

## Valence-electron structure and properties of main phases in Ti(C, N)-based cermets

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### Abstract

Based on the empirical electron theory (EET) of solids and molecules, the valence-electron structures (VESs) of the main phases in Ti(C, N)-based cermets were calculated, and the relationship between the VES and properties was determined. The results indicated that the hardness of the phases with the same crystal structure could be compared using the covalent electron pairs,  $n_a$ , values on the strongest bonds and the plasticity by the sum of  $n_a$  values for the covalent bonds. The dissolution of N in TiC phase could improve the plasticity of TiC phase, and Mo, W and V dissolution could reduce its plasticity. However, Cr dissolution in the rim phase improved the plasticity of the rim phase, which should be advantageous for strengthening Ti(C, N)-based cermets. Based on those results, a Ti(C, N)-based cermet added with Cr<sub>3</sub>C<sub>2</sub> was manufactured; the new cermet had more than twice the transverse rupture strength of a typical cermet.

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**Keywords:** Ti(C, N)-based cermets; Valence-electron structure; Properties

### 1. Introduction

Ti(C, N)-based cermets originated in 1970s. After over 30 years of study, these cermets have been applied in Japan and in Sweden as cutting tools. At present, Ti(C, N)-based cermets are attracting much attention from researchers in other countries because of their excellent wear-resistance, high heat-hardness, perfect chemical stability, very low friction coefficient to metals, superior thermal deformation resistance [1–3]. It has shown great potential as a substitute for the commonly used WC–Co hardmetals.

The microstructure of Ti(C, N)-based cermets is characterized by carbonitrides, exhibiting a core/rim structure, bonded with a metallic phase. Mo, W, Cr and V always exist richly in the rim phase [4]. The characteristics of these phases have great influence on the properties of cermets. In this paper, the relationship between the valence-electron structure (VES) and properties of the main phases was studied.

### 2. Crystalline structure

The results of selected electron diffraction showed that the crystal structure of the solid solutions formed by the

dissolution of nitrogen and other alloying elements into TiC was the same as that of TiC [5].

TiC has a B1-NaCl structure, and belongs to a face-centered-cubic (f.c.c.) lattice. The cell structure and bonding complex are shown in Fig. 1. The international symbol of TiC is Fm3m (no. 225) [6]. The atomic coordinates in the unit cell are as follows:

$$\begin{aligned} \text{Ti (4am3m)} &: (0, 0, 0), (0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0), \\ \text{C (4bm3m)} &: (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, 0), (0, \frac{1}{2}, 0), (0, 0, \frac{1}{2}) \end{aligned}$$

The experimental covalent bond length,  $D(n_a)$ , and identity bond numbers,  $I_a$ , of the TiC unit cell are shown in Table 1. The identity bond numbers were determined using the formula in Ref. [7].

### 3. Calculation of the VES

The crystal structure of Ti(C, N) and the rim phase formed by the dissolution of Mo, Cr to Ti(C, N) are the same as that of TiC [5]. Moreover, some of the C atoms in the TiC were substituted by N atoms, and some of the Ti atoms by other metal atoms. Thus, it is reasonable to consider that C and N atoms have randomly occupied the stations of the C atoms, and Ti and other metal atoms have also randomly occupied that of the Ti atoms. The distribution should be statistical.

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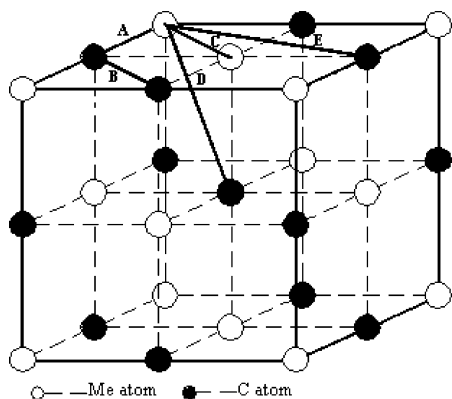


Fig. 1. The unit cell structure of TiC.

