Synthesis of niobium carbide and nitride in air from mechanically activated Nb–C powder mixtures

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Powders of Nb and C mixed in various mole fractions (C = 10–80 mol%) have been ground in a planetary ball mill. When thus mechanically activated mixtures were transferred into a graphite crucible and exposed to air, they ignited spontaneously and self-propagating high-temperature synthesis (SHS) took place. NbC, Nb_2C and Nb_2N were obtained as the main products in the samples with C = 40, 30 and 10 mol%, respectively. From measurement of the lattice constant and XPS spectra, the dissolution of nitrogen into NbC obtained from the mixtures with below C = 50 mol% was observed, while almost stoichiometric NbC formed for the mixtures with C = 50–80 mol%. A possible reaction mechanism for the formation of niobium carbides and nitrides is discussed.

Introduction

Mechanical activation or mechanosynthesis is a promising process for the production of advanced ceramics such as metal carbides and nitrides. Recently, we proposed a novel method for producing aluminium nitride and carbide[1,2] and zirconium nitride and carbide[3] in air. This technique is based on self-propagating high-temperature synthesis (SHS) induced by the energy stored during mechanical activation of Al–C and Zr–C powder mixtures in a ball mill, instead of heating to high combustion temperature. Transition metal carbides and nitrides have many technological applications, because of their high strength, durability, hardness, and even optical, electronic and magnetic properties.[4] The purpose of the present study is to produce niobium carbides and nitrides from Nb–C powder mixtures in air using this technique and to discuss the reaction mechanism.

Experimental

Niobium metal (particle size < 45 μm, 99.9% purity; Kojundo Chemical Laboratory) and natural graphite (mean flake size 5 μm, 97% carbon, 2% ash and 1% volatile component; Nippon Kokuen Industry) powders were used as starting materials. These powders were mixed in various mole fractions (C = 10–80 mol%) in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany) and then ground at a speed of 2700 rpm for 80–135 min. A 25 ml jar and seven balls of tungsten carbide (12 mm diameter) were used for grinding. The amount of powder mixture loaded was 5–24 g, and the mass ratio of powder to balls was 1 : 19–1 : 4. 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. The ground sample was transferred into a graphite crucible (inner diameter 30 mm, depth 40 mm) and allowed to react in air. A graphite crucible was selected for use at temperatures higher than 2000 °C to avoid contamination by crucible materials. The product was separated into two portions, upper and lower, along the depth of the graphite crucible, and each portion was examined by X-ray diffraction (XRD) with a RINT-2000 (Rigaku Denki) instrument using Ni-filtered Cu-Kα radiation. The lattice constants of niobium carbide and nitride obtained were measured under the following conditions: Si(5N) as an internal standard, scanning speed of 0.25° min^{-1} and time constant of 5 s.

Optical microscopy was carried out with a SZH-13 microscope (Olympus). XPS spectra were obtained using an ESCALAB MkII photoelectron spectrometer (VG Science). A powder sample was mounted on the gold mesh and evacuated at a pressure of 10^{-7} Pa for 24 h. The binding energy values measured on the samples were corrected by using the shift of the C 1s line from 285.0 eV.

Results and Discussion

When mechanically activated Al–C or Zr–C powder mixtures were transferred into a graphite crucible and exposed to air, exothermic reactions occurred spontaneously in two successive steps:[1–3] just after exposure to air the first exothermic reaction occurred at several spots, evolving red heat (step 1) and propagated toward neighboring regions, and then a second, violently exothermic reaction occurred, evolving white heat (step 2). In the Nb–C powder mixtures, however, the reaction time for step 1 was extremely short and the reaction of step 2 occurred immediately. The temperatures attained in step 2 in the Nb–C samples with C = 67 and 20 mol% were estimated to be about 1300 and 2200 °C, respectively, from optical pyrometer measurements. As soon as the step 2 reaction started, the graphite crucible was covered with another one to prevent the sample from oxidising. After the reaction, the products were separated into two portions, upper and lower, and identified by XRD as shown in Fig. 1. The morphology and color, as well as the phase identified by XRD, of the final products obtained in the samples with different C mol% were also systematically investigated and are summarized in Table 1. With decreasing C mol%, the grinding time needed for self-ignition changed from 80–120 to 135 min, and the radiance and the evolution time of the white heat due to reaction step 2 tended to increase. The color of the products changed from black to light grey to dark grey. Typical morphologies such as powdery, highly swelled and scale-like, slightly swelled and stratified, and non-swelled brittle lump structures were observed for the products obtained in the samples with C = 80–50, 40–30, 20 and 10 mol%, respectively, though their boundaries were not always clear. These variations in morphology must strongly depend on the reaction behavior in the graphite crucible. Self-propagating high-temperature synthesis (SHS) is a technique in which the synthesis of compounds is accomplished by the propagation of a combustion front

