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# Synthesis of $TiC_{1-x}N_x$ and $TaC_{1-x}N_x$ by spark plasma sintering

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Titanium and tantalum carbonitrides are materials with many interesting properties such as high melting point, good wear resistance, high hardness and high electrical- and thermal conductivity. They have found use as the hard phase in sintered hardmetals and ceramic composites and also as protective coatings on hardmetal substrates. Due to excellent high-temperature strength and good corrosion resistance, they can also be used as high temperature structural materials. Tantalum carbide as well as several other transition metal carbides and nitrides have also been reported to be highly active catalytic materials [1–4].

Transition metal carbonitrides can be produced by several methods from solid, liquid and gaseous state. They can be synthesized as thin films, whiskers, and as bulk materials. The most common synthesis methods are self-propagating high-temperature combustion synthesis (SHS), ion beam assisted deposition (IBAD), carbothermal reduction, plasma enhanced chemical vapor deposition (PECVD), plasma vapor deposition (PVD), chemical vapor deposition (CVD), and high pressure sintering (in HIP furnaces) [3, 5–11].

The aim of this work was to prepare titanium and tantalum carbonitrides ($TiC_{1-x}N_x$ and $TaC_{1-x}N_x$) using the spark plasma sintering (SPS) technique starting with TiC, TiN, TaC, and TaN with no additional sintering aids.

The following starting materials were used: TiC [H. C. Starch GmbH & Co (Germany), grain size $<3$ $\mu$m, purity 99.5%], TaC [ABCR (Germany), grains size $<5$ $\mu$m, purity 99.5%], TiN [Tioxide Chemicals (England), grain size $<0.4$ $\mu$m, purity 99.5%], and TaN [Aldrich Chemical Company, Inc. (U.S.A.), grains size $<5$ $\mu$m, purity 99.5%]. Homogeneous mixtures of the starting powders for preparing $TiC_{1-x}N_x$ and $TaC_{1-x}N_x$ were made in 2-propanol using a planetary mill at a speed of 2000 rev/min for 10 min (Fritsch pulverisette, Germany) with WC milling bodies.

A Dr. Sinter 2050 SPS apparatus (Sumitomo Coal Mining Co., Japan) was used for sintering. Samples of 12 mm in diameter and 4 mm in height were prepared in vacuum under uniaxial mechanical pressure applied from the start of the experiments. The temperature was measured with an optical pyrometer focused on the surface of the graphite die and automatically regulated from 600 °C, once that temperature was reached *via* a pre-set heating program. The reactions took place at 1700 or 1800 °C for 10 min at 50, 75 or 80 MPa. The heating rate from 600 °C up to the plateau was 100 °C/min.

Densities were determined by use of a helium pycnometer (Micromeritics, AccuPyc 1330, U.S.A.). The densities of the sintered compacts where compared to tabulated values for the end compositions assuming a linear dependence.

Unit cell parameters were determined from X-ray powder diffraction patterns recorded with a Huber Imaging Plate Guinier Camera 670 (Huber Diffraktionstechnik GmbH, Germany) and a Guinier-Hägg focusing camera using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.540598$ Å). Si ($a = 5.430879$ Å at 25 °C) was added as an internal standard. The unit cell data was compared with a linear relation from the published data for the end compositions TiC (PDF 32-1383), TiN (PDF 38-1420), TaC (PDF 35-0801), and TaN (PDF 32-1283).

Grain size and porosity of sintered compacts were investigated on polished and fractured surfaces in a scanning electron microscope (SEM), Jeol 820, operated at 10 kV in backscattered electron (BSE) mode and at 20 kV in secondary electron (SE) mode. Electron diffraction (ED) patterns were obtained in a transmission electron microscope (TEM) Jeol 2000FX operating at 200 kV. Chemical analyses of C, O, and N were made with standard combustion techniques.

