Composite Materials

AND REAL PROPERTY.

Ceramic Matrix Composites

General Properties of Ceramics

- High stiffness
- High compressive strength
- High hardness
- Wear resistance
- Brittle fracture
- Low tolerance for stress concentrations or contact stresses
- Wide scatter in mechanical properties due to porosity



Materials Selection in Mechanical Design, Fourth Edition, Michael F. Ashby, Elsevier, 2011, p.7



Ceramic materials \rightarrow brittle fracture !!!

Properties of Some Ceramic and Selected Nonceramic Materials

Material	Melting Point (°C)	Density (g/cm ³)	Hardness (Mohs) ^a	Modulus of Elasticity ^b	Coefficient of Thermal Expansion ^c
Alumina, Al ₂ O ₃	2050	3.8	9	34	8.1
Silicon carbide, SiC	2800	3.2	9	65	4.3
Zirconia, ZrO ₂	2660	5.6	8	24	6.6
Beryllia, BeO	2550	3.0	9	40	10.4
Mild steel	1370	7.9	5	17	15
Aluminum	660	2.7	3	7	24

^aThe Mohs scale is a logarithmic scale based on the relative ability of a material to scratch another softer material. Diamond, the hardest material, is assigned a value of 10.

^bA measure of the stiffness of a material when subjected to a load (MPa \times 10⁴). The larger the number, the stiffer the material.

^cIn units of ($K^{-1} \times 10^{-6}$). The larger the number, the greater the size change upon heating or cooling.



Application areas of Ceramic matrix composites

Ceramic matrix composites (CMCs) have been developed to overcome the intrinsic **brittleness** and **lack of reliability** of monolithic ceramics, with a view to introduce ceramics in structural parts used in severe environments, such as rocket and jet engines, gas turbines for power plants, heat shields for space vehicles, fusion reactor first wall, aircraft brakes, heat treatment furnaces, etc.

Further advantages include weight reductions and higher operating temperatures compared to metals and metal matrix composites

Motivation for Ceramic Matrix Composites

Strength of ceramics depends on pore size, pore volume, grain size, and intrinsic fracture toughness of the material

General approaches for improving the fracture toughness are reducing the pore size, pore volume, grain size and increasing the fracture toughness

Well dispersed reinforcements in the following forms are used to increase the toughness of the ceramic matrix:

Particles Whiskers – microfibers with exceptional mechanical properties Chopped fibres Continuous fibres - much more efficient in toughening the matrix Yarns and mats

Increase in fracture toughness up to approx. 10 MPa \cdot m^{1/2} (maximally up to approx. 20 MPa \cdot m^{1/2} in composites with continuous fibers).

Monolithic ceramics have reasonably high strength and stiffness but are brittle. Thus one of the main objectives in producing ceramic matrix composites is to increase the toughness.

There is also a concomitant rise in strength and stiffness.

The area under the stress-strain curve is the energy of fracture of the sample and is a measure of the toughness. It is clear from the figure that the reinforcement with particulates and continuous fibres has lead to an increase in toughness but that the increase is more significant for the latter.



Schematic force-displacement curves for a monolithic ceramic and CMCs illustrating the greater energy of fracture of the CMCs

M. Rosso, Ceramic and metal matrix composites: Routes and properties, Journal of Materials Processing Technology 175 (2006) 364–375

Both the monolithic and the particulate-reinforced composite fail in a catastrophic manner, which contrast with the failure of the continuous fibre composite where a substantial load carrying capacity is maintained after failure has started.

Therefore not only has the continuous fibre composite a better toughness but the failure mode is more desirable.

However, fibres are more expensive reinforcements than particles and the processing is more complex, therefore the improvement in toughness is associated with an extra cost burden.



Schematic force-displacement curves for a monolithic ceramic and CMCs illustrating the greater energy of fracture of the CMCs

The historical evolution of fibres and ceramic matrix composites, indicating some of the limits to performance or commercial development.



Series in Materials Science and Engineering, Metal and Ceramic Matrix Composites, Edited by Brian Cantor and Fionn Dunne and Ian Stone, IOP Publishing Ltd 2004, Chapter 17: Microstructure and performance limits of ceramic matrix composites, M. H. Lewis

Ceramic matrix composites may be classified into two categories:

One is a group of **toughened ceramics reinforced with particulates and whiskers**. These materials exhibit brittle behavior in spite of considerable improvements in fracture toughness and strength. The maximum in fracture toughness is around 10 MPam^{1/2} or more.

