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Metastable phase relation and phase equilibria in the Cr_2O_3-Fe_2O_3 system

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In order to ascertain the metastable phase relation in the Cr_2O_3-Fe_2O_3 system, the existing phases were investigated by X-ray analysis using samples obtained by heating the coprecipitated powders for 1 h at 600–1000°C. There was a metastable two-phase region of Cr_2O_3-rich (CC) and Fe_2O_3-rich (FC) phases below about 940°C. Equilibrium state of 1:1 composition at 600–900°C was considered to be a single phase of the corundum solid solution. The metastable two-phase CC + FC region was suggested to appear probably due to the compositional inhomogeneity in the coprecipitated powders. © *2003 Kluwer Academic Publishers*

1. Introduction

Phase diagram of the Cr_2O_3-Fe_2O_3 system and formation of the $(Cr,Fe)_2O_3$ solid solutions have been studied by many researchers [1–8]. A continuous solid solution with the corundum structure, $(Cr,Fe)_2O_3$, was reported to exist at 1300–1400°C [1, 2]. Music et al. [3] reported the existence of $(Cr,Fe)_2O_3$ at 1100°C and a two-phase region consisted of Cr_2O_3-rich corundum (abbreviated as CC) and Fe_2O_3-rich corundum (abbreviated as FC) phases at 900°C. Present authors [4] found that the two-phase CC + FC region existed in a compositional range from 35 to 80 mol% Fe_2O_3 at 600°C by measuring the composition dependence of d-spacing of 300 reflection of the corundum structure in this system. However, the maximum temperature of two-phase region is unknown. On the contrary, formation of a single solid solution phase below about 900°C was reported by several authors [5, 6]. Tsokov *et al.* [5] showed that the mechanical treatment of coprecipitated powders decreased the formation temperature of $(Cr,Fe)_2O_3$ to 350°C. Bhattacharya *et al.* [6] found the formation of $(Cr,Fe)_2O_3$ at 600°C in the sol-gel-derived powders. Thus, the question arises whether the two-phase CC + FC region observed in the coprecipitated powders [3, 4] is stable. Then, in this work, we have studied the phase relation in the Cr_2O_3-Fe_2O_3 system by heating the coprecipitated powders at 600–1000°C, showing the existence of metastable two-phase region. And moreover, we have investigated the phase equilibria of equimolar $CrFeO_3$ (1:1) composition at 600–900°C.

2. Experimental procedure

The raw materials used were $Cr(NO_3)_39H_2O$ and $Fe(NO_3)_39H_2O$ with 99.9% purity. The precipitates of mixed hydroxides were prepared by the chemical coprecipitation method [4]. These precipitates were heat-treated for 1 h at 600–1000°C in a platinum crucible to ascertain the phase relation. Similarly, precipitates were heat-treated at 600, 800 and 900°C for 1–1000 h to study the phase equilibria of 1:1 composition. Phases were identified by X-ray diffraction (XRD) analyzing the crystal structure of powders heat-treated at each temperature using a MAC science M21XG diffractometer with monochromatized Cu Kα radiation. In order to prove the existence of two phase region, d-spacing of 300 reflection of the corundum structure was determined by measuring exactly the diffraction angles of 300 XRD peaks using a step scanning technique [4]. Fourier transform infrared (FT-IR) spectra were recorded at room temperature by a FT-IR spectrometer (Nihonbunkou, model FT/IR-620), where the samples were pressed in KBr discs.

3. Results and discussion

3.1. Metastable phase relation

XRD profiles of the powders with 1:1 composition heat-treated for 1 h at 600, 920, 930, 940 and 950°C are revealed in Fig. 1, showing 300 reflection peaks of the corundum structure. At this composition, two-phase mixture consisted of Cr_2O_3-rich corundum (CC) and Fe_2O_3-rich corundum (FC) solid-solution phases was observed at 600–930°C and a single corundum phase was observed at 940 and 950°C. In XRD profiles of samples heat-treated at 940 and 950°C, split of 300 reflections due to Cu Kα_1 and Cu Kα_2 radiations can be observed clearly in Fig. 1.

