JOURNAL OF MATERIALS SCIENCE **39** (2004) 683–685

Influence of ball milling on structure and magnetotransport of chromium dioxide granules

YA-JIE CHEN*, XIAO-YU ZHANG
Department of Physics, Suzhou University, Suzhou 215006, People's Republic of China
E-mail: yjchen@suda.edu.cn

ZHEN-YA LI
Department of Physics, Suzhou University, Suzhou 215006, People's Republic of China;
CCAST (World Laboratory), P.O. Box 8730, Beijing 100080, People's Republic of China

Due to the great potential for application in spin electronic devices, high spin-polarized materials have attracted considerable interest in recent years, theoretically and experimentally [1, 2]. Chromium dioxide is an ideal candidate for spin-polarized electron tunnel junctions, as it is a half-metallic ferromagnet having a Fermi surface in one spin band and a spin gap for the opposite spin direction [3]. Since the discovery of large negative magnetoresistance (MR) in polycrystalline films and powder compacts of CrO_2, many efforts have focused on the investigation of transport mechanism and fabrication techniques [4, 5]. However, the enhanced extrinsic MR can be interpreted in terms of a spin dependent tunneling mechanism, such as in $LaSrMnO_3$, CrO_2 and Fe_3O_4 [6–8]. Therefore, the interface and grain boundary are significantly responsible for the origin of the low field MR. Up to now, there has been relatively little knowledge about the correlation between grain size and magnetotransport properties of acicular half-metallic CrO_2 particles. Thus, the aim of this letter is to study the influence of ball milling on size and crystal structure of CrO_2 grains, and to investigate the electrical, magnetic and magnetotransport properties.

The CrO_2 starting powders (99.5%) were supplied by Micro Magnetics Inc., USA. Ball milling was carried out in a polyflon vial with agate balls. Discs with a diameter of 15 mm and thickness of 2 mm were cold pressed at 1 GPa. Transport properties were measured with a standard four-probe technique at 4 K, 77 K and room temperature, and the contact points were made with silver paste. The average size of the grains from the width of the (110) line was estimated by means of the Scherrer formula $D_{hkl} = k\lambda/\beta\cos\theta$, where D_{hkl} is the diameter of the particles, k is a constant and β is the full width at half maximum (FWHM) of the diffraction peaks. The granules are of acicular shape, as observed using transmission electron microscopy (TEM). The mean length of the granules is about 410 nm, and the diameter is roughly 30.2 nm. Magnetic measurements were performed using a Riken Denshi BHV-55 vibrating sample magnetometer (VSM).

Fig. 1 shows X-ray diffraction patterns for the starting particles and the ball-milled particles. It is observed that all the diffraction peaks of CrO_2 are shifted to lower angles with increasing milling time. This shift is related to lattice expansion of CrO_2. The experimental results indicate that the cell parameter gradually enlarges with increasing milling time, as shown in Fig. 2. This may be attributed to the reduction of the Cr ion during the milling process, due to the formation of a metastable compound of CrO_2 with the chemical valence 4+ of Cr ion. The reduction of the valence of Cr ion leads to the increase of ionic radius and cell parameters. Similar results have also been observed by Wang [9]. The (110) peak not only shifts slightly toward lower angles, but spreads gradually with milling time. This reflects the change of grain size. Hence, the grain size, calculated using Scherrer formula for the (110) peak, is also displayed in Fig. 2. The D_{110} reduces from 21.9 to 15.8 nm. This change is in rough accord with the observation by TEM.

Fig. 3 shows the dependence of the resistivity ρ and specific magnetization σ_s on milling time at room temperature. It is found that the resistivity increases sharply over two orders of magnitude over 50 h of milling time. Subsequently, the samples show slowly increasing resistivity with milling time. This can be interpreted in terms of the reduction of particle size and the increase of specific surface area. However, the reduction of σ_s is remarkable within the initial 50 h, and then exhibits no significant dependence on milling time. The change of σ_s may originate from the lattice expansion and magnetic dead layer on the surface of CrO_2 particles [10].

Since the logarithm of the resistivity at a certain temperature is inversely proportional to the grain size, this implies that the tunneling barrier thickness increases with decreasing grain size. Ballcells [11] has demonstrated that the intergranualr tunneling MR is found to increase with decreasing grain size with constant spin polarization. Here, however, the results indicate that a decrease in MR is found with a decrease in particle size. The MR ratio versus milling time curve is illustrated in Fig. 4, where the MR ratio is defined as

*Author to whom all correspondence should be addressed.

