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Near-surface microstructural modification of (Ti,W)(C,N)/Co hardmetals by nitridation

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Abstract

For developing functional-gradient hardmetals the interaction of nitrogen with (Ti,W)(C,N)/Co hardmetals was investigated. Industrially sintered (Ti,W)(C,N)/Co hardmetals were heat treated above (1500 °C) and below (1200 and 1300 °C) the eutectic temperature using nitrogen pressures up to 25 bar. Above the eutectic temperature compact Ti(C,N) top layers followed by a more or less graded microstructure independent on sample composition were observed. Below the eutectic temperature the microstructure formation is mainly influenced by the sample composition. A Ti(C,N) top diffusion layer forms in materials with a high Ti(C,N) content in which the [N]/[C] ratio decreases towards the interior. Contrary, interaction zones without a layer were obtained in compacts with a high WC content. Cutting tests were performed which showed that such surface-modified hardmetals are superior to non-modified grades of similar overall composition. A ten-fold increase of cutting life time for a surface-modified grade, which has a Ti(C,N) diffusion layer on top, could be observed.

Keywords: Functionally graded materials; Interaction zone; Diffusion layer

1. Introduction

The concept of functionally graded materials has been put forward in the past years [1]. One of the fields of application of this concept is related to hardmetals and cermets used as cutting tools in which special properties such as the ratio of hard phase vs. binder metal, hardness, stress, grain size, ..., change gradually. Because the formation of the graded zone is controlled by diffusion of the various elements in the liquid binder and by the thermodynamic properties of the system the fabrication of a graded hardmetal (cermet) depends strongly on the process parameters such as temperature and gas pressure [2–4].

Several papers concerning the formation of layers and gradients in (Ti,W)(C,N)-based cermets using a diffusion-controlled process have been published [5–8]. Lengauer et al. [7,8] describe a principle classification scheme consisting of four types of the near-surface microstructures formed by sintering in reactive atmosphere, mainly containing N_2. Some of these grades were successively upgraded into the production scale and show excellent cutting performance [9].

Although substantial work has been done in the development of functional gradient hardmetals it mainly deals with gas pressures < 1 bar. The aim of this work is to investigate the influence of higher-than-ambient gas pressures for temperatures above and below the eutectic temperature on the formation of layers and gradients at the surface and in near-surface areas of (Ti,W)(C,N)/Co-based hardmetals.

2. Experimental

Industrially "state of the art" dense-sintered (Ti,W)(C,N)/Co hardmetals, with small amounts of (Ta,Nb)C, were used. The overall composition of the different samples subjected to annealing and sintering experiments in nitrogen atmosphere are listed in Table 1. The hardmetals were annealed in a laboratory autoclave using 5 and 25 bar N_2 at 1200, 1300 and 1500 °C. The reaction time was 1–100 h. In these experiments heating cycles

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Table 1
Composition of the hardmetals

Sample number	Composition (wt.%)			[N]/[C] ratio
	WC	fcc phase	Co	
#7	63.0	27.0	10.0	High
#34	75.0	15.0	10.0	Medium
#28	86.2	7.8	6.0	Zero

were applied which are similar to standard heating cycles and nitrogen was added at special points in the time-temperature profile [8,9]. For characterisation the samples were subjected to optical microscopy, SEM, EPMA, XRD and surface roughness measurements.

3. Results

Various types of different microstructures form in the (Ti,W)(C,N)/Co compacts reacted with N_2 [10]. Some of these can be included in the established scheme of microstructures of vacuum-sintered in situ surface-modified hardmetals and cermets (type 1–4), described by Lengauer et al. [7]. However, due to the application of high pressures in the present study, others show features which do not fit into this scheme.

