June, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1577—1580 (1971) 1577

The Chemical-transport Reaction of Spinel-type Oxides

Koichi NAGASAWA*, Yoshichika BANDO, and Toshio TAKADA
Institute for Chemical Research, Kyoto University, Uji

(Received September 29, 1970)

Single crystals and thin films of spinel-type oxides were prepared by a chemical-transport reaction in a closed system, using HCl gas as the transport agent. This paper will report on the preparation conditions and the reaction process of the chemical-transport reaction. The reaction process of Co_3O_4 was found to be different from that of other oxides, since Co_3O_4 was dissociated into CoO and O_2 in the closed tube. The reaction process was explained by the difference in the dissociated oxygen pressure between the source zone and the crystallization zone in the system. The chemical-transport reaction of $NiFe_2O_4$ was applied to the preparation of thin film. The single-crystal thin films were epitaxially grown on the (110) and (111) surfaces of MgO.

The growth of spinel-type oxides is very important for the fundamental investigation of their physical properties. Therefore, many investigations of the growing method, for instance, the growth from the melt or from the flux, have been made. The growing method from the melt is not suitable for the material dissociated below the melting point, and the method from the flux sometimes causes the flux to be included in the crystals.

The growing method from the gas phase has been expected not to have such defects, and so recently much interest has been directed toward this method. Takei and Takasu[1] prepared single-crystal films of $NiFe_2O_4$ $CoFe_2O_4$, and Fe_3O_4 on the MgO substrate by the decomposition of appropriate mixtures of the metal halides by water vapor. Sputtering in a glow-discharge system from a ceramic cathode of the ferrite also made it possible to prepare single-crystal films of nickel ferrite.[2] In addition, the chemical transport reaction method in a closed system, which was developed by Schäfer and his co-workers,[3] for the growth of single crystals of various solid substances, *e.g.*, Si, Ge, Cu_2O, and Fe_2O_3 is applicable to the growth of ferrite. Hauptmann[4] applied this chemical-transport reaction, using HCl gas as the transport agent, to the preparation of Fe_3O_4 single crystals. In this case, single crystals were presumably grown by this reaction:

$$Fe_3O_4(s) + 8HCl(g) \rightleftharpoons 2FeCl_3(g) + FeCl_2(g) + 4H_2O(g) \tag{1}$$

where (s) and (g) indicate the solid and gaseous states respectively. Moreover, Kleinert[5] reported the growth of $NiFe_2O_4$, $MnFe_2O_4$, and other spinel-type oxides by the same method. In these cases, the materials which were used as the sources were not dissociated in the system. As the cobaltite Co_3O_4 is dissociated into CoO and O_2 at high temperatures, the process of this chemical-transport reaction may be expected to be different from that of other oxides.

In the present investigation, single crystals of Co_3O_4 were synthesized by a chemical-transport reaction using HCl gas, and the reaction process of Co_3O_4 was compared with that of $NiFe_2O_4$. Moreover, $NiFe_2O_4$ thin films were epitaxially grown on the (110) and (111) surfaces of the MgO single crystal. Some parts of this investigation have been already reported in a short note.[6,7] This paper will present the results in detail and will discuss them.

Experimental

Source Materials and Substrates. The source materials for the chemical-transport reaction were Co_3O_4 powder, $NiFe_2O_4$ powder, and sintered $NiFe_2O_4$. The Co_3O_4 powder was obtained by the thermal decomposition of $CoCO_3$ at 700°C in air. α-Fe_2O_3 and NiO were weighed, mixed, and then calcined at 1000°C for 2 hr. Calcination was followed by crushing. This powder was pressed and fired in air at 1200°C for a day. The $NiFe_2O_4$ powder was obtained by crushing this sintered body. $CoCO_3$ and NiO were Wakoo guaranteed reagents, and α-Fe_2O_3 was a product of the Toda Industrial Co., Ltd. (99.9%). Single crystals of MgO were obtained from the New Metals Corp.; a polished (110) or (111) surface or a cleaved (100) surface was used as the substrate for the growth of $NiFe_2O_4$ thin film.

