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Metal reduction of nitrides in a self-propagating way

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HIGHLIGHTS

- Titaniothermic reduction of nitrides to synthesize TiN-based materials.
- Reduction of BN and Si_3N_4 by Ti happens in a self-propagating way.
- Fine crystallite size below 1 μm realized in the products.
- Reduction of nitrides is possible for more metals besides Ti.

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ABSTRACT

Titaniothermic reduction of nitrides in a self-propagating way is reported here to produce TiN-based ceramic powders. In the titaniothermic reaction, where solid nitrides instead of N_2 gas are used as the nitrogen source, N atoms required for the nitridation of Ti do not rely on the infiltration of N_2 gas, but are in-situ supplied by the decomposition of solid nitrides, thus resulting in a higher conversion degree, more homogeneous microstructure, and smaller grain size. In contrast to the well-known aluminothermic and magnesiothermic processes with the reduction of oxides, the titaniothermic reaction involves the reduction of nitrides, which applies to more other metals besides Ti and offers a new way to synthesize nitrides other than direct nitridation of metal powders in a N_2 atmosphere.

1. Introduction

Metal reduction is widely used in pyrometallurgy. For example, Ti can be produced by reduction of $TiCl_4$ by Mg or Na, which is known as the Kroll process [1]. Another example is the thermite reaction between Al and iron oxides (the Goldschmidt process), which was discovered more than one century ago and is still used today for welding rail tracks [2,3]. Compared with the reduction of oxides and halides, metal reduction of nitrides has been less reported.

The thermodynamic basis of metal reduction is the difference in Gibbs energy of formation (ΔG_f) of oxides or halides of different metals. For instance, the ΔG_f of Al_2O_3 is lower than that of Fe_2O_3, and therefore Al can reduce Fe_2O_3, producing Fe and Al_2O_3. Analogously, metal reduction of nitrides should be also possible, because there is a difference in ΔG_f of nitrides of different metals.

This paper deals with metal reduction of nitrides, with reduction of BN and Si_3N_4 by Ti as examples. The reduction reactions take place in a self-propagating way, and the products are TiN-based ceramic composites. TiN is an important refractory compound with high hardness, good chemical and thermal stability, and excellent corrosion resistance, and TiN-based ceramics can be used for applications of cutting tools, wear-resistance components, and high-temperature structural materials [4]. The titaniothermic reduction of nitrides may provide an alternative way to produce TiN besides the direct nitridation of Ti.

2. Experimental

Commercial powders of Ti (99.5%, 325 mesh), BN (98%, O < 1.5 wt%, D_{50} < 2 μm), and Si_3N_4 (95% α, O < 1 wt%, D_{50} < 1 μm) were mixed according to the reaction formula shown in Table 1, and homogenized by ball milling for 8 h in a teflon jar and with agate balls. The reactant powder was pressed into a round compact with a dimension of Ø30 mm × 40 mm and porosity of about 65%, loaded in a graphite crucible, and then placed in a closed reaction chamber. The chamber was evacuated at first and then filled with Ar gas to a

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Table 1
Experimental results of two titaniothermic reactions.

Reactant	Reaction formula	T_{ad} (°C)	T_{exp} (°C)	Phase assemblage
3Ti + 2BN	3Ti+2BN = 2TiN + TiB_2	2375	1810	TiN, TiB_2
4Ti + Si_3N_4	4Ti + Si3N4 = 4TiN+3Si	1619	1337	TiN, $TiSi_2$, Si, α-Si_3N_4

T_{ad}: calculated adiabatic temperature, T_{exp}: experimentally measured temperature.

pressure of 1 atm. The reaction was triggered by passing an electric current of 10 A for 2 s in a tungsten coil at the top of the sample, then continued in a self-propagating way, and completed in a few seconds, during which the reactants were converted into products. The temperature of the sample during the reaction was measured by a W-Re thermocouple. The phase assemblage of the products was examined by X-ray diffraction (XRD; D8 Focus, Bruker, Germany) using Cu Kα radiation and with a scanning rate of 4°/min. The microstructure of the products was observed by scanning electron microscopy (SEM; S-4300, Hitachi, Japan).

3. Results and discussion

To evaluate the possibility of reduction of BN and Si_3N_4 by Ti, the Gibbs energy changes (ΔG) of the reactions of 3Ti+2BN = 2TiN + TiB_2 and 4Ti + Si_3N_4 = 4TiN+3Si are calculated and plotted in Fig. 1. For both the reactions, ΔG is readily negative in a wide temperature range of 300–2700 K, indicating that the reactions will happen from thermodynamic considerations. It is also noticed that the enthalpy changes (ΔH) of the reactions are very negative, implying that the reactions are highly exothermic. The calculated adiabatic temperatures of the reactions (Table 1) are higher than 1800 K, and therefore the reactions can take place in a self-propagating way [5,6].

Fig. 2 shows the temperature profiles of the titaniothermic reactions of Ti with BN and Si_3N_4. Once the reaction starts, the temperature immediately increases and reaches the apex in a few seconds. The measured maximum reaction temperatures are lower than the calculated adiabatic ones (Table 1), due to inevitable heat loss and sometimes incomplete reaction. For example, the reaction between Ti and Si_3N_4 is incomplete and partially differs from the reaction formula of 4Ti + Si_3N_4 = 4TiN+3Si, which will be discussed later.