The second consists of **continuous-fiber composites** exhibiting quasi-ductile fracture behavior accompanied by extensive fiber pull out. The fracture toughness of this class of materials can be higher than 20 MPam^{1/2} when produced with weak interfaces between the fibers and matrix.

The best strengthening effect is provided by dispersed phase in form of continuous monofilament SiC fibers, which are fabricated by chemical vapor deposition (CVD) of silicon carbide on a substrate made of tungsten (W) or carbon (C) fibers.

Monofilament fibers produce stronger interfacial bonding with the matrix material improving its toughness.

Failure of long-fiber ceramic matrix composites is not catastrophic.

Typical Properties of Long-Fiber Ceramic Matrix Composites

- High mechanical strength even at high temperatures;
- High thermal shock resistance;
- High stiffness;
- High toughness;
- High thermal stability;
- Low density;
- High corrosion resistance even at high temperatures.

A variety of ceramic particulates, whiskers (high-strength single crystals with length/diameter ratios of 10 or more), and fibers may be added to the host matrix material to generate a composite with improved fracture toughness.

The presence of these reinforcements appears to disturb the propagation of cracks by at least three mechanisms:

1. When the crack tip encounters a particle or fiber that it cannot easily break or get around, it is deflected off in another direction. Thus, the crack is prevented from propagating cleanly through the structure.

2. If the bond between the reinforcement and the matrix is not too strong, crack propagation energy can be absorbed by pullout of the fiber from its original location.

3. Fibers can bridge a crack, holding the two faces together, and thus prevent further propagation.



Bridging crack growth mechanism in SiC fiberreinforced Ti-metal matrix composite illustrating fiber pull-out, fiber fracture, fiber/matrix interface debonding and matrix cracking. Fatigue crack growth test at 500°C, 10 Hz.

Tamin, M.N., Ghonem, H.: Fatigue Damage Mechanisms of Bridging Fibers in Titanium Metal Matrix Composites. J. Eng. Mater. Technol. Trans. ASME 122, 370–375 (2000)



Fatigue failure surfaces showing (a) fibre pull out and (b) wear of fibres

Series in Materials Science and Engineering, Metal and Ceramic Matrix Composites, Edited by Brian Cantor and Fionn Dunne and Ian Stone, IOP Publishing Ltd 2004, Chapter 5: Ceramic matrix composites for industrial gas turbines, Mark Hazell





Withers, P. J. & Preuss, M. Annu. Rev. Mater. Res. 42, 81–103 (2012)

The secondary phases are chosen to act as barriers to crack propagation.

Whiskers introduced into a ceramic matrix, for example, can retard the crack propagation because the stresses in a whisker spanning the crack plane will tento pull the crack shut. This phenomenon, known as "crack bridging", leads to higher fracture toughness due to the additional stress required for further propagation of the crack. Moreover, continuous fiber composites exhibit quas ductile fracture behavior resulting from extensive fiber bridging.



Fractograph showing extensive matrix cracking and fibres bridging an opened matrix in a fibre reinforced magnesium aluminosilicate ceramic .

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Toughening Due to Fiber Bridging

- Fiber debonding and pullout response
- Closing pressure
- Crack stiffening
- Stress intensity reduction
- Crack closure



http://enpub.fulton.asu.edu/cement/back_up_presentations/baltimore_asce/sld008.htm



Deformation and fracture micromechanisms in front of a notch in a cross-ply glass-fibres epoxy-matrix composite. Fibre pull-out and fibre bridging are clearly visible in the lamina with the fibres perpendicular to the crack plane, while matrix cracking and fibres kinking are dominant in the lamina with fibre parallel to the crack (F. Sket, R. Seltzer, J. M. Molina-Aldareguía).

Cements are frequenctly toughened by additton of polymer fibers due to the advantage of room temperature synthesis

Three mechanisms of fiber reinforcement appeared to be operative in macroporous CPC composites:

First, when the matrix cracked under stress, the fibers bridged the crack to resist its further opening and propagation. The aramid fibers used in this study possessed a high tensile strength and were not cut through by the cracks. Weaker fibers were less effective in this kind of reinforcement.

