研 究

Preparation of ZrB_2 and HfB_2 by Metallurgical Reduction of ZrO_2 , ZrSiO_4 , and HfO_2

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SYNOPSIS

ZrB_2 and HfB_2 were prepared by metallurgical reduction (MTR) of ZrO_2 , ZrSiO_4 , and HfO_2 with Mg or Mg and MgO mixtures. We understood that the theory of function-building fine particle preparation was able to be applied to synthesize nano-atomized fine particles of ZrB_2 . ZrB_2 can also be obtained directly from mixture of ZrSiO_4 , B_2O_3 , and Mg by MTR method. This sample has no borides such as silicon boride except for ZrB_2 . Therefore, this result shows the possibility to obtain ZrB_2 easily from natural source. In addition, HfB_2 can also be synthesized by MTR method using HfO_2 which was calcined over 750 °C.

KEY WORDS

zirconium diboride, hafnium diboride, function-building fine particle preparation, metallurgical reduction

1 Introduction

Metal borides, especially which are composed by transition metals or alkaline earth metals, are indispensable materials to develop electronic or nano-ordered devices, because they are mechanically hard materials with high melting points and good corrosion resistance¹⁾. For instance, the melting point of TiB_2 is quite high (2980 °C) and the mechanical hardness is the highest of all the metal borides²⁻⁵⁾. Also, the electrical conductivity of metal borides is higher than that of each metal crystal. The conductivities of TiB_2 and ZrB_2 , for example, are ten times higher than that of Ti and Zr, respectively⁴⁾. Recently, some reports indicate that some kinds of metal borides show the properties of superconductor⁶⁾. Thus, metal borides are therefore applicable to various fields.

While several preparation methods are known for metal borides, authors have reported that nanoparticles of TiB_2 can be obtained at relatively low temperatures through the reaction of TiO_2 with B_2O_3 in the presence of Mg as the reducing agent^{7,8)}. On the other hand, a function-building fine particle preparation method is one of methods to enhance the atomization of powders⁹⁾.

In this paper, we show the effects of the metallurgical reduction (MTR) method with the function-building fine particle preparation method on the synthesis of ZrB_2 and HfB_2 prepared from ZrO_2 or ZrSiO_4 and HfO_2 , respectively.

2 Experimental

ZrO_2 (mean particle size: 250 nm, Wako Pure Chemical Ind.), ZrSiO_4 (Asahi Glass Ceramics Co. Ltd.), and HfO_2 (mean particle size: 2 μm , Kojundo Chemical Laboratory Co. Ltd.) were used for Zr and Hf sources. Also, B_2O_3 as boron source (40 – 60 mesh), Mg as catalyst (under 100 mesh), and MgO as negative catalyst (mean particle size: 200 nm) were all purchased from Soekawa Chemical Co. and used as supplied.

We tried two methods to mix a metal oxide with B_2O_3 and Mg in our work. We already reported the details called ordered mixture I (OM-I) and II (OM-II) elsewhere⁷⁻⁹⁾, which are based on the ordered mixture theory. Metal oxide and Mg were thoroughly mixed to raise the reactivity of the reducing agent with the oxide before mixing with B_2O_3 to obtain OM-I for ZrO_2 , ZrSiO_4 , and HfO_2 . In the case of OM-II, ZrO_2 and MgO were mixed before mixing with Mg to disperse reactants on the surface of Mg particles. Here, ZrO_2 were mixed with B_2O_3 , Mg, and MgO to obtain OM-II powders in toluene using a 240 ml planetary hard metal ball mill (180 rpm) for 2 hours. Normally, the molar mixing ratio of metal oxides (ZrO_2 , ZrSiO_4 , or HfO_2), B_2O_3 , and Mg was 1 : 1 : 5 in this study. Also, MgO as negative catalyst was added to the mixture to slow down the reaction.

Fifty grams of powder mixture were placed in a graphite reaction boat to obtain ZrB_2 or HfB_2 by the MTR method.