For sintering the $TiC_{1-x}N_x$ samples one series was prepared at 1700 °C for 10 min with an applied pressure

TABLE I $TiC_{1-x}N_x$ sintered at 1700 °C for 10 min. The applied pressures were 50 MPa and 80 MPa respectively

| | 50 MPa | | | 80 MPa | | |
|---|---|---|---|---|---|---|
| $x$-value | Density (g/cm$^3$) | Relative density (%) | $a$-axis (Å) | Density (g/cm$^3$) | Relative density (%) | $a$-axis (Å) |
| 0 | 4.91(1) | 100.0 | 4.3260(2) | 4.88(1) | 99.3 | 4.3249(5) |
| 0.2 | 4.90(1) | 97.8 | 4.3094(4) | 4.91(1) | 98.1 | 4.3080(4) |
| 0.4 | 4.92(1) | 96.5 | 4.2911(3) | 4.98(1) | 97.5 | 4.2918(3) |
| 0.5 | 5.02(1) | 97.4 | 4.2855(5) | 5.06(1) | 98.2 | 4.2838(12) |
| 0.6 | 5.02(1) | 96.6 | 4.2782(6) | 5.07(1) | 97.6 | 4.2764(4) |
| 0.8 | 5.18(1) | 97.8 | 4.2595(2) | 5.14(1) | 97.1 | 4.2599(3) |
| 1 | 5.27(1) | 97.8 | 4.2362(6) | 5.22(1) | 96.9 | 4.2360(7) |

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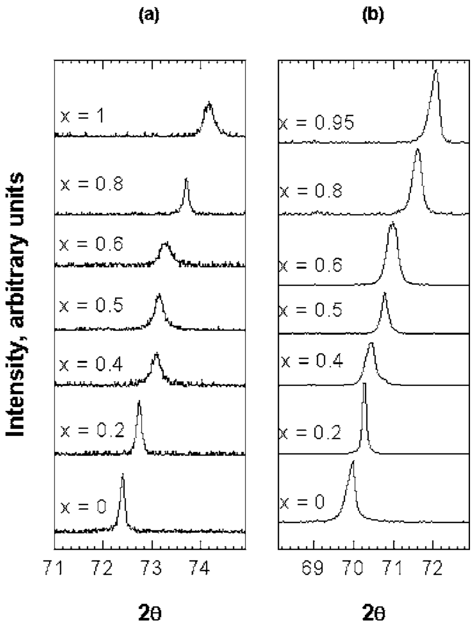


*Figure 1* The change in the $2\theta$ position as a function of the $x$-value for the (311) diffraction peak for (a) the $TiC_{1-x}N_x$ samples prepared at 1700 °C, 50 Mpa. (b) The $TaC_{1-x}N_x$ samples prepared at 1700 °C, 75 MPa.

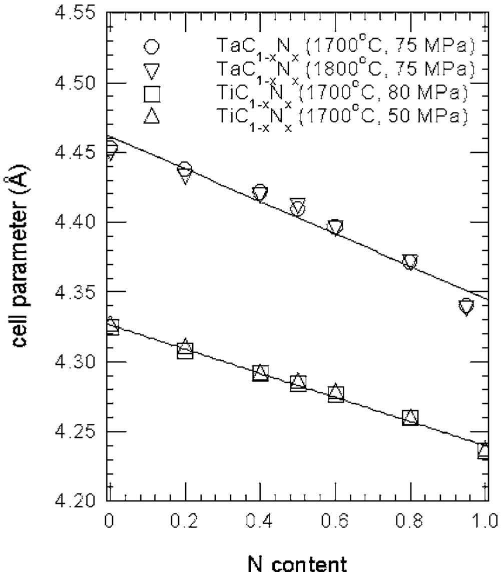


*Figure 2* The unit cell parameter for the two sintering series of $TiC_{1-x}N_x$ and the two series of $TaC_{1-x}N_x$ in comparison with Vegard's law.

of 50 MPa and a second series with 80 MPa applied from start, see Table I. Attempts were also made to apply the pressure only from at 1400 °C, but the final density was then found to be low due to the formation of a sintered rim that entrapped porosity in the samples.

The different experimental series where fully reacted revealing sharp diffraction peaks of the intended solid solution composition with no diffraction peaks from the starting materials. The shift of the (311) peak depending on the composition is shown in Fig. 1a. It was found that $TiC_{1-x}N_x$ follows Vegard's law for the unit cell parameter, see Fig. 2. The Vegard's law behavior of the solid solution $TiC_{1-x}N_x$ is well known [6, 11].

