

# Ti(C,N) Cermets — Metallurgy and Properties

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**Abstract:** An overview of the metallurgical reactions during the vacuum sintering process of powder mixtures for the manufacture of cermets is presented. The relatively complex phase reactions in the multi-component system Ti/Mo/W/Ta/Nb/C,N-Co/Ni are discussed. The liquid binder phase reacts with titanium carbonitride by preferentially dissolving titanium carbide leaving titanium nitride undissolved. The compositions and the amounts of the gas species set free during the sintering process were monitored and led — together with differential thermal analysis — to a better understanding of the mechanisms that govern the sintering behaviour.

The properties and the microstructure of cermets depend on the nature and the alloy status of the prematerials. The composition of the prematerials with respect to the carbon–nitrogen ratio, the stoichiometry of the hard phase and the amount and composition of the binder phase have a decisive influence on the properties and the cutting performances of the final products. Optimization of the properties with respect to the desired performance is possible. Examples of the cermet cutting performance in various applications are discussed.

## 1 INTRODUCTION

Hardmetals based on titanium carbonitride — commonly known as ‘cermets’ — have been successfully introduced in the metal cutting industry.<sup>1</sup> They compare favourably in several respects with conventional WC-based hardmetals and even with coated hardmetals. Several basic features are responsible for the superior cutting performance of cermets:<sup>2</sup>

- high cutting speeds at moderate chip cross-sections;
- high surface quality of the machined work-piece;
- high wear resistance;
- high performance reliability;
- high edge strength and edge sharpness, which are particularly important for meeting demands of near net shape technology and the machining of thin-walled items.

Cermets of the new generation reach standards of fracture toughness and transverse rupture strength comparable to those of conventional hardmetals within the same ISO group of application. The physical and mechanical properties of cermets can be adjusted within certain limits to meet the requirements of the cutting task. Figure 1 schematically outlines the compositional parameters that can be utilized to adjust the properties. Hardness increases within increasing TiC and TiN contents, whereas additions of (Ta,Nb)C appear to improve the cutting performance in interrupted cuts or in milling applications. With increased additions of WC and Mo<sub>2</sub>C, full densification during sintering becomes less of a problem, while additions of higher TiN contents tend to require higher sintering temperatures necessary for obtaining fully dense specimens without residual porosity. The alloy composition of the binder phase with respect to the metal components Ti, Mo and W is dependent on the overall stoichiometry and on the nitrogen content of the hard phase.<sup>3</sup> Deviations from stoichiometry of the

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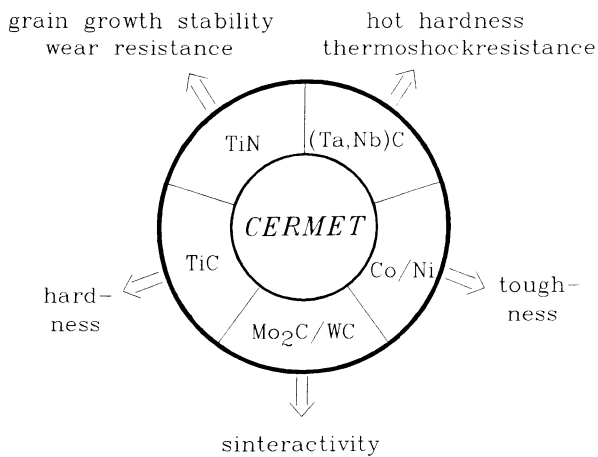


Fig. 1. Graph of the properties of cermet cutting alloys as a function of composition.

hard phase tend to increase the alloy content in the binder phase, whereas nitrogen leads to an increase of the Mo and/or W contents in solid solution in the binder phase. Cermets for cutting applications, now available commercially, are more the product of an industrial optimization process rather than the outcome of systematic metallurgical research. Nevertheless, a few rules of thumb have developed: for applications, where exceptional abrasion and wear resistance is required, cermets usually have high TiC contents with modest TiN additions and low binder contents; for milling applications with high thermal- and shock-stress levels the compositions feature higher binder contents as well as higher nitrogen and Ta/Nb levels in the hard phase.

## 2 METALLURGICAL REACTIONS

The technology for producing cermets corresponds closely to that of conventional hardmetals. As starting materials, usually the binary hard compounds TiC, TiN, Mo<sub>2</sub>C, WC and (Ta,Nb)C are chosen and thoroughly mixed with Co and/or Ni powders for the binder phase. Equally suitable are solid solutions between the hard components such as Ti(C,N), (Ti,Mo)C, (Ti,W)C, (Ti,Ta,Nb,W)C, or even — as recommended by Rudy<sup>4</sup> — complex carbonitride solid solutions (master alloys) incorporating both the nitride and the carbide components in one single phase. The microstructure of cermets that have been sintered with a liquid binder phase such as Ni and/or Co feature structured grains of one single cubic hard

