JOURNAL OF MATERIALS SCIENCE LETTERS 14 (1995) 1078–1081

Densification and characteristics of TiN ceramics

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Among the wide range of nitrogen ceramics, such remarkable properties as high melting point ($T = 2940$ °C), extreme hardness and high room-temperature electrical conductivity make TiN an important technological material [1, 2]. Titanium nitride materials find wide use in several areas of industrial applications. In the last ten years, TiN thin films and coatings have been used to improve wear resistance of cutting tools [1, 3]. Further interest has been focused on this material because of its electrical conductivity (as high as that of metals) and superior heat resistance, which make TiN suitable for electrical discharge machining for the production of complex-shaped components [4] and for the production of high-temperature components [5, 6].

Owing to its high melting point and covalent bonding, some difficulties are encountered in achieving fully dense TiN ceramics [7–11].

Additives such as Ni or Co have been shown to play an important role in promoting densification, and cause the precipitation of a second phase at the grain boundary [8]. In the present work the influence of Ni (3 wt %) and Co (3 wt %; 5 wt %) added to pre-treated commercial powder, on sintering behaviour during hot pressing was investigated. Microstructural changes were studied and compared with the additive-free TiN. On selected samples, mechanical properties and electrical conductivity were evaluated and related to the microstructure characteristics.

The as-received commercial TiN powder has a specific surface area of 3.8 m^2/g and a bimodal particle size distribution containing a high percentage of particle with grain size in the range 0.5–10 μm and a small amount of particle aggregates in the range 50–300 μm. The powder was therefore pre-treated by sedimentation and by sieving in order to obtain particles with a controlled size in the range of some micrometres. The grain size of the powder obtained by the sedimentation method was around 2 μm (in the following this TiN powder will be indicated TiN*); the powder treated by sieving showed a grain size lower than ~3 μm. Starting from the pre-treated TiN powder, five batches constituted of TiN*, TiN, mixture of TiN + 3 wt % Ni, TiN + 3 wt % Co and TiN + 5 wt % Co were prepared (Table I).

For hot pressing, peripheral ram clearance and planar pressing faces were sprayed with a BN lubricant to avoid carbon contamination from the graphite furnace. Shrinkage and densification behaviour were evaluated from ram displacements (Fig. 1a, b). The hot pressing cycles were performed in the range 1700–1850 °C with an applied pressure of 30 MPa.

Bulk densities of the dense samples were measured by the Archimedes method. The theoretical density was calculated by the rule of mixtures. Microstructural analyses were performed by X-ray diffraction and scanning electron microscopy, and the composition was assessed by energy dispersive microanalysis. Analyses and tests were carred out on fractured, polished and etched surfaces.

Young's modulus (E) was calculated using a resonant frequency method [12]. Microhardness (H_v) tests were carried out on polished surfaces with a load of 4.91 N and a loading time of 15 s. The flexural strength (σ) was measured on a four-point bending fixture, outer span 26 mm, inner span 13 mm, with a crosshead speed of 0.5 mm/min on bars 30 mm × 3 mm × 3 mm, with the tensile face ground and the edges chamfered. Fracture toughness (K_{Ic}) was measured by the chevron notch technique [13]. Electrical resistivity was measured,

TABLE I Processing parameters, microstructural characteristics and properties of hot pressed samples at $P = 30$ MPa

Sample	T (°C)	t (min)	Density (g/cc)	(%)	Grain size (μm)	E (GPa)	σ (MPa)	K_{Ic} (MPa $m^{1/2}$)	$H_v0.5$ (GPa)	α (10^{-6}/°C)	ρ (Ωcm) · 10^{-5}
TiN*	1850	30	5.07	93.9	2.56	402	431 ± 24	3.63 ± 0.16	12.1 ± 0.3	8.86	2.00
TiN	1850	30	5.18	96.0	3.10	436	383 ± 41	2.78 ± 0.08	11.7 ± 0.4	8.92	2.30
TiN + 3 wt % Ni	1850	10	5.16	94.5	1.70	404	471 ± 72	6.79 ± 0.74	9.5 ± 0.4	8.79	2.29
TiN + 3 wt % Co	1800	20	5.18	95.0	2.00	406	511 ± 23	5.30 ± 0.09	9.9 ± 0.5	8.79	2.28
TiN + 5 wt % Co	1700	20	5.30	96.2	2.81	394	571 ± 10	5.67 ± 0.05	9.9 ± 0.5	9.24	2.36

TiN*: starting powder pre-treated by sedimentation method; TiN: starting powder pre-treated by sieving;
E: Young's modulus; σ: flexural strength; K_{Ic}: fracture toughness; H_v: Vickers hardness;
α: thermal expansion coefficient (20–1000 °C); ρ: electrical resistivity

