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Review

Microstructure and mechanical properties of TiC–TiN based cermets for tools application

S. Cardinal *, A. Malchère, V. Garnier, G. Fantozzi

MATEIS, INSA de Lyon, bât. Blaise Pascal, 20 Avenue A. Einstein, 69621 Villeurbanne Cedex, France

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ABSTRACT

The objective of this work is to develop materials with both a good hardness and a good toughness. Titanium carbonitride has a significant hardness ($2000H_v$), but its toughness (6 MPa$\sqrt{m}$) is insufficient for tools applications. Toughness can be improved by addition of a metallic binder. Cermets based on TiC and TiN with Ni as binder are the most developed materials. In the present work, the effect of TiN addition and binder content on the microstructure and the properties of the TiC based cermets elaborated by pressureless sintering have been investigated.

Results show that dense cermets with specific core/rim structure have been obtained. The rupture strength and the toughness increase with the addition of Ni. The optimum values of mechanical properties were found for the cermet with 15 wt% Ni and 10 wt% TiN addition, respectively, which exhibits a Vickers hardness over $1400H_{v_{0.3}}$ and a fracture toughness around 13.6 MPa$\sqrt{m}$.

Contents

1. Introduction

Transition metal carbonitrides, especially Ti(C, N) have considerable interest because of their unique combination of properties such as high melting temperature, high hardness, wear resistance, high electrical and thermal conductivities.

TiC and TiN are isomorphous, therefore a continuous solid solution can be prepared: $Ti(C_{1-x}N_x)$ with $0 \leqslant x \leqslant 1$. One of the most common way to prepare titanium carbonitride is to hot press (HP) blended mixture of TiC and TiN powders in vacuum or argon atmosphere at 1700–2400 °C [1–4]. More recently the spark-plasma-sintering (SPS) method has been used to densify titanium carbonitride powders at a relatively lower temperature and shorter sintering time compared to conventional sintering methods [5].

It has been shown that the properties of these compounds can be largely influenced by the [N]/[C] + [N] ratio [6–8]. Physical

* Corresponding author. Tel.: +33(0) 72 43 61 27; fax: +33(0) 72 43 85 28.
E-mail address: Sandrine.cardinal@insa-lyon.fr (S. Cardinal).

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properties have been investigated as a function of nitrogen content and authors have shown that electrical and heat conductivities increase with increasing nitrogen content whereas the microhardness decreases.

In spite of interesting properties of titanium carbonitride, a sintered body of pure Ti(C, N) is rarely used because of its brittleness and low breaking strength. Ti(C, N) is used for application in cermets, where it constitutes the hard phase and is bonded with nickel and/or cobalt to form a tough and wear resistant material.

Cermets elaborated from a Ti(C, N) powder or a combination of TiC and TiN powders with Ni as binder are the most developed materials [9,10]. These cermets are produced by sintering a compacted powders mixture at a temperature where a liquid phase is formed. The metallic additive leads to eutectic reactions with the TiC phase. Chen [11] has studied the melting behaviour of different TiC based cermets and has shown that liquid phase appears at a lower temperature (typically 1350 °C) than the melting temperature of nickel (1455 °C). So, to ensure a liquid phase sintering, the sintering temperatures of titanium carbonitride cermets usually range from 1400 to 1600 °C. Molybdenum is generally added as Mo_2C in the raw powders in order to obtain a good wetting of Ti(C, N) with Ni. During sintering, an intermediate phase between the hard phase and binder phase is formed. This intermediate phase allows to separate the hard phase from the liquid thus preventing the grain growth of the hard phase which is due to the dissolution and reprecipitation mechanisms. In a typical microstructure of titanium carbonitride cermet containing molybdenum carbide, the hard phase is constituted of a undissolved Ti(C, N) core, surrounded by a rim enriched in molybdenum carbide [12,13].

To produce Ti(C, N) cermets, the most commonly used production routes are pressureless sintering, hot pressing, hot isostatic pressing (HIP'ing), or a combination of sintering and HIP'ing, under vacuum, nitrogen or argon atmosphere [8,14]. The SPS emerging technology is used too for the fabrication of cermets [15,16].