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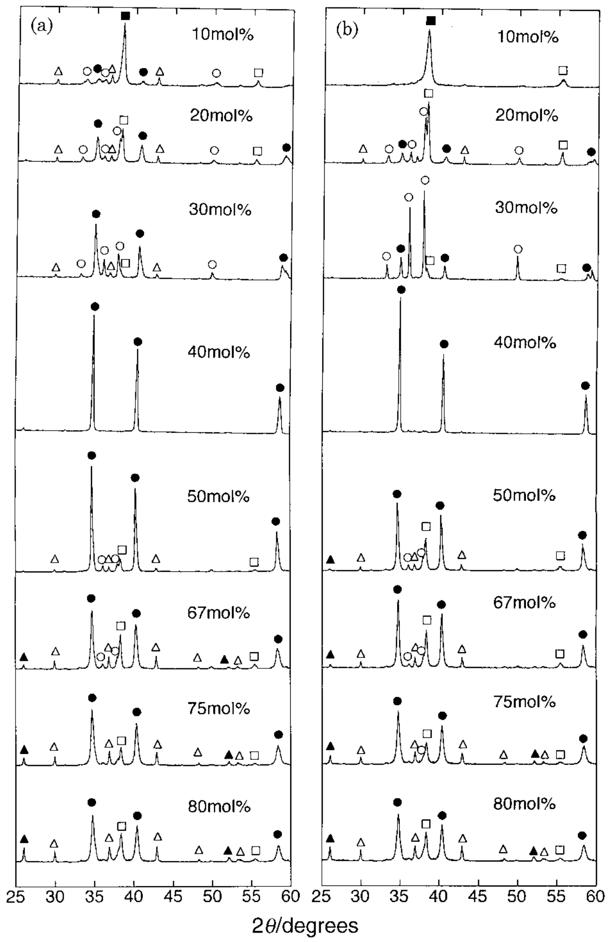

Fig. 1 XRD patterns for (a) the upper and (b) the lower parts of the products obtained in the Nb–C powder mixtures with different C mol%, as indicated. ●, NbC; ○, Nb_2C; □, Nb; ■, Nb_2N; △, NbO; ▲, NbO_2.

through the reactant. The heat to propagate the combustion front is obtained from the heat of the reaction. During unstable combustion, it is known that the propagation velocity is not uniform with time and the combustion front propagates in an oscillatory or spin manner.[5] Although many studies have tried to explain the unstable combustion from the thermodynamic and kinetic points of view, its mechanism has not been elucidated yet because it is influenced by various initial processing parameters such as additives or diluent, initial temperature, particle size, compaction pressure, *etc.*[6]

As can be seen from the XRD patterns of the upper and lower parts of the products in Fig. 1(a) and (b), various carbides and nitride formed depending on the C content in the sample. In the samples with C 80–40 mol%, the main product was cubic NbC, the amount of which increased with decreasing C mol%, and then an almost single phase of NbC was obtained in the sample with C 40 mol%. A small amount of orthorhombic Nb_2C also formed in all samples except for the C 40 mol% sample, the amount of which became a maximum in the lower part of the C 30 mol% sample; the composition of this sample is close to Nb_2C stoichiometry, *i.e.*, C 33.3 mol%. On the other hand, the formation of hexagonal Nb_2N was detected in the C 10 mol% sample. As can be seen from comparison of the XRD patterns for the C 10 and 20 mol% samples, the positions of the Nb_2N 101 ($2\theta = 38.52°$) and Nb 110 ($2\ \theta = 38.50°$) peaks are almost the same, so that it is difficult to distinguish between them. However, after treatment of these samples with 46 mass% HF solution at room temperature for 24 h, the Nb_2N peak still remained, but the Nb peak disappeared. In the lower portion of the C 10 mol% sample, almost single-phase Nb_2N was obtained. It is interesting that the formation of Nb_2N occurred predominantly for the sample with the lowest C mol%, the mechanism of which will be discussed later. Traces of niobium oxides (NbO, NbO_2) were also detected in the upper portion of all the samples. Oxides detected in the lower portion are considered to have been introduced from the upper part as a contaminant when the samples were divided into two portions. Furthermore, a thin white layer of Nb_2O_5 was formed exclusively on the surface of the product obtained from the C 10 mol% sample; this layer was removed before XRD measurement.