The starting temperature for sintering decreases with increasing nitrogen content and was found to be 1180 °C for pure titanium carbide and 940 °C for pure titanium nitride. All $TiC_{1-x}N_x$ samples fractured intergranularly. The highest densities were observed for low $x$-values. The higher the nitrogen content the lower the final density, see Table I. Two types of porosity were observed. For low $x$-values small pores were observed within the grains. A possible explanation for the porosity in the carbon rich samples is that the surfaces of the starting powders could have been partly oxidized yielding CO(g) during sintering. During sintering a rapid grain growth then takes place and gas pores are entrapped in the grains, see Fig. 3a. At higher $x$-values the porosity gradually changes to be mainly concentrated at the grain boundaries, see Fig. 3b. The measured densities (96–100%) were as high as obtained at 8 GPa/1700 °C by hot-pressing [9].

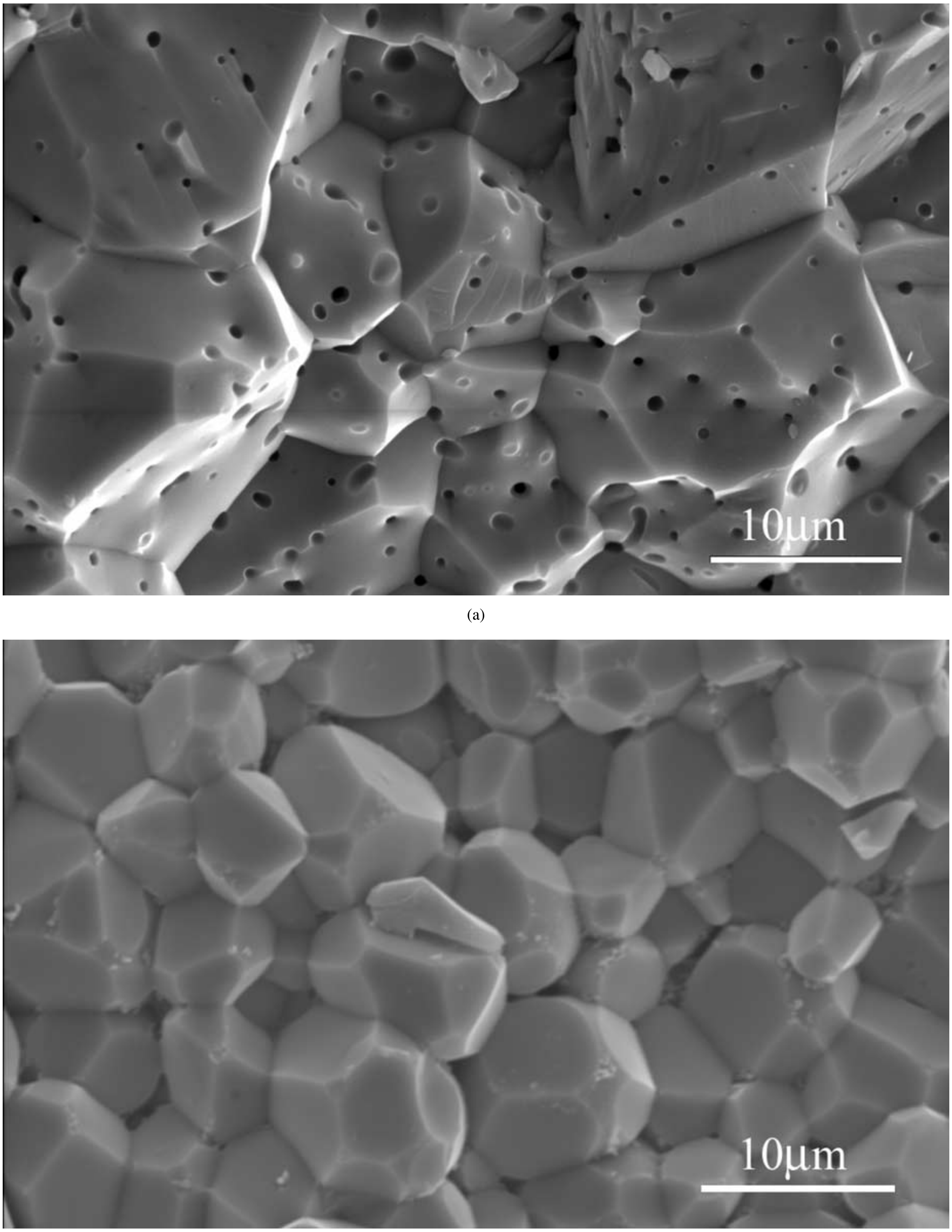
Two series of $TaC_{1-x}N_x$ samples were prepared, one at 1700 and one at 1800 °C for 10 min with an applied pressure of 75 MPa. The sintering of tantalum carbonitrides starts at approximately 1200 °C. There is no clear change in sintering temperature as a function composition. In the pure tantalum carbide there was very limited grain growth. In this sample also an open porosity is observed, see Fig. 4a.