Hardness, toughness and wear resistance can be optimised by varying the material composition. The mechanical properties are influenced by both ceramic and metal phases. The present work consists to elaborate and characterize Ti(C, N) based cermets. The effect of different metal binder additions and the influence of TiN on the microstructures and mechanical properties of cermets have been investigated. The addition of 10 wt% of TiN in the composition of the cermet has been examined. To study the influence of the metal binder Ni, hot pressed Ti(C, N) materials have been produced and their mechanical properties have been compared to those of the Ti(C, N) cermets. The Mo_2C content was fixed.

2. Experimental procedure

2.1. Specimen preparation

The characteristics of the starting powders are given in Table 1. TiN powder was supplied by La Céramique Plastique Company (France). This powder is synthesized by self high temperature synthesis (SHS) process, which allows to obtain fine powders from low cost raw materials [17]. TiC, Mo_2C and Ni are other commercial powders from Starck and Aldrich. Powders density was measured with a helium pycnometer. The mean particle sizes were measured by the Mastersizer laser particle size analyser. Specific surface area measurements were done under argon atmosphere.

Titanium carbonitride materials were prepared as follows: TiC and TiN powders were first blended for 24 h and then hot pressed in graphite die under argon for 1 h at 1850 °C at a pressure of 50 MPa. Samples of 37 mm diameter and about 5 mm height were prepared. Three Ti(C, N) compositions have been studied (70/30, 50/50 and 30/70 at.%).

Table 1
Characteristics of starting powders.

Powder	Supplier	Density (g/cm^3)	Specific surface area (m^2 g)	Particle size (μm)	Lattice parameter (nm)
TiC	Starck	4.9	3.1	1.5	0.4327
TiN	LCP	5.35	7.8	2.9	0.4241
Ni	Aldrich	8.9	–	10	0.3523
Mo_2C	Aldrich	9.2	–	3	$a = b = 0.3012$ $c = 0.4735$

Table 2
Composition of cermets samples (wt%).

Cermet number	TiC	TiN	Mo_2C	Ni
1	70	0	10	20
2	60	10	10	20
3	75	0	10	15
4	65	10	10	15

The cermets were elaborated by conventional powder metallurgy techniques. The compaction is an important step in the fabrication of cermets. Zhang and Lu [18] have studied different types of compaction process and observed the effect of green state on the sintering of Ti(C, N) based cermets. It was concluded that cermets with organic additive, compacted in the two-stage consolidation process (die pressing + cold isostatic pressing) exhibit optimal properties. The cermets were prepared by ball milling using stainless steel balls. The TiN and TiC powders were mixed with Ni and 10 wt% Mo_2C in pure ethanol for 24 h. Polyethylene glycol was added (2 wt%) as a pressing aid. The slurry mixture was dried and sieved (100 μm). Rectangular-shaped specimens were pressed in a steel die at a uniaxial pressure of 100 MPa and thereafter cold compacted by isostatic pressure (350 MPa). Green plates (30×60 mm) with a thickness of 8 mm were produced with a green density of 63%.

Finally, green cermets specimens were dewaxed at 600 °C during 1 h under vacuum and then pressureless sintered under argon atmosphere at 1550 °C during 2 h. Four cermets were prepared using the same method and their composition is given in Table 2.

2.2. Experimental methods

The microstructure of polished specimens was observed by SEM (JEOL 840) in backscattered electron imaging. The chemical compositions of phases were analyzed quantitatively by energy dispersion X-ray analysis (EDX). The morphological parameters of the materials such as grain size and the volume of rims, cores and binder were determined by image analysis (AnalySIS software).

Phases identification was carried out by X-ray diffraction (XRD), using a standard powder diffractometer (Rigaku, Japan) with Cu Kα radiation, a graphite monochromator and a rotating sample holder.