The phases identified in samples obtained by heating the coprecipitated powders for 1 h at 600–1000°C are depicted in Fig. 2. There was a two-phase CC + FC region at temperatures below about 940°C. At 600°C, the CC and FC phases coexisted from 35 to 80 mol% Fe_2O_3 compositional region [4]. At 900°C, the compositional region of CC + FC mixture was about 40 to 70 mol% Fe_2O_3. The apparent critical point for the

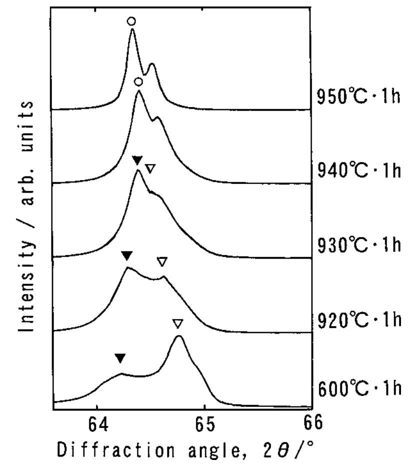

Figure 1 XRD patterns of samples with equimolar $CrFeO_3$ composition heat-treated at various temperatures. ○, ▽ and ▼ represent 300 peaks of single corundum phase, Cr_2O_3-rich corundum (CC) phase and Fe_2O_3-rich corundum (FC) phase, respectively.

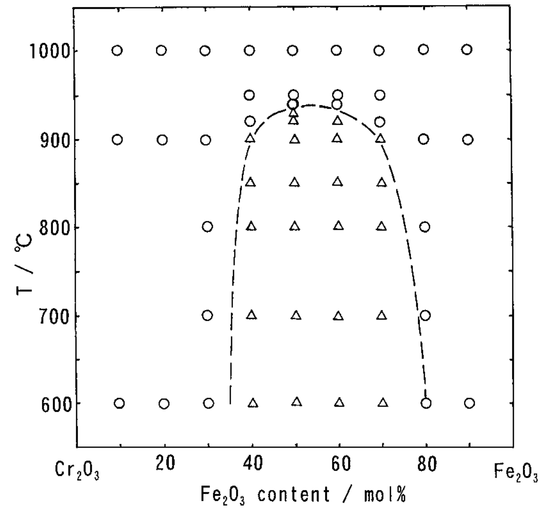

Figure 2 Metastable phase relation of the Cr_2O_3-Fe_2O_3 system obtained by heating the coprecipitated powders for 1 h at each temperature. Dashed line denotes the phase boundary between single corundum phase and two-phase regions. ○ single corundum phase, △ two-phase (CC + FC).

two-phase region was estimated to be about 55 mol% Fe_2O_3, 935 ± 5°C.

3.2. Phase equilibria

Phase equilibria of 1:1 composition were studied by heating the coprecipitated powders at 600, 800 and 900°C for 1–1000 h. The XRD profiles of the samples obtained by heating the as-coprecipitated powders at 900°C for 1, 10 and 20 h showed both 300 reflection peaks of CC Phase (▽ in Fig. 3a) and FC phase (▼ in Fig. 3a), while the sample for 40 h exhibited only a single peak (○ in Fig. 3a) indicating the formation of a single corundum phase. The samples heated at 800°C for 1, 100 and 400 h were CC + FC phases, while that for 1000 h at 800°C was a single corundum phase (Fig. 3b). The samples heated at 600°C for 1–1000 h were CC + FC phases (Fig. 3c).

The d-spacings of 300 reflections, d_{300}, of CC and FC solid solutions approached each other with an increase of the heating time at 600, 800 and 900°C (Fig. 4). It

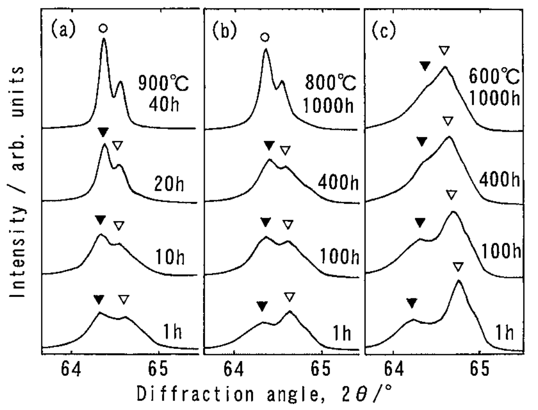

Figure 3 XRD patterns of samples with $CrFeO_3$ composition heat-treated for 1–1000 h at temperatures, (a) 900°C, (b) 800°C and (c) 600°C. ○, ▽ and ▼ show the same symbols as those in Fig. 1.