In contrast, the peak positions of niobium carbide (NbC) obtained for the samples with different C mol% were observed to shift. Therefore, the precise lattice constants, a_0, of NbC were calculated using the 220 and 222 diffraction lines and are shown in Fig. 2, compared with those reported for NbC[7] and NbN.[8] It can be seen from Fig. 2 that the lattice constants of NbC obtained from the samples with C 80–50 mol% were almost constant, 0.4460–0.4463 nm, which agreed with the value of 0.4469 nm reported in the literature.[7] In contrast, the lattice constants of NbC obtained from the samples with C 40–20 mol% decreased with decreasing C mol%, and approached the value of 0.4393 nm reported for NbN.[8] Such changes in the lattice constants of NbC obtained can be explained by assuming the dissolution of nitrogen into the NbC lattice. Therefore, in Fig. 3 the presence of the N 1s spectrum was sought in the XPS spectra of the products obtained from the samples with C 10, 40 and 80 mol%. The intensity of the N 1s signals decreased with increasing C mol% in the samples and was within a trace level for the C 80 mol% sample. The dissolution of oxygen into the NbC lattice is assumed also, depending on the extent of oxygen in air penetrated into the reactant mixtures in the graphite crucible. However, because a strong contribution from niobium oxides coexisted, the O 1s spectra from NbC alone were not able to be distinguished. Constant *et al.*[9] also reported that Zr(C,N,O) solid solutions exist within a wide composition range.

Fig. 4 shows the XRD patterns of the Nb–C powder mixtures with C 50 mol% ground for 0–80 min. With increasing grinding time, the diffraction lines of niobium metal decreased in intensity and broadened, and the 002 line of graphite disap-

Table 1 Morphology, color and phase of the final products obtained in the Nb–C powder mixtures with different C mol%

graphite content (mol%)	grinding time/min	products		
		morphology	color	phase identified by XRD
80	120	powdery	black	NbC > Nb > NbO, NbO_2, Nb_2C
75	90			NbC > Nb > NbO, NbO_2, Nb_2C
67	90			NbC > Nb > NbO, NbO_2, Nb_2C
50	80			NbC ≫ Nb > NbO, NbO_2, Nb_2C
40	80	highly swelled, scale-like;	light grey	NbC ≫ NbO, NbO_2, Nb_2C
30	80	very brittle		NbC, Nb_2C ≫ Nb, NbO, NbO_2
20	90	slightly swelled, stratified; brittle	dark grey	NbC, Nb_2C, Nb ≫ NbO, NbO_2
10	135	non-swelled; brittle		Nb_2N ≫ Nb_2C, Nb, NbC, NbO, NbO_2, Nb_2O_5

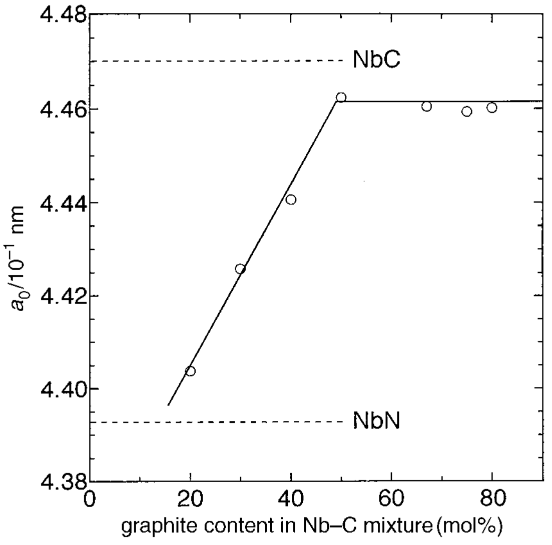

Fig. 2 Variation of the lattice constants, a_0, of niobium carbide obtained with C mol% in the Nb–C powder mixtures. The values shown by the dotted lines are the lattice constants of NbC and NbN reported in the literature.[7,8].

