Abstract
Dense-sintered Ti(C,N)-(Ta,Nb)C-WC-Co-Ni cermet materials were subjected to heat-treatments in nitrogen or vacuum in order to investigate phenomena which help to understand the formation of gradients. The final goal is to achieve a functionally graded near-surface zone in order to increase edge stability upon cutting. The microstructures were characterised by SEM/EDS. Considerable microstructural changes were observed. It was found that the nitrogen-treated cermet surface is rich in titanium nitrides. Nitrogen atmosphere induces a migration of titanium to the surface and of tungsten inside the material. New homogeneous grains without core-rim structure developed. Vacuum treatment leads to nitrogen loss in the surface region but the cubic phase remains stable. If gas removal is retarded, e.g. at the bottom side of the samples, the nitrogen content accumulates in the surface region and a substantial amount of Ti(C,N) is formed.

1 Introduction
Hardmetal cutting tools can consist of more than 90 wt% tungsten carbide. Due to the increasing tungsten price it would be profitable to substitute WC-based hardmetals by Ti(C,N)-based cermets due to their – if any – much lower WC content. Unfortunately, the advantage of cermets – their high hardness – is associated with their greatest disadvantage – their low ductility. Hence, cermets are sensitive to cracks which originate at the surface upon cutting. Apart from different coatings which were not applied in early days of cermet production but are nowadays frequently deposited, a modification of the microstructure in the surface zone by exploiting diffusion phenomena may further improve the cutting-edge properties of cermets. In addition to an appropriate microstructure, the surface should provide a good adhesion for coatings and should be smooth.

The microstructure of Ti(C,N)-based cermets consists of a hard-phase of cubic carbonitride grains in form of a core-rim-structure, embedded in a metallic binder matrix phase [1]. The rim sometimes divides in an inner and an outer rim. In the inner rim the heavier elements such as W are enriched [2]. By nitrogen exposure the carbonitride phase can disintegrate and form WC [3]. Zackrisson et al. [4] found that sintered Ti(C,N)-TiN-WC-Co cermet change their microstructure upon heat-treatment in nitrogen atmosphere (1200 °C, 20 h). In comparison to the bulk the number of TiN-rich dark grains were situated in the surface zone. This zone was also enriched in cobalt and depleted in tungsten and carbon. Kim et al. [5] investigated the binder enrichment on cermet surfaces during sintering. They found that nitrogen introduction in holding or cooling stages prevents binder enrichment. In hardmetals with a substantial amount of carbonitrides, a cubic-free surface can be formed by sintering in an atmosphere of reduced nitrogen activity [6]. Cermets without tungsten form a cubic-carbide-free layer easier and faster than W-containing grades [7]. Doy et al. [8] studied nitridation and de-nitridation of (Ti0.8W0.2)(C0.7N0.3)-Co cermet and found WC-Co and Ti(C,N) layer formation, depending on the nitrogen pressure.

The present study was carried out in order to investigate the microstructural phenomena in near-surface regions of dense-sintered cermets of increased nitrogen content upon vacuum as well as nitrogen treatment at increased temperatures, i.e. under de-nitriding and nitriding conditions.

2 Experimental
Two cermets grades, A and B (Tab.1), with different Ti(C,N) contents were studied. The densely-sintered cermet samples were nitrided and denitrided in various conditions in which holding temperature, time and pressure were varied (Tab.2).

2.1 Starting Materials
The cermet grades were different in their carbide and binder content. Grade A had 60 wt% and grade B 50 wt% submicron Ti(C,N) powder. The industrial production of this powder was recently developed

1 Corresponding author. Tel.: +43 1 58801 16127; fax: +43 1 58801 16490.
E-mail address: walter.lengauer@tuwien.ac.at (W. Lengauer)
and its use for cermets described by Demoly et al. [9]. The $[\text{C}]/([\text{C}]+[\text{N}])$ ratio of this powder was 0.5. Further data are listed in Tab.1. The gross composition of the cubic phase is $(\text{Ti,Ta,Nb,W,Cr})_0.61\text{N}_{0.40}$ for grade A and $(\text{Ti,Ta,Nb,W})_0.66\text{N}_{0.38}$ for grade B, hence the gross $[\text{C}]/[\text{N}]$ ratio of cermet B is higher than that of cermet A.