The density of the samples was measured by using Archimede method. The Vickers hardness with a load of 3 N was performed on polished surfaces. The fracture toughness (K_{IC}) was measured by indentation method under indentation load of 10 kg using the expression derived by Shetty et al. [19]:

$$K_{IC} = 0.0889\left(\frac{H_v P}{4l}\right)^{1/2} \quad (1)$$

where H_v is the Vicker's hardness, P is the indentation load and l is the crack length.

Elastic modulus was determined by the ultrasonic method. Electrical resistivity has been measured by Foucault currents.

The wear behaviour of the samples was studied by reciprocating ball-on-flat sliding test (oscillating TRIBOtester) at room

temperature. The experiments were performed using a ruby ball of 6 mm diameter under an applied load of 3 N. Both TiCN cermets and non-cermets specimens were subjected to wear cycle of 80 mm/mN for 21 h. Two parameters are quantified: friction coefficient and wear rate.

3. Results and discussion

3.1. Hot pressed Ti(C, N)

A good densification (>98%) has been achieved for all the samples and no remarkable porosity or defects were found on the polished surface.

X-ray analyses have confirmed that the two starting powders have reacted during sintering to form a solid solution. Lattice parameters of the solid solution vary linearly with the composition of the materials. From experimental X-ray data, a direct correlation between the lattice parameter "a" and the N/(N + C) ratio can be obtained and allows the assessment of the final composition of the sintered materials and the theoretical densities. Our results confirm those earlier reported by Pastor [20]:

$$a = -0.0857x + 4.3274 \text{ and } d_{th} = 0.45x + 4.9 \quad (2)$$

$$x = \mathrm{N}/(\mathrm{N} + \mathrm{C}) \text{ at.}\%$$

where "a" is the lattice parameter, "d_{th}" is the theoretical density and "x" is the atomic ratio.

The phase composition of the sintered samples was determined from the lattice parameters obtained from XRD spectra using formula (2).

The characteristics obtained for the different materials are presented in Table 3. As expected hardness increases continuously with increasing carbon percentage. These results are in agreement with literature data [3,4], as TiC hardness ($3000H_v$) is higher than TiN hardness ($1800H_v$). However, fracture toughness and bending strength reach maximum value for the $TiN_{0.5}C_{0.5}$ composition. This result can be explained by the observation of the fracture surface. Indeed the $TiN_{0.5}C_{0.5}$ composition presents the finest microstructure compared to the other compositions (Fig. 1a–c). Elastic moduli are quite similar, excepted for $TiC_{0.7}N_{0.3}$ composition, which shows the best value of 510 GPa. Mechanical properties obtained for our materials are better than these in the literature data [21]. However direct comparison between our results and the literature data is difficult because our materials are nearly fully densified compared to those cited by Kral [21]. Furthermore, sample preparation methods and different measurements methods may influence the results and consequently make the comparison risky. That may be the reason why Kral observed a large scatter of the elastic moduli values of transition metal carbonitrides. Electrical resistivity increases with carbon percentage as TiC material is less conducting than TiN.

3.2. Ti(C, N) based cermets

3.2.1. Microstructure

Microstructures of cermets were studied by SEM, using backscattered electron images (BEI) (Fig. 2). Based on grey levels of those images, we can easily deduce that cermets are composed of three phases: a typical specific core/rim structure is embedded into a metal binder network.

The morphological parameters of the materials such as grain size and the volume of rims and cores are given in Table 4.

For all cermets, the value of the standard deviation is quite high compared to the grain size, showing that distribution is not very homogeneous. The grain size increases when the formulation contains TiN. When TiN is added (cermets 2 and 4) the binder phase percentage and the rim thickness increase whatever the initial Ni percentage. The fact that the presence of nitrogen (TiN) causes an increase of the binder phase volume, is in accordance with the Roebuck's results [22]. On the other hand, the fact that in our samples the grain size and the rim thickness are not decreasing with TiN addition disagrees with literature data [23]. We can suppose that in our compositions, the [N]/[C] + [N] ratio is not sufficient to have an obvious effect and cermets with more than 10 wt% of TiN must be tested.

