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Preparation of Nanoparticle Mixture of Nitride and Boride by Induction Thermal Plasmas

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Nanoparticles of boride and nitride have attractive characteristic because of their high thermal conductivity. The purpose of this paper is to prepare nanoparticle mixture of nitride and boride by induction thermal plasmas. Another purpose is to correlate the prepared particle composition with thermodynamic parameters. For B-N-Ti system that has low Gibbs free energy of nitrization and boridation, boride and nitride nanoparticles were prepared. For B-N-M (M = Ta, Nb) system that has middle Gibbs free energy of nitrization with higher nucleation temperature than boron, nitride nanoparticles were more prepared than boride. While B-N-M (M = Co, Fe and Mo) system that has high Gibbs free energy of nitrization, only boride nanoparticles were prepared. The composition of prepared boride and nitride nanoparticles depends on the Gibbs free energy, the nucleation temperature.
Key words: Thermal Plasma, Nitrogen Plasma, Nitride, Boride, Nanoparticle

1. INTRODUCTION

Attractive material process with thermal plasmas have been proposed for production of nanoparticles, because thermal plasmas offer unique advantages; these advantages include high enthalpy and high chemical reactivity to enhance reaction kinetics. Investigation of physical and chemical processes in thermal plasma processing is indispensable for production of nanoparticles.

Induction thermal plasmas provide effective preparation of nitrides. TiN(1) and AlN(2) were prepared by Ar-N_2 induction plasmas. Si_3N_4 were prepared through the vapor-phase reaction between $SiCl_4$ and NH_3 in induction plasmas(3). Besides, preparation of boride nanoparticles has been reported. YB_{66} were prepared by plasma chemical process using starting powders of YB_4 and B(4). TiB_2 were synthesized in the vapor-phase reaction of sodium with $TiCl_4$ and BCl_3 (5).

The purpose of this paper is to prepare nanoparticles mixture of nitride and boride by induction thermal plasmas. Another purpose is to correlate prepared particle composition with thermodynamic parameters.

2. THERMODYNAMIC CONSIDERATION

2.1 Vapor pressure

The vapor pressure ratio of metal to boron was shown in **Fig. 1.** The vapor pressure ratio of Ti/B is on the order of 10^2 at the melting point of Ti. That of Co/B is on the order of 5×10^3 at the melting point of Co. Preparation of borides having large vapor pressure difference is quite difficult. Therefore, control of condensation process is very important for preparation boride nanoparticles.

2.2 Nucleation Temperature

The nucleation rate expression proposed by Girshick et al (6) was used for the estimation of critical saturation ratio. **Relationship between the nucleation rate and saturation ratio was shown in Fig. 2. The nucleation rate**

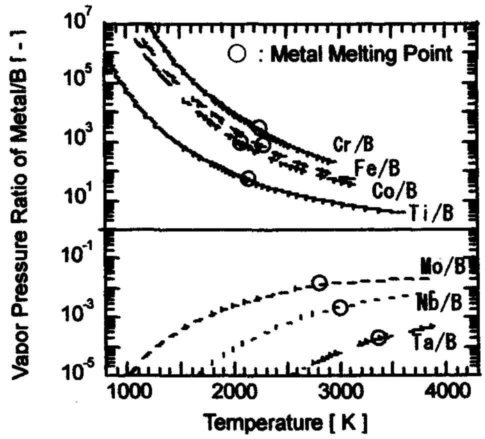

Fig. 1. Temperature dependence of vapor pressure ratio.

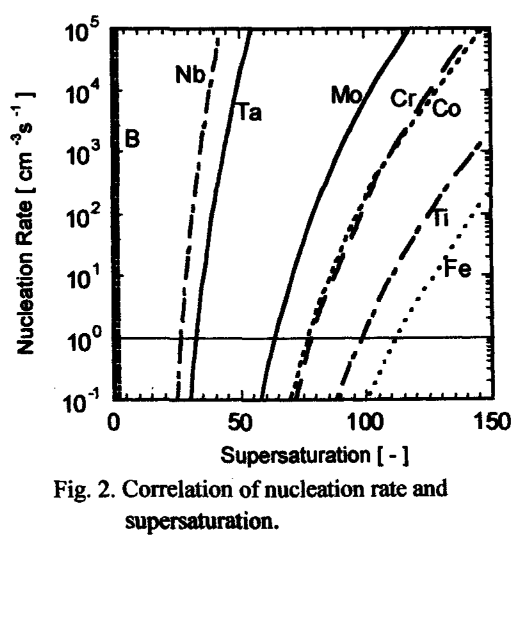

Fig. 2. Correlation of nucleation rate and supersaturation.

