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Preparation and characterization of nanocrystalline chromium boride

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Abstract Nanocrystalline chromium boride (CrB) powders were successfully synthesized at 600 °C through a solid-state reaction. The synthesis was carried out in an autoclave by using $CrCl_3$, Mg and MgB_2 as the reactants. The X-ray powder diffraction pattern indicates the formation of orthorhombic CrB. Transmission electron microscopy image shows that typical CrB crystallites are composed of floss-like particles with less than 10 nm in diameter and about 50–100 nm in length. Thermogravimetric analysis revealed that the oxidation resistance for nanocrystalline CrB is much lower than that of bulk CrB.

Introduction

Borides of transition metals are well known for their high melting point, outstanding hardness, low specific weight, high modulus, high chemical stability, good wear resistance and so forth [1–3]. Due to these attractive properties, Borides of transition metals have extensive applications in many areas. For example they have been used as high temperature materials, surface protection materials and wear resistant materials.

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Traditionally, metal borides were prepared by various high temperature reactions such as the direct combination of boron with metal elements at high temperatures, electrolysis of molten salt baths, and various thermal reduction processes [4, 5]. Recently, various efforts have been made to synthesize metal borides at lower temperatures, control the morphology of metal borides or simplify the reaction procedures. For example, Y. Gu and co-workers have prepared nanocrystalline titanium diboride via a benzene-thermal reaction of metallic sodium with amorphous boron powder and titanium tetrachloride at 400 °C [6], A. Latini et al. reported a rapid single step synthesis of light lanthanide borides through borothermic reduction of oxides enhanced by electron beam bombardment [7].

In this work, we report a novel chemical route to synthesize nanocrystalline Chromium boride (CrB). The reaction was carried out in an autoclave and can be described as follows:

$$2CrCl_3 + MgB_2 + 2Mg \rightarrow 2CrB + 3MgCl_2$$

Experimental

In a typical procedure, an appropriate amount of anhydrous $CrCl_3$ (0.025 mol), Mg (0.025 mol) and MgB_2 (0.0125 mol) were put into a stainless steel autoclave of 50 ml capacity. The autoclave was sealed and maintained at 600 °C for 8 h, then cooled to room temperature. The product was washed with dilute hydrochloric acid (its concentration: 0.01 M) and distilled water respectively to remove $MgCl_2$ and other

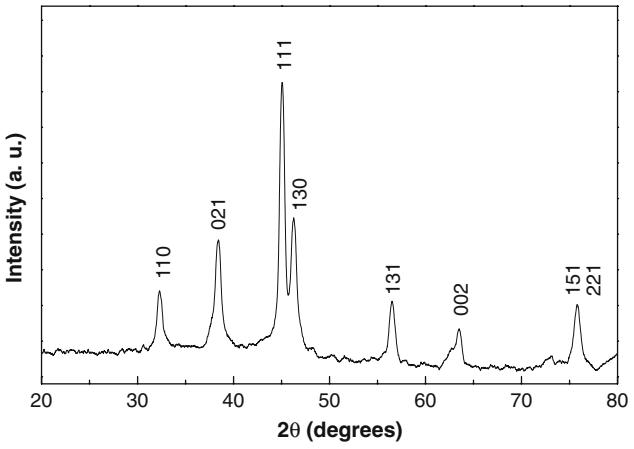

Fig. 1 XRD pattern of the CrB sample

impurities. After drying in vacuum at 60 °C for 4 h, the final gray powder product was obtained.

X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax-γA X-ray diffractometer with CuKα radiation (λ = 1.54178 Å). The morphology of CrB was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X-rays as the excitation source. Thermogravimetric analysis (TGA) profile was collected with a Shimadzu-50 thermoanalyzer apparatus under airflow. UV–vis absorption spectrum was recorded on a Shimadzu UV-2410PC UV–vis spectrophotometer.