In order to have information concerning the phases composition in the cermets, EDX line scans in SEM have been done, crossing metal binder, rim and core in cermets 3 and 4. A low primary electron beam energy (10 kV) has been chosen, in order to reduce X-rays generation volume. Fig. 4 shows net intensities evolution of CK, NK, NiL, MoL and TiK peaks.

The core corresponds to TiC. NK intensity detected in the core of cermet 4 is close to zero, while this core is certainly composed of a Ti(C, N) solid solution. However, any intensity to detect the pres-

Table 3
Mechanical properties of TiC + TiN powders hot pressed 1H at 1850 °C.

	d/d_{th} (%)	Lattice parameters (nm)	K_{IC} (MPa$\sqrt{m}$)	σ_f (MPa)	$H_{v_{0.3}}$ (kg/mm^2)	E (GPa)	Electrical resistivity (μΩ cm)
$TiC_{0.3}N_{0.7}$	>98	0.4265	5.4 ± 0.62	360 ± 30	1740 ± 150	467	52.3
$TiC_{0.5}N_{0.5}$	>98	0.4280	6.3 ± 0.03	435 ± 10	2100 ± 165	473	76.6
$TiC_{0.7}N_{0.3}$	>98	0.4296	5.7 ± 0.1	330 ± 40	2120 ± 84	510	95.1

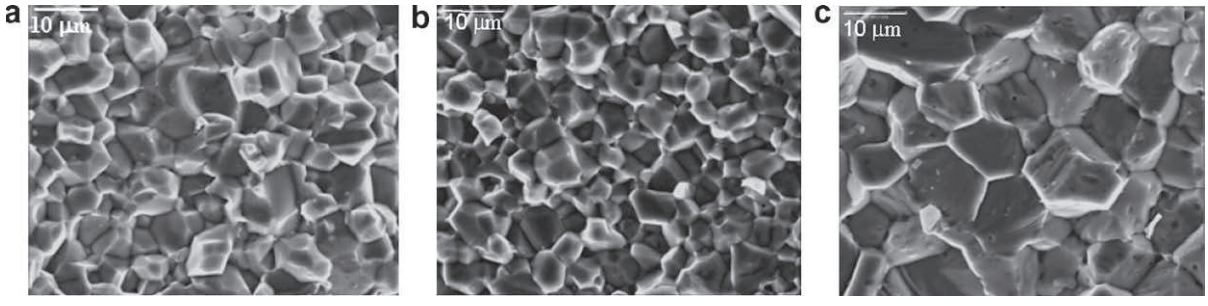

Fig. 1. Fracture surfaces of Ti(C, N) based materials observed by SEM. (a) $TiC_{0.3}N_{0.7}$ (b) $TiC_{0.5}N_{0.5}$ and (c) $TiC_{0.7}N_{0.3}$.

