

# Compaction of Titanium Carbonitride powder samples of various C/N ratio by Spark-Plasma-Sintering (SPS) and by conventional hot-pressing

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## Abstract

Several Spark-Plasma-Sintering (SPS) compaction experiments of nanostructured and conventional titanium carbonitride powders of various stoichiometric composition (C/N ratio) have been performed at different sintering conditions. The nanostructured samples have been synthesized by ultra-rapid condensation from the gas phase in a high frequency plasma. The results were compared with data obtained by different conventional sintering techniques e.g. pressureless sintering, gas pressure sintering, and hot pressing. The phase composition and the crystallite size of the compacted samples were investigated by X-ray diffraction (XRD). The fracture surface was inspected by scanning electron microscopy (SEM). The capability of the SPS method to obtain a high sintering density combined with a reduced grain growth was evaluated.

## 1. Introduction

Cemented carbides with titanium carbonitride as an additive have several potential advantages compared with conventional tungsten carbide based materials especially for the production of cutting tools. For this purpose an increased hardness, a high wear resistance, and a high resistance against the decomposition of the cutting edge is of big importance. The addition of nanodispersed titanium carbonitride powders to the WC-Co cermets can cause a finer structure in these materials and therefore enhance these properties. The characteristics of the Ti(C,N) cermet compounds are detailed discussed in Ref. [1].

The general problem of obtaining fully dense nanostructured bulk materials is of essential significance in various fields of materials engineering due to their special physical parameter. Aim of this study is the investigation of the sintering process of nanostructured titanium carbonitride samples of various chemical composition by means of the spark-plasma-sintering method and to compare the results with data obtained using the conventional hot pressing sintering technique.

The spark-plasma-sintering method can be roughly compared with the conventional hot press. Additionally a pulsed electric current is applied directly to the graphite mold. The SPS method comprises three main mechanisms of action: a) the application of uniaxial pressure, b) the application of pulsed voltage, and c) the resistance heating of graphite dies and sample. Nevertheless, an exact interpretation of the microscopic effect of the SPS has not been achieved. A description of this method and its related modifications including a summary of the historical developments has been given in Ref. [2].

Sintering experiments by means of the SPS method with the very close related compound nanostructured titanium nitride were already performed [3]. A study dealing with the synthesis and sintering behaviour of titanium nitride can be found in [4] and [5].

### **Experimental procedure**

Several titanium carbonitride nanopowder samples from the producer Plasma Ceramics Technologies Inc. (PCT) in Riga, Latvia with various chemical compositions were used for the compaction experiments. These samples were synthesized by ultra-rapid condensation from the gas phase as described in [6]. The evaporation of the raw materials was performed by means of an inductively coupled radio frequency plasma of 5.28 MHz (generator power 65-80 kW). The synthesis experiments were performed using nitrogen as a plasma forming gas (flow rate 7-8 m<sup>3</sup> h<sup>-1</sup>), various gaseous hydrocarbons as methane, propane or butane, and metallic titanium as a raw powder. The chemical composition and homogeneity and the grain size distribution of the products is specifically influenced by the adjustment of the synthesis parameter. Additionally a Ti(C<sub>0.5</sub>N<sub>0.5</sub>) powder from Nanostructured & Amorphous Materials Inc. (N&AM) in Los Alamos, USA, which was prepared by plasma assisted chemical vapour deposition, and conventional microstructured carbonitride powders (samples St70/30C and St30/70B) of H.C.Starck G.m.b.H., Germany with the nominal composition Ti(C<sub>0.7</sub>N<sub>0.3</sub>) and Ti(C<sub>0.3</sub>N<sub>0.7</sub>) were examined for the purpose of comparison.

The spark-plasma-sintering-experiments were performed using an SPS-1050 apparatus (Sumitomo Coal Mining, Japan). About 2 g of the original powders were loaded without adding any pressure aids in a graphite die (15mm diameter) and punch unit. During the beginning of the sintering experiment the gas pressure (air) in the apparatus was in the range of several Pa. During the sintering process the pressure increases to 300 Pa while reaching maximum temperature. The mechanic pressure applied at the punch unit reached a maximum of 20 to 30 MPa. The used electric current was typically 1350A at 1600°C and 1650A at 1800°C. The corresponding voltage has been between 4 and 6 V, respectively. The electric current was pulsed periodically with 14 pulses /sec (2 of 14 pulses off as a recovery time). The temperature was measured by means of a pyrometer on the surface of the graphite die cylinder. The parameters voltage, current, temperature of the graphite die, mechanic force on the graphite punch, and position and displacement of the punch were recorded during the experiment. The heating rate was at 100°C/min, the holding time was 1 min.

