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Mechanical activation assisted self-propagating high-temperature synthesis of ZrC and ZrB_2 in air from Zr/B/C powder mixtures

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Abstract

When the powder mixture of Zr/B/C = 1/1/1 in molar ratio was mechanically activated by grinding in a planetary ball mill and then exposed to air, it self-ignited spontaneously and the self-propagating high-temperature synthesis (SHS) of ZrC and ZrB_2 was simultaneously occurred. In this mechanical activation assisted self-propagating high-temperature synthesis in air (MA-SHS in Air), it was found that high reactivity of disordered carbon formed by mechanical activation of graphite played a decisively important role. On the other hand, the isothermal solid-state reaction of the unground powder mixture of Zr/B/C = 1/1/1 in argon formed ZrB_2 at 800 °C and then ZrC at 1000 °C. The reaction mechanism and the morphology of the products in both processes are discussed. The product with fine, homogeneous microstructure obtained in MA-SHS in Air is expected to be a promising candidate as precursor of ZrC–ZrB_2 composites.

Keywords: Borides; Carbides; Mechanical activation; Milling; SHS; ZrB_2; ZrC

1. Introduction

Carbide and boride of zirconium show a number of excellent properties such as high melting temperature, high strength, high thermal and electrical conductivity, and chemical stability. Therefore, the use of these ceramics in composites can be expected to offer potential candidates for a variety of high-temperature structural applications.[1–4] Furthermore, it is important to prepare the powder mixture of ZrC-ZrB_2 with fine, homogeneous microstructure, because it is known that ceramic materials with fine microstructures, especially nanocomposites, exhibit improved mechanical properties.[5]

Mechanical activation or mechanosynthesis is a potential process for the production of advanced materials such as metal carbides, nitrides and borides. We have recently developed a technique combining mechanical activation (MA) by grinding and self-propagating high-temperature synthesis (SHS) in air, which is called MA-SHS in air in this study. This technique is based on SHS induced by exposing the metal-graphite powder mixtures mechanically activated to air and has been successfully applied to the synthesis of carbides and nitrides of Al, Zr and Nb,[6–12] and borocarbides of Al_3BC.[13]

In the present study an application of this MA-SHS in air technique has been developed for the simultaneous synthesis of carbide and boride of zirconium from the powder mixtures of Zr/B/C = 1/1/1. In contrast, a traditional isothermal solid-state reaction in the powder mixture of Zr/B/C = 1/1/1 was investigated as well. The reaction mechanism and the microstructure of the products obtained in both processes are discussed. In general, it is well known that the mechanical activation enhances the reactivity of solids as well as their mixing homogeneity, and lowers remarkably reaction temperature. In most cases, a major drawback of this process is powder contamination from milling equipment (vial, balls and grinding medium) during grinding. However, in the present study, the use of graphite as a reactant can be expected to minimize contamination of the powder, because of its excellent lubricant ability.

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2. Experimental procedures

The powders of zirconium metal (particle size of less than 150 μm, 98% purity, Kojundo Chemical Laboratory), amorphous boron (practical grade, Sigma Chemical Company) and natural graphite (mean flake size 5 μm, 97% carbon, 2% ash and 1% volatile component, Nippon Kokuen Industry) were used as starting materials. These powders were mixed in a mole ratio of Zr/B/C = 1/1/1, Zr/C = 1/1 and Zr/B = 1/1, respectively, in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany) and then ground for 15–120 min. A 25 ml jar and seven balls of 12 mm in diameter of tungsten carbide were used for grinding. The amount of powder mixture loaded was 5.6–8.1 g, and the weight ratio of powder to balls was about 1:16–1:11. The grinding was interrupted every 15 min, and the sample was scraped from the balls and the side walls of the jar and then reloaded to continue grinding. After grinding, the ground sample was transferred into a graphite crucible (inner diameter of 30 mm and depth of 40 mm) and exposed to air. Just then, it self-ignited and the exothermic reactions propagated into the reactant powders. As soon as the reactions started, the graphite crucible was covered with another one to prevent the sample from oxidizing. After the reaction, a swelled lump of the product formed and a small amount of the unreacted sample remained in a crucible. It was ground in an agate mortar and then subjected to X-ray diffraction. An isothermal solid-state reaction of the unground powder mixture of Zr/B/C = 1/1/1, which was mixed in an agate mortar, was also investigated in argon atmosphere at 600–1200 °C for 60 min.