is strongly dependent on the surface tension and the saturation ratio. When the nucleation rate is over 1.0 $cm^{-3}\ s^{-1}$, particle formation can be conveniently observed experimentally. Therefore the corresponding value of saturation ratio is defined as the critical saturation ratio [7]. The critical saturation ratio of B was estimated to be 2, while the other metals have the critical saturation ratio from 30 to 120.

The nucleation temperature at the critical saturation ratio was presented in **Fig. 3** for constituent materials of boride and nitride. The nucleation temperature of the metal almost corresponds to the melting temperature, while B has wide liquid range between the nucleation and melting temperature.

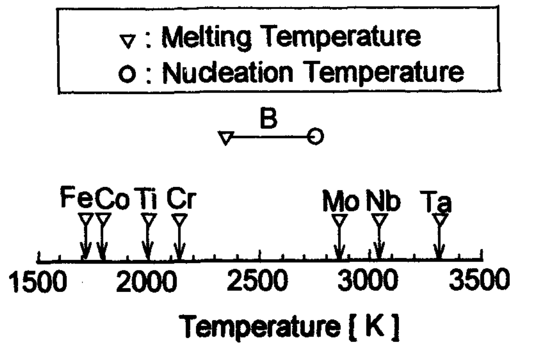

Fig. 3. Nucleation and melting temperature.

2.3 Gibbs free energy

Gibbs free energy of nitrization and boridation at the metal melting temperature were summarized in **Fig. 4**. Gibbs free energies of nitrization and boridation for Ti are the lowest among metals, while Co has relatively high value in these Gibbs free energies. In this paper, we selected Ti-B-N and Co-B-N system to investigate the effect of Gibbs free energy on nucleation mechanism of nanoparticles.

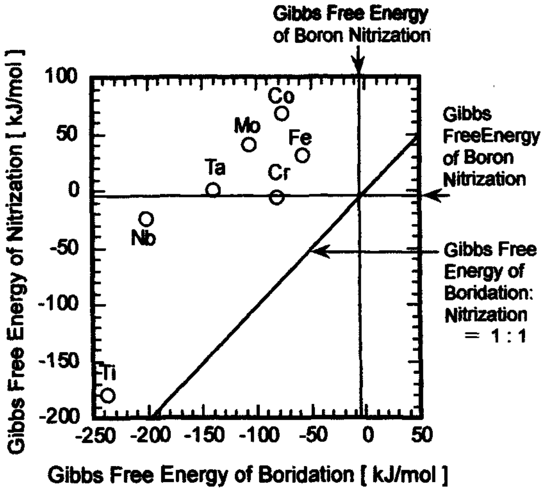

Fig. 4. Gibbs free energy of nitrization and boridation at metal melting temperature.

3. EXPERIMENT PROCEDURES

3.1 Experimental set-ups

A schematic diagram of the experimental apparatus is shown in **Fig. 5**. Total system was evacuated and then Ar was introduced up to a pressure of 101 kPa. Raw material powder of B and metal powder were premixed and introduced into the plasma at feed rate of 0.1 g/min. Typical operating conditions were as follows; plate power: 20 kW for Ar plasma, 25 kW for Ar-N_2 plasma; total pressure: 101 kPa; Ar flow rate: 34 L/min, and N_2 flow rate: 0, 2 or 4 L/min.

3.2 Injection powders

Raw material powders used in this study are B (average: 15 μm), Cr (0.7-25 μm, average: 9.6 μm), Co (average: 5 μm), Fe (1-13 μm, average: 6.6 μm), Mo (2-4 μm, average: 3 μm), Nb (1-25 μm, average: 15.5 μm), Ti (1-25 μm, average: 9.1 μm) and Ta (2-25 μm, average: 11.6 μm). In the thermal plasma, premixed powder was evaporated immediately and nanoparticles were prepared through the cooling process. The nanoparticles were collected on condition that metal vapor was quickly quenched by the water-cooled coil. Nanoparticles were collected at two quenching positions; one is upper quenching in Ar plasma, while the other is lower quenching in Ar-N_2 plasma. These positions were 207mm and 267mm from the bottom of plasma torch.