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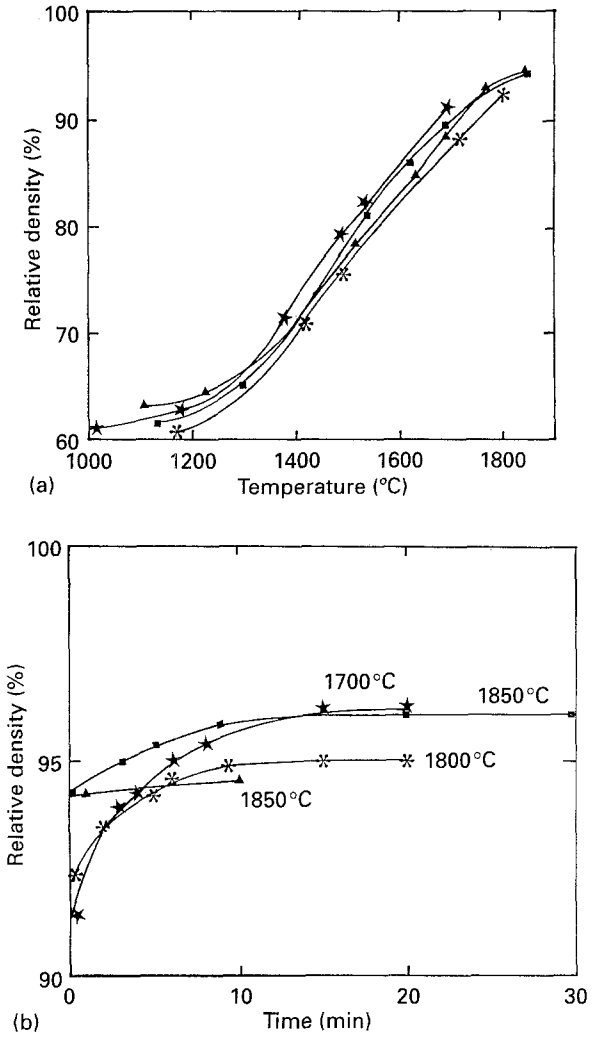

Figure 1 Densification behaviour as a function of temperature (a) and time (b) during hot pressing at 30 MPa: ■ TiN; ▲ TiN-3 wt % Ni; * TiN-3 wt % Co; × TiN-5 wt % Co.

at room temperature, by a four-linear-probes method, with a distance between the contact points of 3.78 mm. The thermal expansion was investigated in the range 20–1000 °C with a heating rate of 5 °C/min.

Table I reports experimental data and processing parameters for the hot pressed samples. The densification behaviour related to the hot pressing parameters (temperature and time) for all specimens are shown in Fig. 1a, b. The difference in densification between TiN* and TiN is presumably due to the lower amount of oxygen in TiN* (the oxygen contents, measured by infrared absorption, are 0.90 wt % and 1.15 wt % for TiN* and TiN, respectively) according to previous results on the effects of oxygen impurities on sintering behaviour [2, 11, 14, 15].

Fig. 1a, b show a significant shrinkage attributable to a sintering mechanism controlled by volume diffusion which should allow matter transport from the grain boundaries to the neck regions [16]. The addition of different quantities of metal dopant such as Ni or Co contributes to reducing the grain size in all the dense specimens owing to the reduced sintering time. This follows from the consequent enhanced volume diffusion, as the self-diffusion coefficient is—in the assumed analytical relation proposed by Kingery and Berg [17]—strictly dependent on the radius of the particles [2].

In the case of Co addition, dense products have been obtained at lower temperature (Table I). This is due to some liquid phase formation during eutectic reaction between Co and TiN. In spite of the addition of Ni or Co, the final densities do not exceed 96%. It can be hypothesized that partial solution of Co and Ni into TiN limits the wettability between the metal and the titanium nitride. As previously reported [11] when the wetting of the solid by the liquid is incomplete, then some contact exists among the solid particles rather than the achievement of a complete dispersion in the liquid, and as a consequence a skeleton is formed. If this skeleton occurs early in the sintering process then densification can be limited. Microstructure changes with the sintering temperature, time and composition are shown in Figs 2, 3 and 4a, b for TiN, TiN-3 wt % Ni, TiN-3 wt % Co and TiN-5 wt % Co compositions. The large number of pores enclosed within grains, some defects and cracks could be related to the initial fast densification, which leads to the trapping of pores in the grains [11]. Moreover the addition of 5 wt % of Co causes areas of enhanced grain growth.

