

Ti(C,N)-Based Cermets: Critical Review of Achievements and Recent Developments

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Keywords: titanium carbonitride, titanium carbide, solid-state properties, cutting tools, hardmetal, hardness, fracture toughness, transverse rupture strength, sintering

Abstract. The paper describes briefly the historical development and presents in more detail solid-state properties such as hardness, heat conductivity, thermal expansion and mechanical properties of titanium carbonitride Ti(C,N), the basis of the hard phase of cermets. The metallurgy of Ti(C,N)-based cermets with respect to microstructure formation during sintering and the impact on properties are presented in more detail. The various influences such as W and/or Mo content, Mo/W ratio, C content and C/N ratio, binder phase content and binder phase composition (Co/Ni), sintering time, dwell time, alloy state of powders and grain size were critically evaluated and are presented in form of fracture toughness vs. hardness graphs. A table gives a reference list on the study of these influences. TRS data on cermets were collected and summarised in a separate table, too.

The focus is put on grades which have the potential of being fabricated soon in industrial processes for production of cermet tools. Application examples for metal cutting, sawing and chip bonding are presented.

In two final sections recent modifications and achievements such as graded microstructures, multicomponent binder, and hybrid microstructures are also briefly presented together with an outlook on the future potential of cermet applications.

1. Introduction

Cermet is an artificial word that designates the combination of a brittle hard phase ('ceramic') with a ductile binder phase ('metal') to form a composite material. In the metal cutting industry cermet is always designated as a TiC- or Ti(C,N)-based composite with an *fcc* hard phase and a Co-, Ni- or Co/Ni-based binder phase. In the cutting tool industry this designation differentiates cermets from 'hardmetals' (English) or 'cemented carbides' (American). The latter are composed of a hexagonal WC phase and a ductile binder, mainly composed of Co. Both types of materials are employed in metal cutting processes. The consumption of cermets in this field is only at a level of 3-5% in the western hemisphere, whereas in Japan cermets make up around 25-30% of metal cutting inserts. Hence, cermets are always compared to hardmetals in view of service performance. Generally, they are more brittle and less ductile than hardmetals, located between the latter and ceramics in terms of the toughness vs. hardness, or a feed-rate and cutting depth vs. cutting-speed relation (Fig.1). There are a few applications outside classical metal cutting which will be addressed briefly later in this review. Tab.1 presents the advantages and disadvantages of cermets as compared to hardmetals.

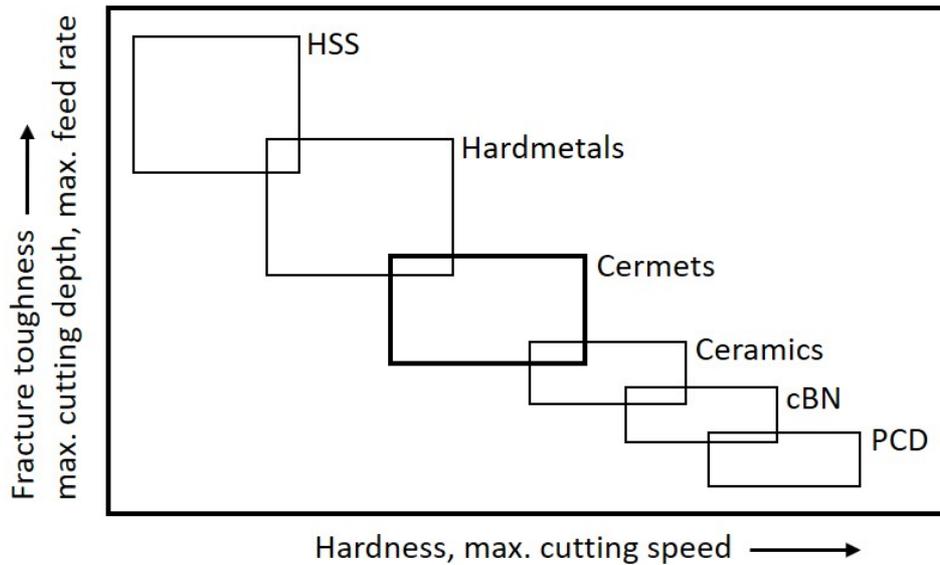


Figure 1

Scheme of fracture toughness vs. hardness and – parallel – feed rate vs. cutting speed of various materials used in cutting tools. The cermets are located in between of more brittle ceramics and more ductile hardmetals. HSS: High-speed steel, cBN: cubic boron nitride, PCD: polycrystalline diamond (bonded).

Table 1

Properties of cermets when compared to hardmetals.

Characteristics	Hardmetal	Cermet
Toughness	+	–
Hardness	–	+
Specific density	–	+
Thermal conductivity	+	–
Production chain	+	–
Characterisation	+	–
Cutting depth	+	–
Feed rate	+	–
Cutting speed	–	+
Flank wear	+	–
Crater wear	–	+
Friction, tool – workpiece interaction	–	+
Dimensional accuracy of manufactured parts	–	+
Raw material supply risk	–	+

2. Brief Historical Review

It was only about four years after the fabrication of hardmetals in 1926 according to Schröter's patent of 1923 [1], that TiC-based composites were invented by Schwarzkopf and Hirschl [2] and marketed by *Plansee* under the brand *Titanit S*. One of the best grades in this invention was a composite of 62% TiC, 27% Mo₂C, 10% Ni and 1% Cr. At that time, these materials were called tungsten-free hardmetals. It took about another 20 years before the word cermet entered into the usage of metal cutting industry when TiC-NbC-TaC-Ni,Co,Cr,Mo,Al alloys were investigated for turbine-blade applications in the late 1940s, as invented by Kieffer and Kölbl [3] as well as by Redmond and Graham [4]. Various companies such as *Plansee* (brand name: *WZ Alloys*), *Kennametal* (*Kentanium*), *Firth-Sterling* and *Metropolitan-Vickers* have investigated and/or produced similar materials. Nowadays such types of grades are again interesting, both due to NbC

additions to the hard phase and/or establishing a multi-component high-entropy alloy binder phase (see chapter “recent research”). Mo was not beneficial to the above-mentioned alloys with respect to oxidation resistance but was a further major step in the development of cermet grades by Ford Motor Co. under the guidance of Moskowitz and Humenik [5], who were able to increase the wetting behaviour and thus enhance sintering properties. One of the most important idea and achievement was the introduction of nitrogen into the starting formulation. This was first achieved in a thesis at TU Vienna [6, 7]. Nitrogen is a grain refining element and rises the hardness substantially. Since then, nitrogen is mainly added in form of Ti(C,N) as well as quaternary carbonitrides powders such as (Ti,Mo)(C,N) or in form of a nitrogen-containing sintering atmosphere at relatively low temperatures to nitride the carbide powders in a stage when open porosity in the body still prevails. Also, the invention of Rudy [8] to form spinodal alloys by decomposition of (Ti,Mo)(C,N) into two *fcc* phases with very similar lattice parameters involved the presence of nitrogen. The hard phase structure was claimed to be a result of this decomposition. However, a spinodal alloy would have had a much finer structure than prevailing in the hard-phase grains of cermets.

Another step was the formation of intermetallic aluminide phases within the binder phase to strengthen it [9-12]. This can be achieved by adding binary and ternary Al compounds such as AlN or Ti₂AlC, which form aluminides with the metals of the binder phase. The composition of the binder phase is important in view of a desired high deformation and crack resistance. For this strengthening, alloying elements play an important role. Several authors have investigated the binder composition. For TiC-Mo₂C-based cermets the composition is dependent on the hard phase composition of nitrogen-free cermets [5]. Interestingly, in case of nitrogen-containing cermets, the Mo content in the binder phase is higher than that of nitrogen-free cermets [5, 13-15] (see also chapter 4.2). The stoichiometry of the hard phase and the concentration of alloying elements in the binder are interdependent of each other: the higher the deviation from stoichiometry of the hard phase is, i.e. from $([C]+[N])/[\text{sum of metals}] = 1$, the higher is the solubility in the binder phase.

With the development of various microanalytical tools, it has been possible to measure the concentration in the binder phase and the hard phase grains also of more complicated cermets [16-18]. However, hard phases and the binder phase are not in thermodynamic equilibrium, hence the concentration in the binder depends on sintering conditions, too [19]. It is therefore questionable whether such data can be used for modelling, like it is possible for hardmetals [20].

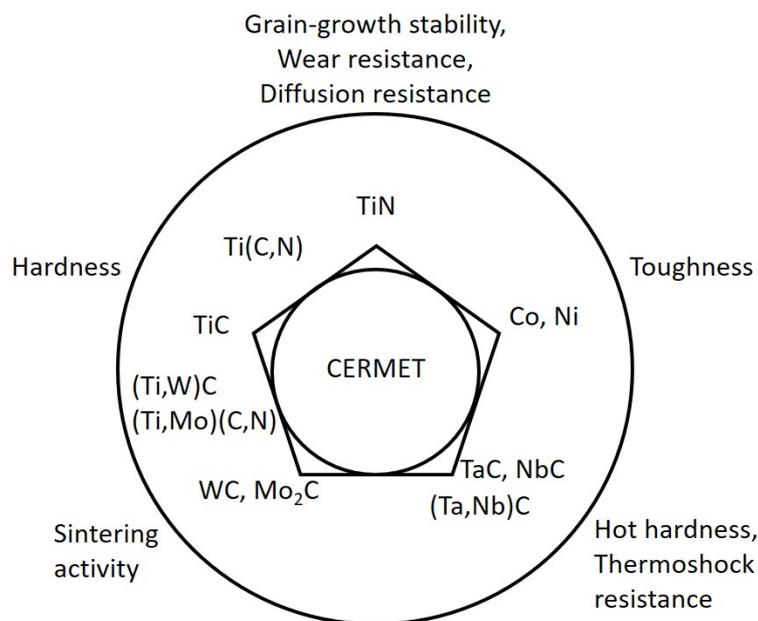
Tab. 2 presents a historical summary of the above-mentioned steps which was published in 1989 [21]. The detailed formulations of the various grades investigated nowadays are documented in the next chapters.

Today, the formulations of cermets are relatively complicated mixtures of high-quality carbide, nitride, carbonitride and metal powders with low oxygen content. There exist industrial grades which do not contain molybdenum, added in form of powders like Mo₂C, (Ti,Mo)C or (Ti,Mo)(C,N) in the starting formulation, but instead tungsten for which WC, (Ti,W)C powders are added. Also, TaC, NbC and (Ta,Nb)C are often added in a relatively high percentage, up to around 10wt% of the starting formulation. The powders are prepared by carbothermal synthesis by mixing oxides with carbon black and subjecting the mixtures to high temperatures of around 2000°C. If carbonitrides are prepared nitrogen is inserted via the gas phase. For the preparation of Ti(C,N) powder TiO₂ (usually rutile) is mixed with carbon black and heated in nitrogen atmosphere [22, 23] or by reaction of Ti with N and C in a so-called metal process. Fig.2 gives condensed information of the various constituents of cermets and their impact on the properties and sintering behaviour of cermets [24].

Table 2

Historical development as summarised by Ettmayer and Lengauer [21]. After 1990 many different grades appeared which are discussed in the following text.

Year	Principal Composition	Manufacturer
1926	WC-Co	Krupp-Widia
1930	TiC-Mo ₂ C-Ni,Mo,Cr	Plansee
1930	TaC-Ni	Fansteel Corp.
1933	TiC-TaC-Ni	Siemens
1938-45	TiC-VC-Fe,Co,Ni	Plansee
1949-55	TiC-NbC-Ni,Co,Cr,Mo,Al	Plansee, Kennametal
1952-54	TiC-steel	Chromalloy
1960	TiC-Ni,Mo	Ford Motor Co.
1970	TiC-TiN-Ni,Mo	TU Vienna
1974	(Ti,Mo)(C,N)-Ni,Mo	Teledyne
1975	TiC-TiN-WC-Mo ₂ C-VC-Ni,Co	Kyocera
1977-80	TiC-Mo ₂ C-Ni,Mo,Al	Ford Motor Co.
1980-83	(Ti,Mo,W)(C,N)-Ni,Mo,Al	Mitsubishi
1988	(Ti,Ta,Nb,V,Mo,W)(C,N)-Ni,Co-Ti ₂ AlN/Ti ₂ AlC	Krupp Widia

**Figure 2**

Scheme of the influence of various constituents of the starting formulation on sintering and properties of powders in a typical cermet formulation [24].

3. Preparation and Characterisation

3.1 Starting formulation and sintering

The industrial fabrication of cermets is essentially the same as for hardmetals. First, the starting powders are weighed and mixed in a drum or attritor mill with the aid of hardmetal balls and a dispersive liquid or, in recent developments, with water together with corrosion inhibitors to prevent hydrolysis of the hard phase powders. Pressing aids such as paraffine wax on the order of 2-4wt% of the powder weight is added in this step, too. Recent developments in this process try to lower the amount of dispersing liquids ("dry mixing"). Then the mixture is spray dried to uniform

granules of a narrow particle size to provide excellent flowability for the automated pressing step. Pressing is performed in hardmetal dies at static pressures in the range of 10-20 kN/cm².

The sintering step is more complicated than that of hardmetals with respect to the various temperature dwells as well as to the sintering atmosphere. Usually, the highest sintering temperature is on the order of 1460 – 1540°C, which is higher than that of hardmetals. Because of the more stable character of cermet hard phases, even CO is formed at higher temperatures than upon sintering of hardmetals. Furthermore, if nitrogen is in the starting formulation, the outgassing of nitrogen at higher temperature than the CO outgassing temperature can give rise to nitrogen porosity.

Today, modern sintering technology always makes use of a so-called sinterHIP cycle, in which a first part of the sintering cycle is performed at vacuum conditions, sometimes adding some nitrogen counter-pressure, and a final part is performed at elevated Ar pressure (e.g. 30-60 bar) in order to isostatically densify the material and squeeze any pores to obtain a material with zero porosity. However, even by using sinterHIP technology, high-quality carbide and carbonitride powders together with a well-tailored sintering profile are necessary for obtaining a uniform and pore-free microstructure. If just the pores are filled up by application of high pressure, the cermet would not be of high quality, i.e. mechanical properties such as transverse rupture strength (TRS), hardness, and fracture toughness are lowered. Thus, vacuum sintering investigations are a valuable prerequisite to establish an almost pore-free and homogeneous microstructure. This sintering behaviour is best investigated by a combination of methods of thermal analysis [25, 26] such as Differential Thermal Analysis (DTA) for measurement of the formation temperature of the liquid phase as well as dilatometry (shrinkage as a function of temperature), which both can be performed under various atmosphere conditions. As mentioned previously, the formation of CO takes place during cermet sintering due to the starting oxygen content of the raw powders and reaction with carbon. Thus, mass-spectrometric analysis of delubing (outgassing) is another important investigation technique in which the CO production of various constituents of the starting formulation, including the ones of the binder powders, can be investigated. Nitrogen can be measured at the same time although CO and N₂ have practically the same mass of 28amu, the small difference cannot be resolved by a quadrupole mass spectrometer. Hence, ¹²C and ¹⁴N are additionally recorded. Another obstacle is the constant, relatively high pressure in the sintering chamber, whereas the pressure in the spectrometer is below 10⁻⁵mbar. The two parts must be separated by a small orifice. Starting in 1990, Ettmayer et al. [24] were the first who employed such a design of mass-spectrometric outgassing analysis to characterise the sintering phenomena in situ and they have summarised the various metallurgical phenomena occurring upon sintering. In their work, the sintering chamber can carry much larger samples than usually used in MS-coupled techniques (DIL-MS, DTA-MS) and was separated by an orifice to separate the two chambers. This method was further developed [27] and recently applied in a laboratory sintering furnace, which compares better to industrial sintering furnaces, to study the behaviour of industrially produced Ti(C,N) powders grades [28]. The results showed that this technique delivers important information for carbonitride powder production, too. Nowadays, the use of reference gases for calibration and more sophisticated hardware makes quantitative information of the concentration of delubed gases within ±10rel% possible [29].

Fig.3 shows a representation of results of various important in-situ investigations techniques to study the sintering behaviour of cermets together with a sintering profile of a cermet in which also nitrogen was added at certain temperatures and results in completely dense-sintered cermets. A drawback of such investigation techniques is often a much different environment as compared to a sintering furnace of production. Together with the small sample size, this can result in different behaviour of cermet under laboratory investigation as compared to production.

After sintering, cermets are ground by use of diamond disks and are sometimes PVD or CVD coated, depending on the final application.

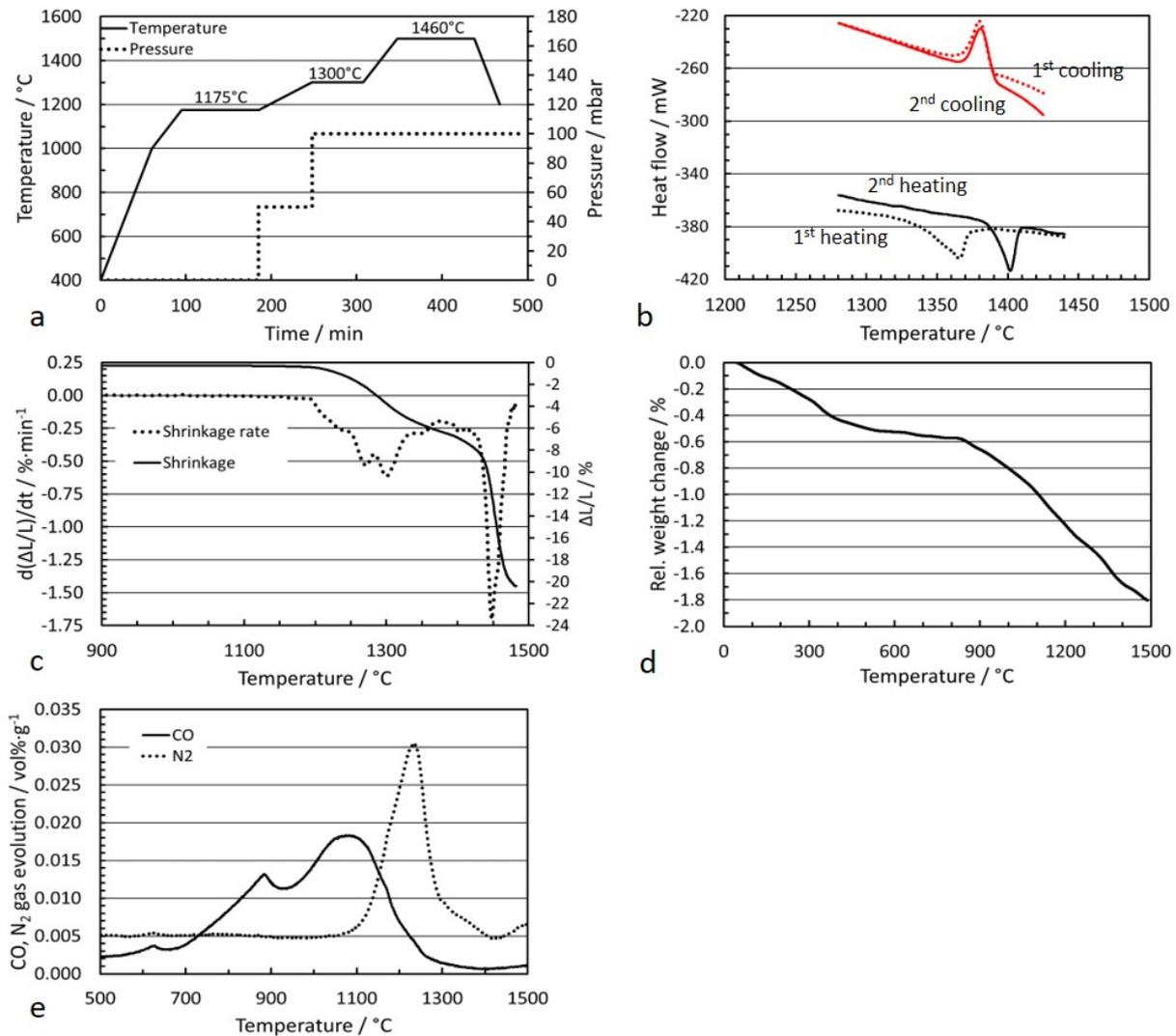


Figure 3

Sintering profile (a) and representation of the output of various in-situ investigations techniques important to study the sintering behaviour of cermets: (b) DTA for investigation of liquid-phase formation temperature, (c) dilatometry for measurement of shrinkage and shrinkage rate, (d) TG for measurement of mass change, (e) delubing behaviour of CO and N₂ studied by mass spectrometry.

3.2 Characterisation

3.2.1 Metallography, mechanical properties

A detailed inspection of cermets makes use of diamond-polished samples to characterise for porosity, presence of graphite or eta phase, and binder-phase distribution by light-optical microscopy (LOM) and to get insight into the structure of the hard-phase grains by scanning-electron microscopy (SEM). Fig.4 shows images of both techniques [30, 31]. Eta phase in cermets is only formed when the sub-stoichiometry of employed carbides or carbonitrides is very high (i.e. $[\text{non-metals}]/[\text{metals}] < 1$) or a high amount of carbide-forming metals is admixed. In contrast, free carbon can be easily formed upon too high carbon balance or if a too high nitrogen pressure is adjusted upon sintering. Nitrogen squeezes out carbon from the *fcc* lattice and carbon precipitates as graphite (for nitrogen pressure ranges see 4.1). LOM images are also a necessary prerequisite to determine porosity in the sintered samples by using a standardised procedure for a clear specification of porosity. For example, the ISO code A00B00C00 (DIN ISO 4505) designates a material with no visible porosity at 100x and 200x magnification of small pores (A), large pores (B), and free carbon (C).

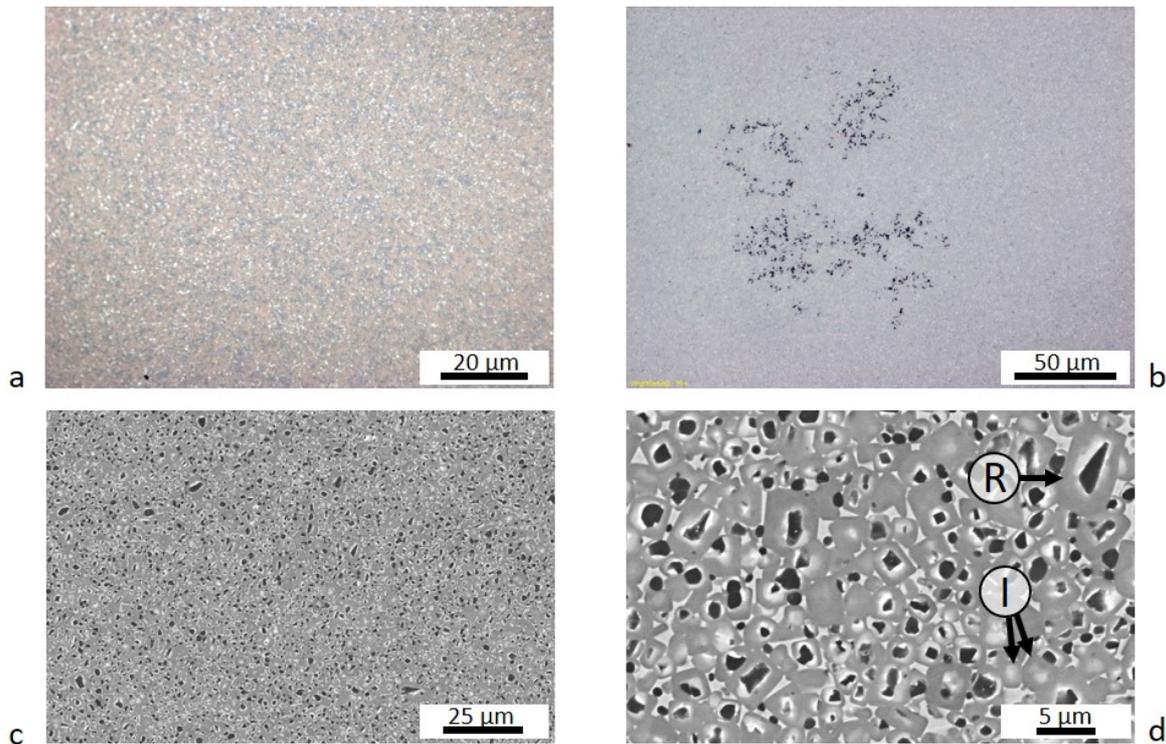


Figure 4

Microstructure of cermets, (a) light-optical microscopy (LOM) image proving a perfect distribution of binder phase and zero porosity A00B00C00, (b) LOM image of a cermet with an unwanted content of free C (graphite) and (c,d) SEM images by use of backscattered electrons (BSE) in different magnifications. The BSE images show the relative atomic weight average within the image (black: light elements; grey: average in atomic weight, white: heavy elements). R: regular threefold core-rim type grain, I: inverse twofold core-rim-type grain.

