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# Elastic constants of Al and TiN calculated by *ab initio* method<sup>①</sup>

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**[Abstract]** The elastic constants of Al single crystal were calculated by *ab initio* method for calibration. Three deformation directions were selected in order to obtain the different constants of  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ . The cohesion energy curves of the three deformation directions were calculated. The results of the second order partial differential at the equilibrium point of the cohesion energy curve provide the elastic constants of the Al single crystal. The changes of crystal symmetry and lattice can lead to the deviations of the calculated cohesion energy curves and the accurate elastic constants can not be obtained, but when the correction is taken into calculation, the calculated results are very close to the literature data. It is very difficult to obtain the elastic constants of thin films by experiment and the data from the handbook are scattered in a large scale. However, the elastic constants calculated by this method can be served as a standard. Though the errors of TiN elastic constants calculated by this method are a little higher than that for Al, the results are acceptable.

**[Key words]** Al; TiN; elastic constant; *ab initio* method

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## 1 INTRODUCTION

The residual stress of the thin film is usually measured by X-ray diffraction, by which only the lattice strain is obtained and the elastic constants are required to calculate the stress value. So elastic constant is a key parameter for calculating internal stress by XRD method. The elastic constants of a thin film may be obtained by different means. If the film is of the same composition as the bulk material, the elastic constants can be found from the handbook. If no bulk material is available, the elastic constant should be determined by experiment. However, the values from different sources deviate greatly, it may result from different techniques of the measurement. For example, for well known thin film TiN, its value of elastic modulus was widely accepted as 250 GPa<sup>[1,2]</sup> in Japan, but in Europe the value was 640 GPa<sup>[3]</sup>. In other words, with the same X-ray measurement method, the reported values of residual stress may differ more than two times.

If the elastic constant of a film has to be measured, many factors such as composition, microstructure, defects, texture etc could affect its value. Thus the theoretical calculation is important for calibrating the experimental value. However, yet very little study can be found in literature.

In this paper, the elastic constants of pure Al was first calculated and its result was examined with the data in the handbook, then the TiN film was se-

lected for calculation. If the result also agrees well with that of the experimental results widely accepted in literature, we can make further approach to the other kinds of thin films.

In this study, the calculated elastic constants of the polycrystalline aggregate are checked with the experimental data.

## 2 PRINCIPLE OF CALCULATION

The elastic constants of Al and TiN crystals are calculated by *ab initio* method. Because their lattice is cubic, three deformation directions are selected in order to obtain the different constants of  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ . The three deformations are first expanding or shrinking along the three axes simultaneously; second, stretching or compressing along axis  $a$  only; and third shearing parallel to the  $XOY$  plane. The cohesion energy curves in the three deformation directions are also calculated and the effects of the Position's ratio and the lattice distortion must be taken into consideration in order to obtain the lowest cohesion energy curves. The results of the second order partial differential at the equilibrium point of the cohesion energy curve lead to the elastic constants of the Al and TiN crystals<sup>[4]</sup>.

The cohesion energy curves are calculated by means of the CASTEP (Cambridge Serial Total Energy Package) software<sup>[5]</sup>, which can calculate the total energy of the different lattice parameters using the

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regular conservation method and the LDA (Local Density Approximation) method.

According to the Hooke's law and the nature of the cubic crystal,

$$\left. \begin{aligned} K &= (c_{11} + 2c_{12})/3 \\ \sigma_{11} &= c_{11} \cdot \varepsilon_{11} \\ \sigma_{12} &= c_{44} \cdot 2\varepsilon_{12} \end{aligned} \right\} \quad (1)$$

At first, the crystal cell is expanded along three coordinates simultaneously.  $u$  and  $v$  represent the potential energy and the dimension of the primitive cell. If the dimension of cell has increased  $\Delta v$ , let the function of potential energy expand at the equilibrium point by Talar series, the pressure  $p$  reads

$$p = - \frac{\partial u}{\partial v} = - \left( \frac{\partial u}{\partial v} \right)_{v_0} - \left( \frac{\partial^2 u}{\partial v^2} \right)_{v_0} \cdot \Delta v - \dots \quad (2)$$

At the equilibrium point, the first item equals to zero. When the change of the dimension is very small, the items higher than the second order can be neglected. So Eqn. (2) is

$$p = - \left( \frac{\partial^2 u}{\partial v^2} \right)_{v_0} \cdot v_0 \cdot \frac{\Delta v}{v_0} \quad (3)$$