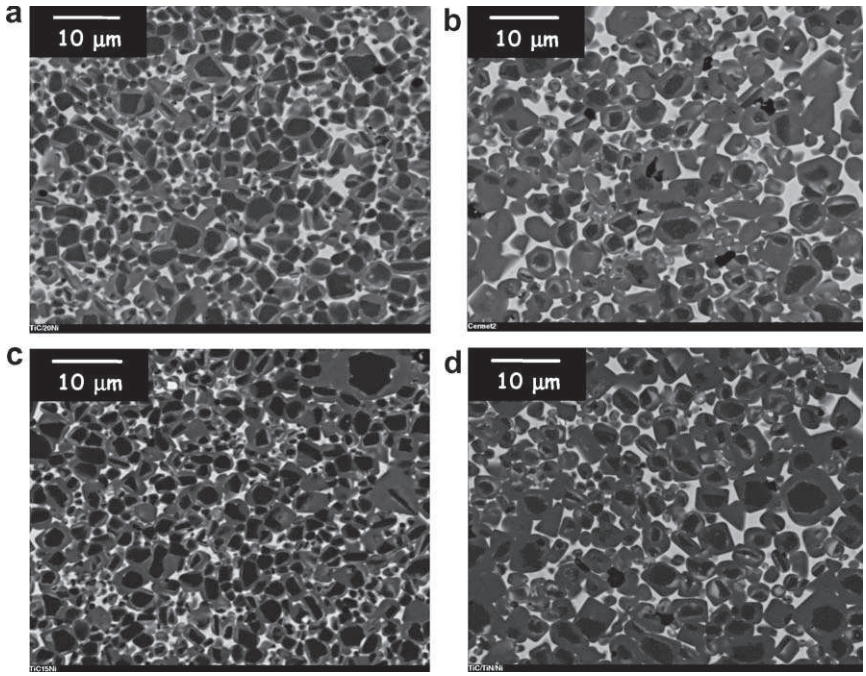

Fig. 2. Polished surface of cermets observed by SEM in BEI mode. (a) Cermet 1: 0% TiN 20% Ni, (b) cermet 2: 10% TiN 20% Ni, (c) cermet 3: 0% TiN 15% Ni and (d) cermet 4: 10% TiN 15% Ni.

Table 4
Average grain size and related standard deviation (SD); volumic proportions of rims, cores and binder.

Cermet number	1	2	3	4
Grain size (µm)	2.3	3.2	2.8	3.6
SD (µm)	1	1.4	1.3	1.5
Binder (%)	11.2	13	8.7	10
Core (%)	30.4	18	26.8	11
Rim (%)	58.4	69	64.5	79

ence of nitrogen is measured in the whole cermet. This null intensity can be explained by three factors: first, the difficulty to separate TiL (E_{TiL} = 0.452 keV) and NK (E_{NK} = 0.392 keV) peaks which overlap; secondly, NK X-ray peak is highly absorbed by carbon atoms contained in the sample; and finally, nitrogen is present in a rather low content in this cermet 4. The rim consists in a solid solution of (Ti, Mo)C (cermets 1 and 3) or (Ti, Mo)(C, N) (cermets 2 and 4). Figs. 3 and 4, clearly show that molybdenum is only detected into the rim. The molybdenum content is not constant in the rim and a maximum concentration is located in the inner rim side at the interface with the core. This corresponds to the white ring around the core, observed on BEI images (Fig. 2).

The metal binder is mainly composed of nickel. Nevertheless, EDX spot analysis done on this metal phase (Table 5) show the presence of metallic atoms (Mo, Ti) in a rather low content (around 1 wt% for Mo and 4.5 wt% for Ti). Detection of Mo and Ti in this metal binder is explained by the dissolution of hard phases during sintering. These quantitative analyses make also appear an iron contamination due to ball milling.

3.2.2. XRD analysis

The XRD patterns of the starting powders mixture and of the sintered cermet 2 are presented in Fig. 5. Before sintering, each raw constituent is identified, in spite of overlapping of some peaks of nickel, titanium carbide, titanium nitride and molybdenum carbide.

After sintering, the peaks of Mo_2C have disappeared and only two phases are present, a ceramic phase and a metal phase. Qian and Lim [24] have shown that Mo_2C dissolves during solid state

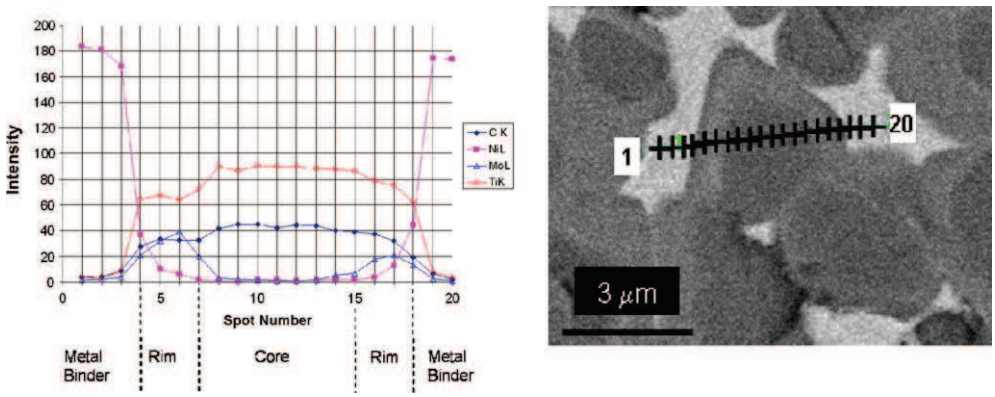

Fig. 3. EDX Intensity profile on cermet 3 obtained after 20 spots, along the line drawn on the BEI image.

