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MA-SHS of NbC and NbB_2 in air from the Nb/B/C powder mixtures

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Abstract

When the Nb/B/C powder mixture with different molar ratios was mechanically activated by grinding for 60–150 min in a planetary ball mill and exposed to air, it self-ignited spontaneously and the self-propagating high-temperature synthesis (SHS) of NbC and NbB_2 was induced. This mechanical activation assisted SHS (MA-SHS in air process) depended strongly on the particle size of Nb metal, the mixing ratio of Nb/B/C and the weight ratio of sample to balls. The product of NbC and NbB_2 with fine, homogeneous microstructure is expected to be a promising candidate as precursor of NbC–NbB_2 composites.

Keyword: Mechanical activation (MA); Carbide (NbC); Boride (NbB2)

1. Introduction

Carbide and boride of niobium 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 NbC and NbB_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 grinding and self-propagating high-temperature synthesis (SHS) in air, which is called the MA-SHS in air process 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, nitrides and borides of Al, Nb and Zr,[2–4] and borocarbides of Al_3BC.[5] In the latest paper,[6] an application of this MA-SHS in air process has been developed for the first time for the simultaneous synthesis of NbC and NbB_2 from the powder mixtures of Nb/B/C = 2/2/1. In addition, a traditional isothermal solid-state reaction in the same powder mixture of Nb/B/C = 2/2/1 was also investigated, and the reaction mechanism and the microstructure of the products obtained in both processes were discussed. The purpose of the present study is to investigate in detail the effect of the particle size of Nb metal, the mixing ratio of Nb/B/C and the weight ratio of sample to balls on the MA-SHS in air process.

2. Experimental procedures

The powders of niobium metal (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. The reactivity of two niobium metals having different particle sizes of 5–50 and 50–130 μm, which are designated hereafter as Nb(S) and Nb(L), respectively, was compared. These powders were mixed in molar ratios of Nb/B/C = 1/1/1, 2/2/1, 3/2/2 and 3/4/1 in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany) and then ground for 15–180 min. A 25 ml jar and seven balls of 12 mm in diameter of tungsten carbide were used for grinding. The amounts of powder mixture loaded were ca. 9.0, 6.0 and 3.0 g, and the weight ratios of powder to balls (R) were about 1/10, 1/15 and 1/30, respectively. The grinding was interrupted every 15 min, and the sample was scraped from the balls and the sidewalls of the jar, and then reloaded to continue grinding. After grinding, the ground sample was transferred into a graphite crucible (inner diameter of

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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. The product formed in a crucible was ground in an agate mortar and then subjected to X-ray diffraction. X-ray diffraction (XRD) was done with a RINT-2000 (Rigaku Denki) using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were carried out with a JSM-5410-SEM-EPMA-WDX combined microanalyzer (JEOL).

3. Results and discussion

Fig. 1(A) and (B) show the change in XRD patterns of the samples of Nb(S)/B/C = 2/2/1 with different weight ratios of sample to balls, i.e., $R = 1/15$ and 1/30, with grinding time. After grinding both samples for 30 min, the 0 0 2 peak of graphite at $2\theta = 26.3^\circ$ completely disappeared and the Nb peaks decreased in intensity and broadened with increasing grinding time. These results indicate the disappearance of the stacking order of the graphite layers and the formation of disordered carbon with finely divided grains, and the size reduction and the increase in the lattice strain in Nb metal particles. After the grinding of 75 min, the sample of Nb(S)/B/C = 2/2/1 ($R = 1/15$) was transferred into a graphite crucible and exposed to air, just then it self-ignited and exothermic reactions spontaneously occurred in the successive steps, evolving red heat initially and then white heat. After the reaction, the formation of NbC and NbB_2 was confirmed as shown in Fig. 1(A), though accompanying with a trace of NbO. It seems to be a first study for simultaneous formation of NbC and NbB_2 from elemental Nb, B and C by the MA-SHS in air process. On the other hand, even after grinding the sample of Nb(S)/B/C = 2/2/1 ($R = 1/30$) for 150 min and exposing to air, the self-ignition and the MA-SHS process were not observed. Instead, as shown in Fig. 1(B), the 1 1 1 peak of NbC at $2\theta = 34.8^\circ$ was detected after 60-min grinding, and its intensity increased with an increase in grinding time up to 150 min. In addition, the peak of Nb, which was remained unreacted, shifted to lower angle, maybe indicating the formation of solid solution, Nb_{ss}. In fact, the same behavior was also observed in the sample of Nb(S)/B = 1/1 ($R = 1/12$) ground for 180–270 min.[6] The formation mechanism and the solubility limit of Nb_{ss} in the Nb-B system under the mechanical stress seem to be a next interesting subject matter. From these results it was found that the MA-SHS in air process was extremely influenced by the weight ratio of sample to balls, R. Therefore, the effect of the particle size of Nb metal, the mixing ratio of Nb/B/C and the weight ratio of sample to balls on the MA-SHS in air process was investigated in detail.