Table 1

The experimental covalent bond lengths and identity bond numbers of the TiC unit cell

Bond	$D(n_a)$ (Å)	$I_a$
C–Ti (A)	$D(n_A) = \frac{1}{2}a = 2.1200$	12
C–C (B)	$D(n_B) = \frac{1}{2}\sqrt{2}a = 2.9981$	12
Ti–Ti (C)	$D(n_C) = \frac{1}{2}\sqrt{2}a = 2.9981$	12
Ti–C (D)	$D(n_D) = \frac{1}{2}\sqrt{3}a = 3.6719$	16
Ti–C (E)	$D(n_E) = \frac{1}{2}\sqrt{5}a = 4.7405$	48

The single-bond semilengths,  $R^S(I)$ , and the total covalence-electron pairs,  $n_c^S(I)$ , of the solid solutions can be calculated according to the average atom theory [8]. The equations for calculating  $R^S(I)$  and  $n_c^S(I)$  are as follows [8]:

$$R^S(I) = R^A(I)x + R^B(I)(1-x) \quad (1)$$

$$n_c^S(I) = n_c^A x + n_c^B(1-x) \quad (2)$$

Here,  $R^S(I)$ ,  $R^A(I)$ , and  $R^B(I)$  represent the single-bond semilengths of the solid solution, the solute, and the solvent, respectively;  $x$  denotes the content of A atoms; and  $n_c^S(I)$ ,  $n_c^A(I)$ , and  $n_c^B(I)$  denote the total number of covalent electron pairs in the solid solution, the solute, and the solvent, respectively.

Then, the individual theoretical bond distance,  $\bar{D}(n_a)$ , of each bond in various phases can be determined by the empirical electron theory (EET) of solids and molecules formulated by Yu [7], which is the further development of L. Pauling's chemical bond theory. Yu's theory mainly includes the bond length difference (BLD) method, which

makes it possible to calculate the crystal VES [7]. The basic thought of the BLD method is described as follows [7]: the equation for calculating the bond distance,  $D(n_a)$ , is

$$D(n_a) = R^u(I) + R^v(I) - 0.6 \log n_a \quad (3)$$

Here  $a$  represents a different bond, with  $n_a$  the covalent electron pairs in the bond between the  $u$  and  $v$  atoms, and  $a = A, B, C, D, \dots, N$ , where  $N$  is the number of bonds calculated in a unit structure;  $R(I)$  the single-bond semilength of an atom. We can obtain the  $(N-1)$  BLD equations if  $D(n_A)$  corresponding to the shortest bond distance is used for the subtraction of  $D(n_\alpha)$  ( $\alpha = B, C, D, \dots, N$ ). In addition, the sum of the covalent electron number derived from all the covalent bonds in the unit cell (designated as  $n_A \sum_{\alpha=A}^N I_\alpha \gamma_\alpha$ ) is equal to the total covalent electron number out of all atoms in the unit cell (designated as  $\sum n_C$ ), so an equation for  $n_A$  can be established, which is expressed as

$$n_A = \frac{\sum n_C}{\sum_{\alpha=A}^N I_\alpha \gamma_\alpha} \quad (4)$$

where the values of  $\gamma_\alpha$  reflect the relative values of  $n_B, n_C, \dots, n_N$  with respect to  $n_A$  in each bond B, C,  $\dots$ , and N, respectively.

From these equations,  $N$  different theoretical bond lengths  $\bar{D}(n_a)$  ( $a = A, B, \dots, N$ ) can be calculated through selecting hybrid states of the various kinds of atoms.