All samples in the two $TaC_{1-x}N_x$ series were fully reacted revealing sharp diffraction peaks and no remaining diffraction peaks from the starting materials were observed. The shift of the (311) peak as a function of composition is shown in Fig. 1b. It was found that the unit cell parameter for $TaC_{1-x}N_x$ follows Vegard's law, see Fig. 2. Chemical analysis shows that some oxygen is present and that it increases with increasing nitrogen

TABLE II $TaC_{1-x}N_x$ sintered at 1700 °C and 1800 °C for 10 min. The applied pressure was 75 MPa

| | 1700 °C | | | 1800 °C | | |
|---|---|---|---|---|---|---|
| $x$-value | Density (g/cm$^3$) | Relative density (%) | $a$-axis (Å) | Density (g/cm$^3$) | Relative density (%) | $a$-axis (Å) |
| 0 | 14.40(1) | 99.4 | 4.4526(2) | 14.17(1) | 97.7 | 4.4511(9) |
| 0.2 | 14.08(1) | 95.2 | 4.4377(23) | 14.03(1) | 94.9 | 4.4338(3) |
| 0.4 | 14.64(1) | 97.1 | 4.4213(23) | 14.63(1) | 97.0 | 4.4207(3) |
| 0.5 | 14.65(1) | 96.2 | 4.4088(10) | 14.65(1) | 96.2 | 4.4125(4) |
| 0.6 | 14.59(1) | 94.9 | 4.3967(1) | 14.59(1) | 95.0 | 4.3972(4) |
| 0.8 | 14.39(2) | 91.9 | 4.3708(10) | 14.39(2) | 91.9 | 4.3726(67) |
| 0.95[a] | 14.29(1) | 90.0 | 4.3399(17) | 14.25(1) | 89.8 | 4.3399(2) |

[a] The applied pressure was 100 MPa.



(a)

(b)

*Figure 3* SEM micrograph of (a) $TiC_{0.8}N_{0.2}$ showing entrapped porosity in the grains. (b) $TiC_{0.2}N_{0.8}$ showing porosity mainly in the grain boundaries.

content, see Table III. The presence of oxygen in the samples is also indicated by the ED-TEM studies that revealed traces of an impurity phase with a TTB related structure. This structure is very common among tantalum oxides.

The $TaC_{1-x}N_x$ samples fractured both transgranularly and intergranularly, see Fig. 4b. No entrapped

TABLE III Chemical analysis of $TaC_{1-x}N_x$ sintered at 1700 °C/75 MPa for 10 min

| | $x = 0.2$ | $x = 0.4$ | $x = 0.5$ | $x = 0.6$ | $x = 0.8$ |
|---|---|---|---|---|---|
| C (wt%) | 4.77 | 3.69 | 3.09 | 2.44 | 1.2 |
| O (wt%) | 0.09 | 0.14 | 0.15 | 0.2 | 0.27 |
| N (wt%) | 0.99 | 2.47 | 3.26 | 3.9 | 5.46 |

