Nanocarbon-dependent synthesis of ZrB_2 in a binary ZrO_2 and boron system

Ruixing Li[a,*], Haijie Lou[a], Shu Yin[b], Yun Zhang[a], Yanshan Jiang[a], Bin Zhao[a], Junping Li[c], Zhihai Feng[c], Tsugio Sato[b]

[a] Key Laboratory of Aerospace Materials and Performance (Ministry of Education), School of Materials Science and Engineering, Beihang University, Beijing 100191, China
[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[c] Aerospace Research Institute of Materials & Processing Technology, No. 1 Nan Da Hong Men Road, Fengtai District, Beijing 100076, China

HIGHLIGHTS

- A reaction system of ZrO_2, boron, and carbon has not been found in literature.
- ZrO_2 reacts with B, thermodynamic possibility at 25 °C, can not yet end till 1550 °C.
- A complete reaction was achieved by adding nano-carbon at 1550 °C.
- The metastable reactants strongly affected the kinetics of solid-state reactions.
- Single crystal and plate-like ZrB_2 particles were obtained.
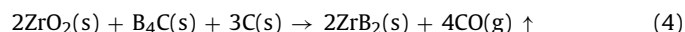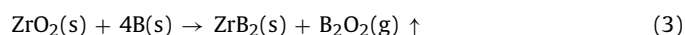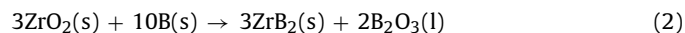
ARTICLE INFO

ABSTRACT

Thermodynamically, ZrO_2 may react with boron to form B_2O_3/B_2O_2 and ZrB_2 at room temperature. However, this reaction is incomplete at temperatures lower than 1550 °C, even with the use of metastable reactants, i.e., as-synthesized amorphous hydrous nano-ZrO_2 and amorphous boron powders. In this study, a complete disintegration of ZrO_2 was achieved by introducing nanocarbon to the binary system of ZrO_2 and boron at 1550 °C. The metastable reactants affected the temperature required for the solid-state reactions and also strongly affected the kinetics of the transformation. Single crystal and plate-like ZrB_2 particles with a uniform distribution and a size of ca. 1.0 μm in two-dimensions were obtained using 5 wt.% nanocarbon and a B/Zr molar ratio of 4.

1. Introduction

A range of excellent physicochemical properties such as high melting temperature, high electrical conductivity, superior mechanical properties and oxidation resistance make ZrB_2 a promising material for use in thermal protection systems [1–3]. ZrB_2 powder can be obtained by different routes [1–5] and two main routes are used commercially: (1) the direct chemical combination of elemental zirconium and boron and (2) the borothermal or carbothermal reduction (BCTR). The basic reactions are:

$$Zr(s) + 2B(s) \rightarrow ZrB_2(s) \quad (1)$$

$$3ZrO_2(s) + 10B(s) \rightarrow 3ZrB_2(s) + 2B_2O_3(l) \quad (2)$$

$$ZrO_2(s) + 4B(s) \rightarrow ZrB_2(s) + B_2O_2(g) \uparrow \quad (3)$$

$$2ZrO_2(s) + B_4C(s) + 3C(s) \rightarrow 2ZrB_2(s) + 4CO(g) \uparrow \quad (4)$$

Actually, B_2O_2 is known to be unstable and it may decompose to B_2O_3 and boron [6].

$$3B_2O_2(g) \rightarrow 2B_2O_3(g) + 2B(s) \quad (5)$$

Reaction (1) is a simple chemical reaction and, therefore, we focused on BCTR for this study. Many researchers have prepared ZrB_2 powder by BCTR. Submicron-ZrB_2 powder has been synthesized by the borothermal reduction of nano-ZrO_2 with boron and some H_3BO_3 under hot press conditions [3]. Millet and Hwang [4] synthesized ZrB_2 powder with residual ZrO_2 using amorphous boron and ZrO_2 based on Reaction (3). They proved that mechanical treatment was an effective way to decrease the required reaction
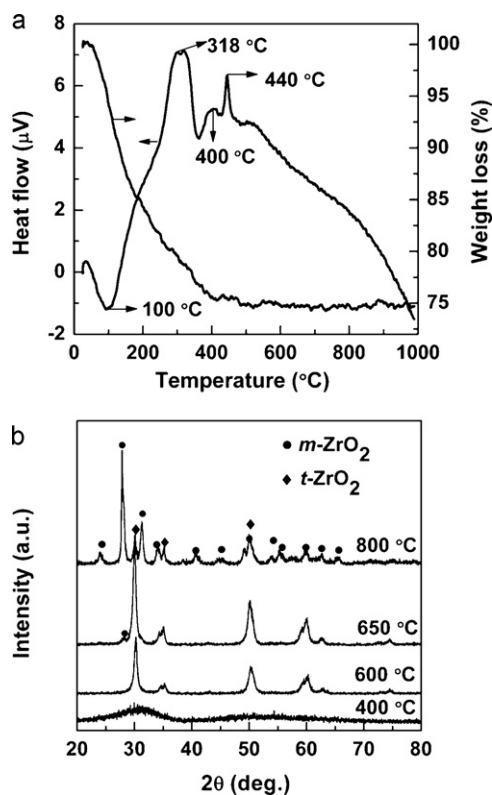
Fig. 1. (a) TG–DTA curves of the as-synthesized precursor and (b) XRD patterns of the precursor before and after calcination.