X-ray diffraction (XRD) was done with a RINT-2000 (Rigaku Denki) using Ni-filtered $\mathrm{CuK}\alpha$ radiation (30 kV, 15 mA). Optical microscopy, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out with a VH-7000 digital HD microscope (Keyence) and a JSM-5410-SEM-EPMA-WDX combined microanalyzer (Jeol). Prior to the observation, the powder sample was dispersed in ethanol by ultrasonication, and was placed as a drop on a glass plate or a brass stub and then dried.

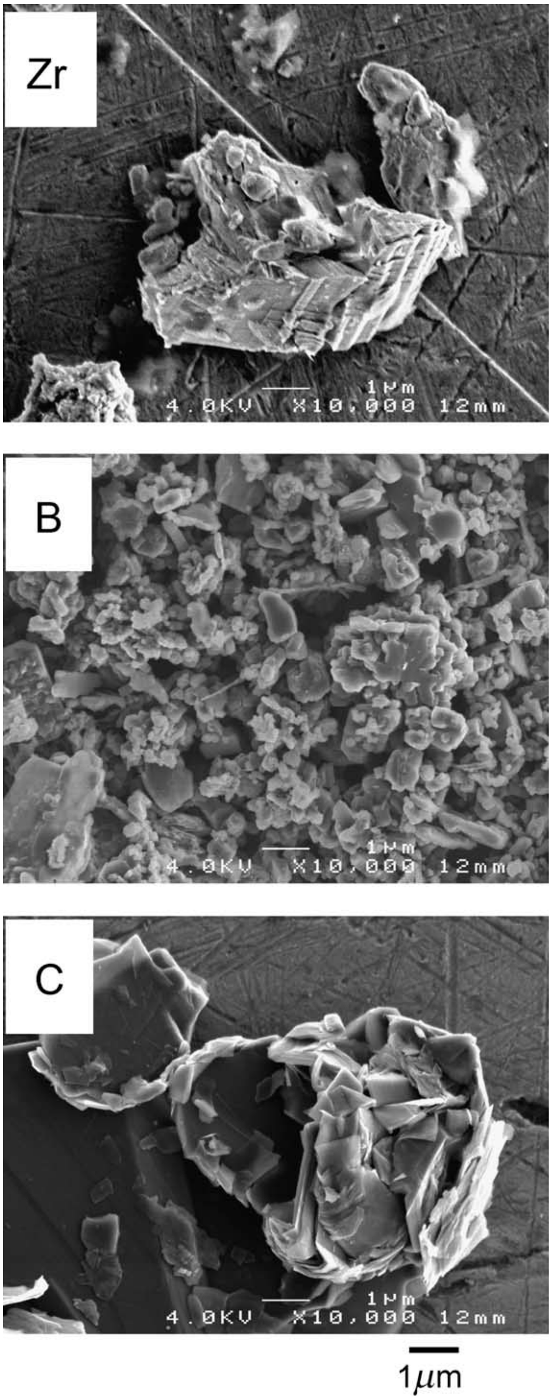

Fig. 1. The SEM microphotographs of the particles of Zr, B and C (graphite).

3. Results and discussion

Fig. 1 shows the SEM microphotographs of the particles of Zr, B and graphite. Characteristic forms of bulky zirconium and flaky graphite with the size of ca. 6 μm can be observed. Amorphous boron shows the smallest size, consisting of particles that are smaller than 1 μm.

Fig. 2 (a)–(d) show the XRD patterns of the samples of Zr/B/C = 1/1/1 which were ground for 0 (unground)–45 min, respectively. The α-Zr peaks apparently decreased in intensity and broadened with increasing grinding time and the 002 peak of graphite at $2\theta = 26.3^\circ$ disappeared after the grinding of 30 min. These results indicate the size reduction and the increase in the lattice strain of Zr metal particles, and the disappearance of the stacking order of the graphite layers and the formation of disordered carbon with finely divided grains.[6] After the grinding of 45 min, when the temperature of the jar was cooled to room temperature and then the ground sample was transferred into a graphite crucible and exposed to air, it did not self-ignite as shown in Fig. 2(d). In contrast, as soon as the jar was opened immediately after grinding and the sample was exposed to air, it self-ignited instantly and exothermic reactions spontaneously occurred in the successive steps, evolving red heat initially and then white heat. After the reaction, the products was obtained in a morphology of the swelled and stratified structure, which was almost the same morphology as obtained previously in the Zr/C powder mixtures with C = 45 mol% [11]. The product was ground in an agate mortar, and subjected to XRD, and the formation of ZrC and ZrB_2 was confirmed as shown in Fig. 2(e). No literature data are available about simultaneous formation of ZrC and ZrB_2 by MA-SHS in air through elemental Zr, B and C. Furthermore, it is very interesting to elucidate what kind of reactions occurred as a self-ignition and subsequent MA-SHS reaction. In order to do this, therefore, MA-SHS in air processes in the powder mixtures of Zr/C = 1/1 and Zr/B = 1/1 were investigated as well.

