

Titanium Carbonitride–Zirconia Composites: Formation and Characterization*

E. Barbier & F. Thevenot

Laboratoire Céramiques Spéciales, Ecole Nationale Supérieure des Mines de Saint-Etienne, 158, cours Fauriel, 42023 Saint-Etienne, Cédex 2, France

(Received 18 December 1990; revised version received 7 March 1991; accepted 15 March 1991)

Abstract

Sintering by hot-pressing and mechanical properties of the $TiC_{1-x}N_x-ZrO_2$ ($ZrO_2 < 50$ vol.%, partially stabilized by 3 mol% Y_2O_3) system are investigated by methodology of research using optimal design. This method allows the description and prediction of the bending strength, fracture toughness, microhardness and the temperature of the end of densification with only 13 samples for the whole system.

For a $TiC_{0.33}N_{0.67}-50$ vol.% ZrO_2 composite, the surface area and the yttria content of the zirconia powder has been optimized. The best properties are obtained using a $12\text{ m}^2/\text{g}$ zirconia powder partially stabilized with 3 mol% Y_2O_3 . Using a fractional factorial matrix, hot-pressing cycle parameters are also optimized.

Im System $TiC_{1-x}N_x-ZrO_2$ ($ZrO_2 < 50$ Vol.%, teilstabilisiert mit 3 mol% Y_2O_3) wurden mittels methodischer Probenauswahl und optimierter experimenteller Vorgehensweise das Sinterverhalten beim Heipressen und die mechanischen Eigenschaften untersucht. Diese Methode ermglicht es, fr das gesamte System mit nur 13 Proben die Biegefestigkeit, Bruchzhigkeit, Mikrohrte und die Temperatur am Ende der Verdichtung zu beschreiben und vorherzusagen.

Fr den Werkstoff $TiC_{0.33}N_{0.67}$ mit 50 Vol.% ZrO_2 wurde die spezifische Oberflche und der Y_2O_3 Gehalt des ZrO_2 Pulvers optimiert. Die besten Eigenschaften ergaben sich bei einem ZrO_2 Pulver mit $12\text{ m}^2/\text{g}$ das mit 3 mol% Y_2O_3 teilstabilisiert wurde. Durch Zusammenfassung der Daten in Matrixschreibweise konnten die Heipreparameter ebenso optimiert werden.

* This work is a part of the PhD thesis of E. Barbier, Ecole des Mines de Saint-Etienne, France, 20 March 1991.

Le frittage par compression à chaud et les propriétés mécaniques du composite $TiC_{1-x}N_x-ZrO_2$ ($ZrO_2 < 50$ vol.%, partiellement stabilisé par 3 mol% de Y_2O_3) sont étudiés à l'aide de la méthodologie de la recherche expérimentale en utilisant des plans d'expériences. Cette méthodologie permet de décrire et de prédire dans le domaine étudié, à l'aide de 13 compositions seulement, l'évolution de la contrainte de flexion, de la ténacité, de la dureté et de la température de fin de densification.

Pour un composite $TiC_{0.33}N_{0.67}-50$ vol.% ZrO_2 , la surface spécifique et le pourcentage molaire en Y_2O_3 de la poudre de zirconie ont été optimisés. Les meilleures propriétés sont obtenues en utilisant une poudre de zirconie de $12\text{ m}^2/\text{g}$ partiellement stabilisée avec 3 mol% de Y_2O_3 . Les paramètres du cycle de compression à chaud ont été également optimisés en utilisant une matrice factorielle fractionnaire.

1 Introduction

The solid solution TiC_xN_{1-x} combines the particularly attractive properties of TiC and TiN, such as high melting point, hardness, good thermal and electrical conductivity.¹ So titanium carbonitride is excellent for thermomechanical applications and has been used as cutting tools² and wear-resistant materials, but only mixed with other elements (Mo, Ni)³ or in coating shapes obtained by CVD or PVD. In fact the brittleness and high sintering temperature of TiCN as a pure phase are the two most important factors in the shortcomings for its elaboration and use under high stress fields.

A dispersion of zirconia particles increases toughness of a large number of composites ($Al_2O_3-ZrO_2$, mullite ZrO_2 , $Si_3N_4-ZrO_2$, etc.) according to the well-known mechanisms of microcrack form-

ation and stress-induced phase transformation.⁴ A recent investigation⁵ shows that an addition of ZrO₂ improves the densification and the mechanical properties of titanium carbonitride.

