論文・Paper

Synthesis of LaCrO_3 Under Hydrothermal Conditions

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The synthesis of LaCrO_3 from the mixture of chromium hydroxide and La_2O_3 was studied under hydrothermal conditions and in air. LaCrO_3 was directly prepared under hydrothermal conditions of above 400°C under 100 MPa H_2O pressure in contrast to the formation of LaCrO_3 via La_2CrO_6 above 700°C in air. LaCrO_3 synthesized under hydrothermal conditions was well crystallized with homogeneous grain size of $0.7 \pm 0.2 \mu\text{m}$ at temperatures of $700^\circ\text{C} \sim 1000^\circ\text{C}$, while that synthesized in air was an aggregate with irregular grains.

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水熱条件下における LaCrO_3 の合成

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水熱条件下における水酸化クロム水合物と La_2O_3 の混合物からの LaCrO_3 の合成反応を調べ、空気中における合成反応と比較した。水熱条件下では 100 MPa, 400°C 以上で LaCrO_3 を直接合成することができたが、空気中では低温で中間化合物 La_2CrO_6 を生成し、 700°C 以上でのみ LaCrO_3 の生成が認められた。 $700^\circ\text{C} \sim 1000^\circ\text{C}$ の水熱条件下で合成された LaCrO_3 生成物は $0.7 \pm 0.2 \mu\text{m}$ の均一な微粒子であったが、空気中で合成された LaCrO_3 は大きさ形状ともに不規則な粒子の集合体であった。

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Key-words : LaCrO_3 , Hydrothermal synthesis, Fine powder, La_2CrO_6

1. Introduction

Lanthanum chromite LaCrO_3 had been studied earlier from electromagnetic or crystallographic interest^{(1), (2)}. In recent years, LaCrO_3 or doped LaCrO_3 have widely been studied as a refractory conducting material because of its electronic conductivity, high melting point ($>2400^\circ\text{C}$) and oxidation or corrosion resistivity. Particularly, the doped LaCrO_3 materials with high electronic conductance have been interested as an electrode for MHD^{(3), (4)}, fuel cell⁽⁵⁾ or electric arc⁽⁶⁾, and a heating element⁽⁷⁾ or a conducting lead for ZrO_2 -base heating elements⁽⁸⁾. In these studies or applications, LaCrO_3 and doped LaCrO_3 have generally been synthesized by solid state reac-

tions of oxide mixtures with heating at high temperatures above 1000°C in air. These procedures need repeat firing and grinding to complete the reaction due to slow diffusion processes in solids. Therefore we have studied the synthesis of LaCrO_3 under hydrothermal conditions in comparison with the usual firing under atmospheric pressure. Here the effects of the temperatures and atmospheres on the synthesis of LaCrO_3 is described.

2. Experimental

Chromium hydroxide was used as a starting material to improve the reactivity with La_2O_3 . The chromium hydroxide was precipitated from 3 N chromic nitrate solution prepared from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (guaranteed reagent grade, Kanto Chem. Co., Ltd., Tokyo, Japan)

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by adding into 8 N NH_4OH solution. The precipitate was filtered, washed by distilled water thoroughly, then dried at 90°C for 24 h in air. The contents of Cr_2O_3 in this hydroxide were analyzed by TG-DTA (Thermoflex TG-DTA, Rigaku Denki Co., Ltd., Tokyo, Japan) and ignition loss measurements. This chromium hydroxide was mixed with lanthanum oxide (>99.9%, Shinetsu Chem. Co., Ltd., Japan), of which La_2O_3 contents were also analyzed by TG-DTA and ignition loss measurements, to the exact composition of $\text{La}_2\text{O}_3:\text{Cr}_2\text{O}_3=1:1$ (mol) thoroughly in an agate mortar with acetone.

The mixture of about 0.1 g was sealed with an electric arc in a Pt capsule 2.7 mm ID, 0.15 mm thick and 35 mm long. The capsule was heated in a test-tube type pressure vessel of Stellite 25 under the pressure of 100 MPa H_2O at $300^\circ\sim 700^\circ\text{C}$ for 3~24 h. The temperature was measured by calibrated Platinel thermocouples attached on the outside wall of the vessel.

In order to study the influences of atmospheres, additional experiments were carried out where ~0.06 g chromium powder (>99%, Wako Pure Chem. Co., Ltd., Tokyo) was added on the top of the mixture in the capsule, Chromium would react with H_2O to produce Cr_2O_3 and H_2 at high temperatures, so that a reducing atmosphere was created in the capsule.

The synthesis of LaCrO_3 from the starting mixture was also studied in air by the TG-DTA equipment. The mixture was heated at $600^\circ\sim 1200^\circ\text{C}$ for 3 h in a Pt crucible then cooled rapidly.

All samples prepared were examined by X-ray powder diffraction using a diffractometer with a rotating Cu anode and a graphite monochromator (RU-7, Rigaku Denki Co., Ltd., Japan) and scanning electron microscopy using an equipment (JSM T-200, JEOL Co. Ltd., Japan).