We used the oven with thermocouple and water jacket shown in elsewhere. Heating was continued at a rate of $5^\circ\text{C}/\text{min.}$ up to definite temperature and then the temperature was kept for 30 minutes. After completion of the reaction, the boat was moved to the water-cooled part of the tube and taken out of the tube after being thoroughly cooled.

The sample after calcination was scraped out of the tube and purified in the following way. The calcined sample was treated with 1 N HCl at 100°C for an hour and the solid separated by filtration was washed with distilled water and ethanol. The washed solid was then treated with 1 N NH_4Cl at 100°C for three hours. The final product was obtained after another filtration and washing with water and ethanol followed by drying.

Powder X-ray diffraction (XRD) profiles were measured to determine the lattice constants of the samples by Cu $\text{K}\alpha$ radiation at 40 kV and 25 mA using Rigaku RINT-1100 instrument. Particle-size distributions were measured with a dynamic light scattering (DLS) apparatus (NICOMP 380ZLS; Particle Sizing Systems). Also, we observed the reactants directly by scanning electron microscope (SEM; S-510, Hitachi Co. Ltd.) and transmission electron microscope (TEM; JEM-1200EX, JEOL) observations.

3 Results and Discussion

3.1 Preparation of ZrB_2 from OM-I and OM-II of ZrO_2

Fig. 1 (a) and (b) show SEM images of OM-I (composed of ZrO_2 and Mg) and OM-II (composed of ZrO_2 , Mg, and MgO). Particles of ZrO_2 and particle mixture of ZrO_2 and MgO were found to uniformly cover the surface of Mg particles. We calcined these particles at different temperatures. Fig. 2 shows calcined OM-I powders of ZrO_2 with B_2O_3 treated at different temperatures. This

figure clearly shows that we cannot obtain ZrB_2 from OM-I up to 500°C . On the other hand, Fig. 3 shows calcined OM-II with B_2O_3 at different temperatures and strongly indicates that ZrB_2 can be synthesized over 600°C if we use OM-II as a source of Zr. Also, the temperature to start the reaction for OM-II is higher than that for OM-I

Fig.1 SEM images of (a) OM-I and (b) OM-II covered with ZrO_2 .

Fig.2 Calcined OM-I of ZrO_2 with B_2O_3 at different temperatures.

Fig.3 Calcined OM-II of ZrO_2 with B_2O_3 at different temperatures.

because of the existence of the negative catalyst, MgO . Although we can understand the differences between before and after the reaction from the change of their color qualitatively, quantitative discussion for the reaction is needed to decide the reaction condition to prepare ZrB_2 . Therefore, we measured powder XRD patterns for these samples to determine the impurities such as Mg and ZrO_2 quantitatively.

Fig. 4 shows powder XRD profiles of OM-I and calcined OM-I after addition of B_2O_3 as a function of reaction temperature. This figure indicates that Mg and ZrO_2 are remained if the OM-I sample is treated less than 700°C , though the reaction starts over 500°C . Similarly, powder XRD patterns of OM-II and calcined OM-II after addition of B_2O_3 as a function of reaction temperature were obtained as shown in Fig. 5. The temperature finishing the reaction from ZrO_2 to ZrB_2 is similar to that of OM-I, however, the reaction for OM-II is milder than that of OM-I because of the negative catalyst and, therefore, the structural change between ZrO_2 and ZrB_2 for OM-II occurred from 600°C to 750°C , whose change for OM-I was between 700°C and 750°C .

Fig. 6 shows particle-size distributions of ZrB_2 obtained by OM-I and OM-II. Peak positions synthesized from OM-II shifted to smaller sizes compared to that from OM-I. Also, the peak position of smaller one for OM-II is similar to that of ZrO_2 which was used as a source of Zr . This result indicate that, in the case of OM-II, it is able to disperse ZrO_2 with MgO on the surface of Mg particles, though ZrO_2 particles gathered to each other by mixing process for OM-I. In addition, MgO effectively decreased the activity of reducing reaction. Therefore, ZrB_2 particles

Fig.4 Powder XRD patterns of OM-I and calcined OM-I of ZrO_2 after addition of B_2O_3 .

produced by OM-II can keep their particle size without aggregation even after the reaction.