3.1. Sintering above the eutectic temperature

A compact Ti(C,N) top layer followed by a more or less graded structure was observed in (Ti,W)(C,N)/Co samples annealed above the eutectic temperature at 1500 °C at 5 and 25 bar N_2 for 1 h, independent on the sample composition (Figs. 1–3). This corresponds to a type 4 microstructure as described previously [7]. Although the microstructure type remains the same, several important features such as the thickness of the Ti(C,N) top layer, the surface roughness and the porosity increase with increasing Ti(C,N) content (Figs. 1–3 and Table 2). Compacts with high TiN content

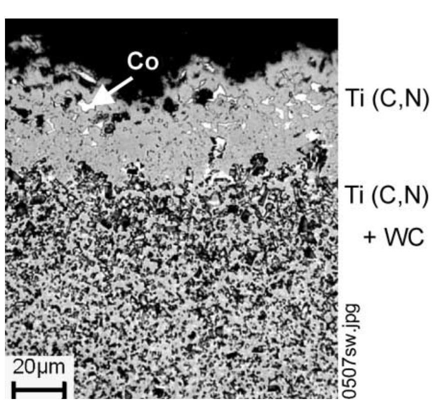

Fig. 1. Microstructure of a (Ti,W)(C,N)/Co hardmetal (sample #7) sintered at 1500 °C with 5 bar N_2 for 1 h.

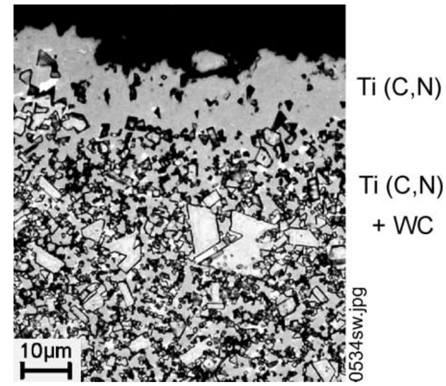

Fig. 2. Microstructure of a (Ti,W)(C,N)/Co hardmetal (sample #34) sintered at 1500 °C with 5 bar N_2 for 1 h.

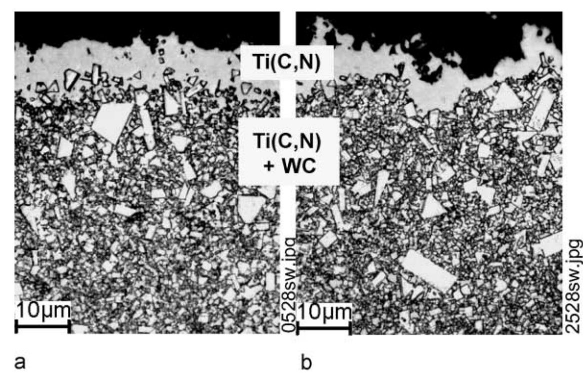

Fig. 3. Microstructure of sample #28, sintered at 1500 °C for 1 h: (a) at 5 bar N_2 and (b) at 25 bar N_2.

Table 2
Layer thickness and R_a values of the samples sintered at 1500 °C with 5 bar N_2 and 25 bar N_2 for 1 h

Sample number	Ti(C,N) layer thickness (μm)		R_a (μm)	
	5 bar N_2	25 bar N_2	5 bar N_2	25 bar N_2
#7	~50	~55	4.5	5
#34	~15	~25	4.6	3.6
#28	~10	~7	1.2	2.1

(sample #7 and #34) form up to 55 μm thick Ti(C,N) top layers (Figs. 1 and 2). These layers can contain a substantial amount of Co and they also show porosity and rough surfaces with R_a values up to 5 μm (Table 2). In the case of sample #28, a compact with a high WC content and no TiN in the starting formulation, a quite smooth and compact Ti(C,N) top layer of about 10 μm thickness and with a surface roughness of 1.2–2.1 μm formed at 5 bar N_2. An increased nitrogen pressure of 25 bar N_2 causes no substantial difference in layer-thickness for all investigated samples but the surface roughness (R_a) was increased as compared to 5 bar N_2 (Table 2, for sample #28 compare Fig. 3).

Because of the presence of a liquid phase at 1500 °C causing a high mobility of the diffusing species (the eutectic temperature is about 150 °C below this temperature [2]), layers and gradients form quite fast (within 1 h). If the annealing temperature is decreased to temperatures were no liquid phase appears (1300 and 1200 °C) the annealing time has to be increased (up to 100 h) in order to modify the near-surface microstructure so as to form zones or diffusion layers above a few µm thickness.