The conventional hot pressing experiments were performed with an inductive heated hot pressing device temperature range from 1600°C to 1800°C, dwelling time 60 min and a uniaxial pressure of 30 MPa under atmospheric pressure of 1-10 Pa. The temperature was also measured by means of a pyrometer.

### **Characterization**

The determination of the density of the compacted samples was performed using Archimedes method in absolute ethanol and in distilled water. The micrograph of the uncompacted nanopowder was obtained with a transmission electron microscope (TEM) CM 20 (Philips, Netherlands) using an acceleration voltage of 200 kV.

The phase characterisation of the samples and the subsequent crystallite size determination by means of X-ray powder diffractometry (XRD) were performed using an Philips X'Pert Powder diffractometer using Copper K $\alpha_{1,2}$  radiation at 40 kV and 40 mA. This instrument is equipped with an automatic divergence slit, a sample spinner, a diffracted beam curved graphite monochromator, and a scintillation counter. A receiving slit of 0.1 mm (= 0.033° 2 $\theta$ ) and an antiscatter slit of 4° was selected. On both sides of the sample sollar slits (0.04 rad) were inserted. The measurements were performed in step-scan mode over the range 5 – 85 ° 2 $\theta$  with a step size of 0.02° and a counting time of 3 s/step.

The crystallite size determination was carried out using Scherrer's formula in the form  $d = K \cdot \lambda / (B-b) \cdot \cos \theta$ , where  $d$  denotes the average crystallite size,  $K$  is the shape factor (normally between 0.9 and 1),  $\lambda = 1.54056 \text{ \AA}$ , is the wavelength of the used copper radiation,  $B$  is the peak width (FWHM or integral breadth),  $b = 0.08^\circ 2\theta$  is the instrumental standard profile width, and  $\theta$  denotes the diffracting angle. For the determination of the crystallite size the main titanium carbonitride diffraction peaks at  $36.5^\circ 2\theta$  (1 1 1),  $42.2^\circ 2\theta$  (2 0 0), and  $61.2^\circ 2\theta$  (2 2 0) were applied.

The chemical analysis of the samples was performed by quantitative IR-absorption method in a LECO-device. The specific surface area was determined by the BET adsorption-desorption method.

## Results and discussion

In figure 1 transmission electron microscopy (TEM) micrographs of the pristine nanopowder PCT7 and N&AM are shown. The main components in the PCT samples are idiomorph cubic shaped particles. The diameter of these particles varies between 25 and 100 nm. Regardless of their various chemical composition all these products differ only slightly in their fine-grained areas. In contrast the N&AM powder consists of globular shaped particles.

Analytical data of various carbonitride powders are given in table 1. In figure 2 the diffractograms of the samples PCT 1, 2, 5, and 7 and N&AM are shown. The shape of the diffraction maxima indicates a non-homogenous chemical composition. Samples PCT 1 and PCT 2 display a "shoulder" towards the higher  $2\theta$  angle which suggests a minor amount of a more nitrogen rich phase. The samples PCT 5 and 7 seem to be composed of two separate components with a different chemical composition. Therefore the determination of the crystallite size of the pristine powders is complicated by the chemical inhomogeneity of the samples. At powder PCT 1, which seems most homogeneous, a crystallite size of  $\approx 40$  nm can be deduced. During the sintering process the FWHM of the diffraction maxima is decreasing rapidly and no chemical inhomogeneity is observed (diagrams not shown here). This can be explained by crystal-growth combined with chemical homogenisation. The crystallite sizes given in tables 2 and 3 can be easily calculated from these data.

The recorded displacement velocity of the graphite punch ( $dx/dt$ ) plotted as a function of the measured temperature represents a good characterisation of the sintering behaviour of a sample. In figure 3  $dx/dt$  is plotted vs. temperature for several SPS and conventional HP experiments. The HP experiments display a broad variance: the temperature of the maximum shift of the punch, which corresponds with the sintering process ranges from  $1190^\circ\text{C}$  (N&AM, nanostructured) to  $1560^\circ\text{C}$  (PCT 7) and  $1720^\circ\text{C}$  (PCT 1). The conventional powder samples fit between these borders:  $1430^\circ\text{C}$  (St70/30C) and  $1470^\circ\text{C}$  (St30/70B). Additionally some of the curves show a bimodal broadening of the sintering maximum, which can be explained by the chemical inhomogeneity of these samples.