Fig. 3 shows the XRD patterns of the samples of Zr/C = 1/1 which were ground for 0 (unground)–45 min, respectively. The variation in XRD patterns with grinding time in Fig. 3(a)–(c) was very similar to that in the sample of Zr/B/C = 1/1/1 shown in Fig. 2. As shown in Fig.3 (d), when the sample was exposed to air just after the grinding of 45 min, it self-ignited and subsequently the highly exothermic reactions occurred and then ZrC was formed in a form of the swelled and stratified structure. On the other hand, as shown in Fig. 4, in the sample of Zr/B = 1/1, any self-ignition reaction and any formation of borides were not detected even after the grinding of 120 min, although the Zr peaks decreased in intensity and broadened with increasing grinding time. These results suggest that the self-ignition reaction is due to the oxidation reaction of disordered carbon formed by grinding with oxygen in air, followed by the reaction between zirconium and disordered carbon as MA-SHS process.

From this and the experimental results obtained hitherto in the Al/C, Zr/C and Nb/C systems,[6–12] a possible reaction process can be estimated as follows. First of all, when the sample of Zr/B/C = 1/1/1 ground for 45 min was exposed to air, on the surface of the samples in the graphite crucible, an ignition reaction of disordered carbon formed by grinding with oxygen in air is initiated. In order to cause the oxidation, carbon has to be not only in an amorphous state, but also mechanically activated. Although the oxidation of Zr in

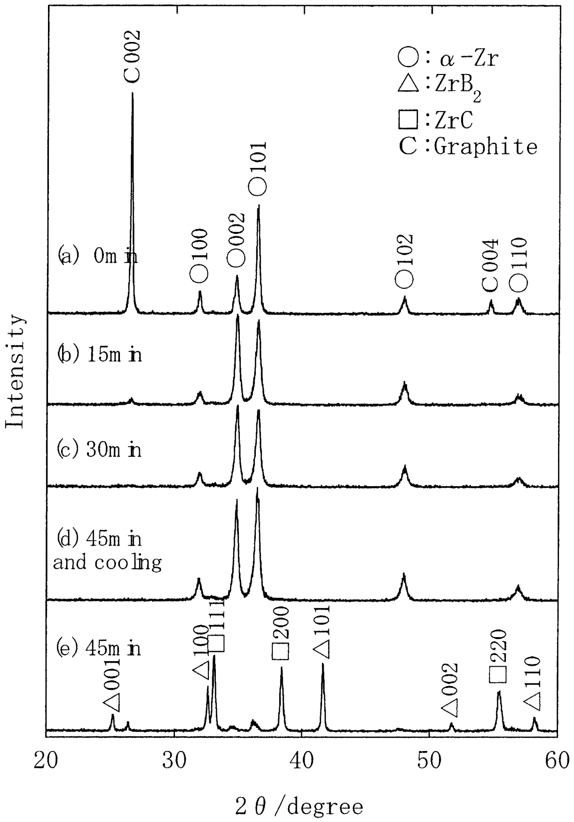

Fig. 2. The XRD patterns of the samples of Zr/B/C = 1/1/1 which were ground for (a)–(d) 0–45 min, and (e) the product obtained by MA-SHS in air of the sample ground for 45 min, which is described in detail in text.