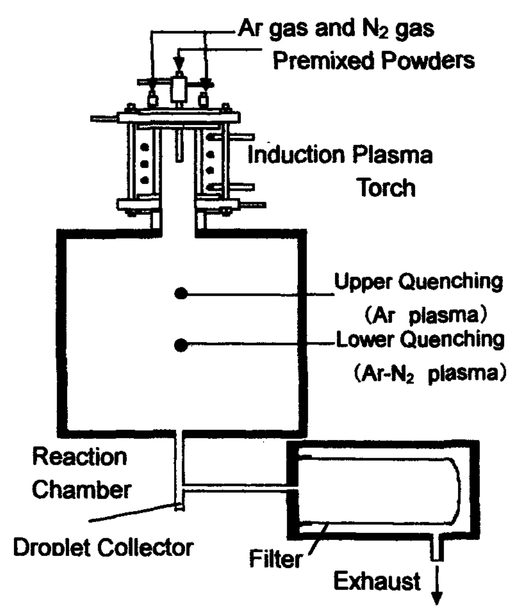

Fig. 5. Schematic diagram of the experimental apparatus for nanoparticle preparation.

3.3 Analysis

Prepared nanoparticles were characterized by X-ray diffraction (XRD). XRD was carried out on an MXP3TA (Mac Science). The particle size, morphology and electron diffraction were determined by transmission electron microscope (TEM). TEM observation were performed on an JEM-2010 (JEOL) operated at an accelerating voltage of 200 kV. Sample for TEM analysis were prepared by dispersing particles on to carbon copper meshes.

4. EXPERIMENTAL RESULTS

4.1 Ti-B-N system

The XRD spectrum chart of the prepared nanoparticles for Ti-B-N system was shown in **Fig. 6.** TiN, TiB_2, h-BN, Ti_2N as well as unreacted Ti were identified from XRD spectrum peak. TEM photograph reveals that the average particle diameter is 11.4 nm. TiB_2 and TiN of the nanoparticles were identified with electron diffraction.

Figure 7 shows the effect of initial B content in the feed powder on the relative XRD intensity of boride at different flow rates of N_2 in the plasma. Relative XRD intensity was defined as the ratio of boride first peak to the identified all first peaks (Ti, TiN, TiB_2, Ti_2N and h-BN). Preparation of TiB_2 nanoparticle was most successful at B content in the feed powder of 0.66.

Figure 8 shows the effect of initial B content on the relative XRD intensity of nitride, metal or h-BN at different flow rates of N_2 in the plasma. Smaller amount of TiN particles was prepared at larger B content in the feed powders.

These results in Ti-B-N system are attributed to the lowest Gibbs free energies of nitrization and boridation among the metals, and to small vapor pressure ratio of Ti to B.

4.2 Co-B-N system.

The XRD spectrum chart of the nanoparticles for Co-B-N system was shown in **Fig. 9.** Co_2B, CoB, h-BN as well as unreacted Co, B were identified from XRD spectrum peak.

Figure 10 shows the effect of initial B content on the relative XRD intensity of boride at different flow rates of N_2 in the plasma. Preparation of Co_2B nanoparticles was most successful at B mole fraction of 0.50, and CoB nanoparticles was most successful at B mole fraction of 0.75. **Figure 11** shows the effect of initial B content on the relative XRD intensity of metal or h-BN at different flow rates of N_2 in the plasma. The amount of unreacted Co particles was smaller at larger B content in the feed powders.

Similar results were obtained for B-N-M (M = Fe and Mo) system that has high Gibbs free energy of nitrization.