In the present paper, firstly, the authors try to describe and forecast mechanical properties (flexural bending strength, fracture toughness and hardness) of any hot-pressed TiC_{1-x}N_x-ZrO₂ composites (0 < x < 1) containing less than 50 vol.% of tetragonal zirconia polycrystalline (TZP) (3 mol% Y₂O₃). Secondly, one specific composite, presenting good mechanical properties, has been selected after the investigations carried out in Section 4.3. The variation of the mechanical properties of this composite (containing 50 vol.% ZrO₂) are studied in relation to the content of Y₂O₃ stabilizer in zirconia, the surface area of the zirconia powder and the parameters of hot-pressing cycle (temperature, pressure, threshold time...) (cf. Section 4.4).

2 Methodology of Research

The aim of this study is to find, in the considered domain (Fig. 1), a composition or a zone offering the best mechanical properties. For this optimization it will be long and tedious to investigate all of the domain using a classical way. Therefore a methodology of research using optimal designs^{6,7} is employed. This methodology has been already successfully applied to the mixture problem in the ternary diagram TiB₂-TiC-SiC.⁸⁻¹⁰

The main point of the methodology consists in describing predicting or explaining the studied phenomena, i.e. finding the relation between the factors (here, the compositions of the composites) and the responses (the mechanical properties in this study). For instance, in this study, experimental responses (*Y*) can be connected to the volume fraction (*X*) of each constituent *i* (with 1 = ZrO₂, 2 = TiN, 3 = TiC) through a polynomial function, whose numerical coefficients (*b*) must be calculated. The

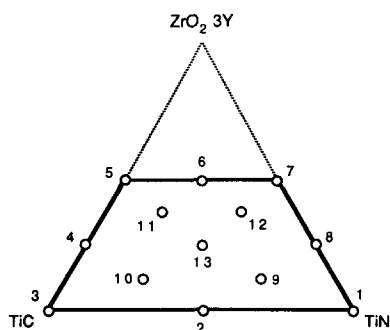


Fig. 1. Domain studied in the TiC_{1-x}N_x-ZrO₂ system and positions of the thirteen compositions elaborated.

following eqn (1) represents a reduced cubic model which is the highest order polynomial used in this study:

$$Y = b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \quad (1)$$

It would be more logical to express the response *Y* as a function of the volumic fraction of ZrO₂ and TiC_xN_{1-x}. But it is easier to have *Y* as a function of the volumic fraction of the two extremities of the solid solution.

The distribution of the points necessary for the calculation of the polynomials have to respect a kind of 'symmetry' and 'regularity' in the space to allow the determination of a model with the best accuracy. To develop a linear model, the four compositions at the summits are sufficient, and with the addition of four other points at the middle of the edges, a second order polynomial can be generated; finally a reduced cubic model is built up with a supplementary point at the centre of the domain (Fig. 1).

The coefficients of the models are calculated using experimental data and the help of software (NEMROD¹¹) which permits a computation of the coefficients of the models by the least squares method. Then the validity of the polynomial is verified comparing theoretical values given by the polynomial and experimental ones for test compositions.

The well-known fractional factorial matrices¹⁰ are employed to observe how the different parameters of a hot-pressing cycle affect the mechanical properties of the material.

3 Experimental Procedures

The starting powders are: TiC, TiN, TiC_{0.33}N_{0.67}, TiC_{0.5}N_{0.5} and TiC_{0.67}N_{0.33} (H. C. Starck, Germany) with a mean particle size equal to 1.35, 1.6, 1.2, 1.7 and 1.6 μm, respectively.

Table 1. Zirconia powders characteristics

Powder name	Surface area (m ² /g) ^a	Mean agglomerate size (μm) ^b	m-zirconia (vol.%)
Z3Y6	8.5	0.7	83
Z3Y12	12.7	0.48	67
Z3Y18	17.3	0.27	33
Z3Y30	29	0.19	16
Z0Y12	12.8	—	≥99

^a BET measure given by the supplier.

^b Sedimentation measure (Sedigraph) given by the supplier.