3.2. Annealing below the eutectic temperature

Below the eutectic temperature the microstructure formation is mainly influenced by the sample composition. Compact or extremely porous and thick (up to 90 µm) Ti(C,N) top layers and/or interaction zones which show a smooth variation of particle distribution in near-surface areas were observed. Ti(C,N) top layers formed in (Ti,W)(C,N)/Co compacts with a high Ti(C,N) content. Contrary, interaction zones without a layer were obtained in compacts with a high WC content.

3.2.1. Annealing below the eutectic temperature: 1300 °C

As mentioned, before depending on the composition, interaction zones or layers can form below the eutectic temperature upon reaction with nitrogen. In compacts with high amount of WC the action of nitrogen changes the composition of the Ti(C,N) phase only, leaving other features almost unchanged. This is shown in Fig. 4 for sample #28. The nitrogen content in Ti(C,N) changes gradually from a high concentration at the surface and in near-surface areas to lower amounts in the core (in sample #28 it actually attains pure TiC, Fig. 4a). This feature can be easily detected by the intensive colour change of titanium carbonitrides as a function of [C]/[N] ratio (e.g.: TiN: golden yellow; $TiC_{0.2}N_{0.8}$: violet; TiC: dark grey [11]). Dark yellow particles at the surface transform to violet and finally dark grey colour as the interior is approached (Fig. 4a, for a colour version of the photographs of this work, please connect to www.tuwien.ac.at/physmet/microstructures).

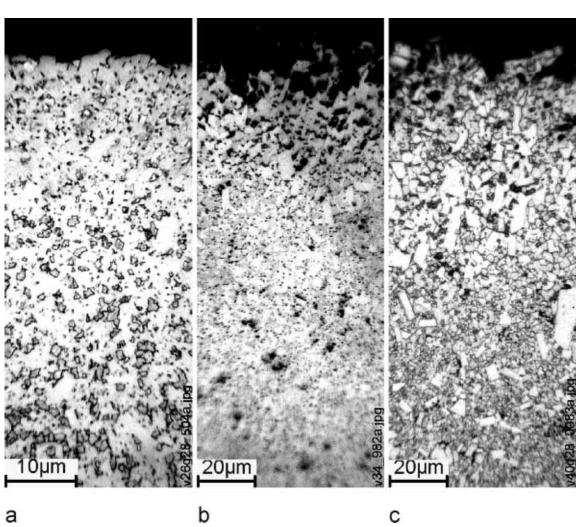

Fig. 4. Microstructures of sample #28 annealed at 1300 °C with 25 bar N_2: (a) 10 h, (b) 20 h and (c) 100 h.

Further increase of the annealing time of compact #28 at 1300 °C (to 20 and 100 h, respectively) yields a rough and porous surface zone with higher amount of nitrogen-rich Ti(C,N) grains. These near-surface areas also show a distinct change in particle size upon interaction with nitrogen. Large WC crystallites (up to 20 µm) can be identified followed by a graded zone in which the WC crystallites become much smaller (Fig. 4b and c). For the annealing temperature of 1300 °C and annealing times >10 h this microstructural feature is observed in all investigated compacts independent on composition. The compacts containing a high amount of Ti(C,N) (sample #7) additionally form a Ti(C,N) layer on top of this graded zone. Hence, an interface is visible (Fig. 5). It has to be noted, that the about 90 µm thick Ti(C,N) top layer formed in this sample has very high porosity and also contains large WC crystallites.