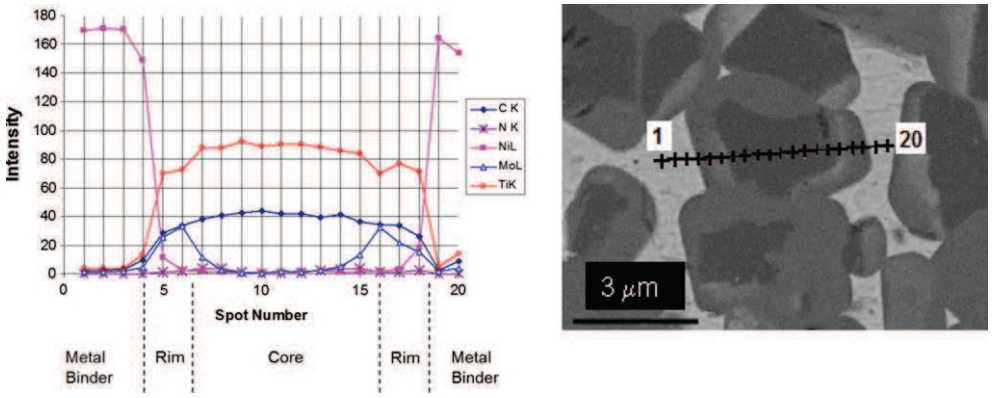

Fig. 4. EDX Intensity profile on cermet 4 obtained after 20 spots, along the line drawn on the BEI image.

Table 5
Results in weight percents obtained from EDX analysis done on the metal binder (conditions: 15 kV – quantification without standards – ZAF quantification model).

	Cermet 3			Cermet 4		
MoL	0	0	0.70	0.96	0.79	1.02
NiL	87.89	87.19	88.38	81.64	83.37	82.10
TiK	4.68	5.31	3.88	4.80	4.34	4.29
FeK	7.43	7.50	7.04	12.60	11.50	12.59

sintering at 1200 °C and then reprecipitates on TiC, or TiCN particles to form the corresponding (Ti, Mo)C or (Ti, Mo)(C, N). The ceramic phase is mainly composed of a solid solution formed from TiC and TiN. Lattice parameter of hard phase in cermet 2 (a = 0.4311 nm) is smaller than those of the TiC phase (a = 0.4327 nm), as TiC has been nitrided to form TiCN. The metal phase is mainly composed of Ni. The peaks of Ni are shifted toward lower angles. The expanded lattice parameter of metal binder phase (a = 0.3578 nm instead of 0.3524 nm for standard Ni) is in agreement with the presence of titanium and molybdenum. The same results are obtained for the TiC based cermets 1 and 3: lattice parameter of hard phase decreases after sintering (0.4307 nm) due to incorporation of Mo. The lattice parameter of Ni increases (0.3555 nm) but less than in TiC–TiN based cermet. Indeed, the Mo content in the binder is much larger with TiC–TiN–Ni–Mo cermets than with TiC–Ni–Mo cermets. These results are in accordance with the investigations of Doï [9], who has studied the evolution of lattice parameters of metal and ceramic phases for various TiN and Mo additions in TiC based cermets.