In the SEM images a peculiar grain-structure of hard particles can be identified, a so-called core-rim structure. In so-called “regular” grains R (Fig.4d) there is a three-fold structure with a dark core composed of light elements (such as Ti, C, N) then a bright inner rim of a higher concentration of heavy elements (such as Mo, W, Ta), and finally a grey rim of an intermediate average atomic weight. Occasionally, so-called “inverse” grains “I” (Fig.4d) are formed with a core of heavier elements than that of the grey rim. The amount and presence of inverse grains is not always clear because the dark core can be located below the polished surface or could have been above. Ion beam sputtering techniques with successive imaging could help to clarify this issue. However, the amount of inverse grains is substantially enhanced if pre-alloyed powders are employed [32], a proof of their existence (see also 4.2). All parts of the hard phase grains are *fcc* carbides or carbonitrides, often with an almost identical lattice parameter which often cannot be easily distinguished by standard XRD. The different parts of the hard-phase grains have the same lattice orientation, thus it is not possible to distinguish them by electron-back scattering (EBSD).

Hardness and fracture toughness data are very important information for both the development of cermets and the quality insurance in production. Usually, Vickers hardness (HV) is used applying a load of typically 10 or 30kgf and the size of indent is measured to calculate HV10 or HV30, respectively. Upon measurement of the cracks occurring at the corners of the Vickers indents, the so-called Palmqvist fracture toughness (K_{IC}) is calculated using the modification of Shetty and Wright [33]:

$$K_{IC} = 0.0275 * \sqrt{\frac{HV*P}{l}} \quad (1)$$

where $l = \sum \text{length of cracks}$ [m], HV is the Vickers hardness and $P = 10$ [kgf].

The HV and K_{IC} are thus easily measured, so that many studies in literature refer to such data. Therefore, we have evaluated the existing literature on potentially industrially competitive cermets grades referring to these data in form of a function K_{IC} vs. HV. The general behaviour of this function is that the K_{IC} decreases with increasing HV (see 4.3).

A much more time-consuming and costly procedure is the measurement of transverse rupture strength (TRS) of cermets. It requires careful processing of at least around 20 test bodies for bending test. The sample must be prepared in a well-defined geometry by grinding and polishing to avoid fissures. A statistical Weibull analysis should follow, reflecting strength and probability of fracture. TRS data are not often reported in literature although they are an excellent information for the quality of the material and is a preceding step before final application testing of a cermet grade is employed. Nowadays, rods of typically 3mm in diameter and 20mm in length were proposed to avoid any edges that are difficult to prepare without pre-damage.

3.2.2 Magnetic properties

Magnetic measurements are non-destructive investigation methods and are employed to characterise the alloy status of the magnetic binder phase. The specific saturation magnetisation (M_s) is reduced by dissolved elements in the binder phase [34]. Thus, it serves as an indication of the amount of hard phase constituents (metals, carbon) picked up by the binder phase upon sintering. If the Ni content is not too high, and the concentration of dissolved elements is not too large, the measurements can be performed at room temperature [35]. Because of many constituents in a cermet, a quantitative relationship between the concentrations of dissolved elements is not accessible without simplifications, nor is a general statement possible whether a cermet sample contains phases like free carbon. This is a drawback as compared to quality control of hardmetals for preparing uniform series with precise carbon level, which defines the desired properties. In WC-Co hardmetals, only W and C are present in the Co binder phase, and W and C concentrations are coupled. Hence, there is a direct relationship with a single M_s value. Such a general relation does not exist in cermets because the binder is composed of many more elements. For quality assurance of a certain cermet grade, M_s measurements can, however, detect deviations in the process chain and ensure homogeneity in production lots.

Another magnetic information, the coercive force H_c , which is a measure of the binder phase thickness between the hard-phase grains and thus indirectly a measure for the grain size in hardmetals, cannot be used for cermets in a straightforward manner, too.

Although high temperatures occur in most application of cermets such as metal cutting, there are not too many studies on high temperature properties. Especially, Mari and co-workers (e.g. [36]) have investigated the deformation behaviour of various types of cermets at high temperatures using a so-called high-temperature mechanical spectroscopy to measure internal friction and evaluate the deformation behaviour (stress-strain curves). Cermets are more rigid as compared to hardmetals and four different temperatures zones of their mechanical behaviour were identified, i.e. brittle and elastic behaviour up to around 600°C, deformation of the binder at $\approx 600 - 800^\circ\text{C}$, deformation of the hard phase at $\approx 800 - 1100^\circ\text{C}$ and plasticity by grain boundary sliding at temperatures higher than $\approx 1100^\circ\text{C}$. Interestingly, the deformation of the hard phase was not observed in hardmetals which is probably due to the higher high-temperature hardness of WC as compared to Ti(C,N). The grain-boundary sliding occurs at 1030°C in cermets (depending on composition) and at 830°C in hardmetals.

4. Metallurgy and Properties

4.1 Phase equilibria and solid-state properties of Ti(C,N)

The properties of cermets are of course greatly influenced by the properties of the Ti(C,N) phase that is a carbonitride resulting from a complete miscibility of TiC and TiN, represented in the phase diagram (Fig.5) [37]. This diagram shows that Ti(C,N) can be even more sub-stoichiometric than the binary compounds.

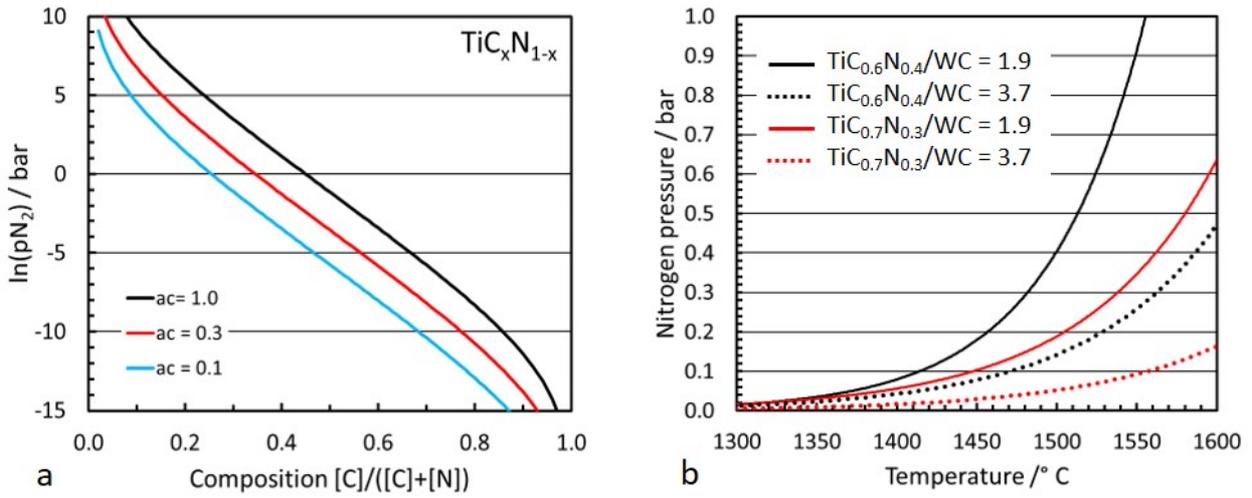


Figure 6

(a) Nitrogen equilibrium pressure of Ti(C,N) at 1500°C for three carbon activities. The equilibrium pressure lowers upon decreasing carbon activity. Calculation performed with data of Jonsson [38].
 (b) Nitrogen equilibrium pressure of Ti(C_{0.6}N_{0.4}) and Ti(C_{0.7}N_{0.3}) in equilibrium with a high and low amount of WC (in wt%) and with a Co/Ni binder phase [39].

The heat conductivity of Ti(C,N) is increased by increasing nitrogen content (Fig.7a) [41]. At levels interesting for Ti(C,N) cermets, in the range [C]/([C]+[N]) = 0.5 – 0.8, it is not much changing. Generally, it is much lower than that of WC so that cermets have a much lower heat conductivity (10-15Wm⁻¹K⁻¹) than hardmetals (25-80Wm⁻¹K⁻¹). By insertion of metals such as W, Nb, Ta, Cr, V into the lattice of Ti(C,N) during sintering the solid-state properties can be considerably influenced. This was shown amongst others for the systems (Ti,Me)(C,N) for V, Nb, and Ta for large replacement of Ti [42]. In a recent study [43] the heat conductivity of W-, Nb- and Ta-containing TiC and Ti(C,N), such as prevailing in hardmetals as a free *fcc* phase was reported (Fig.7b). With respect to composition, such *fcc* phases can be compared to that of a cermet. It was found that a higher amount of W and N increases and sub-stoichiometry, i.e. [Me]/([C]+[N]) < 1, lowers the heat conductivity of (Ti,Ta,Nb,W)(C,N). Furthermore, small amounts of Cr, V decrease the heat conductivity.

Thermal expansion (Fig.8) is also a function of the [C]/([C]+[N]) ratio, i.e. the higher the carbon content, the lower the expansion coefficient [44]. The authors reported that the Ti(C_xN_{1-x}) lattice parameters versus composition were found to fit Eq.2 in the temperature region 298-1473K:

$$a\left(\frac{[C]}{[C+N]}, T\right) = 0.42313 + 0.008 * \frac{[C]}{[C+N]} + \left(2.338 - 0.122 * \frac{[C]}{[C+N]}\right) * 10^{-6} * T + \left(1.0717 - 0.2258 * \frac{[C]}{[C+N]}\right) * 10^{-9} * T^2 \pm 0.0002 \text{ nm} \quad (2)$$

where a is the lattice parameter in nm and T the absolute temperature.
 The linear thermal expansion coefficient α is:

$$\alpha\left(\frac{[C]}{[C+N]}, T\right) = \frac{\left(\left(2.338 - 0.122 * \frac{[C]}{[C+N]}\right) * 10^{-6} + \left(2.143 - 0.451 * \frac{[C]}{[C+N]}\right) * 10^{-9} * T\right)}{a\left(\frac{[C]}{[C+N]}, T\right)} \quad (3)$$

where α is the temperature-dependent thermal expansion coefficient in K⁻¹.

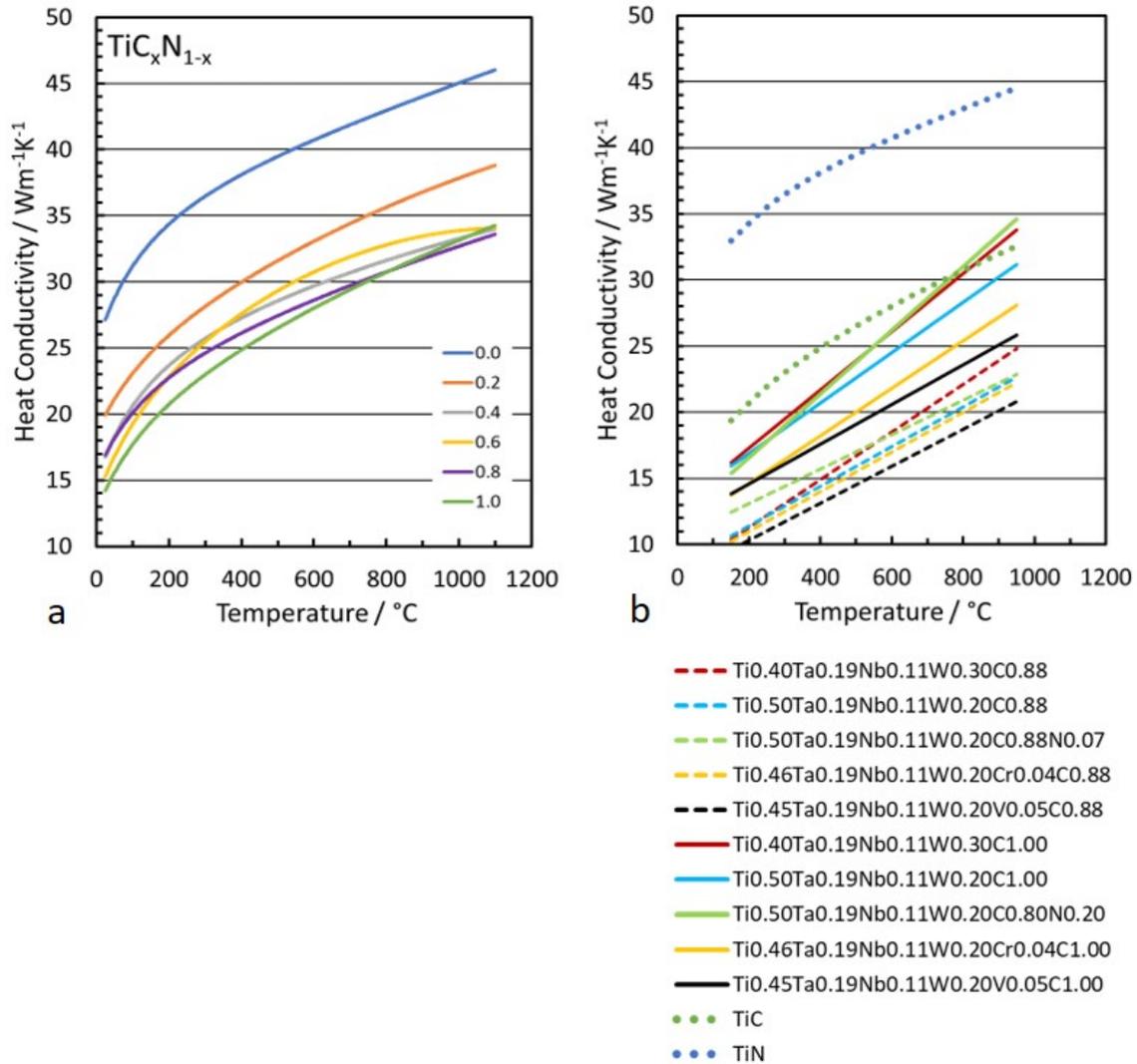


Figure 7

(a) Heat conductivity of Ti(C,N) as a function of temperature and for various $[C]/([C]+[N])$ ratios [41]. TiN has the highest heat conductivity, TiC the lowest. (b) Heat conductivity of TiC- and Ti(C,N) based compounds with addition of W, Nb and Ta as well as the influence of small Cr and V additions [43].

The hardness of Ti(C,N) is a function of the $[C]/([C]+[N])$ ratio, too. Fig.9 shows an increase of hardness, both with a very small load (nanohardness, with a Berkovich indenter) and a higher load (microhardness, with a Vickers indenter) with an increase of the $[C]/([C]+[N])$ ratio, hence the maximum is at the nitrogen-free composition TiC [45].

At room temperature, the Young's as well as the bulk modulus is decreased with increasing $[C]/([C]+[N])$ ratio, whereas the shear modulus shows a weak maximum at around $[C]/([C]+[N]) = 0.60$ (Fig.10a). Fig.10b shows for TiC, TiN, and Ti(C_{0.4}N_{0.6}) the dependency on temperature. At increasing temperature these moduli are decreasing [46, 47, 48].

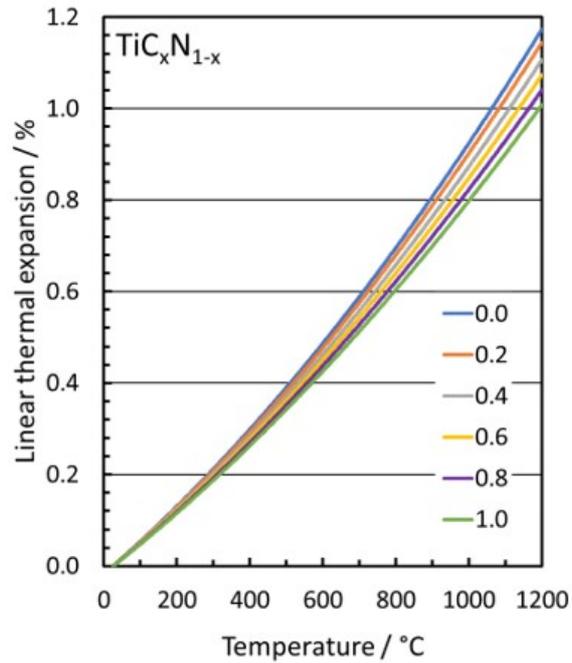


Figure 8

Thermal expansion of $\text{Ti}(\text{C},\text{N})$ as a function of temperature and $[\text{C}]/([\text{C}]+[\text{N}])$ ratio calculated with Eq. 2, corrected formula from [44].

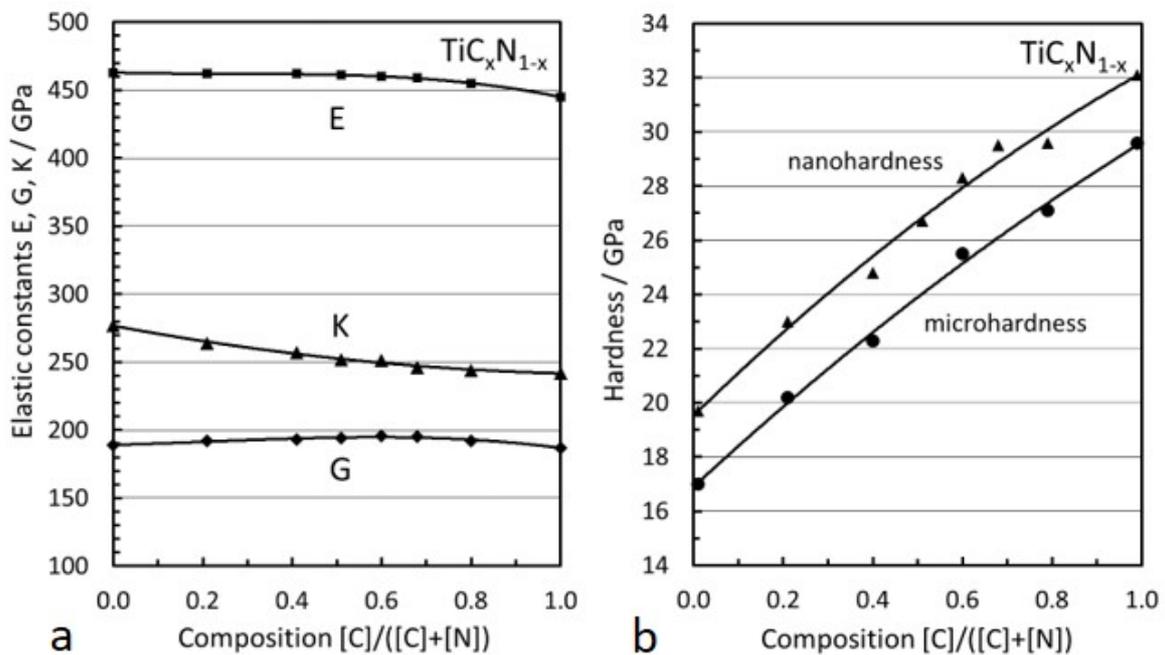


Figure 9

(a) Hardness of $\text{Ti}(\text{C},\text{N})$, and (b) Young's modulus (E) and bulk (K) and shear modulus (G) at room temperature as a function of $[\text{C}]/([\text{C}]+[\text{N}])$ ratio [45].

Further solid-state properties of $\text{Ti}(\text{C},\text{N})$, of minor importance here, such as electrical conductivity and colour are contained in [47, 41].

Because of the complicated hard-phase grain structure of cermets, the overall solid-state properties of the hard phase are a combination of the different *fcc* phases which form upon sintering.

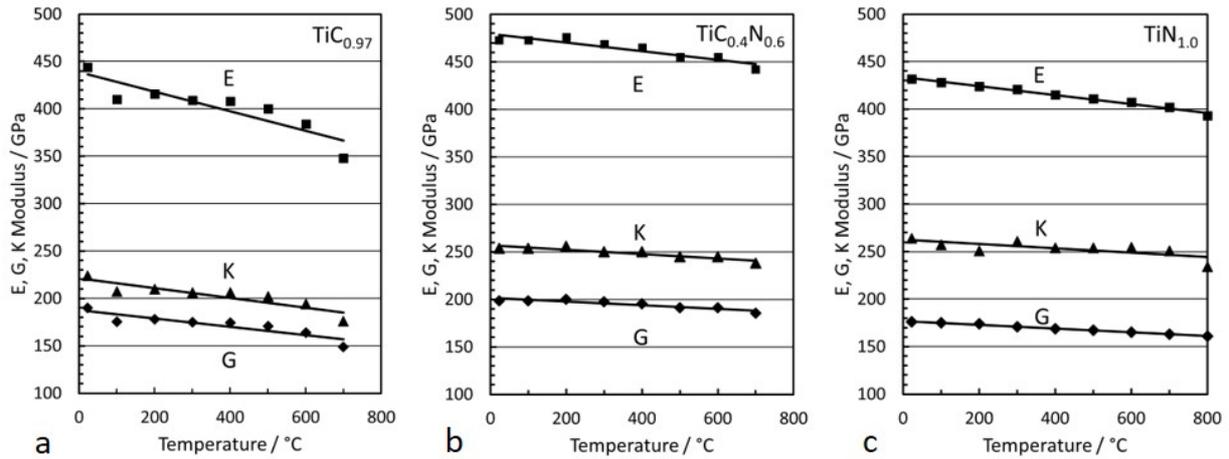


Figure 10

Young's (E), bulk (K), and shear modulus (G) of a) $\text{TiC}_{0.97}$, b) $\text{Ti}(\text{C}_{0.4}\text{N}_{0.6})$, and c) TiN as a function of temperature [47, 48].

4.2 Metallurgy of cermets

The first stages of sintering are represented by CO formation at around 400-600°C. Carbon originates from the carbides or carbonitrides and oxygen from binder phase powders Co and Ni (Fig.3e). At higher temperatures CO is released by reduction of oxygen which stems from carbide powders such as WC and Mo_2C and at higher temperatures from strongly-bonded oxygen of Ti- and Ta-based carbides and carbonitrides [49]. This CO formation is a necessary pre-requisite for good wetting and finally dense sintering of cermets. The addition of carbides like WC and Mo_2C , which dissolve in the binder phase at relatively low temperature still in solid-state conditions, is helpful for oxygen reduction. A small part of oxygen is certainly not released but incorporated into the *fcc* lattice of the hard phase because of a strong Ti-O bond.

The dark core (Fig.4d) originates from the lower solubility of nitrogen-rich $\text{Ti}(\text{C},\text{N})$ as compared to WC or Mo_2C . The latter are responsible for the good wetting of the hard phase Ti-based particles [5, 8, 11] by forming an *fcc* shell around the Ti-rich core. It is still questionable whether the inner rim forms in the solid state such as several authors believe [18, 50-56] or in the liquid state [57]. Supported by various analyses in our laboratory by use of interrupted sintering investigations, XRD, metallography, and outgassing experiments [24, 28, 31, 49, 55], the formation of inner rim starts in the solid state but continues in the liquid eutectic. Because of rather low diffusion rates of metals [47] it could not form in the solid state only, with such a thickness and uniformity as observed in cermets. In a first step, WC and/or Mo_2C are readily dissolved by the binder (as compared to $\text{Ti}(\text{C},\text{N})$ which is much more stable against the binder, especially at high nitrogen content [58]). W and/or Mo do not enter in the hard phase lattice as long as the nitrogen content in the $\text{Ti}(\text{C},\text{N})$ particles is high due to their instability in a nitrogen-rich lattice (Mo-N and especially W-N bonds are very unstable). Hence, for starting the formation of the inner rim, nitrogen is released by the interaction of hard-phase carbonitrides with the W- and/or Mo-containing binder phase. This release starts in the solid state as recent mass-spectroscopic investigations show [28, 29]. The nitrogen evolution maximum is about 100-200°C below the formation of the liquid phase. In parallel with nitrogen outgassing W and/or Mo are inserted into the perimeter of the $\text{Ti}(\text{C},\text{N})$ particles. The composition of this inner-rim phase is relatively W- and/or Mo-rich and N-poor as compared to the core composition. This is due to the phase equilibria in Ti-W-C-N [59] and Ti-Mo-C-N [8] systems, respectively, in which two phases α' and α'' coexist in a large miscibility gap. These two phases have an almost identical lattice parameter so that the α'' phase (inner rim) grows epitaxially onto the α' phase (core).

