Characterization of Si_3N_4 -TiN Composites Prepared by Spark Plasma Sintering

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Spark plasma sintering (SPS) was applied to produce electroconductive Si_3N_4 -20 vol%TiN composites. The sintering mechanism for SPS was a hybrid of dissolution-reprecipitation and viscous flow at 1450 and 1500 °C and viscous flow at 1600 °C. At temperatures higher than 1550 °C, nearly full density (relative density of 98%) was achieved. The Vickers micro-hardness reached a maximum (21.7 GPa) at 1550 °C. Homogeneous distribution without the agglomeration of TiN particles in the Si_3N_4 matrix was achieved by SPS at 1600 °C. The composites prepared by SPS at 1550 and 1600 °C had low electrical resistivity and could be machined by electrical discharge machining.

Key words: Spark Plasma Sintering, Silicon Nitride/Titanium Nitride Composite, Machinability

1. INTRODUCTION

Silicon nitride-based materials have promising high temperature properties such as strength, creep resistance and oxidation resistance. A successful approach for the possibility of mass production at a lower manufacturing cost is to incorporate an electrically conductive reinforcement such as TiN [1]. TiN has a high melting temperature (2950 °C), high hardness (21 GPa), and good electroconductivity ($2.5 \times 10^{-5} \Omega\text{cm}$) [2]. Depending on the amount of TiN particles added and the type of TiN subnetwork formed in the composite, it is possible to make a composite that is sufficiently electroconductive to be machined by electrical discharge machining (EDM), thus avoiding the expensive grinding operation for the final shaping and surface finishing of components [3, 4]. The electrical resistivity of the Si_3N_4 /TiN composite is affected by the initial size of the powder, the sintering method and the microstructure formed during sintering. Si_3N_4 /TiN composites have been produced by various methods including hot pressing (HP) [3, 4], gas pressure sintering (GPS) [5, 6], in situ processing [7], and self-propagating high temperature synthesis (SHS) [8]. However these methods require a high temperature and a long processing time.

A new rapid sintering method, spark plasma sintering (SPS) has been applied to produce hard sintered materials via the application of a large pulsed current using a graphite mold under a high compressive stress [9]. In SPS, rapid heating due to the large current shortens the densification time, thereby making this process suitable for the sintering of materials. However, there have been few reports on the application of SPS to electroconductive Si_3N_4 /TiN composites. The aim of the present study was to evaluate the applicability of SPS to the consolidation of Si_3N_4 -TiN nano powders. The

influences of sintering temperature on electrical resistivity were investigated and correlated with the microstructure.

2. EXPERIMENTAL PROCEDURE

The starting materials used for this study were Si_3N_4 containing 5 mass% Y_2O_3 and 2 mass% Al_2O_3 (Wako Co. Ltd.) and TiN powders (Wako Co. Ltd.). Fig.1 shows secondary electron (SE) images of the starting materials. The mean particle size of Si_3N_4 and TiN was approximately 50 nm. The amount of TiN added should be as small as possible because TiN is readily oxidized at 600 °C, leading to the degradation of oxidation resistance [10]. On the other hand, the percolation concentration at which the electrical resistivity of Si_3N_4 /TiN composites decreased drastically is nearly 20 vol%TiN [7]. Therefore, Si_3N_4 -20 vol%TiN powders were mixed by ultrasonic vibration, followed by planetary ball milling (Pulverisette 6, Fritsch Co. Ltd.) at a rotation speed of 100 rpm for 6 h in ethanol using ZrO_2 balls.

The mixed powders of 2 g were put into a graphite die with an inner diameter of 15 mm. A graphite sheet of 0.25 mm thickness was used to prevent powder/die and powder/punch reactions. The unit was rapidly heated to 1450-1600 °C by SPS (SPS-3.20 MK-4, Sumitomo Coal Co. Ltd.) under a compressive stress of 40 MPa in vacuum (10 Pa). The temperature was monitored and regulated by an infrared ray thermometer focused on the surface of the graphite die. The temperature was increased at a rate of 100 °C/min from 600 °C up to the sintering temperature, followed by holding for 10 min at the sintering temperature.