Second, crack deflection by the fibers caused multiple cracking in the matrix. In comparison, CPC without fibers failed by a single crack with a flat fracture surface. Multiple cracking produced numerous fractured pieces of the matrix, consuming the applied energy in creating new surfaces, thus contributing to the toughness.

Third, the frictional sliding of fibers against the matrix during pullout further consumed the applied energy and further increased the fracture resistance of the composite. The effectiveness of the fiber in this composite was dependent on fiber type, fiber volume fraction, and fiber length



H. H. K. Xu, J. B. Quinn, S. Takagi, L. C. Chow, F. C. Eichmiller, "Strong and macroporous calcium phosphate cement: Effects of porosity and fiber reinforcement on mechanical properties", J Biomed Mater Res 57: 457–466, 2001

Addition of carbon, aramid, e-glass and polyglactin fibers to calcium phosphate cements Fiber reinforcement resulted fourfold increase in strength of CPC composite and an increase of nearly two orders of magnitude in work-of-fracture. The results showed that for each fiber, the ultimate strength generally increased with volume fraction and length. The ultimate strength and work-of fracture first increased with fiber length; the ultimate strength then slightly decreased at 200 mm fiber length, while the work-of-fracture leveled off at fiber length > 25 mm.

A valid correlation for the elastic modulus of the composite, for randomly oriented short fibers:

 $E_{c} = (3/8) E_{L} + (5/8) E_{T}$ $E_{L} = E_{m} [1 + \eta_{L} V_{f} (2L/d)] / [1 - \eta_{L} V_{f}]$

 $E_{T} = E_{m} [1 + 2 \eta_{T} V_{f}] / [1 - \eta_{T} V_{f}]$



where E_L and E_T are moduli of unidirectional shortfiber composites in the longitudinal and transverse directions, E_c , E_f , and E_m are elastic moduli of composite, fiber, and matrix, respectively. V_f is fiber volume fraction, L is fiber length, and d is fiber diameter.

H. H. K. Xu, F. C. Eichmiller, A. A. Giuseppetti, "Reinforcement of a self-setting calcium phosphate cement with different fibers", J Biomed Mater Res, 52, 107–114, 2000

An empirical equation that relates the cement strength as a function of fiber strength: $S_C = S_m + \alpha S_F$

This is further refined as $S_C = S_m + \beta S_m S_F = S_m (1 + \beta S_F)$

When the fiber type, fiber length and fiber volume fraction were kept constant, the composite strength increased linearly when the matrix strength was increased and the calcium phosphate cement composite strength was, in general, 2.16 times higher than the strength of calcium phosphate cement without fibers

Xu investigated the relationship between fiber strength and composite strength and came up with the equation:

 $S_{C} = 14.1 + 0.047 S_{F}$ This equation shows that a key to increasing the cement composite strength is to develop stronger fibers.



Scanning electron microscopy images of fractured surfaces of hydroxyapatite whisker-reinforced calciumphosphate cement

If α_R for a particulate reinforcement is greater than that for the matrix α_M then the circumferential cracks may be produced in the matrix, and for $\alpha_R < \alpha_M$ radial cracks may be found.

With a fibre reinforcement, when $\alpha_R > \alpha_M$ the axial tensile stresses induced in the fibres produce an overall net residual compressive stresses in the matrix and, as the fibres contract, there is a tendency for them to pull away from the matrix.

The stress situation is reversed when $\alpha_R < \alpha_M$ and cracking of the matrix due to the axial tensile stresses may occur. Clearly there has to be some matching of the coefficients of thermal expansion in order to limit these problems.



Typical failure modes: (a) 4layer FFRP-PC, (b) 4-layer FFRP-CFRC, (c) CFRC core, (d) PC core and (e) coir fibre bridging.

ZrO₂ is used commonly as a biomaterial due to its mechanical strength, as well as its chemical and dimensional stability and elastic modulus similar to stainless steel









Crystal structure of monoclic (a), tetragonal (b) and cubic zirconia(c).

Depending on the temperature, zirconia can exist in three forms. Pure zirconia has a cubic structure at temperatures greater than 2,370° C. The cubic phase has a cubic form with square sides and moderate mechanical properties with a density of 6.27 g/cm².