Method. The source material, Co_3O_4 or $NiFe_2O_4$

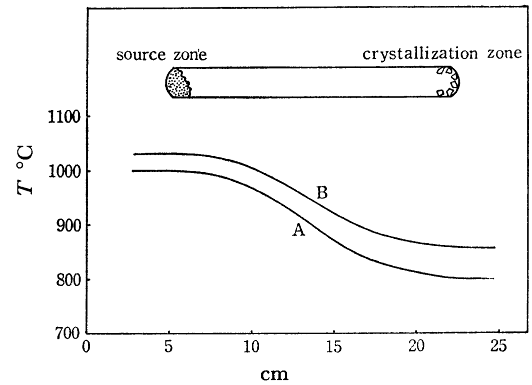


Fig. 1. Temperature gradient of the furnace and position of the closed silica tube. A is the gradient in the preparation of Co_3O_4 and $NiFe_2O_4$ single crystals and B $NiFe_2O_4$ single crystal thin films.

---

* Present address: Central Research Laboratory, Mitsubishi Electric Corp., Amagasaki, Hyogo.

[1] H. Takei and S. Takasu, *Jap. J. Appl. Phys.*, **3**, 175 (1964).

[2] W. D. Westwood, H. K. Eastwood, R. G. Poulson, and S. G. Sadler, *J. Amer. Ceram. Soc.*, **50**, 119 (1967).

[3] H. Schäfer, H. Jacob, and K. Etzel, *Z. Anorg. Allg. Chem.*, **286**, 27 (1956).

[4] Z. Hauptman, *Czech. J. Physics*, **12**, 148 (1962).

[5] D. Kleinert, *Z. Chem.*, **3**, 353 (1968).

[6] T. Takada, Y. Bando, N. Yamamoto, and K. Nagasawa, *Jap. J. Appl. Phys.*, **8**, 619 (1969).

[7] K. Nagasawa, Y. Bando, and T. Takada, *ibid.*, **7**, 174 (1968).

powder, was loaded into one end of a silica tube 18 cm in length and 1.4 cm in diameter. After the tube had then been evacuated to 10^{-6} mmHg, 40 mmHg of HCl gas was admitted and the other end of the tube was sealed off. The tube was heated for 2—3 days in a furnace with a temperature gradient, as is shown in Fig. 1, and then quenched in water within a minute. The temperatures of the source zone and crystallization zone were 1000°C and 800°C respectively. The tube was then broken, and the crystals obtained in the crystallization zone were removed from the wall of the tube.

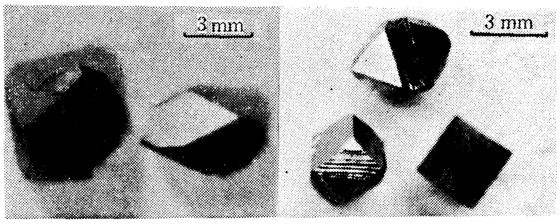
In the growth of $NiFe_2O_4$ thin films, the source material was sintered $NiFe_2O_4$, 8 mm in diameter and 3 mm thick. The silica tube used was 17 cm in length and 9 mm in diameter. In the crystallization zone, a substrate of MgO single crystal having a polished (110) or (111) surface or a cleaved (100) surface was mounted. The pressure of the HCl gas admitted was 50 mmHg. The temperature in the source zone was 1030°C, and at the substrate zone, 860°C, as is shown in Fig. 1. The tube was heated for two days, pulled out of the furnace, and cooled in air. The film grown on the surface of the substrate could be separated from the substrate by treating it in a hot 2—5% aqueous solution of nitric acid. The surface area and weight of the film were measured, and the film thickness was calculated from the density of $NiFe_2O_4$.