According to the definition of the body modulus  $K$ ,

$$p = K \cdot \frac{\Delta v}{v_0} \quad (4)$$

Combine Eqn. (3) with Eqn. (4),  $K$  is as follows:

$$K = \left( \frac{\partial^2 u}{\partial v^2} \right)_{v_0} \cdot v_0 \quad (5)$$

When the crystal cell is stretched along axis  $a$  only, its elongation strain is  $\Delta a$  under the stress of  $\sigma$ . The energy change is  $\Delta u = f \cdot \Delta a$ , let the function of potential energy expands at the equilibrium point by Talar series

$$f = \frac{\partial u}{\partial a} = \left( \frac{\partial u}{\partial a} \right)_{a_0} + \left( \frac{\partial^2 u}{\partial a^2} \right)_{a_0} \cdot \Delta a + \dots \quad (6)$$

Neglecting the items higher than the second order, the expression is

$$f = \left( \frac{\partial^2 u}{\partial a^2} \right)_{a_0} \cdot \Delta a = \left( \frac{\partial^2 u}{\partial a^2} \right)_{a_0} \cdot \frac{\Delta a}{a_0} \cdot a_0 \quad (7)$$

Because  $f = \sigma \cdot a_0^2$ , and  $\sigma$  expands at the equilibrium point,

$$\begin{aligned} \sigma &= \frac{1}{a_0^2} \cdot \left( \frac{\partial^2 u}{\partial a^2} \right)_{a_0} \cdot \frac{\Delta a}{a_0} \cdot a_0 \\ &= \frac{1}{a_0} \cdot \left( \frac{\partial^2 u}{\partial a^2} \right)_{a_0} \cdot \varepsilon \end{aligned} \quad (8)$$

Comparing Eqn. (8) with Eqn. (1),  $c_{11}$  can be obtained:

$$c_{11} = \frac{1}{a_0} \cdot \left( \frac{\partial^2 u}{\partial a^2} \right)_{a_0} \quad (9)$$

Similar to the derivations of  $K$  and  $c_{11}$ , when shearing parallel to the  $XOY$  plane, the relation between the force  $f$  and shearing angle  $\Delta\theta$  will be

$$f = \left( \frac{\partial^2 u}{\partial \theta^2} \right)_{\theta_0} \cdot \Delta\theta \cdot \frac{1}{a_0} \quad (10)$$

The stress  $\sigma$  can be

$$\sigma = \frac{1}{a_0^3} \cdot \left( \frac{\partial^2 u}{\partial \theta^2} \right)_{\theta_0} \cdot \Delta\theta \quad (11)$$

According to the definition of strain,

$$\varepsilon_{12} = \frac{1}{2} \left( \frac{\partial X}{\partial y} + \frac{\partial Y}{\partial x} \right) \quad (12)$$

where  $X$  and  $Y$  denote the  $x$ ,  $y$  components after the crystal cell has been sheared. Substitute Eqn. (11), Eqn. (12) into Eqn. (1),  $c_{44}$  is

$$c_{44} = \frac{1}{a_0^3} \cdot \left( \frac{\partial^2 u}{\partial \theta^2} \right)_{\theta_0} \quad (13)$$

Substitute Eqn. (5) and Eqn. (9) into Eqn. (1),  $c_{12}$  also can be obtained. Thus all independent tensors of elastic matrix are achieved.