Table 1 shows the results obtained by the MA-SHS in air process in the Nb(S) or Nb(L)/B/C samples with various mixing

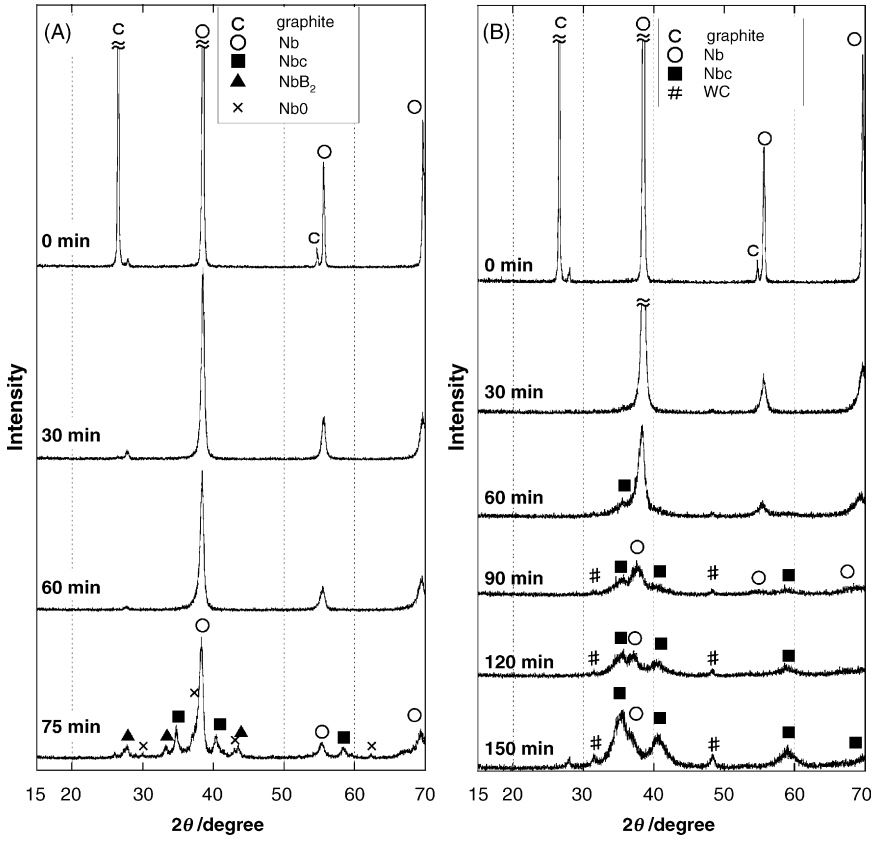

Fig. 1. The change in XRD patterns of the samples of Nb(S)/B/C = 2/2/1 with the weight ratios of sample to balls, (A) $R = 1/15$ and (B) $R = 1/30$, with grinding time. After 75-min grinding, the MA-SHS in air process was induced in the sample of Nb(S)/B/C = 2/2/1 with $R = 1/15$ and NbC and NbB_2 were formed, which is described in detail in text.

Table 1
The effect of particle size of Nb metal (Nb(S) or Nb(L)), mixing ratio of Nb(S) or Nb(L)/B/C and weight ratio of sample to balls (*R*) on the products obtained by MA-SHS in air process

Samples	*R* ratios	Ignition time (min)[a]	Products
Nb(S)/B/C = 1/1/1	1/15	105	$Nb = NbC \gg NbB_2$
Nb(S)/B/C = 3/2/2	1/15	60	$Nb \gg NbC > NbB_2$
Nb(S)/B/C = 2/2/1	1/15	75	$Nb \gg NbC = NbB_2$
Nb(L)/B/C = 3/2/2	1/15	75	$NbC \gg NbB_2 > Nb$
Nb(L)/B/C = 2/2/1	1/10	105	$NbC = NbB_2 \gg Nb$
Nb(L)/B/C = 2/2/1	1/15	60	$NbC = NbB_2 = Nb$
Nb(L)/B/C = 3/4/1	1/10	180[b]	Nb
Nb(L)/B/C = 3/4/1	1/15	120[b]	Nb

[a] Ignition time corresponds to grinding time required for sample to self-ignite in air.
[b] These samples did not self-ignite even after 180- and 120-min grinding.