Fig. 2. XRD patterns of the samples synthesized using as-synthesized ZrO_2, boron, and (a) 5 wt.% nanocarbon; (b) without carbon at different temperatures.

temperature. Guo and Zhang [5] prepared ZrB_2 powder based on Reaction (4). They obtained ZrB_2 at 1650 °C using a 20–25 wt.% excess of B_4C. In conclusion, previous studies about the BCTR mostly followed Reactions (2)–(4). Using Reactions (2) and (3), we intended to introduce a small amount of carbon into the binary system of ZrO_2 and boron.

There are five reasons for this. First, thermodynamic calculations show that Reaction (2) may occur at room temperature [3] and Reaction (6) may thus ignite at higher than 1490 °C [7]. Consequently, it is likely that ZrO_2 will react with boron to form B_2O_3/B_2O_2 and ZrB_2 [Reactions (2) and (3)] initially during heating. With an increase in temperature, B_2O_3 and residual ZrO_2 tend to react with carbon to form ZrB_2 and this is based on Reaction (6).

$$ZrO_2(s) + B_2O_3(g) + 5C(s) \rightarrow ZrB_2(s) + 5CO(g) \qquad (6)$$

Second, a chemical reaction in which the forward and reverse reactions reach equilibrium is characterized by the concentration of the reactants and products, which do not change over time. The decrease in product concentration would benefit the forward reaction and inhibit the reverse reaction. For Reactions (2) and (3), B_2O_3/B_2O_2 is one of the main products. If it is consumed by Reaction (6) the equilibrium in Reactions (2) and (3) would change and the forward reaction would be promoted. Third, Reactions (2) and (3) are solid redox reactions. If carbon is introduced, Reaction (6) tends to occur and the chemical process shifts to a gas–liquid–solid ternary system from a unique solid system. Here, the existence of both liquid and gaseous B_2O_3 is possible since B_2O_3 has a high vapor pressure [8]. Moreover, the final product, CO, in Reaction (6) is an efficient reducing agent. Fourth, B_2O_3/B_2O_2 and boron are products of Reactions (2), (3) and (5) can be used as recycle feeds. As a consequence, the amount of boron used can be reduced and the forward reactions will be more favorable. Fifth, the selection of starting materials, e.g., metastable reactants affect the temperature required for the solid-state reaction and also strongly affect
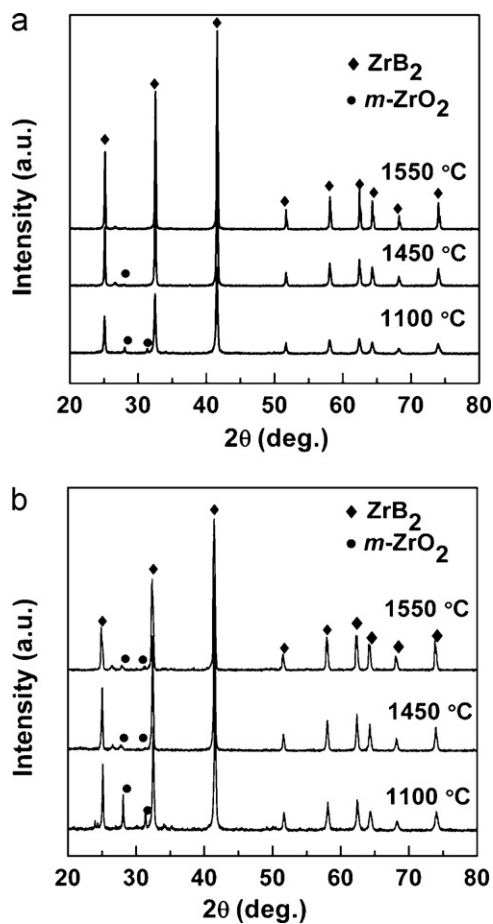
the kinetics of transformation. In this study, we used nanocarbon, which is a popular metastable material. Additionally, hydrous nano-ZrO_2 and amorphous boron were also selected as starting materials. We thus conducted experiments wherein nanocarbon was incorporated into a binary ZrO_2 and boron system.