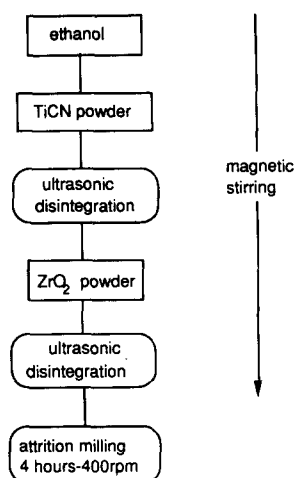


Fig. 2. Elaboration process algorithm.

The characteristics of the zirconia powder (Pechiney, Criceram, France) employed in the study are presented in Table 1.

3.1 Preparation of powders

To obtain a uniform dispersion of ZrO_2 particles a good mix of the starting powders is necessary. For that, powder batches of 100 g are prepared according to the process shown in Fig. 2. To help the deagglomeration an ultrasonic disintegration stage is used. Attrition milling is carried out in a 500 ml vessel coated with an organic material. Zirconia milling balls (1100 g fully stabilized by MgO) of about 2 mm diameter and a Teflon-coated rotor with a 400 rpm velocity are used. A milling time of 4 h is chosen in concordance with a good dispersion and the grain size fineness. X-Ray fluorescence showed an addition of ZrO_2 picked up from the milling balls and a longer attrition time would have increased the ZrO_2 pick-up too much. After attrition the mixture was vacuum dried and sieved. Because of the ZrO_2 pick-up, the compositions of mixtures are a little different from those expected.

3.2 Hot-pressing technique

Powder samples (16–18 g) were first cold-compacted in a graphite die (20 mm inner diameter) and uniaxially hot-pressed using a graphite resistor (VS Pgr 7/10, laboratory press, Degussa, Germany). The press is fully controlled and monitored by computer (temperature, pressure, shrinkage).

A first hot-pressing was performed for all the mixtures under 40 MPa in N_2 atmosphere to determine the maximum densification rate and the end of sintering.

These data allow the execution of a second hot-pressing cycle, so as to obtain samples having more than 98% of theoretical density and to avoid grain

growth. A typical hot-pressing cycle consisted of:

- heating and cooling rates of $30^\circ\text{C}/\text{min}$;
- a soaking temperature fixed between the temperature of the maximum densification rate and the temperature at the end of sintering;
- a soaking time of 15 min;
- a 40 MPa pressure applied from 1000°C to the end of the soaking time;
- a nitrogen atmosphere.

3.3 Mechanical tests

Once hot-pressed the sample densities are evaluated and samples are cut in four bars of $3 \times 4 \times 17 \text{ mm}^3$. The face of these bars charged in tension is carefully polished with a diamond paste (down to $1 \mu\text{m}$ size) to release the stresses due to machining. Then the flexural bending strength is measured by the three-point bending test, microhardness is determined with a Vickers indenter (500 g) and fracture toughness is evaluated using the Vickers indentation technique and the Evan's formula.¹²

4 Results and Discussion

4.1 Sintering of the composites

Every composite reached a relative density of approximately 98%. From the densification rate versus temperature curves, the end of sintering temperatures could be established. The most favourable model to describe the phenomenon was a reduced cubic one:

$$Y = 1300X_1 + 1667X_2 + 1821X_3 - 333X_1X_2 - 564X_1X_3 - 289X_2X_3 + 2368X_1X_2X_3 \quad (2)$$

where Y is the temperature of the end of densification ($^\circ\text{C}$) and X_i the volume fraction of the component i with $1 = ZrO_2$, $2 = TiN$, $3 = TiC$ (cf. eqn (1)).

Figure 3 shows the predicted iso-temperature of densification end curves in a complete ternary diagram. This figure points out an obvious increase of the composite sinterability with the zirconia content. Barnier & Thévenot¹³ have already observed an improvement of the sintering behaviour of ZrC and ZrO_xC_y composites with ZrO_2 additions.