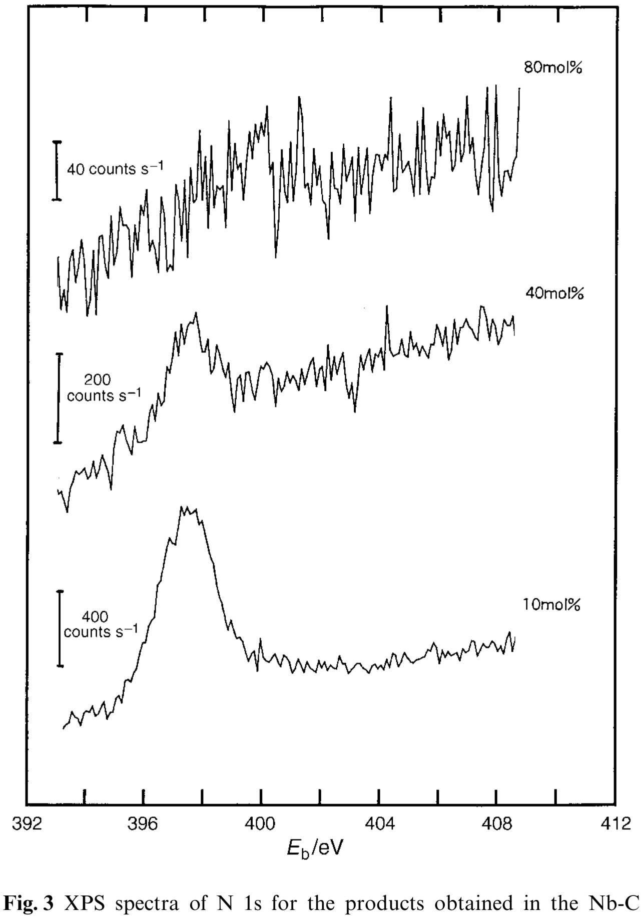

Fig. 3 XPS spectra of N 1s for the products obtained in the Nb-C powder mixtures with C 10, 40 and 80 mol%, respectively

peared after grinding for 30 min. These results suggest the size diminution and the increase in lattice strain of the Nb particles, and the disappearance of the stacking order of the graphite layers. The optical micrographs of these ground samples showed the decrease in particle size of Nb and C, and coating of Nb particles with disordered carbon; a similar result was observed in Al–C powder mixtures.[1] When thus mechanically activated samples were exposed to air, the exothermic reactions occurred spontaneously.

From these experimental results, a possible reaction process was estimated, by comparison to the results obtained for the Al–C and Zr–C powder mixtures.[1–3] First of all, on the surface of the samples in the graphite crucible, reaction step 1 is initiated by ignition reaction of disordered carbon covering the surface of the Nb metal particles with oxygen in air.