The tetragonal phase exists at temperatures ranging from 1,170° C to 2,370° C. The tetragonal structure has a straight prism with rectangular sides and the most satisfactory mechanical properties with a density of 6.1 g/cm².

The monoclinic phase occurs at temperatures below 1,170° C and has a deformed parallelepipedonal (ie, a prism with six faces) shape, as well as the weakest mechanical properties with a density of 5.6 g/cm².



In terms of strength, it is essential to limit the amount of the monoclinic phase because of its lower density.

To stabilize tetragonal zirconia at room temperature and control phase transformations. metal oxides, such as yttria (Y_2O_3) or ceria (CeO_2), are added to the crystal structure. The addition of "stabilizing oxides" vields called multiphase materials partially stabilized zirconia. Technically, if yttria is added for stabilization, then it is referred to as yttria-stabilized tetragonal polycrystals (Y-TZP).



Vacancy transport in YSZ



Phase diagram of partially stabilized zirconia (PSZ): Partially stabilized zirconia (PSZ) is a mixture of zirconia polymorphs: a cubic and a metastable tetragonal ZrO₂ phase is obtained, since an insufficient amount of stabilizer has been added. PSZ is a transformation-toughened material since the induced microcracks and stress fields absorb energy.

PSZ is used for crucibles because it has a low thermal conductivity and a high melting temperature. The addition of 16 mol% CaO or 16 mol% MgO or 8 mol% Y_2O_3 (8YSZ) is enough to form fully stabilized zirconia. The structure becomes cubic solid solution, which has no phase transformation when heating from room temperature up to 2500 °C.



A unique characteristic of zirconia is its ability to stop crack growth, which is "transformation toughening".

Particles changing from tetragonal to monoclinic

Monoclinic phase particle

Tetragonal phase particle

crack

An ensuing crack generates tensile stresses that induce a change from a tetragonal configuration to a monoclinic configuration and a localized volume increase of 3% to 5%.

This volume increase results in a change of tensile stresses to compressive stresses generated around the tip of the crack. The compressive forces counter the external tensile forces and stop the further advancement of the crack. This characteristic accounts for the material's low susceptibility to stress fatigue and high flexural strength of 900 MPa to 1,200 MPa.



The ZrO_2 addition to Al_2O_3 increases its toughness via the tetragonal to monoclinic ZrO_2 transformation, so called transformation toughening and microcracking. The bright zirconia can be inter- or intra-granular. Oxide powder mixtures are hot pressed or pressureless sintered at <1600°C.

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There is a wide spectrum of CMCs depending on the chemical composition of the matrix and reinforcement. **Non-oxide CMCs are those which have been the most studied**.

Such a choice could appear surprising since the atmosphere in service is often oxidizing. That choice could be explained as follows. The **most performant fibres**, in terms of stiffness, failure strength, refractoriness and density **are non-oxide fibres**, i.e. carbon and silicon carbide fibres. Further, carbon fibres are extensively used in volume production of polymer-matrix composites. As a result, they are much cheaper than all the other fibres (except glass fibres).

Second, **in order to avoid compatibility problems**, which are crucial at high temperatures, non-oxide fibres are preferably embedded in non-oxide matrices. Hence, the first non-oxide CMCs have been carbon/carbon (C/C) composites. They have been initially designed and produced for use in rocket engines and re-entry heat shields, i.e. under extremely severe service conditions but short lifetimes. In a second step, C/SiC and SiC/SiC composites were developed in order to increase the oxidation resistance of the materials and hence their lifetimes in oxidizing atmospheres. Silicon nitride was also used as matrix although it is less stable at high temperatures than silicon carbide.

Oxide-CMCs would obviously be the best choice, from a thermodynamic standpoint, for long term applications in oxidizing atmospheres.

Unfortunately, oxide fibres, although they are refractory, **tend to undergo grain growth** at high temperatures, (which results in a fibre strength degradation) and exhibit a poor creep resistance.

Further, they display **much higher densities** than for example carbon fibres (4 g/cm³ for alumina versus 2 g/cm³ for carbon).

Attempts have been made to improve the high temperature properties of oxide fibres with limited success. Despite these disadvantages, AI_2O_3/AI_2O_3 and derived CMCs have been, and are still, extensively studied.