At this point, the chemical inertness of the carbonitride and zirconia phases present has been tested. Several authors^{5,14,15} have pointed out the existence of a $(Ti, Zr)_2O_4$ solid solution by diffusion of Ti into ZrO_2 . In the present case no reaction between the two phases has been observed by X-ray

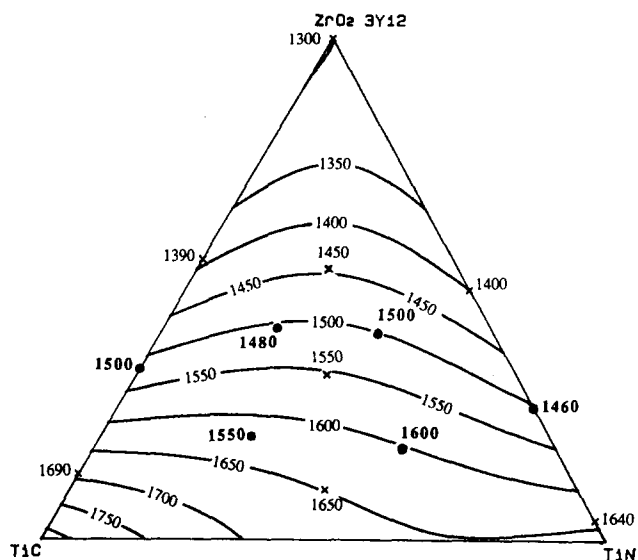


Fig. 3. Iso-temperature of densification end ($^{\circ}\text{C}$) curves plotted with a reduced cubic polynomial model and experimental values of the 14 compositions elaborated. The black points are test points.

diffraction, or by energy dispersive X-ray spectroscopy (EDXS). In another test, dense cylinders of zirconia and $\text{TiC}_{0.3}\text{N}_{0.7}$, $\text{TiC}_{0.5}\text{N}_{0.5}$, $\text{TiC}_{0.7}\text{N}_{0.3}$, TiC, TiN were held tightly in contact at 1700°C for 30 min under 40 MPa and did not join together. That proved once more the absence of reaction for the temperatures, pressure and soaking times used in this study.

4.2 Stabilization of the zirconia phase

The amount of monoclinic zirconia ($m\text{-ZrO}_2$) measured by X-ray diffraction after sintering is always followed by a decrease of the modulus of rupture and an increase of the fracture toughness of the sample, which implies the existence of microcracking. If only tetragonal zirconia ($t\text{-ZrO}_2$) is detected after sintering for a composition, but $m\text{-ZrO}_2$ appears on a second XRD pattern after machining, then this signifies that a part of $t\text{-ZrO}_2$ can be transformed under stress. No cubic zirconia has ever been detected in any sample. So, according to XRD patterns and mechanical properties evolution, three distinct areas are shown in the studied ternary diagram (Fig. 4).

It can be observed that tetragonal zirconia (t or t') stability increases with the sintering temperature and the nitrogen content in the TiCN phase. This phenomenon could be explained by a stabilization of $t\text{-ZrO}_2$ by nitrogen with the temperature. In fact Claussen & Jahn¹⁶ have already noticed that nitrogen could stabilize cubic ZrO_2 in $\text{Si}_3\text{N}_4\text{-ZrO}_2$. According to Cheng & Thompson¹⁷ partially stabilized tetragonal zirconia sintered in a nitrogen

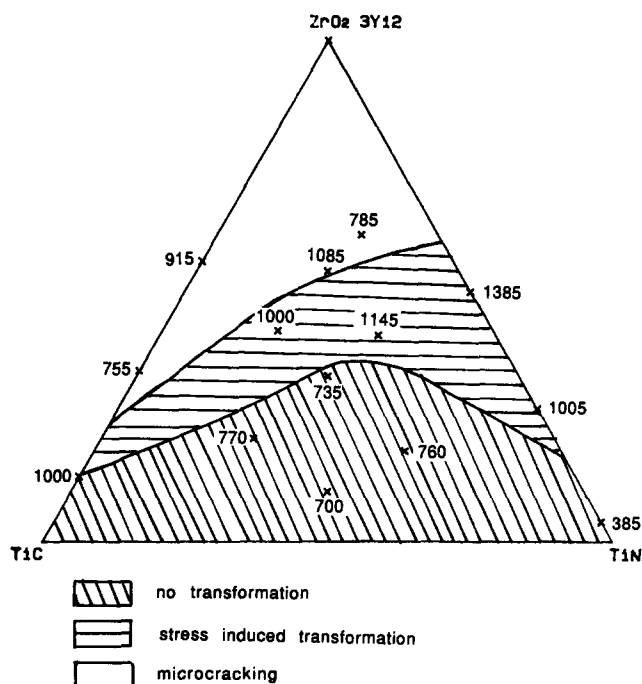


Fig. 4. Evolution of the tetragonal zirconia stability in the ternary diagram and experimental values of the bending strength (MPa) of each composite hot-pressed.

atmosphere reacts with nitrogen above 1400°C and gives a non-transformable $t'\text{-ZrO}_2$.

