

Method for the synthesis of CrO₂ at ambient pressure and temperature

著者	角田 匡清
journal or publication title	Journal of applied physics
volume	93
number	10
page range	6856-6858
year	2003
URL	http://hdl.handle.net/10097/35374

doi: 10.1063/1.1555988

Method for the synthesis of CrO₂ at ambient pressure and temperature

H. Ye

College of Chemistry and Chemical Engineering, Central-South University, Changsha 410083, People's Republic of China

Q. Zhang and F. Saito

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

B. Jeyadevan^{a)} and K. Tohji

Department of Geoscience and Technology, Tohoku University, Sendai 980-8579, Japan

M. Tsunoda

Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan

(Presented on 12 November 2002)

In this article, we report the synthesis of metastable chromium dioxide at ambient temperature and pressure. The formulation of this method is based on the fact that the CrO₂ particles used in magnetic recording tapes are chemically unstable and react with the organic binder, leading to a disproportionate reaction that produces nonmagnetic Cr(III)OOH and H₂Cr(VI)O₄ compounds. This suggests that it is also possible to synthesize CrO₂ by reacting Cr(III) with Cr(VI) under appropriate conditions. Thus, metastable chromium dioxide (CrO₂) powder was synthesized by mechanically grinding a mixture of CrO₃ and Cr(OH)₃ to induce a solid–solid reaction at atmospheric temperature and pressure. The characteristics of the product obtained after mechanical grinding of the above mixture depended on parameters such as the preparation conditions for the starting material Cr(OH)₃, the grinding time, the rotational speed of the mill and the mole ratio of CrO₃ and Cr(OH)₃. An x-ray diffraction pattern of the product obtained under optimum conditions was in excellent agreement with the profile of CrO₂. Furthermore, the powder was strongly ferromagnetic, with saturation magnetization of 63 emu/g in an applied field of 1 T. © 2003 American Institute of Physics. [DOI: 10.1063/1.1555988]

I. INTRODUCTION

Of several oxidation states of chromium, CrO₂ is the only chromium oxide that is strongly ferromagnetic at room temperature (Cr⁴⁺ is a 3d² ion). And this has been of some interest technologically as a magnetic recording medium.¹ However, CrO₂ is metastable at atmospheric pressure and temperature and synthesis with these requires stringent conditions.^{2,3} Recently, it was reported that CrO₂ could be prepared by decomposing Cr(NO₃)₃ impregnated in a polycrystalline rutile (TiO₂) support under ambient pressure.⁴ Another report claimed that CrO₂ could be produced by reducing CrO₃ with NH₄I/NH₄Br at temperatures between 120 and 150 °C and annealing the solid product at temperatures below the decomposition point of CrO₂.⁵ However, further simplification of the synthesis process is very much desired to study the intrinsic properties of this oxide and also the effect of potential dopants that could enhance the above properties. In this article, we report a method by which to synthesize CrO₂ by reacting Cr(III) with Cr(VI) compounds mechanochemically. It was found that CrO₂ can be synthesized by grinding a mixture of CrO₃ and Cr(OH)₃·nH₂O at ambient pressure and temperature conditions. The product obtained was strongly ferromagnetic and its x-ray diffraction pattern was in excellent agreement with the pattern reported for CrO₂ in the literature.

^{a)}Electronic mail: jeya@ni4.earth.tohoku.ac.jp

II. EXPERIMENT

The raw materials for Cr(VI) and Cr(III) were reagent grade CrO₃ and Cr(OH)₃·nH₂O, respectively (supplied by Wako Chemical Co. Ltd., Japan). A planetary ball mill (Fritch Pulverisette-7, Germany) with two zirconia vials was used to mechanically mill the mixture of reagents. The inner diameter and volume of each vial were 80 mm and 45 cm³, respectively. In our experiments, zirconia balls 15 mm in diameter were used as the grinding media, and about 2 g of a Cr(VI) and Cr(III) mixture was used as the starting material. The ball/powder ratio was about 35:1. The phases present in the ground products were identified by x-ray diffraction (XRD) (Cu-MultiFlux, Rigaku, Japan) analysis. The magnetic properties were determined by a vibrating sample magnetometer (VSM) (Tamakawa model TM-VSM1230-HHHS). Thermal gradient/differential thermal gradient (TG/DTG) analysis of the samples was performed at various stages of grinding in a thermal balance (Rigaku Thermoplus TG-8120). The morphology of the product was monitored by a scanning electron microscope (SEM) (Hitachi S-4100).