A high purity silicon (>99.99%, Kinzoku Kagaku Lab., Tokyo) was added as an internal standard to determine the lattice parameters of LaCrO_3 .

3. Results and discussion

3.1 Characterization of starting materials

The chromium hydroxide prepared was fine-grained aggregate as seen in Fig. 1, and amorphous on the basis of the X-ray diffraction. The composition of this material appeared to be $\text{Cr}_2\text{O}_3\cdot 6.42\text{H}_2\text{O}$ from the ignition loss measurements. Based upon the X-ray diffraction, small amount of $\text{La}(\text{OH})_3$ was detected in used La_2O_3 (Fig. 2). The water contents of this material was determined to be $\text{La}_2\text{O}_3\cdot 0.95\text{H}_2\text{O}$ by ignition loss measurements and TG-DTA. Table 1 summarizes the characterization of the starting materials.

3.2 Synthesis of LaCrO_3 under hydrothermal conditions

Table 2 shows the results of hydrothermal experiments. The product heated at 300°C was identified to be crystallized $\text{La}(\text{OH})_3$ and small amount of $\text{LaCO}_3\text{OH}^{(9)}$ by X-ray diffraction.

Fig. 1. SEM photograph of prepared chromium hydroxide.

Fig. 2. SEM photograph of lanthanum oxide.

Table 1. Characterization of starting materials.

Material	X-ray analysis	Water contents n values in $\text{N}_2\text{O}_3\cdot n\text{H}_2\text{O}$
Chromium hydroxide	Amorphous	6.42
Lanthanum oxide	$\text{La}_2\text{O}_3 + \text{La}(\text{OH})_3^*$	0.95

* A small amount of CO_2 might be absorbed though no CO_2 containing phases could be detected.

reaction (Fig. 3). Chromium hydroxide might exist still in amorphous state because no crystallized chromium compounds could be detected in this product. The formation of LaCO_3OH indicates the contamination of starting La_2O_3 by CO_2 gas absorbed from atmosphere. Similar phenomena have often been observed in the studies in the system $\text{La}_2\text{O}_3\text{-H}_2\text{O}$ under hydrothermal conditions^{(10), (11)}. The crystal LaCO_3OH is significantly stable under hydrothermal conditions particularly high pressures as 100 MPa or above⁽¹⁰⁾ in the presence of CO_2 components, even they were in a small amount, in the system. LaCO_3OH remained at 500°C and traced at 600°C, but has not been detected above 700°C. The product of 400°C was almost well crystallized LaCrO_3 indicating the reaction between $\text{La}(\text{OH})_3$ and chromium hydroxide with the release of H_2O . Scanning

Table 2. X-ray diffraction analysis of the products prepared hydrothermally under 100 MPa.

Temperature (°C)	Period (hr)	Identified phases
300	3	$\text{La}(\text{OH})_3$ (vs), LaCO_3OH (w)
400	3	LaCrO_3 (vs), LaCO_3OH (vw)
400	24	LaCrO_3 (vs), LaCO_3OH (v)
500	3	LaCrO_3 (vs), LaCO_3OH (vw)
600	3	LaCrO_3 (vs), LaCO_3OH (tr)
700	3	LaCrO_3 (vs)

vs—very strong, w—weak, vw—very weak, tr—trace

Fig. 3. X-ray powder pattern of the products prepared under hydrothermal conditions.

electron photomicrograph of this product (Fig. 4) revealed fine-grained LaCrO_3 of about 0.1 μm in diameter and hydrothermally grown LaCO_3OH crystals of 1~3 μm in edge. As the reaction temperature elevated, the amount and the size of LaCO_3OH crystals decreased while the production of LaCrO_3 increased. Only well crystallized LaCrO_3 could be observed in the product at 700°C. The LaCrO_3 crystals has homogeneous grain size of $0.7 \pm 0.2 \mu\text{m}$ (Fig. 5). The hydrothermally prepared LaCrO_3 has an orthorhombic symmetry ($Pbmm$) with the lattice parameters $a=5.477 \text{ \AA}$, $b=5.511 \text{ \AA}$ and $c=7.758 \text{ \AA}$, which are in good agreement with the previous data^{(2), (12)~(14)}, $a=5.476\sim5.479 \text{ \AA}$, $b=5.512\sim5.515 \text{ \AA}$ and $c=7.752\sim7.758 \text{ \AA}$ for pure LaCrO_3 prepared in air at high temperatures above 1000°C. These results indicate that formation of LaCrO_3 has been completed in a short period of 3 h at temperatures as low as 700°C under hydrothermal conditions due to the action of supercritical water as a mineralizer.

Fig. 4. SEM photograph of the product prepared under hydrothermal condition (at 400°C, 100 MPa, for 3 h).

Fig. 5. SEM photograph of the product prepared under hydrothermal condition (at 700°C, 100 MPa, for 3 h).