#### 4. Results

While performing calculation for a known structure, the data in the hybridization list of atoms can be scanned using a computer so as to find all resolutions. The more detail calculative process may be found in Ref. [7]. When  $\Delta D(n_a) = |\bar{D}(n_a) - D(n_a)| \leq 0.05 \text{ \AA}$ , it is thought that the theoretical bond length is consistent with the experimental covalent bond length [7], and the resolution can be considered as the actual state of selected hybrid step coincidence atoms in the cell. After analysis and comparison with the calculated results, the hybrid steps of all atoms of various phases were determined. Ti, C, N, Mo W, V and Cr occurred separately in B11, 6, 1, B6, 2 A14 and 7. The VES of  $\text{Ti}(\text{C}_{0.8}, \text{N}_{0.2})$ ,  $(\text{Ti}_{0.9}, \text{Mo}_{0.1})(\text{C}_{0.8}, \text{N}_{0.2})$ ,  $(\text{Ti}_{0.8}, \text{Mo}_{0.1}, \text{W}_{0.1})(\text{C}_{0.8}, \text{N}_{0.2})$   $(\text{Ti}_{0.7}, \text{Mo}_{0.1}, \text{W}_{0.1}, \text{V}_{0.1})(\text{C}_{0.8}, \text{N}_{0.2})$  and  $(\text{Ti}_{0.7}, \text{Mo}_{0.1}, \text{W}_{0.1},$

Table 2

VES of the solid solution  $\text{Ti}(\text{C}_{0.8}, \text{N}_{0.2})$  unit cell

Bond	Atoms to form bond	$I_a$	$n_a$	$\bar{D}(n_a)$ (Å)	$D(n_a)$ (Å)	$\Delta D$ (Å)
A	C(N)–Ti	12	0.51998	2.10011	2.1200	0.01989
B	C(N)–C(N)	12	0.00354	2.97821	2.9981	0.01989
C	Ti–Ti	12	0.09043	2.97821	2.9981	0.01989
D	Ti–C(N)	16	0.00135	3.65201	3.6719	0.01989
E	Ti–C(N)	48	$2.231 \times 10^{-5}$	4.72061	4.7405	0.01989

Table 3  
VES of the solid solution (Ti<sub>0.9</sub>, Mo<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>) unit cell

Bond	Atoms to form bond	$I_a$	$n_a$	$\bar{D}(n_a)$ (Å)	$D(n_a)$ (Å)	$\Delta D$ (Å)
A	C(N)–Ti(Mo)	12	0.52049	2.10813	2.1200	0.01187
B	C(N)–C(N)	12	0.00343	2.98623	2.9981	0.01187
C	Ti(Mo)–Ti(Mo)	12	0.09344	2.98623	2.9981	0.01187
D	Ti(Mo)–C(N)	16	0.00135	3.65003	3.6719	0.01187
E	Ti(Mo)–C(N)	48	$2.233 \times 10^{-5}$	4.72863	4.7405	0.01187

Table 4  
VES of the solid solution (Ti<sub>0.8</sub>, Mo<sub>0.1</sub>, W<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>) unit cell

Bond	Atoms to form bond	$I_a$	$n_a$	$\bar{D}(n_a)$ (Å)	$D(n_a)$ (Å)	$\Delta D$ (Å)
A	C(N)–Ti(Mo, W)	12	0.51901	2.12347	2.1200	0.00347
B	C(N)–C(N)	12	0.00323	3.00157	2.9981	0.00347
C	Ti(Mo, W)–Ti(Mo, W)	12	0.09854	3.00157	2.9981	0.00347
D	Ti(Mo, W)–C(N)	16	0.00134	3.67537	3.6719	0.00347
E	Ti(Mo, W)–C(N)	48	$2.227 \times 10^{-5}$	4.74397	4.7405	0.00347

Table 5  
VES of the solid solution (Ti<sub>0.7</sub>, Mo<sub>0.1</sub>, W<sub>0.1</sub>, V<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>) unit cell

Bond	Atoms to form bond	$I_a$	$n_a$	$\bar{D}(n_a)$ (Å)	$D(n_a)$ (Å)	$\Delta D$ (Å)
A	C(N)–Ti(Mo, W, V)	12	0.52761	2.12078	2.1200	0.00078
B	C(N)–C(N)	12	0.00327	2.99888	2.9981	0.00078
C	Ti(Mo, W, V)–Ti(Mo, W, V)	12	0.10079	2.99888	2.9981	0.00078
D	Ti(Mo, W, V)–C(N)	16	0.00137	3.67268	3.6719	0.00078
E	Ti(Mo, W, V)–C(N)	48	$2.263 \times 10^{-5}$	4.74128	4.7405	0.00078