phase embedded in a matrix of the binder phase. The grains of the hard phase show the typical structured appearance with a core-and-rim-type microstructure. With unalloyed prematerials the cores usually do not contain any of the heavier elements such as Mo, W, Ta, Nb, etc., which can only be found in the rims. Whenever pre-alloyed starting materials such as (Ti,Mo)C, (Ti,W)C or (Ti,Ta,Nb,W)C are used, the cores of the hard particles may contain substantial amounts of the heavier elements, but at the same time other grains whose cores contain only the lighter elements, Ti, C and N are also present in the microstructure. The same holds true for cermet formulations with prealloyed complex carbonitride solid solutions. The nitrogen content in cermet formulations gives rise to a certain microporosity which can be decreased or avoided by hot isostatic pressing or by a sinter-HIP treatment.

During the heating up period, several metallurgical reactions, between the hard components themselves on the one hand and between the hard components and the binder metals on the other, begin to occur. They start well before even the first liquid phase is formed. The metallurgical reactions in the solid state comprise degassing reactions, diffusional processes and shrinkage of the powder compacts.<sup>5</sup> At even higher temperatures the binder metals start to react metallurgically with the hard phases and form a liquid phase well below the melting points of the pure metals. The metal melt dissolves the carbide components and dissolution reprecipitation mechanisms set in. These processes have a decisive influence on the microstructures of the cermets. In order to arrive at a better understanding of the metallurgical processes occurring during the liquid-phase sintering stage of cermet alloys specific experiments were devised to obtain more detailed and systematic information on this aspect of their behaviour. Additional experiments with more conventional compositions were also performed and the results are presented.

### 2.1 Interaction between nickel melt and Ti(C,N)

Ti(C,N) is a solid solution between the boundary phases TiC and TiN. While the phase equilibria between TiC and Ni or Co are sufficiently established,<sup>6</sup> the phase diagrams for Ni-Ti-N and Co-Ti-N are still largely unexplored.<sup>7</sup> Similarities

between the systems Ni–Ti–C and Ni–Ti–N exist with respect to the phase equilibria in the solid state. While between TiC and Ni, or between Co and TiC, pseudobinary eutectic points have been reported, analogous eutectic points between Ni and TiN or Co and TiN are either not known or observations by some authors are highly questionable. Since the solubility of TiN in liquid metals such as Fe, Co and Ni is much lower than the solubility of TiC, it can be safely assumed that the eutectic compositions will be very near to the metal corner of the ternary systems and the melting point depression will consequently be relatively slight.<sup>7</sup> Compact pure TiN is wetted excellently by nickel (cobalt) melts and the metal melt has been observed to penetrate along the grain boundaries into the bulk material. Apparently the interphase energy between the metal melt and TiN is lower than the grain boundary energy between TiN crystallites.

The reactions between Ti(C,N) and the liquid metals Ni and Co have not yet been extensively investigated, but it can be safely assumed that the phase equilibria will not be substantially different from those in the Fe–Ti–C–N system. According to the report by Ozturk and Fruehan,<sup>8</sup> Ti(C,N) reacts with Fe melts in such a way that TiC is preferentially dissolved in the iron melt, whereas a residue of relatively carbon-poor Ti(C,N) remains undissolved. The nitrogen partial pressure in the atmosphere, of course, has a decisive influence on phase equilibria; in any case the solubility of TiC in the liquid metal will be much higher than that of TiN. Upon liquid-phase sintering of powder compacts consisting of Ti(C,N) and Ni and/or Co — or equally well, of TiC + TiN + Co/Ni — there will be a preferential solubility of TiC in the liquid phase. Undissolved TiN residues will remain and serve as nuclei for the precipitation of dissolved carbides upon solidification of the liquid phase.

For a nitrogen pressure of 10 mbar at 1773°C, for instance, the carbonitride  $\text{Ti}(\text{C}_{0.84}\text{N}_{0.16})$  is in equilibrium with a nickel melt that contains approx. 8 at% Ti and 13.3 at% C but only about 0.002 at% N. Under the same conditions TiN is in equilibrium with a nickel melt containing approx. 10 at% Ti and nearly no nitrogen. Ti(C,N) between those extreme compositions is — under identical conditions — in any case in equilibrium with a nickel melt that contains relatively much more TiC in liquid solution than TiN.