2. Experimental

We used zirconyl nitrate (AR), amorphous boron ($D_{50} = 0.82$ μm, 95% purity) and carbon ($D_{50} = 30$ nm, 99.5% purity) in our work. In a typical synthesis, the precursor was prepared by dropping 0.25 mol/L zirconyl nitrate solution into stirred ammonia at 0.5 mL/s. The precipitate was repeatedly centrifuged, washed with methanol and then dried at 60 °C. Afterwards, the precipitated precursor and amorphous boron with a B/Zr molar ratio of 4 were wet mixed for 4 h and then dried. The mixed powder and 5 wt.% (total weight of dry hydrous ZrO_2 and boron) nanocarbon were hand ground and pressed into a disk. Finally, the disk was transferred into a crucible with a cover and placed in an alumina tube furnace. It was initially kept at 400 and 1100 °C, respectively, and then at 1450 or 1550 °C for 2 h.

The mass and heat flow of the samples were monitored by thermal analysis (TG–DTA, HCR-2). The crystallographic structure was identified by X-ray diffractometry (XRD, D/MAX 2200 PC). The specific surface area of the powder was determined using a NOVA-2200e analyzer. The size and morphology of the particles were characterized by SEM (JEOL JSM-6700F) and TEM (JEM-2100F) microscopies.

3. Results and discussion

Fig. 1a shows the TG–DTA results of the precipitated precursor using zirconyl nitrate and ammonia after drying at 60 °C. At temperatures lower than 400 °C a loss of weight was evident as the temperature increased, which probably resulted from the loss of water in hydrous ZrO_2. A strong endothermic peak was observed in the DTA curve at 100 °C, which corresponds to the evapora-
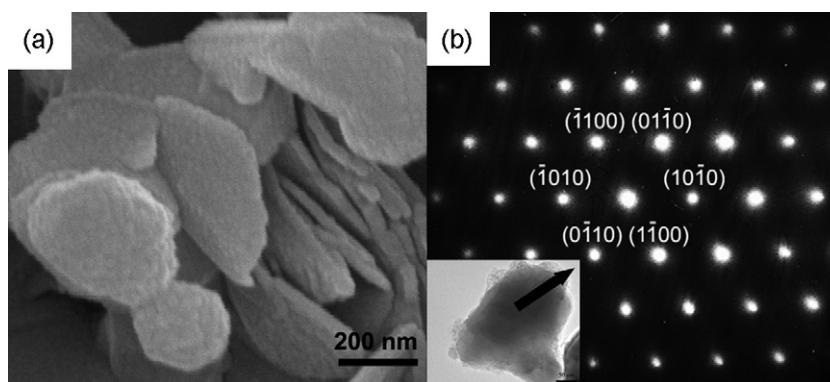
Fig. 3. (a) SEM image and (b) SAED pattern of the ZrB_2 powder synthesized at 1550 °C, the inset in (b) is a TEM image of the ZrB_2 particle used to obtain the SAED pattern.

tion of physically absorbed water. The exothermic peaks centered at 318 and 400 °C are attributed to the decomposition of zirconium hydroxide and the formation of amorphous ZrO_2 [9]. Another exothermic peak centered at 440 °C was also present. We attribute this to a phase transformation of amorphous ZrO_2 [10]. An in-depth discussion is to follow.

Further XRD analysis was conducted to understand the phase composition of the precipitated precursor after calcination. We found that the precipitated precursor that was dried at 60 °C was amorphous and that this state was retained at up to 400 °C, as shown in Fig. 1b. It then transformed to t-ZrO_2 at 600 °C. Since we found an exothermic peak at 440 °C using TG–DTA, t-ZrO_2 likely starts to form at about 440 °C. Additionally, the diffraction peak centered at 28.1° is assigned to m-ZrO_2, which was obtained after calcination at 650 °C. With an increase in temperature, the diffraction intensity of m-ZrO_2 became stronger whereas that of t-ZrO_2 decreased. These results indicate that the precipitated precursor initially transforms to t-ZrO_2 and then to m-ZrO_2. In other words, TG-DTA and XRD show that as-synthesized hydrous ZrO_2 is amorphous and it undergoes several changes in lattice structure during calcination. These continuous nascent states would benefit the synthesis of ZrB_2. In addition, the specific surface area of the precipitated precursor was found to be 322 m^2/g and, therefore, the as-synthesized hydrous ZrO_2 is fine.