0022–2461

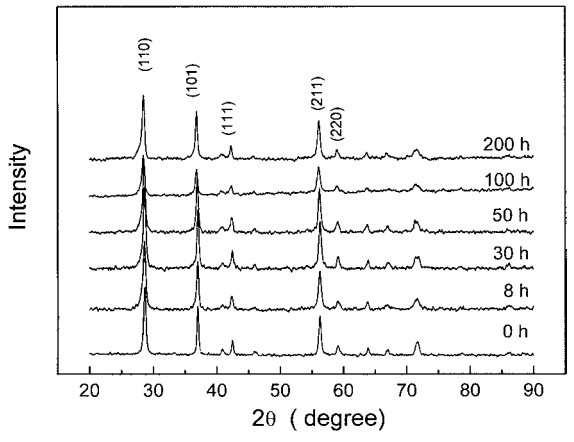

Figure 1 XRD patterns of CrO_2 powder after ball milling.

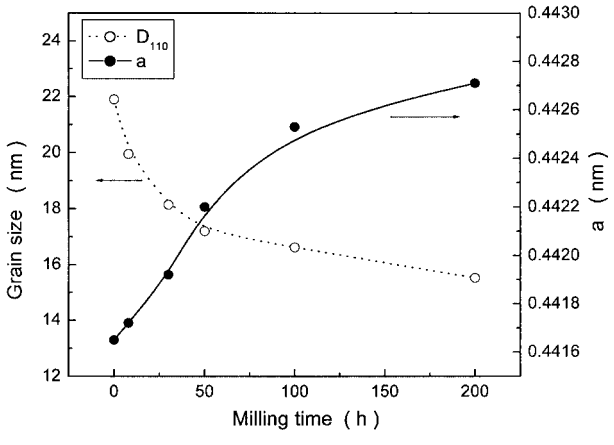

Figure 2 The variation of grain size and cell parameter of CrO_2 grains with ball milling time.

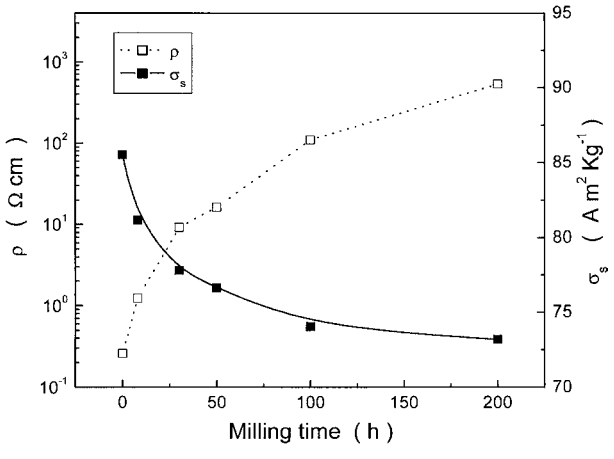

Figure 3 Dependence of the resistivity (ρ) and the specific magnetization (σ_s) of the CrO_2 powder compacts on milling time.

$MR = (R_m - R_H)/R_m$ where R_m and R_H are resistance at 0.7 T and in an applied field, respectively. No significant orientation dependence is observed in any samples. It is worth noting that the MR ratio declines monotonically with milling time, and that the decreased MR is apparently associated with a change in grain size. However, the intergranular tunneling MR may be generally attributed to two factors: the tunneling barrier, formed by the interface between particles, and the spin polarization of CrO_2 grains. Thus, ball milling leads to a change in the barrier between particles due to the change of

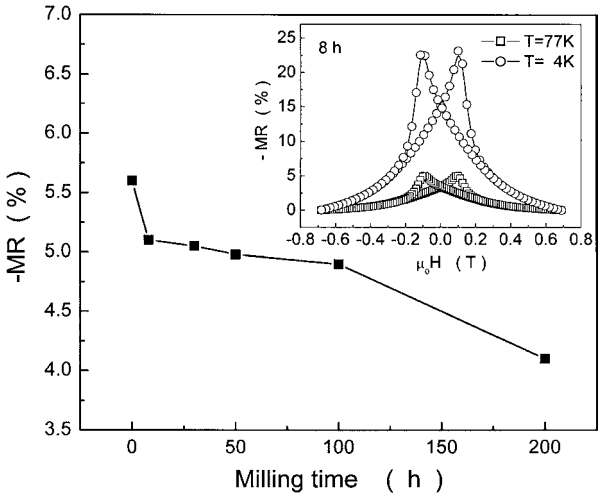

Figure 4 The variation of the magnetoresistance (MR) of CrO_2 grains with ball milling time. The inset is the magnetoresistance as a function of applied field at 4 K and 77 K for the sample milled for 8 h.