Effect of SiC-reinforcement fibers on the properties of selected ceramic materials						
Material	Flexural Strength (psi)	Fracture Toughness (psi $\sqrt{in.}$)				
Al ₂ O ₃	80,000	5,000				
Al ₂ O ₃ /SiC	115,000	8,000				
SiC	72,000	4,000				
SiC/SiC	110,000	23,000				
ZrO ₂	30,000	5,000				
ZrO ₂ /SiC	65,000	20,200				
Si ₃ N ₄	68,000	4,000				
Si ₃ N ₄ /SiC	115,000	51,000				
Glass	9,000	1,000				
Glass/SiC	120,000	17,000				
Glass ceramic	30,000	2,000				
Glass ceramic/SiC	120,000	16,000				

Types of ceramic-matrix composites

- Al₂O₃-ZrO₂ composites
- SiC particulate / Si₃N₄ matrix composites
- SiC whisker / Al₂O₃ matrix composites
- SiC whisker / Si₃N₄ matrix composites
- Continuous fiber / glass matrix composites
- Carbon / carbon composites
- SiC / SiC composites
- Oxide / oxide composites.

Properties of selected reinforcing materials*								
Material	Density (g/cm ³)	Tensile Strength (ksi)	Modulus of Elasticity (×10 ⁶ psi)	Melting Temperature (°C)	Specific Modulus (×10 ⁷ in.)	Specific Strength (×10 ⁶ in.		
Polymers:								
Kevlar TM	1.44	650	18.0	500	34.7	12.5		
Nylon	1.14	12	0.5	249	1.0	2.9		
Polyethylene	0.97	3-7	0.04-0.1	147	7.1	13.7		
Metals:								
Be composites	1.83	40-50	44.0	1277	77.5	2.8		
Boron	2.36	500	55.0	2030	64.7	4.7		
W	19.40	580	59.0	3410	8.5	0.8		
Glass:								
E-glass	2.55	500	10.5	<1725	11.4	5.6		
S-glass	2.50	650	12.6	<1725	14.0	7.2		
Carbon:								
HS (high strength)	1.75	820	40.0	3700	63.5	13.0		
HM (high modulus)	1.90	270	77.0	3700	112.0	3.9		
Ceramics:								
Al ₂ O ₃	3.95	300	55.0	2015	38.8	2.1		
B ₄ C	2.36	330	70.0	2450	82.4	3.9		
SiC	3.00	570	70.0	2700	47.3	5.3		
ZrO ₂	4.84	300	50.0	2677	28.6	1.7		
Whiskers:								
Al ₂ O ₃	3.96	3000	62.0	1982	43.4	21.0		
Cr	7.20	1290	35.0	1890	13.4	4.9		
Graphite	1.66	3000	102.0	3700	170.0	50.2		
SiC	3.18	3000	70.0	2700	60.8	26.2		
Si ₃ N ₄	3.18	2000	55.0		47.8	17.5		

 $1\frac{gm}{cm^3} = 0.0361\frac{lb}{ln^3}$

Oxide Matrices

	Comparative typical property guide for oxide matrices.								
Matrix	Crystal structure	Melting point in pure form, (°C)	Onset of reduction in reducing atmospheres, (°C)	Theoretical density, (Mg m ⁻³)	Elastic modulus, (GPa)	Typical flexural strength, (MPa)	Thermal expansion coefficient, 10 ⁻⁶ K ⁻¹ (25 1000 °C)	Thermal conductivity, W m ⁻¹ K ⁻¹ (25 °C)	Electrical conduction ^c
Alumina, Al ₂ O ₃	Hexagonal	2060	1400	3.986	400	300	8	≈38	Insulator
Y TZP ^a	Tetragonal	2300	400 (darkens)	6.10	210	800	10	≈1.5	Insulator/oxygen ion conductor
PSZ ^b	Cubic/ tetragonal	2300	400 (darkens)	6.05	200	500	10	≈1.5	Insulator/oxygen ion conductor
Mullite, 3Al ₂ O ₃ ,2SiO ₂	Orthorhombic	1934	1000 (darkens)	3.1	300	250	5	≈ 10	Insulator
Yttrium aluminum garnet (YAG)	Cubic	2000	1400		280	250	8	≈15	Insulator
Spinel, MgO.Al ₂ O ₃	Cubic	2135	1400	3.59	280	250	8	≈15	Insulator
Na beta alumina	Hexagonal			≈3.5	320	300	8		Sodium ion conductor