### Tab.1: Cermet compositions

<table>
<thead>
<tr>
<th>Grade</th>
<th>Ti(C,N)</th>
<th>(Ta,Nb)C</th>
<th>WC</th>
<th>Cr$_3$C$_2$</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grade A</td>
<td>60</td>
<td>10</td>
<td>16</td>
<td>1</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Grade B</td>
<td>50</td>
<td>15</td>
<td>20</td>
<td>0</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Fig.1 shows the composition of grade A and B cermets within the isothermal phase diagram of the system Ti-W-C-N calculated by Jonsson [10]. Here, $\delta$ marks the cubic (fcc) $(\text{Ti,W})(\text{C,N})$ phase, whereas $\gamma_W$ means the molar ratio $[n_\text{W}] / ([n_\text{W}]+[n_\text{Ti}]+[n_\text{Ta,Nb}]+[n_\text{Cr}])$. It should be noted that Ta, Nb and Cr were not considered by Jonsson. According to this phase diagram both grades should be located in the phase field where one fcc carbonitride phase coexists with WC. Since in both of our grades no WC was found but have a core-rim type structure our sample are rather located in the $\delta_1 + \delta_2$ phase field. The cited study of Doi et al. [8] is based on WC-rich samples and does not consider two fcc phases.

![Fig.1: Cermet grades A and B mapped in the isothermal section of the Ti-W-C-N phase diagram of Jonsson [10]](image)

### 2.2 Preparation of green bodies

Powder mixtures were milled for 72 h in a ball-mill filled with hardmetal grinding bodies and cyclohexane as milling aid, dried and sieved (1.2 mm mesh). Afterwards, green cylindrical bodies (12 mm diameter) were uniaxially pressed (150 MPa).

### 2.3 Sintering

The cermets were sintered in a graphite crucible in an induction furnace. The process was started with vacuum conditions and ended with a partial $\text{N}_2$ pressure of 100 mbar. The applied sintering profile was already presented in [9]. The samples were placed on an alumina plate to avoid contact with graphite.

### 2.4 Nitriding and De-nitriding

For post-treatment und vacuum and nitrogen (Fig.2), respectively, the samples were again placed on alumina plates and rapidly heated under 100 mbar $\text{N}_2$ partial pressure to the vertex temperature. At
this temperature a higher N\textsubscript{2} partial pressure (line a) or dynamic vacuum (b) was applied for various dwell times. The conditions are summarised in table Tab.2.

![Graph showing temperature and N\textsubscript{2} partial pressure over time.]

**Tab.2: Treatment conditions**

<table>
<thead>
<tr>
<th></th>
<th>T2 / °C</th>
<th>t / min</th>
<th>Pressure / mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Nitriding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1)</td>
<td>1280</td>
<td>120</td>
<td>400</td>
</tr>
<tr>
<td>2)</td>
<td>1300</td>
<td>120</td>
<td>400</td>
</tr>
<tr>
<td>3)</td>
<td>1380</td>
<td>60</td>
<td>400</td>
</tr>
<tr>
<td>4)</td>
<td>1460</td>
<td>30</td>
<td>400</td>
</tr>
<tr>
<td>b) De-nitriding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5)</td>
<td>1380</td>
<td>60</td>
<td>vacuum</td>
</tr>
<tr>
<td>6)</td>
<td>1380</td>
<td>120</td>
<td>vacuum</td>
</tr>
<tr>
<td>7)</td>
<td>1460</td>
<td>30</td>
<td>vacuum</td>
</tr>
</tbody>
</table>

2.5 Microstructure

The samples were cut, ground and polished with diamond paste finally to 1 µm. For final polishing a colloidal silica suspension was used. The microstructure of bulk and surface of the cerments were characterised by light-optical microscopy (LOM) with magnification of 1000x. The microstructure was also characterised by SEM (Quanta 200 FEGSEM, FEI), using a BSE detector and magnifications of 2000x and 15000x. The element concentrations at several positions were measured by EDX (energy dispersive X-ray spectroscopy).

3 Results

3.1 Near-surface zone after sintering

The samples show a grey surface after sintering. The comparison of the near-surface cross sections (Fig.3a with Fig.3c) shows that this zone is thicker for grade A than for grade B cerments. For both samples the layer at bottom (right column) is smoother than at the top face (left column).

Fig.4 shows typical cerment microstructure by SEM with core-rim structure in the bulk. The dark cores are rich in Ti and N, whereas the grey coloured rims are intermediate in metal composition and low in nitrogen. No WC grains are detected in the bulk.