By X-ray analyses only cubic TiN and traces of the metallic additives have been detected for TiN-3 wt % Ni and TiN-3 wt % Co compositions. In the case of TiN doped with 5 wt % of Co, some peaks were attributed to an intermediate phase such as $Co_{0.3}Ti_{0.7}Ni$. Fig. 5 (white areas) shows an irregular distribution of this intergranular phase. X-ray spectra give evidence of a slight orientation for the basal plane (220) of TiN, owing to the stress applied during hot pressing (30 MPa).

Thermal, mechanical and electrical characteristics are shown in Table I. The discrepancy between

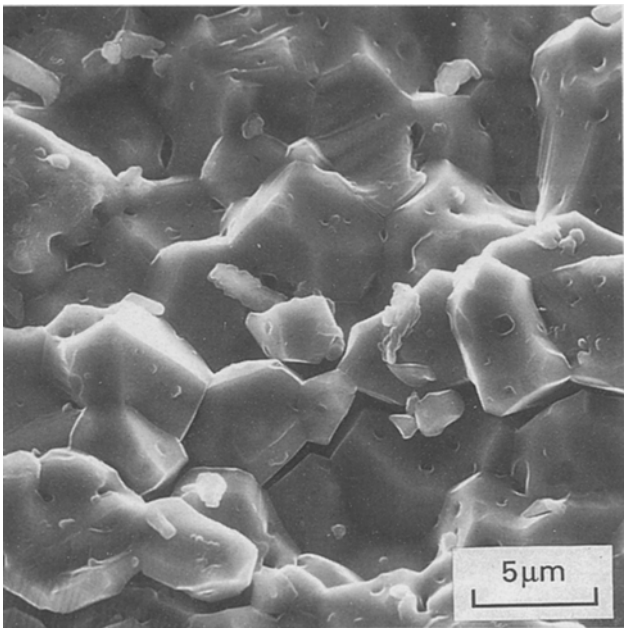

Figure 2 SEM morphology of fracture surface of monolithic TiN hot pressed at 1850 °C for 30 min at 30 MPa.

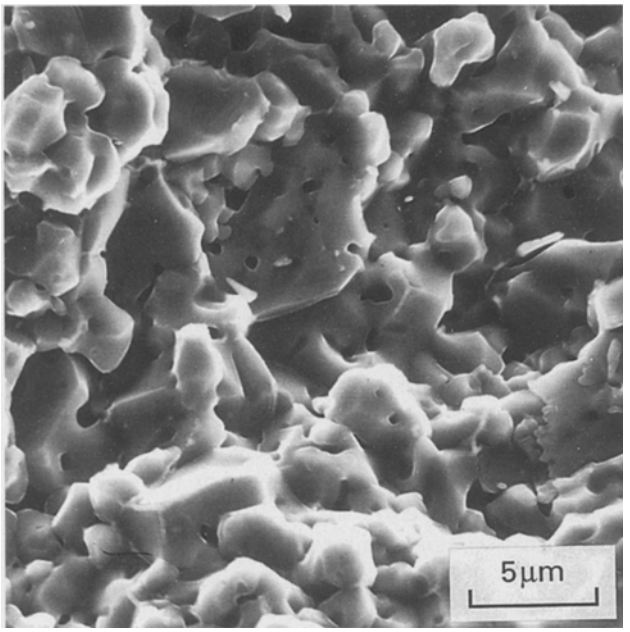

Figure 3 Fracture surface of TiN-3 wt % Ni hot pressed at 1850 °C for 10 min at 30 MPa.

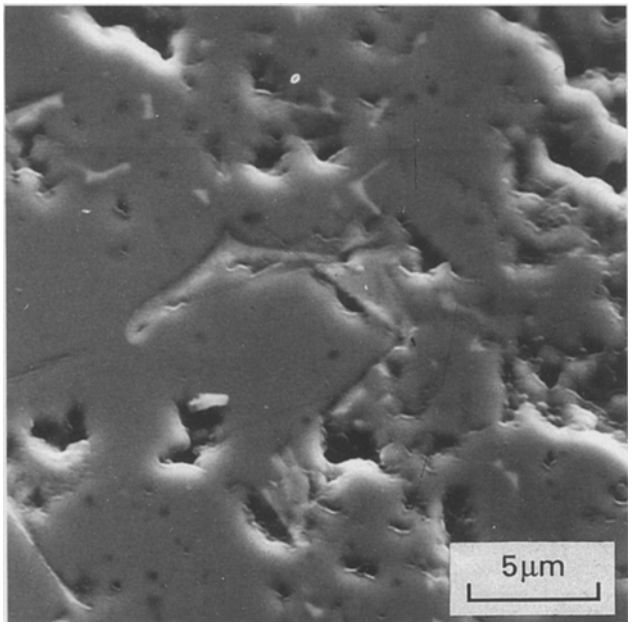

Figure 5 Polished surface of TiN-5 wt % Co composition hot pressed at 1700 °C for 20 min at 30 MPa.