The outgassing of nitrogen is substantially reduced and often ends abruptly upon formation of the liquid phase (by a eutectic reaction between hard phase and binder phase), because the liquid closes porosity. In the eutectic liquid, the α'' phase continues to precipitate, and the surrounding binder

phase is depleted in W and Mo. For these reasons, an outer rim with a composition lower in W or Mo and higher in Ti forms.

The outgassing of nitrogen is reduced if the cermet is sintered in nitrogen atmosphere. In this case, W and Mo cannot be incorporated to form a rim and most of the black cores remain separated. Fig.11 shows two microstructures of a cermet of identical starting composition but sintered in Ar (Fig.11a) and sintered in nitrogen (Fig.11b) atmosphere, reflecting the above described phenomena. It is especially interesting that the Ti- and N-rich particles are well-embedded, too [30, 31].

The grey outer rim growths in the liquid state and upon cooling [55]. If pre-alloyed powders such as (Ti,W)C and (Ti,Mo)(C,N) are used in the starting formulation the inverse grains are much more frequent because the heavy elements are already present in the same lattice as Ti from the very beginning. Much less nitrogen outgassing in case of using pre-alloyed powders occurs [28] because the amount of inner rim formation, as explained above, is much less and the formation of a rim around W- and Mo-rich particles does not force nitrogen to outdiffuse. In addition, a generally lower nitrogen equilibrium pressure is prevailing because the nitrogen is distributed more evenly amongst the different phases rather than concentrated in the core of the particles.

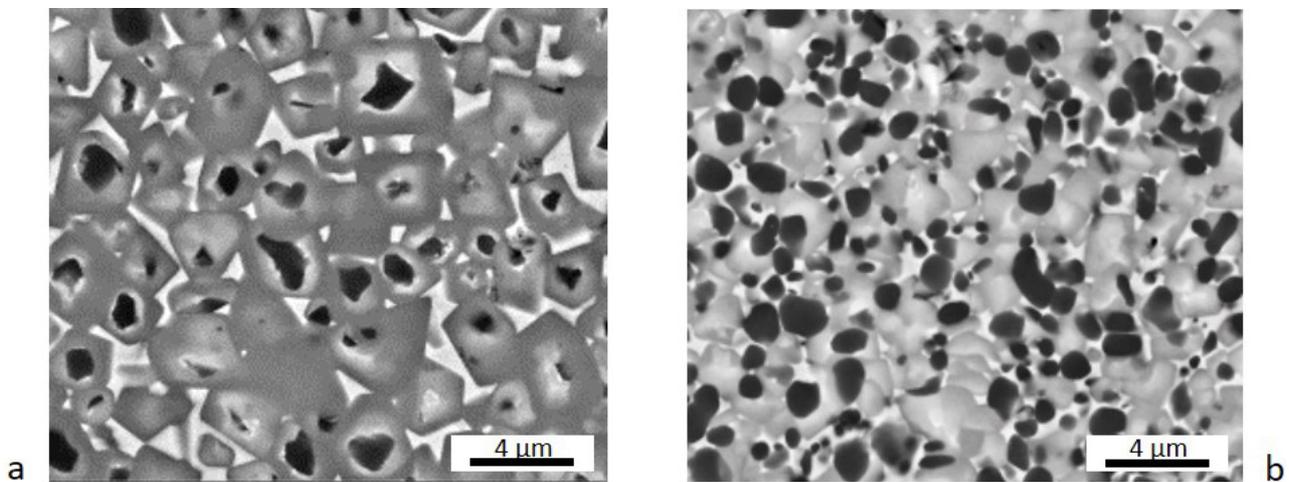


Figure 11

Microstructure of cermets with identical starting composition sintered in a) Ar atmosphere and b) in nitrogen atmosphere. The core-rim structure observed in an Ar-sintered sample vanishes in N_2 , many nitrogen-rich grains are more isolated, and a typical inner rim does not form (compare to Fig.4d). SEM-BSE images.

It has been shown, that in some cermets a pronounced core-rim-structure does not form within regular sintering time, if so-called solid solution carbides are used [60]. It was claimed that because of reduction of the number of interfaces these solid-solution cermets should have better mechanical properties, which was not yet proven. As mentioned above, the core and the rim of the hard phase have a very small lattice mismatch, too, so that an interface in the usual sense is not present. Furthermore, a complete absence of core-rim structure is not present in the solid-solution carbides because of the still existing preferential dissolution of some metals even if a more homogeneous starting compound is employed.

Another important impact of the nitrogen pressure is the solubility of various metals in the binder phase. If nitrogen is present in the sintering atmosphere, the Ti content in the binder will be lowered because of the high affinity of Ti, and N. Nishigaki and Doi [14] reported a higher Mo content in the binder phase upon increasing the nitrogen content of the starting formulations. This can only be explained by a kinetic retardation of Mo, dissolved in the binder, taken up by the hard phase and/or the presence of a sub-stoichiometric hard phase. The use of sub-stoichiometric hard-phase powders increases the concentration of dissolved elements in the binder phase because the sub-stoichiometric powders tend to reach the stoichiometry. This can happen or by taking up C or N from the atmosphere, or by releasing metals (more easily than in case of stoichiometric powders) to the

binder under dissolution. In our investigations of successive replacement of W by Mo we observed a substantial increase of specific saturation magnetisation (M_s) if nitrogen is used instead of Ar atmosphere. It increases substantially with increasing nitrogen pressure (Fig.12). The fact that M_s is decreased with increasing concentration of elements in the binder phase is a strong indication that the concentration of dissolved elements is much lower in nitrogen atmosphere, in contrast to what was observed by [14].

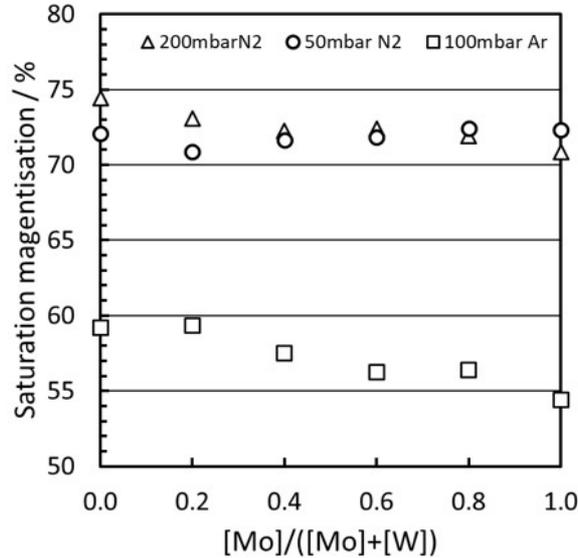


Figure 12

Specific saturation magnetisation (M_s) relative to a pure Co/Ni=1:1 alloy of the binder of Ti(C,N)-WC-Mo₂C-(Ta,Nb)C-Co/Ni cermets as a function of the $[Mo]/([Mo]+[W])$ ratio (from left to right: replacement of W by Mo in mol). The cermets have the same binder content in vol% and were sintered in different atmospheres [31].

The nitrogen pressure has not only impact on the stoichiometry of the hard phase but also on the microstructure, as nitrogen can lead to a depletion of C in the *fcc* lattice and dissolve in the binder phase. If the binder phase is saturated, free C can form (compare Fig.4b). In addition, N plays a very important role as a grain growth inhibitor. Work on the interdependency of binder phase composition (with the solubility of the various elements), hard-phase composition (with varying C/N and non-metal/metal ratio – “stoichiometry”), together with the activity of C, N and O in the gas phase is still needed for a better description of cermet systems.

4.3 Properties of cermets

As already mentioned, the competitive materials with which cermets are compared are WC-Co hardmetals. Sometimes these hardmetals contain a substantial amount of *fcc* phases such as TiC, Ti(C,N), and (Ta,Nb)C with the benefit of higher oxidation resistance, lower plastic deformation (especially at higher temperatures), and are of ISO application classes P and M [61]. WC-Co hardmetal grades without such carbides are typically of ISO class K. In Tab.3 some general solid-state properties are listed for cermet grades of which the composition is specified and compared to hardmetal grades P and K [62].

Table 3

Comparison of properties of some cermet grades with some hardmetal grades P and K[62].

Cermets				Hardmetal			
Composition wt%	P05	P10	P20	Composition wt%	P10	P25	K10
Carbonitrides	89.0	85.7	82.3	WC	60.0	72.7	>92
Other carbides	0.6	0.8	1.0	(Ti, Ta, Nb)C	31.0	17.3	<2
Co/Ni	10.4	13.5	16.7	Co	9.0	10.0	6.0
Co/Ni / vol%	4.0	10.6	13.0	Co / vol%	10.9	14.0	10.0
Density g/cm ³	6.1	7.0	7.0	Density g/cm ³	10.6	12.6	14.9
Hardness HV 30	1650	1600	1450	Hardness HV 30	1560	1490	1580
Compression Strength / MPa	5000	4700	4600	Compression Strength / MPa	4500	4600	5400
TRS MPa	2000	2300	2500	TRS MPa	1700	2200	2000
Young's Modulus GPa	460	450	440	Young's Modulus GPa	520	550	630
Fracture toughness MPa.m ^{-1/2}	7.2	7.9	10.0	Fracture toughness MPa.m ^{-1/2}	8.1	10	9.6
Poisson number ν	0.21	0.22	0.21	Poisson number ν	0.22	0.22	0.22
Heat conductivity Wm ⁻¹ K ⁻¹	9.8	11.0	15.7	Heat conductivity Wm ⁻¹ K ⁻¹	25	45	80
Thermal expansion coeff. 10 ⁻⁶ K ⁻¹	9.5	9.4	9.1	Thermal expansion coeff. 10 ⁻⁶ K ⁻¹	7.2	6.7	5.5

Because of the multicomponent character of cermets, we have screened the literature concerning the various influences of constituents and preparation conditions. The number of journal papers published in the last years has increased drastically and cannot be overlooked easily. An overview of various studies on cermets is presented in Tab.4 and the detailed data on composition (where “%” is intended as “wt%” in any part of this work, if not differently specified), hardness HV10, and fracture toughness K_{IC} are discussed in the following graphs. Most of the data were measured using different methods and loads (i.e. HRA, HV30, HV20, etc.). For making a comparison possible, a conversion based on empirical correlations obtained in our laboratory was applied. This fact, together with the usual instrumental accuracy, must be always taken into account in the next chapters.

Table 4

Literature survey on Palmqvist fracture toughness and hardness of Ti(C,N)-based cermets, also some nitrogen-free grades are contained. References were considered only for grades which have the potential of a relatively direct and soon implementation in existing production technology.

Ref.	Properties									Ti-based compound	Secondary carbides & additions	Binder
	HV & / or K_{IC}	TRS	Magn. data	E/G/v	XRD [a]	Phase comp.	Grain size	Wear [b]	Other			
[30]	●	-	-	-	●	-	-	-	-	f, s Ti(C _{0.5} N _{0.5})	(Ta,Nb)C, WC, Cr ₃ C ₂	Co, Ni
[31]	○	-	-	-	-	-	-	-	-	Ti(C _{0.7} N _{0.3}), Ti(C _{0.5} N _{0.5})	[c]	Co, Ni
[36] *	●	-	-	-	-	-	●	-	-	Ti(C _{0.7} N _{0.3}) [d]	Mo ₂ C	Co, Ni
[55]	●	-	●	-	●	-	-	-	-	f, s Ti(C _{0.5} N _{0.5})	(Ta,Nb)C, WC, Cr ₃ C ₂	Co, Ni
[64] *	●	-	-	●	●	●	●	-	-	Ti(C _{0.7} N _{0.3})-Ti(C _{0.5} N _{0.5})	Mo ₂ C	Co, Ni
[65] *	○	-	-	-	X	●	-	-	-	Ti(C _{0.7} N _{0.3})	WC	Ni
[66] *	●	-	-	-	-	X	-	-	X	Ti(C _{0.7} N _{0.3})	Mo ₂ C, Mo	Ni
[67]	●	○	-	-	-	●	-	-	-	[e]	[e]	[e]
[68]	● [f]	-	-	●	-	X	●	○	-	TiC, TiN	Mo ₂ C	Ni
[69] ◇	○ [g]	-	○	-	-	○	-	-	-	Ti(C _{0.7} N _{0.3})	WC, NbC	Ni
[70] *	○	○	●	-	-	-	●	○	-	Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C, (Ta _{0.7} Nb _{0.3})C	Co
[71] *	○	○	-	-	X	●	-	-	-	TiC, TiN	WC, C	Co
[72] *	○	○	-	-	X	●	-	-	-	TiC, TiN	WC, Mo, C	Co
[73] □	○	○	-	-	X	-	-	-	-	Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C	Co, Ni [h]
[74] □	●	●	●	-	●	●	-	-	-	TiC, TiN	WC, Mo, C	Ni
[75] □	○	○	-	-	○	●	-	-	-	Ti(C _{0.5} N _{0.5})	WC, Mo, Cr ₃ C ₂ , C	Ni
[76] □	○	○	-	-	●	●	-	-	-	TiC, TiN	WC, TaC, Mo, Cr ₃ C ₂ , C	Co, Ni [h]
[77] *	○	-	-	-	○	○	-	-	-	(Ti _{0.7} W _{0.3})C _x	-	Ni
[78] □	●	●	-	-	●	-	-	-	-	n TiC, n TiN	WC, Mo ₂ C	Ni
[79] □	●	●	-	-	X	-	-	○	-	Ti(C _{0.7} N _{0.3})	Mo ₂ C, Cr ₃ C ₂	Ni
[80] ◇	● [i]	-	-	●	●	-	●	-	○	(Ti _{1-x} Ta _x)(C _{0.5} N _{0.5})	-	Co
[81] ◇	● [i]	-	-	-	●	-	-	-	-	(Ti _{1-x} Ta _x)(C _{0.7} N _{0.3})	-	Ni
[82] *	○	-	-	-	-	-	○	-	-	(Ti _{0.93} W _{0.07})C, (Ti _{0.93} W _{0.07})(C _{0.7} N _{0.3})	Mo ₂ C	Ni
[83] *	○	○	-	-	X	●	○	-	-	(Ti,W)C	Mo, C	Ni
[84] *	○	○	-	-	●	●	-	-	-	Ti(C _{0.5} N _{0.5})	WC, Mo ₂ C	Co, Ni
[85] □	●	●	-	-	X	○	-	-	-	Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C, TaC	α, βCo
[86] *	●	-	-	-	X	●	●	-	-	Ti(C _{0.7} N _{0.3}), (Ti _{0.88} W _{0.12})C, - (C _{0.7} N _{0.3})	WC, Mo ₂ C, NbC	Co, Ni
[87] *	○	-	-	-	X	X	●	-	-	Ti(C _{0.7} N _{0.3}), (Ti _{0.88} W _{0.12})C, - (C _{0.7} N _{0.3})	WC, Mo ₂ C, NbC	Co, Ni
[88] ◇	○ [j]	○	-	-	-	X	-	-	-	TiC, TiN	WC, Mo	Ni
[89] *	●	-	-	-	-	●	●	-	-	Ti(C _{0.5} N _{0.5}), (Ti _{0.93} W _{0.07})C	WC, Mo ₂ C, TaC	Co, Ni
[90]	●	●	-	●	-	-	●	-	-	(Ti _{0.8} Ta _{0.2})(C _{0.5} N _{0.5})	-	Co
[91] ■	●	●	-	-	-	●	-	-	-	Ti(C _{0.7} N _{0.3})	WC, Mo, TaC, HfC	Co, Ni
[92] *	●	-	-	-	X	●	-	-	-	Ti(C _{0.5} N _{0.5})	WC, Mo ₂ C, TaC	Co, Ni
[93] ◇	● [g]	●	-	●	-	-	-	●	-	Ti(C _{0.5} N _{0.5})	WC	Co, Ni
[94] ◇	● [g]	●	-	●	-	-	-	○	-	TiC	-	[k]
[95] *	●	-	-	-	-	-	-	○	-	Ti(C _{0.5} N _{0.5})	-	steel
[96] ◇	● [g]	●	-	●	-	-	-	○	-	TiC	-	[k]
[97] *	●	●	-	-	-	-	-	-	-	Ti(C _{0.5} N _{0.5})	Mo	Ni

● numerical data available

○ numerical data can be extracted from graphs

X only graphs presented or no easy/accurate data extraction possible

- no data

◇ not used in any graph due to missing or non-convertible HV/K_{IC} units specifications (e.g. HV0.2, HV0.3, HV5)

* HV10 calculated from HV30 data

■ HV10 calculated from HV20 data

□ HV10 calculated from HRA data

[a] XRD pattern and/or lattice parameter

[b] wear, friction, and/or corrosion data

[c] WC, Mo₂C, Cr₃C₂, (Ta_{0.6}Nb_{0.4})C, C

[d] specifications given in [98]

[e] only specifications on final at% per each chemical element were given

[f] HV0.3 measurements

[g] missing HV specifications

[h] Co/Ni ratio not specified, just total Co+Ni amount indicated

n: nano, f: fine, s: submicron powders

We have sorted out many of those studies which deal with materials and processes which are obviously not capable of a soon introduction into industrial cermet production.

Another important factor is the porosity influence on hardness and fracture toughness. Many authors do not show appropriate images from which the porosity level can be judged nor communicate an ISO code. ISO EN 4499 [63] standards listed in Tab.5 were used to specify the grain sizes in the next chapters, as well as in Tab.4 and Tab.6.

Table 5

Grain-size classification for raw powders used for hardmetals [63] adopted in the in the present review.

Grain-size range	Designation	Abbreviation
< 0.2 μm	nano	n
0.2 – 0.5 μm	ultra fine	u
0.5 – 0.8 μm	submicron	s
0.8 – 1.3 μm	fine	f
1.3 – 2.5 μm	medium	m
2.5 – 6.0 μm	coarse	c
> 6.0 μm	extra coarse	xc

4.3.1 Influence of WC content

The graph in Fig.13 shows HV- K_{IC} data of cermets with different WC content for various cermet mixtures. Li et al. [71] studied the influence of WC additions on nanoTiC-nanoTiN-WC-Co-C and found that an increase of WC lead to an increase in hardness and a decrease in toughness. The difference is significant up to 10% WC addition and becomes less remarkable between 10 and 20%WC.

A similar trend was measured by Wu et al. [65] upon investigation of $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -WC-Ni cermets by varying the amount of WC. In their study, the addition of WC was tested within the range of 10 - 30%, revealing in fact the same behaviour of [71] up to 25% WC addition. This trend was attributed to a reduction of the mean free path of the binder and a reduction of the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ grain size, due to the WC dissolution in the binder resulting in a solution hardening of the metal binder.

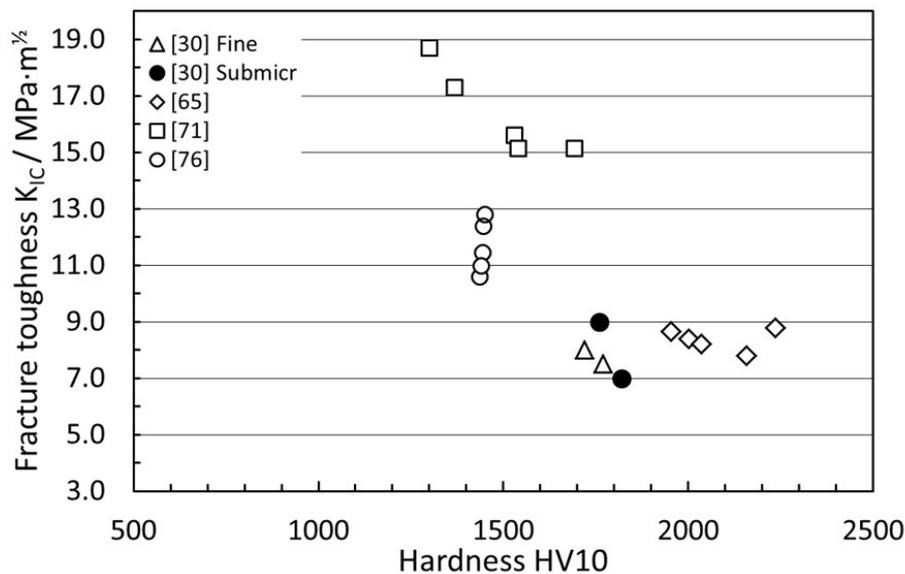


Figure 13

Fracture toughness vs. hardness relationship of cermets with variations of the WC content. [30] Fine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})-(\text{Ta},\text{Nb})\text{C}-\text{WC}-\text{Cr}_3\text{C}_2-\text{Co}-\text{Ni}$; [30] submicron $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})-(\text{Ta},\text{Nb})\text{C}-\text{WC}-\text{Cr}_3\text{C}_2-\text{Co}-\text{Ni}$; [65] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})-\text{WC}-\text{Ni}$; [71] $\text{TiC}-\text{TiN}-\text{WC}-\text{C}-\text{Co}$; [76] $\text{TiC}-\text{TiN}-\text{WC}-\text{TaC}-\text{Mo}-\text{Cr}_3\text{C}_2-\text{C}$.

On the other hand, with 30% WC addition the cermet showed a significant increase of K_{IC} (around $1 \text{ MPa}\cdot\text{m}^{1/2}$ higher than the sample with 25% WC), together with a further increase in hardness. Thus, the 30%WC cermet was found to be the best sample concerning these two mechanical properties. The behaviour was attributed by the authors to the existence of “free-WC phase” inside the microstructure after XRD evaluations. Probably the hardness increase is due to a precipitation strengthening effect of WC.

Demoly et al. [30] reported a small decrease in hardness and a small increase in toughness when increasing the WC addition in fine or sub $\mu\text{mTi}(\text{C}_{0.5}\text{N}_{0.5})\text{-(Ta,Nb)C-WC-Cr}_3\text{C}_2\text{-Co-Ni}$ cermets. Tungsten did not form a free WC phase in this case. In their study, focused on investigating the applicability of industrially prepared powders, also other factors were modified at the same time (e.g. $\text{Ti}(\text{C,N})$ grain size, amount of $(\text{Ta,Nb})\text{C}$, amount and Co/Ni ratio of binder phase), therefore, the results cannot be considered as affected by the variation of WC content only, but it is important to highlight that the variation in K_{IC} is larger in case of submicron $\text{Ti}(\text{C,N})$ -based cermets.

In case of partial substitution of WC by TaC, the results found by Wu et al. [76] indicate that both HV and K_{IC} decreased with increasing TaC substitution.

4.3.2 Influence of Mo content and of Mo/W ratio

Cutard et al. [64] analysed the influence of Mo on both, $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ - and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermets with Co or Ni binder (all the compositions reported from this paper are in vol%). As shown in Fig.14, for part of their samples the increase of Mo content causes an increase in hardness and a decrease in toughness, with two exceptions. The first in case of a $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -Co based cermet, for which the toughness had a maximum at 6.4vol% Mo addition, with almost the same hardness of the 3.2vol% Mo sample. In case of a further increase of Mo content, the general trend of hardness increase and fracture toughness decrease applies. The second exception regards $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -Co based samples, for which almost no variation in K_{IC} was found upon Mo increase from 1.5vol% to 3.2vol%Mo, while the hardness increased.

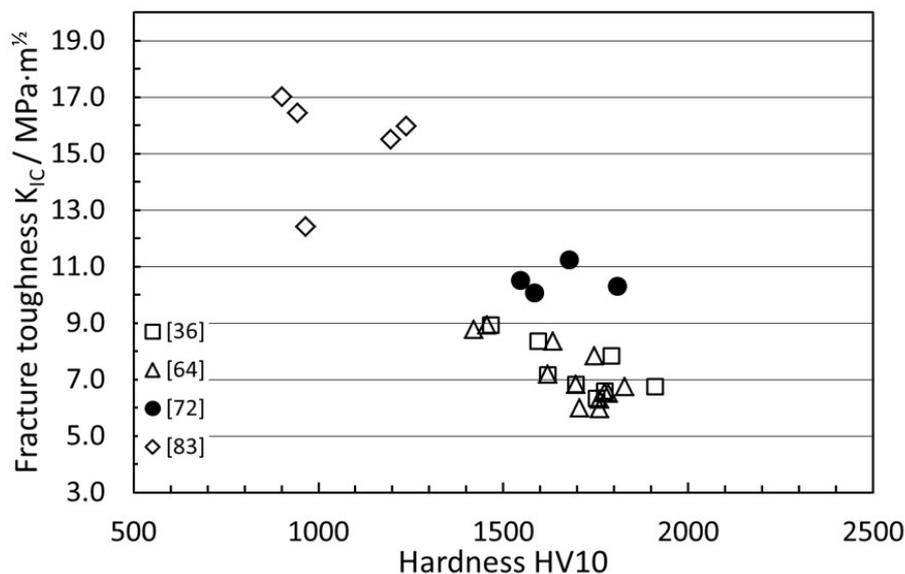


Figure 14

Fracture toughness vs. hardness comparisons on Mo content variations. [36] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-Mo}_2\text{C-Co}$ or -Ni ; [64] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-Mo}_2\text{C-Co}$ or -Ni and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-Mo}_2\text{C-Co}$ or -Ni ; [72] $\text{TiC-TiN-WC-Mo-C-Co}$; [83] $(\text{Ti,W})\text{C-Mo-C-Ni}$.