The SPS sintering experiments display the maximum of sintering activity shifted to lower temperatures (around  $1400^\circ\text{C}$ ) both the nanostructured sample PCT 7 and the conventional powder St70/30C. Additionally there is no significant bimodal broadening of the maximum of  $dx/dt$ , homogenous sintering is observed.

It is not clear if this effect is induced only by the specific sintering mechanism of the SPS process or if it is also influenced by the different heating conditions.

The sintering densities of the SPS and HP compaction experiments and some crystallite size values (as obtained by XRD) are given in tables 2 and 3.

The SPS results show that a bigger sintering density is correlated with an increased grain growth. In addition it can be concluded, that the SPS process is capable to produce samples with somewhat smaller crystallite size in comparison with conventional hot pressing if similar sintering densities are considered.

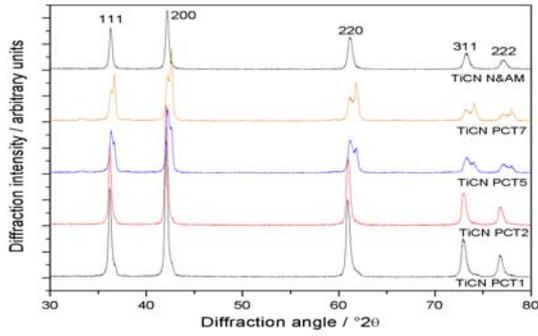


Figure 2: XRD diffractograms between 30° and 80°2θ for the pristine titanium carbonitride samples obtained by plasmachemical synthesis. The crystallographic indices of the diffraction maxima are given. The position of the diffraction maxima shows a minor variation in the overall chemical composition. The shape of the diffraction maxima is caused by chemical inhomogeneity and by particle size distribution.

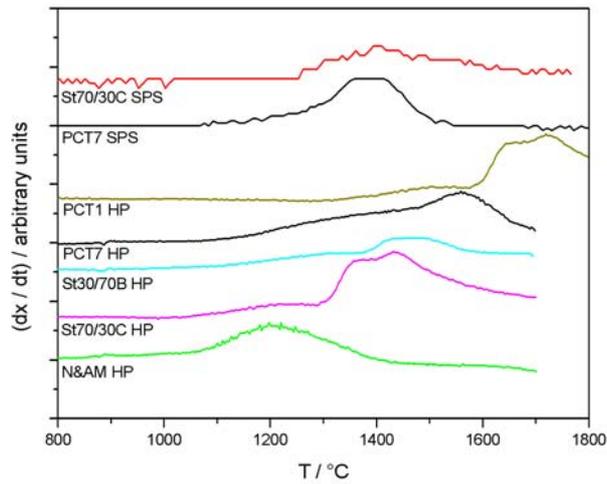


Figure 3: displacement velocity of the lower punch during the SPS and the conventional HP experiments shown as a function of the measured temperature (sample designation and compaction method is indicated).

sample designation	Chemical analysis				SSA m <sup>2</sup> /g	formula	C/(C+N)
	C <sub>total</sub> wt. %	C <sub>free</sub> wt. %	N wt. %	O wt. %			
PCT 1	13.5	0.8	7.9	2.1	29.1	Ti(C <sub>0.66</sub> N <sub>0.35</sub> )	0.65
PCT 2	14.0	n.d.	7.8	1.6	n.d.	Ti(C <sub>0.73</sub> N <sub>0.35</sub> )	0.66
PCT 4	8.1	0.6	10.2	3.0	32	Ti(C <sub>0.38</sub> N <sub>0.44</sub> )	0.46
PCT 5	6.7	0.3	15.6	3.5	33	Ti(C <sub>0.34</sub> N <sub>0.72</sub> )	0.32
PCT 6	4.4	n.d.	17.1	n.d.	38.5	Ti(C <sub>0.22</sub> N <sub>0.74</sub> )	0.23
PCT 7	5.9	0.9	16.5	2.8	34.4	Ti(C <sub>0.27</sub> N <sub>0.75</sub> )	0.26
N&AM	9.0	0.5	10.6	4.4	21.1	Ti(C <sub>0.44</sub> N <sub>0.47</sub> )	0.48
St30/70B	5.6- 6.6	<0.05	14-15	<1.0	n.d.	Ti(C <sub>0.30</sub> N <sub>0.70</sub> )	0.30
St70/30C	13-14	<0.05	6.8- 7.8	<1.5	n.d.	Ti(C <sub>0.70</sub> N <sub>0.30</sub> )	0.70

Table 1: chemical composition of various titanium carbonitride samples

Regardless of the higher sintering density (HP) of the samples PCT 4 and N&AM (with similar  $C/(C+N) \approx 0.5$ ) the sintering behaviour with hot pressing of the carbonitride powder samples show no noticeable relationship between chemical composition, analytical oxygen content, or crystallite size.