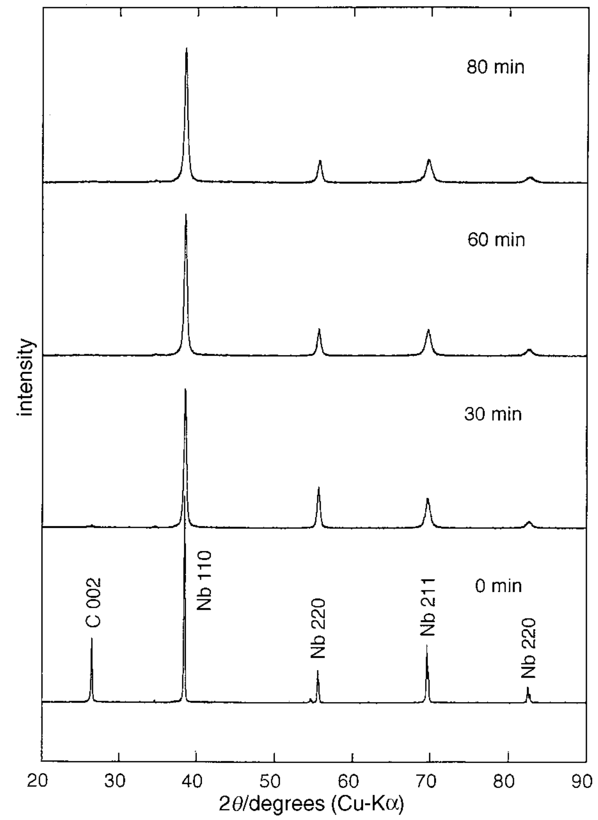

Fig. 4 XRD patterns of the Nb–C powder mixtures with C 50 mol% ground for 0–80 min

$$C + O_2 \rightarrow CO_2 + \Delta H_1 \qquad (1)$$

In order to cause the oxidation, carbon has to be not only in an amorphous 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 carbon particles, and hence its oxidation may be inhibited. In fact, the formation of niobium oxides (NbO, NbO_2) was detected in trace amounts. Furthermore, in the cases of Al–C[10] and Zr–C[3] powder mixtures with C 50 mol%, when the mechanically activated sample was heated in flowing nitrogen containing a small amount of oxygen in TG–DTA runs, it was found that the exothermic reaction due to the oxidation of the disordered carbon was initiated at around 100 °C, accompanying a mass decrease and followed by the concurrent oxidation of Al or Zr metal above 200 °C. 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. This is the case for the Nb–C powder mixtures.

Then, the heat evolved by the oxidation of carbon is transferred to the inside of the crucible, and the reaction propagates into the Nb–C powder mixtures. That is, at the expense of ΔH_1, in step 2 Nb metal reacts with C to form NbC and Nb_2C, evolving ΔH_2 and ΔH_3.

$$Nb + C \rightarrow NbC + \Delta H_2 \qquad (2)$$

$$2Nb + C \rightarrow Nb_2C + \Delta H_3 \qquad (3)$$

In the case of the C 10 mol% sample, excess Nb metal reacts also with nitrogen in air.

$$4Nb + N_2 \rightarrow 2Nb_2N + \Delta H_4 \qquad (4)$$

Reaction (4) is also an exothermic reaction with ΔH_4 and evolves white heat as well. As described above, Nb_2O_5 was formed exclusively near the surface of the product as a thin white layer. This result shows that the oxidation of excess Nb metal, because of insufficient carbon coverage in the Nb-rich samples, took place on the surface of the reactant, and consequently a nitrogen-rich atmosphere is achieved just under the product layer of Nb_2O_5. Then the reaction of the excess Nb metal with nitrogen occurs by using the heat released by the exothermic reactions in steps 1, *i.e.*, ΔH_1, and the oxidation reaction of Nb metal. Thus, it is understandable that the formation of niobium nitride, Nb_2N, occurred predominantly in the sample with the lowest C mol%. In the inner part of reactants with C 50–80 mol%, the particles of Nb metal are intimately surrounded by fine particles of disordered carbon and the nitridation as well as the oxidation of them is inhibited, so the carbonization reaction of Nb metal occurs exclusively. However, as can be seen from Fig. 2 and 3 the dissolution of nitrogen into NbC obtained from the samples with C 40–20 mol% could not be inhibited perfectly. In addition, the penetration of oxygen into the sample may not be avoided. Although the concentration gradient of nitrogen and oxygen decreases abruptly just under the niobium oxide surface layer formed, it still exists from the top to the bottom of the crucible. Depending on this gradient, the formation of solid solutions of Nb(C,N,O) is estimated.

In conclusion, it is emphasized that almost stoichiometric NbC and Nb_2N were easily formed as a single phase in air in a graphite crucible from mechanically activated Nb–C powder mixtures with C 50–80 mol% and C 10 mol%, respectively.

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Paper 7/04235C; *Received* 17*th June*, 1997