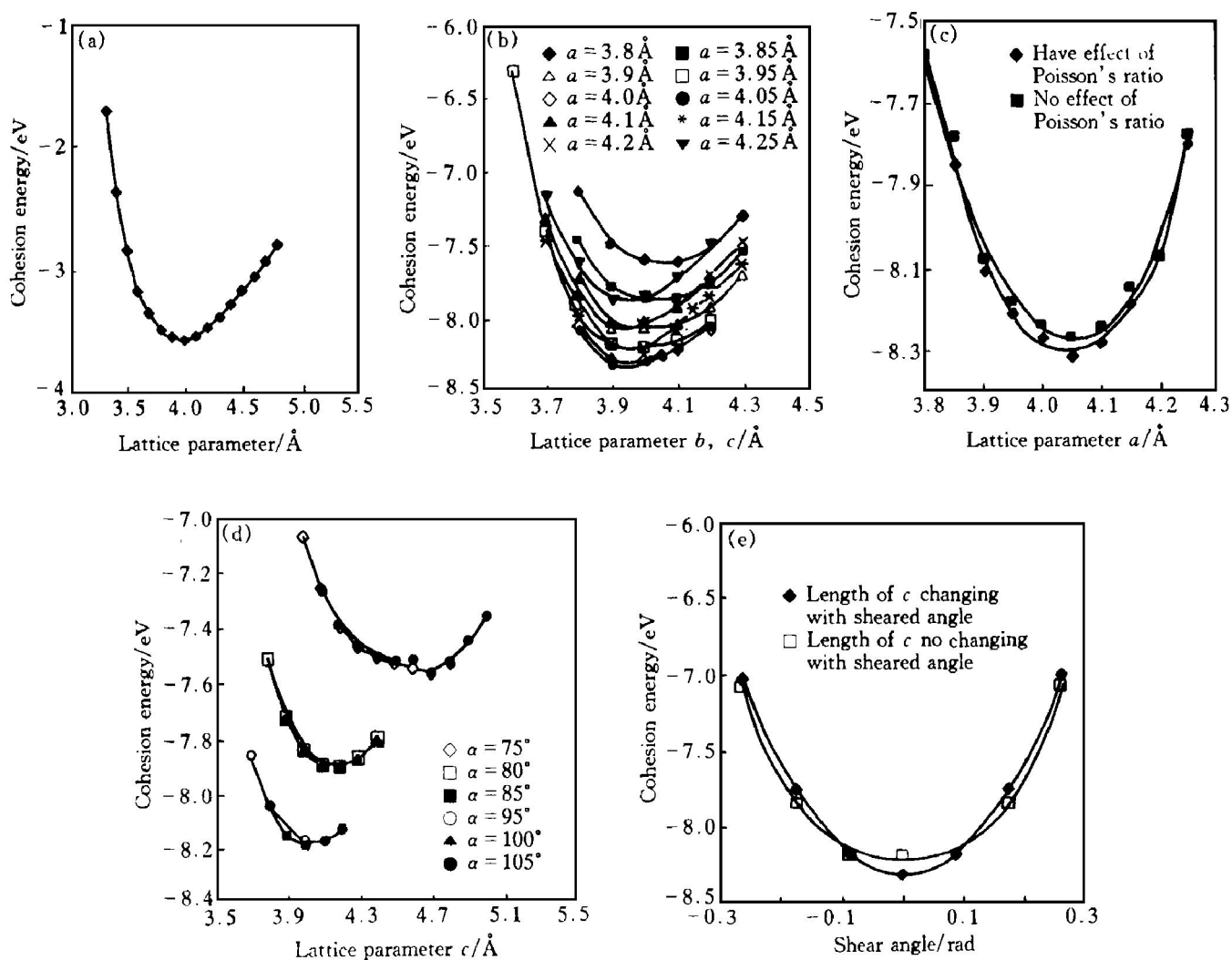
The elastic constants of an ( $hkl$ ) plane for a single crystal can be found in the handbook, but the value differs from that in an aggregate, since the grain is in constraint with its surroundings. There are different models to calculate the elastic constant of an ( $hkl$ ) plane in the polycrystal using single crystal data<sup>[6]</sup>. Kroner model<sup>[7~10]</sup> as a self-consistent model has been widely accepted for theoretical analysis. In this paper, Kroner model is employed to obtain the elastic constants of polycrystalline aggregates Al and TiN.

### 3 RESULTS AND DISCUSSION

Fig. 1(a) shows the calculated cohesion energy of pure Al when the cell is expanded simultaneously along three axes, whose lengths change at the same time and the Poisson's ratio does not play any role. According to Eqn. (3) and Eqn. (5), the lattice parameter,  $a_0$ , and the bulk modulus,  $K$ , can be obtained from the cohesion energy curve.

When the cell is stretched along axis  $a$ , the lengths of axes  $b$  and  $c$  will change. The effect of Poisson's ratio must be taken into consideration when the cohesion energy curve is calculated. The procedure is as follows: at first, the cell is stretched along axis  $a$  to a designated value and the lengths of axes  $b$  and  $c$  change step by step to calculate the cohesion energy curve. Then set another length of axis  $a$  and repeat the calculation. All calculated results are shown in Fig. 1(b). In this case, the obtained lattice space at the lowest energy point of every curve differs from that in Fig. 1(a). If all points at the lowest energy in the cohesion energy curves are connected, we can find the real lowest cohesion energy curve. For comparison, the cohesion energy curve without the effect of Poisson's ratio is calculated and the result is also shown in Fig. 1(c). The two curves deviate from each other, obviously, the results with the effect of Poisson's ratio are substantial.