5.DISCUSSION

Investigation of correlation between the composition of prepared nanoparticles and the thermodynamic parameters are important for the control of the particle compositions. **Figure 12** shows the relationships between the relative XRD intensity ratio of nitride to boride and the thermophysical properties; the nucleation temperature ratio of metal to boron and the Gibbs free energy ratio of nitrization to boridation are selected as the thermophysical properties in this study. Gibbs free energy of boridation is negative for all metals in this study, therefore larger ratio of Gibbs free energy of nitrization to boridation indicates that nitrides are more stable thermodynamically than the borides. For Ti, Cr, Mn, Fe, Co, Al and Si, which have lower nucleation temperature than B, larger amount of nitrides was prepared at larger ratio of Gibbs free energy of nitrization to boridation and the thermophysical properties. The wide liquid range between the nucleation

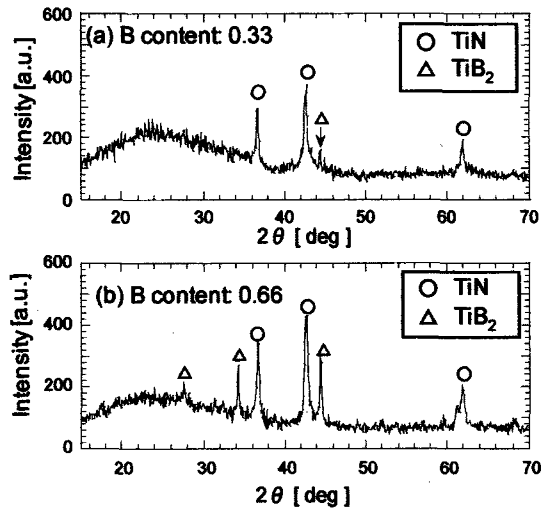

Fig. 6. XRD spectrum chart of nanoparticles for Ti-B-N system; B content in feed powders: (a) 0.33, (b) 0.66; N_2: 2.0 L/min.

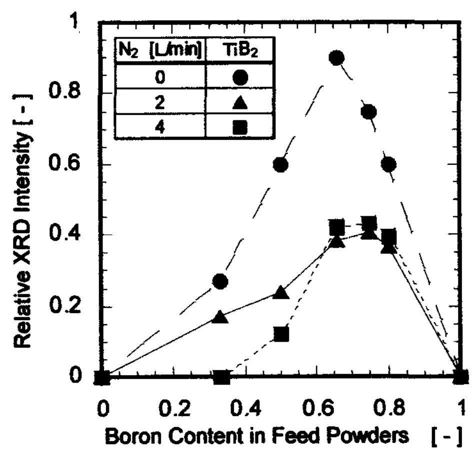

Fig. 7. Effect of boron content in feed powders on the prepared boride particle composition for Ti-B-N system.

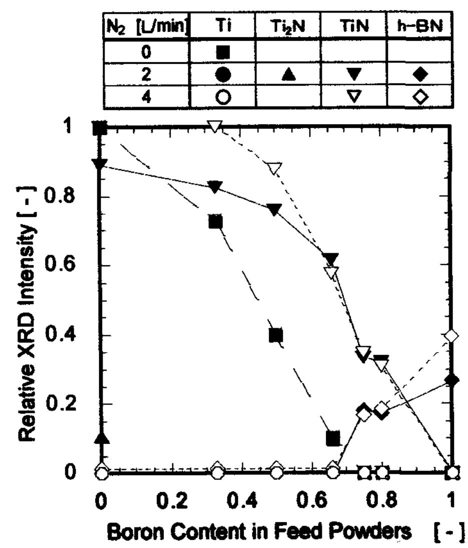

Fig. 8. Effect of boron content in feed powders on the prepared nitride and unreacted metal particle composition for Ti-B-N system.

and the melting temperature of B would have considerable effect on the nucleation mechanism.

On the other hand, nucleation temperatures of Nb, Mo and Ta are higher than that of B. These metals having higher nucleation temperature nucleate faster than B, therefore nucleation mechanism of these metals is different from the metals having lower nucleation temperature than B.

6. CONCLUSIONS

Experiments were carried out to prepare nanoparticle mixture of nitride and boride, and to correlate these compositions with thermodynamic parameters.

For B-N-Ti system that has low free energy of boridation and nitrization, boride and nitride nanoparticles were prepared. For B-N-M (M = Ta, Nb) system that has middle Gibbs free energy of nitrization with higher nucleation temperature than boron, nitride nanoparticles were more prepared than boride. While B-N-M (M = Co, Fe and Mo) system that has high Gibbs free energy of nitrization, only boride nanoparticles were prepared. The composition of prepared boride and nitride nanoparticles depend on the Gibbs free energy, the nucleation temperature.