Table 6  
VES of the solid solution (Ti<sub>0.7</sub>, Mo<sub>0.1</sub>, W<sub>0.1</sub>, Cr<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>) unit cell

Bond	Atoms to form bond	$I_a$	$n_a$	$\bar{D}(n_a)$ (Å)	$D(n_a)$ (Å)	$\Delta D$ (Å)
A	C(N)–Ti(Mo, W, Cr)	12	0.50294	2.12662	2.1200	0.00662
B	C(N)–C(N)	12	0.00319	3.00472	2.9981	0.00662
C	Ti(Mo, W, Cr)–Ti(Mo, W, Cr)	12	0.09366	3.00472	2.9981	0.00662
D	Ti(Mo, W, Cr)–C(N)	16	0.00130	3.67852	3.6719	0.00662
E	Ti(Mo, W, Cr)–C(N)	48	$2.158 \times 10^{-5}$	4.74712	4.7405	0.00662

Cr<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>) then were established and summarized in Tables 2–6, respectively.

## 5. Discussion

### 5.1. Relationship between the VES and hardness

A crystal with high hardness means that the crystal is not easy to deform under loading. In the view of crystallography, it is deduced that the bonds forming between the atoms in the same plane or different planes are not easy to debond. The more the covalent electron pairs are, the stronger the ability of the crystal to resist deformation is. So the product of the number of the strongest bond and that of covalent electron pairs on this bond can be the criterion to compare the hardness.

As for the (Ti, M)(C, N) solid solutions with the same structure and various compositions, the numbers of the strongest bonds are the same in respective unit cells, so the number of covalent electron pairs on the strongest bond can reflect the hardness. This deduction has been verified by a series of experiments. For example, both of TiC and TiN belong to NaCl structure, and (Ti, W)C formed by a small amount of WC dissolution in TiC is also [9]. The numbers of covalent electron pairs on the strongest bond formed between Ti atom and the other nearest atoms are listed as follows [10]:  $n_A^{\text{TiC}} = 0.5367$ ,  $n_A^{\text{TiN}} = 0.4358$ , and  $n_A^{(\text{Ti,W})\text{C}} = 0.53486$ . It can be determined from the EET of solid and molecules that the hardness is TiC > (Ti, W)C > TiN. The tested hardness of TiC, (Ti, W)C and TiN were HV30000 [11], HV2100–2900 [12] and HV2000 [13], respectively, which is consistent with the above deduction.

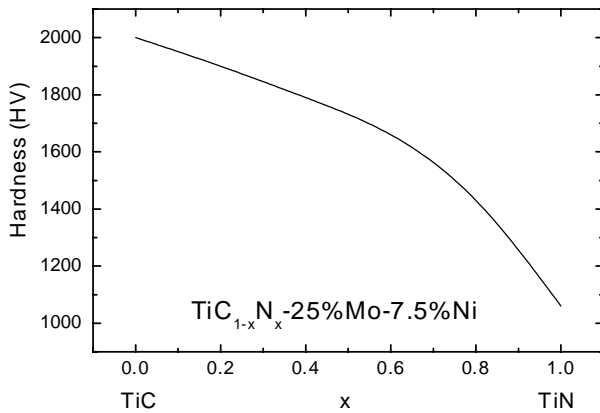


Fig. 2. Hardness vs. amount of nitrogen of Ti(C, N) cermets.

In the case of the solid solutions, TiC, Ti(C<sub>0.8</sub>, N<sub>0.2</sub>), (Ti<sub>0.9</sub>, Mo<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>), (Ti<sub>0.8</sub>, Mo<sub>0.1</sub>, W<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>), (Ti<sub>0.7</sub>, Mo<sub>0.1</sub>, W<sub>0.1</sub>, V<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>), (Ti<sub>0.7</sub>, Mo<sub>0.1</sub>, W<sub>0.1</sub>, Cr<sub>0.1</sub>)(C<sub>0.8</sub>, N<sub>0.2</sub>), concerned in this paper, the numbers of covalent electron pairs on the strongest bonds of each solid solution are 0.53670, 0.51998, 0.52049, 0.51901, 0.52761 and 0.50294, respectively. It is concluded that the formation of Ti(C, N) in TiC cermets by the dissolution of N into TiC may reduce the hardness of the cermets, which was verified by the experimental results shown in Fig. 2 [14]. It can also be concluded that the hardness of the rim phase (Ti, Mo)(C, N) enriched in Mo is higher than that of Ti(C, N) core, and the dissolution of W in (Ti, Mo)(C, N) reduces the hardness of the rim phase. In addition, the dissolution of V in the rim phase may increase the hardness of the rim phase further. However, the dissolution of Cr may reduce the hardness of the rim phases, because the numbers of covalent electron pairs on the strongest bonds of the rim phase (Ti, Mo, W)(C, N) is reduced.