4.3 Mechanical properties

4.3.1 Flexural bending strength

In this case, it has been impossible to find a polynomial model predicting the evolution of flexural bending strength correctly. The evolution of this property is indeed too intricate, depending on numerous parameters (sintering temperature, nitrogen and zirconia contents, etc.), to be described by a simple polynomial.

Nevertheless the evolution of the modulus of rupture can be explained with the help of the $m\text{-ZrO}_2$ content (Fig. 4). In the zone of the domain where no transformation occurred, the bending strength increase is low. When stress-induced transformation of zirconia appears bending strengths reach relatively high values. The presence of monoclinic ZrO_2 after sintering involves microcracking and a decrease of the modulus of rupture. On the TiC– ZrO_2 axis bending strength reaches a minimum with the composite containing the most important amount of $m\text{-ZrO}_2$ ($\sigma_f \text{TiC-34 vol.}\% \text{ZrO}_2\text{-3Y12} = 755 \text{ MPa}$).

4.3.2 Fracture toughness

Although the fracture toughness values show very often high deviation and are not measured with a very reliable technique, a quadratic model has been

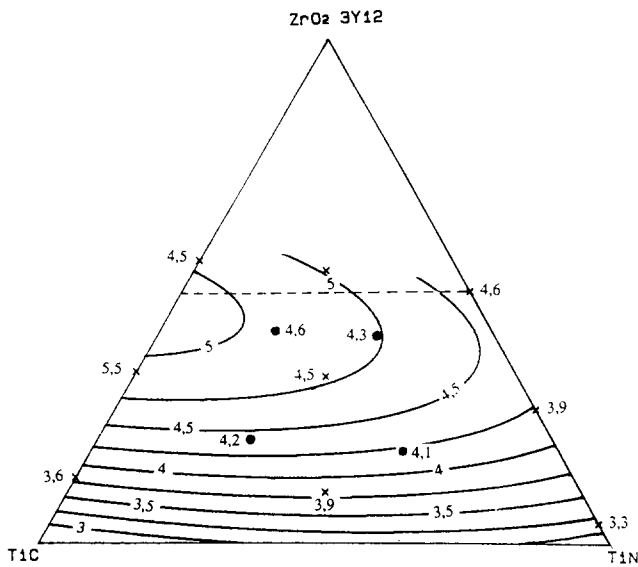


Fig. 5. Iso-fracture toughness ($\text{MPa}\sqrt{\text{m}}$) curves plotted using a quadratic polynomial model. Experimental fracture toughness for each material. The black points are test points.

found to described this property in the studied diagram:

$$Y = 1.5X_1 + 2.9X_2 + 2.6X_3 + 8.8X_1X_2 + 12X_1X_3 + 1.3X_2X_3 \quad (3)$$

where Y is the fracture toughness ($\text{MPa}\sqrt{\text{m}}$) and X_i the volume fraction of the constituent i with $1 = \text{ZrO}_2$, $2 = \text{TiN}$, $3 = \text{TiC}$ (cf. eqn (1)).

The experimental values of the four test points are in good agreement with the theoretical data (see black points and iso-fracture toughness curves on Fig. 5) if a deviation up to 10% is accepted. Considering experimental data standard deviation and errors introduced by the Vicker's indentation technique, such accuracy seems reasonable.

A regular increase of fracture toughness is noticed with an increasing amount of ZrO_2 . This phenomenon has already been observed in the TiN-ZrO_2 system.¹⁸

The low value observed for TiC-34% ZrO_2 is attributed to the existence of microcracks, this sample containing 10% of $m\text{-ZrO}_2$ after sintering.