The density was measured by the Archimedes method (MD-300S, Alfa Mirage Co. Ltd.). The microstructure

Fig.1 SE images of the as-received powders (a) Si_3N_4 and (b) TiN

of the polished and plasma-etched (Tensec SP10, Horiba Co. Ltd.) specimen was examined using a scanning electron microscope (ESEM XL-30 Series, Philips Co. Ltd.) and an energy dispersive X-ray spectrometer (EDX) installed in the ESEM. The crystalline structure was examined by X-ray diffraction (XRD-6000S, Shimadzu Co. Ltd.), which was performed with Cu $K\alpha$ -ray at a scanning rate of 3 °/min. The Vickers micro-hardness of the composites under a load of 9.807 N was measured using Vickers hardness tester (HVM, Shimadzu Co. Ltd.). The electrical resistivity was measured at room temperature on the polished surface of the specimen ($2 \times 3 \times 14$ mm) using a four-point probe method. The machinability of the composites was examined by EDM (Robocut α -OA, Fanuc Co. Ltd.) with 0.25 mm diameter of Cu wire at a speed of 0.2 mm/min

3. RESULTS AND DISCUSSION

Fig.2 shows the relationships between logarithmic shrinkage ($\log \Delta L/L_0$) and holding time ($\log t$) for the composites prepared by SPS at 1450, 1500 and 1600 °C. A dense composite was obtained by SPS at 1600 °C for 80 s but was not achieved at 1450 or 1500 °C, even when the holding time was 10 min. Kingery et al [11, 12] proposed a linear relation between shrinkage and holding time based on a theoretical consideration during the initial stage of sintering. According to the relationships, the slope k is 0.5 for dissolution-reprecipitation mechanism [11] and the slope k is 1 for viscous flow [12]. From Fig.2, the slopes in the early stage (~ 62 s) of sintering are 0.71, 0.78 and 0.90 at 1450, 1500 and 1600 °C, respectively. This implies that the dominant mechanisms for SPS are a hybrid of dissolution-reprecipitation and viscous flow at 1450 and 1500 °C and viscous flow at 1600 °C.

Fig.2 Relationships between log shrinkage and log holding time.

Fig.3 shows back-scattered electron (BSE) images of the Si_3N_4 -20vol%TiN composites prepared by SPS and Fig.4 shows the EDX analyses of (a) grey region and (b) white region of composite prepared by SPS at 1600 °C. It is found that the grey region is Si_3N_4 (matrix) and white grains are TiN. It was observed in Figs.3(a) and (b) that a black part are pores. Porosity decreased with the increase in sintering temperature. No pores were found in the composites prepared by SPS at temperatures higher than 1550 °C. As shown in Figs. 3(a) and (b), the agglomeration of TiN particles were observed, although there was less agglomeration at 1550 °C (Fig.3(c)). A homogeneous distribution without the agglomeration of TiN particles was achieved by SPS at 1600 °C, while the grain growth of TiN particles was observed (Fig.3 (d)). This is because the sintering mechanism is governed by viscous flow as shown by $k = 0.9$.

Fig.5 shows the relative density and Vickers micro-hardness of Si_3N_4 -20 vol%TiN composites plotted against sintering temperature. The full density was calculated on the basis of the densities of 3.18, 5.44, 4.84 and 3.98 g/cm³ for Si_3N_4 , TiN, Y_2O_3 and Al_2O_3 , respectively. The relative density increased with increasing sintering temperature up to 1550 °C, reaching 98 % at 1550 and 1600 °C. This result corresponds to the microstructure of the composites (Figs. 3(c) and (d)). These findings are in good agreement with the results of Gao et al [7]; dense Si_3N_4 -20 vol%TiN composites were achieved by HP at 1550-1800 °C for 1 h under a compressive stress of 30 MPa. Thus, the total processing time required for SPS was less than that required for HP. This suggests that SPS is an efficient sintering process for consolidating Si_3N_4 -20 vol%TiN powders. The maximum hardness (21.7 GPa) was achieved at 1550 °C. This is because porosity decreases with increasing sintering temperature. However, a slight decrease in hardness was found at 1600 °C. It is thought that not only the growth of TiN particles but also the grain growth of the Si_3N_4 matrix may occur at 1600 °C.

Fig.6 shows XRD patterns of the starting powders and composites prepared by SPS at different temperatures. α - and β - Si_3N_4 phases were present in the as-received Si_3N_4 powder and in the composite sintered at 1450 °C. No α - Si_3N_4 peaks were detected in the composites sintered at higher temperatures (1500-1600 °C), only the β - Si_3N_4 was present in these composites. These findings are in good agreement with the results of Hojo [13], who showed that the complete transformation of α - Si_3N_4 to β -

Fig.3 BSE images of Si_3N_4 -20vol%TiN composites prepared by SPS at different temperatures. (a) 1450 °C, (b) 1500 °C, (c) 1550 °C and (d) 1600 °C.