The microstructures of the near-surface areas of both grades look similar if the same side (top – bottom) is regarded (compare Fig.4a with 4c, and 4b with 4d). However, on top side of grade A (Fig.4a) a light grey coating above the grains was observed (which can also be seen in LOM microstructure Fig.3a). The EDX analysis shows that this coating consists of cobalt-nickel binder which came out of the bulk material. This phenomenon was recently investigated by Janisch et al. [11] on hardmetals to occur upon solidification.

The top face in each grade (Fig.4a and c) shows a core-rim type structure with a very small difference in average chemical composition between core and rim as can be concluded from the almost identical grey scale. This would mean a very close composition of $\delta_1$ and $\delta_2$ phases in the two-phase field (Fig.1) with some nitrogen loss.
Interestingly, the bottom side of both grades A and B (Fig.4b and 4d) is significantly different from the top side and shows a larger difference of average chemical composition. Without representing a typical core-rim structure there are dark parts of increased Ti and N content which are rather elongated than spherical with a much finer structure as compared to the bulk. The N- and Ti-rich parts increase towards the surface. This structure is due to restricted nitrogen evolution from the bottom face. Obviously, N diffuses out of the sample, leading to a N-poor coreless structure at the inner part of the zone (δ₁ and δ₂ phases close in composition), but cannot completely evolve from the sample and accumulates near the surface (δ₁ and δ₂ phases more separated in composition).

From a recent study [9] it could be concluded that the enrichment of rim phase, such as it is observed on top faces of both grades in Fig.4a and 4c, could slightly increase both, hardness and the fracture toughness. Also the very peculiar structure on both bottom faces with very small and intermixed phases could give increased mechanical properties. This will be investigated by micro-indentation measurements which will show whether hardness and elastic properties change in these layers as compared to bulk properties.

![Image of sample surfaces](image1)

**Fig.3:** As sintered samples, LOM 1000x; Grade A surface zone thicker than B, top face rougher than bottom side

![Image of sample surfaces](image2)

**Fig.4:** As sintered samples of grade A and B, SEM 15000x, Grade A sample top face has cobalt-nickel capping
3.2 Nitriding

3.2.1 Nitriding of unground samples

Fig. 5 shows the near-surface microstructure of grade A and B cermet samples as obtained from sintering (named “unground”) after nitriding at 1300 °C, 120 min, 400 mbar (treatment 1). Grade A (Fig. 5a) formed two layers. Near the bulk was a grey Ti(C,N) layer (less nitrogen), and above that, a red coloured Ti(C,N) layer (more nitrogen). In the red N-rich Ti(C,N) layer white crystallites were formed which were identified by EDX to be WC. The image of the near-surface zone of grade B cermet (Fig. 5b) shows only a red coloured N-rich Ti(C,N) layer, no grey one. In comparison with grade A it can be seen that the surface of grade B is smoother. The WC crystallites are located on top of the layer of grade B.

![c) Grade B top face](image1)

![d) Grade B bottom](image2)

Fig. 4 continued: As sintered samples of grade A and B, SEM 15000x, Grade A sample top face has cobalt-nickel capping

![a) Grade A, top face](image3)

![b) Grade B, top face](image4)

Fig. 5: Unground samples, treatment 1, (nitriding 1300 °C/120 min/400 mbar) LOM 1000x

Depending on the nitrogen pressure, the reaction of fcc carbonitrides with nitrogen can result in the formation of free hexagonal WC. Hence, a slight difference in WC content of the starting formulation can cause different bulk microstructure upon nitridation due to different nitrogen equilibrium pressures. Because of the higher WC content, free WC was indeed formed in grade B but not in grade A. Grade A would require a higher nitrogen pressure to form WC.

3.2.2 Nitriding of ground samples

In order to observe effects on the near-surface microstructure without interference with a surface layer from sintering some samples were ground before treatment. Fig. 6 shows grade A and B cermet samples treated at 1300 °C for 120 min at 400 mbar (treatment 2, treatment 1 samples look similar). Cermet A (treatment 1 and 2) has a red N-rich Ti(C,N) layer after nitriding, no grey one like in unground samples. In the N-rich Ti(C,N) layer a significant amount of binder phase (white) can be seen, especially at the bottom side. The EDX analysis of this phase is 39 wt% Co, 40 wt% Ni and 7 wt% W, remainder C, N. In contact with this binder phase faceted Ti(C,N) crystallites form although a liquid phase was never formed upon post treatment (Fig. 7b). By means of EDX the composition of this
phase is \((\text{Ti}_{0.77}\text{W}_{0.09}\text{Ta}_{0.05}\text{Nb}_{0.09})(\text{C}_{0.63}\text{N}_{0.49})\). Below the Ti(C,N) layer a binder-depleted zone exists (Fig.6a, b).