Finally the authors agree with the conclusion proposed for the TiN-ZrO_2 system by Haylock *et al.*:

' K_{Ic} is not simply related to the amount of zirconia present and crack pinning has been suggested as a possible toughening mechanism along with martensitic transformation'.¹⁸

4.3.3 Microhardness

In this case too the difference between the experimental values and the theoretical ones calculated with the model should not exceed 10%. According

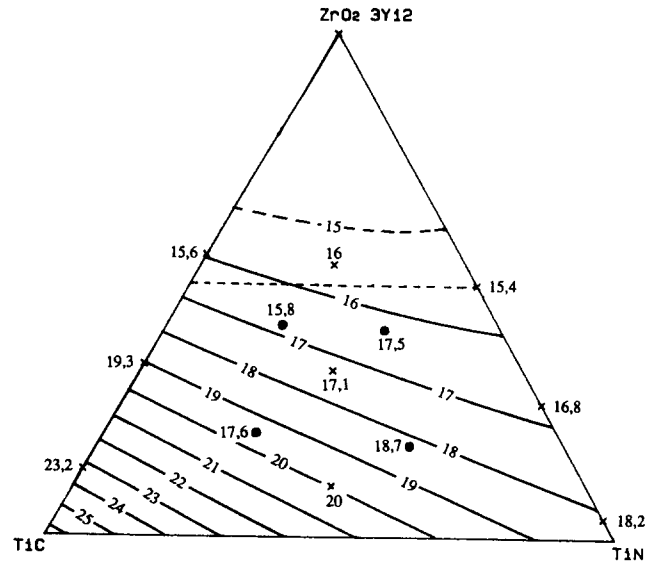


Fig. 6. Iso-hardness (GPa) curves plotted with a quadratic polynomial model and experimental hardness of the 13 compositions. The black points are test points.

to these circumstances, microhardness is correctly described by a second-order polynomial model:

$$Y = 13.6X_1 + 18.5X_2 + 26.5X_3 - 1.9X_1X_2 - 13.5X_1X_3 - 4.3X_2X_3 \quad (4)$$

where Y is the microhardness (GPa) and X_i the volume fraction of the constituent i with $1 = \text{ZrO}_2$, $2 = \text{TiN}$, $3 = \text{TiC}$ (cf. eqn (1)).

It may be seen from the iso-hardness curves (Fig. 6) that the hardness of the composites decreases while the ZrO_2 content increases, due to the low hardness of zirconia. If pure TiC is harder than pure TiN , the difference in hardness disappears by adding approximately 50% ZrO_2 .

The composite $\text{TiC}_{0.33}\text{N}_{0.67}\text{-50 vol.}\% \text{ZrO}_2$ is situated in a region of the diagram where the bending strength is relatively high (over 1000 MPa). By an optimization of this composition the fracture toughness could be improved without a big decrease of the bending strength.

4.4 Optimization of the $\text{TiC}_{0.33}\text{N}_{0.67}\text{-50 vol.}\% \text{ZrO}_2$ composite mechanical properties

4.4.1 Influence of the stabilizer content in ZrO_2

$\text{TiC}_{0.33}\text{N}_{0.67}\text{-50 vol.}\% \text{ZrO}_2$ (12 m^2/g) composites with different amounts of Y_2O_3 (Rhone-Poulenc, Paris) are hot-pressed at 1450°C under 40 MPa during 15 min. Table 2 presents the flexural bending strength and the fracture toughness of these composites. With these results it becomes evident that titanium carbonitride is very sensitive to microcracking and even a low transformed zirconia amount can damage the material. The best properties are obtained with 3 mol% of yttria due to the

Table 2. m-ZrO₂ amount and mechanical properties of TiC_{0.33}N_{0.67}-50% ZrO₂ as a function of Y₂O₃ content

Y ₂ O ₃ (mol%)	m-ZrO ₂ after sintering ^a	m-ZrO ₂ after machining ^a	Flexural bending strength (MPa)	Fracture toughness (MPa√m)
1	87	97	Crushed	—
2	28	50	Macrocracked	—
3	0	9	1050 ± 90	4.6 ± 0.4
6	0	0	815 ± 85	4.3 ± 0.3

^a Remaining zirconia is t-ZrO₂.

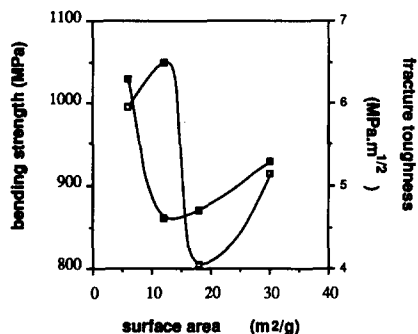


Fig. 7. □, Bending strength and ■, fracture toughness of the final composite (TiC_{0.33}N_{0.67}-50 vol.% ZrO₂) versus surface area of the starting zirconia powder (partially stabilized with 3 mol% Y₂O₃).

stress-induced transformation. With 6 mol% of yttria the bending strength is lower because, in this case, there is no reinforcement due to the stress-induced transformation of zirconia, which is fully stabilized by Y₂O₃ (t-ZrO₂).