Analysis. The phases of the source material remaining in the source zone after the reaction, which will here after be called the "residue", and the single crystals obtained were identified by means of X-ray powder diffraction using Mn-filtered Fe-radiation. The lattice constants of the single crystals were measured by the X-ray powder pattern, using {721} reflection. A Laue photograph was taken of a face of a crystal obtained using copper radiation.

In the case of the $NiFe_2O_4$ thin film, a Laue photograph was taken by means of the transmitted diffracted lines. As an electron beam could pass through the edge of the film, the lattice constant of the films was measured by means of usual electron diffraction, using Au polycrystalline film as a standard sample. The atomic ratios of iron to nickel in the films were measured by chemical analysis.

Results and Discussion

Chemical-transport Reaction of Co_3O_4. The transport of Co_3O_4 and $NiFe_2O_4$ by HCl yielded some black and bright crystals 2—5 mm in size. Figure 2 shows photographs of representative crystals. The Laue photograph showed that the best developed faces were {111}. The {110} planes were also observed in some $NiFe_2O_4$ single crystals. The X-ray powder diffraction of the single crystals indicated that they had a spinel structure and that the lattice constant was 8.080 Å in Co_3O_4 and 8.352 Å in $NiFe_2O_4$ respectively. These values agreed approximately with the A.S.T.M. value.



(A) (B)

Fig. 2. Photographs of (A) Co_3O_4 single crystals and (B) $NiFe_2O_4$ single crystals.

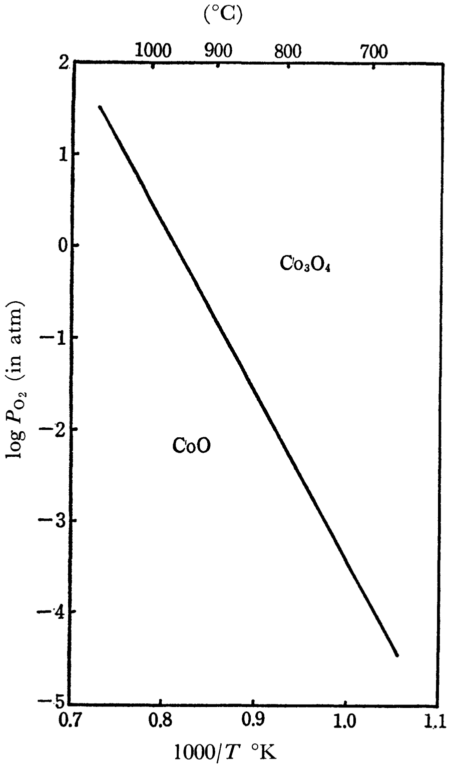


Fig. 3. Oxygen pressure in equilibrium with Co_3O_4 and CoO as a function of 1000/T°K.

TABLE 1. CONDITIONS EMPLOYED IN PREPARATION OF SPINEL-TYPE OXIDE SINGLE CRYSTALS BY CHEMICAL TRANSPORT REACTION AND RESULTS

Run No.	Source material	Weight of source material charged (g)	Phase of residues at the source zone	Phase of single crystals obtained	Admitted HCl gas (mmHg)	Reaction time (day)	Temperature gradient (°C)
1	Co_3O_4	0.40	CoO	Co_3O_4	40	2	1000—800
2	Co_3O_4	0.15	CoO	Co_3O_4	40	2	1000—800
3	Co_3O_4	0.70	Co_3O_4+CoO	Co_3O_4	40	3	1000—800
4	Co_3O_4	0.50	Co_3O_4+CoO	Co_3O_4	40	3	1000—800
5	$NiFe_2O_4$	0.15	$NiFe_2O_4$	$NiFe_2O_4$	40	3	1000—800
6	$NiFe_2O_4$	0.30	$NiFe_2O_4$	$NiFe_2O_4$	40	3	1000—800
7	$NiFe_2O_4$	0.50	$NiFe_2O_4$	$NiFe_2O_4$	40	3	1000—800