Further investigations were carried out by Mari et al. [36] (covering some results identical to [64], but others were re-measured or are different. Also, in this case, all the compositions reported from this paper are in vol%), confirming the previous results of [64] and revealing that $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-Co}$

based cermet with 6.4vol%Mo addition has in fact a higher hardness than the 3.2vol%Mo sample, with a maximum value for the K_{IC} .

Li et al. [72] discussed the influence of Mo content in case of nanoTiC-nanoTiN-WC-Mo-20Co-2C, finding the highest hardness in case of a 10wt% Mo addition, whereas the highest K_{IC} is reached at 5wt% Mo addition. For both properties, deviations from these values lead to a decrease of each property. However, due to the fixed amount of C used, the stoichiometry ($[\text{non-metals}]/[\text{metals}]$ ratio) of the hard phase was not steady with the variation of the Mo content and this could have had a large effect on the measured final properties.

The same consideration is valid for the study of Zhang et al. [83], where the influence of the Mo content on (Ti,W)C-Mo-30Ni-1C cermets was discussed. The fracture toughness was higher without Mo addition and slightly decreased with the increase of Mo until 15wt% Mo, and was more significant at 20wt% Mo. On the other hand, the hardness increased with the addition of Mo, showing a maximum at 15wt%Mo, with a subsequent drop for higher contents.

Recently, Schwarz et al. [31] investigated cermets with changing Mo/W ratio. This was done on three series with Ti(C,N) powders different in C/N ratio. The alloy composition was calculated in such a way that the molar $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratio changed in steps of 0.2 from 0 to 1 (molar exchange of W by Mo) and keeping the vol% of binder constant to make all the prepared grades comparable with respect to K_{IC} and hardness data. The necessary condition of keeping the volume of binder constant, while studying properties other than influence of binder content, was neglected in many studies.

The sintering was done in both Ar atmosphere as well as nitrogen (see 4.3.3). The K_{IC} and HV10 data from this work are summarised for two series, in Fig.15a for Ti(C_{0.7}N_{0.3})-based and Fig.15b for Ti(C_{0.5}N_{0.5})-based cermets.

In case of nitrogen atmosphere, the $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratio increase lead to a general increment of the hardness and to an almost constant behaviour for the toughness for both Ti(C_{0.7}N_{0.3})- and Ti(C_{0.5}N_{0.5})-based cermets. On the other hand, in case of Ar atmosphere, the hardness is almost constant (for the Ti(C_{0.7}N_{0.3}) grades) or increased only slightly (for the Ti(C_{0.5}N_{0.5}) grades) when increasing the $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratio, while toughness kept almost constant for both series, except for Ti(C_{0.7}N_{0.3}) cermets in case of $[\text{Mo}]/([\text{Mo}]+[\text{W}])=1$, where a significant decrease in toughness occurred.

Other investigations concerning, directly or indirectly, the variation of the Mo/W ratio were done by some other authors. As mentioned previously, Li et al. [72] investigated the effect of Mo addition on nanoTiC-nanoTiN-WC-Mo-20Co-2C. The variation in composition involved Mo and Ti(C,N), while all the other components were kept constant. Thus, a variation in Mo/W ratio obviously occurs, but the experiments were not designed for this specific purpose and the influence of changing the amount of Ti(C,N) is unclear.

WC additions to Ti(C_{0.7}N_{0.3})-WC-Mo-15(Co+Ni) cermets with increasing WC and decreasing Ti(C_{0.7}N_{0.3}) contents were studied by Jung et al. [73]. The other factors, including the Mo content, were kept constant, thus Mo/W ratio variations take place in the series analysed, but again not due to specific designing of the composition, and Ti(C_{0.7}N_{0.3}) variations effects cannot be separated, too. Similar analysis about WC influence was carried out by Qu et al. [75] on Ti(C_{0.5}N_{0.5})-WC-Mo-Cr₃C₂-C-Ni and by Dong et al. [78] on TiC-TiN-WC-Mo₂C-Ni, but same considerations can be applied concerning Mo/W variations and simultaneous Ti(C_{0.5}N_{0.5}) variations occurring. Lin et al. [99] compared two samples having WC-(W,Ti)C-Mo-C-Ni compositions, one with 1%Mo and another one without Mo. The WC amount was reduced to include Mo in the composition, thus a Mo/W variation takes place keeping all the other factors constant, but the grade developed by the authors is a WC-based material and not a typical cermet.

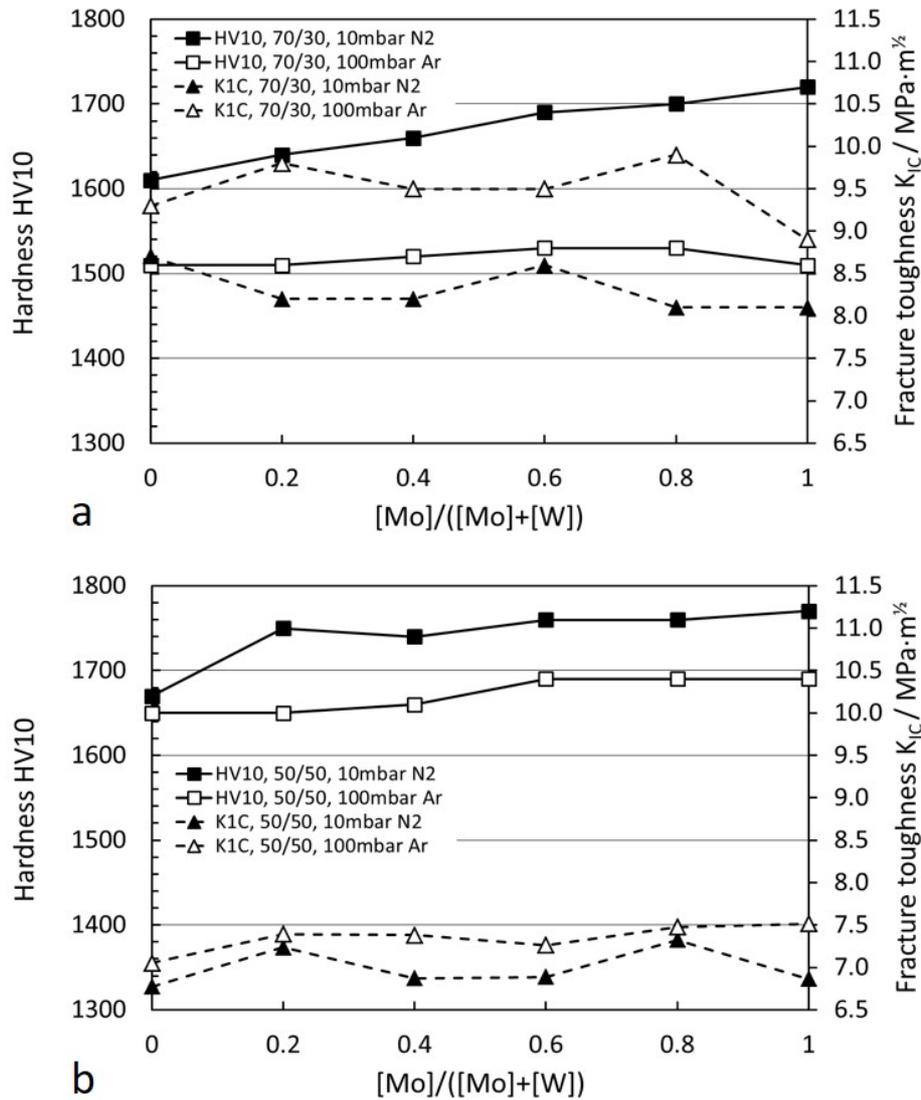


Figure 15

Fracture toughness and hardness vs. $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratio for different sintering atmospheres (100mbar Ar or 10mbar N₂) for (a) Ti(C_{0.7}N_{0.3})-based and (b) Ti(C_{0.5}N_{0.5})-based grades [31].

The gradual replacement of (Ti_{0.93}W_{0.07})C-20wt%Ni ‘CSS’ (Complete Solid Solution) cermets by conventional Ti(C,N)-based cermets ‘TCC’ with a composition of Ti(C_{0.5}N_{0.5})-20WC-7TaC-3Mo₂C-9Co-9Ni was investigated by Kim et al. [89]. Due to the substitution of TCC with CSS, the tested grades showed a variation of all the components, including a variation in the Mo/W ratio. As a matter of fact, the contents of WC, Mo₂C, and Ti(C,N) decrease, while that of (Ti,W)C increases, thus a clear understanding on the effect of just Mo/W variations is not possible.

Some more relevant results concerning Mo/W ratio are provided by Zhang et al. [83] about (Ti,W)C-Mo-C-Ni cermets. The authors analysed the effect of increasing Mo content by 5wt% steps from 0 to 20wt%, decreasing the (Ti,W)C accordingly. The Mo/W ratio varies, whereas the Ti/W ratio is fixed due to the use of the same (Ti,W)C raw powder. All the other raw powder contents were kept constant, including the C additions. Therefore, in this case two additional effects that could interfere with the pure Mo/W variation are present: the Ti content and the overall stoichiometry variations.

4.3.3 Influence of C/N ratio

As cited above Schwarz et al. [31] also studied the influence of nitrogen, both by using different Ti(C,N) powders, i.e. Ti(C_{0.5}N_{0.5}), Ti(C_{0.6}N_{0.4}), and Ti(C_{0.7}N_{0.3}) as well as using Ar or N₂ sintering atmosphere.

This influence was most pronounced in the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ cermet grade which had the lowest nitrogen content (Fig.11). Upon sintering in Ar the typical core-rim structure developed in form of rather coarse grains (Fig.11a). The influence of nitrogen atmosphere resulted in a microstructure where the typical core-rim structure was absent, and the nitrogen-rich particles were rather isolated than incorporated in the hard-phase grains (Fig.11b). Such a microstructure could also be obtained in Ar atmosphere when the nitrogen content of $\text{Ti}(\text{C},\text{N})$ was increased to $\text{Ti}(\text{C}_{0.6}\text{N}_{0.4})$ or $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ powder. This is proof of the grain-refining behaviour of nitrogen and of the above discussed formation mechanisms of the inner rim (see 4.2). At high nitrogen activity the $\text{Ti}(\text{C},\text{N})$ does not incorporate W and/or Mo unless nitrogen is not released in the peripheric region of carbonitride grains. The nitrogen release takes place at solid-state conditions before forming the eutectic but a sufficient nitrogen pressure or a high nitrogen content prevents the $\text{Ti}(\text{C},\text{N})$ from achieving a sufficiently low nitrogen potential where W and/or Mo can be inserted into the lattice. Thus, an inner rim cannot form. Obviously, if no inner rim is present, an outer-rim composition with average atomic weight (grey) does not form onto the nitrogen-rich particles. Moreover, grains with an average outer-rim composition form separately leaving dark Ti- and N-rich particles isolated. As can be seen from Fig.11b average atomic mass particles formed rather large grains because of the lower nitrogen content and the absence of its grain-refining effect.

Fig.15 gives information on the influence of C/N ratio on fracture toughness and hardness if the data are compared at the same $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratio. It is seen that (Fig.15a) nitrogen atmosphere sintering lead $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -based cermets to become a remarkable harder material for any $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratios, while the toughness decreases as compared to Ar atmosphere sintered samples. Same behaviour is true also for $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based grades (Fig.15b), but the difference in hardness between nitrogen and argon atmospheres in this case was almost constant when Mo was added in different amounts, while for $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -based cermets this difference was increasing as the $[\text{Mo}]/([\text{Mo}]+[\text{W}])$ ratio increased. In addition, toughness in case of $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based grades showed only a small or even almost no decrease when N_2 was used as sintering atmosphere. Comparing $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ - with $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermets, the lower C/N ratio of $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ grades lead to higher hardness and lower toughness for each $[\text{Mo}]/([\text{Mo}]+[\text{W}])$, regardless to the sintering atmosphere

As previously mentioned, Cutard et al. [64] analysed the influence of Mo content on both $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ - and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermets with Co or Ni binder (all the compositions reported from this paper are in vol%). Therefore, comparisons between cermets with different C/N ratios can be done, and results are presented in Fig.16. While the K_{IC} always decreased with the decreasing C/N ratio, the influence of C/N ratio on hardness was not that clear. Comparing two couples of grades of $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -6.4 Mo_2C -Co and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -6.4 Mo_2C -Co cermets, with 6.4% Co and 18.0% Co, respectively, the hardness showed an opposite trend. In case of a cermet with 6.4% Co, the hardness was lower for $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ as compared to $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$, while in case of 18.0% Co the contrary was observed. For $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -3.2 Mo_2C -6.4Co and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -3.2 Mo_2C -6.4Co grades the hardness values were almost the same.

Russias et al. [68] studied two different cermet grades, TiC -10 Mo_2C -25Ni and TiC -10TiN-10 Mo_2C -25Ni, to understand the influence of TiN additions in TiC-based cermets. The microhardness HV0.3 of the material decreased by around 240 HV0.3 when 10wt% of TiN was added, while the toughness increased by 4 $\text{MPa}\cdot\text{m}^{1/2}$ (measured with a 5kg load indentation).

The influence of partial substitution of $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ and WC with $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ or $(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})$ on $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -WC- Mo_2C -NbC-Co-Ni cermets was investigated by Park et al. [86]. The use of $(\text{Ti},\text{W})\text{C}$ influences also C/N ratio and lead to achieve both, higher hardness and substantially higher toughness, as compared to $(\text{Ti},\text{W})(\text{C}_{0.7}\text{N}_{0.3})$ addition. As can be read from their graph, the increase in hardness is in the order of 50 HV10, the increment in toughness is about 2.25 $\text{MPa}\cdot\text{m}^{1/2}$ for $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ -containing cermets.

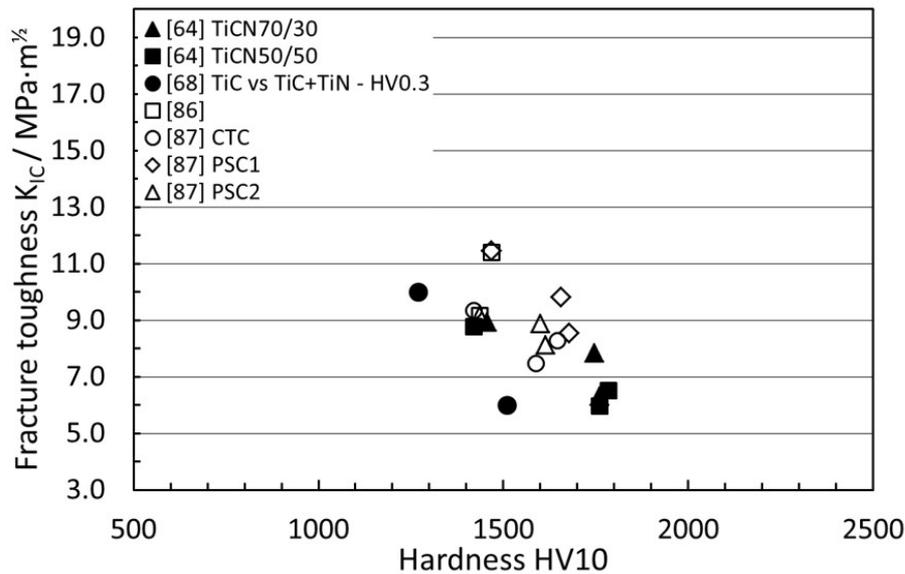


Figure 16

Fracture toughness vs. hardness comparisons on C/N ratio variations. [64] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-Mo}_2\text{C-Co}$ or -Ni ; [64] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-Mo}_2\text{C-Co}$ or -Ni ; [68] TiC- or $(\text{TiC-TiN})\text{-Mo}_2\text{C-Ni}$, HV0.3; [86] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-(Ti}_{0.88}\text{W}_{0.12})\text{C-}$ and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-(Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$; [87] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$; [87] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-(Ti}_{0.88}\text{W}_{0.12})\text{C-WC-Mo}_2\text{C-NbC-Co-Ni}$; [87] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-(Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$.

An additional contribution was given by the authors in a second paper [87], where a comparison between the three grades $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$, $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-(Ti}_{0.88}\text{W}_{0.12})\text{C-WC-Mo}_2\text{C-NbC-Co-Ni}$, and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-(Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$ was performed making a series of samples with different binder content (12wt%, 15wt%, and 20wt% (Co+Ni) with Co/Ni 1:1, respectively) per each grade. The binder content comparison will be discussed later (see 4.3.7). Considering the C/N ratio variations effects, the grades with $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ additions (higher C/N ratio) show both, highest hardness and toughness for each binder content, even in case of 15wt% binder, where the hardness of $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$ sample is lower but very close to the one with $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ additions. Again, the largest increment was found for the toughness, confirming results achieved by the authors [86]. The grades with $(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})$ additions do not differ from to the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$ ones by C/N ratio, thus the small differences in both hardness and fracture toughness between those two grades are caused only by the different pre-alloyed status of the powders (see 4.3.5).

Kim et al. [89] investigated the effect of substituting partially and fully $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ and WC with $(\text{Ti}_{0.93}\text{W}_{0.07})\text{C}$ on $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-20WC-7TaC-3Mo}_2\text{C-9Co-9Ni}$ cermets. The C/N ratio varied due to the decrease of the $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ phase amount, but the Co/Ni ratio was varied as well, from 1:1 to 100% Ni along the tested series. Therefore, the results achieved by the authors are affected by both ratios and the binder variation contribution cannot be distinguished from the C/N variation one. For this reason, data from this paper [89] are not shown in Fig.16.

4.3.4 Influence of C content

Seo et al. [77] analysed the influence of carbon content on $(\text{Ti}_{0.7}\text{W}_{0.3})\text{C}_x\text{-Ni}$ cermets, the corresponding data of which are shown in the K_{IC} vs. hardness plot in Fig.17. Generally, their hardness level is significantly below and the fracture toughness data above the usual values. Although a relatively good K_{IC}/HV relationship was achieved with a stoichiometric mixture, with the relatively highest hardness and the highest toughness (1216 HV10 - 10.47 MPa·m^{1/2}), sub-stoichiometric cermets were able to keep relatively good hardness even with a high carbon deficiency (values between 1091 and 1132 HV10). The toughness first increased slightly (10.81 MPa·m^{1/2}) and then considerably decreased with decreasing amount of C. On the other side,

increasing the C content over the stoichiometric ratio (i.e. excess of C) leads first to a slightly increase in toughness ($10.71 \text{ MPa}\cdot\text{m}^{1/2}$) and then a significant decrease occurred, while the hardness always decreased. Although quite high fracture toughness values were achieved, the low hardness values make these materials inappropriate for applications in cutting.

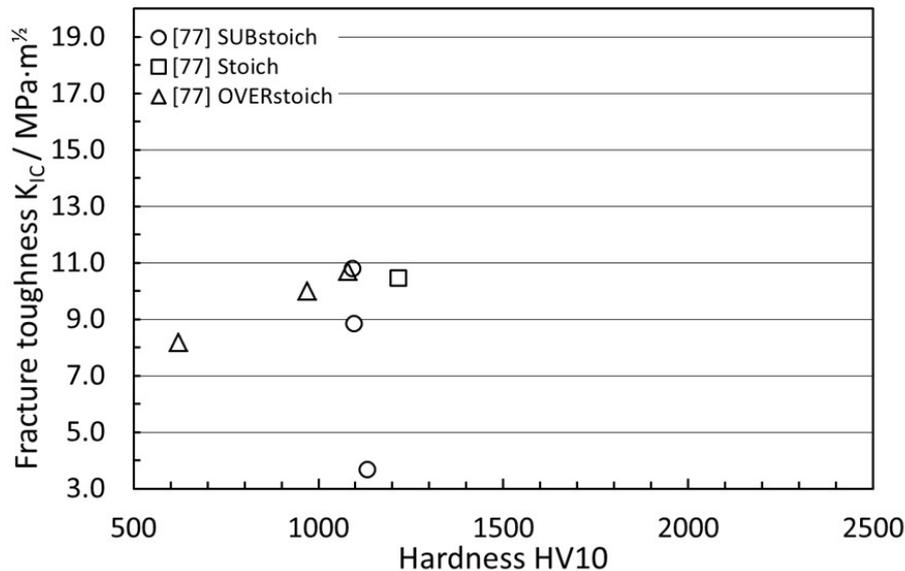


Figure 17

Fracture toughness vs. hardness comparisons on C content variations. [77] SUBstoichiometric ($\text{Ti}_{0.7}\text{W}_{0.3}\text{C}_x\text{-Ni}$); [77] Stoichiometric ($\text{Ti}_{0.7}\text{W}_{0.3}\text{C}_x\text{-Ni}$); [77] OVERstoichiometric ($\text{Ti}_{0.7}\text{W}_{0.3}\text{C}_x\text{-Ni}$).

4.3.5 Influence of the raw powder alloy state

Pre-alloyed powders for preparation of $\text{Ti}(\text{C,N})\text{-(Ti,W)C-WC-TaC-Mo}_2\text{C-Co-Ni}$ cermets were investigated by Kim et al. [89]. The experiments aimed to compare a series of cermets with increasing addition of complete solid solution phases (CSSs), i.e. $(\text{Ti}_{0.93}\text{W}_{0.07})\text{C}$, mixed with 20wt%Ni, as a partial substitution in the standard $\text{Ti}(\text{C,N})\text{-WC-TaC-Mo}_2\text{C-Co-Ni}$ cermet. According to their results (Fig.18), adding CSSs cermets (i.e. $\text{CSS}+20\text{wt}\%\text{Ni}$) slightly decreased the hardness, while at the same time increased the K_{IC} significantly. The maximum K_{IC} was reached in case of addition of 50wt% CSSs cermets, where also the hardness was comparable with the one of the cermet without any CSSs cermets. Both properties decreased when a 100% CSS cermet is prepared. Nevertheless, the toughness was still higher than the conventional cermet without CSSs cermets.

Research on this topic was further carried on by Park et al. [86, 87]. The focus in their first work was put on comparing the effects of adding 32wt% $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ or 32wt% $(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})$ to a $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Ni-Co}$ cermet. The addition of $(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})$ led to a small decrease in hardness and a substantial increase of around $1 \text{ MPa}\cdot\text{m}^{1/2}$ in K_{IC} compared to a commercial cermet composition (i.e. without $(\text{Ti,W})\text{C}$ carbides or carbonitrides), while the use of $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ allowed to obtain almost the same hardness but with large increase in toughness of around $3.5 \text{ MPa}\cdot\text{m}^{1/2}$ compared to conventional cermets.

Better results obtained with $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ additions were additionally confirmed in the second study published by the authors [87], comparing also the influence of the CSSs additions in case of a binder content variation from 10 to 20wt%. The general trend regarding a decrease in hardness and an increase of toughness when increasing the binder content was valid for all the cermet samples prepared, except for the hardness values relative to a common cermet composition (i.e. a $\text{Ti}(\text{CN})$ -based one), where the highest value was reached for 15wt% binder. For any binder content, cermets with $(\text{Ti}_{0.88}\text{W}_{0.12})\text{C}$ showed a better K_{IC}/HV behaviour than the comparable cermet compositions and the $(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})$ -based ones, respectively. $(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})$ -based cermets did not always show an improvement, when compared to a common cermet composition. As a matter of

fact, for 15wt% binder content, the hardness is lower, and for 20wt% binder the toughness results are slightly lower than that of a conventional cermet formulation.

