ray photoelectron spectroscopy. About 70% of deposited carbon was assigned to graphite.

1. Introduction

A synthetic magnetite with a carbon-iron(II) oxide layer (CIO layer) showed its reactivity for water splitting at substantially low temperature of 350°C [1]. It can be synthesized by the carbon-deposition reaction from CO₂ gas on oxygen-deficient magnetite, composing of the stoichiometric magnetite (Fe₃O₄)_{1-δ} and a CIO layer represented by (Fe₃O₃)_δC₁. The latter portion on CIO layer serves water splitting to form H₂ gas at 350°C. Recently, complete decomposition of CO₂ to carbon with oxygen-deficient ferrites (ODFs) at 300°C has been reported [2]. The ODF can be synthesized by H₂ reduction of spinel ferrite at 300°C and is represented by a general formula M_xFe_{3-x}O_{4-δ} where M is a bivalent metal ion such as Zn, Co, Mn and Ni; δ denotes the oxygen deficiency. The carbon of CO₂ is deposited on the material surface and oxygen ions are incorporated into the crystal lattice of the ODF. Ni(II) ferrite revealed the highest reactivity among oxygen-deficient Zn(II), Mn(II), Co(II) and Ni(II) ferrites.

In this paper, a carbon-bearing Ni(II) ferrite (CBNF) is synthesized by CO₂-decomposition reaction on H₂-reduced Ni(II) ferrite. The CBNF is characterized by X-ray diffractometry, Mössbauer spectroscopy, X-ray photoelectron spectroscopy and chemical analysis.

2. Experimental

Ni(II) ferrite (NF) (Ni:Fe mole ratio, 0.15) was synthesized by the air-oxidizing Fe(II)/Ni(II) mixed hydroxide suspension for 6 h at pH 9 and at 65°C according to the previous reports [3]. The product was washed successively with distilled water and acetone, and then heated to remove adsorbed water and acetone in an N₂ gas stream at 300°C for 3 h. CBNF, Ni_xFe_{3-x}O_{4-δ}C₁, was prepared by repeated CO₂ decomposition on NF as follows: A 5.0 g portion of the NF was partially reduced to form an oxygen-deficient Ni(II) ferrite (Ni_xFe_{3-x}O_{4-δ}) in a quartz tube reactor by passing H₂ for 30 min at 300°C. After evacuation of the reactor, 80 cm³ of CO₂ gas was injected to react with the oxygen-deficient NF for 4 h at the same temperature. This procedure was repeated 10 times to form the CBNF. The solid phase was identified by X-ray diffractometry (XRD) with Fe Kα radiation, X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy.

Mössbauer spectra were recorded at room temperature with a ⁵⁷Co source diffused in metallic Rh, which was oscillated in constant acceleration mode. The spectra were calibrated with an iron foil absorber. The surface of the CBNF was characterized by XPS. Monochromatic Al-Kα radiation at 350 W was used to obtain the C 1s spectra. The Fe²⁺:Fe_{total} mole ratio of the samples was determined by colorimetry using 2,2'-bipyridyl and Inductively coupled plasma (ICP) spectrometry. The oxygen content was determined by thermogravimetry. Carbon was determined using an elemental analyzer.

3. Results and discussion

The chemical composition of the NF prepared by the wet method was determined to be Ni_{0.382}Fe_{2.618}O_{3.992}. The Ni:Fe mole ratio was equal to that used at preparation. The XRD pattern of the NF showed only those peaks characteristic of the spinel

type structure, retaining the single phase. The lattice constant was 0.8376 nm, which is in agreement with that of the stoichiometric NF with an Ni:Fe mole ratio of 0.146 ($\text{Ni}_{0.382}\text{Fe}_{2.618}\text{O}_4$, $a_0 = 0.8375$ nm) reported previously. The CBNF was also a single phase of the spinel type structure and did not contain any metallic or carbide phases. The lattice constant was 0.8380 nm and larger than that of the stoichiometric NF. The chemical composition was determined to be $\text{Ni}^{2+}_{0.382}\text{Fe}^{2+}_{1.118}\text{Fe}^{3+}_{1.502}\text{O}^{2-}_{4.8}\text{C}_\tau$ ($\delta = 0.249$, $\tau = 0.280$). The maximum δ value of the oxygen-deficient NF is 0.16-0.19, indicating that the CBNF was more reduced. The lattice constant of the CBNF (0.8380 nm) is larger than that of the stoichiometric NF with the same Ni:Fe mole ratio of 0.146 (0.8375 nm), a value which has been smoothed using the lattice constants reported in the JCPDS cards.