In the case of the chemical-transport reaction of Co_3O_4, the phases of the residue changed with the amount of the source material present before the reaction. Table 1 gives a survey of the growth experiments. Runs 1 and 2, in which the weights of the source material were 0.40 and 0.15 g respectively, gave only CoO as the residue. However, runs 3 and 4, in which these weights were 0.50 g and 0.70 g, gave two phases of CoO and Co_3O_4 as the residue. Such phenomena could be explained by the dissociation reaction of Co_3O_4, $Co_3O_4 \rightarrow 3CoO + 1/2O_2$. In this case, the dissociation oxygen pressure is given by the equation[8]: $\log P_{O_2} = -19150/T + 15.48$. Figure 3 shows the dissociation pressure *versus* the temperature. According to Fig. 3, the dissociation pressure of Co_3O_4 is 2.78 atm at 1000°C and 5.6×10^{-3} atm at 800°C. Co_3O_4 at the source zone is perhaps dissociated into CoO and O_2 at 1000°C until the oxygen pressure reaches 2.78 atm in the closed system. If the Co_3O_4 is assumed to be completely dissociated into CoO and O_2 in the system whose volume is estimated to be about 27 m*l*, the oxygen pressures of runs 1—4 can be calculated to be 3.2, 1.2, 4.0, and 5.5 atm respectively. The calculated dissociated pressure of run 2, 1.2 atm, is lower than the dissociation pressure, 2.78 atm, at 1000°C. Therefore, it is considered that, in run 2, the Co_3O_4 is completely dissociated into CoO and O_2, and that then $CoCl_2$ gas is prepared by the reaction of CoO and HCl in the source zone. However, in this experiment, Co_3O_4 crystals were prepared in the crystallization zone. As the oxygen pressure in the tube should be higher than the dissociation pressure of Co_3O_4 in the crystallization zone of 800°C, this reaction may occur as follows:
in the source zone of 1000°C:

$$Co_3O_4(s) \rightarrow 3CoO(s) + \frac{1}{2}O_2(g) \qquad (2)$$

$$3CoO(s) + 6HCl(g) \rightarrow 3CoCl_2(g) + 3H_2O(g) \qquad (3)$$

and in the crystallization zone of 800°C:

$$2CoCl_2(g) + 3H_2O(g) + \frac{1}{2}O_2(g) \rightarrow Co_3O_4(s) + 6HCl(g) \qquad (4)$$

The calculated oxygen pressures of runs 3 and 4, 4.0 and 5.5 atm respectively, are much higher than 2.78 atm, and in the source zone Co_3O_4 should be partially dissociated into CoO and O_2 until the oxygen pressure amounts to 2.78 atm. Therefore, the reaction proceeds with a source material consisting of CoO and Co_3O_4. In runs 3 and 4 the following reaction may be added to the above-mentioned reaction in the source zone:

$$Co_3O_4(s) + 8HCl(g) \rightleftharpoons CoCl_2(g) + 2CoCl_3(g) + 4H_2O(g). \qquad (5)$$

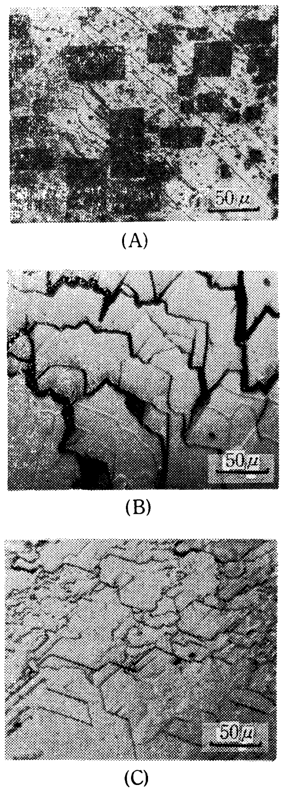
The reverse reaction may occur in the crystallization zone.