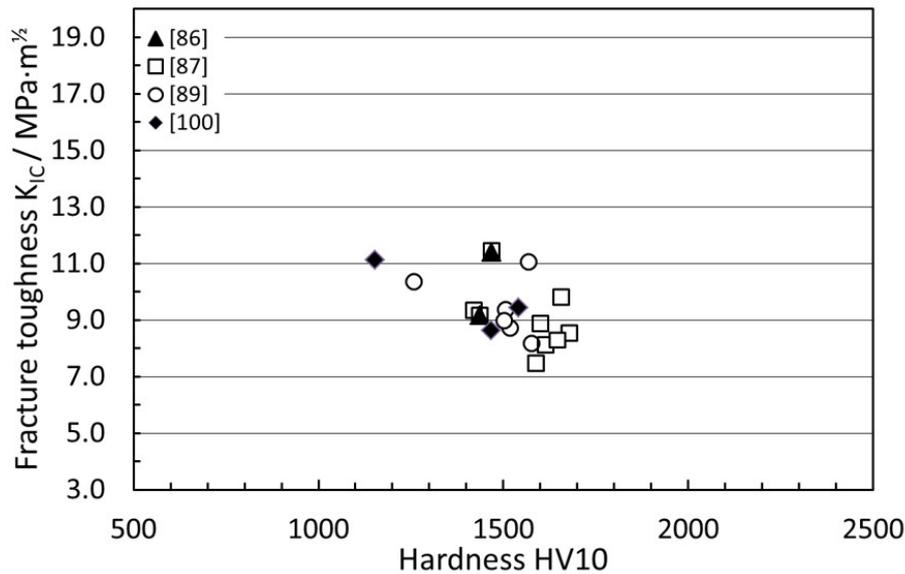


Figure 18

Fracture toughness vs. hardness comparisons on different raw powder alloy states. [86] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-}(\text{Ti}_{0.88}\text{W}_{0.12})\text{C-}$ and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-}(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$; [87] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-}$ and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-}(\text{Ti}_{0.88}\text{W}_{0.12})\text{C-}$ and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-}(\text{Ti}_{0.88}\text{W}_{0.12})(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo}_2\text{C-NbC-Co-Ni}$; [89] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-}$ and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-}(\text{Ti}_{0.93}\text{W}_{0.07})\text{C-}$ and $(\text{Ti}_{0.93}\text{W}_{0.07})\text{C-WC-Mo}_2\text{C-TaC-Co-Ni}$; [100] $(\text{Ti},\text{M})(\text{C},\text{N})\text{-M}_x\text{C-Co/Ni}$, $\text{Ti}(\text{C},\text{N})\text{-M}_y\text{C-Co/Ni}$, and $(\text{Ti},\text{M}_z)(\text{C},\text{N})\text{-Co/Ni}$.

Different pre-alloyed raw powders were tested also by Liu et al. [100] comparing three cermets $(\text{Ti},\text{M})(\text{C},\text{N})\text{-M}_x\text{C-Co/Ni}$, $\text{Ti}(\text{C},\text{N})\text{-M}_y\text{C-Co/Ni}$ and $(\text{Ti},\text{M}_z)(\text{C},\text{N})\text{-Co/Ni}$. All three grades had finally the same overall composition of $\text{Ti}(\text{C},\text{N})\text{-16WC-12Mo}_2\text{C-0.13/0.16VC-9Co-11Ni}$. The highest hardness was achieved by the $(\text{Ti},\text{M})(\text{C},\text{N})\text{-M}_x\text{C}$ -based sample with a value of 1541 HV10, while the other two grades $\text{Ti}(\text{C},\text{N})\text{-M}_y\text{C}$ and $(\text{Ti},\text{M}_z)(\text{C},\text{N})$ reached 1467 HV10 and 1153 HV10, respectively. The K_{IC} was $9.4 \text{ MPa}\cdot\text{m}^{1/2}$ for $(\text{Ti},\text{M})(\text{C},\text{N})\text{-M}_x\text{C-Co/Ni}$, $8.6 \text{ MPa}\cdot\text{m}^{1/2}$ for $\text{Ti}(\text{C},\text{N})\text{-M}_y\text{C-Co/Ni}$, and $11.1 \text{ MPa}\cdot\text{m}^{1/2}$ for $(\text{Ti},\text{M}_z)(\text{C},\text{N})\text{-Co/Ni}$. The authors attribute the high fracture toughness and high hardness of the $(\text{Ti},\text{M})(\text{C},\text{N})\text{-M}_x\text{C}$ sample to the reduction of stress concentration at the core/rim interface due to the disappearance of the inner rims, and to the submicron microstructure.

4.3.6 Influence of raw powders' grain size

A comparison between cermets prepared with different grain size of industrially fabricated raw powders was carried out by Demoly et al. [30]. In particular, two different $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-}(\text{Ta},\text{Nb})\text{C-WC-Cr}_3\text{C}_2\text{-Co-Ni}$ cermet compositions were prepared with fine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$, and two additional versions with the same overall compositions, but substituting the fine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ by submicron $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ raw powders. After sintering all the four samples under the same conditions, the results showed in both cases that the use of submicron $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ lead to an increase in hardness (Fig.19). The toughness increased only for one mixture (grade B) when comparing the fine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ with the submicron $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ cermet, while for the other mixture (grade A), the toughness of the submicron $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ version was slightly lower than the corresponding fine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ one (even almost the same if the standard deviation of the measurement is taken into account).

The grade A was further tested by the authors [55] and the results confirmed the aforementioned mechanical properties behaviour of fine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ and submicron $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ versions, with 1820 HV10 - $8 \text{ MPa}\cdot\text{m}^{1/2}$ and 1850 HV10 - $7.5 \text{ MPa}\cdot\text{m}^{1/2}$, respectively.

Chai et al. [97] investigated a series of influencing factors on cermets in their study, including the grain size of the starting raw powders. In this respect, when keeping all the other factors constant,

the results for a $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -Mo-Ni cermet composition showed an increase of hardness and a decrease in toughness, in case a $0.2\mu\text{m}$ $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermet (1990 HV10 – $6.09 \text{ MPa}\cdot\text{m}^{1/2}$) is compared to a $0.5\mu\text{m}$ $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermet (1937 HV10 – $6.26 \text{ MPa}\cdot\text{m}^{1/2}$).

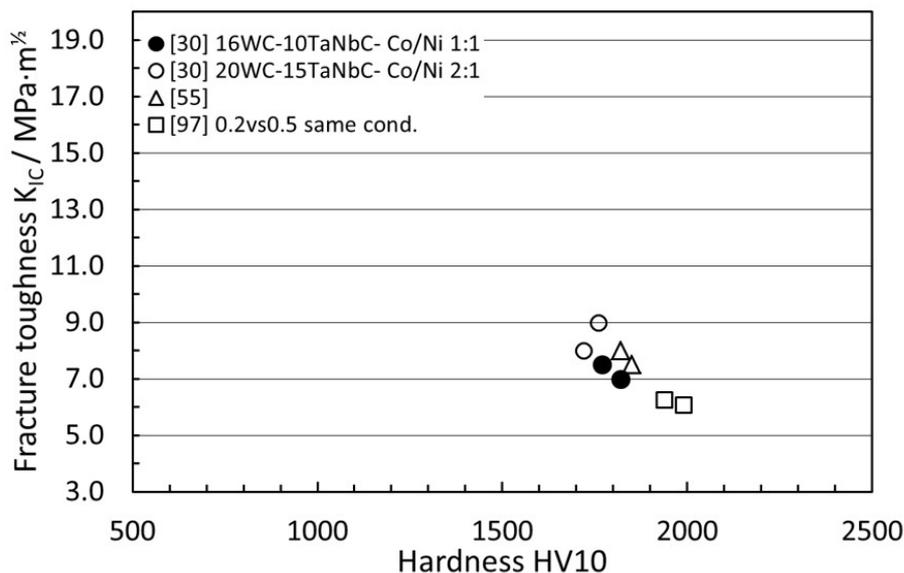


Figure 19

Fracture toughness vs. hardness comparisons on different raw powders grain sizes. [30] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -10(Ta,Nb)C-16WC- Cr_3C_2 -Co-Ni (Co/Ni 1:1); [30] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -15(Ta,Nb)C-20WC- Cr_3C_2 -Co-Ni (Co/Ni 2:1); [55] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -(Ta,Nb)C-WC- Cr_3C_2 -Co-Ni; [97] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -Mo-Ni, 2 stage holding, 1500°C .

An analysis of the grain size influence of TiC and TiN raw powders was carried out by Liu et al. [101]. The tested composition was 55TiC-10TiN-15WC-4Mo-1C-7.5Co-7.5Ni, preparing four samples (A, B, C, and D) using TiC-TiN, TiC-nano TiN, nano TiC-TiN, and nano TiC-nano TiN, respectively. Although the study shows interesting results concerning microstructure and crack propagations images, the data concerning the hardness / toughness ratio are outside the usual relationship, e.g. 1570-1720 HV10 and 14.5 - $16.1 \text{ MPa}\cdot\text{m}^{1/2}$ for K_{IC} . We consider that they are not reliable compared to data for both experimental and commercial grades, and thus we have not included them into Fig.19.

4.3.7 Influence of binder content

Cutard et al. [64] analysed the influence of the binder content and binder composition, as well as addition of various amounts of Mo, on both $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ - and $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermets (all the compositions reported from this paper are in vol%). Fig.20 shows that an increase of the binder content leads to a decrease in hardness and an increase in K_{IC} , as expected, for $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -based grades ($\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -6.4Mo₂C-grades with 6.4% Co, 13.0% Co, and 18.0% Co). The trend is confirmed also by the samples belonging to the $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based grades ($\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -6.4Mo₂C with 6.4% Co and 18.0% Co), showing even a stronger decrease in hardness compared to the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -based grades. In fact, due to the higher N content, $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermets are expected to be harder if all the other components are kept constant (compare [31]), and this is confirmed in this case as well comparing $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -6.4Mo₂C-6.4% Co sample with $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -6.4Mo₂C-6.4% Co sample. However, increasing the binder content up to 18% lead the $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermet to reach a lower hardness and a lower toughness compared to the similar grade prepared with $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ (sample $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -6.4Mo₂C-18.0% Co and $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})$ -6.4Mo₂C-18.0% Co, respectively).

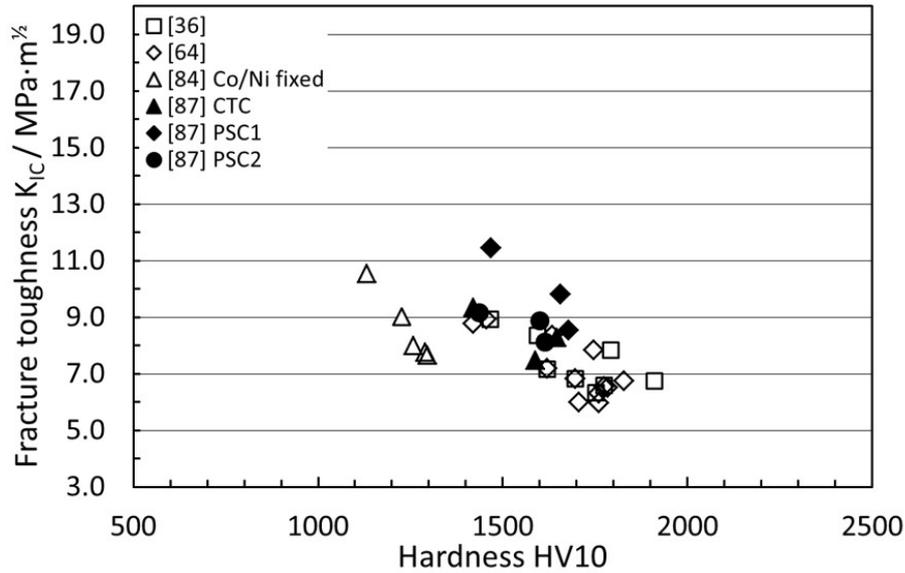


Figure 20

Fracture toughness vs. hardness comparisons on various binder contents. [36] $Ti(C_{0.7}N_{0.3})-Mo_2C-Co$ or $-Ni$; [64] $Ti(C_{0.7}N_{0.3})-Mo_2C-Co$ or $-Ni$ and $Ti(C_{0.5}N_{0.5})-Mo_2C-Co$ or $-Ni$; [84] $Ti(C_{0.5}N_{0.5})-WC-Mo_2C-Co-Ni$ (Co/Ni constant); [87] $Ti(C_{0.7}N_{0.3})-WC-Mo_2C-NbC-Co-Ni$; [87] $Ti(C_{0.7}N_{0.3})-(Ti_{0.88}W_{0.12})C-WC-Mo_2C-NbC-Co-Ni$; [87] $Ti(C_{0.7}N_{0.3})-(Ti_{0.88}W_{0.12})(C_{0.7}N_{0.3})-WC-Mo_2C-NbC-Co-Ni$.

Material softening caused by an increased binder content was proved in a work by Mari et al. [36], too. The results of Xu et al. [84] on different binder content and composition are also in agreement with this trend. The variation became larger as the binder content increased, particularly for the toughness increment. Furthermore, all three series tested by Park et al. [87] confirm these results.

4.3.8 Influence of binder composition, mainly the Co/Ni ratio

Investigations made by Cutard et al. [64] and Mari et al. [36] include, as previously mentioned, also binder composition variations (all the compositions reported from these two papers are in vol%). Grades $Ti(C_{0.7}N_{0.3})-6.4Mo_2C-6.4Co$ and $Ti(C_{0.7}N_{0.3})-6.4Mo_2C-6.4Ni$ can be directly compared, having only the type of binder as a difference. Results are shown in Fig.21. The hardness was slightly lowered when substituting Co by Ni, while the toughness showed a steeper decrease.

The study of Xu et al. [84] on the Co/Ni ratio variation revealed that the best K_{IC}/HV combination is reached when both, Co and Ni, are present. The tested samples had a fixed amount of both hard phase (75wt%) and overall binder phase (25wt%). K_{IC} always increased when increasing the Ni content, while the hardness showed first an increase until 10wt%Ni + 15wt%Co, and then decreased upon further Ni increase.

Demoly et al. [30] tested two different cermet grades with 1:1 and 2:1 Co/Ni ratios, both made in two versions with submicron $Ti(C_{0.5}N_{0.5})$ and fine $Ti(C_{0.5}N_{0.5})$, respectively. Both the submicron and the fine series showed a decrease in hardness and an increase in toughness when moving from 1:1 to 2:1 Co/Ni binder ratio. Slightly larger influence of Co/Ni was found in case of submicron $Ti(C_{0.5}N_{0.5})$ compared to fine $Ti(C_{0.5}N_{0.5})$ grades.

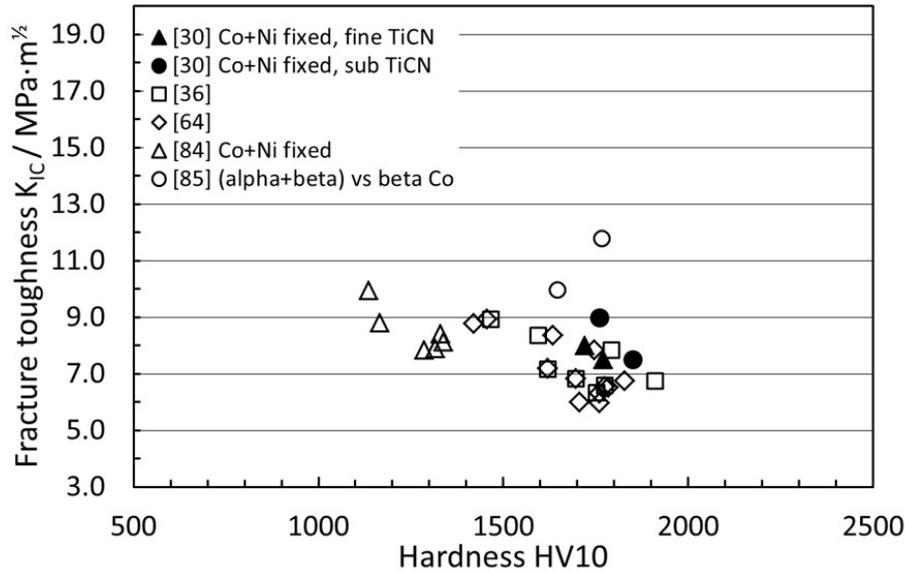


Figure 21

Fracture toughness vs. hardness comparisons on different binder compositions. [30] fine $Ti(C_{0.5}N_{0.5})-(Ta,Nb)C-WC-Cr_3C_2-Co-Ni$; [30] submicron $Ti(C_{0.5}N_{0.5})-(Ta,Nb)C-WC-Cr_3C_2-Co-Ni$; [36] $Ti(C_{0.7}N_{0.3})-Mo_2C-Co$ or $-Ni$; [64] $Ti(C_{0.7}N_{0.3})-Mo_2C-Co$ or $-Ni$ and $Ti(C_{0.5}N_{0.5})-Mo_2C-Co$ or $-Ni$; [84] $Ti(C_{0.5}N_{0.5})-WC-Mo_2C-Co-Ni$ (Co+Ni constant); [85] $Ti(C_{0.7}N_{0.3})-WC-Mo_2C-TaC-(\alpha Co+\beta Co)$ or $-\beta Co$.

An interesting evaluation of binder phase structure was carried out by Deng et al. [85]. The tests consisted in the preparation of the same $Ti(C_{0.7}N_{0.3})-WC-Mo_2C-TaC-Co$ cermet grade with two different Co phases. One grade had mainly a hexagonal phase (α) with some face-centred cubic (β) phase, the other only pure β phase. A significant difference between these two samples was found in their mechanical properties. Both, the hardness and the K_{IC} increased in case of only pure β -Co phase binder on the order of around 100 HV10 and $1.8 MPa.m^{1/2}$, respectively. It should be noted here, that in cermets the binder is composed of 100% β phase if Ni is present.

4.3.9 Influence of the sintering temperature

In Fig.22 results on the influence of the sintering temperature on K_{IC} and hardness of various cermets are represented.

Zhou et al. [91] studied the influence of the sintering dwell at the highest temperature on two different cermets grades, $Ti(C_{0.7}N_{0.3})-Mo-Ni-Co$ (grade TMNC) and $Ti(C_{0.7}N_{0.3})-WC-Mo-Ni-Co-TaC-HfC$ (grade TWMNCTH), respectively. The results revealed no significant difference of the hardness for the TMNC grade, while that of TWMNCTH one showed a slight increase when the sintering temperature was increased from 1380°C to 1450°C. At higher temperature than the latter no significant further change of hardness was detected. The toughness had a similar behaviour for both grades, being almost constant until 1400°C, then decreased as the sintering temperature increased.

High-pressure sintering of a $Ti(C_{0.5}N_{0.5})-WC-Mo_2C-TaC-Ni-Co$ cermet with fixed 5 GPa pressure (applied by a NaCl media) and variable sintering temperature between 900°C and 1600°C was investigated by Wang et al. [92]. The hardness increased linearly with the temperature with a small rate until 1300°C and then steeper until the maximum sintering temperature was reached (1600°C). K_{IC} oscillated around an almost linear trend, increasing with the increase of temperature. A good combination of K_{IC} and hardness belonged to a sample sintered at 1600°C, reaching 1775 HV10 and $6.73 MPa.m^{1/2}$. The highest toughness was achieved for a sample sintered at 1500°C (1707 HV10 – $6.92 MPa.m^{1/2}$).

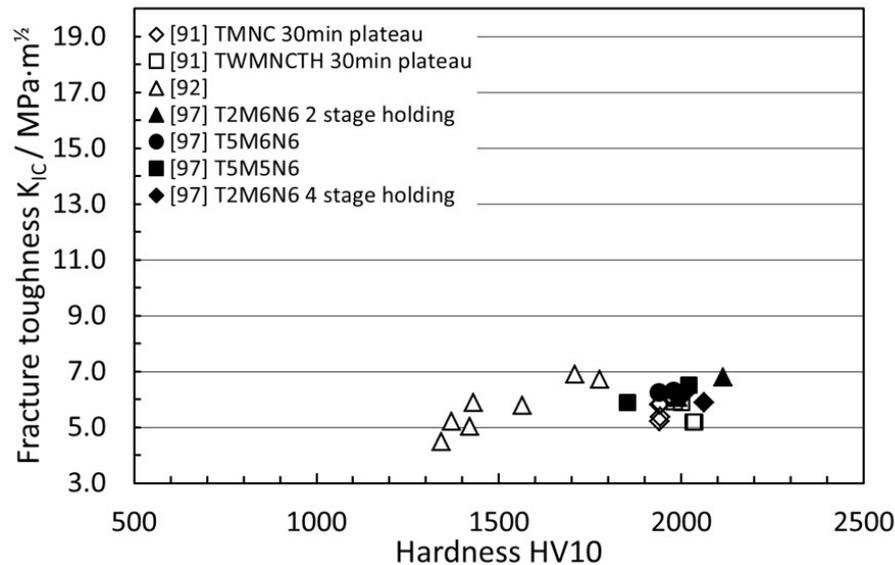


Figure 22

Fracture toughness vs. hardness comparisons on influence of sintering temperature. [91] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-Mo-Co-Ni}$, 30min dwell; [91] $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-WC-Mo-TaC-HfC-Co-Ni}$, 30min dwell; [92] $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-WC-Mo}_2\text{C-TaC-Co-Ni}$; [97] $0.2\mu\text{m Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-6.5Mo-Ni}$, 2 stage holding; [97] $0.5\mu\text{m Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-6.5Mo-Ni}$, 2 stage holding; [97] $0.5\mu\text{m Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-5.4Mo-Ni}$, 2 stage holding; [97] $0.2\mu\text{m Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-6.5Mo-Ni}$, 4 stage holding.

The study of Chai et al. [97] included interesting information also on the influence of the sintering temperature on mechanical properties. The investigated cermet was $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-Mo-Ni}$, as reported in 4.3.6. The nano $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based grade (i.e. $0.2\mu\text{m Ti}(\text{C}_{0.5}\text{N}_{0.5})$) sintered with two dwells showed a decrease of both, hardness and toughness, when increasing the sintering temperature from 1450°C to 1500°C ($2114 \text{ HV}_{10} - 6.82 \text{ MPa}\cdot\text{m}^{1/2}$ for the lower temperature, $1990 \text{ HV}_{10} - 6.09 \text{ MPa}\cdot\text{m}^{1/2}$ for 1500°C). Nevertheless, the same grade sintered with a four-dwell sintering profile showed a decrease in hardness but an increase in toughness upon increasing sintering temperature from 1500°C to 1550°C ($2060 \text{ HV}_{10} - 5.89 \text{ MPa}\cdot\text{m}^{1/2}$ and $2007 \text{ HV}_{10} - 6.22 \text{ MPa}\cdot\text{m}^{1/2}$, respectively). According to the authors, the ultrafine $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})$ -based cermet (i.e. $0.5\mu\text{m Ti}(\text{C}_{0.5}\text{N}_{0.5})$) showed an opposite behaviour compared to the nano grade when increasing the sintering temperature (in this case from 1500°C to 1550°C) with an increase in hardness and an increase in toughness, from $1937 \text{ HV}_{10} - 6.26 \text{ MPa}\cdot\text{m}^{1/2}$ to $1977 \text{ HV}_{10} - 6.31 \text{ MPa}\cdot\text{m}^{1/2}$, respectively.

In case of an ultrafine cermet grade with a lower amount of Mo, both, the toughness and especially the hardness, decreased upon increasing sintering temperature from 1500°C to 1550°C (from $2018 \text{ HV}_{10} - 6.53 \text{ MPa}\cdot\text{m}^{1/2}$ to $1851 \text{ HV}_{10} - 5.91 \text{ MPa}\cdot\text{m}^{1/2}$).

4.3.10 Influence of the sintering holding time

The influence of sintering dwell time on $(\text{Ti}_{0.8}\text{Ta}_{0.2})(\text{C}_{0.5}\text{N}_{0.5})\text{-20Co}$ cermets at 1550°C was analysed by Chicardi et al. [90]. The study revealed that the hardness tends to increase and reach the maximum for 30min holding time, after that it slightly decreased if the dwell time is doubled and keeps constant until 180min (Fig.23). On the other hand, the toughness increased between 0 and 30min and between 60 and 180min, while the toughness value kept constant between 30 and 60min. Thus, the highest toughness was reached with the longest dwell.

