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MA-SHS of ZrC and ZrB_2 in Air from The Zr/B/C Powder Mixtures

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Keywords: Mechanical activation (MA), Self-propagating high-temperature synthesis (SHS), ZrC, ZrB_2, Zr/B/C powder mixtures

Abstract. When the powder mixtures of Zr/B/C=3/2/2~6/10/1 in molar ratio were mechanically activated (MA) by ball milling and then exposed to air, they self-ignited spontaneously and the self-propagating high-temperature synthesis (SHS) was occurred to form ZrC and ZrB_2 simultaneously. In this MA-SHS process in air, it is essential that graphite is converted into disordered carbon by mechanical activation and mixed with the particles of Zr and B in an intimate contact state. A fine, homogeneous microstructure of the product is expected to be a promising candidate as precursor of ZrC-ZrB_2 composites.

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. 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 [1]. 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 ball milling and self-propagating high-temperature synthesis (SHS) in air. This MA-SHS technique is based on SHS induced by exposing the mechanically activated metal-graphite powder mixtures to air and has been successfully applied to the synthesis of carbides, nitrides and borides of Al, Zr and Nb [2-5], and borocarbides of Al_3BC [6]. 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=3/2/2~6/10/1. On the other hand, a traditional isothermal solid-state reaction in the powder mixture of Zr/B/C=2/2/1 was investigated as well. The reaction mechanism and the microstructure of the products in both processes are discussed.

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 molar ratios of Zr/B/C=3/2/2~6/10/1 in an agate mortar, loaded in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany) in air and then ground for 45~60 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 6.0-10.8 g, and the weight ratio of powder to balls was about 1:15-1:9. 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 in a crucible. An isothermal solid-state reaction of the unground powder mixture of Zr/B/C=2/2/1 was also investigated in argon atmosphere at 600~1200ºC for 60 min. X-ray diffraction (XRD) was done with a RINT-2000 (Rigaku Denki) using Ni-filtered CuKα 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).

Results and Discussion

Fig.1 shows the X-ray diffraction patterns of the samples of Zr/B/C=2/2/1 ground for 0~45 min and the product obtained in MA-SHS after grinding of 60 min. The α-Zr peaks apparently decreased in intensity and broadened with increasing grinding time and the 002 peak of graphite 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. After the grinding of 60 min, when the temperature of the jar was cooled to room temperature and the ground sample was transferred into a graphite crucible and exposed to air, it did not self-ignite. In contrast, when 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 product was obtained in a morphology of the swelled and stratified structure. As can be seen in Fig.1(e), the product was consisted of ZrC and ZrB_2. No literature data can be found about simultaneous formation of ZrC and ZrB_2 by MA-SHS in air through elemental Zr, B and C. In order to elucidate the mechanism of MA-SHS process, the reaction was investigated in the powder mixtures of Zr/C=1/1 and Zr/B=1/1 as well. In the former, the sample self-ignited in air after the grinding of 45 min and formed ZrC, while in the latter, it did not self-ignite even after the grinding of 120 min. This result suggests that the self-ignition reaction corresponds to the oxidation reaction of disordered carbon formed by grinding. From these results, a possible reaction process can be estimated as follows. First of all, when the ground sample of Zr/B/C was exposed to air, on the outermost surface of the samples in the graphite crucible, an ignition reaction of disordered carbon mechanically activated by grinding is initiated. For the oxidation, carbon has to be not only in an amorphous state, but also mechanically activated. 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, can be sufficiently expected. This is the reason why it is well known that the reactivity of the nanosized particles, such as disordered carbon formed by mechanical grinding, is extremely high. Then, the heat evolved by the oxidation of disordered carbon is transferred into the sample in the crucible, and SHS reactions is induced. Formation reactions of ZrC and ZrB_2 are also highly exothermic, so that the reactions become self-sustaining and propagate through the reactant mixture in the form of combustion wave. On the other hand, an