The TEM images of ZrB_2 obtained from OM-I and OM-II are shown in Fig. 7. The nano-ordered particles of ZrB_2 were formed in the case of OM-II, although highly ordered crystalline structure was formed for OM-I. This result also supports that we can obtain smaller particles from

Fig.5 Powder XRD patterns of calcined OM-II of ZrO_2 after addition of B_2O_3 .

OM-II which was already shown in Fig. 6. Hence, the activity of reducing reaction from ZrO_2 to ZrB_2 can be controlled by adding MgO which is also used to keep the particle size of ZrB_2 , and then we can produce nano-ordered ZrB_2 with this method.

3.2 Preparation of ZrB_2 from OM-I of ZrSiO_4

It is so difficult to synthesis ZrB_2 and HfB_2 with the OM-II samples of ZrSiO_4 or HfO_2 because of less reactivity of OM-II that we tried to synthesize ZrB_2 and HfB_2 from

Fig.6 Particle size distributions of ZrB_2 obtained from (a) OM-I and (b) OM-II.

ZrSiO_4 and HfO_2 by using OM-I with B_2O_3 samples. Here, ZrSiO_4 is one of natural minerals that includes Zr element, however, it is widely said that it is quite difficult to synthesize ZrB_2 from ZrSiO_4 directly because of the stability of ZrSiO_4 .

Fig. 8 shows powder XRD profiles of calcined OM-I of ZrSiO_4 with B_2O_3 at 750°C . This result indicates that it can be synthesized ZrB_2 even if we use ZrSiO_4 as a source of Zr. Also, the XRD profiles of calcined OM-I of ZrSiO_4 with B_2O_3 are similar to that obtained from ZrO_2 as a source of Zr, and no peak assigned for silicon boride such as SiB_4 or SiB_6 when we increase the ratio of B_2O_3 . Therefore, ZrB_2 can be directly synthesized by using ZrSiO_4 as a source of Zr.

3.3 Preparation of HfB_2 from OM-I of HfO_2

Fig. 9 shows before and after calcined OM-I powders of HfO_2 with B_2O_3 treated at different temperatures. This figure shows that the reaction occurs over 700°C . However, HfB_2 cannot be obtained under 700°C supported by powder XRD profiles shown in Fig. 9. The powder XRD pattern of OM-I with B_2O_3 calcined at 700°C clearly shows some peaks stemming from HfO_2 and no peaks assigned by HfB_2 . Therefore, HfB_2 can also be synthesized from OM-I of HfO_2 over 750°C that is similar to that of ZrO_2 .

Fig.7 TEM images of ZrB_2 synthesized from (a) OM-I and (b) OM-II.

Fig.8 Powder XRD patterns of calcined OM-I of ZrO_2 and ZrSiO_4 after addition of B_2O_3 at 750°C .

4 Conclusion

We showed the effects of the MTR method with the function-building fine particle preparation method on the synthesis of ZrB_2 and HfB_2 prepared from ZrO_2 , ZrSiO_4 , and HfO_2 . The ZrB_2 sample having smaller particle size

Fig.9 Calcined OM-I of HfO_2 with B_2O_3 at different temperatures.

Fig.10 Powder XRD patterns of OM-I and calcined OM-I of HfO_2 after addition of B_2O_3 .

can be obtained from OM-II of ZrO_2 with B_2O_3 compared with that of OM-I because of the effect of MgO which

decreases the activity of the reaction. ZrB_2 synthesized from ZrSiO_4 was also characterized by powder XRD measurements. This sample includes no silicon boride, therefore, we can obtain ZrB_2 from ZrSiO_4 directly and selectively from natural source of Zr. In addition, HfB_2 can be synthesized from calcination of OM-I of HfO_2 with B_2O_3 . The reaction temperature is similar to that for ZrB_2 . Hence, MTR method with function-building fine particle preparation method is useful to prepare the ZrB_2 and HfB_2 from their oxides.

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