Young's modulus values of TiN* and TiN are mainly related to the residual porosity and to the presence of some cracks. The addition of 5 wt % of Co depresses Young's modulus, maybe owing to the presence of areas of microstructural defects: irregular grain growth and the presence of cracks. With regard to flexural strength and fracture toughness, the low values of the undoped TiN sample are related to the presence of microcracks. In the case of Ni or Co-doped specimens, strength and toughness are strongly improved. These values are higher than the data reported in the literature [18], also extrapolated to the level of the theoretical density. This improvement can be attributed to the reduction of critical defects and the reduced mean grain size. The addition of Ni or Co lowers the microhardness values which are, anyway, in agreement with those found in the literature for hot pressed TiN without sintering aids [18].

The presence of the metal dopants in amount of 3 wt % shows no significant influence on the thermal expansion values; the composition with higher content of Co (5 wt %) has a higher thermal expansion. The electrical resistivity measurements are not affected by the metallic additions and are lower than the values reported in the literature for undoped TiN ceramics [18].

From the experimental results, the following conclusions can be drawn. The sintering behaviour is affected by the amount of oxygen in the starting

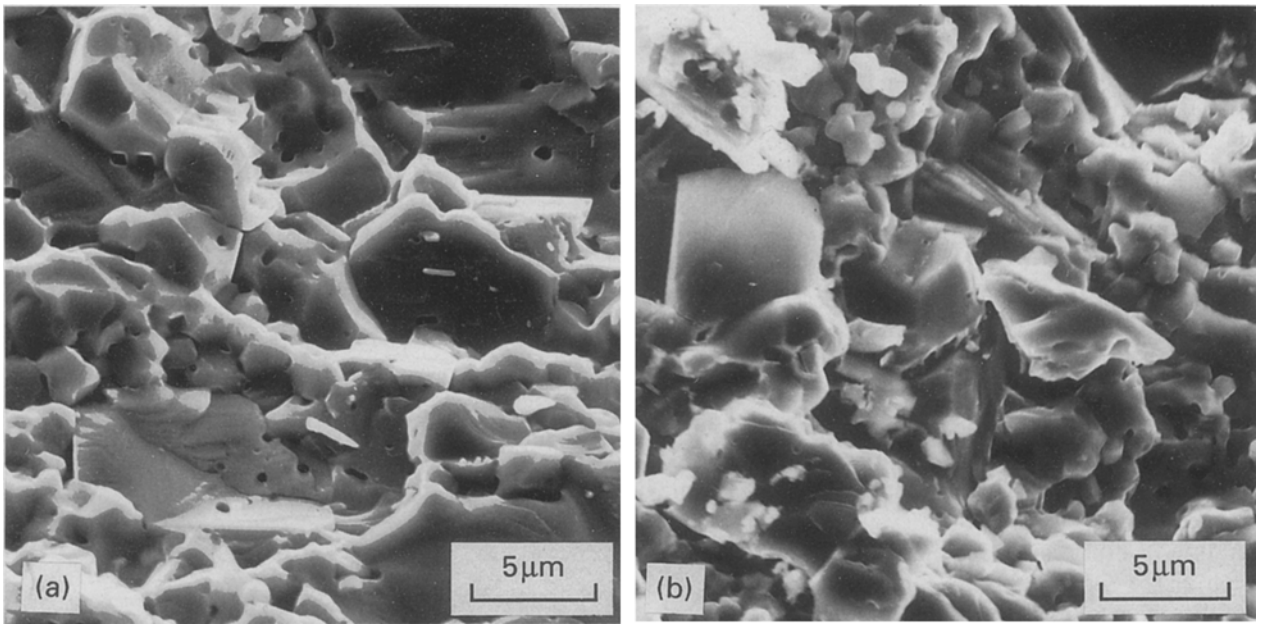

Figure 4 Fracture surface of (a) TiN-3 wt % Co hot pressed at 1800 °C for 20 min at 30 MPa; (b) TiN-5 wt % Co hot pressed at 1700 °C for 20 min at 30 MPa.

powder, and type and content of metal dopants. Ni and Co additions (3 wt %, 5 wt %) allow TiN to densify at lower temperature and in a reduced sintering time. As a consequence they strongly affect the microstructure of the sintered samples, which show a reduced grain size in comparison with additive-free TiN. The positive effect of Ni and Co addition is, moreover, confirmed by the increased values of flexural strength and fracture toughness.

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Received 1 November 1994
and accepted 8 February 1995