### 5.2. Relationship between the VES and plasticity

(Ti, M)(C, N) solid solutions belong to B1-NaCl structure, the closed-packed plane of which is {1 1 1}, and the closed-packed orientation of which is <1 1 0>. If slid occurs, it is necessary to overcome the coalescence of the bonding complex listed below (see Fig. 1): C(N)–Ti(M) ( $D(n_a) = a/2$ ), Ti(M)–Ti(M) ( $D(n_a) = \sqrt{2}a/2$ ), C(N)–Ti(M) ( $D(n_a) = \sqrt{3}a/2$ ), C(N)–Ti(M) ( $D(n_a) = \sqrt{5}a/2$ ). The values of  $n_a$  for the above bonding complex are  $n_A$ ,  $n_C$ ,  $n_D$ ,  $n_E$ , respectively. In a cell,  $n_a$  reflects the bond strength, which is the resistance of the atoms to sliding. If the resistance of the atom planes in (Ti, M)(C, N) solid solution to shear along {1 1 1} is expressed as  $\sum n_a^{(Ti,M)(C,N)} = n_A + n_C + n_D + n_E$ , the resistance of the atom planes in TiC, TiN, (Ti, M)(C, N), all of which belong to B1-NaCl structure, to shear along {1 1 1}, can be expressed as  $\sum n_a^{TiC}$ ,  $n_a^{TiN}$  and  $\sum n_a^{(Ti,M)(C,N)}$ , respectively. It was calculated that  $\sum n_a^{TiC} = 0.6282$  [9] and  $\sum n_a^{TiN} = 0.5460$  [15]. In addition, from Tables 2–6, it was determined that the

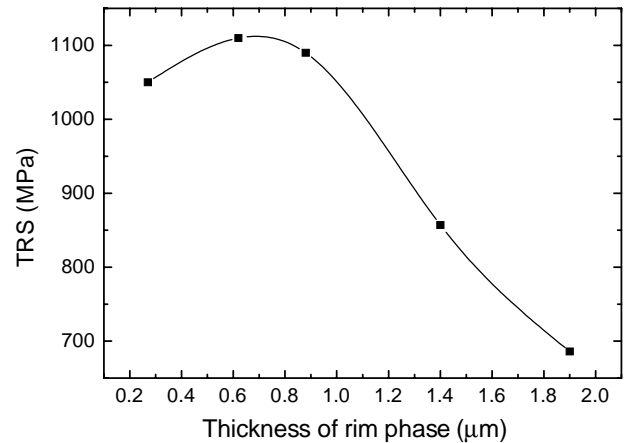


Fig. 3. TRS vs. thickness of rim phase of cermets.

values of  $\sum n_a^{Ti(C_{0.8},N_{0.2})} = 0.61178$ ,  $\sum n_a^{(Ti_{0.9},Mo_{0.1})(C_{0.8},N_{0.2})} = 0.61530$ ,  $\sum n_a^{(Ti_{0.8},Mo_{0.1},W_{0.1})(C_{0.8},N_{0.2})} = 0.61892$ ,  $\sum n_a^{(Ti_{0.7},Mo_{0.1},W_{0.1},V_{0.1})(C_{0.8},N_{0.2})} = 0.62979$  and  $\sum n_a^{(Ti_{0.7},Mo_{0.1},W_{0.1},Cr_{0.1})(C_{0.8},N_{0.2})} = 0.59792$ . Clearly, the shear along {1 1 1} was easier to achieve in Ti(C, N) than in TiC, which explained why the dissolution of TiN in TiC can improve the plasticity of TiC. The dissolution of Mo, W, especially V in Ti(C, N) reduced the plasticity of Ti(C, N), which should reduce the strength of Ti(C, N)-based cermets. However, the dissolution of Cr in the rim phase, (Ti, Mo)(C, N), improved the plasticity of the rim phase, which should be advantageous to strengthening Ti(C, N)-based cermets because the plastic rim phase is able to deform in concert with the metal binder phase.