In contrast to cermet A, the near-surface microstructure of cermet B shows only a small red-coloured layer of almost pure Ti(C,N). There is no free WC within this Ti(C,N) but WC is enriched just below this layer (Fig.6c, d, white phase).

The Ti(C,N) layers in both grades are thicker in the top face than in the bottom face. Since the post-treatment temperatures are well below the eutectic temperature the layer formation occurs in both cases by solid-state diffusion. The grains of the layers do not show the core-rim-structure under the influence of nitrogen, they are very homogeneous. During treatment 1 and 2 the binder phase is pressed out of the bulk from grade A samples. Most interestingly, this binder phase migration does not occur at higher temperatures (1380 and 1460°C).

In Fig. 7 the phenomena are sketched for cermets of grade A. At the beginning near-surface Co/Ni enrichment can be seen (Fig.7a). This binder phase stems from the outer region of the sample and is thus depleted there (compare microstructure in Fig.6a). Upon increasing time more binder migrates to the surface and also Ti(C,N) is formed upon nitridation. A large part of essentially Ti(C,N) is formed below the enriched binder phase because nitrogen can diffuse easily through Co/Ni. Only a small amount of Ti(C,N) is formed on top representative of Ti which was dissolved in the binder (Fig.7b and Fig.6b).

Interestingly, cermets of grade B do not form a binder-enriched layer upon nitridation. Here, the Ti(C,N) layer is uniform. The absence of a binder enrichment in the surface is probably due to the formation of free WC upon nitridation, which migrates towards the interior (sketch Fig.8) and is enriched below the Ti(C,N) layer. Obviously the WC holds the binder phase within the bulk. Doi et al. [8] observed an extremely irregular Ti(C,N) layer. The fact that a uniform Ti(C,N) layer formed in our samples is due to the increased Ti(C,N) content in the starting formulation.
3.3 De-nitriding

3.3.1 De-nitriding ground samples

In order to cause near-surface phase reactions of at least 5-10µm by vacuum conditions within an acceptable time it was necessary to increase the treatment temperature to at least 1380 °C, which is substantially higher than that of nitridation temperatures causing similar spatial influence. Denitrided ground samples (treatment 6) show a thin and rough light grey layer at the top side. At the bottom side the layer is darker and very smooth (no further details could be observed in LOM investigations because of the restricted resolution). SEM investigations (Fig.9) show for grade A (left) at the top face grains of cubic phase of intermediate composition. Dark (N-rich) grains are missing. EDX measurements showed that almost no nitrogen is present in this outermost region. No WC-Co/Ni surface zone forms. A WC-Co zone was observed by Doi et al. [8] which is due to the much higher WC concentration in their starting formulation.

While the top sides of both cermet grades are very similar, the bottom sides are not. Cermets of grade A show nitrogen enrichment whereas cermets of grade B show a depletion of nitrogen similar to its top face. This behaviour is again due to the different nitrogen equilibrium pressures and the different tendency of both samples to de-nitride. Grade A has a lower WC content and hence a lower nitrogen equilibrium pressure than grade B. As the small gap between the sample and the alumina plate does not allow the nitrogen to evolve completely the nitrogen pressure in the gap is thus sufficient for nitriding grade A but insufficient for nitriding grade B.
4 Conclusions

The experiments show that a diffusion-controlled layer formation on cermets is possible by both, nitriding and de-nitriding (vacuum) conditions. While nitriding can take place at temperatures ≤1300°C and form uniform carbonitride layers, de-nitriding must take place at least at 50-100°C higher temperatures in order to influence the microstructure within the same depth of around 10µm. However, the de-nitriding conditions do not cause WC-Co/Ni layer at the surface. For such a layer the WC content of the starting formulation has to be increased. This is due to the high stability of carbonitrides which do not readily decompose upon vacuum treatment. Only a small difference in composition can cause substantially different layers. Due to this small difference, a homogeneous Ti(C,N) layer as well as a Ti(C,N) layer with a substantial amount of binder phase can be formed in nitrided samples. Also the precipitation of WC within the layer as well as in the
bulk just below the layer is sensitive to overall formulation of the cermet. In one grade WC depleted just below the diffusion-induced layer, in the other WC was enriched. Though substantially more work is needed to clearly understand the diffusion phenomena in near surface zones (also because of the very complicated multi-component, multi-phase structure of cermets) these phenomena can be used to tailor specific mechanical edge properties of cermet cutting tools.

References


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