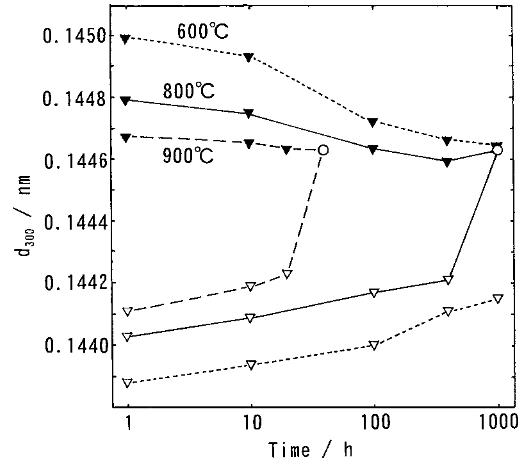

Figure 4 Dependence of d-spacing, d_{300}, of the corundum structure in samples with $CrFeO_3$ composition on holding time at 600, 800 and 900°C. ○, ▽ and ▼ represent d_{300}-values of single corundum phase, CC phase and FC phase, respectively.

took 40 and 1000 h to form the single phase at 900 and 800°C, respectively. In samples heated at 600°C, the d_{300}-value of CC phase increased, while that of FC phase decreased with an increase of the heating time (Fig. 4). Then, it is expected that a single corundum phase will be obtained in the sample heat-treated longer than 1000 h at 600°C. Moreover, in the homogeneous sample obtained by heating the sol-gel-derived powders up to 600°C, a single solid-solution phase was found at 1:1 composition [6]; this result supported the existence of a single corundum phase at 600°C. From these results, the equilibrium state of 1:1 composition is considered to be a single phase of the corundum solid solution at 600–900°C. The d_{300}-value of a single corundum phase (○ in Fig. 4) is larger than the average value of those of CC and FC phases (▽ and ▼ in Fig. 4). This reason is not clear at present.

We have obtained a phase relation of the Cr_2O_3-Fe_2O_3 system with an CC + FC two-phase region below about 940°C (Fig. 2). However, the two-phase coexistence is not stable but metastable at 1:1 composition. In fact, the stable phase was confirmed to be a single corundum solid-solution phase (Figs 3 and 4). Thus, Fig. 2 is not an equilibrium phase diagram with miscibility gap but a metastable phase relation. It is

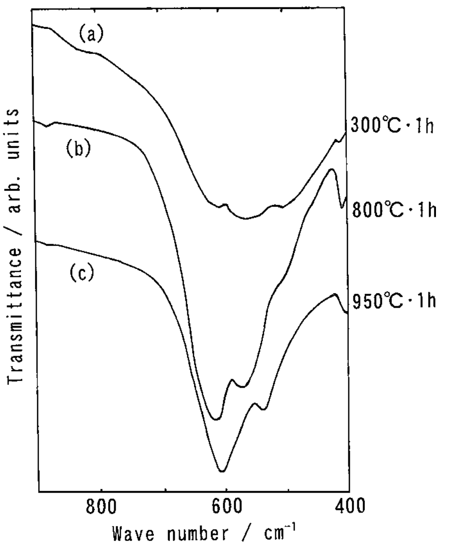

Figure 5 FT-IR spectra of powders with $CrFeO_3$ composition heat-treated at various temperatures.

suggested that the two-phase CC + FC coexistence in the earlier works [3, 4, 7] was in the metastable state.

3.3. FT-IR spectra

FT-IR spectra of the powders with 1:1 composition heat-treated for 1 h at 300. 800 and 950°C are revealed in Fig. 5. Samples heated at 300°C were found to be amorphous oxides in a previous paper [4]. In the FT-IR spectrum of amorphous oxides (Fig. 5a), very broad bands with transmittance minima at 410, 505, 563 and 610 cm^{-1} were observed. In the FT-IR spectrum of two-phase CC + FC mixture (Fig. 5b), broad bands at 410, 572 and 616 cm^{-1} are attributed to CC phase [3, 7], and a broad band at 572 cm^{-1} and a shoulder at 510 cm^{-1} are attributed to FC phase [3, 7]. In oxides with single corundum phase (Fig. 5c), broad bands were observed at 607 and 539 cm^{-1}, which were similar to the results of other researchers [5, 7]. The positions for transmittance minima in the FT-IR spectrum of amorphous oxides are close to those of two-phase CC + FC mixture but different from those of single corundum phase. Then, there is a possibility that the coprecipitated powders have some inhomogeneity. This inhomogeneity may cause the formation of metastable two-phase mixture during heating the as-coprecipitated powders.

4. Conclusion

(1) Metastable phase relation in the Cr_2O_3-Fe_2O_3 system was studied by identifying the existing phases in the samples obtained by heating the coprecipitated powders for 1 h at 600–1000°C. There was a metastable two-phase region of Cr_2O_3-rich and Fe_2O_3-rich corundum phases below about 940°C.

(2) Equilibrium state of 1:1 composition in the temperature range from 600 to 900°C was considered to be a single phase of the corundum solid solution.

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