Processing Research

Sintering of attrition-milled TiN powders using a spark plasma sintering technique

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Poorly sinterable TiN powders have been fully densified using a spark plasma sintering (SPS) technique. Sintering characteristics and microstructural evolution during SPS processing were evaluated using electron microscopy. It was found that Al_2O_3 incorporated as a contaminant during the milling process reacted with TiN particles at temperatures above 1700°C to form a secondary phase containing Al_2O_3 that accelerated the mass transport. This secondary phase makes it possible to start sintering at a lower temperature. It also enables the growth of TiN grains to be controlled. This phenomenon could be confirmed by the presence of the round or curved grain boundaries and the presence of Al_2O_3 containing secondary phase clusters in grain boundary triple junctions.

Key words: Spark plasma sintering, TiN, Microstructures, Grain size distribution

Introduction

Titanium nitride (TiN) has a high melting temperature, high hardness, good thermal stability, good resistance to acids and alkalis, and good electrical conductivity at high temperatures [1]. Because of its excellent properties, TiN has been used as tool materials with high strength and hardness, as corrosion-resistant coatings for Cu electrodes in semiconductor processes, and as abrasive materials with a sensing functionality [2]. It also has been used to increase the value of components through its aesthetically pleasing golden color [3].

In common with other non-oxide ceramics, pure TiN powders are very difficult to fully densify because of strong covalent bonding, a very low self-diffusion coefficient for mass transport and tendency to decompose at high temperature [4]. A number of strategies have been proposed to overcome the problem of poor sinterability, such as heating of the TiN green body while it is embedded in BN or Si_3N_4 powders [5], the addition of oxides as sintering aids [2] and the application of high nitrogen gas pressure during the sintering [6].

Moriyama *et al.* [2] reported that they could obtain an 86% dense material after hot-pressing at 1950 for 1 hour at a pressure of 14 MPa. Although the addition of Al_2O_3 or BN at about 10 wt% addition can increase the relative density of TiN up to 97.7%, the mechanical properties of the resulting TiN body tend to be degraded, depending on the characteristics of the additives. Here we report the sintering behavior of TiN densified using spark plasma sintering. This procedure uses a transient high temperature plasma to help densify ceramics. The plasma is generated by the application of a pulsed direct current [7].

This study aimed to investigate the sintering characteristics of pure TiN powders when spark plasma sintering (SPS), a newly developed sintering technique, was used. The SPS process can make a sintered body at lower temperature and in shorter times compared to conventional sintering processes through a high temperature spark plasma created between powder particles by the application of a pulsed direct current. In fact, SPS is similar to self-propagating high temperature sintering (SHS) and microwave sintering in terms of the use of self-heating action between particles inside the powders. Also, this process has many advantages compared to hot-pressing (HP) and pressureless sintering (PLS), including ease of operation and accurate control of sintering energy as well as high sintering speed, high reproducibility, safety and reliability [7, 8].

Experimental procedure

The starting material was commercially available TiN powder that is typically 99% pure with an average particle size of $3.36 \,\mu\text{m}$. The as-received powders were attrition-milled with Al₂O₃ balls in distilled water for 3 hours. The milled powders were then dried at 150°C for 24 hours in a drying oven.

The dried TiN powders were put into a graphite mold in the chamber of a spark plasma sintering apparatus (Model SPS 515S, Izumi Tech Co. Ltd., Japan). The sintering condition was typically at a pressure of 50

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MPa under a pulsed direct current of about 1500A in a vacuum atmosphere and in the temperature range of 1500°C to 1800°C.

The particle size of the initial and attrition-milled TiN powders were measured by a particle size analyzer (Model 9300 X100, Honeywell, USA). Relative densities of the samples were determined by the Archimedes method. The linear intercept method was used to calculate the mean grain size of sintered bodies. X-ray diffraction was used to identify the phases in the sintered body. The microstructure of the sintered body was analyzed using a scanning electron microscope (Model JSM-6330F, JEOL, Japan) and an energy dispersive X-ray spectrometer (Model INCA Energy, Oxford Instrument, United Kingdom). The microstructure was further investigated using a transmission electron microscope (Model JEM-2010F, JEOL, Japan).