The Gibbs free energy and nucleation temperature have considerable effect on the composition of the prepared nanoparticles of mixture of borides and nitrides.

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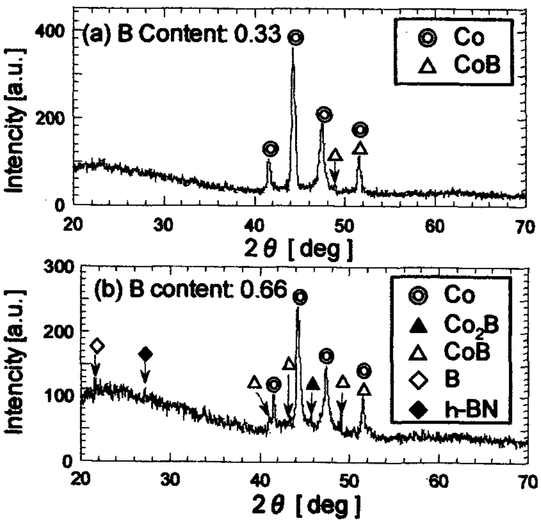

Fig. 9. XRD spectrum chart of nanoparticles for Co-B-N system; B content in feed powders: (a) 0.33, (b) 0.66; N_2: 2.0 L/min.

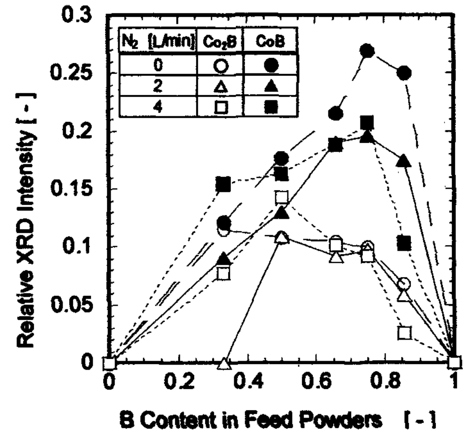

Fig. 10. Effect of boron content in feed powders on the prepared boride particle composition for Co-B-N system.

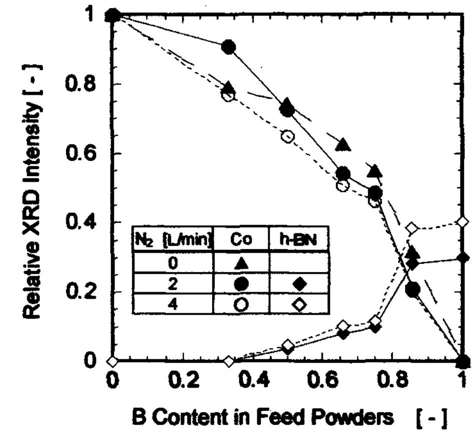

Fig. 11. Effect of boron content in feed powders on the prepared particle composition for Co-B-N system.

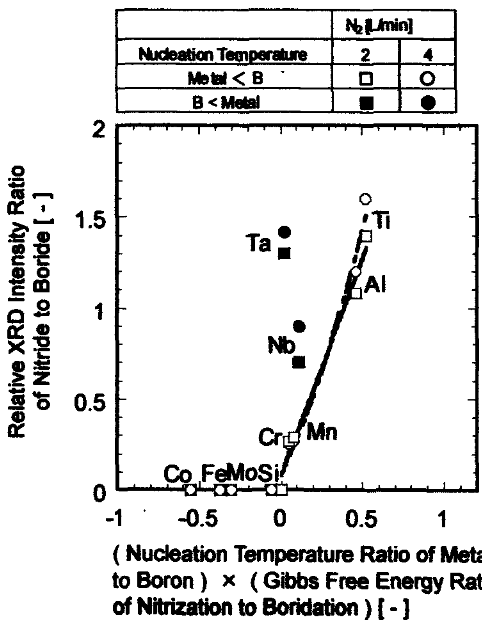

Fig. 12. The relationships between the relative XRD intensity ratio and the thermophysical properties.

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