The results of the thermochemical estimation of these phase equilibria have been confirmed, at

least qualitatively, by experimental work in which nickel melt was brought into contact with fully dense hot-pressed specimens of Ti(C,N). These were prepared from Ti(C,N) powders of various compositions by hot-pressing in graphite dies at 2200–2500°C under a pressure of 30 MPa yielding compact polycrystalline hard materials with residual porosities between 0.9 and 4.3%. The cylindrical specimens were cut with a diamond saw. The sections were reacted at 1500°C with nickel melt in  $\text{Al}_2\text{O}_3$  crucibles for a period of 20 min. High-purity Ar served as a protective gas. After cooling down, the contact zone between Ni melt and the hard phase was investigated by metallography and by electron beam microanalysis. It was found that the reaction between Ti(C,N) and liquid Ni proceeds as expected: liquid nickel penetrates along the grain boundaries into the solid Ti(C,N) specimen and preferentially dissolves TiC, which in turn is transported via the liquid phase out of the hard material, while undissolved nitrogen-rich Ti(C,N) residues remain undissolved along the original grain boundaries of the hard phase. In the microsection Fig. 2(a) this reaction becomes visible. The larger original Ti(C,N) grains, as yet unattacked by the nickel melt, are surrounded by carbonitride grains which can be distinguished from the original carbonitride grains by their brighter colour. As revealed by the ESMA analysis in Fig. 2(b), the nitrogen content of the precipitated carbonitride grains is much higher than that of the original bulk carbonitride. With very nitrogen-rich Ti(C,N) compacts the nickel melt penetrates along the grain boundaries into the bulk material but without disintegrating it. Instead, liquid nickel only leads to the formation of nitrogen-rich seams. In powder metallurgical compacts, the metallurgical reactions will proceed similarly: the higher solubility of TiC in the liquid metal compared to the low solubility of TiN will result in the formation of nitrogen-rich nuclei around which the dissolved (Ti,Mo)C will precipitate epitaxially in the course of a dissolution–reprecipitation process. This phenomenon could even be a basis for an explanation of the well-known fact that the grain growth rate in nitrogen-containing cermets is so much lower than in nitrogen-free alloys.<sup>9</sup> Since the volume portion of the liquid binder phase in cermet cutting alloys is much smaller than that in the contact reaction experiments, the saturation concentration of the liquid phase with respect to the TiC, Mo-carbide and

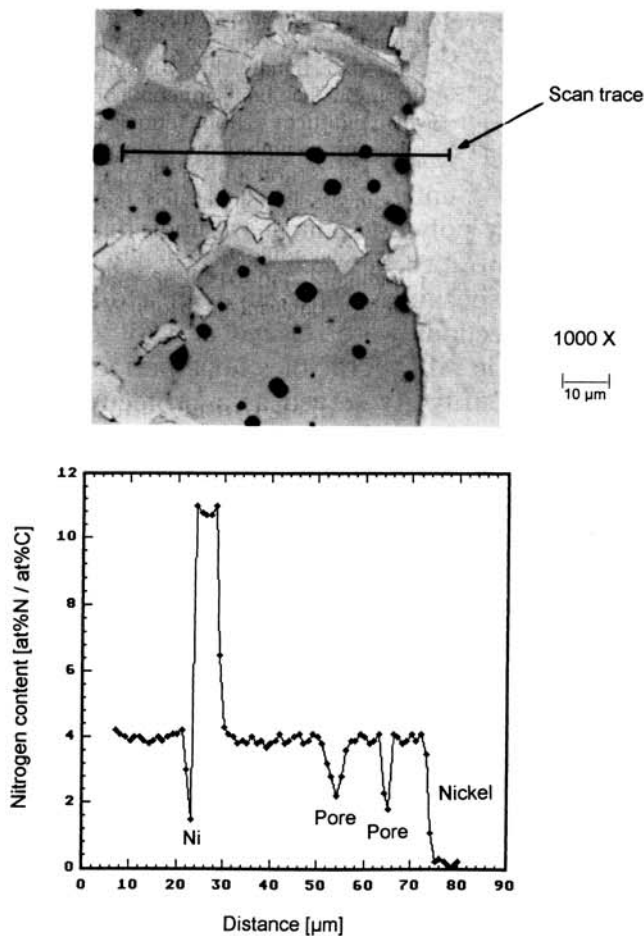


Fig. 2. Microsection through the contact zone between nickel melt and  $Ti(C_{0.2}N_{0.8})$ . Upper part: bright — Ni, light grey —  $Ti(C_{0.09}N_{0.91})$ , grey —  $Ti(C_{0.2}N_{0.8})$ , ESMA — scan across the reaction zone. Lower part: ESMA signals across the reaction zone. Y-axis — N/C ratio.

W-carbide concentrations will soon be reached and not every hard particle can completely go into solution. Thus, if they were present in the starting powder mixture, some of the Mo, W, Ta-containing TiC particles will quite probably survive, unchanged, the liquid phase sintering process.