To clarify the above-mentioned supposition the effects of nanocarbon on the processes of the two different reaction systems were investigated by excluding and including nanocarbon in the binary system of the as-synthesized hydrous nano-ZrO_2 and amorphous boron (B/Zr (mol.) = 4). XRD patterns of the final products synthesized at 1100, 1450 and 1550 °C with 5 wt.% nanocarbon are shown in Fig. 2a. The product obtained after calcination at 1100 °C showed strong diffraction peaks of ZrB_2 and the peaks centered at 28.1° and 31.4° are assigned to m-ZrO_2. With an increase in temperature, the diffraction intensity of m-ZrO_2 became weaker (*see* Fig. 2a, 1450 °C) and finally a single phase of ZrB_2 was present at 1550 °C.

Fig. 2b shows XRD patterns of the products synthesized without nanocarbon. ZrB_2 and m-ZrO_2 were observed at calcination temperatures up to 1550 °C. Therefore, we conclude that the results of the synthesis at 1100 °C were independent of the presence or absence of nanocarbon. However, an increase in the synthesis temperature up to 1550 °C gave different results: the complete disintegration of ZrO_2 was observed in the presence of nanocarbon and the residuum of ZrO_2 was present in the absence of nanocarbon. Therefore, the effects of nanocarbon on the reduction of ZrO_2 are evident. As noted above, Reactions (2) and (6) can occur at higher than room temper-

ature and 1490 °C, respectively. Therefore, Reactions (2) and (3) might occur initially and this is accompanied by the production of B_2O_3/B_2O_2, and then Reaction (6) is induced with a further increase in temperature. Therefore, an understanding of the many factors that affect the reaction process is required to understand why the synthesis of a single ZrB_2 phase might occur at 1550 °C over 2 h. The three kinds of metastable reactants affect the temperature required for the solid-state reactions and also strongly affect the kinetics of the transformation.

Fig. 3a shows a SEM image of the ZrB_2 powder synthesized using the as-synthesized hydrous nano-ZrO_2, boron and 5 wt.% nanocarbon at 1550 °C over 2 h. It reveals a plate-like morphology for the ZrB_2 particles with a uniform size distribution and average particle size of *ca.* 1.0 μm in two-dimensions. Additionally, a TEM image and SAED pattern are shown in Fig. 3b. The ZrB_2 particles are, therefore, single crystals and well crystallized.

4. Conclusions

A single phase of ZrB_2 powder was successfully synthesized with B/Zr (mol.) = 4, and 5 wt.% carbon by BCTR using as-synthesized amorphous hydrous nano-ZrO_2, amorphous boron and nanocarbon at 1550 °C over 2 h. The morphology was plate-like and the average size of the ZrB_2 particles was *ca.* 1.0 μm in two-dimensions.

References

[1] L. Chen, Y. Gu, Z. Yang, L. Shi, J. Ma, Y. Qian, Scripta Mater. 50 (2004) 959–961.
[2] M. Brochu, B.D. Gauntt, L. Boyer, R.E. Loehman, J. Eur. Ceram. Soc. 29 (2009) 1493–1499.
[3] S.L. Ran, O.V. Biest, J. Vleugels, J. Am. Ceram. Soc. 93 (2010) 1586–1590.
[4] P. Millet, T. Hwang, J. Mater. Sci. 31 (1996) 351–355.
[5] W.M. Guo, G.J. Zhang, J. Am. Ceram. Soc. 92 (2009) 264–267.
[6] Z. Jiang, W.E. Rhine, Chem. Mater. 4 (1992) 497–500.
[7] H. Zhao, Y. He, Z.Z. Jin, J. Am. Ceram. Soc. 78 (1995) 2534–2536.
[8] W.G. Fahrenholtz, J. Am. Ceram. Soc. 88 (2005) 3509–3512.
[9] A. Mondal, S. Ram, Ceram. Int. 30 (2004) 239–249.
[10] H.Y. Zhu, B. Liu, M.M. Shen, Y. Kong, X. Hong, Y.H. Hu, W.P. Ding, L. Dong, Y. Chen, Mater. Lett. 58 (2004) 3107–3110.