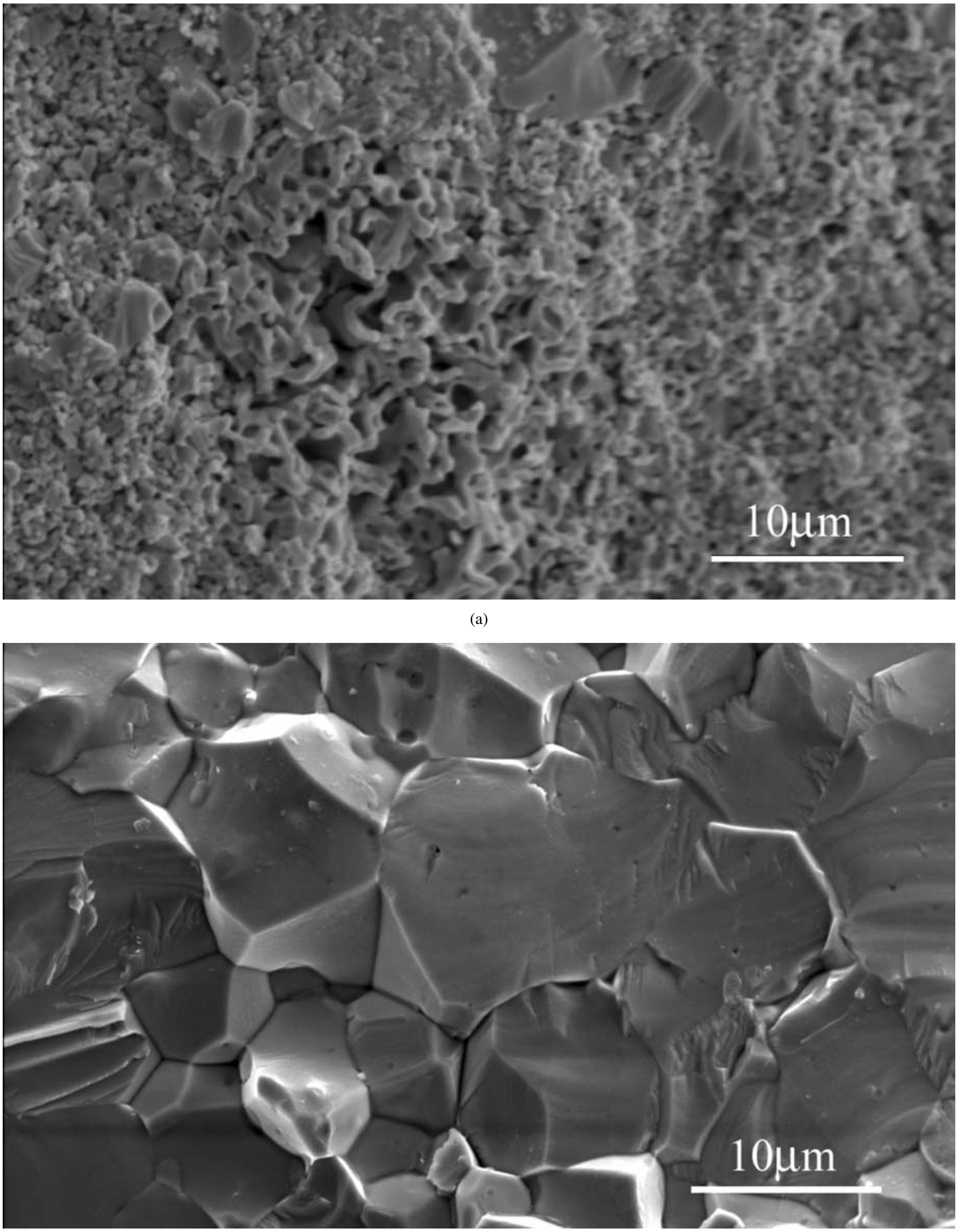


*Figure 4* SEM micrograph of (a) TaC showing some open porosity. (b) $TaC_{0.5}N_{0.5}$ showing both transgranular and intergranular fracture. The porosity is concentrated on the grain boundaries.

pores were observed inside the grains. The relative density decreases with increasing $x$-value, see Table II, thus showing the same tendency as for $TiC_{1-x}N_x$.

The results show that the SPS technique allow rapid synthesis of $TiC_{1-x}N_x$ and $TaC_{1-x}N_x$ solid solutions resulting in highly dense and stoichiometric compacts.

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