III. RESULTS AND DISCUSSION

It has been reported⁵ that the CrO₂ particles used in magnetic recording tapes are chemically unstable and react with the organic binder, leading to a noticeable loss in magnetization. Although the mechanism is yet to be completely

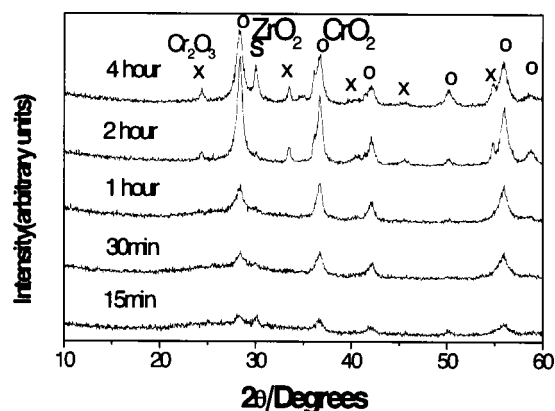
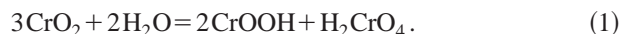


FIG. 1. X-ray diffraction patterns of ground products obtained for different grinding times.

understood, it is well established that a disproportionate reaction produces nonmagnetic compounds given by



It can be noticed that part of Cr(IV)O₂ is converted into Cr(III)OOH and the rest into H₂Cr(VI)O₄. This implies that it is also possible to synthesize CrO₂ by reacting Cr(III) with Cr(VI) under appropriate conditions.

According to the reverse reaction in Eq. (1), an oxidizing agent, H₂CrO₄, and a reducing agent, CrOOH, were necessary to synthesize CrO₂. Here, we selected CrO₃, which can form H₂CrO₄ easily in the presence of water. Furthermore, CrO₃ has a high electron affinity (EA) and could act as a strong oxidizing agent. As for CrOOH, Cr(OH)₃·nH₂O was annealed at a predetermined temperature for a specified period of time. Based on the reaction Cr⁶⁺ + 2Cr³⁺ = 3Cr⁴⁺, the mixture of CrO₃ and Cr(OH)₃ with molar ratio equivalent of 1:2 was ground in the mill.

The XRD patterns of the ground powders obtained for different grinding times are shown in Fig. 1. The diffraction peaks corresponding to CrO₂ began to appear within 15 min of grinding, and their intensities rose according to the amount of grinding. However, it should be noted that for grinding periods longer than 2 h, peaks corresponding to Cr₂O₃ and ZrO₂ (grinding media) began to appear. On the other hand, the peak intensities of CrO₂ also depended on the rotation speed of the mill for a fixed grinding time of 2 h, and reached a maximum at 700 rpm.

The saturation magnetization *M_s* in 1 T applied field as a function of the grinding time is shown in Fig. 2. The ferromagnetic fraction in the ground powder increased with grinding time with *M_s* reaching a maximum of 48 emu/g after 2 h. On the other hand, the *M_s* of the products obtained for different rotation speeds reached a maximum of 48 emu/g at 700 rpm. Thus, the optimum grinding time and rotation speed were fixed as 2 h and 700 rpm, respectively.

Based on the above results, it is reasonable to assume that the following solid–solid reaction has taken place during milling:

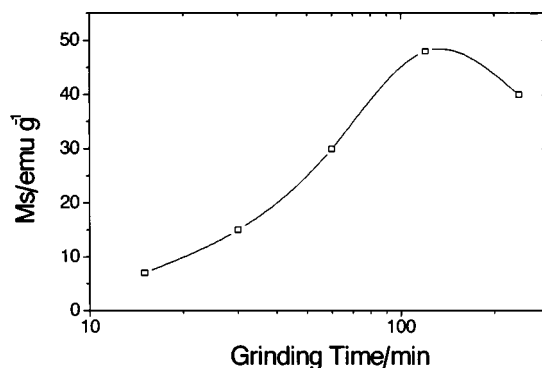
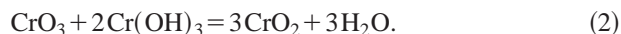


FIG. 2. Magnetization at 1 T of ground products obtained for different grinding times.

However, diffraction peaks corresponding to Cr₂O₃ appeared for powders ground for 2 h or more, irrespective of the rotation speed. The formation of Cr₂O₃ could have been due to overannealing of Cr(OH)₃·nH₂O, nonstoichiometric ratio between the starting material in Eq. (2) and/or the reduction of CrO₂. In order to inhibit the formation of Cr₂O₃, milling was carried out under varying initial molar ratios of CrO₃:Cr(OH)₃ and the XRD patterns of the ground product are given in Fig. 3. It is clear that the intensity of the peak corresponding to Cr₂O₃ was due to the nonstoichiometry of reaction (2). The addition of CrO₃ in quantities slightly over the stoichiometric requirement effectively inhibited the formation of Cr₂O₃ in the ground product. It is believed that when there was an excess of Cr(OH)₃, dehydration of it would form Cr₂O₃ according to the reaction.