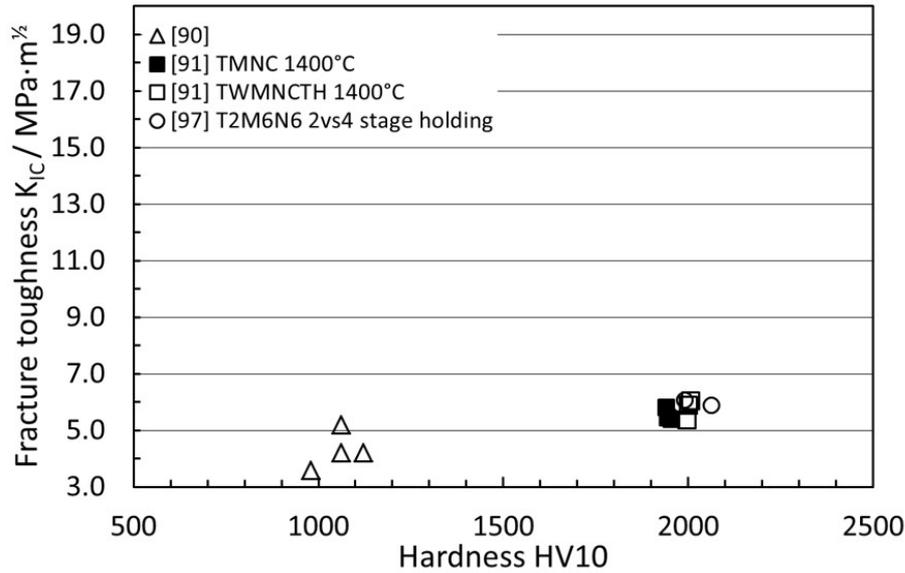


Figure 23

Fracture toughness vs. hardness comparisons on influence of sintering dwell time. [90] $(Ti_{0.8}Ta_{0.2})(C_{0.5}N_{0.5})-Co$; [91] $Ti(C_{0.7}N_{0.3})-Mo-Co-Ni$, 1400°C; [91] $Ti(C_{0.7}N_{0.3})-WC-Mo-TaC-HfC-Co-Ni$, 1400°C; [97] $0.2\mu m Ti(C_{0.5}N_{0.5})-6.5Mo-Ni$, 1500°C.

As mentioned above, Zhou et al. [91] compared different sintering temperatures, but conducted also experiments on dwell time keeping constant the 1400°C sintering temperature. In case of their TMNC series, hardness did not significantly vary with different dwell time, reaching a maximum for 45min, while the toughness had a maximum for 30min and then decreased for 45min, remaining almost stable when the dwell time was further increased up to 60min. On the other hand, results from the TWMNCTH series showed again almost no variation for the hardness when increasing the dwell time, while the toughness first increased until 45min reaching the maximum value there, and then decreased for longer dwell time (60min).

Chai et al. [97] tested also two sintering profiles, which differ by the presence of two or four dwells during the heating phase. The first cycle had a dwell at 1300°C and one at the sintering temperature of 1450°C. The second had two more additional dwells at 400°C and 800°C, respectively. It must be noted that in all cases the dwell time at the sintering temperature was kept the same, thus the results cannot be compared directly with the previously mentioned studies with respect to dwell time variations. The nano $Ti(C_{0.5}N_{0.5})$ -based grade was tested after these two cycles, resulting in slightly higher hardness and slightly lower toughness in case of four dwells cycle compared to the two dwells case.

4.3.11 General comparison in a fracture toughness – hardness map

In Fig.24 all the above-cited data were introduced in a K_{IC} vs. hardness plot together with the data from commercial cermets collected and measured in our laboratory over the last years. As mentioned above, the various cermet grades considered in this work were selected because of their high potential of industrialisation. The data set is differentiated between grades given in academic studies and commercial grades. The latter are concentrated at hardness values between ca. 1400 and 1700 HV10 and show a much steeper K_{IC} increase upon lower hardness than the samples contained in the literature. It is assumed that these commercial grades are practically free of pores, whereas in case of literature data, porosity data were often not reported.

Because of the real application of industrial grades in various cutting processes we conclude that the low K_{IC} at low hardness is less appropriate for such an application. Of course, also a hardness lower than 1400 HV10 seems not acceptable for any cutting application.

As mentioned above, TRS data are most interesting because they reflect the properties of cermets over a larger volume and thus are a well-suited quality indicator of the material. Therefore, we have

screened the literature on TRS data which are included in Tab.6. Optimum values of TRS are located in the region 2400-2800 MPa, lower values than 2000 MPa cannot be considered as appropriate for cutting tool applications. They are probably influenced by porosity, too. Since different authors prepared different grades even in case of studying the influence of adding the same compound to a cermet, a comparison between the achieved results is not possible in most of the cases. Anyway, some general considerations can be done.

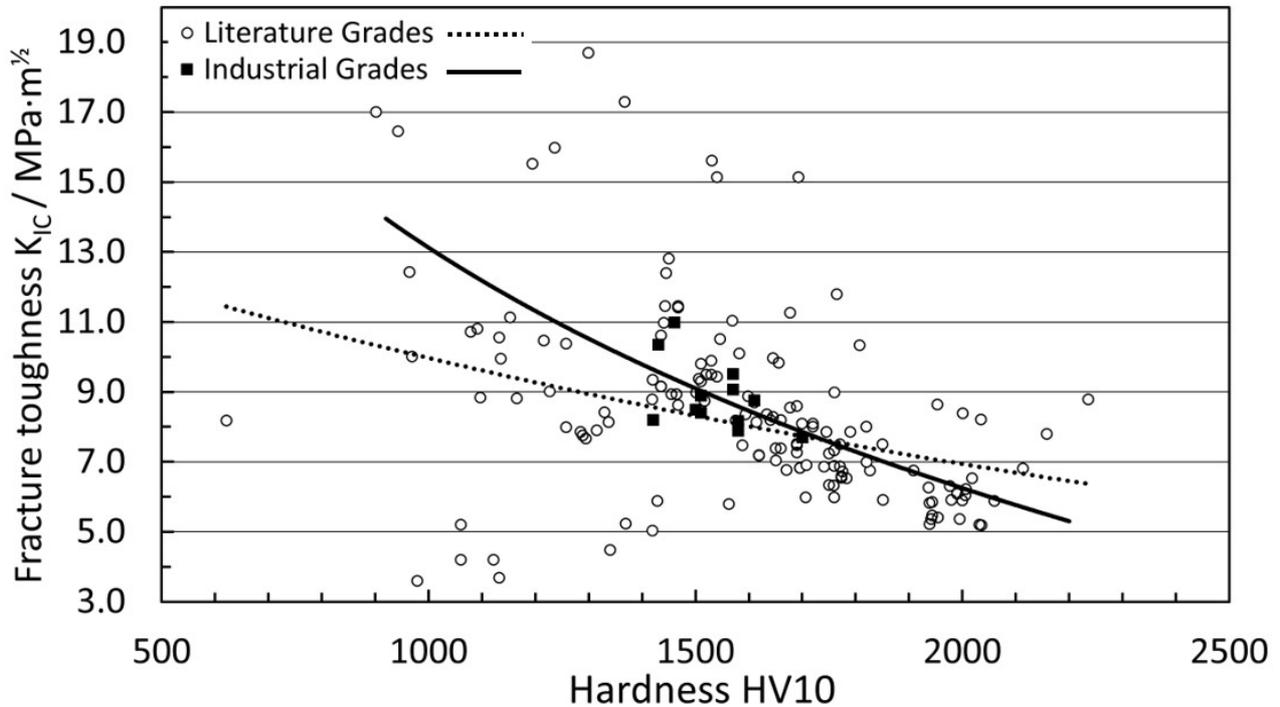


Figure 24

Fracture toughness K_{IC} and hardness data condensed into one diagram of the above-cited studies together with data from industrial grades (measured in our laboratory).

Additions of secondary carbides or carbide formers like Mo, lead to an increase in the TRS values compared to grades without these additions [71-73, 75, 76, 78, 79, 83, 102]. According to Rahimi et al. [70], Mo_2C is more effective than WC or $(Ta_{0.7}Nb_{0.3})C$ in increasing the TRS.

N_2 atmosphere is generally not beneficial for the TRS, especially if added before the cooling stage. This procedure, leading to a nitrogen enrichment near the surface and a higher hardness, obviously decreases TRS [88].

With respect to the sintering temperature and dwell time, 1400°C and 30min of dwell resulted in the highest TRS value for both the grades tested by Zhou et al. [91]. This is certainly an interesting result which must be verified, considering the low sintering temperature together with a short dwell time.

Clearer is the higher TRS when increasing the amount of binder phase [94]. Concerning the preparation technique, it was found that spray drying together with uniaxial pressing give better results rather than slip casting or slip casting combined with CIP [103].

Table 6
Transverse rupture strength (TRS) data collection on cermets.

Ref.	Sample number/name	Main Feature	TRS [MPa]	Ti-based compound	Secondary carbides	Binder
[67]	A	η phase	2373 ^[a]	[b]	[b]	[b]
	B	-	2327 ^[a]			
	C	-	2536 ^[a]			
	D	-	2800 ^[a]			
	E	free C	1336 ^[a]			
[70]	M5	5wt% Mo ₂ C	1792	Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C, (Ta _{0.7} Nb _{0.3})C	Co
	M8	8wt% Mo ₂ C	2063			
	M10	10wt% Mo ₂ C	2021			
	M15	15wt% Mo ₂ C	1800			
	W5	5wt% WC	1417			
	W12	12wt% WC	1583			
	W15	15wt% WC	1542			
	W20	20wt% WC	1479			
T15	15wt% (Ta _{0.7} Nb _{0.3})C	1104				
[71]	A	no WC	800	TiC, TiN	WC, C	Co
	B	5wt% WC	853			
	C	10wt% WC	863			
	D	15wt% WC	879			
	E	20wt% WC	1026			
[72]	A	no Mo	874	TiC, TiN	WC, Mo, C	Co
	B	5wt% Mo	908			
	C	10wt% Mo	944			
	D	15wt% Mo	971			
[73]	A	no WC	1309	Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C	Co, Ni _[e]
	B	10wt% WC	1982			
	C	20wt% WC	2064			
	D	30wt% WC	2082			
[74]	A1	sintering + annealing	1575	TiC, TiN	WC, Mo, C	Ni
	A2	sintering	1860			
	B1	sintering + annealing, +1wt% C	1663			
	B2	sintering, +1wt% C	2023			
[75]	A	no WC	1016	Ti(C _{0.5} N _{0.5})	WC, Mo, Cr ₃ C ₂ , C	Ni
	B	5wt% WC	1531			
	C	10wt% WC	1778			
	D	15wt% WC	2000			
	E	25wt% WC	2097			
[76]	A	no TaC	1836	TiC, TiN	WC, TaC, Mo, Cr ₃ C ₂ , C	Co, Ni _[e]
	B	1wt% TaC	1800			
	C	3wt% TaC	1831			
	D	5wt% TaC	2202			
	E	7wt% TaC	1788			
[78]	W0	no WC	2130	nano TiC, nano TiN	WC, Mo ₂ C	Ni
	W1	5wt% WC	2260			
	W2	10wt% WC	2330			
	W3	15wt% WC	2390			
[79]	G0	no Cr ₃ C ₂	1300	Ti(C _{0.7} N _{0.3})	Mo ₂ C, Cr ₃ C ₂	Ni
	G1	1wt% Cr ₃ C ₂	1340			
	G2	3wt% Cr ₃ C ₂	1380			
	G3	5wt% Cr ₃ C ₂	1430			
	G4	7wt% Cr ₃ C ₂	1490			
[83]	A	no Mo	1423	(Ti,W)C	Mo, C	Ni
	B	5%Mo	1552			
	C	10%Mo	1800			
	D	15%Mo	1880			
	E	20%Mo	1458			

[84]	A	22.5wt% binder (fixed Co/Ni)	825	Ti(C _{0.5} N _{0.5})	WC, Mo ₂ C	Co, Ni
	B	24.0wt% binder (fixed Co/Ni)	1340			
	C	25.0wt% binder (fixed Co/Ni)	1450			
	D	26.0wt% binder (fixed Co/Ni)	1455			
	E	27.5wt% binder (fixed Co/Ni)	1480			
	F	no Co, 25.0Ni	1460			
	G	5.0Co, 20.0Ni	1848			
	H	10.0Co, 15.0Ni	1145			
	I	15.0Co, 10.0Ni	1185			
	J	20.0Co, 5.0Ni	1295			
	K	25.0Co, no Ni	1767			
[85]	A	alpha+beta Co	2015	Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C, TaC	α, βCo
	B	beta Co	2155			
[88]	A	vacuum	2075	TiC, TiN	WC, Mo	Ni
	B	N ₂ during entire cycle	1155			
	C	N ₂ during heating	1570			
	D	N ₂ during final sintering	1775			
	E	N ₂ during cooling	2000			
[90]	CSCs - 0min	0min	281 ^[d]	(Ti _{0.8} Ta _{0.2})(C _{0.5} N _{0.5})	-	Co
	CSCs - 30min	30min	319 ^[d]			
	CSCs - 60min	60min	354 ^[d]			
	CSCs - 180min	180min	307 ^[d]			
[91]	TMNC-1380°C-30 min	Mo, 1380°C - 30 min	1370	Ti(C _{0.7} N _{0.3})	WC, Mo, TaC, HfC	Co, Ni
	TMNC-1400°C-30 min	Mo, 1400°C - 30 min	1787			
	TMNC-1450°C-30 min	Mo, 1450°C - 30 min	1530			
	TMNC-1500°C-30 min	Mo, 1500°C - 30 min	1410			
	TMNC-1400°C-45 min	Mo, 1400°C - 45 min	1465			
	TMNC-1400°C-60 min	Mo, 1400°C - 60 min	1265			
	TWMNCTH-1380°C-30 min	Mo, WC, TaC, HfC, 1380°C - 30 min	1295			
	TWMNCTH-1400°C-30 min	Mo, WC, TaC, HfC, 1400°C - 30 min	1563			
	TWMNCTH-1450°C-30 min	Mo, WC, TaC, HfC, 1450°C - 30 min	1280			
	TWMNCTH-1500°C-30 min	Mo, WC, TaC, HfC, 1500°C - 30 min	1130			
	TWMNCTH-1400°C-45 min	Mo, WC, TaC, HfC, 1400°C - 45 min	1305			
TWMNCTH-1400°C-60 min	Mo, WC, TaC, HfC, 1400°C - 60 min	1345				
[93]	A	WC-5wt% Co	910	Ti(C _{0.5} N _{0.5})	WC	Co, Ni
	B	WC-5wt% Co + 2.1wt% Co + 6.2wt% Ni	1290			
[94]	T80/14	86.5 vol% TiC, 14Ni-steel, austenite-bainite	1500, 2100 ^[e]	TiC	-	[f]
	T75/14	83.0 vol% TiC, 14Ni-steel, austenite-bainite	1800, 2400 ^[e]			
	T70/14	79.0 vol% TiC, 14Ni-steel, austenite-bainite	2300			
	T60/14	74.0 vol% TiC, 14Ni-steel, austenite-bainite	2400			
	T60/8	74.0 vol% TiC, 14Ni-steel, martensite	2200			
	TN30	83.0 vol% TiC, Ni:Mo (2:1)	1700			
	TN40	74.0 vol% TiC, Ni:Mo (2:1)	1900			
	TN40	74.0 vol% TiC, Ni:Mo (4:1)	2200			
TN50	65.0 vol% TiC, Ni:Mo (2:1)	2200				
[96]	TN20 ^[g]	86.5 vol% TiC, Ni:Mo (2:1)	1450	TiC	-	[f]
[97]	T2M6N6 - 1	Ti(C,N) 0.2μm, 2 stage dwell, 1450°C	1034	Ti(C _{0.5} N _{0.5})	Mo	Ni
	T2M6N6 - 2	Ti(C,N) 0.2μm, 4 stage dwell, 1500°C	1356			
	T2M6N6 - 3	Ti(C,N) 0.2μm, 2 stage dwell, 1500°C	1461			
	T2M6N6 - 4	Ti(C,N) 0.2μm, 4 stage dwell, 1550°C	1121			
	T5M6N6 - 3	Ti(C,N) 0.5μm, 2 stage dwell, 1500°C	1108			

	T5M6N6 – 5	Ti(C,N) 0.5 μ m, 2 stage dwell, 1550°C	1342			
	T5M5N6 – 3	Ti(C,N) 0.5 μ m, 2 stage dwell, 1500°C	1348			
	T5M5N6 - 5	Ti(C,N) 0.5 μ m, 2 stage dwell, 1550°C	966			
[100]	(Ti,M)(C,N)-M _x C	(Ti,15W,5Mo,0.2V)(C,N), Mo ₂ C, WC	2210	(Ti,15W,5Mo,0.2V)(C,N), Ti(C,N), (Ti,20W,15Mo,0.2V)(C,N)	WC, Mo ₂ C, VC	Co, Ni
	Ti(C,N)-M _y C	Ti(C,N), VC, Mo ₂ C, WC	1842			
	(Ti,M ₂)(C,N)	(Ti,20W,15Mo,0.2V)(C,N)	1293			
[101]	A	TiC, TiN	982	TiC, TiN, n TiC, n TiN	WC, Mo, C	Co, Ni
	B	TiC, nano TiN	1096			
	C	nano TiC, TiN	1327			
	D	nano TiC, nano TiN	1624			
[102]	FT1	with Mo ₂ C	1560	Ti(C _{0.7} N _{0.3})	Mo ₂ C	Fe
	FT2	without Mo ₂ C	1020			
[103]	SC 15FeNiC	slip casting, 15.0 vol% FeNi, 0.5wt%C	1088	Ti(C _{0.5} N _{0.5})	C	Fe, Ni
	SC-CIP 15FeNi	slip casting + CIP, 15.0 vol% FeNi	1374			
	SC-CIP 15FeNiC	slip casting + CIP, 15vol% FeNi, 0.5wt%C	1375			
	SDP 15FeNi	spray dry + uniax. press, 15.0 vol% FeNi	1529			
	SDP 15FeNiC	spray dry + uniax. press, 15.0 vol% FeNi, 0.5wt%C	1528			
	SDP 20FeNi	spray dry + uniax. press, 20.0 vol% FeNi	1529			
	SDP 20FeNiC	spray dry + uniax. press, 20.0 vol% FeNi, 0.5wt%C	1867			
[104] ^[b]	-	-	2350	-	-	-
[105]	A-HP	Mo ₂ C, HIP	1160	Ti(C,N), TiC	WC, Mo ₂ C, Mo	Co, Ni
	B-HP	TiC, Mo, HIP	1160			
	A-PLS	Mo ₂ C, pressureless sintering	1325			
	B-PLS	TiC, Mo, pressureless sintering	1295			
[106]	1	no C	1041	Ti(C _{0.5} N _{0.5})	Cr ₃ C ₂ , Mo ₂ C, C	Fe
	2	0.5wt%C	1757			
	3	1.0wt%C	2435			
	4	1.5wt%C	2055			
	5	no C + quenching + tempering	1234			
	6	0.5wt%C + quenching + tempering	2179			
	7	1.0wt%C + quenching + tempering	2483			
	8	1.5wt%C + quenching + tempering	1964			
[107]	NT6A	Ti(C _{0.7} N _{0.3})	1361	Ti(C _{0.7} N _{0.3}), nano Ti(C _{0.7} N _{0.3})	WC, Mo ₂ C, TaC	Co, Ni
	NT6A	Ti(C _{0.7} N _{0.3}), postHIP 30min	1451			
	NT6A	Ti(C _{0.7} N _{0.3}), postHIP 90min	1235			
	NT6B	nano Ti(C _{0.7} N _{0.3})	965			
	NT6B	nano Ti(C _{0.7} N _{0.3}), postHIP 30min	1235			
	NT6B	nano Ti(C _{0.7} N _{0.3}), postHIP 90min	1740			

^[a] TRS value related to 50% of probability of fracture. This value is usually taken as a reference value in estimating the TRS of a material starting from a Weibull plot (authors have tested and measured 30 specimens per each grade)

^[b] only specifications on final at% per each chemical element were given

^[c] Co/Ni ratio not specified, just total Co+Ni amount indicated

^[d] biaxial flexural strength

^[e] value after HIP

^[f] 14Ni-steel austenite-bainite, 14Ni-steel martensite, Ni, Mo

^[g] [94] and [96] reported the same samples results, except for this sample which was added in [96] investigations. Thus, only TRS value concerning this additional sample is listed here

^[h] data taken from the paper's abstract

5. Application Examples

As cermets are more brittle than hardmetals, with a higher hardness lower fracture toughness and lower TRS their application is restricted to finishing operations with relatively high cutting speeds and low cutting depth. Because of their higher stiffness, increased oxidation resistance and chemical resistivity towards the workpiece material, as well as their increased plastic deformation resistance, the workpiece surfaces are generally smoother and of higher quality than that machined with hardmetals. In some cases, a coating is not applied to cermets, which means a higher geometrical precision because of the existence of very sharp edges. Hence, for some applications, they can outperform coated hardmetals.

5.1 Metal cutting

In their theses Cassel [108] and Gerschwiler [62] have made extensive studies on intermittent turning as well as turning and milling, respectively. Because of their chemical stability cermets are well-suited for cutting of ferritic-pearlitic steels, tempered steel and cast-iron grades and much less-suited for cutting austenitic steels and Ni-basis alloys. Cratering as a wear mechanism is of much minor importance than abrasive flank wear. Hence, the latter determines the lifetime. Generally, cermets show a more continuous wear than hardmetals.

The large thermal expansion and low heat conductivity can lead to high tensile stresses, in turn leading to formation of thermal cracks, which are often not a criterion for reduced cutting time. This wear phenomenon is especially observed in milling operations. Dry cutting, is therefore proposed to avoid conditions of thermal shock. If the cutting depth is reduced the tendency of cracking upon thermal shock is substantially reduced. In case of cermets containing Al or when Al is contained in the workpiece material, an interesting phenomenon of Al compounds enrichment on the tool surface was observed, causing an improvement of the cutting performances. Similar observations were made for Ca compounds.

As for hardmetals, application of coatings is generally beneficial to the cermet performance, too. Any coating technique which is applied to hardmetals can also be applied to cermets. With coatings abrasion resistance is minimised and resistance to diffusion and adhesion wear further enhanced. The special benefit of cermets is that after consumption of the coating upon wear the material below has still a high oxidation, diffusion and adhesion resistance. However, without coating a sharper cutting edge is obtained, which is a benefit for high-precision applications and an advantage of cermets as compared to hardmetals that must be, on contrary, coated.

Examples for parts machined with cermets are given in Fig.25 [109]. In these parts high-precision boreholes are shown, together with a sketch of the tools and the cermet insert. The workpiece materials are various steels. The tolerances of the boreholes are on the order of 40 – 100µm. The tolerance in roundness is 8µm. By use of cermets instead of hardmetals the tool life was increase from 400 to 1200 pieces per cutting edge.

Cermets with an appreciable amount of W in the starting composition have been successfully tested for milling and gear hobbing [110] and had a better performance than a commercial grade, presumably without such a high W content in the starting composition. Upon addition of a high W content, the hard phase composition tends to achieve a sub-stoichiometric composition, because part of W is inserted into the hard phase. A comparison of an uncoated cermet with a coated hardmetal grade upon cutting of hardened steel was performed by Chen et al. [111] and showed that at lower cutting depth the cermet outperformed the coated comparison grade. This was true also for larger cutting depth but only up to a certain cutting time. The latter is related to the higher brittleness of cermets.

For microtools such as micro end-mills, Kim et al. [112] have tested so-called solid solution cermets, showing no core-rim structure in the hard phase and being nitrogen free. The best grades with a composition of $(Ti_{0.88}W_{0.12})C-7.5\%Co-7.5\%Ni$ showed some potential for application.

Fine grain cermets were tested by Liu et al. [113] on medium carbon steel. The grade without addition of nano TiN having a higher hardness showed better performance, although having lower TRS and K_{IC} . The presented HV and K_{IC} data of the fine grades are lower than that of the cermets

with conventional grain size so that the benefit of use of nano powders (according to Tab.5) is not reflected by these data.

An interesting study of Zhang et al. [114] revealed optimum relationships of the WC/Ti(C,N) and $[C]/([C]+[N])$ ratios of the employed Ti(C,N) and the Co/Ni ratio. The flank was lowest at WC/Ti(C,N) = 0.30, $[C]/([C]+[N]) = 0.6$ and Co/Ni = 2/1.

