Fabrication of Bulk Chromium Nitrides Using Self-Propagating High-Temperature Synthesis and Hot Isostatic Pressing

Yoshihiro Shoji, Masaru Yoshinaka, Ken Hirota and Osamu Yamaguchi
Dept. of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyo-Tanabe 610-0321.

SYNOPSIS
Cr$_2$N, CrN and their mixtures with desired fractions were prepared by self-propagating high-temperature synthesis (SHS) under controlled nitrogen pressure and then followed by hot isostatic pressing at 1300°C and 196 MPa under argon gas. The combustion temperature increased with increasing nitrogen pressure. Single-phase Cr$_2$N and CrN were formed at 1040°C under 0.18 MPa N$_2$ and 1730°C under 2 MPa N$_2$, respectively. The mechanical properties of chromium nitride ceramics with relative density of 99.2% were examined; Vickers hardness $H_v$ (CrN: 11.2 GPa and Cr$_2$N: 14.5 GPa) linearly increased with increasing fraction of Cr$_2$N, whereas fracture toughness $K_{IC}$ ($\sim$4.7 MPa$\cdot$m$^{1/2}$) and bending strength $\sigma_b$ ($\sim$355 MPa) were constant regardless of the fraction of Cr$_2$N/CrN.

KEY WORDS
self-propagating high-temperature synthesis (SHS), chromium nitrides, hot-isostatic pressing (HIP)

1 Introduction
Chromium coatings have been widely studied in the field of hard coating for wear and corrosion resistance. In particular, CrN films have many superior properties such as hardness, dense particles, good adhesion and corrosion resistance. Two compounds of CrN (cubic) and Cr$_2$N (hexagonal) exist in the Cr-N system. They were formed by heating Cr metal for long times at 735 to 1180°C in a stream of either NH$_3$ or N$_2$. Recently, Braverman et al. studied the combustion of Cr in nitrogen and reported that adiabatic combustion temperatures for the formation of Cr$_2$N and CrN were 1290°C and 2063°C, respectively, in a solid phase. Self-propagating high-temperature synthesis (SHS) is an interesting process, in which initial reactants, when ignited, instantaneously transform into products because of a high exothermic heat of reaction. In the present study, Cr$_2$N, CrN and selected powder mixtures were successfully prepared by SHS under controlled nitrogen pressure. The experiments described below deal with the formation and sintering of them.

2 Experimental Procedure
As-received Cr metal (99.9% pure) with an average particle size of 2 μm was used as a starting material. The loose powder was put into a carbon crucible; then, the crucible was placed in a stainless-steel chamber. SHS was performed under a different nitrogen pressure between 0–2 MPa. Nitrogen gas (99.99% pure) was introduced into the chamber after evacuation, then the powder was ignited by heating a carbon ribbon. An electric voltage of ~50 V and a current of ~20 A were applied for ignition.

Densification was performed by hot isostatic pressing (HIPing) under argon gas as the pressure-transmitting medium. Before HIPing, the powders obtained by SHS were pressed into pellets at 98 MPa and then cold isostatically pressed at 343 MPa. The green compacts, covered with boron nitride powders, were sealed in a Pyrex-glass tube under vacuum. HIPing conditions were as follows: heating rate of 400°C/h; increasing pressure rate of ~180 MPa/h above 800°C; and sintering for 2 h at 1300°C and 196 MPa.

Scanning electron microscopy (SEM) was used for microstructural observations. Bulk densities after polishing with diamond paste (nominal size 1 to 3 μm) were determined by the Archimedes method. Test samples (~3 × 3 × 20 mm) for mechanical measurements were cut from the sintered compacts with a diamond saw and then lapped with diamond paste. Vickers hardness ($H_v$) and fracture toughness ($K_{IC}$) were determined by the micro-indentation technique with a 19.8-N load. Three-point bending strength ($\sigma_b$) was evaluated with a 16-mm span and a crosshead speed of 0.5 mm/min. Ten measurement
runs were carried out to determine the average values for each mechanical property.