Carbon-bearing iron(II) oxide layer (referred to as CIO layer) has been reported which can be formed on magnetite by repeated H_2 -reduction/ CO_2 -decomposition processes at 300°C, being a constituent of the carbon-bearing magnetite (CBM) [1]. The CIO layer is essentially amorphous and can be represented by $(\text{Fe}_3\text{O}_3)_x\text{C}_\tau$. It is possible to assume that two components of the bulk NF and the CIO-like surface layer will constitute the CBNF, as is the case for CBM. First, the chemical composition of the bulk NF is that corresponding to the lattice constant $a_0 = 0.8380$ nm and can be given as $\text{Ni}_{0.30}\text{Fe}_{2.70}\text{O}_4$ using the relationship between the lattice constants of NF and the Ni(II) content. The other portion forms the CIO-like layer represented by $\text{Ni}^{2+}_{0.63}\text{Fe}^{2+}_{2.37}\text{O}^{2-}_3$. Thus, the chemical composition of the CBNF may be tentatively represented by $(\text{Ni}_{0.30}\text{Fe}_{2.70}\text{O}_4)_{1-x}(\text{Ni}^{2+}_{0.63}\text{Fe}^{2+}_{2.37}\text{O}^{2-}_3)_x\text{C}_\tau$ ($x = 0.249$, $\tau = 0.280$).

Figure 1: Mössbauer spectrum of the CBNF

Figure 2: C1s binding energy of the CBNF

Mössbauer spectra of the NF and CBNF corroborate the absence of a metallic iron phase within experimental error (Fig. 1). The spectrum for the NF showed almost the same pattern as that of the CBNF, which is not shown. They could be well fitted to two sextets, a and b, assigned to the tetrahedral (A) and octahedral (B) sites, respectively, as well as to NF. Site assignments of iron ions can be made on the basis of an interpretation made on magnetite Fe_3O_4 . The absorption intensity ratio I_a/I_b was 0.85 for the NF and 0.79 for the CBNF. The other Mössbauer parameters of the CBNF were in agreement with those of the NF. As mentioned above, the bulk composition of the CBNF is given by $\text{Ni}_{0.30}\text{Fe}_{2.70}\text{O}_4$. Assuming that there are Fe^{3+} ions which are not in a mixed valence state in the B sites and which contribute to sextet a as is the case of NF [4], the cation distribution of the bulk can be written as $[\text{Fe}^{3+}_{1.00}]_A(\text{Ni}^{2+}_{0.30}\text{Fe}^{3+}_{0.19}\text{Fe}_{1.51})_B\text{O}_4$, by using $I_a/I_b = 0.79$ and then adjusting the mixed valence of $\text{Fe}_{1.51}$ in B sites to 2.54. The valence is nearly equal to that for magnetite (2.50). Therefore the above chemical formula can be concluded to be reasonable.

The carbon deposited on the CBNF was characterized using XPS. The C 1s core level spectrum could be well fitted to three peaks (Fig. 2). A main peak at 284.6 eV was assigned to graphite; other peaks at 286.3 and 288.7 eV were due to the contribution of bound CO and CO_2 , respectively. Peaks attributed to carbide should be observed at 282 to 283 eV, but they were not found in the spectrum. Therefore, the possibility of presence of the carbide phases (Fe_3C and/or Fe_2C) was discounted. Most of the deposited carbon atoms from CO_2 were polymerized and formed graphite on the surface of the CBNF.

References

1. Y. Tamaura, K. Akanuma, N. Hasegawa and M. Tsuji, *J. Mater. Sci.* **29** (1994) 6175.
2. M. Tsuji, H. Kato, T. Kodama, S. G. Chang, N. Hasegawa and Y. Tamaura, *J. Mater. Sci.* **29** (1994) 6227.
3. T. Katsura, Y. Tamaura and G. S. Chyo, *Bull. Chem. Soc. Jpn.*, **52** (1979) 96.
4. T. Kodama, M. Tabata, T. Sano, M. Tsuji and Y. Tamaura, *J. Solid State Chem.* **120** (1995) 64.