Si_3N_4 occurs during the dissolution-precipitation process at 1600 °C. No rodlike β - Si_3N_4 was observed in the microstructure (Fig. 3). It is thought that the added TiN particles inhibit the formation of rodlike β - Si_3N_4 .

Fig.7 shows the room temperature DC electrical resistivity of composites prepared by SPS. The electrical resistivity of the composites decreased with the increase in sintering temperature. The composite prepared at 1450 °C ($5 \times 10^{13} \Omega\text{cm}$) had the same order of electrical resistivity as that of monolithic Si_3N_4 . Microstructural factors such as the grain shape and size of the matrix, the distribution and size of TiN particles and the porosity influence the electrical resistivity of the composites. Rodlike β - Si_3N_4 improves the fracture toughness of the composite but increases its electrical resistivity [5]. The electrical resistivity decreases with decreasing matrix

Fig.4 EDX analyses of composite prepared by SPS at 1600 °C. (a) grey region and (b) white region

Fig.5 Relative density and Vickers hardness of Si_3N_4 -20 vol%TiN composites versus sintering temperature.

Fig.6 XRD patterns of the starting powders and composites prepared by SPS at different temperatures.

grain size because electrons flow through the grain boundaries containing TiN particles. The porosity increases the electrical resistivity. The composite prepared by SPS at 1450 °C has many pores and a long TiN-to-TiN distance due to the large amount of agglomeration, resulting in high electrical resistivity. The decrease in electrical resistivity at higher SPS temperatures is attributed to both the reduction of porosity (Fig. 5) and the shorter TiN-to-TiN distance due to the decrease in agglomeration. In SPS at 1600 °C, a homogeneous TiN distribution without the agglomeration was achieved (Fig. 3(d)). As a result, the TiN-to-TiN distance decreased and the electrical resistivity was considerably reduced. The value of electrical resistivity (3.46 Ωcm) of the composite prepared by SPS at 1600 °C is small compared with that of composites obtained by HP (10^9 -order Ωcm , 20 vol%TiN, 1850 °C for 1 h) [4] and GPS (10^3 -order Ωcm , 20 vol%TiN, 1950 °C for 3.5 h) [6], and is equivalent to that of the composite produced by in situ processing (about 2 Ωcm , 20 vol%TiN, in situ direct nitridation + HP at 1650 °C for 1 h) [7].

Fig.7 Electrical resistivity versus sintering temperature of Si_3N_4 -20 vol%TiN composites.

The composites prepared by SPS at 1450 and 1500 °C could not be machined by EDM, while the composites prepared at 1550 and 1600 °C could be machined by EDM. Fig.8 shows an optical micrograph of the composites prepared by SPS at 1450 °C and at 1600 °C after machined by EDM. Liu [4] reported that TiN content higher than 30 vol% must be added to produce the composites with a low electrical resistivity (approximately 10^{-2} Ωcm) to facilitate EDM. In this study, the amount of TiN required for the composite to be machinable by EDM was only 20 vol%. This is because a homogeneous distribution of TiN particles in the matrix was achieved, resulting in a low electrical resistivity

4. CONCLUSIONS

Si_3N_4 with additives (Y_2O_3 and Al_2O_3) and 20 vol%TiN powders were mixed using a planetary ball mill, then subjected to SPS at 1450-1600 °C for 10 min under a compressive stress of 40 MPa. The sintering mechanism for SPS was a hybrid of dissolution-reprecipitation and viscous flow at 1450 and 1500 °C and viscous flow at 1600 °C. At temperatures higher

Fig.8 Optical micrograph of the composites prepared by SPS at (a) 1450 and (b) 1600 °C after machined by EDM.

than 1550 °C, nearly full density (relative density of 98%) was achieved. The Vickers micro-hardness reached a maximum (21.7 GPa) at 1550 °C then decreased slightly when the temperature was increased to 1600 °C. The transformation of α - Si_3N_4 to β - Si_3N_4 occurred at temperatures higher than 1500 °C. A homogeneous distribution without the agglomeration of TiN particles in the Si_3N_4 matrix was achieved by SPS at 1600 °C. The electrical resistivity was related to the microstructure of the composites. The composites prepared by SPS at 1550 and 1600 °C had a low electrical resistivity and could be easily machined by EDM

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