Low-Temperature Synthesis of Nanocrystalline ZrB_2 via Co-reduction of $ZrCl_4$ and BBr_3

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Nanocrystalline zirconium diboride (ZrB_2) has been synthesized via a sodium co-reduction of $ZrCl_4$ and BBr_3 at 400 °C. The XRD patterns can be indexed as hexagonal ZrB_2 with the lattice constants $a = 3.167$ and $c = 3.527$ Å. The TEM image indicates the product has particle morphology, with size of about 20 nm.

Zirconium diboride (ZrB_2) is a potential advanced ceramic material for use at high temperatures requiring resistance to wear, oxidation, and corrosion. It has a very good thermal and electrical conductivity.[1,2] However, there have been few reports on the composition, structure, and physical properties of the ZrB_2 nanocrystallites, indicating that there is a great challenge in synthesis and characterization of nanocrystalline ZrB_2.

Traditionally, ZrB_2 powder was synthesized by various high temperature methods, such as the carbothermal reduction of ZrO_2 and B_4C (1400 °C)[3] and the mechano-chemistry treatment of a mixture of zirconia powder and amorphous boron followed by annealing (1100 °C).[4] In addition, other methods have been developed to prepare zirconium diboride. Andrievskii et al. obtained amorphous powder of $ZrB_{2.76}$ with mean particle size 40 nm by thermolysis of $Zr(BH_4)_4$ at 573–623 °C;[5] Berthon et al. synthesized ZrB_2 by CVD from a mixture of $ZrCl_4$, BCl_3, and H_2;[6] Devyatkin researched electrosynthesis from cryolite–alumina melts containing zirconium and boron oxides;[7] Reich et al. synthesized zirconium boride by plasma enhanced chemical vapor deposition;[8] Otani et al. prepared ZrB_2 single crystals by the floating zone method.[9]

Herein, we report a low-temperature route to nanocrystalline ZrB_2 by co-reduction of $ZrCl_4$ and BBr_3 using metallic sodium as reductant and solvent. The reaction can be described as follows:

$$ZrCl_4 + 2BBr_3 + 10Na \xrightarrow{400\ ^\circ C} ZrB_2 + 4NaCl + 6NaBr. \quad (1)$$

In this reaction, nascent zirconium and boron are generated in the reaction of $ZrCl_4$ (boiling point = 331 °C) and BBr_3 (boiling point = 90 °C) by metallic sodium (melting point = 98 °C), and they combine to form nanocrystalline ZrB_2.

In the typical process, 0.01 mol $ZrCl_4$ (analytical pure grade), 0.02 mol BBr_3 (99.99%, shanghai pharmaceutical corporation), and 0.1 mol sodium were placed into a stainless steel autoclave with a quartz liner. And then, the autoclave was sealed and heated at 400 °C for 6 h, followed by naturally cooling to room temperature. The product in the quartz liner was washed with distilled water and absolute ethanol for several times to remove the impurities. The final product was vacuum-dried at 60 °C for 2 h. Black powders were obtained.

X-ray powder diffraction (XRD) pattern was carried out on a Rigaku Dmax-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of nanocrystalline ZrB_2 was observed from transmission electron microscopy (TEM) images taken with a Hitachi H-800 transmission electron microscope.

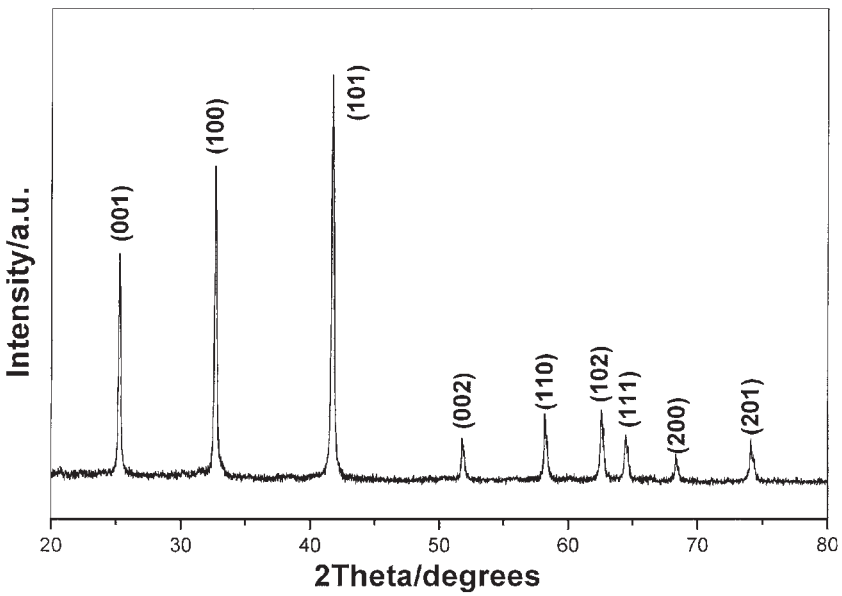

Fig. 1. XRD pattern of nanocrystalline ZrB_2 obtained from co-reduction of $ZrCl_4$ and BBr_3 using metallic sodium.