ratios and R ratios. In addition, the representative XRD patterns of the products obtained in the samples of Nb(L)/B/C = 2/2/1, 3/2/2 and 3/4/1 are shown in Fig. 2. As can be seen from Table 1, the larger amount of NbC and NbB_2 was formed in the Nb(L)/B/C samples rather than in the Nb(S)/B/C samples, indicating the higher reactivity of the large particles of Nb(L) than the small particles of Nb(S). This result seems to be strange in view of the fact that the larger particle is generally less reactive than the smaller one. However, it can be explained by following mechanochemical effects: the particles of Nb metal are usually covered with a thin oxide layer, but it was destroyed under mechanical activation and a lot of fresh and active metal surfaces were created in the larger particles of Nb rather than in the smaller ones. Furthermore, only NbC and NbB_2 phases were obtained in the samples of Nb(L)/B/C = 2/2/1 and 3/2/2 in Fig. 2,

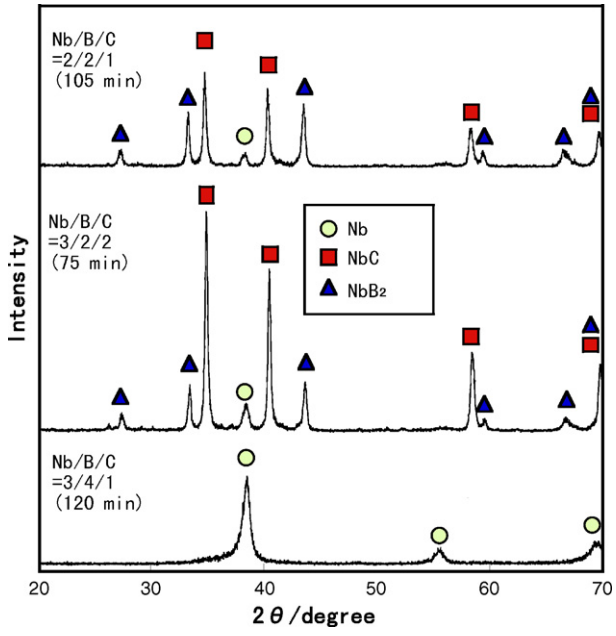

Fig. 2. The XRD patterns of the products obtained by the MA-SHS in air process in the samples of Nb(L)/B/C = 2/2/1, 3/2/2 and 3/4/1, respectively.

though very small amount of Nb remained unreacted. In the latter sample, the remarkable increase in NbC peaks compared with NbB_2 peaks was admitted. It can be explained by the estimation that the ratios of the Nb(L)/B/C = 2/2/1 and 3/2/2 in the starting samples correspond to the ratios of NbB_2/NbC = 1/1 and 1/2 expected as the product phases. On the other hand, as shown in Table 1 and Fig. 2, in the sample of Nb(L)/B/C = 3/4/1 corresponding to the product ratio of NbB_2/NbC = 2/1, the MA-SHS reaction was not induced even after 180-min grinding (*R* = 1/10) and 120-min grinding (*R* = 1/15). This result shows the presence of the optimal mixing ratio of Nb/B/C, particularly the presence of the critical amount of C, for the self-ignition and subsequent MA-SHS in air process.

Taking into account the results obtained hitherto in the Al/C, Nb/C and Zr/C samples,[2–4] a possible reaction process in the Nb/B/C sample can be estimated as follows. Firstly, as soon as the Nb/B/C sample was mechanically activated by grinding and exposed to air, an ignition reaction of the disordered carbon formed by grinding with oxygen in air is initiated on the surface of the sample in the graphite crucible. In order to cause that oxidation, graphite has to be not only in a disordered state, but also mechanically activated. Although the oxidation of Nb in air is expected to occur preferentially based on the thermodynamic data, the particles of Nb 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.[7] This result verified that the disordered carbon served as an igniter for the SHS process. Secondary, the heat evolved by the oxidation of disordered carbon is transferred to the inside of the crucible, and SHS reactions in the Nb/B/C powder mixture are induced. That is, at the expense of enthalpy of evolved by the oxidation of carbon, Nb metal reacts simultaneously with C and B to form NbC and NbB_2. Both formation reactions of NbC and NbB_2 are also so highly exothermic that the reactions become self-sustaining and propagate through the reactant mixture in the form of combustion wave.

In addition, the SEM microphotographs of the products obtained by the MA-SHS in air process show the agglomerate of fine particles of NbC and NbB_2 consisting of a few micrometers, indicating the perfect destruction of original Nb particle into the fine particles. Therefore, the fine, homogeneous microstructure of the products obtained in the MA-SHS in air process is considered to be attractive precursor for NbC–NbB_2 composites. The synthesis and mechanical properties of the NbC–NbB_2 composite will be reported in near future.

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