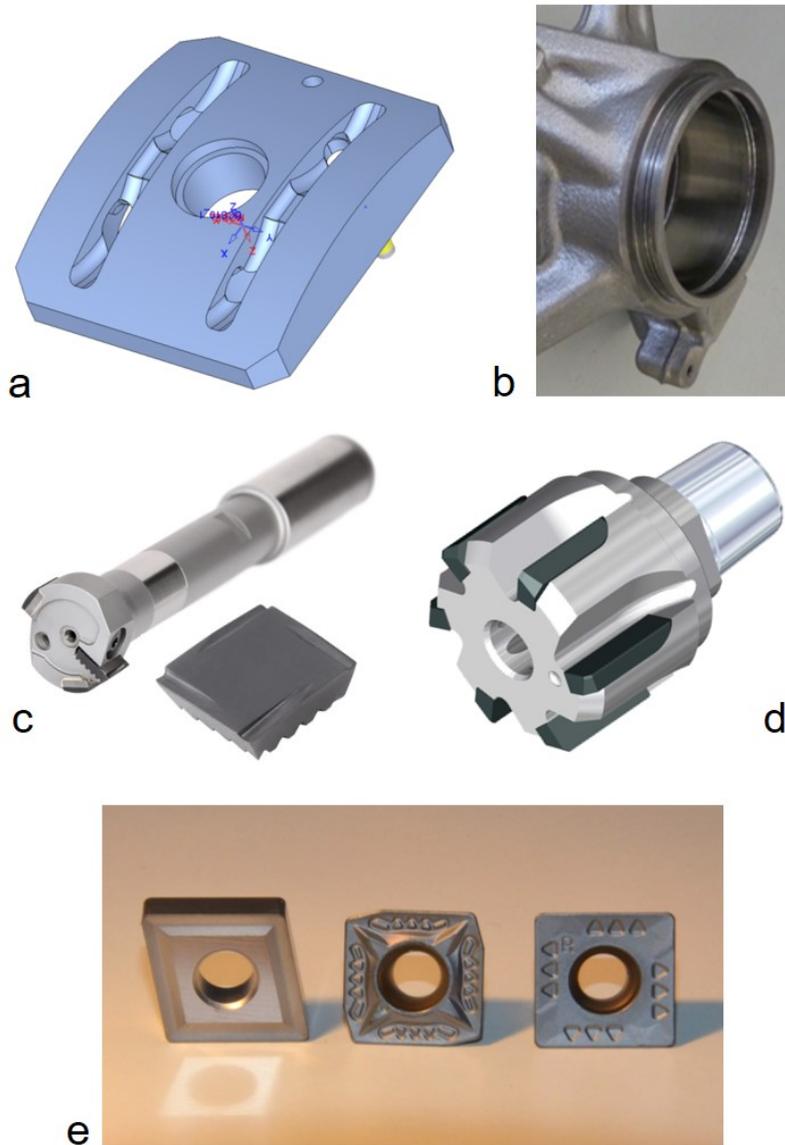


Figure 25

Application examples for metal cutting with cermet inserts, a) and b) parts which contain cylindrical holes having very small tolerances and are machined with cermets, c) and d) round tools with cermet inserts, e) cermets for turning, Kennametal Inc. [109].

5.2 Sawing

Hardmetal and cermet tips for sawing are employed in uncoated form. Hence, the performance of cermets is directly comparable to that of the hardmetal, rather than a coating or coated hardmetal. The tips are brazed with Ag-based alloys towards a steel blade and then ground to achieve the desired geometry. Cermet-tipped saw blades are used for both metal and wood cutting such as their hardmetal counterparts. An example of a circular blade is shown in Fig.26. The low density of cermets as compared to hardmetals (Tab.3) is especially beneficial for high speed circular saws causing less vibrations because of lower radial forces. Hence, the saw runs quieter, too. This was proven by tests of Abrão et al. [115] who compared cermets with two hardmetal grades and found that blades equipped with cermet teeth produced cuts with the narrowest slot width.

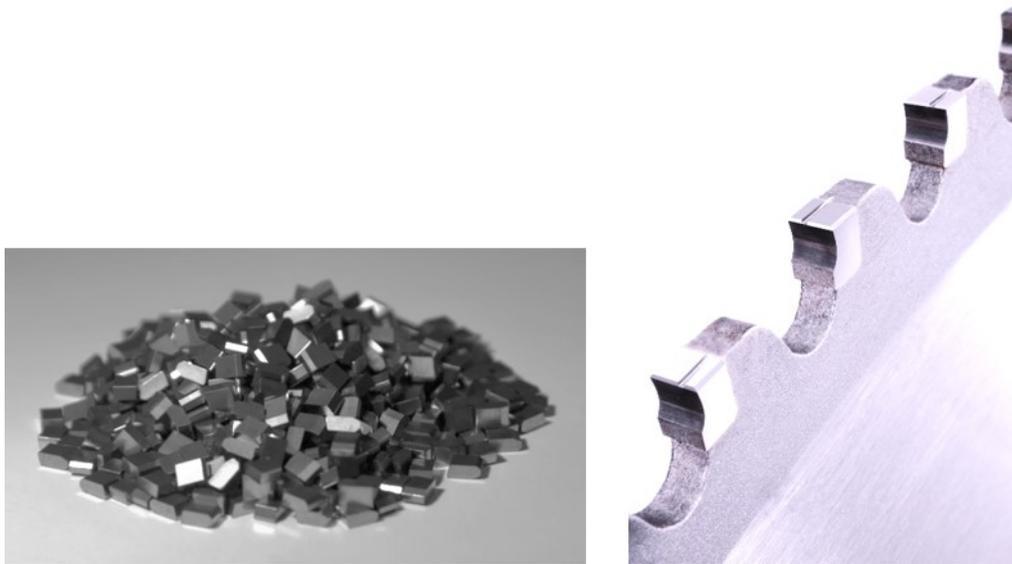


Figure 26

Cermets for sawing, (a) cermet teeth, (b) brazed on circular saw blade.

Cermet-tipped circular saw blades for wood cutting were reported to show a much cleaner cut, edges with less whiskering, and much less wear of the teeth than hardmetal equipped blades [116]. In addition, the fastest cuts were possible with cermet blades. Such blades also proved to be beneficial for cutting particle boards.

5.3 Chip bonding

A non-cutting application is the use of cermets as tools for wire bonding in the fabrication of electronic devices [117]. This is because of the restricted wetting properties which prevents cermets from sticking to the wire with which an electronic chip is connected to the surrounding PDC (Fig.27a). Principally, the geometry of these bonding tools is of wedge type or of capillary type, whereas cermets are used for wedge-type tools. The tools are high-precision parts (Fig.27b) and are processed by various techniques such as honing and EDM machining after sintering.

6. Recent Research on Special Modifications and Alternatives

In the following, some interesting and relatively new topics in the field of Ti(C,N)-based cermets are summarised, which could play some stronger role soon. Again, only such materials are considered, which have the potential of soon implementation into an industry process within the existing technology. Hence, the use of extremely fine-grained powders is not considered here because a lot of precautions are necessary to prevent fine Ti compounds from rapid hydrolysis, oxidation and even burning upon contact with ambient air.

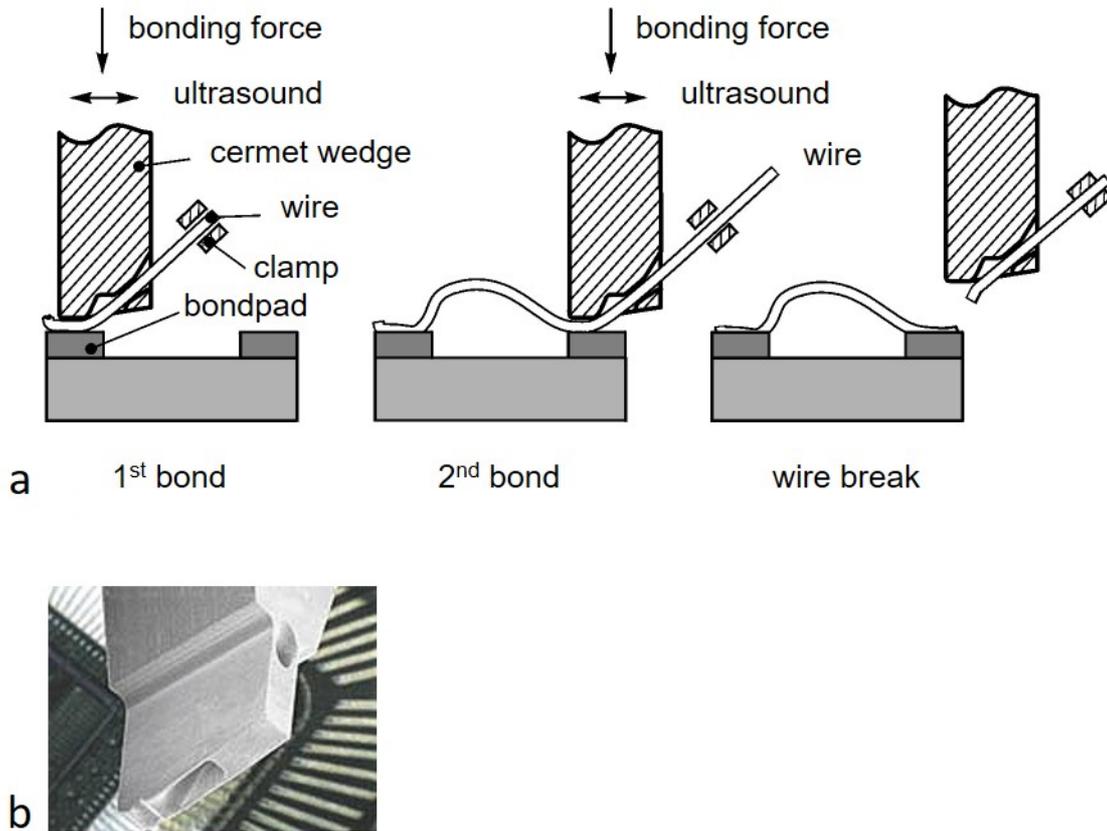


Figure 27

Top: Scheme of wedge-bonding procedure (<http://deacademic.com/pictures/dewiki/87/WEDGE-WEDGE.jpg>) and bottom: small wedge bonding tool (SPT, Switzerland) for chip bonding with Au wires of less than $75\mu\text{m}$.

6.1 Solid-solution cermets

These types of cermets contain a simple microstructure in that they have a very faint core-rim structure [60, 118] with a much finer grain size if Ni is used as the only metal binder. Several data of such a type of cermets were cited above (4.3.5). The uniform hard-phase structure is achieved by a low amount of W in the (Ti,W)C starting powder, rather than using TiC and WC separately. It was claimed that, because of the absence of interfaces within the hard phase grains, the properties are enhanced.

6.2 Hybrid composites and laminates

There is a continuous transition between a cermet with *fcc* hard grains and hardmetals with hexagonal WC as a hard phase. In fact, the above-mentioned class P hardmetals contain sometimes already a huge amount of *fcc* carbides and carbonitrides, especially if the concentration is considered in vol%. The reverse proportion, i.e. a low amount of free hexagonal WC in a matrix of essentially *fcc* hard phase, can be established, too [49, 64, 119, 120]. After a maximum solubility of WC in the Ti(C,N) phase has been reached, which depends on the nitrogen activity, free WC will form and increase its presence as far as the WC in the starting formulation is increased (Fig.28). The so-obtained hybrid composites are fully dense and combine an interesting combination of properties that has not yet been exploited in technical applications.

In laminates, a combination of cermet and hardmetals form such microstructures in the transition zone, too. Such laminates could be candidate materials for replacement of WC upon supply shortage or increase the stiffness of bodies [39,121].

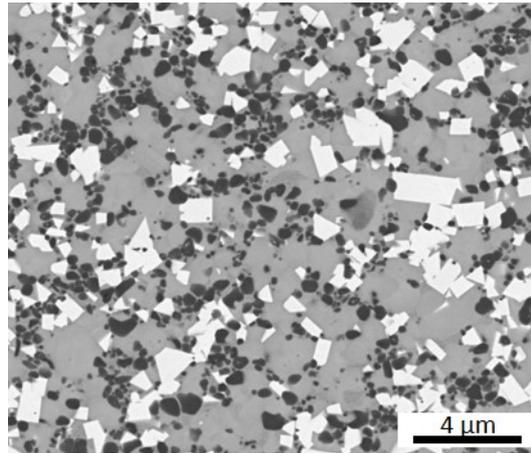


Figure 28

Microstructure of a hybrid material, which shows features of a cermet (dark and grey Ti(C,N) particles) and a hardmetal (white WC crystallites). Realised by the combination of cermet with hardmetal body to form a laminate [39]. SEM-BSE image.

6.3 Graded microstructures

A few cermet grades with graded microstructure are already on the market, with an increased nitrogen content at near-surface positions by use of a nitrogen-containing atmosphere [122]. Such a microstructure is shown in Fig.29a. Because of nitrogen in-diffusion, nitride-rich particles (dark) are more frequent in the near surface zone. In addition, the reverse diffusion – nitrogen out-diffusion – produces a nitrogen-depleted surface zone, leaving a WC-Co layer at the surface, Fig.29b.

Basics of diffusional nitrogen enrichment and depletion have been presented already several years ago in various studies on *fcc*-rich hardmetals [123-125]. Nitride-enriched surfaces have higher hardness than the interior and can also serve as a well-prepared substrate for enhanced adhesion of coatings. Nitride-depleted surface have a lower hardness, but a high toughness [125]. The latter could be very interesting if a high abrasion resistance is desired for which WC-Co is well suited.

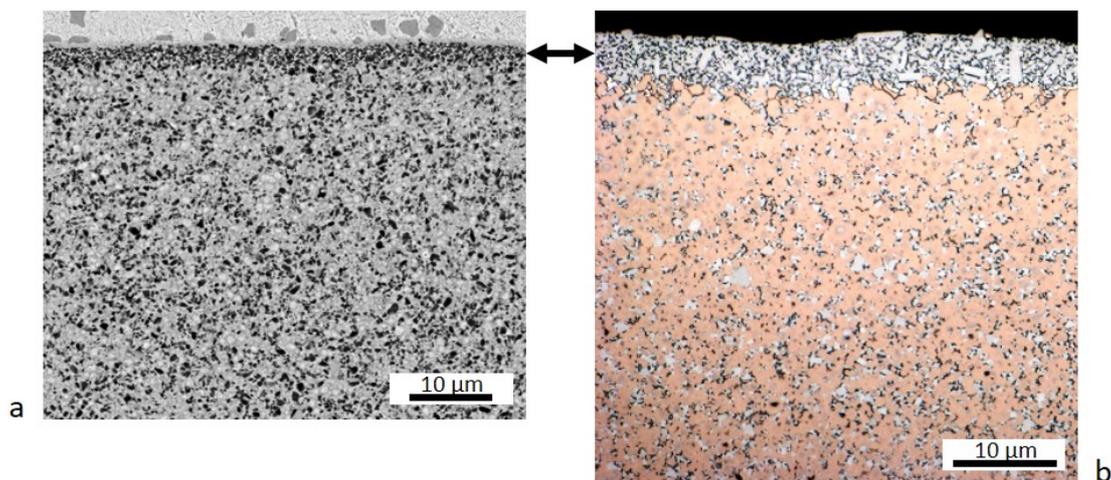


Figure 29

(a) Commercial cermet with an enrichment of nitride particles near the surface (arrow), SEM-BSE image. (b) cermet with a high amount of WC in the starting formulation and a nitrogen-depleted surface composed of a typical hardmetal microstructure WC-Co, LOM image.

In addition, also pure binder phase enrichment, so-called ‘capping’ could be produced on the surface of cermets [126-128] that is most helpful for cermet parts which are brazed to a steel body like in the production of circular or band saw blades. The formation and thickness can be tailored by sintering conditions, as well as the C and N activities in the gas phase and in the cermet.

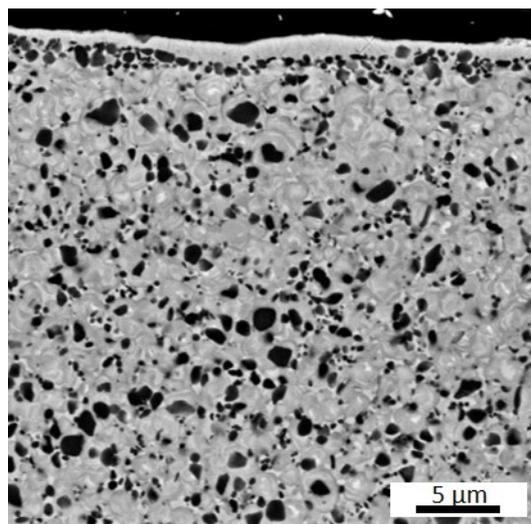


Figure 30

Formation binder phase layer (Co/Ni) on top of a cermet, SEM-BSE image [126].

6.4 Alternative binders and high-entropy alloy (HEA) binder

Binders composed of an alloy of the iron metals Fe, Co, Ni were already proposed long time ago for hardmetals [129] and there are some very specific applications. Such a binder phase, with and without Co, could thus be introduced into the production of cermets in a quite straightforward way, too.

In recent years, also multi-component binders such as Co,Ni,Fe,Cr,V,Al which form a uniform *fcc* solid solution have been proposed [130]. Such binders were considered already in the late 1940s when oxidation-resistant binders for TiC were a target material for turbine blades [3, 4]. This material combination was never used for the desired application in turbines but was further studied for cutting applications in which the word *cermet* originated. Also, the addition of high amounts of refractory metals [131] to achieve a high-temperature resistance is interesting. As discussed above, the solubility of W and Mo can be influenced by the nitrogen composition and pressure upon sintering. In addition to this, hard phase powders with different non-metal/metal ratio and addition of W and/or Mo powders was used to modify the binder-phase composition (compare [110, 132]). Nevertheless, such materials could easily enter in production if some specific application occurs and the benefit is large enough to replace existent grades.

7. Outlook

Because of the multiphase character of Ti(C,N)-based cermets, there are a lot of variables in research and development of these materials already for the starting formulations. These are multiplied by the fact that the hard-phase powders show often a complete solid solubility and can be alloyed with each other to end up with a very large number of compounds that can be employed in the starting formulation. Because of this, the potential of property enhancement is very large already from the view of raw materials and considerably larger than that of WC-Co based hardmetals.

Together with a deeper knowledge and an expected further progress on the metallurgy of cermets, which will enhance the service properties, cermets could increase their proportion among cutting tools. This is especially true if it is considered that on the one hand the world's raw material situation of cermet constituents is much less problematic than that of hardmetals [133] and the machining industry trend goes to near-net shape production of raw parts for which only a smaller volume removed from the workpiece is necessary in production of end parts. Especially in the automobile industry the trend goes to electric cars, powered by batteries and in near future by fuel cells, in which much smaller parts are assembled than for combustion engines.

The rapidly developing additive manufacturing technology will certainly have positive impact on the proportion of cermets amongst cutting tools, too. This technology cannot not only supply small parts but even large near-net shape bodies for which only finishing operations are needed.

References

- [1] Schröter K 1923 Gesinterte harte Metallegierung und Verfahren zu ihrer Herstellung *German Patent* DE420689
- [2] Schwarzkopf P, Hirschl I 1931 Mehrere Metallkarbide enthaltendes Hartmetall, insbesondere für Formkörper oder Werkzeugeile *Austrian Patent* AT160172
- [3] Kieffer R and Kölbl F 1952 Über die Entwicklung und Eigenschaften warm- und zunderfester Hartlegierungen auf Titankarbidbasis mit Nickel-Kobalt-Chrom-Bindern *Planseeber. Pulvermetall.* 1, 17-35
- [4] Redmond J C and Graham J W 1952 *Met. Progr.* 61(4), 67-70
- [5] Moskowitz D and Humenic M 1966 Cemented titanium carbide cutting tools, in: *Modern Developments in P/M* 3, 83-94, Hausner H.H. (eds). Springer, Boston, MA
- [6] Freudhofmeier M 1970 Über die Herstellung von Hartmetallen auf der Basis von Nitriden und Karbonitriden der IVa und Va Metalle *Thesis*, TH Vienna
- [7] Kieffer R, Ettmayer P, Freudhofmeier M 1971 Über neuartige Nitrid- und Karbonitrid-Hartmetalle *Metall* 25(12), 1335-1342
- [8] Rudy E 1973 Boundary phase stability and critical phenomena in higher-order solid solution systems *J. Less-Common Met.* 33, 43-70
- [9] Doi H, Nishigaki K 1976 Binder phase strengthening through precipitation of intermetallic compounds in titanium carbide base cermet with high binder concentration, in: *Modern developments in P/M* 11, 525-542, Plenum Press
- [10] Nishigaki K, Yoshimura H, Doi H 1980 For the purpose of improving mechanical and cutting properties of Ti(C_{0.7}N_{0.3})-15Ni-8Mo alloy AlN was added to the alloy *J.Jap. Soc. Powd. Metall.* 27(2), 50-55
- [11] Moskowitz D, Humenic M 1980 Cemented TiC base tools with improved deformation resistance, in: *Modern Developments in P/M* 14, ed. H.H.Hausner et al. 307-320
- [12] Ettmayer P, Kolaska H 1989 Cermets der neuen Generation *Metall* 43(8), 742-749
- [13] Snell P O 1974 Effect of carbon content and sintering temperature on structure formation and properties of a TiC-24%Mo-15% Ni alloy *Planseeber. Pulvermetall.* 22(2), 91-104
- [14] Nishigaki K, Doi, H 1980 Effect of Additional Carbon Content on Mechanical and Cutting Properties of TiC_{0.7}N_{0.3}-15Ni-8Mo Alloy *J. Jap.Soc. Powd. Metall.* 27(4) 130-136
- [15] Suzuki H, Hayashi K, Matsubara, H, Tokumoto, K 1983 High Temperature Strength of TiC-Mo₂C-Ni Alloys Containing Nitrogen *J. Jap. Soc. Powd. Metall.* 30(3), 106-111
- [16] Gee M G, Reece M J, Roebuck B 1992 High resolution electron microscopy of Ti(C,N) cermets *J. Hard Mater.* 3(2), 119-143
- [17] Andrén H-O, Rolander U, Lindahl P 1993/1994 Phase composition in cemented carbides and cermets *Int. J. Refract. Met.&Hard Mater.* 12(3), 107-113
- [18] Zackrisson J, Rolander U, Andrén H-O 2001 Development of cermet microstructures during sintering *Metall.Mater.Trans. A* 32(1), 85-94

-
- [19] Córdoba J M, Chicardi E, Gotor F J 2013 Liquid-phase sintering of Ti(C,N)-based cermets. The effects of binder nature and content on the solubility and wettability of hard ceramic phases *J. Alloys Compds.* 559, 34–38
- [20] Peng Y, Buchegger C, Lengauer W, Du Y, Zhou P 2016 Solubilities of grain-growth inhibitors in WC-Co-based cemented carbides: Thermodynamic calculations compared to experimental data *Int. J. Refract. Met. & Hard Mater.* 61 121–127
- [21] Ettmayer P, Lengauer W 1989 The Story of Cermets *powd. metall. intern.* 21(2), 37-38
- [22] Berger L M, Ettmayer P, Schultrich B 1994 Influencing factors on the carbothermal reduction of titanium dioxide without and with simultaneous nitridation *Int. J. Refract. Met. Hard Mater.* 12, 161–172
- [23] Steinkellner P, Etschmaier A, Rabitsch K, Lengauer W 2008 Carbothermal Synthesis of TiC and Ti(C,N) powders in a lab-scale reactor *Proc. 2nd Int. Congress on Ceramics ICC2 Verona (I)*, CD edition
- [24] Ettmayer P, Kolaska H, Lengauer W, Dreyer K 1995 Ti(C,N) Cermets – Metallurgy and Properties *Int.J.Refr.Met.& Hard.Mater.* 13, 343-351 (1995)
- [25] Leitner G, Jaenicke-Roessler K, Gestrich T, Breuning T 1997 Shrinkage, liquid phase formation, phase transformation and gas reactions during the sintering of WC-Co hard metals *Proc Int. Conf. Powder Metall. Particulate Mater.* 2, 12-15
- [26] Chen L, Lengauer W, Dreyer K 2000 Advances in modern nitrogen-containing hardmetals and cermets *Int.J.Refract.Met.& Hard Mater.* 18, 153-161.
- [27] Garcia J, Lengauer W 2001 Quantitative Mass Spectrometry of Decarburisation and Denitridation of Cemented Carbonitrides During Sintering *Mikrochim Acta* 136, 83-89
- [28] Findenig G, Buchegger C, Lengauer W, Veitsch C, Demoly A 2017 Investigation of the main influencing parameters on the degassing behaviour of titanium carbonitrides using mass spectrometry *Int.J.Refr.Met.&Hard Mater.* 63, 38-46
- [29] Schwarz V, Scagnetto F, Lengauer W 2018 Influence of composition on the outgassing behaviour of Ti(C,N)-based cermets, *Proc.EuroPM 2018*, in press
- [30] Demoly A, Veitsch C, Lengauer W, Rabitsch K 2011 Effect of submicron Ti(C,N) on the microstructure and the mechanical properties of Ti(C,N)-based cermets *Int.J.Refr.Met.&Hard Mater.* 29(6), 716-723
- [31] Schwarz V, Zivadinovic I, Lisnard B, Traxler F, Viala R, Lengauer W 2016 Optimised properties of Ti(C,N)-based cermets by variation of the W/Mo ratio *Proc. WorldPM 2016*, 9.-13.10.2016, Hamburg (D), Session 45 HM – Cermets, USB Version, EPMA, Shrewsbury, UK, ISBN 978-1-899072-47-7
- [32] Lindahl P, Rosén A E, Gustafson P, Rolander U, Andrén H-O 2000 Effect of pre-alloyed raw materials on the microstructure of a (Ti,W)(C,N)-Co cermet *Int.J. Refract.Met.& Hard Mater.* 18, 273-279 (2000)
- [33] Shetty, D K , Wright, I G 1986 On estimating fracture toughness of cemented carbides from Palmqvist crack sizes *J. Mater. Sci. Lett.* 5(3), 365-368.
- [34] Roebuck B 1996 Magnetic moment (saturation) measurements on hardmetals *Int.J.Refract. Met. Hard Mater.* 14(5-6), 419-424
- [35] Zhang M, Yang Q, Xiong W, Huang B, Ruan L, Moa Q, Li S 2018 Effect of graphite content on magnetic and mechanical properties of TiC-TiN-Mo-Ni cermets *J. Magnet. Magnet. Mater.* 451, 385-390