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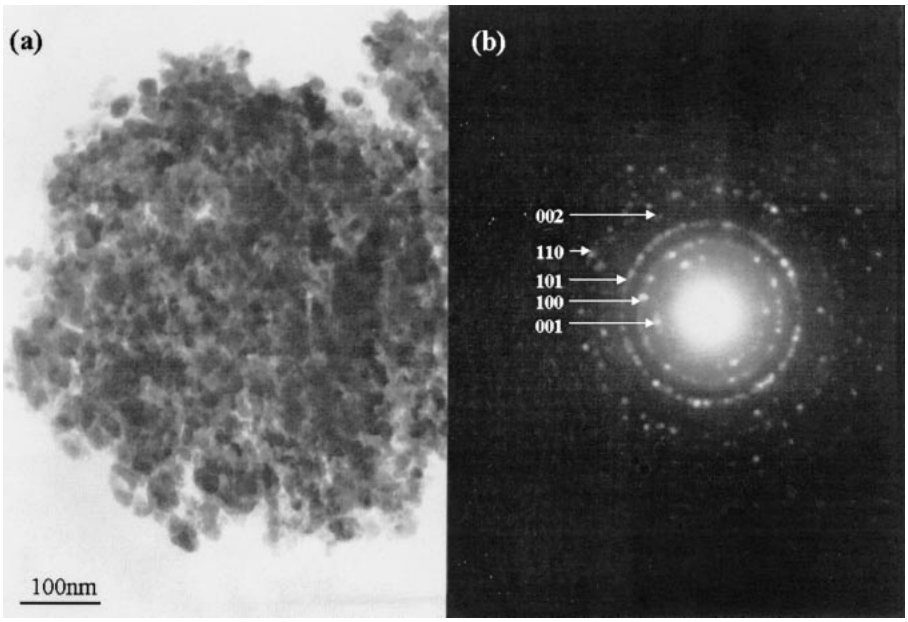

Fig. 2. TEM image (a) and ED pattern (b) of nanocrystalline ZrB_2 obtained from co-reduction of $ZrCl_4$ and BBr_3 using metallic sodium.

Figure 1 shows the XRD pattern of the sample. In Fig. 1, all of the nine peaks at *d*-spacings can be indexed as hexagonal ZrB_2. The lattice constants are $a = 3.167$ and $c = 3.527$ Å, in good agreement with $a = 3.170$ and $c = 3.530$ Å (JCPDS card# 75-1050). No evidence of crystalline Zr, ZrO_2, NaCl, and other impurities are observed.

TEM image and selected area electron diffraction (ED) pattern of crystalline ZrB_2 are shown in Fig. 2. In Fig. 2a, the material exhibits uniform particle with about 20 nm in size. In Fig. 2b, the diffraction rings from inner to outer, at *d*-spacings of 3.53, 2.74, 2.17, 1.76, and 1.58 Å, match hexagonal ZrB_2 (001), (100), (101), (002), and (110) planes, in good agreement with the XRD results.

The influences of reaction temperature and reaction time on the formation of the nanocrystalline ZrB_2 were investigated. The reaction is thermodynamically spontaneous (calculated $\Delta G = -2352.71\ \mathrm{kJ\,mol^{-1}}$) and exothermic (calculated $\Delta H = -2881.29\ \mathrm{kJ\,mol^{-1}}$).[10] It was found that an optimum reaction condition for the nanocrystalline ZrB_2 was at the temperature of 400 °C for longer than 6 h. If the temperature was lower than 300 °C, the yield of ZrB_2 was less than 20%. As the temperature was higher than 350 °C, the crystallinity of ZrB_2 increased evidently. If the temperature is higher than 500 °C, the grain size grew easily up and agglomerated. A suitable temperature for nanocrystalline ZrB_2 was about 400 °C. The reaction time of longer than 6 h at 400 °C did not obviously affect the crystallinity and the yield (90%). However, when reaction time was less than 3 h, the reaction was incomplete and the yield (30%) and crystallinity was poor.

In summary, nanocrystalline hexagonal ZrB_2 has been successfully synthesized via a sodium co-reduction of $ZrCl_4$ and BBr_3 at 400 °C for 6 h. The present route allows the fabrication of ZrB_2 powder with higher crystallinity and a narrow particle-size distribution. This route described may be extended to synthesize other transition metal boride, which may offer opportunity for technological applications.

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