Results and discussion

Figure 1 shows the XRD pattern of the as-prepared CrB sample, all the peaks can be indexed as orthorhombic CrB. After refinement, the lattice constants, a = 2.969 Å, b = 7.874 Å, c = 2.932 Å, is very close to the reported value for CrB (a = 2.966 Å, b = 7.866 Å, c = 2.932 Å, JCPDS card, No. 32–0277).

Figure 2 gives the XPS spectra of the as-prepared CrB sample. The B1s and Cr2p core-level regions were examined. It is found that the binding energies of B1s at 187.8 eV and Cr2p3 at 574.4 eV accord with the reported binding energies for CrB [8]. The quantification of the peak intensities reveals that the atomic ratio of B to Cr is 1.12:1.0, which is close to the chemical stoichiometric relation between B and Cr.

The morphology of CrB sample was investigated by TEM. Figure 3(a) shows a typical image of the

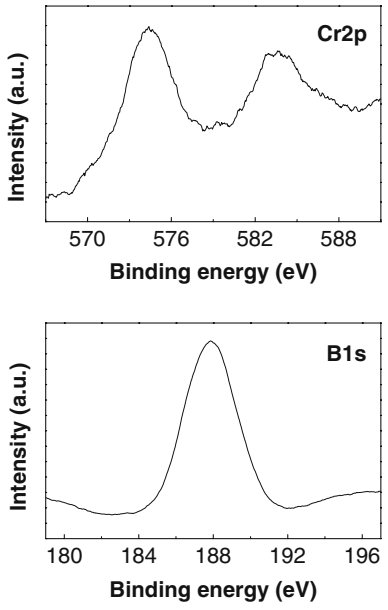

Fig. 2 XPS spectra of the CrB sample

as-prepared CrB, which exhibits that the CrB sample has a floss-like morphology. The diameter of the CrB floss is less than 10 nm and the length is about 50–100 nm. Figure 3(b) shows the selected area electron diffraction pattern of CrB, which is consistent with the high crystallinity of the sample. The diffraction rings from inner to outer, at d-spacings of 2.01 and 1.25 Å, match CrB (111) and (221) planes, in good agreement with the XRD results.

To investigate the oxidation resistance of the as-prepared CrB, the Thermogravimetric analysis (TGA) was carried out in air at atmospheric pressure. Figure 4 shows the TGA curve of the CrB. It can be seen that two obvious weight gain steps occurred centered around 709 °C and 844 °C respectively, which can be attributed to the oxidation of CrB. This suggests that the oxidation of CrB is composed of two steps, which has been reported for CrB film [9]. In the first weight gain step (around 709 °C), a protective layer of mixed oxides forms on the surface, which slows the oxidation rate. With the temperature increasing to 844 °C, the protective layer is destroyed, which causes the oxidation rate increasing rapidly [10]. A small weight loss step can also be observed around 100 °C, which may arise from the evaporation of absorbed water on the surface of the sample. The TGA data reveal that the initial oxidation temperature of nanocrystallien CrB is about 300 °C lower than that of bulk CrB [10]. The decrease of oxidation resistance for nanocrystalline CrB may be due to its small grain size. The ratio of the surface to volume increases remarkably when the particle's size decreases. This will lead to more defects