3 Results and Discussion

Fig. 1 shows the combustion temperature measured with a W-Re thermocouple (0.125 mm in wire-diameter); it increased with increasing nitrogen pressure. No ignition occurred under nitrogen pressure <0.18 MPa. The resulting products were ground for 5 min by a dry process using an agate mortar and pestle. Phases were examined by X-ray diffraction (XRD) analysis using Ni-filtered CuKα radiation. A wide range of variation in nitrogen pressure resulted in the formation of Cr₂N, CrN and their mixtures. Fig. 2 shows the fraction of Cr₂N(CrN) as a function of nitrogen pressure. The fraction of Cr₂N and CrN were determined by measuring the diffraction peak heights, (111) for Cr₂N\(^{10}\) and (200) for CrN\(^{11}\), of the strongest lines in the spectra, followed by using a calibration curve. Interplanar spacings were measured with the aid of an internal standard of high-purity silicon, and unit-cell values were determined by a least-squares refinement. The diffraction lines for Cr₂N were reasonably indexed by a hexagonal unit cell with \(a = 0.4811\) and \(c = 0.4484\) nm. The

---

![Fig. 1](image1.png)

**Fig. 1** Combustion temperature as a function of nitrogen pressure.

![Fig. 2](image2.png)

**Fig. 2** Cr₂N/CrN fraction as a function of nitrogen pressure.

![Fig. 3](image3.png)

**Fig. 3** XRD patterns of (a) Cr₂N and (b) CrN powders.
lattice parameter of CrN was \( a = 0.4139 \text{ nm} \). These data agreed with those (Cr\(_2\)N: \( a = 0.48113 \text{ and } c = 0.44841 \text{ nm} \)\(^{10}\), CrN: \( a = 0.4140 \text{ nm} \)\(^{11}\)) reported previously. Single-phase Cr\(_2\)N and CrN, consisting of aggregates in which the primary particle sizes were \( \sim 2.3 \mu \text{m} \) for the latter powders, were formed at 1040 ° under 0.18 MPa and 1730 °C under 2 MPa, respectively (Figs. 3 and 4). Intermediate nitrogen pressures gave the mixtures of both nitrides. With increasing nitrogen pressure the fraction of CrN rapidly increased up to \( \sim 0.5 \text{ MPa} \) and slowly at \( \sim 0.5 \) to 2 MPa, in inverse proportion to that of Cr\(_2\)N.

The XRD results of the samples obtained by grinding sintered compacts revealed that the fraction of Cr\(_2\)N/CrN gave the same data as shown in Fig. 2, with an error of \( \pm 0.4\% \). The relative densities calculated using the theoretical densities of Cr\(_2\)N (6.539 Mg/m\(^3\))\(^{10}\) and CrN (6.178 Mg/m\(^3\))\(^{11}\) were 99.2 \( \pm 0.1\% \) for all the ceramics. Fig. 5 shows SEM photographs for the fracture surfaces of pure Cr\(_2\)N and CrN ceramics, indicating the grain sizes of \( \sim 11 \) and \( \sim 9 \mu \text{m} \) for the former and latter nitrides, respectively. Fig. 6 shows the Vickers hardness \( (H_v) \) of the ceramics.
Pure CrN ceramics gave a value of 11.2 GPa. The hardness linearly increased with increased fraction of Cr$_2$N; finally, a value of 14.5 GPa was obtained for pure Cr$_2$N ceramics. This result indicated that the hardness obeys the rule-of-mixtures. The values of $K_{ic} (\sim 4.7\, \text{MPa\cdot m}^{1/2})$ and bending strength $\sigma_b (\sim 355\, \text{MPa})$ were constant for all the ceramics, regardless of the fraction of Cr$_2$N/CrN (Fig. 7). The results suggest that among ceramics, except for ZrO$_2$-based materials, chromium nitrides have a higher fracture toughness.

4 Summary

Bulk Cr$_2$N, CrN and their mixtures with desired fractions, were fabricated by hot isostatic pressing (HIP) for 2 h at 1300°C and 196 MPa using the chromium nitride powders prepared by self-propagating high-temperature synthesis (SHS) under controlled nitrogen pressure at 0.18 to 2 MPa. Dense ceramics with relative density of 99.2% thus obtained exhibited homogeneous microstructures consisting chromium nitride grains ($\sim 11\, \mu m$ for Cr$_2$N, $\sim 9\, \mu m$ for CrN). Their mechanical properties were evaluated; Vickers hardness $H_v$ increased from 11.2 (CrN) to 14.5 GPa (Cr$_2$N) with increasing Cr$_2$N fraction. However, their fracture toughness $K_{ic} (\sim 4.7\, \text{MPa\cdot m}^{1/2})$ and three-point bending strength $\sigma_b (\sim 355\, \text{MPa})$ were constant in spite of the Cr$_2$N/CrN fractions.

References