The reaction between hot-pressed compact quaternary solid solutions of (Ti,Mo) (C,N) or (Ti,W) (C,N) with liquid nickel are currently under investigation. While the phase equilibria are considerably more complicated in a quaternary system, the first results appear to indicate that, even in such cases, nitrogen-rich titanium carbonitride segregates from the melt, while TiC, Mo-carbide and W-carbide are preferentially dissolved in the melt. Whenever Mo or W carbides are present as components in the starting powder mixture, because of their high solubilities

Table 1. Solubilities of carbides and TiN in liquid binder metals at 1400°C

System	Solubility of the carbide/nitride (wt %)
Co-TiC	10
Co-TiN	<0.5
Co-VC	19
Co-NbC	8.5
Co-TaC	6.3
Co-Mo <sub>2</sub> C	39
Co-WC	39
Ni-TiC	11
Ni-TiN	<0.5
Ni-VC	14
Ni-NbC	7.0
Ni-TaC	6.3
Ni-Mo <sub>2</sub> C	36
Ni-WC	27

they are dissolved in the liquid phase. Therefore, the melt that results during the first few minutes after the liquid phase is formed is relatively rich in Mo and/or W. (See Table 1 for the solubilities of various carbides in liquid Ni or Co.) From this melt containing TiC, Mo<sub>2</sub>C, WC, etc., in liquid solution (Ti,Mo)C or (Ti,W)C phase precipitates, probably epitaxially, around undissolved TiN nuclei. Since in the first stage the melt is rich in Mo (and/or W), the first layer surrounding the TiN nucleus will definitely be richer in Mo (and/or W) than would correspond to the gross composition of the powder mixture. Such enrichments of Mo and/or W around the core of the hard particles have been frequently observed and are reported in the literature.<sup>10</sup>

## 2.2. Degassing experiments

During the sintering of powder compacts with nitrogen containing components, when carried out in vacuum, several gaseous species are set free which influence the stoichiometries of the hard phases. Even the alloy status of the binder phase can be affected.<sup>11</sup> In order to be able to identify the gaseous species and monitor the quantities given off during the heating-up period, a special experiment was devised for measuring these gases with respect to both composition and absolute amounts. In industrial sintering furnaces this task is complicated by the tendency of the conventional graphite heating elements and insulating materials to absorb and to give off gases, particularly CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and hydrocarbons,

which are uncontrollably desorbed during the heating up period. In order to avoid these possibly disturbing influences, the green compacts were heated inductively in a quartz tube and the evaporating gases were analysed in a quadrupole mass spectrometer. The relative ion intensities of the ion currents for the mass units  $^{12}\text{C}^+$ ,  $^{14}\text{N}^+$ ,  $^{28}\text{CO}^+$  and  $^{28}\text{N}_2^+$  were utilized to determine the relative amounts of  $\text{N}_2$  and  $\text{CO}$ . The ion intensities, together with their fragmentation patterns of pure component gases, made it possible to arrive at a set of equations which led to information about the kinds and the amounts of gases present in the sintering atmosphere.<sup>12</sup> The results of the experiments are shown graphically in Fig. 3 and are summarized as follows:

- The oxygen contamination of the powder mixture, probably as chemisorbed or chemically bonded oxygen, begins to react with carbon present in the mixture as carbides or free carbon. It is reduced to  $\text{CO}$  which is given off into the gas atmosphere. With increasing temperature the rate of reaction

increases gradually until it reaches a maximum at  $1100^\circ\text{C}$ . With a further rise in temperature the rate decreases, probably because of oxygen depletion of the powder particles.

Nickel and cobalt increase the rate of  $\text{CO}$  formation and enhance the removal of the anti-wetting oxide layers on the surfaces of the nitride and carbide particles.

- The evolution of nitrogen sets in at about  $1200^\circ\text{C}$  and reaches a very pronounced maximum at about  $1300^\circ\text{C}$ . With further increasing temperatures the rate of nitrogen evolution decreases again and comes to a near standstill. Only at temperatures exceeding  $1500^\circ\text{C}$  does the rate start to increase again.
- The onset of the liquid phase formation is clearly reflected in the differential thermal analysis: it coincides with the temperature at which the nitrogen evolution is abruptly discontinued. It would appear that the formation of the liquid phase and the decrease in