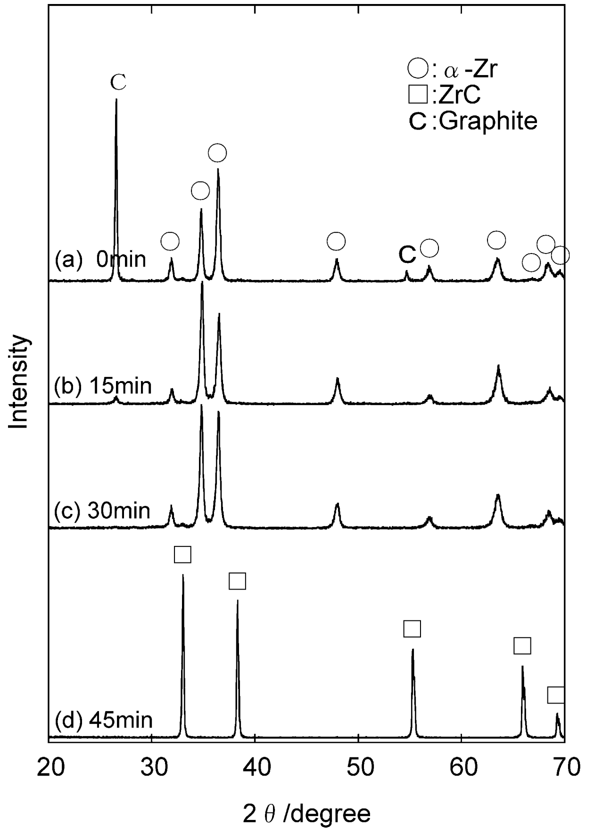

Fig. 3. The XRD patterns of the samples of Zr/C = 1/1 which were ground for (a)–(c) 0–30 min, and (d) the product obtained by MA-SHS in air of the sample ground for 45 min.

air is expected to occur preferentially, based on the thermodynamic data, the particles of Zr metal are surrounded by the finely divided particles of disordered carbon and amorphous boron, therefore its oxidation must be inhibited. In fact, when the mechanically activated powder mixtures of Al/C = 1/1 and Zr/C = 1/1 were heated in a flowing nitrogen containing a very small amount of oxygen in TG-DTA-MS runs, it was found that the exothermic reaction due to the oxidation of the disordered carbon was initiated at around 100 °C, accompanying with a weight decrease and a release of CO_2 and/or CO.[8,11] This result verified that the disordered carbon served as an igniter for the SHS reaction induced by mechanical activation of Al/C and Zr/C powder mixtures. Then, the heat evolved by the oxidation of disordered carbon is transferred to the inside of the crucible, and SHS reactions in the powder mixture of Zr/B/C = 1/1/1 are induced. That is, at the expense of enthalpy of evolved by the oxidation of carbon, Zr metal reacts simultaneously with C and B to form ZrC and ZrB_2. Both formation reactions of ZrC and ZrB_2 are highly exothermic, so that the reactions become self-sustaining and propagate through the reactant mixture in the form of combustion wave.

Furthermore, it is important from the standpoint of technology, to compare the reaction behavior and the morphology of the products obtained in MA-SHS process with those in a traditional isothermal solid-state reaction. Fig. 5 shows the results of the isothermal solid-state reaction of the unground sample of Zr/B/C = 1/1/1, in which the samples were heated at 600–1200 °C for 60 min in argon atmosphere. At 600 °C, no reaction occurred. At 800 °C, the formation of ZrB_2 was detected firstly and at 1000 °C the formation of ZrC was also noticed, and then, at 1200 °C, as shown in Fig. 5(d), the intensity in XRD lines of ZrB_2 and ZrC became almost same. Thus, such a reaction behavior in the isothermal solid-state reaction in argon is apparently different to that in MA-SHS in air. Practically, the free energies of the formation of ZrB_2 and ZrC (in unit per one mole of Zr, according to the reaction $Zr + 2B = ZrB_2$ and $Zr + C = ZrC$) were calculated to be about −300 and −200 kJ mol^{-1}, respectively, in the temperature range of 100 to 1100 °C [14]. From this thermodynamic data, therefore, a predominant formation of ZrB_2 can be readily understood. On the other hand, though not shown in figure, the isothermal solid-state reaction of the sample of Zr/B/C = 1/1/1 ground in a ball mill for 45 min was also investigated at 600–1000 °C in argon. In this case, the formation of a small amount of ZrC was noticed firstly at 600 °C and then ZrB_2 was detected at