In run 1, the calculated oxygen pressure, 3.2 atm, is slightly higher than 2.78 atm. However, in this experiment, the residue was CoO. This can be explained by considering the following process. In the initial stage, the reaction should proceed with two phases of CoO and Co_3O_4 in the source zone, and the oxygen pressure seems to be kept at 2.78 atm in the tube. As the growth of Co_3O_4 single crystals consumes the O_2 gas in the crystallization zone, as is shown in Eq. (4), the Co_3O_4 at the source zone should be dissociated into CoO and O_2 by the quantity of Co_3O_4 prepared in the crystallization zone, thus keeping the oxygen pressure 2.78 atm. Therefore, the quantity of Co_3O_4 in the source zone should decrease with the growth of Co_3O_4 single crystals in the crystallization zone, and only CoO should come to exist as the residue in the source zone. In every case from run 1 to run 4, it is considered that Co_3O_4 single crystals grow under the oxygen pressure dissociated in the source zone.

In the case of $NiFe_2O_4$, the phases of single crystals and the residue did not change with the amount of the source before the reaction, as is shown in runs 5, 6, and 7. The chemical-transport reaction seems to proceed with source material of a single phase, according to this simple reversible reaction:

$$NiFe_2O_4(s) + 8HCl(g) \rightleftharpoons NiCl_2(g) + 2FeCl_3(g) + 4H_2O(g). \qquad (6)$$

Preparation of Thin Film of $NiFe_2O_4$. Figure 4 shows the surfaces of the MgO (100), (110), and (111) substrates on which $NiFe_2O_4$ was deposited by the chemical-transport reaction. On the (100) MgO

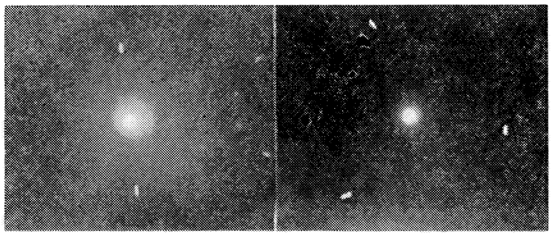


(A)
(B)
(C)

Fig. 4. Photomicrographs of (A) (100), (B) (110), and (C) (111) surface of MgO single crystals on which $NiFe_2O_4$ was deposited.

---

[8] O. Kubaschewski and LL. Evans, " Metallugical Thermochemistry," London Pergamon Press (1956), p. 331.



(A) (B)

Fig. 5. Laue patterns of film using copper radiation. (A) film on (110) surface of MgO. (B) film on (111) surface of MgO.

substrate, many oriented pyramid-like microcrystals were observed, as is shown in Fig. 4(A). On the contrary, thin films were observed on the (110) and (111) MgO substrates. The film was shiny and opaque brown, and it overlaid the substrate. The films removed from the substrate was composed of a ferromagnetic material. The film thickness was about 5000 Å, and the growing speeds were about 100 Å/hour. Laue patterns obtained using copper radiation are shown in Fig. 5. The pattern of the film on the (110) surface of MgO consisted of reflections with a two-fold axis; the film was a (110) plane with a cubic structure. The pattern of the film on the (111) surface of MgO corresponded to that of the single crystal film with a (111) surface with a cubic structure. The electron diffraction of the film removed from the (111) surface of MgO gave spots with a six-fold axis. The lattice constant calculated by means of the diffraction spots was 8.38 Å. This value agrees within 0.5% with the A.S.T.M. value of $NiFe_2O_4$. The atomic ratio of iron to nickel in the film was determined to be 1.97±0.04 from the chemical analysis. Therefore, it may be concluded that the film was nickel ferrite deposited epitaxially on the (110) and (111) planes of MgO.

When the $NiFe_2O_4$ powder was charged as the source, thin films were not grown, and many small crystals were found on the substrate. The rate of surface reaction may be much higher in the powdered source material than in the sintered one, as the surface area of the powdered material is larger than that of the sintered one. It is considered that the high rate of surface reaction results in much transport. In this case, the great deal of transport seems to cause the overgrowth of $NiFe_2O_4$ crystals on the substrate.

The authors wish to express their thanks to Dr. N. Yamamoto for his fruitful discussions.