3.2.2. Annealing below the eutectic temperature: 1200 °C

While after 10 h annealing time at 1300 °C a nitrogen-affected zone is present in samples with a high WC content (sample #28) no such zone forms or is at least visible in the optical microscope after the same time at 1200 °C (compare Figs. 4a and 6a). At 1200 °C and annealing times up to 100 h very smooth surfaces and much smaller interaction zones were obtained (Figs. 6 and 7). The rugged and porous Ti(C,N) zones obtained at 1300 °C do not form at this decreased annealing temperature in the investigated period of time. This can again be explained by the decreased mobility of elements at lower temperatures. The annealing-time dependency

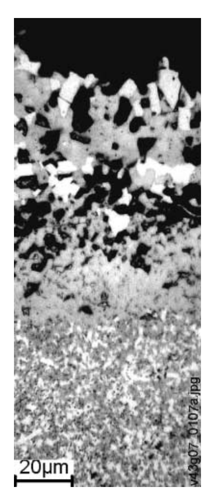

Fig. 5. Microstructure of sample #7 annealed at 1300 °C for 40 h at 25 bar N_2.

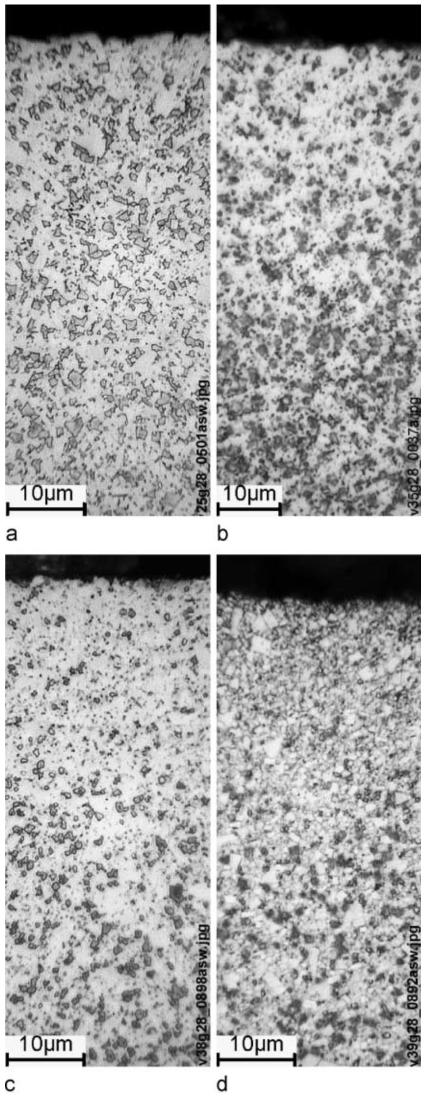

Fig. 6. Microstructures of sample #28 annealed at 1200 °C with 25 bar N_2: (a) 10 h, (b) 20 h, (c) 40 h and (d) 100 h.

on formation of interaction zones for a compact with a high WC content (sample #28) annealed at 1200 °C with 25 bar N_2 is presented in Fig. 6. Interestingly an interaction zone of about 30 μm independent of annealing time (within the limit of 20–100 h) forms. This interaction zone has an increased amount of nitrogen-rich Ti(C,N) in comparison with the core zone. However, the grain size of the WC crystallites increases (compare Fig. 6c and d).

The formation of interaction zones and/or layers at 1200 °C is mainly influenced by the composition of the starting formulation. In compacts with a high WC content (sample #28 and #34) a nitrogen-rich reaction zone occurs at the outermost surface but no distinctive Ti(C,N) top layer forms (see Figs. 6c and 7). This can be explained by the fact that at 1200 °C no liquid phase is present so that Ti cannot diffuse fast enough to the surface which is required to form a Ti(C,N) layer. At the same annealing conditions a Ti(C,N) top layer forms in compacts with a high Ti(C,N) amount such as in sample #7 (Fig. 8b). This is because of the high Ti content present in the surface region and the exceed of the solubility product which promotes TiN precipitation. At 25 bar N_2 an about 7 μm thick monolithic Ti(C,N) top layer formed in this sample after 100 h. Then, a zone rich in fcc phase follows (Fig. 8b). If a nitrogen pressure of 5 bar is applied, again a Ti(C,N) top layer occurs although the annealing time was only 20 h (Fig. 8a). Upon a closer look at the Ti(C,N) top layers which occur in samples with high Ti(C,N) content a composition gradient in these layers can be found. This becomes clearly visible already by light optical inspection which shows a transition of the dark yellow colour to a violet colour ($[N]/[C] \approx 0.80$).