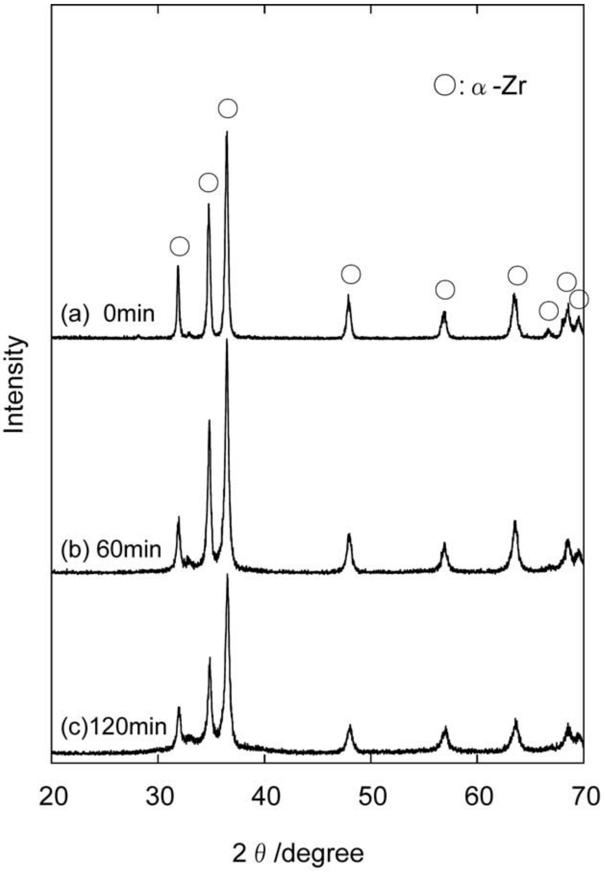

Fig. 4. The XRD patterns of the samples of Zr/B = 1/1 which were ground for (a)–(c) 0–120 min.

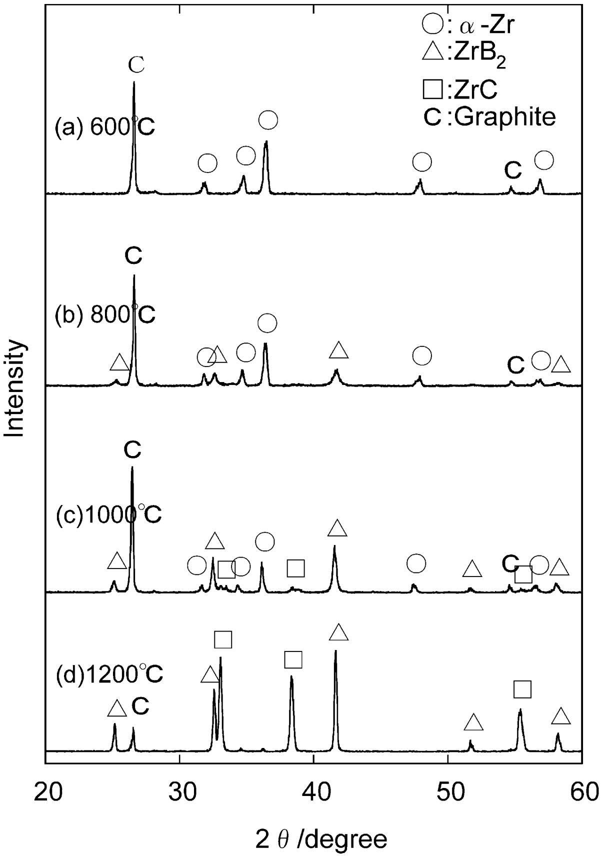

Fig. 5. The XRD patterns of the unground samples of Zr/B/C = 1/1/1 which were isothermally heated at 600–1200 °C for 60 min in argon.