^a TZP tetragonal zirconia polycrystals, containing a high proportion of metastable tetragonal ZrO_2 , see Section 4.01.5.5. ^b PSZ partially stabilized zirconia, with insufficient stabilizer to form an all-cubic phase material, see Section 5.5. ^c Given in general descriptive terms; actual values are usually strong functions of composition, phase distribution, and temperature. Most oxides are electronic insulators. Those indicated become ionically conducting at raised temperature, typically above 300 400 °C.

Oxide Matrices

Oxide matrices and typical useful reinforcements.						
Matrix	Particulates	Platelets	Whiskers	Fibers		
Alumina, Al ₂ O ₃	ZrO_2 , SiC, TiC, TiN, TiB ₂ , ZrB_2 , metals	SiC	SiC, B ₄ C	SiC, Al ₂ O ₃ , 3Al ₂ O ₃ .2SiO ₂		
Y TZP ^a	Al_2O_3	Al_2O_3	Al_2O_3	2 5 2		
PSZ ^b	$Al_2 O_3$	SiC				
Mullite,	Al_2O_3 , ZrO_2	Al_2O_3	SiC	SiC, Al_2O_3		
$3Al_2O_3.2SiO_2$						
Yttrium aluminum garnet (YAG)			Al_2O_3	Al_2O_3		
Spinel, MgO.Al ₂ O ₃	$Al_2 O_3$					
Na beta alumina	ZrO_2					

Non-oxide Matrices

			Comparative	typical pro	perty gui	de for nonoxide	matrices.		
Matrix	Crystal structure	Melting point in pure form (°C)	Onset of active oxidation (°C)	Theoretical density (Mg m ⁻³)	Elastic modulus (GPa)	Typical flexural strength (MPa)	Thermal expansion coefficient, 10 ⁻⁶ K ⁻¹ (25 1000°C)	<i>Thermal</i> <i>conductivity</i> Wm ⁻¹ K ⁻¹ (25 °C)	Electrical conduction ^a
SiC	α: hexagonal β: cubic	> 2200 (sublimes)	900 ^b	3.19	440	300	4	30	Insulator
Si ₃ N ₄	α , β : hexagonal	≈ 1750 (sublimes)	900 ^b	3.20	320	300 800	3	100	Insulator/ semiconductor
MoSi ₂	tetragonal	2030	1000^{b}	6.25		380	8	60	Conductor
B ₄ C	rhombohedral	2420	800	2.52	450	350	5	30	Insulator
BN	hexagonal	> 2500 (sublimes)	800	2.27	40 60	40 60	7	20	Insulator
CVD // deposition							25	150	
CVD ⊥ deposition					150	150	0.4	2	
AlN	hexagonal (wurtzite)	> 2000 (decomposes)	900°	3.26	350	400	5.6	> 150	Insulator
TiB ₂	hexagonal	2870	700	4.50	500	600	6		Conductor
TiN	cubic	2950 (sublimes in vacuum at > 1450)	700	5.44	450		8		Conductor
TiC	cubic	3065	700	4.92	460	800	8	30	Conductor

^a Given in general descriptive terms; actual values are usually strong functions of composition, phase distribution, and temperature. ^b Forms a passivating silica layer. ^c Forms a passivating alumina layer.

Comprehensive Composite Materials, Volume 4: Carbon/Carbon, Cement, and Ceramic Matrix Composites, 4.01 Matrix Materials, R. MORRELL

Non-oxide Matrices

Matrix	Particulates	Platelets	Whiskers	Fibers
SiC		SiC	$B_4 C$	C, SiC
Si_3N_4	SiC, TiC, TiN, TiB ₂	Si_3N_4	Si ₃ N ₄	SiC, Al_2O_3 , C
MoSi ₂	ZrO_2 , TiB_2 , Nb, SiC , Si_3N_4	Al_2O_3	SiC	SiC, Al_2O_3
B ₄ C	TiB_2 , Al_2O_3	SiC	SiC	C, SiC
BN (hexagonal) AlN	B_4C		SiC	
TiB ₂	B_4C, BN			
TiN ¹ TiC ¹				