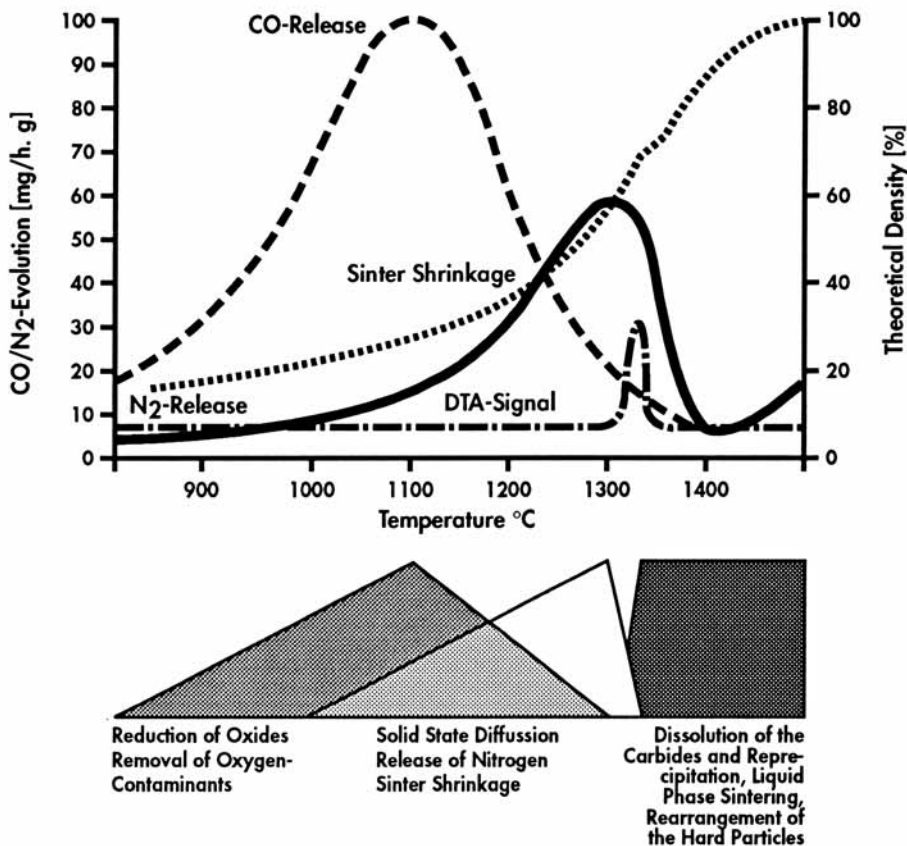


Fig. 3. Schematic diagram of the metallurgical reactions during a sinter cycle.

the evolution rate of nitrogen are causally linked. Obviously, the liquid phase promotes or even triggers the formation of the core/shell type-structure of the hard particles. Since the shell contains little or no nitrogen the direct contact between the nitride-containing core and the diffusion-promoting liquid phase is disrupted by the shell. Because of the protective action of the shell the rate of nitrogen evolution is drastically reduced.

### 3 CERMETS SINTERED WITH DIFFERENT STARTING MATERIALS

In order to optimize the cutting performance of cermet tools the influence of various starting materials has been investigated. The starting materials were chosen so that the gross composition of the hard phase was kept constant. Mixtures of the unalloyed binary carbides with titanium nitride, mixtures of prealloyed carbides with titanium nitride or titanium carbonitride, and even prealloyed multicomponent carbonitrides were used. The influence of the binder phase with respect to the Ni/Co mixing ratio and of the conditions during sintering were investigated.

The influence of different starting materials manifests itself in the microstructures of the sintered cermets: with unalloyed binary components as starting materials the microstructures as they appear in the BSE (back-scattered electron) images in the scanning electron microscope (SEM) are characterized by the exclusive presence of dark, titanium-rich cores and brighter rims containing the heavier elements Mo, W, Ta, Nb, Ti and C. However, with prealloyed carbides such as (Ti,W)C or (Ti,W,Ta,Nb)C, some of the hard particles in the cermet microstructure do have dark cores, while others have bright cores. The same observations can also be made if quaternary or even more complex prealloyed carbonitrides are used.

The mechanical properties of these cermets, such as hardness, transverse rupture strength and rupture toughness, do not appear to be significantly influenced by the choice of the starting hard materials if the same gross composition is maintained. For cermets with the nominal composition (wt%): 26.0% TiC, 27.0% TiN, 20.0% WC, 8.6% TaC, 1.1% NbC, 1.0% Ti<sub>2</sub>AlC, 8.2% Ni,

8.6% Co, the hardness values HV30 are ~ 1440–1460 and the transverse rupture strength values ~ 1400–1600 MPa for sintered specimens and up to ~ 2200–2400 MPa for hot-pressed specimens. Coarse carbides and nitrides result in slightly higher transverse rupture values, while hardness values remain unaffected.

The magnetic properties of cermets — specific saturation magnetization and coercive force — are dependent on the binder content and binder composition, especially with respect to the relative amounts of cobalt and nickel, but are also influenced by the alloy content (Ti,Mo,W,Nb,Ta,Al, etc.) within the binder phase. The coercive force and the interdependence between coercive force and mean free path of the binder phase appear to be not as clear as for conventional WC-Co hardmetals.

A series of experimental alloys with varying Ni/Co ratios but with identical volume portions of binder phase were sintered in order to study the influence of binder composition. The results clearly show that cermet alloys can be sintered to full density irrespective of binder composition — from pure nickel over nickel-cobalt alloys to pure cobalt binder. With increasing cobalt content the hardness increases slightly while rupture toughness values tend to decrease (see Figs 4 and 5). With transverse rupture strength values, the trends are somewhat less clear but they too seem to generally decrease with increasing Co content (see Fig. 6). A possible explanation might be found in the observation that the grain size of the hard phase becomes somewhat finer with increasing Co content. The shape of the hard particle grains and the alloy status of the binder phase could also influence these values.