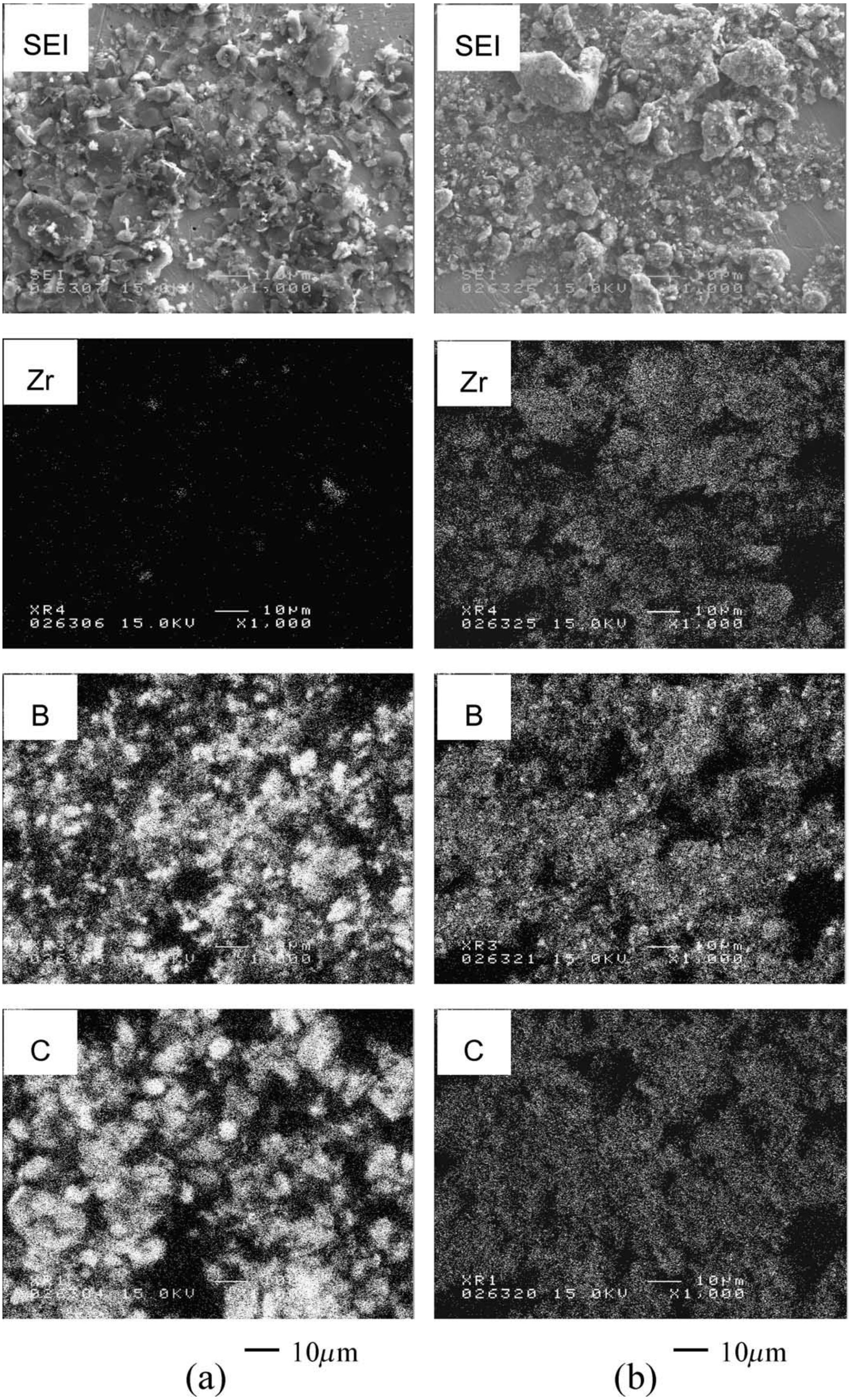

Fig. 6. The secondary electron images (SEI) and associated elemental maps of the samples of Zr/B/C = 1/1/1 ground for (a) 0 (unground) and (b) 45 min. The XRD patterns of these samples are shown in Fig. 2(a) and (d), respectively.

700 °C. A preferential formation of ZrC rather than ZrB_2 seems to depend on the high reactivity of disordered carbon formed by grinding. In graphite, during mechanical activation by grinding, the breaking down of graphite grains into nanocrystallites was often observed and the introduction of lattice defects, such as shearing and turbostratic stackings of 002 planes into the crystallites,[15] can be sufficiently expected. This is because it is well known that the reactivity of the nanosized particles, such as disordered carbon formed by mechanical grinding, is extremely high.