3.2.3. Mechanical properties

The results obtained for density, elastic modulus, hardness and toughness are reported in Table 6. Comparing cermets 1 and 2, with cermets 3 and 4, the addition of TiN has no significant influence on density. On the other hand, the density of nickel is higher than those of TiC and TiN, and as expected, cermets density decreases from 5.58 to 5.42 as nickel content decreases, respectively, from 20 to 15 wt%. Similar elastic moduli are obtained for all the tested compositions, however the small differences observed between the cermets are attributed to the various binder content in the cermets and to the different values of ceramic and metal elastic moduli (E_{TiN} = 450 GPa, E_{TiC} = 470 GPa and E_{Ni} = 215 GPa). The cermet 3 with the lowest content of binder (8.7 vol.%) (see Table 4) exhibits the highest elastic modulus (410 GPa). If we compare cermets 2 and 4 with cermets 1 and 3, we can observe that the pres-

Table 6
Mechanical properties of cermets.

Cermet number	Density (g/cm^3)	E (GPa)	$H_{V_{0.3}}$ (kg/mm^2)	K_{IC} (MPa$\sqrt{m}$)
1	5.58	400 ± 10	1360 ± 130	13.8 ± 0.7
2	5.56	390 ± 9	1235 ± 95	14.2 ± 0.9
3	5.42	410 ± 10	1520 ± 100	10.3 ± 0.5
4	5.41	396 ± 9	1420 ± 115	13.6 ± 0.5

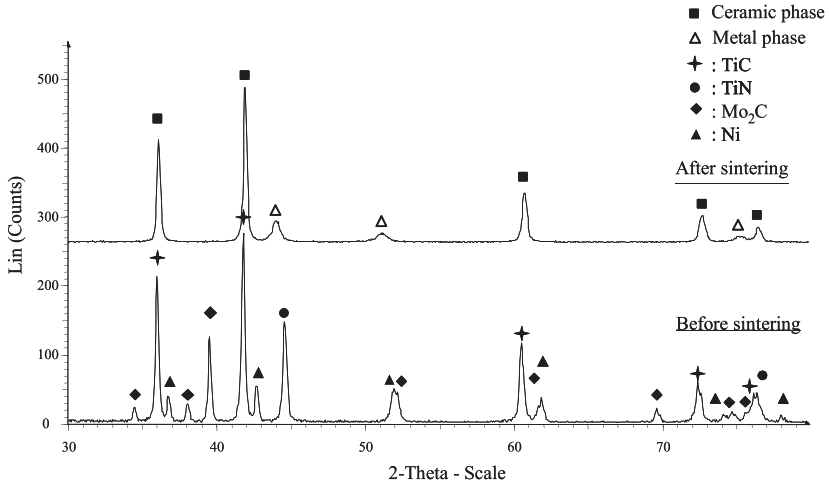

Fig. 5. XRD patterns of cermet 2 before and after sintering.

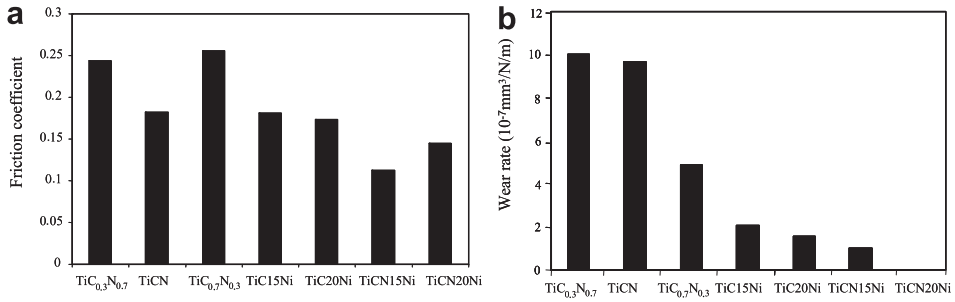

Fig. 6. Comparison of friction coefficient (a) and wear rate (b) of TiC–TiN based materials and cermets.