4.4.2 Influence of the zirconia powder specific area

Figure 7 gives the mechanical properties of a composite TiC_{0.33}N_{0.67} with 50 vol.% ZrO₂ of different surface areas (6, 12, 18, 30 m²/g) stabilized by 3 mol% Y₂O₃. These materials are hot-pressed in the same conditions as described in Section 4.4.1.

No transformation is observed by XRD for surface areas of 18 and 30 m²/g. A sample containing

ZrO₂ with a surface area of 6 m²/g shows 9 vol% m-ZrO₂ immediately after sintering and 25% after machining. The presence of microcracks allows the understanding of the high fracture toughness and the lower bending strength comparatively to those obtained with a 12 m²/g ZrO₂ powder. At the end of the curves, the mechanical properties increase slightly probably due to the finer and finer grain size of zirconia.

4.4.3 Hot pressing cycle optimization

From both the previous sections it is concluded that the best properties are obtained using a 6 m²/g zirconia starting powder containing 3 mol% of yttria. In this part of the study the authors try to improve the mechanical properties thanks to the optimization of hot-pressing cycle parameters.

The four factors considered as important are the soaking time and temperature, the pressure and the cooling rate. Each of these four parameters can take two extreme values during this study. To determine the influence of each factor on the mechanical properties a fractional factorial matrix constituted by eight experiments (Table 3) is used. Considering these influences four types of composites can be characterized, depending on hot-pressing factors.

At low sintering temperature and high pressure, a part of zirconia is transformed during cooling,

Table 3. Fractional factorial matrix of eight experiments for four factors (bending strength, fracture toughness and m-ZrO₂ amount are given for each experiment)

Experiment number	Cooling rate (°C/min)	Sintering temperature (°C)	Threshold time (min)	Pressure (MPa)	m-ZrO ₂ (vol.%)		Bending strength (MPa)	Fracture toughness ± 10% (MPa√m)
					After sintering	After machining		
1	10	1500	20	20	0	14	1010 ± 140	4.5
2	30	1500	20	40	6	25	830 ± 60	6.8
3	10	1700	20	40	0	0	1055 ± 150	4.2
4	30	1700	20	20	0	0	800 ± 70	4.4
5	10	1500	60	40	12	32	705 ± 90	7
6	30	1500	60	20	0	16	900 ± 60	4.7
7	10	1700	60	20	0	0	955 ± 125	4.3
8	30	1700	60	40	0	0	735 ± 70	3.9

involving a microcracking, which decreases strength and increases fracture toughness of the composite (experiments 2 and 5).

At low sintering temperature but low pressure, only stress-induced transformation is possible; so bending strength is increased but fracture toughness value is moderate (experiments 1 and 6). For the two previous composites types, both cooling rate and soaking time have no effective influence.

For high sintering temperature, no transformation of ZrO_2 occurred because of stabilization by nitrogen, so fracture toughness is low but bending strength depends on the cooling rate. At a cooling rate of $30^\circ C/min$, bending strength is low (experiments 4 and 8) while at $10^\circ C/min$ bending strength is relatively high (experiments 3 and 7). Soaking time and pressure have no significant influence.

5 Conclusions

The methodology of research has allowed the study of the reinforcement of TiC_xN_{1-x} by ZrO_2 (ZrO_2 content < 50 vol.% containing 3 mol% Y_2O_3), and the description and prediction of the mechanical properties in the whole domain studied using only thirteen compositions.

Zirconia addition to TiC_xN_{1-x} ($0 < x < 1$) improves sinterability and fracture toughness but significantly reduces hardness. Bending strength is generally increased by ZrO_2 addition, but is strongly dependent on the stability of zirconia, so the evolution of this property is not simple. For the higher sintering temperature zirconia is fully stabilized by nitrogen.