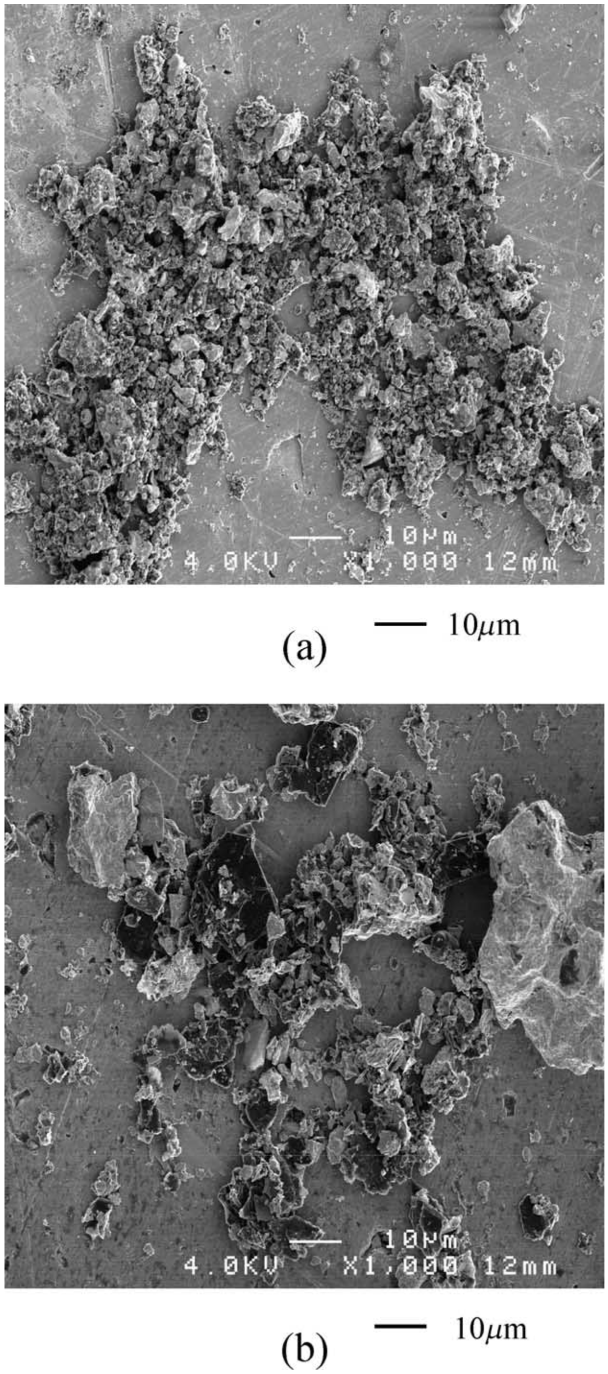

Fig. 7. The SEM microphotographs of the products obtained from the sample of Zr/B/C = 1/1/1 by (a) MA-SHS in air and (b) isothermal solid-state reaction heated at 1200 °C for 60 min in argon. The XRD patterns of these samples are shown in Figs. 2(e) and 5(d), respectively.

In addition, the mixing homogeneity of the elemental components of Zr, B and C in the reactants just before the reaction is also another important factor controlling the reaction behaviors in MA-SHS and solid-state reaction. Fig. 6 shows the secondary electron images (SEI) and associated elemental maps of the samples of Zr/B/C = 1/1/1 ground for 0 and 45 min. In Fig. 6(a), in the unground sample of Zr/B/C = 1/1/1, neither a homogeneous distribution nor an intimate contact among the component particles of Zr, B and C can be seen. However, much smaller particle size of B than C, as shown in Fig. 1, might produce a number of contact points between the particles of Zr and B, which provides favorable conditions for the formation of ZrB_2. In contrast, in Fig. 6(b) after grinding of 45 min, the particle sizes of the three components decreased remarkably and their mixing homogeneity was much improved. Therefore, such a creation of homogeneous distribution and intimate contact among the mechanically activated particles of Zr, B and C is considered to be essential to the simultaneous formation of ZrC and ZrB_2 in MA-SHS in air process.

Fig. 7 shows the SEM microphotographs of the products obtained by MA-SHS in air and isothermal solid-state reaction in argon, respectively. The former shows a homogeneous distribution of smaller particles of a few μm of ZrC and ZrB_2 with a small amount of unreacted Zr and C, but the latter shows polydispersed particles ranging from a few μm to few tens μm. Therefore, the fine, homogeneous microstructure of the products obtained in MA-SHS in air process is considered to be attractive precursor for ZrC–ZrB_2 composites.

From the above results, it is concluded that the mechanical activation assisted self-propagating high-temperature synthesis (MA-SHS) in air is a useful process to synthesize carbide and boride of Zr simultaneously, and to offer the fine, homogeneous microstructure required for the precursor of ZrC–ZrB_2 composites.

Acknowledgements

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