The SEM analysis of the samples ground for different durations clearly showed the progress of size reduction in the mechanochemical reaction. Although the particle size of the ground powder was reduced to submicron size with the grinding time, agglomeration of the particles became very pronounced as shown in Fig. 4. TG/DTG analysis of the sample ground at 700 rpm for 2 h revealed that the product was thermally stable until 400 °C and the loss of weight below this temperature was due to the loss of water. However, at temperatures higher than 400 °C, the CrO₂ decomposed

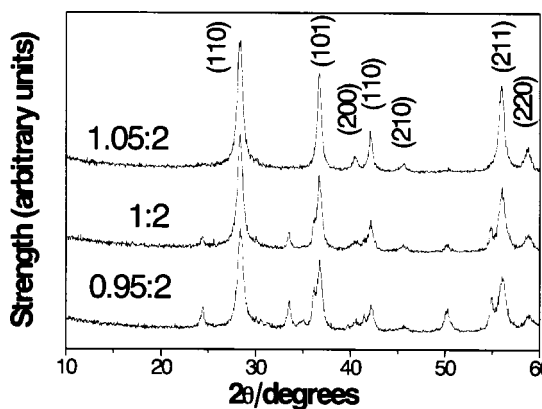


FIG. 3. X-ray diffraction patterns of ground products obtained for different CrO₃ and Cr(OH)₃·nH₂O mole ratios.

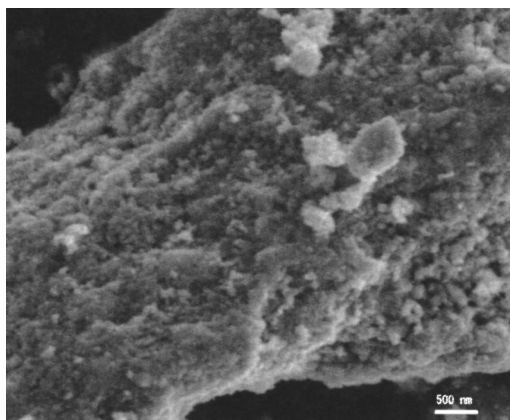


FIG. 4. SEM micrograph of the Cr_2O_3 sample synthesized by ball milling for 2 hours at 700 rpm.

into Cr_2O_3 and the corresponding weight loss was recorded. This was confirmed by XRD of the sample treated at 500°C . It is known that bound water in raw material of $\text{CrOOH}\cdot n\text{H}_2\text{O}$ is necessary in order for it to react with CrO_3 and form CrO_2 magnetic powder. And 16% of the water is contained in $\text{Cr}(\text{OH})_3$. Therefore, the saturation magnetization of the powder could be improved by drying it at a specific temperature. Thus the sample was annealed at 300°C for 5 h. The magnetic hysteresis loops of the samples before and after drying are shown in Fig. 5. The magnetization improved by about 30% and the M_s increased from 48 to 63 emu/g and H_c from 128 to 190 Oe. However, the change in weight was only 6%. The additional increase in magnetization is believed to be due to CrO_2 crystal grain growth induced by thermal annealing.

IV. CONCLUSION

Metastable CrO_2 magnetic powder was synthesized by grinding a mixture of CrO_3 and $\text{CrOOH}\cdot n\text{H}_2\text{O}$. The XRD analysis and the magnetic properties of the powder con-

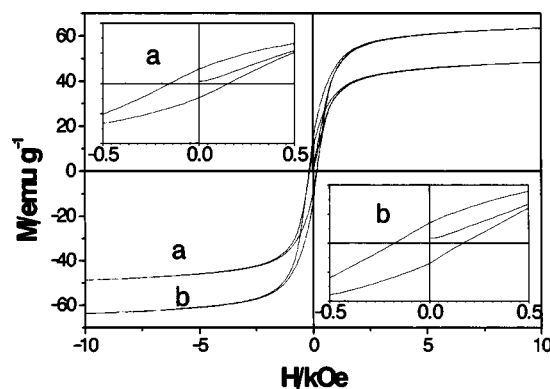


FIG. 5. Magnetic hysteresis loops (a) before and (b) after annealing the product obtained by grinding a CrO_3 and $\text{Cr}(\text{OH})_3\cdot n\text{H}_2\text{O}$ mixture with ratio of 1.05:2 for 2 h at 700 rpm.

firmed the formation of CrO_2 . The quality of the product depended on the mole ratio of CrO_3 and $\text{CrOOH}\cdot n\text{H}_2\text{O}$, the grinding time, and the speed of rotation of the mill. Further enhancement of the magnetic properties of the powder was obtained by annealing the sample at temperatures below the decomposition temperature of CrO_2 . This synthesis method is of practical importance for its simplicity, especially since there is no requirement for the high pressure used in traditional methods.

ACKNOWLEDGMENT

The Education Ministry of China is gratefully acknowledged for its financial support.

¹J. Kubota, J. Am. Ceram. Soc. **44**, 239 (1961).

²B. L. Chamberland, CRC Crit. Rev. Solid State Mater. Sci. **7**, 1 (1977).

³R. G. Egdell, E. Brand, and D. Kellett, J. Mater. Chem. **9**, 2717 (1999).

⁴K. Ramesha and J. Gopalakrishnan, Chem. Commun. (Cambridge) **1999**, 1173 (1999).

⁵G. Basile, G. C. Boero, F. Garbassi, E. M. Ceresa, and F. Montino, MRS Bull. **17**, 1197 (1982).