In the experiments with Cr powder, LaCrO_3 was also synthesized in the capsule at temperatures above 400°C . The products in the experiments with Cr powder were entirely identical with those in the experiments without Cr powder. A reducing atmosphere created by the hydrogen produced by the reaction

at temperatures above $600^\circ\text{C}^{15)}$, had little effect on the formation of LaCrO_3 . These results indicate that LaCrO_3 is stable under a reducing conditions, though oxygen deficient Ca-doped LaCrO_3 has been prepared¹⁶⁾ under a similar hydrothermal conditions employed in the present study. The water was decomposed into hydrogen which could permeate through the wall of the Pt capsule at high temperatures, so that a weight loss could be observed after hydrothermal treatments. The elimination of water contents, 12% or 18% at 600°C , corresponding to the observed weight losses did also show no significant effects on the formation and the crystal growth of LaCrO_3 .

3.3 Synthesis of LaCrO_3 in an atmospheric pressure

When the same starting mixture of La_2O_3 and chromium hydroxide as that in hydrothermal experiments was heated in air with an atmospheric pressure, the formation of LaCrO_3 was observed at higher temperatures above 700°C as seen in Table 3. At lower temperatures as 600°C , no LaCrO_3 was detected but the mixture of La_2CrO_6 and small amounts of La_2O_3 and Cr_2O_3 . According to the results by TG-DTA and X-ray diffraction for the samples heated at various temperatures, the reaction process to form LaCrO_3 in air appeared to be as follows,

Table 3. X-ray diffraction analysis of the products prepared in air (0.1 MPa).

Temperature ($^\circ\text{C}$)	Period (hr)	Identified phases
300°C	3	La_2O_3 (vs), $\text{La}(\text{OH})_3$ (s)
400°C	3	La_2O_3 (vs), LaCO_3 (s), Cr_2O_3 (vs)
500°C	3	La_2O_3 (vs), LaCO_3 (s), Cr_2O_3 (vs)
550°C	3	La_2O_3 (vs), Cr_2O_3 (vs)
600°C	3	La_2CrO_6 (vs), La_2O_3 (w), Cr_2O_3 (w)
700°C	3	LaCrO_3 (vs), La_2CrO_6 (w), La_2O_3 (vs), Cr_2O_3 (vs)
800°C	3	LaCrO_3 (vs), La_2CrO_6 (vs)
900°C	3	LaCrO_3 (vs)
1200°C	3	LaCrO_3 (vs)

vs—very strong, s—strong, w—weak, vs—very weak

Fig. 6. SEM photograph of the product prepared in air (at 1200°C , 0.1 MPa, for 3 h).

The formation of La_2CrO_6 with the oxidation of chromic oxide is characteristic¹⁷⁾ in the reaction between La_2O_3 and Cr_2O_3 in air. The powder of LaCrO_3 prepared in air at temperatures above 900°C aggregated irregularly as shown in Fig. 6.

4. Summary

Pure LaCrO_3 was synthesized at low temperatures as 700°C under hydrothermal conditions with 100 MPa pressure for 3 h from La_2O_3 and chromium hydroxide. LaCrO_3 was well crystallized with homogeneous grain size of $0.7 \pm 0.2 \mu\text{m}$. The water seemed to accelerate the reaction between La_2O_3 or La hydroxide and Cr_2O_3 or Cr hydroxide as a mineralizer. The formation process under hydrothermal conditions appears to be simpler than that via the formation of La_2CrO_6 as an intermediate compound in air.

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実験・技術・調査報告・Report

マグネシア質断熱耐火物の試作 (マグネシア多泡粒の研究, その 2)

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酢酸液滴からのマグネシアまたはマグネシアクロム鉄鉱多泡粒を用いて断熱耐火煉瓦を調製することができる。すなわち、バルクな多泡粒を水で湿らすと、若干可塑性が現れて加圧成形を容易にし、乾燥するとかなりの強度を発生、高温焼成すれば、比較的小さな焼成収縮で軽量のマグネシアまたはマグネシアクロム鉄鉱系多孔質煉瓦が得られる。

本実験に用いた多泡粒は、0.42~1.7 mm 粒分 30 wt% 1.7~3.3 mm 粒分 50 wt% また 3.3~4.7 mm 粒分 20 wt% の粒度分布をもち、成形に好ましい水分量は、成形圧 10 kg/cm² の場合、約 5 wt% であった。105°C で乾燥した成形体の圧縮強さは 27 kg/cm² である。加熱すると、約 300°C で酢酸塩が分解してアセトンと炭酸ガスを発生し、続いて 1500°C 加熱で線収縮 4.5%、圧縮強さ 50 kg/cm² の軽量焼成体（かさ比重、1.2 g/cm³）を得た。熱伝導率は 1000°C で、0.95 kcal/m・h・°C、これは普通のマグネシア煉瓦の約 1/4 である。平炉及び転炉スラグの浸食性を調べたところ焼成体組織へわずかに浸透したものの良い耐食性を示した。

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Trial Preparation of Heat Insulating Magnesia Refractories (Study on Porous Magnesia Grains, Part 2)

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A heat insulating fire brick made of magnesia or magnesia-chromite mixture can successfully be produced from the respective porous grains prepared by use of acetic acid droplets