Results and discussion

Sintering behavior of pure and attrition-milled TiN powders

Figure 1 shows commercially available TiN after attrition milling in which the average TiN particle size was reduced from $3.36 \,\mu\text{m}$ for the initial powder to $1.00 \,\mu\text{m}$. The particle size distribution exhibited a bi-modal shape. Even though X-ray diffraction analysis did not detect significant contamination of the pure TiN powder



Fig. 1. SEM image of the attrition milled TiN powder.

from the Al_2O_3 balls used as milling media, a small amount of Al_2O_3 could be expected to be incorporated into the TiN powder during the milling process.

Figure 2 shows the Z-axis displacement of the specimen as a function of sintering temperature during the entire SPS process. The initial decrease in the Z-position arises from the initial expansion of the graphite mold die. In case of as-received TiN powder, the sintering shrinkage started at about 1000 to 1050°C and finished at about 1700°C (Fig. 2(a) and Fig. 2(b)) and the Zposition continuously increased at sintering temperature below 1600°C. This result confirms that pure TiN powder



Fig. 2. Z-position variation during SPS process for various final sintering temperatures. □ : as-received ■ : attrition milled.



Fig. 3. Relative density of bodies sintered at different temperatures.

needs to be heated over 1700°C in order to densify.

By comparison, milled TiN powder started to conpact in volume in the temperature range of 900 to 950°C, densifying completely in the temperature range of 1600 to 1650°C. Figure 3 shows relative densities of the sintered TiN bodies as a function of sintering temperature. The as-received pure TiN powder could reach only 94.7% relative density at 1500°C but reached sintered densities over 98% above 1600°C. These results indicate that the SPS process is very effective in densifying pure TiN powders in comparison with other sintering processes such as hot-pressing [2]. It can be emphasized that even at 1500°C the attrition-milled TiN powders reached 97.7% relative density and, over 1600°C, both powders were densified to similar relative densities. The enhancement of the densification of TiN powder during the SPS process needs to be investigated further.

Microstructure of Sintered bodies

Figure 4 shows the chemically etched surfaces of bodies sintered at different temperatures. Most of the TiN grains were slightly rounded polygons. Many intragranular pores were found in the specimens sintered over 1600°C. As expected, the grain size of the sintered bodies tends to increase with the sintering temperature but no significant tendency for abnormal grain growth was detected.

The average grain sizes in the TiN specimens are given in Fig. 5. It is evident from this figure that the grain sizes of the compact produced from milled powder are consistently lower than those from compact produced from as-received powder for the same SPS condition.

Figure 6 shows TEM images of sintered bodies at 1800°C. It was found that the specimen sintered from as-received powders contained many intergranular micropores indicating excessive grain growth. Specimens from the milled powder typically displayed clean grain boundaries. The secondary intergranular phase containing Al_2O_3 was observed at the triple junctions and on grain boundaries. The secondary phases seem to originate



Fig. 4. Optical micrographs of TiN bodies sintered by SPS at various temperatures: (a) as-received powders (b) attrition milled powders.



Fig. 5. Average grain size of TiN bodies sintered at different temperatures.

from the incorporation of the Al_2O_3 during the milling process.

Figure 7 shows the Al_2O_3 containing secondary phase formed at a grain boundary triple junction. Sometimes these phases formed on the curved grain boundaries, as shown in Fig. 8, indicating the localized melting of the Al_2O_3 particles during the initial stage of the SPS process.

During the SPS process the spark plasma, due to the



Fig. 6. TEM images of TiN sintered at 1800°C: (a) as-received powders (b) attrition-milled powders.



Fig. 7. TEM-EDS image of triple junction in TiN sintered at 1800° C.



Fig. 8. TEM image of curved grain boundary.



Fig. 9. TEM image of triple junction containing Al₂O₃.

direct current flowing through the surface of the TiN powder, could melt the Al_2O_3 particles to form liquid or gaseous phases to activate the mass transport between TiN particles. These phases then recrystallize during cooling process to form secondary phases at the grain boundary triple junctions as shown in Fig. 9.

Conclusion

Fully densified TiN bodies were successfully obtained using a spark plasma sintering technique. Pure TiN powder could reach over 98% of relative density with only five minutes at 1600°C. The milling process was very effective to improve the sintering behavior of pure TiN. The phase containing Al₂O₃, which incorporated Al_2O_3 from the milling process, played an important role in reducing the initial stage sintering temperature and the inhibiting grain growth in the final stages of the SPS process.

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