size and surface nature of the particles. Furthermore, the increased barrier height of CrO_2 grains should have enhanced the MR effect [12]. The experimental results however are beyond expectation, and the reduction of MR may be mainly attributed to the decrease of spin polarization of CrO_2 grains. The oxygen deficiency and the change of average chromium valence may cause, the lattice expansion which may give rise to a change in spin-polarized state away from the ideal high spin polarization. Kämper [13] has indicated that spin polarization is closely related to the structural disorder induced during ball milling. Slight disorder may arise from the lattice expansion and decrease in crystallinity. In addition, the spin-polarization is proportional to the surface magnetization.

The plots showing MR as a function of field reveal that at $T = 77$ K and $T = 4$ K, a typical butterfly shape curve can be seen for the sample milled for 8 h (see the inset of Fig. 4). It is noted that the MR is sensitive to the applied field within 0.2 T. There is consensus that the low field MR is due to spin-polarized tunneling between grains with different orientations. From 4 K to 77 K, the magnitude of MR drops steeply from -23 to -5% at a lower applied field of 0.7 T. The temperature dependence of MR can be explained with an intergranular tunneling model [14], which suggests that the intergranular contacts are mostly tunnel barriers, rather than metallic point contacts. The model predicts that the spin dependent tunneling effect is inversely proportional to increase in temperature. In the tunneling transport system, however, an important interpretation of decreasing MR is in terms of the decay of spin-polarization with increasing temperature.

In conclusion, a lattice expansion occurs during ball milling. This leads to a decrease in the specific magnetization. The low field magnetoresistance (MR) decreases with increasing milling time, which may be attributed to the lattice expansion and the reduction of spin polarization of CrO_2. However, the grain size affects the resistivity, due to the increase of specific surface area and changes to the surface nature of CrO_2 grains.

Acknowledgments

This work was supported by the National Natural Science Foundation of China under Grant No. 10174049.

References

1. H. Y. HWANG and S. W. CHEONG, *Science* **278** (1997) 1607.
2. L. H. V. LEUKEN and R. A. D. GROOT, *Phys. Rev.* B **51** (1995) 7176.
3. J. M. D. COEY, J. J. VERSLUIJS and M. VENKATESAN, *J. Phys. D: Appl. Phys.* **35** (2002) 2457.
4. J. M. D. COEY, A. E. BERKOWITZ, L. L. BALCELLS, F. F. PUTRIS and A. BARRY, *Phys. Rev. Lett.* **80** (1998) 3815.
5. A. GUPTA, X. W. LI and G. XIAO, *J. Appl. Phys.* **87** (2000) 6073.
6. H. Y. HWANG, S. W. CHEONG, N. P. ONG and B. BATLOGG, *Phys. Rev. Lett.* **77** (1996) 2041.
7. Y. J. CHEN, X. Y. ZHANG and Z. Y. LI, *J. Magn. Magn. Mater.* (2003) (in press).
8. X. W. LI, A. GUPTA, G. XIAO and G. Q. GONG, *J. Appl. Phys.* **83** (1998) 7049.
9. K. Y. WANG, L. SPINU, J. HE, W. ZHOU, W. WANG and J. TANG, *ibid.* **91** (2002) 8204.
10. J. H. PARK, E. VESCOVO, H. J. KIM, C. KWON, R. RAMESH and T. VENKATESAN, *Phys. Rev. Lett.* **81** (1998) 1953.
11. LL. BALCELLS, J. FONTCUBERTA, B. MARTÍNEZ and X. OBRADORS, *Phys. Rev.* B **58** (1998) R14697.
12. R. H. CHENG, B. XU, C. N. BORCA, A. SOKOLOV, C. S. YANG, L. YUAN, S. H. LIOU, B. DOUDIN and P. A. DOWBEN, *Appl. Phys. Lett.* **79** (2001) 3122.
13. K. P. KÄMPER, W. SCHMITT, G. GÜNTHERODT, R. J. GAMBINO and R. RUF, *Phys. Rev. Lett.* **59** (1987) 2788.
14. J. S. HELMAN and B. ABELES, *ibid.* **37** (1976) 1429.

Received 30 May
and accepted 14 August 2003