An optimization shows that a ZrO_2 starting powder of $12 m^2/g$ containing 3 mol% of yttria gives the best mechanical properties. A $TiC_{0.33}N_{0.67}$ -50 vol.% ZrO_2 ($12 m^2/g$, 3 mol% of Y_2O_3) composite can reach a fracture toughness of $7 MPa\sqrt{m}$ or a bending strength of 1000 MPa, depending on the hot-pressing cycle.

References

1. Toth, L. E., *Transition Metal Carbides and Nitrides, Refractory Materials*, Academic Press, New York, 1971.

2. Watanabe, T., Doutsu, T., Shoubu, K. & Kai, Y., Hot pressing and cutting tool performance of Ti(C, N)-based ceramics. *Mat. Sci. Forum*, **34-36** (1988) 561-5.
3. Pastor, H., Titanium carbonitride-based hard alloys for cutting tools. *Mat. Sci. Eng.*, **A105/106** (1988) 401-9.
4. Claussen, N. & Rühle, M., Design of transformation toughened ceramics; science and technology of zirconia. *Advances in Ceramics*, Vol. 3. The American Ceramic Society, Inc., Columbus, OH, 1981. pp. 137-63.
5. Gross, V., Haylock, J. & Swain, M. V., Transformation toughened titanium carbonitride zirconia composite. *Mat. Sci. Forum*, **34-36** (1988) 555-9.
6. Fargin, E., Sergent, M., Mathieu, D. & Phan-Tan-Luu, R., Approche méthodologique de la recherche expérimentale. *Bio-Sciences*, **4** (1985) 77-8.
7. Phan-TanLuu, R., Mathieu, D. & Fencuille, D., Méthodologie de la recherche expérimentale. Part of course at Laboratoire de Prospective Reactionnelle et Analyse de l'Information (LPRAI), Université d'Aix-Marseille, 1983.
8. De Mestral, F. & Thévenot, F., Optimization of mechanical properties in the ternary system TiB_2 -TiC-SiC, using optimal design. In *Proc. 12th Plansee Seminar*, Reutte, Austria, May 1989. **2**, pp. 557-75.
9. De Mestral, F. & Thévenot, F., Ceramic composites: TiB_2 -TiC-SiC Part I. Properties and microstructures in the ternary system. *J. Mat. Sci.*, **26** (1991).
10. De Mestral, F., PhD Thesis No 41 TD. Elaboration et caractérisation de céramiques composites dans le système ternaire TiB_2 -TiC-SiC; application de la méthodologie de la recherche expérimentale. Ecole Nationale Supérieure des Mines, Saint-Etienne, France, 1990.
11. Mathieu, D. & Phan-Tan-Luu, R., Programme NEMROD (new efficient methodology for research using optimal design) L.P.R.A.I., Université d'Aix-Marseille, 1988.
12. Anstis, G. R., Chantikul, P., Lawn, B. R. & Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture toughness: 1. Direct crack measurements. *J. Am. Ceram. Soc.*, **64** (1981) 533-8.
13. Barnier, P. & Thévenot, F., Synthesis and hot-pressing of single phase ZrC_xO_y and two phases ZrC_xO_y - ZrO_2 materials. *Int. J. High Tech. Ceram.*, **2** (1986) 291-307. Frittage et caractérisation mécanique de céramiques dans le système Zr-C-O. *Silic. Indus.*, **9-10** (1988) 133-42.
14. Hannink, R. H. J. & Muddle, B. C., Microstructures of zirconia/non-oxide composites. *Mat. Sci. Forum*, **34-36** (1988) 543-7.
15. Bannister, M. J. & Barnes, J. M., Solubility of TiO_2 in ZrO_2 . *J. Am. Ceram. Soc.*, **69** (1986) C269-271.
16. Claussen, N. & Jahn, J., Mechanical properties of sintered and hot-pressed Si_3N_4 - ZrO_2 composites. *J. Am. Ceram. Soc.*, **61** (1978) 94-5.
17. Cheng, Y. & Thompson, D. P., Nitrogen-containing tetragonal zirconia. Communication to the 8th Journées d'Etudes sur les Nitrures, JENI 8, Saint-Etienne, 11-12 October 1990.
18. Haylock, J., Horvath, S. & Swain, M. V., Comparative fracture toughness measurements of transformation toughened TiN- ZrO_2 composite. *Materials Forum*, **13** (1989) 101-7.