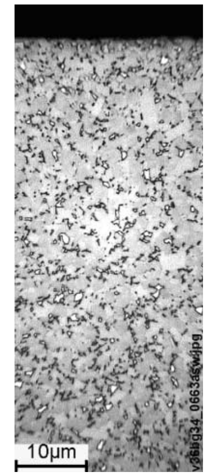

Fig. 7. Microstructure of sample #34 annealed at 1200 °C for 20 h at 5 bar N_2.

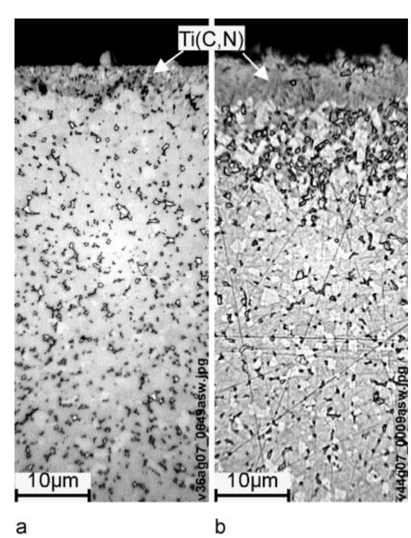

Fig. 8. Microstructure of sample #7 annealed at 1200 °C: (a) 20 h, 5 bar N_2 and (b) 100 h, 25 bar N_2.

Table 3
R_a-values of sample #28 for different annealing conditions

T (°C)	pN_2 (bar)	R_a (±0.2) (μm)			
		10 h	20 h	40 h	100 h
1300 °C	5 bar N_2	–	2.4	–	4.6
1300 °C	25 bar N_2	0.6	2.3	–	7.7
1200 °C	5 bar N_2	–	0.1	–	–
1200 °C	25 bar N_2	0.5	0.4	0.2	0.2

Also for the samples annealed at 1200 °C it was observed (compare the R_a values of the samples annealed above the eutectic temperature) that the surface roughness increases with increasing annealing temperature and/or annealing time or nitrogen pressure. The R_a values as a function of temperature and nitrogen pressure of one (Ti,W)(C,N)/Co compact (sample #28) are presented in Table 3.

3.3. Cutting tests

First cutting tests of two different surface modified inserts of the geometry SNUN 120408 were done. The first insert, sample #28 annealed at 1200 °C for 20 h using 5 bar N_2 (microstructure similar to the microstructure presented in Fig. 6b), shows a interaction zone with a smooth change in particle distribution. The microstructure of the second insert, sample #7 (for the microstructure compare Fig. 8a), shows a diffusion layer of about 5 μm on top of a graded structure.

The width of wear land (Fig. 9) and the depth of crater (Fig. 10) were measured as a function of cutting time during continuous turning of steel CK45N. For comparison two commercial grades, TTM and TTR, of which the composition is near the sample #7 and sample #28, respectively, were measured. Sample #28 did not show an improved performance compared with the commercial grades. But sample #7, with the diffusion layer on top, had a substantial lower wear than the commercial grades. In industry a common tool life criterion for an insert is about 0.3 for VB_{max}, if this limit is reached the inserts are replaced. The surface modified grade with the diffusion layer on top (sample #7) reached this limit after 59 min while the commercial grades reached it after 3 and 6 min (compare Fig. 9). This means a substantial increase of the cutting performance by at least one order of magnitude. For the crater depth sample #7 shows also excellent wear behaviour with almost imperceptible cratering after 6 min. This is also extremely interesting from a commercial standpoint. While CVD or PVD layer deposition amount up to 30% of the total production costs of an indexable insert a nitrogen treatment costs only a few percents of these total costs. Since a sinterHIP process is well established in hardmetal technology as a post-treatment to reduce porosity such a second step can easily be performed. However, the production costs could be even further reduced if the nitrogen treatment to create a diffusion layer is not performed in a separate process but performed in situ in a post-treatment within the sintering cycle and if the post-treatment cycle is shortened which is under investigation.

