Rapid Consolidation of TiN–Cr2N–(Ti,Cr)N Nanoparticles Using Pulsed Current Activated Sintering and the Mechanical Properties of Sintered Product

Wonbaek Kim1, Chang-Yul Suh1, Ki-Min Roh1, Jae-Won Lim1, Song-Lee Du2 and In-Jin Shon2,*

1Minerals and Materials Processing Division, Korea Institute of Geoscience, Mining and Materials Resources, Daejeon, Korea
2Division of Advanced Materials Engineering, Research Center of Advanced Materials Development, Chonbuk National University, Jeonbuk 561-756, Korea

We previously reported that the electrical explosion of Cr-plated Ti wires in N2 gas produced nanoparticles composed of cube-shaped TiN, sphere-shaped Cr2N and extremely fine (Ti,Cr)N particles. In this study, the mixture powders were consolidated by pulsed current activated sintering (PCAS). A near-full density compact could be obtained within five minutes at 1600°C. The shrinkage-time profile revealed an abnormally high contraction of the compact at 1500°C after the typical sintering period observed at temperatures between 700 to 1300°C. The sudden shrinkage at 1500°C turned out to be the consequence of the eutectic melting of Cr2N particles which decomposed to Cr and N2. The metallic Cr phase was located mostly at triple points and grain boundaries prohibiting the grain growth of TiN grains. The microhardness of the compact (13.6 GPa) was lower than that of pure TiN compact (16.2 GPa) due to the soft Cr phase. Nevertheless, the fracture toughness of the compact (6.0 MPa·m1/2) was higher than that of the pure TiN compact (6.0 MPa·m1/2) probably because the metallic Cr along grain boundary may deter the crack propagation.

Keywords: TiN, Cr2N, (Ti,Cr)N, wire explosion, mechanical properties, sintering

1. Introduction

(Ti,Cr)N has many attractive properties, such as high hardness, excellent abrasive wear, oxidation and corrosion resistance.1,2) However, in contrast to the numerous studies on (Ti,Cr)N coatings, little attention has been paid to the fabrication and properties of bulk (Ti,Cr)N ceramics, probably because of the difficulty in the preparation of particulates and subsequent densification without binder.

Nanocrystalline materials have potential as advanced engineering materials with improved physical and mechanical properties.3,4) Recently, nanocrystalline powders have been developed by thermochemical and thermomechanical processes such as the spray conversion process (SCP), co-precipitation, high energy milling and electrical wire explosion.5–8) Of these, electrical wire explosion appears to be the simplest and most feasible method for synthesis of various compounds.9,10) However, the grain sizes in sintered materials are much larger than in pre-sintered powders due to rapid grain growth that occurs during conventional sintering. Controlling grain growth during sintering is a key to the commercial success of nanostructured materials. Various sintering techniques have been proposed to overcome the problem of grain growth. These include high-pressure densification, magnetic pulse compaction and shock densification.11–13)

The pulsed current activated sintering (PCAS) method has emerged recently as an effective technique for sintering and consolidating high temperature materials.14,15) PCAS is similar to traditional hot-pressing, but the sample is heated by a pulsed electric current that flows through the sample and a die. This process increases the heating rate (up to 1000°C/min) to a degree much higher than that of traditional hot-press sintering.

In the course of our previous attempt to synthesize (Ti,Cr)N nanopowders, we reported that the electrical explosion of Cr-plated Ti wires in N2 gas produced nanoparticles of TiN, Cr2N and extremely fine (Ti,Cr)N particles. In this study, the mixture particles were consolidated by PCAS and evaluated its mechanical properties.

2. Experimental Procedures

The Ti–Cr wire for electrical wire explosion was prepared by electrodeposition of Cr on a 0.289 mm diameter Ti wire. Specific details regarding the continuous electrodeposition set-up and the fabrication of raw powders are described in Refs. 16 and 17). The final diameter of the Cr-coated Ti wire was 0.320 mm which should give an average composition of about 25 at% Cr.

The powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 10 mm; height, 40 mm) and placed in a pulsed current activated sintering system (Eltek, South Korea) shown in Refs. 14) and 15). The sintering was conducted in four stages. The system was evacuated (stage 1) and subjected to an uniaxial pressure of 80 MPa (stage 2). An induced current was activated and maintained until densification as indicated by a linear gauge measuring sample shrinkage (stage 3). The temperature was measured by an optical pyrometer that was focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature (stage 4).

Microstructural information was obtained from product samples that were polished and etched using H2O (100 mL),...
HF (5 mL) and H₂SO₄ (7 mL) for 30 s at room temperature. Product compositional and microstructural analyses were conducted by X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness of the sintered samples was measured by indentations at load of 10 kg and a dwell time of 15 s.

3. Results and Discussion

3.1 Explosion products

The explosion of Cr-plated Ti wire in N₂ gas produced mixture phases of nanosized particles. Figure 1 shows a typical FE-SEM image of the particles. The particles consisted of the cube-shaped TiN, sphere-shaped Cr₂N, and clusters of extremely fine (Ti,Cr)N nanoparticles. Figure 2 shows the diffraction pattern of the reaction product on which TiN and Cr₂N peaks are marked by □ and ○, respectively. Ti or Cr peaks are not observed. More detailed description of the phases are provided in Ref. 17). Obviously, simple comparison of the peak intensity appears to suggest that the major phase is TiN together with small amount of Cr₂N phase. However, (Ti,Cr)N phase, which was verified in our previous study using FE-TEM, could not be identified by X-ray diffraction due to its small quantity and the possible peak broadening originated from its fine size. The average Cr content in the mixture powder was close to 25 at% within experimental error.