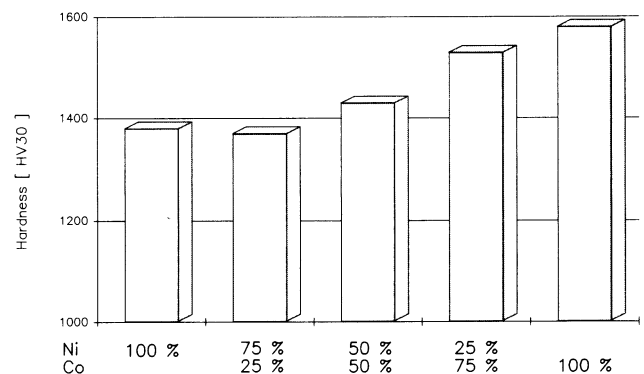


Fig. 4. Hardness values of cermet cutting tools vs Ni/Co binder composition.

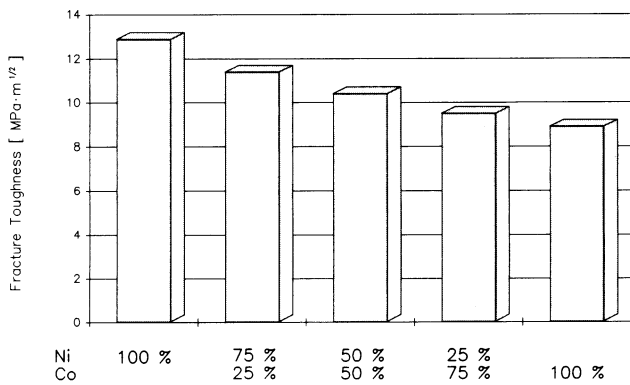


Fig. 5. Fracture toughness of cermet cutting tools vs Ni/Co binder composition.

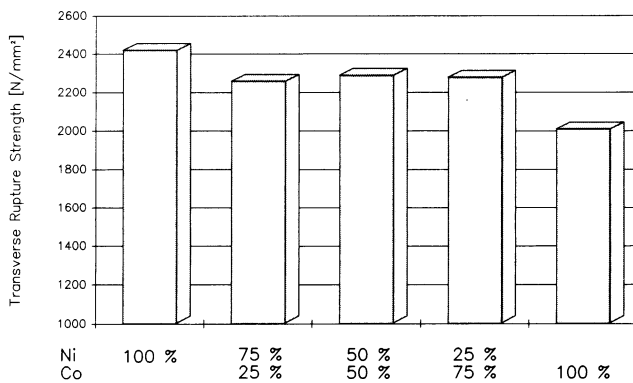
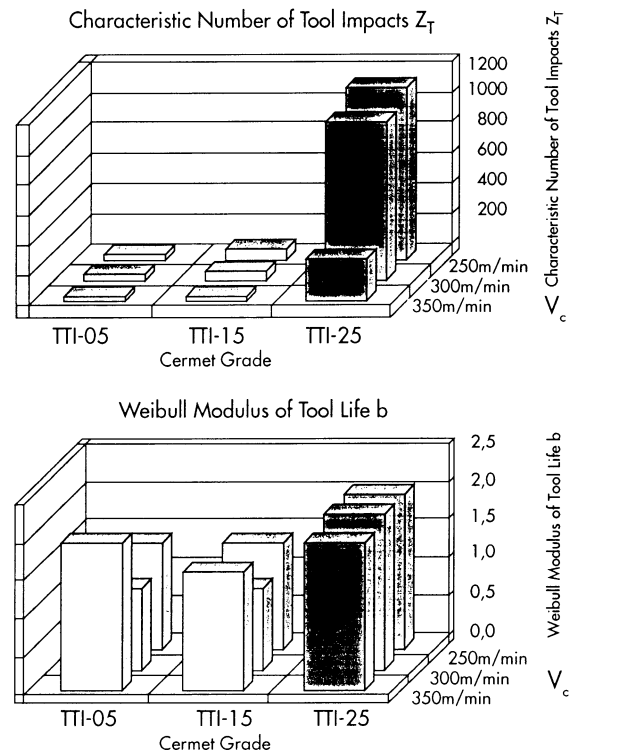


Fig. 6. Transverse rupture strength of cermet cutting alloys vs Ni/Co binder composition.

