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Spark plasma sintering of titanium nitride in nitrogen: Does it affect the sinterability and the mechanical properties?

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ABSTRACT

Titanium nitride ceramics have an intrinsic interest due to its optical and structural applications. However, the conditions for sintering of dense pieces are not still clarified. This research work is focused on the spark plasma sintering (SPS) of near-fully dense fine-grained TiN. The main goal is giving a response to a longstanding debate: can the external atmosphere favor sintering? Different sintering atmospheres, either vacuum or a nitrogen flow, have been used during SPS heating to this purpose. X ray diffraction analysis has showed the presence of TiN as the main phase with traces of Ti_4O_7 in optimal SPS conditions (1600 °C, one minute dwell time). Our results show that the use of a nitrogen flow while heating can improve sinterability very slightly, but mechanical properties are essentially unaltered within the experimental uncertainty. The hardness reaches values as high as 20GPa whereas fracture toughness can be evaluated around 4 $MPam^{1/2}$.

1. Introduction

Titanium nitride (TiN) is widely accepted as one of the most interesting engineering ceramic materials today. This is due to a large variety of applications in many different fields thanks to its high melting point (3223 K), high thermal conductivity (1.92–2.09 $Jm^{-1}s^{-1}K^{-1}$), low electrical resistivity (10^{-3}–$10^{-4}\,\Omega$ cm) and isotropic expansion coefficient ($9.3 \times 10^{-6}\,K^{-1}$) [1–3]. From a structural point of view, it has only one crystalline phase: this is a fcc structure (NaCl type) in which N atoms partly occupy interstitial sites, leaving the remaining sites vacant. This is the reason why TiN ceramics exhibit both covalent and metallic characteristics depending on the Ti:N ratio. For example, when the Ti:N ratio is more than 1, it exhibits a more metallic character, which diminishes when the N occupancy in the lattice increases [3]. Nowadays, TiN is commonly used in film and coatings (such as cutting tools, solar control films, microelectronic and optical devices) rather than as a monolithic ceramic [4–9]. This is due to its low sinterability and therefore the poor mechanical properties of bulk pieces. This is a consequence of the strong tendency of TiN to oxidize while heating at high temperatures. Nevertheless, consolidation of dense bulk ceramics has been attempted by means of several sintering techniques [10–15]: in one approach, TiN ceramics have been prepared by hot-press at 1850 °C with a relative density ~96% (and a final hardness and fracture toughness of 12 GPa and 3.63 MPa $m^{0.5}$ respectively.) [10]. In another study, bulk TiN was sintered by hot-press with a DC electric field applied directly through a graphite die and punches yielding a maximum relative density equal to 97% at 1750 °C. Therefore, an improved hardness of 20 GPa and toughness of 4.28 MPa $m^{0.5}$ was obtained) [11]. This last study has motivated the use of field-assisted sintering approaches: at this point, Groza et al. have fabricated TiN ceramics (~97% density by assuming at least 10% of Ti_3O_5 in the microstructure) by field-assisted sintering at 1350 °C at 66 MPa under vacuum. A value of hardness of 20 GPa is just reported in this study [12]. Unfortunately, the conditions for optimal fabrication of nanostructured TiN (i.e. the lowest temperatures and stresses) with improved mechanical properties are not well-known: the reported values on the degree of densification are quite scattered and the effect of the use of vacuum or nitrogen atmosphere is unknown. For instance, Kawano et al. found that the use of spark plasma sintering under nitrogen atmosphere at 1600 °C can permit the fabrication of TiN ceramics with a relative density of 98% and enhanced grain growth to 1–2 μm or 10–20 μm depending on starting powders [13]. In another study by Wang et al. titanium nitride nanopowders were sintered by SPS at 1380 °C [14] in vacuum and dense TiN ceramics > 78% with mean grain sizes of 100–150 nm were obtained.

Furthermore, Suárez-Vázquez prepared stoichiometric and non-stoichiometric titanium nitride ceramics by reaction of TiH_2 with TiN in SPS at 1600–1800 °C under vacuum. They showed that the highest relative density remains near 95%, even with temperatures as high as 1800 °C and a dwell-time equal to 20 min. The final average grain size

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was 1.2 μm and the room-temperature mechanical performance had an upper bound of hardness equal to 20.15 GPa and toughness equal to 3.25 MPa $m^{0.5}$. Moreover, the addition of TiH_2 promoted the densification of TiN_{1-x} and also grain growth [15].

This study is focused on the analysis of the optimal conditions to fabricate TiN nanoceramics with near-fully dense ending, with a special emphasis on the role of the external atmosphere during sintering.

2. Experimental procedure

The starting material was a commercially available TiN nanopowder with an average particle size of ~20 nm as indicated by the manufacturer (Plasma Chem GmbH, Germany) with a purity over 97% (%: O < 3; C < 0.1; Fe < 0.02; Si < 0.01). The powders were densified by SPS (Dr. Sinter SPS-515S, Sumitomo Coal Mining Co., Japan) using a single-step cycle at peak temperatures in the range between 1200–1600 °C (as measured by an optical pyrometer focused on die) with heating ramp of 100 °C/min and a uniaxial pressure of 75 MPa (kept constant from the beginning), and one min holding time. Two sets of experiments were conducted: one set comprises experiments made in a dynamic-vacuum atmosphere, whereas the other set corresponds to those made under nitrogen atmosphere; i.e. a flow of nitrogen during sintering. This aim of this strategy is twofold: first, analysis of the possible densification enhancement of TiN under a nitrogen atmosphere, and secondly, the possible elimination of the titanium oxide layer on the surface of the TiN nanopowder during heating. Table 1 lists the specific SPS variables used, with the DC pulse sequence always being 12(on):2(off) with pulses of 3.3 ms. After the completion of the SPS cycle, the electrical power was shut off to allow rapid cooling to room temperature (i.e. in 1–2 min). The flow of nitrogen gas was fixed to 4 l/min in all experiments under nitrogen.