3.2 Pulsed current activated sintering

The progress of sintering process can be trailed by the shrinkage displacement-time (temperature) curve. Figure 3 shows the shrinkage curve at 1600°C under the applied pressure of 80 MPa. Under the applied pulse current, the powder compact contracted almost nearly from 700 to 1300°C and remained constant up to 1460°C. Afterwards, the shrinkage curve reveals an unexpectedly high contraction period in the narrow temperature ranges of 1470–1510°C. It remains steady afterwards up to 1600°C suggesting the completion of the consolidation. Later on, this subsequent contraction was related to the eutectic melting of Cr₂N phase. The average Cr content measured on the surface was very low as 3.42 ± 0.31 at%. Therefore, it is evident that significant amount of Cr was reduced probably by evaporation during sintering.

The apparent density of the compact was calculated to be 6.897 g/cm³. This is extremely high value considering the density of TiN (5.43 g/cm³) and that of Cr₂N (6.539 g/cm³). This high value can only be explained by the presence of metallic Cr in the compact (density of Cr is 7.14 g/cm³). Figure 4 shows the X-ray diffraction pattern of the sintered compact at 1600°C. TiN peaks was observed while either Cr₂N or Cr peaks could not be identified.

The morphology and composition of the sintered compact was further investigated using SEM/EDS. Figure 5 shows SEM/EDS result for the compact sintered at 1600°C. Here, (a) is the SEM image of the polished and etched surface of the compact, (b) is a typical EDS spectrum from the phases
marked by arrows on the micrograph and (c) is the Cr-K\textsubscript{\alpha} mapped image. The Cr-K\textsubscript{\alpha} mapped image clearly shows the presence of Cr-rich phase along grain boundaries. A few % Ti was also detected in the phase. It may be originated from the TiN matrix grains. However, it does not detect any nitrogen suggesting the grain boundary precipitates are virtually Cr metal.

Cr\textsubscript{2}N phase is known to melt eutectically at about 1600\textdegree C.\textsuperscript{18} Apparently, it melted and segregated along grain boundaries. It is quite probable considering the fact that the actual temperature of the compact should be higher than 1600\textdegree C. This is because the temperature measurement was conducted on the surface of the mold which should be cooler than the sample inside. The liquid Cr phase appears to prohibit the grain growth of TiN grains. Figures 6(a) and 6(b) show the SEM micrographs of the polished and etched surface of sintered compacts from (a) TiN–Cr\textsubscript{2}N–(Ti,Cr)N and (b) pure TiN particles. The average grain size of the mixture powder and pure TiN was measured as 6.5 and 17.9 \textmu m, respectively. This result suggests that the presence of liquid Cr phase obviously hindered the growth of TiN grains. The Cr phase also affected the microhardness and fracture toughness of the compact.

3.3 Mechanical properties

Vickers hardness was measured on the polished surface of the compact using a 98N load and 15-s dwell time. The calculated hardness values of the (Ti,Cr)N sintered 1600\textdegree C was 13.6 GPa. This value represents an average of five measurements. Indentations produced with sufficiently large loads were characterized by median cracks around the indent. According to the lengths of these cracks we can estimate the fracture toughness of the material with the following expression:\textsuperscript{19}

$$K_{\text{IC}} = 0.023(c/a)^{-3/2} \cdot H_v \cdot a^{1/2}$$

(1)
Table 1 Mechanical properties of mixture and pure TiN compacts.

<table>
<thead>
<tr>
<th></th>
<th>1600°C</th>
<th>TiN(1600°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density, d/(g/cm³)</td>
<td>6.897</td>
<td>5.267</td>
</tr>
<tr>
<td>Vickers hardness, Hv/(GPa)</td>
<td>13.6</td>
<td>16.2</td>
</tr>
<tr>
<td>Fracture toughness KIC/(MPa·m¹/²)</td>
<td>6.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Grain size, D/(µm)</td>
<td>6.5</td>
<td>17.9</td>
</tr>
</tbody>
</table>

where c is the trace length of the crack measured from the center of the indentation, a is half the average length of the two indent diagonals, and Hv is the hardness.

The Vickers hardness and fracture toughness of the mixture (TiN–Cr₂N–(Ti,Cr)N) compact and pure TiN compact are summarized in Table 1. The microhardness of the mixture compact (13.6 GPa) was significantly lower than that of pure TiN compact (16.2 GPa). This was not expected because the grain size of pure TiN was 3 times larger than the mixture compact. Therefore, it is obvious that the hardness of mixture compact is lower than that of pure TiN compact due to the soft Cr phase. Regardless of its lower hardness, the fracture toughness of the mixture compact (6.6 MPa·m¹/²) was higher than that of pure TiN compact (6.0 MPa·m¹/²). This is believed to suggest that soft Cr phase on grain boundary may deter the propagation of cracks.

4. Conclusions

The wire explosion products of Cr-plated Ti wire, which consisted of TiN, Cr₂N and (Ti,Cr)N nanoparticles, were rapidly consolidated by PCAS. A near-full density compact was obtained after sintering at 1600°C within 5 min. The Cr₂N phase was melted eutectically at around 1500°C to metallic Cr. The metallic Cr was solidified and segregated along grain boundaries. The Cr phase at grain boundaries hindered the growth of TiN grains during sintering. The microhardness of the compact (1390 kg/mm²) was lower than that of pure TiN compact (1650 kg/mm²). The lower hardness of mixture compact is due to the metallic Cr. The fracture toughness of the mixture compact (6.6 MPa·m¹/²) was higher than that of pure TiN compact (6.6 MPa·m¹/²). The metallic Cr appears to hinder the propagation of crack enhancing the fracture toughness.

Acknowledgments

This study was supported by a grant from basic research project of Korea Institute of Geoscience and Mineral Resources and by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20114030200060).

REFERENCES