Fig. 3 shows the XRD patterns of the products. The reaction between Ti and BN is complete and produces TiN and TiB_2, which follows the reaction formula of 3Ti+2BN = 2TiN + TiB_2 and agrees well with

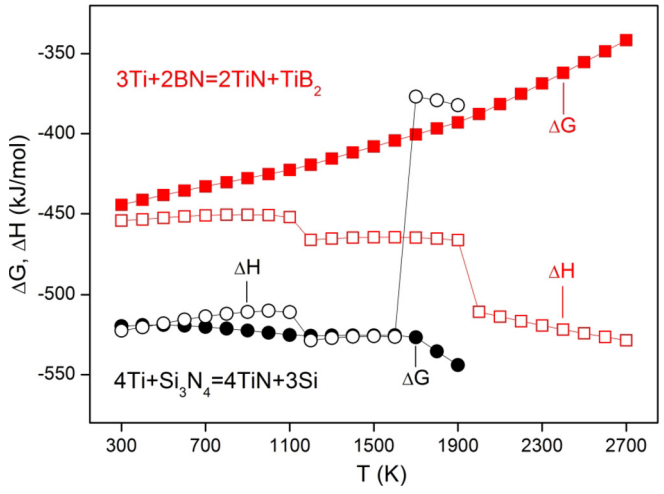

Fig. 1. Gibbs energy change (ΔG) and enthalpy change (ΔH) of the reactions of 3Ti+2BN = 2TiN + TiB_2 and 4Ti + Si_3N_4 = 4TiN+3Si. (P = 1 atm).

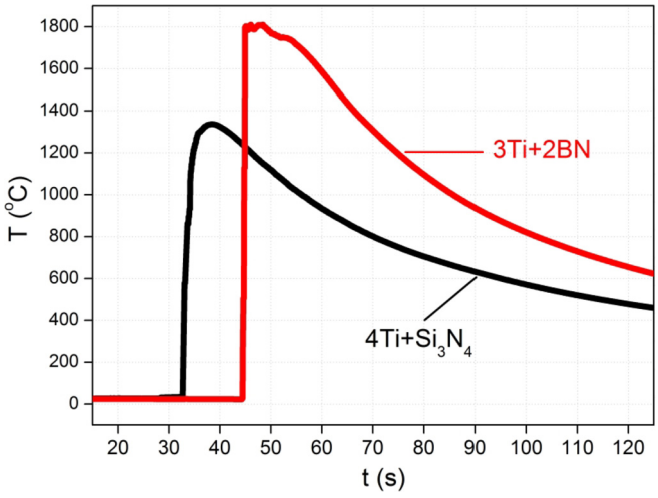

Fig. 2. Temperature profiles during the reactions of Ti with BN and Si_3N_4 in 1 atm Ar atmosphere.

previous studies [7–9]. The reaction can be regarded as a combination of two reactions of Ti + BN=TiN + B and Ti+2B = 2TiN + TiB_2, where Ti reduces BN at first to produce B and then reacts with B to form TiB_2. From XRD data, the lattice parameter of TiN (cubic, Fm-3m, 225) is a = 4.249 ± 0.001 Å, which is very close to the value of 4.25 Å in PDF #65–5759. The lattice parameters of TiB_2 (hexagonal, P6/mmm, 191) are a = 3.030 ± 0.001 Å and c = 3.231 ± 0.001 Å, which are also consistent with those in PDF #35–0741. The reaction between Ti and Si_3N_4 is not complete and some unreacted α-Si_3N_4 remains, partially deviating from the reaction formula of 4Ti + Si_3N_4 = 4TiN+3Si. Nevertheless, TiN is the major phase and Si is also present in the product, confirming that the reduction of Si_3N_4 by Ti has taken place. The lattice parameter of TiN is a = 4.246 ± 0.001 Å and agrees well with that in the standard PDF card, indicating that the synthesized TiN in principle keeps the nominal stoichiometry. In the product, besides the major phase of TiN, minor $TiSi_2$ phase is observed. The formation of Ti-Si intermetallic compounds in the reaction between Ti and Si_3N_4 has been also observed before [10], and is fulfilled by the reaction between Ti and Si extracted from Si_3N_4.

After the reduction of BN and Si_3N_4 by Ti, the products are loose compacts and can be readily pulverized into powders, in which each particle consists of many fine crystallites, as shown in Fig. 4. The crystallites are much smaller than those in TiN powders produced by combustion of Ti in N_2 atmosphere [11], where faceted crystals larger than 10 μm are observed. In the TiN-TiB_2 powders produced by reaction between BN and Ti, most crystallites are smaller than 2 μm. In the product by reaction between Ti and Si_3N_4, the average crystallite size is below 1 μm and many grains are smaller than 0.5 μm.

The reduction of BN and Si_3N_4 by Ti is similar to the well-known aluminothermic and magnesiothermic reactions [3,12–14] in two aspects. At first, the reaction involves extraction of one element from its compound by another element. Secondly, the reaction is highly exothermic and takes place in a self-propagating way. In this