#### 4 APPLICATION OF CERMET CUTTING ALLOYS

Today cermet cutting alloys are mainly applied for finishing and rough-finishing of unalloyed and alloyed steels and ductile globular cast iron. Particularly in machining centers cermet cutting tools have proven superior with respect to their reliability. A multitude of cutting operations can be performed within one single fixture. Machining operations with aluminium or Al/Si alloys result in the formation of built-up edges. Cermet cutting tools applied for machining very hard materials appear to be operating at the borderline of their applicability. Quench-tempered steels with strength values up to  $1000 \text{ N mm}^{-2}$  can satisfactorily be machined with cermet cutting tools in both turning and milling operations. In Fig. 7 the characteristic figures (characteristic number of total tool impacts and Weibull modulus of lifetime) with respect to the specific type of cermet are shown. The machining tests were performed

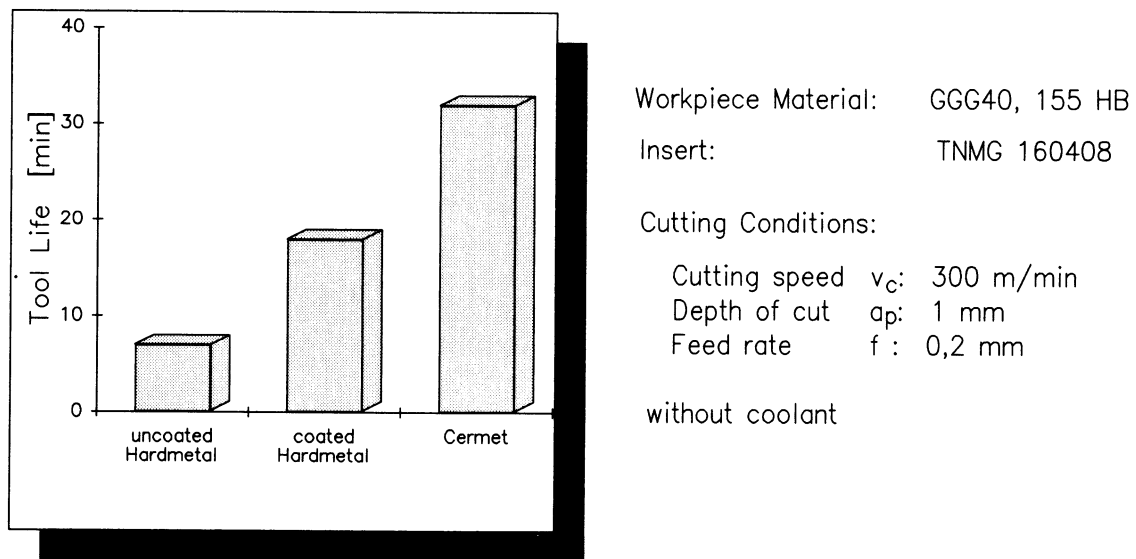


Cutting Material: Cermets  
 Workpiece Material: 42 CrMo 4 V  
 $R_m$  ca.  $950 \text{ N/mm}^2$   
 Cutting Test: VDI Stripe Turning Test  
 © 1991

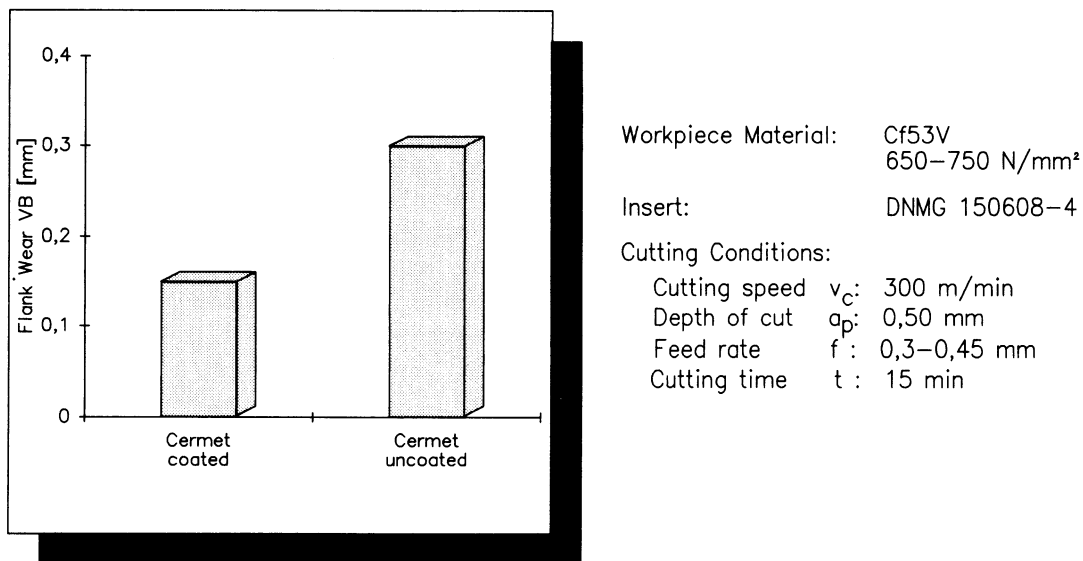
Cutting Conditions:  
 $f = 0,1 \text{ mm}$   
 $a_p = 2,5 \text{ mm}$   
 Insert: SPUN 120308