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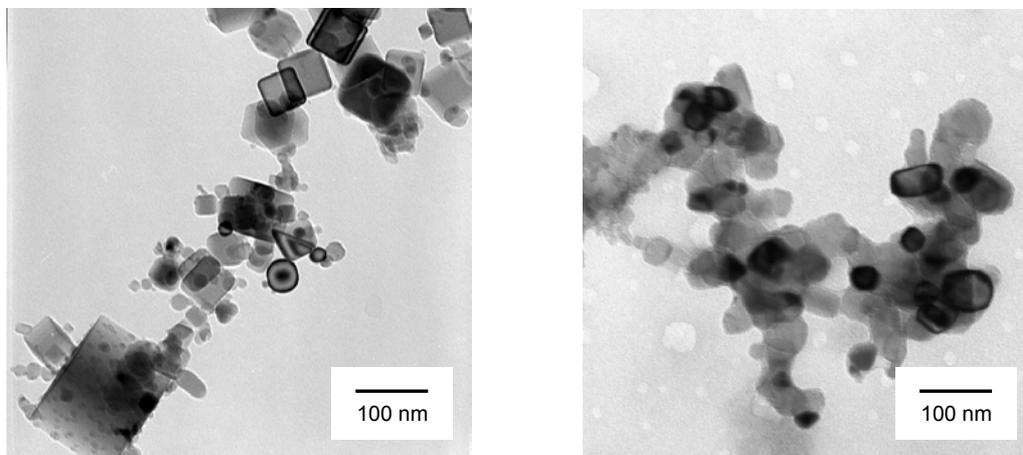


Figure 1: TEM micrograph of the uncompact PCT7 (left) and the N&AM titanium carbonitride powder sample (right).

Sample designation as used in this work, SSA = specific surface area, formula = stoichiometric formula calculated from the analytic data, assuming that no oxygen is integrated in the structure, C/(C+N) value calculated from the stoichiometric formula; the data for the Starck samples are assumed as supported by the producer; n.d. = not determined

sample designation	T / °C	dwell / min	$\rho$ / g·cm <sup>-3</sup> Archimedes	d(cryst) / nm
PCT 1	1600	1	4.78 (96%)	205
PCT 1	1800	1	4.76 (95%)	246
PCT 7	1600	1	4.85 (95%)	71
PCT 7	1800	1	4.89 (96%)	131
St70/30C	1600	1	4.60 (92%)	159
St70/30C	1800	1	4.74 (95%)	326
St30/70B	1600	1	4.34 (85%)	165
St30/70B	1800	1	4.60 (90%)	208

Table 2: summary of various titanium carbonitride samples compacted by SPS

Sample designation as used in this work, T = sintering temperature, dwell = dwell time,  $\rho$  = density obtained by means of method of Archimedes, d(cryst) = crystallite size calculated by Scherrer's equation

sample designation	HP-Nr.	T / °C	dwell / min	$\rho$ / g·cm <sup>-3</sup> Archimedes	d(cryst) / nm
PCT 1	19	1700	60	4.76 (95%)	
PCT 1	12	1800	60	4.45 (89%)	205
PCT 2	41	1800	60	4.41 (89%)	
PCT 4	92	1800	60	4.94 (97%)	
PCT 5	70	1700	60	4.84 (94%)	
PCT 5	90	1800	60	4.71 (92%)	
PCT 7	81	1700	60	4.77 (94%)	
PCT 7	82	1800	60	4.83 (95%)	151
St30/70B	13	1800	60	4.40 (86%)	
St30/70B	89	1700	60	4.94 (97%)	
St70/30C	85	1700	60	4.91 (98%)	
St70/30C	91	1800	60	4.89 (98%)	>1800
N&AM	102	1800	60	4.97 (97%)	300

Table 3: summary of various titanium carbonitride samples compacted by conventional hot pressing

Sample designation as used in this work, T = sintering temperature, dwell = dwell time,  $\rho$  = density obtained by means of method of Archimedes, d(cryst) = crystallite size calculated by Scherrer's equation