-
- [36] Mari D, Bolognini S, Feusier G, Cutard T, Viatte T, Benoit W 2003 TiMoCN based cermets Part II. Microstructure and room temperature mechanical properties *Int.J. Refract.Met. & Hard Mater.* 21, 47-53
- [37] Binder S, Lengauer W, Ettmayer P, Bauer J, Debuigne J, Bohn M 1995 Phase Equilibria in the Systems Ti-C-N, Zr-C-N and Hf-C-N *J.Alloys Compds.* 217, 128-136
- [38] Jonsson S 1996 Calculation of the Ti-C-N system *Z. Metallk.* 87(9), 713-720
- [39] Wawrzik S, Zhou P, Buchegger C, Lengauer W 2015 Metallurgy and thermochemistry of cermet/hardmetal laminates *Int.J.Refr.Met.& Hard Mater.* 50, 282-289
- [40] Doi H, Nomura T, Tobioka M, Takahashi K, Hara A 1985 Thermodynamic evaluation of equilibrium nitrogen pressure and WC separation in Ti-W-C-N system carbonitride *Proc. 11th Plansee Seminar* 1, 825-843
- [41] Lengauer W, Binder S, Aigner K, Ettmayer P, Guillou A, Debuigne J, Groboth G 1995 Solid-State Properties of Group IVb Carbonitrides *J.Alloys Compds.* 217, 137-147
- [42] Königshofer R, Liersch A, Lengauer W, Koch T, Scheerer M, Hohenauer W 2004 Solid-state properties of binary, ternary and quaternary transition metal carbonitrides *Proc. WorldPM 2004*, Vienna (A), Vol.3, p.593-598 (CD-ROM: p.575-508), EPMA Shrewsbury UK, ISBN 1899072 15 2
- [43] Hohenauer R, Lengauer W 2017 Structure and Properties of WC-MC-Co hardmetals and of their MC and M(C,N) phases *Proc. EuroPM 2017*, 01.-05.10.2017 Milano (I), Session 26, USB, EPMA, Shrewsbury, UK, ISBN 978-1-1899072
- [44] Aigner K, Lengauer W, Rafaja D, Ettmayer P 1994 Lattice Parameters and Thermal Expansion of Ti(C_xN_{1-x}), Zr(C_xN_{1-x}), Hf(C_xN_{1-x}) and TiN_{1-x} from 298-1473K Measured by High-Temperature X-ray Diffraction *J.Alloys Compds.* 215, 121-126
- [45] Yang Q, Lengauer W, Koch T, Scheerer M, Smid I 2000 Hardness and Elastic Properties of Ti(C_xN_{1-x}), Zr(C_xN_{1-x}) and Hf(C_xN_{1-x}) *J.Alloys Compds.* 309, L5-L9 (2000)
- [46] Kral C, Lengauer W, Rafaja D, Ettmayer P 1998 Critical Review on Elastic Properties of Transition Metal Carbides, Nitrides and Carbonitrides, *J.Alloys Compds.* 265(1-2), 215-233 (1998)
- [47] Lengauer W 2000 Transition Metal Carbides, Nitrides and Carbonitrides, in: Handbook of Ceramic Hard Materials, Vol.I, p.202-252, ed. R.Riedel, Wiley-VCH, Weinheim (2000)
- [48] Mathe B A, Comins J D, Every A G, Lengauer W 2014 Thermal dependence of elastic properties of polycrystalline TiC_{0.97} and TiC_{0.40}N_{0.60} alloys studied by surface Brillouin scattering *Int.J.Refr.Met.&Hard Mater.* 45, 212-217
- [49] Chen L, Lengauer W, Ettmayer P 2000 Metallurgical Reactions and Microstructure Developments During Sintering of Modern Cermets and Cemented Carbonitrides *Proc. Advances in Powder Metallurgy and Particulate Materials*, Part 8, p.51-71
- [50] Yoshimura H, Sugizawa T, Nishigaki K, Doi H 1983 Reaction occurring during sintering and the characteristics of TiC-20TiN-15WC-10TaC9Mo-5.5Ni-11Co cermet *Int.J.Refract. Met&Hard Mater.* 2(4), 170-174
- [51] Yang J K, Lee H-C 1996 Microstructural evolution during the sintering of a Ti(C,N)-Mo₂C-Ni alloy *Mater. Sci. Engineer. A* 209, 213-217
- [52] Lindhal P, Gustafson P, Rolander U, Stals L, Andrén H-O 1999 Microstructure of model cermets with high Mo or W content *Int.J.Refract.Met.& Hard Mater.* 17, 411-421
- [53] Ahn S, Kang S 2000 Formation of Core/Rim Structures in Ti(C,N)-WC-Ni Cermets via Dissolution and Precipitation Process *J. Am. Ceram. Soc.* 83, 1489-1494

-
- [54] Li P, Ye J, Liu Y, Yang D, Yu H 2012 Study on the formation of core-rim structure in Ti(CN)-based cermets *Int.J.Refract.Met.&Hard Mater.* 35, 27-31
- [55] Demoly A, Veitsch C, Lengauer W, Rabitsch K 2012 Cermets based on new submicron Ti(C,N) powder: microstructural development during sintering and mechanical properties, in: *Advances in Sintering Science and Technology II: Ceram. Trans.* 232, p.57-69, ed. S.-J.L.Kang et al., John Wiley & Sons, Hoboken NJ, print ISBN 9781118273753, online ISBN 9781118486955
- [56] Iparraguirre I, Rodriguez N, Ibarreta F, Martinez R, Sanchez J M 2014 Effect of the Cr content on the sintering behaviour of TiCN-WC-Ni-Cr₃C₂ powder mixtures *Int.J.Refract.Met.&Hard Mater.* 43, 125-131
- [57] Min K, Kang S 2003 Rim structure in Ti(C_{0.7}N_{0.3})-CW-Ni Systems *J. Amer. Ceram. Soc.* 86, 1761-1766
- [58] Lengauer W 1995 Multiphase Reaction Diffusion in Transition Metal-Carbon and Transition Metal-Nitrogen Systems *J.Alloys Compds.* 229, 80-92 (1995)
- [59] Jonsson S 1996 Assessment of the Ti-W-C system and calculations in the Ti-W-C-N system *Z. Metallk.* 87(10), 788-795.
- [60] Park S, Kang S 2005 Toughened ultrafine (Ti,W)(C,N)-Ni cermets *Scripta Mater.* 52, 129-133
- [61] Brookes K 1998 *Hardmetals and other Hard Materials*, Int. Carbide Data, East Barnet, UK, ISBN 0950899569
- [62] Gerschwiler K 1998 *Untersuchungen zum Verschleißverhalten von Cermets beim Drehen und Fräsen*, Shaker Verlag Band 28/98, Aachen ISBN 3-8265-4346-7
- [63] DIN EN ISO 4499-2 2010 Deutsches Institut für Normung e.V.
- [64] Cutard T, Bolognini S, Feusier G, Verdon C, Viatte T, Benoit W 1997 Microstructure and mechanical properties of Ti(C,N)-Mo₂C-(Ni,Co) cermets as a function of their chemical composition *Key Engineer. Mater.* 132-136, 747-750
- [65] Wu Y, Xiong J, Guo Z, Yang M, Chen J, Xiong S, Fan H, Luo J 2011 Microstructure and fracture toughness of Ti(C_{0.7}N_{0.3})-WC-Ni cermets *Int.J.Refract.Met.&Hard Mater.* 29, 85-89
- [66] Cutard T, Viatte T, Feusier G, Benoit W 1996 Microstructure and high temperature mechanical properties of Ti(C_{0.7}N_{0.3})-Mo₂C-Ni cermets *Mater. Sci. Engineer.* A 209, 218-227
- [67] Zackrisson J, Andrén H-O 1999 Effect of carbon content on the microstructure and mechanical properties of (Ti,W,Ta,Mo)(C,N)-(Co,Ni) cermets *Int.J.Refract.Met.& Hard Mater.* 17, 265-273
- [68] Russias J, Cardinal S, Aguni Y, Fantozzi G, Bienvenu K, Fontaine J 2005 Influence of titanium nitride addition on the microstructure and mechanical properties of TiC-based cermets *Int.J.Refract.Met.&Hard Mater.* 23, 358-362
- [69] Ahn S, Kim H, Kang S 2007 Effect of secondary carbide addition on properties of Ti(C_{0.7}N_{0.3})-Ni cermets *Mater. Sci. Forum* 534-536, 1165-1168
- [70] Rahimi Dizaji V, Rahmani M, Faghihi Sani M, Nemati Z, Akbari J 2007 Microstructure and cutting performance investigation of Ti(C,N)-based cermets containing various types of secondary carbides *Int.J.Machin.Tools & Manufact.* 47, 768-772
- [71] Li Y, Liu N, Zhang X, Rong C 2008 Effect of WC content on the microstructure and mechanical properties of (Ti,W)(C,N)-Co cermets *Int.J.Refract.Met.&Hard Mater.* 26, 33-40
- [72] Li Y, Liu N, Zhang X, Rong C 2008 Effect of Mo addition on the microstructure and mechanical properties of ultra-fine grade TiC-TiN-WC-Mo₂C-Co cermets *Int.J.Refract. Met.&Hard Mater.* 26, 190-196

-
- [73] Jun W, Ying L, Ping Z, Jiancai P, Jinwen Y, Minjing T, 2009 Effect of WC on the microstructure and mechanical properties in the $\text{Ti}(\text{C}_{0.7}\text{N}_{0.3})\text{-xWC-Mo}_2\text{C-(Co,Ni)}$ system *Int.J.Refract.Met.&Hard Mater.* 27, 9-13
- [74] Zhang Y, Zheng Y, Zhong J, Yuan Q, Wu P 2009 Effect of carbon content and cooling mode on the microstructure and properties of Ti(C,N)-based cermets *Int.J.Refract.Met.&Hard Mater.* 27, 1009-1013
- [75] Qu J, Xiong W, Ye D, Yao Z, Liu W, Lin S 2010 Effect of WC content on the microstructure and mechanical properties of $\text{Ti}(\text{C}_{0.5}\text{N}_{0.5})\text{-WC-Mo-Ni}$ cermets *Int.J.Refract.Met.&Hard Mater.* 28, 243-249
- [76] Wu P, Zheng Y, Zhao Y, Yu H 2010 Effect of TaC addition on the microstructures and mechanical properties of Ti(C,N)-based cermets *Mater. Design* 31, 3537-3541
- [77] Seo M, Kim J, Kang S 2011 Effect of carbon content on the microstructure and properties of $(\text{Ti}_{0.7}\text{W}_{0.3})\text{C-Ni}$ cermet *Int.J.Refract.Met.&Hard Mater.* 29, 424-428
- [78] Dong G, Xiong J, Chen J, Guo Z, Wan W, Yi C, Chen H 2012 Effect of WC on the microstructure and mechanical properties of nano Ti(C,N)-based cermets *Int.J.Refract.Met.&Hard Mater.* 35, 159-162
- [79] Wan W, Xiong J, Yang M, Guo Z, Dong G, Yi C 2012 Effect of Cr_3C_2 addition on the corrosion behavior of Ti(C,N)-based cermets *Int.J.Refract.Met.&Hard Mater.* 31, 179-186
- [80] Chicardi E, Torres Y, Córdoba J M, Hvizdoš P, Gotor F J 2014 Effect of tantalum content on the microstructure and mechanical behavior of cermets based on $(\text{Ti}_x\text{Ta}_{1-x})(\text{C}_{0.5}\text{N}_{0.5})$ solid solutions *Mater. Design* 53, 435-444
- [81] Naidoo M, Johnson O, Sigalas I, Herrmann M 2014 Influence of tantalum on the microstructure and properties of Ti(C,N)-Ni cermets *Int.J.Refract.Met.&Hard Mater.* 42, 97-102
- [82] Rafiaei S M, Kim J-H, Kang S 2014 Effect of nitrogen and secondary carbide on the microstructure and properties of $(\text{Ti}_{0.93}\text{W}_{0.07})\text{C-Ni}$ cermets *Int.J.Refract. Met.&Hard Mater.* 44, 123-128
- [83] Zhang G, Xiong W, Yang Q, Yao Z, Chen S, Chen X 2014 Effect of Mo addition on microstructure and mechanical properties (Ti,W)C solid solution based cermets *Int.J.Refract.Met.&Hard Mater.* 43, 77-82
- [84] Xu Q, Ai X, Zhao J, Gong F, Pang J, Wang Y 2015 Effects of metal binder on the microstructure and mechanical properties of Ti(C,N)-based cermets *J.Alloys Compds.* 644, 663-672
- [85] Deng Y, Jiang X Q, Zhang Y H, Chen H, Tu M J, Deng L, Zou J P 2016 The effect of Co particle structures on the mechanical properties and microstructure of TiCN-based cermets *Mater. Sci. Engineer. A* 675, 164-170
- [86] Park C, Nam S, Kang S 2016 Carbide/binder interfaces in Ti(CN)-(Ti,W)C/(Ti,W)(CN)-based cermets *J. Alloys Compds.* 657, 671-677
- [87] Park C, Nam S, Kang S 2016 Enhanced toughness of titanium carbonitride-based cermets by addition of (Ti,W)C carbides *Mater. Sci. Engineer. A* 649, 400-406
- [88] Zhao Y, Zheng Y, Li Y, Zhou W, Zhang G, Zhang J, Xiong W 2017 Microstructure and performance of graded Ti(C,N)-based cermets modified by nitriding treatment during different sintering stages *Int.J.Refract.Met.&Hard Mater.* 62, 1-8
- [89] Kim J W, Ahn S Y, Kang S 2009 Effect of the complete solid-solution phase on the microstructure of Ti(CN)-based cermet *Int.J.Refract.Met.&Hard Mater.* 27, 224-228

-
- [90] Chicardi E, Torres Y, Córdoba J M, Sayagués MJ, Rodríguez J A, Gotor F J 2013 Effect of sintering time on the microstructure and mechanical properties of (Ti,Ta)(C,N)-based cermets *Int.J.Refract.Met.&Hard Mater.* 38, 73-80
- [91] Zhou H, Huang C, Zou B, Liu H, Zhu H, Yao P, Wang J 2014 Effects of sintering processes on the mechanical properties and microstructure of Ti(C,N)-based cermet cutting tool materials *Int.J.Refract.Met. & Hard Mater.* 47, 71-79
- [92] Wang Y, Kou Z, Liu Y, Liu F, Duan W, Deng J, Ma Y, Ma D, Tan L, Li C, Zhang Y, He D 2016 Ti(C,N)-based cermets sintered under high pressure *Int.J.Refract. Met.&Hard Mater.* 54, 203-209 (2016)
- [93] Bellosi A, Calzavarini R, Faga M G, Monteverde F, Zancolò C, D'Errico G E 2003 Characterisation and application of titanium carbonitride-based cutting tools *J. Mater. Process. Technol.* 143-144, 527-532
- [94] Roosaar T, Kübarsepp J, Klaasen H, Viljus M 2008 Wear performance of TiC-base cermets *Mater. Sci.* 14(3), 238-241
- [95] Canteli J A, Cantero J L, Marín N C, Gómez B, Gordo E, Miguélez M H 2010 Cutting performance of TiCN-HSS cermet in dry machining *J. Mater. Process. Technol.* 210, 122-128
- [96] Klaasen H, Kübarsepp J, Roosaar T, Viljus M, Traksmaa R 2010 Adhesive wear performance of hardmetals and cermets *Wear* 268, 1122-1128
- [97] Chai Y, Liu H, Huang C, Zou B, Liu H 2013 Study of influencing factors of mechanical properties of Ti(C,N)-based cermets *Key Engineer. Mater.* 589-590, 578-583
- [98] Mari D, Bolognini S, Feusier G, Cutard T, Verdon C, Viatte T, Benoit W 2003 TiMoCN based cermets Part I. Morphology and phase composition *Int.J. Refract.Met.&Hard Mater.* 21, 37-46
- [99] Lin N, Wu C H, He Y H, Zhang D F 2012 Effect of Mo and Co additions on the microstructure and properties of WC-TiC-Ni cemented carbides *Int.J.Refract.Met.&Hard Mater.* 30, 107-113
- [100] Liu Y, Jin Y, Yu H, Ye J 2011 Ultrafine (Ti,M)(C,N)-based cermets with optimal mechanical properties *Int.J.Refract.Met.&Hard Mater.* 29, 104-107
- [101] Liu N, Yin W, Zhu L 2007 Effect of TiC/TiN powder size on microstructure and properties of Ti(C,N)-based cermets *Mater. Sci. Engineer. A* 445-446, 707-716
- [102] Guo Z, Xiong J, Yang M, Wang J, Sun L, Wu Y, Chen J, Xiong S 2009 Microstructure and properties of Ti(C,N)-Mo₂C-Fe cermets *Int. J.Refract. Met. & Hard Mater.* 27, 781-783
- [103] Dios M, Kraveva I, González, Alvaredo P, Ferrari B, Gordo E, Bermejo R 2018 Mechanical characterization of Ti(C,N)-based cermets fabricated through different colloidal processing routes *J.Alloys Compds.* 732, 806-817
- [104] Wang X, Liu Y 2017 Weibull analysis on transverse rupture strength of Ti(C,N)-based cermets *Mat.Science & Engineering of Powder Metallurgy* 22(4), 546-555
- [105] Xu Q, Ai X, Zhao J, Qin W, Wang Y, Gong F 2015 Comparison of Ti(C,N)-based cermets processed by hot-pressing sintering and conventional pressureless sintering *J.Alloys Compds.* 619, 538-543
- [106] Chen M, Zhuang Q, Lin N, He Y 2017 Improvement in microstructure and mechanical properties of Ti(C,N)-Fe cermets with the carbon additions *J.Alloys Compds.* 701, 408-415
- [107] Xiong J, Guo Z, Yang M, Shen B 2008 Preparation of ultra-fine TiC_{0.7}N_{0.3}-based cermets *Int.J.Refract.Met.&Hard Mater.* 26, 212-219

-
- [108] Cassel C 1994 Einsatzverhalten von Cermet-Schneidstoffe bei der Drehbearbeitung, Fortschritt-Berichte VDI, Reihe 2: Fertigungstechnik, Nr.318
- [109] Kennametal Inc 2017 *private communication* M. Wolf, Mistelgau, Germany
- [110] Vicenzi B, Risso L, Calzavarini R, 2001 High performance milling and gear hobbing by means of cermet tools with a tough (Ti,W,Ta)(C,N)-Co,Ni,W composition *Int.J.Refract.Met.&Hard Mater.* 19, 11-16
- [111] Chen X, Xu J, Xiao Q 2015 Cutting performance and wear characteristics of Ti(C,N)-based cermet tool in machining hardened steel *Int.J.Refract.Met. & Hard Mater.* 52, 143-50
- [112] Kim J, Kim M, Kang M, Kang S 2013 Material properties and tool performance of Ti-based solid solution cermets for micro end-mill applications *Int.J.Refract.Met.& Hard Mater.* 36, 278-282
- [113] Liu N, Chao S, Yang H 2006 Cutting performances, mechanical property and microstructure of ultra-fine grade Ti(C,N)-based cermets *Int.J.Refract.Met.Hard Mater.* 24, 445-452
- [114] Zhang H, Tang S, Yan J, Hu X 2007 Cutting performance of titanium carbonitride cermet tools *Int.J.Refract.Met.&Hard Mater.* 25, 440-444
- [115] Abrão A M, Moreira M C, Faria P E, Campos Rubio J C 2014 High-performance circular sawing of AISI 1045 steel with cermet and tungsten carbide inserts *J. Mechan. Sci. Technol.* 28(10), 4275-4282
- [116] <http://www.carbideprocessors.com/pages/carbide-parts/cermet-ii-saw-blades-in-industrial-applications.html>
- [117] Brokelmann M, McKeown M 2016 Heavy copper wire bonding ready for industrial mass production *Proc. 1st Int. Symp. 3D Power Electron. Integration and Manufact.* NC State University, Raleigh, Article 7570581
- [118] de la Obra A G, Avilés M A, Torres Y, Chicardi E, Gotor F J 2017 A new family of cermets: Chemically complex but microstructurally simple *Int.J. Refract. Met. & Hard Mater.* 63(1), 17-25
- [119] Yoon B-K, Lee B-A, Kang S-J L 2005 Growth behavior of rounded (Ti,W)C and faceted WC grains in a Co matrix during liquid phase sintering *Acta Mater.* 53(17), 4677-4685
- [120] Kang Y, Kang S 2010 WC-reinforced (Ti,W)(CN) *J.Europ. Ceram. Soc.* 30, 793-798
- [121] Gotor F J, Bermejo R, Córdoba J M, Chicardi E, Medri V, Dalle Fabbriche D, Torres Y 2014 Processing and characterisation of cermet/hardmetal laminates with strong interfaces *Mater. Design* 58, 226-233
- [122] Kang Y, Kang S 2010 The surface microstructure of TiC-(Ti,W)C-WC-Ni cermets sintered in a nitrogen atmosphere *Mater. Sci. Engineer. A* 527, 7241-7246
- [123] Lengauer W, Dreyer K 2002 Functionally Graded Hardmetals *J.Alloys Compds.* 338(1-2), 194-212
- [124] Ucakar V, Kral C, Dreyer K, Lengauer W 2002 Near-Surface Microstructural Modification of (Ti,W)(C,N) Hardmetals by Nitridation *Int.J.Refr.Met.&Hard Mater.* 20, 195-200
- [125] Lengauer W, Dreyer K 2006 Tailoring hardness and fracture toughness gradients in functional gradient hardmetals *Int.J.Refract.Met.&Hard Mater.* 24, 155-161
- [126] Wawrzik S, Demoly A, Veitsch C, Lengauer W 2011 Ti(C,N)-Based Cermets: Evolution and Stability of Microstructure within Sintering and High-Temperature/High-Pressure Annealing *Proc. EuroPM 2011*, Barcelona (E), Vol.1, paper 170, CD-ROM Edition, EPMA, Shrewsbury, UK, ISBN 978-1-899072-23-1

- [127] Janisch D, Lengauer W, Rödiger K, Dreyer K, van den Berg H 2010 Co capping: Why is sintered hardmetal sometimes covered with binder? *Int.J.Refract.Met.&Hard Mater.* 28, 466-471
- [128] García J, Englund S, Haglöf F 2017 Controlling cobalt capping in sintering process of cermets *Int.J.Refract.Met.&Hard Mater.* 62, 126-133
- [129] Prakash L J 2014 Properties and applications of WC hardmetals with iron based binders *Proc. 9th Int. Conf. on Tungsten, Refractory and Hardmaterials* 113-125
- [130] Zhu G, Liu Y, Ye J 2013 Fabrication and properties of Ti(C,N)-based cermets with multi-component AlCoCrFeNi high-entropy alloys binder *Mater. Lett.* 113, 80-82
- [131] Liu B, Wang J, Chen J, Fang Q, Liu Y 2017 Ultra-High Strength TiC/Refractory High-Entropy-Alloy Composite Prepared by Powder Metallurgy *JOM* 69(4) 651-656
- [132] Ettmayer P, Hörmanseder W 1986 Phase equilibria between high melting nitrides and refractory binder metals *High Temp. High Press.* 18(2), 161-172
- [133] British Geological Survey 2015 Risk List
<http://www.bgs.ac.uk/mineralsuk/statistics/riskList.html>