Fig. 7. Characteristic number of tool impacts according to the VDI-stripe turning test and Weibull modulus of lifetime for various cermet cutting alloys and cutting speeds.

at the RWTH Aachen according to the VDI stripe-turning test. With the hard and wear-resistant cermet alloys, TTi05 and TTi15, the characteristic number of tool impacts is significantly below 100. The tougher cermet TTi25 features a much higher number of tool impacts. At a cutting speed of  $250 \text{ m min}^{-1}$  the figures are above 1000. With increasing cutting speed this number decreases, but even at  $350 \text{ m min}^{-1}$ , numbers of 200 can be reached. With respect to the Weibull modulus all three cermets have similar values. The benefits of the application of cermet cutting tools in comparison with coated and uncoated conventional hardmetals of the identical ISO application group can be readily demonstrated, for instance, with the finish-turning of ductile globular gray cast iron GGG 40. A cermet alloy outperforms a conventional coated hardmetal (see Fig. 8) with respect to both tool life as well as with respect to the surface finish of the machined workpiece. With a harder material, GGG 70, the outcome is reversed. Here the



**Fig. 8.** Finish turning of globular cast iron GGG 40 with cermet cutting tools compared to uncoated and coated hardmetal grades.



**Fig. 9.** Copy-turning of a gear shaft with coated and uncoated cermet grades.

coated hardmetal proves to be superior to the cermet alloy. The further development of cermet alloys will however lead to coated cermet grades with even better wear resistance and applicability for the machining of even harder materials and workpieces (see Fig. 9). As for the hot wear resistance, a further increase in the nitrogen content is expected to improve it as well.

## 5 CONCLUSIONS AND PERSPECTIVES

The metallurgical reactions during liquid-phase sintering or cermet alloys are extraordinarily

complex. They include reactions of the solid hard particles with the liquid binder phase on the one hand and reactions of the sinter compact with the sinter atmosphere on the other. The great variety of process parameters in cermet alloy production makes it difficult to correlate the actual performance of cermet cutting tools with process parameters such as the choice of starting materials, their composition, alloy status, grain size and grain size distribution, carbon and nitrogen contents and stoichiometry. Furthermore, the sintering conditions and the alloy status of the binder phase after the sintering process probably



influence the cutting performance too. Notwithstanding these difficulties, the manufacturers of cermets have been able to achieve a very high level of quality and reliability for their alloys by applying rigorous standards of process control and optimization strategies.

### ACKNOWLEDGEMENTS

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### REFERENCES

1. Ettmayer, P. & Kolaska, H., Cermets der neuen Generation. *Metall*, **43** (8) (1989) 742–9.
2. Kolaska, H., Cermets — modern und leistungsfähig. *Chemische Produktion*, **3/92** (1992) 37–9.
3. Ettmayer, P. & Kolaska, H., Cermets (Wolframcarbidgefreie Hartmetalle). In *Pulvermetallurgie in Wissenschaft u. Praxis*, ed. H. Kolaska, Band 4. Verlag Schmid, Freiburg/B, 1988, pp. 163–93.
4. US Patent 3971656 (1976).
5. Ettmayer, P., Kolaska, H. & Groschner, M., Titanium carbonitride-based hardmetals: metallurgical reactions during sintering and properties of Ti(C,N)-based cermets. *Proc. of the 8th Int. Conf. on Powder Metallurgy in the CSFR*, Piestany, October 1992.
6. Bäckerud, L., Carlson, B., Oscarsson, R. & Mikus, M., A study of the nickel-rich and cobalt-rich corners of the systems Ni-Ti-C and Co-Ti-C. *Scand. J. Metallurgy*, **3** (1974) 225–35.
7. Binder, S., Lengauer, W. & Ettmayer, P., The Ti-N-Ni system: Investigations relevant for cermet sintering. *J. Alloys & Compounds*, **177** (1991) 119–27.
8. Ozturk, B., & Fruehan, R. J., Thermodynamics of inclusion formation in Fe-Ti-C-N alloys. *Metallurgical Trans. B.*, **21B** (1990) 879–84.
9. Matsubara, H., Shin, S. G. & Sakuma, T., Grain growth of TiC- and Ti(C,N)-based cermets during liquid phase sintering. *Proc 1991 Int. Symp. on the Science and Technology of Sintering*, Vancouver, Canada, 1991.
10. Ettmayer, P., Kolaska, H. & Dreyer, K., Effect of the sintering atmosphere on the properties of cermets. *pmi*, **23** (1991) 224–30.
11. Gee, M. G., Reece, M. J. & Roebuck, B., High resolution electron microscopy of Ti(C,N) cermets. *J. Hard Materials*, **3** (1992) 119–41.
12. Groschner, M., Metallurgische Reaktionen bei der Sinterung von Titancarbonitrid-Hartmetallen. Dissertation, TU Wien, 1992.