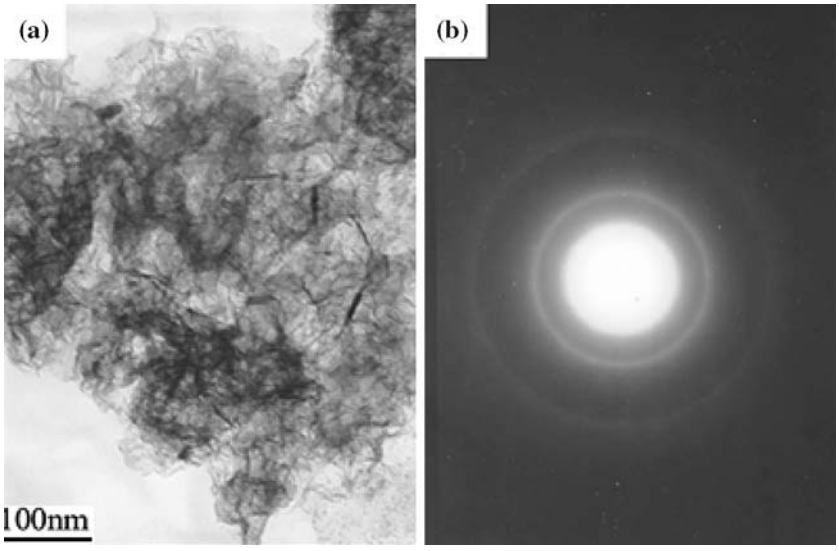

Fig. 3 (**a**) TEM image of CrB sample. (**b**) Selected area electron diffraction pattern of CrB

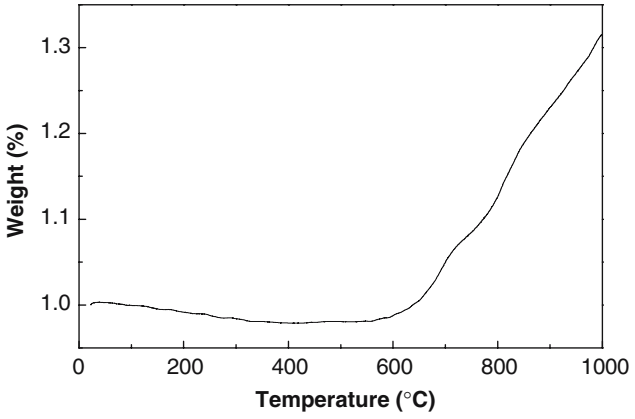

Fig. 4 TGA curve for CrB sample

and strains exposed on the crystal surface, which is not beneficial to oxidation resistance.

In the present route, no CrB could be detected in the product if the temperature is below 500 °C. Heating at a higher temperature such as 650 °C will result in an increase of the crystalline CrB sizes. An optimum temperature for nanocrystalline CrB is about 600 °C. A reaction time at 600 °C in the range of 3–10 h did not significantly affect the crystallite size and morphology. If the time is shorter than 2 h, the reaction becomes very incomplete and the crystallinity is very poor due to too short reaction time.

Conclusions

In summary, floss-like nanocrystalline CrB powders were successful synthesized in an autoclave by using Mg, $CrCl_3$ and MgB_2 as the reactants at 600 °C. An atomic ratio of B to Cr of 1.12:1.0 was determined from X-ray photoelectron spectra. The decrease of oxidation resistance for nanocrystalline CrB may be due to its small grain size.

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References

1. Erdemir A, Halter M, Fenske GR (1997) Wear 205:236
2. Bulfon C, Leithe-Jasper A, Sassik H, Rogl P (1997) J Solid State Chem 133:113
3. Adams RM (1964) Boron, metallo-boron compounds, and boranes. Interscience, New York, pp 335
4. Aronsson B, Lundstrom T, Rundqvist S (1965) Borides, silicides, and phosphides: a critical review of their preparation, properties and crystal chemistry. Methuen, London, p 3
5. Thomson R (1990) In: Freer R (ed) The physics and chemistry of carbides, nitrides and borides, vol 185, Kluwer Academic Pub., Boston, MA, NATO ASI Series E, p113
6. Gu Y, Yitai Q, Chen L, Zhou F (2003) J Alloy Compd 352:325
7. Latini A, Pascasio FD, Gozzi D (2002) J Alloy Compd 346:311
8. Aleshin VG (1979) J Less Common Metals 67:173
9. Zhou M, Nose M, Makino Y, Nogi K (1999) Thin Solid Films 343–344:234
10. Matkovich VI (1977) Boron and refractory borides. Springe, New York