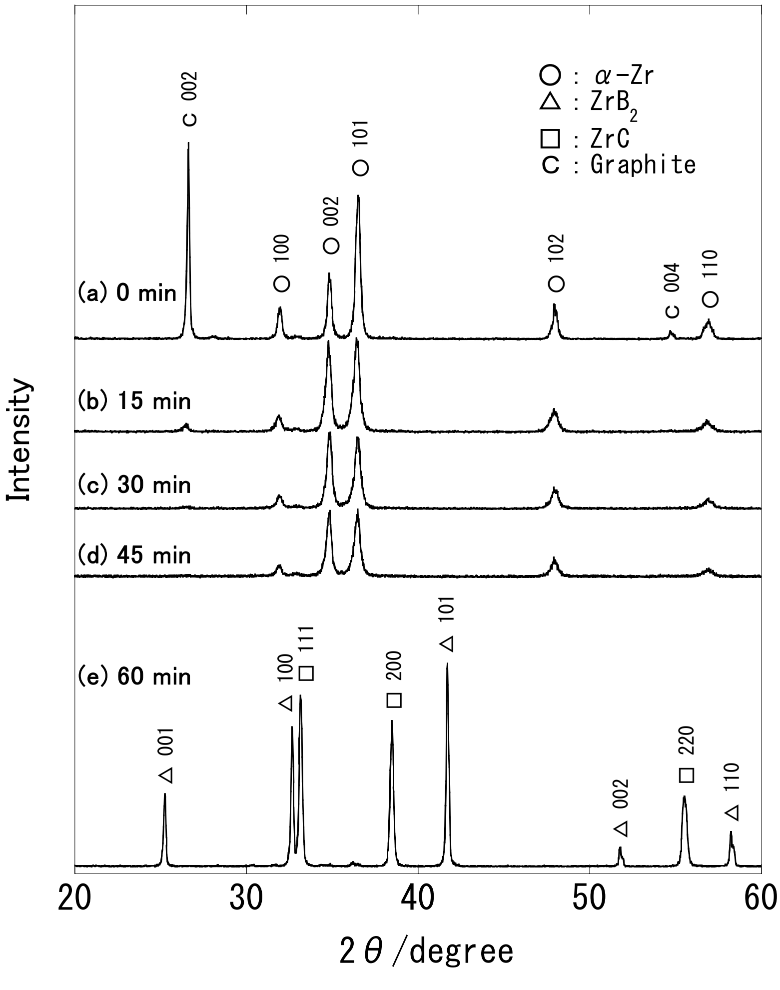

Fig.1.The X-ray diffraction patterns of the samples of Zr/B/C=2/2/1 ground for (a)-(d) 0~45 min and (e) the product obtained in MA-SHS after grinding of 60 min.

isothermal solid-state reaction of the unground sample of Zr/B/C=2/2/1 was carried out at 600~1200ºC for 60 min in argon atmosphere. At 600ºC, no reaction occurred. At 800ºC, the formation of ZrB_2 was detected firstly and at 1000 and 1200ºC the formation of ZrC as well as ZrB_2 proceeded. A predominant formation of ZrB_2 can be understood from the free energy data of the formation of ZrB_2 and ZrC, i.e., -300 kJ mol^{-1} for the reaction $Zr + 2B = ZrB_2$ and -200 kJ mol^{-1} for the reaction $Zr + C = ZrC$ in the temperature range of 100 to 1100ºC [7].

Furthermore, it is found from the SEM microphotographs of the products obtained by MA-SHS in air and isothermal solid-state reaction in argon, that the former shows a homogeneous distribution of smaller particles of a few μm of ZrC and ZrB_2, but the latter shows polydispersed particles ranging from a few μm to few tens μm. In the former, the homogeneous distribution and intimate contact among the mechanically activated, fine particles of Zr, B and C is considered to be reflected on the homogeneous morphology of the product. Such a fine, homogeneous microstructure of the products obtained in MA-SHS in air process is expected to be attractive precursor for ZrC-ZrB_2 composites.

Summary

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.

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