The relative density of the resulting TiN ceramics was measured by the Archimedes method using distilled water as the immersion media. The as-SPSed specimens were ground off and polished to a 1-μm finish using routine ceramographic methods for the microstructural analyses and mechanical tests. The microstructures were characterized using scanning-electron microscopy (SEM; S5200, Hitachi, Japan), X-ray diffractometry (XRD; D8 Advance, Bruker AXS, Germany). The SEM observations were driven by mean of secondary electrons (SE) to infer information on the presence of residual porosity and morphology of grain sizes on polished surfaces that had previously been chemically etched with 46%HF solution at room temperature. SEM observations also were made on fracture surfaces. The XRD patterns were acquired over a wide angular range (15–115°2θ) using pure Cu-Kα_1 incident radiation (λ = 1.5406 Å).

The mechanical characterization was carried out by Vickers-indentation tests (Duramin, Struers A/S, Denmark) under a load (P) of 19.62 N (10 indentations per specimen), under ambient conditions. The hardness and fracture toughness were calculated from the length of the diagonal of the residual impression (a) and the semi-length of the surface trace of the radial cracks (c), using the standard Anstis expressions [16,17].

$$H_v = 2P/a^2$$
$$K_{IC\,(Anstis)} = 0.016(E/H)^{0.5}Pc^{-1.5} \quad (1)$$

A Young's modulus (E) of 550 GPa was used in the calculations of the fracture toughness values [18,19]. However, the modulus increases steadily in the presence of nitrogen to reach values around 640 GPa [18]. This fact can introduce a significant error in the fracture toughness determinations. To skip this potential artifact, the fracture toughness was also calculated by means of the Tanaka equation [20,21].

$$K_{IC\,(Tanaka)} = APc^{-1.5} \quad (2)$$

where A is in the interval from 0.0513 and 0.1018. In most cases, the mean value is adopted: A = 0.0725 (This value is used here). The Tanaka equation is derived from a theoretical calculation of the residual stress field of the elastic/plastic contact applying the internal spherical inclusion model. By contrast, Anstis equation makes use of a semi-empirical calibration factor proportional to $(E/H)^{0.5}$. A comparison between them is provided in [21]. In most cases, the values derived from Anstis equation are within the interval of values permitted by Eq. (2) although more close to the upper bound [21].

It is very important to emphasize that the Vickers hardness technique is a semi-quantitative technique to measure fracture toughness. Taking into account the assumptions made in the formulation of both equations, absolute values of the fracture toughness cannot be determined accurately. However, the method is useful because it gives an estimate and it offers comparative values among specimens tested under the same conditions. A more accurate method such as SEVNB tested in bending configuration is too difficult to implement in this case, because the fabrication of dense specimens of a reproducible microstructure with the dimensions required by international standards is not available by SPS.

3. Results and discussion

3.1. Sintering properties

A XRD pattern of the initial TiN nanopowder is shown in Fig. 1 confirming that this powder is essentially formed by TiN. Titanium oxide phases (at least 3% indicated by manufacturer) were not detected in this pattern. This supports the fact that titanium oxide phases are not crystalline ones and they just increase the background of the pattern and/or the quantity is less than the accuracy of the XRD diffractometer.

XRD analyses of TiN ceramics at different SPS sintering

Table 1
Processing conditions, microstructural features and room-temperature mechanical properties of fine-grained TiN ceramics prepared in this study.

Sample designation	Measured density (g/cm^3)	Relative density (assuming 100%TiN)	Ave. Grain size (nm)	Grain size dispersiom (nm)	Hardness (GPa)	Fracture toughness (MPa$m^{0.5}$) Tanaka formula	Fracture toughness (MPa$m^{0.5}$) Anstis formula
SPS 1600 °C^{-1} min in Vac	5.00	96.0	680	240–1380	18.1 ± 1	4.35 ± 0.20	5.30 ± 0.23
SPS 1600 °C^{-1} min in N_2	5.00	96.0	730	260–1660	20.6 ± 1	4.35 ± 0.26	4.97 ± 0.30
SPS 1500 °C^{-1} min in Vac	4.90	94.0	440	200–870	16.0 ± 1	3.91 ± 0.46	5.05 ± 0.60
SPS 1500 °C^{-1} min in N2	4.96	95.2	445	200–906	18.1 ± 1	4.19 ± 0.49	5.10 ± 0.60
SPS 1400 °C^{-1} min in V	4.86	93.3	330	150–570	–	–	–
SPS 1300 °C^{-1} min in Vac	4.83	92.7	200	100–325	15.2 ± 1	4.10 ± 0.46	5.45 ± 0.61
SPS 1300 °C^{-1} min in N_2	4.85	93.1	192	100–330	15.8 ± 1	4.32 ± 0.35	5.63 ± 0.0.46
SPS 1200 °C^{-1} min in Vac	4.82	92.4	180	100–260	–	–	–