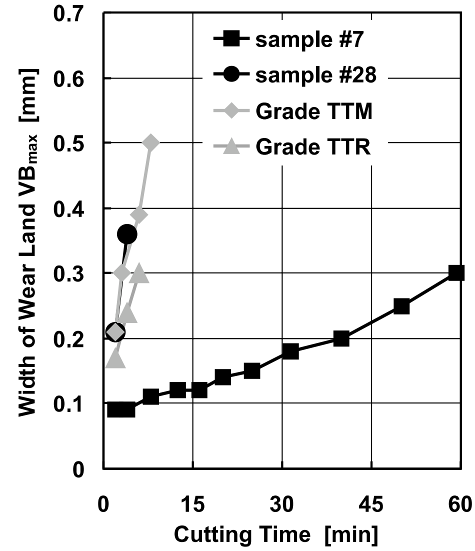

Fig. 9. Results of a cutting test: width of wear land versus cutting time; continuous turning of steel CK45N; $R_m = 618$ N/mm, Insert: SNUN 120408, cutting conditions: $V_c = 180$ m/min, $a_p = 2.0$ mm, $f = 0.2$ mm/U.

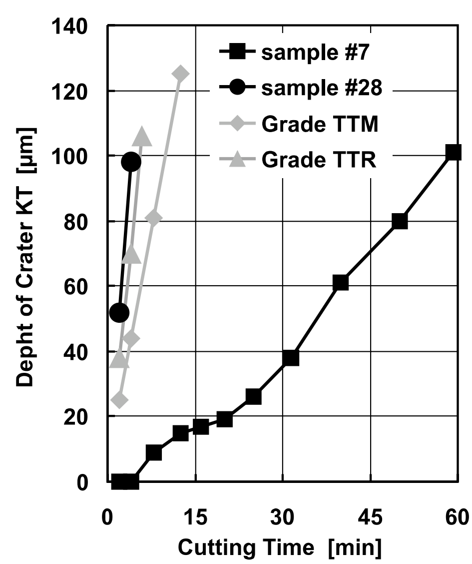

Fig. 10. Results of a cutting test: depth of crater versus cutting time; continuous turning of steel CK45N; $R_m = 618$ N/mm, Insert: SNUN 120408, cutting conditions: $V_c = 180$ m/min, $a_p = 2.0$ mm, $f = 0.2$ mm/U.

4. Conclusion

In (Ti,W)(C,N)/Co hardmetals modified with high-pressure nitrogen either form compact Ti(C,N) top layers and/or interaction zones. Above the eutectic temperature compact Ti(C,N) top layers independent on sample composition were observed. Below the eutectic temperature the microstructure formation is mainly influenced by the sample composition. A Ti(C,N) top layer forms in (Ti,W)(C,N)/Co hardmetals with a high Ti(C,N) content. Contrary, interaction zones without a layer were obtained in compacts with high WC content. These interaction zones show a smooth variation of particle distribution in near surface areas. The porosity, increased particle sizes and rough surfaces of interaction zones obtained at an annealing temperature of 1300 °C can be explained by the increased mobility of the elements compared to an annealing temperature of 1200 °C. The two different nitrogen pressure applied, 25 bar N_2 and 5 bar N_2, respectively cause no substantial difference in the microstructure type for all investigated temperatures.

The surface roughness plays an important role in the cutting performance of indexable inserts. Some of the structures formed below the eutectic temperature show surface roughness lower than 0.5 μm and therefore as low as the roughness of deposited layers. Although some nitrogen-reacted compacts show features, such as rugged and porous influence zones and big WC crystallites, which make them not suitable for use in metal cutting operations. First cutting tests showed a tremendous increase of cutting performance for the sample which has the Ti(C,N) diffusion layer on top while the sample with the interaction zone do not show an increase in performance.

Some microstructural features were observed which are very interesting for the development of new gradient types formed by diffusional in situ surface modification. They show surfaces and particle sizes favourable for a cutting tool. The low temperatures of solid-state modification of these compacts allow not only the formation of zones with changing particle composition but also the formation of graded interlocked carbonitride layers the production of which is much less costly than of deposited layers.

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