The influence of the thickness of the rim phase enriched in Mo and W on the strength of Ti(C, N)-based cermets were studied, and the results were summarized in Fig. 3 [16]. The rim phase with adequate thickness was necessary to ensure good wettability between hard cores and the binder, so it improved the strength of the cermet. However, too thick rim phase reduced the strength of the cermet, which was consistent with the results calculated by the EET of solid and molecules.

## 6. Experimental and results

### 6.1. Experimental

The compositions of the three cermets in the present study are given in Table 7. A small amount of VC and Cr<sub>3</sub>C<sub>2</sub> were added in cermets B and C, respectively. These powders were dispersed homogeneously and mixed in a planetary ball-mill for 12 h at a speed of 150 rpm (rotations per minute). The slurry was dried and pressed into the shapes of test specimens for the transverse rupture strength (TRS) of ceramics. The green compacts were sintered at 1683 K in vacuum for 1 h. The vacuum was controlled at 10<sup>-2</sup> to

Table 7  
Nominal compositions of the three materials (wt.%)

Cermet	TiC	TiN	Ni	Mo	WC	C	Cr <sub>3</sub> C <sub>2</sub>	VC
A	33	10	32	16	7.5	1.5	0	0
B	33	10	32	16	6.9	1.5	0	0.6
C	33	10	32	16	6.9	1.5	0.6	0

Table 8  
Mechanical properties of the three cermets

Cermet	Addition	TRS (MPa)	Hardness (HRA)
A	0	860.9	89.8
B	0.6 wt.% VC	947.5	89.0
C	0.6 wt.% Cr <sub>3</sub> C <sub>2</sub>	1831.6	90.2

1 Pa during liquid sintering. The hardness and TRS at 298 K were measured. The distribution of the elements was determined by an Oxford Inca energy dispersive X-ray analysis (EDAX) in combination with JEM-2000FX II transmission electron microscopy (TEM).

## 6.2. Results

The distributions of V and Cr were determined. The content of V in the rim phase in cermet B was within 1.78–2.56 wt.% and that of Cr in cermet C within 1.16–1.98 wt.%. Most of the V and Cr resided richly in the rim phases.

The TRS and hardness at 298 K are given in Table 8. Although the microstructures of the three cermets were nearly the same [5], the addition of a small amount of Cr<sub>3</sub>C<sub>2</sub> improved the TRS greatly, which reflects that Cr<sub>3</sub>C<sub>2</sub> improved the plasticity of the rim phase and its ability to deform in concert with the metal phase. The slight improvement of the TRS of cermet B is due to fining of the grains.

## 7. Conclusions

- (1) Based on the principles of crystal science and the EET of solids and molecules, the VESs of the main phases in Ti(C, N)-based cermets were calculated. It was determined that the hardness for the phase with the same crystal structure could be compared using the covalent electron pairs  $n_a$  on the strongest bonds.
- (2) When being loaded, the relative resistance of the atoms to sliding along the closed-packed planes and the plasticity of the materials with the same crystal structure, could be compared using the sum of the  $n_a$  values for the covalent bonds.
- (3) The dissolution of TiN in TiC improved the plasticity of TiC. The dissolution of Mo, W, especially V, in

Ti(C, N) reduced the plasticity of Ti(C, N). The dissolution of Cr in the rim phase, (Ti, Mo)(C, N), improved the plasticity of the rim phase. A Ti(C, N)-based cermet manufactured with added Cr<sub>3</sub>C<sub>2</sub>, had more than two times the TRS of a typical cermet.

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