ence of TiN decreases the hardness but increases the toughness whatever the starting binder content. These results could be explained by the increasing of binder phase volume in the cermet when TiN is present [22] (Table 4) and by the lower hardness of TiCN, compared to TiC. Toughness values reported in Table 6 show a direct correlation with the binder volume fraction (Table 4); i.e., higher binder volume higher toughness. Our toughness values are better than those reported by Mari for Ni cermets [10]. This difference was expected as our samples contain more binder phase. Moreover, comparing samples 1 and 4 shows similar toughness values 13.8 and 13.6 MPa$\sqrt{}$m, respectively, even if the binder phase content is higher for sample 1 than sample 4; this particular result could be explained with the higher grain size of the sample 4 which may improve the toughness. Indeed, it is found that cermets with coarse grains have higher fracture toughness than that of cermets with finer grains [25]. The reasons are due to the higher bonding force in the transcrystalline fracture of coarse grains than that of in the intergranular fracture of fine grains. The best compromise between hardness and toughness is obtained for the TiC–TiN–Mo_2C–15Ni composition (cermet 4). A bending strength of 1080 MPa has been measured for this material. If we compare the mechanical properties of cermets with those of Ti(C, N) based materials, we can observe that: as expected, the addition of a metallic binder improves the bending strength and the toughness, for example cermet 4 exhibits a toughness of 13.6 MPa$\sqrt{}$m in comparison with 6.3 MPa$\sqrt{}$m for TiCN. Hardness decreases with Ni content, from 2100H_v for TiCN to 1420H_v for TiCN cermet with 15 wt% of Ni binder. Electrical resistivity values are very low, 125 and 170 μΩ cm for TiCN/10Mo_2C/20Ni and TiC/10Mo_2C/20Ni materials, respectively. Therefore, these materials are available for EDM machining.

3.3. Tribological test

The reciprocating sliding test allows to measure tangential force and hence to deduce the friction coefficient. The wear rate has been calculated from the wear volume and the tested conditions. The Ti(C, N) based materials and their corresponding cermets have been tested and compared together. In Fig. 6a, the friction coefficient is reported for the different materials. It can observed that low friction coefficients values are obtained for all Ti(C, N) based materials (<0.25) and in particular for TiCN composition. The cermets exhibit friction coefficient inferior to 0.2, the lowest friction coefficient of 0.11 being obtained for the TiCN15Ni composition.

The wear rate results are given in Fig. 6b. The results are given from the highest to the smallest values. The wear rate significantly decreases with the presence of metal binder. If we compare the different compositions, cermets containing nitrogen exhibit the best wear behaviour, especially the composition with 20 wt% of Ni, which shows negligible wear volume. According to these results, wear rate is not only dependent to the hardness but also to the toughness. Indeed cermets which exhibit higher toughness but lower hardness than TiCN materials present a better wear behaviour.

4. Conclusions

Dense Ti(C, N) solid solutions samples in the TiC–TiN binary system were elaborated by hot pressing for 1H at 1850 °C under 50 MPa. Lattice parameters and mechanical properties were measured as a function of N/(N + C) atomic ratio. TiCN composition exhibits the finest microstructure and the best properties, hardness of 2100H_v and toughness of 6.3 MPa$\sqrt{}$m.

Four compositions of TiC based cermets have been prepared by addition of Ni (15 and 20 wt%) and TiN (0 and 10 wt%). Cermets were first cold pressed and then pressureless sintered at 1550 °C under argon atmosphere.

Dense materials with specific core/rim structure have been obtained. The influence of Ni and TiN on microstructure and mechanical properties has been clearly observed. The presence of TiN in the cermet leads to a decrease of hardness but to an increase of toughness.

If we compare Ti(C, N) based materials with the corresponding cermets the addition of a metallic binder has improved the bending strength and the toughness (>10 MPa$\sqrt{}$m), and decreases the hardness from 2100H_v for TiCN to 1420H_v for TiCN cermet with 15 wt% of Ni binder.

Wear test has shown that cermets containing TiN are the most interesting materials as they exhibit the best friction coefficient and the lowest wear rate.

The properties of Ti(C, N) based cermets fulfil the objectives of this work (hardness > 1500H_v and toughness > 8 MPa$\sqrt{}$m) and in particular the cermet with 10 wt% of TiN and 15 wt% of Ni is a good candidate to substitute cemented carbide parts.

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