When the cell is sheared parallel to the  $XOY$  plane, the length of axis  $c$  changes as the sheared



**Fig. 1** Cohesion energy curves of Al calculated by CASTEP software

- (a) —Expanding along three axes simultaneously; (b) —Stretching along  $a$  axis only and  $a$ ,  $b$  and  $c$  are three lattice parameters; (c) —Stretching along  $a$  axis only; (d) —Shearing parallel to  $XOY$  plane,  $\alpha$  is shearing angle and  $c$  is lattice parameter; (e) —Shearing parallel to  $XOY$  plane

angle increases. Using the similar method, the lowest cohesion energy curve of the sheared cell is obtained. Fig. 1(d) and Fig. 1(e) show the cohesion energy curves when the cell is sheared parallel to  $XOY$  plane and Fig. 1(e) gives the results with and without change of  $c$  length. It shows again that the lowest energy curve is obtained as the length of axis  $c$  changes with increasing the sheared angle.

The calculated elastic constants of single crystal Al are summarized in Table 1. Group A is the results with the effect of Poisson's ratio and group B not. Group C is from Ref. [11]. The  $c_{ij}$ ,  $K$ ,  $a_0$  and  $\nu$  are the stiffness, bulk modulus, lattice parameter and Poisson's ratio. Because the data of  $K$  and  $a_0$  are obtained from the cohesion energy curve of that the cell is expanded along three axes simultaneously and there is no effect of the Poisson's ratio. Table 1 shows that the values of  $a_0$  and  $K$  of group A are the same as that in group B, yet the others differ in about 20% with and without correction. Clearly, the group A is

close to group C.

**Table 1** Elastic constants of Al single crystal

	$c_{11}/\text{GPa}$	$c_{12}/\text{GPa}$	$c_{44}/\text{GPa}$	$K/\text{GPa}$	$a_0/\text{\AA}$	$\nu$
A	104.82	58.17	25.53	73.44	4.00	0.358
B	123.86	48.62	21.38	73.44	4.00	0.284
C	108.00	62.20	28.40	78.00	4.02	0.345

According to the Kroner model and using the data of group A and C of Table 1, the elastic constants of polycrystalline Al are obtained (Table 2). In comparison with literature data, the largest error of  $c_{11}$ ,  $c_{12}$  and  $c_{44}$  by our calculation is less than 6%.

All calculated results of single crystal and polycrystalline aggregate are in good agreement with that in literature. It convinces that a combination of *ab initio* method with Kroner model is appreciable. This method was applied to calculate the elastic constants of TiN<sup>[12~14]</sup>, of which the elastic constants differ in a big range in Ref. [3~5]. Fig. 2(a) shows the

**Table 2** Elastic constants of Al polycrystalline (GPa)

	Calculated result			Literature result		
	$c_{11}$	$c_{12}$	$c_{44}$	$c_{11}$	$c_{12}$	$c_{44}$
Voigt	106.52	57.24	24.64	112.34	60.01	26.21
Reuss	103.76	54.50	24.56	112.17	60.20	26.36
Kroner	105.83	56.13	24.76	112.34	60.12	26.29

cohesion energy curve when the cell of TiN is expanded along three axes simultaneously. Fig. 2(b) and Fig. 2(c) show the cohesion energy curves when the cell is stretched along  $a$  axis, and Fig. 2(c) shows the results with and without the effect of the Poisson's ratio. Fig. 2(d) and Fig. 2(e) show the cohesion energy curves when the cell is sheared paralleling to  $XOY$  plane and Fig. 2(e) is the results with and without change of  $c$  length.

The data of group C of Table 3 was obtained using the acoustic experiment<sup>[14]</sup>, the data are widely accepted now<sup>[15, 16]</sup>. Table 3 gives group B data for that the effect of Poisson's ratio has not been considered and larger errors are involved, the largest rela-

tive error is about 30%. Using the Kroner model and the data of group C of Table 3, the literature results can be obtained as in Table 4.

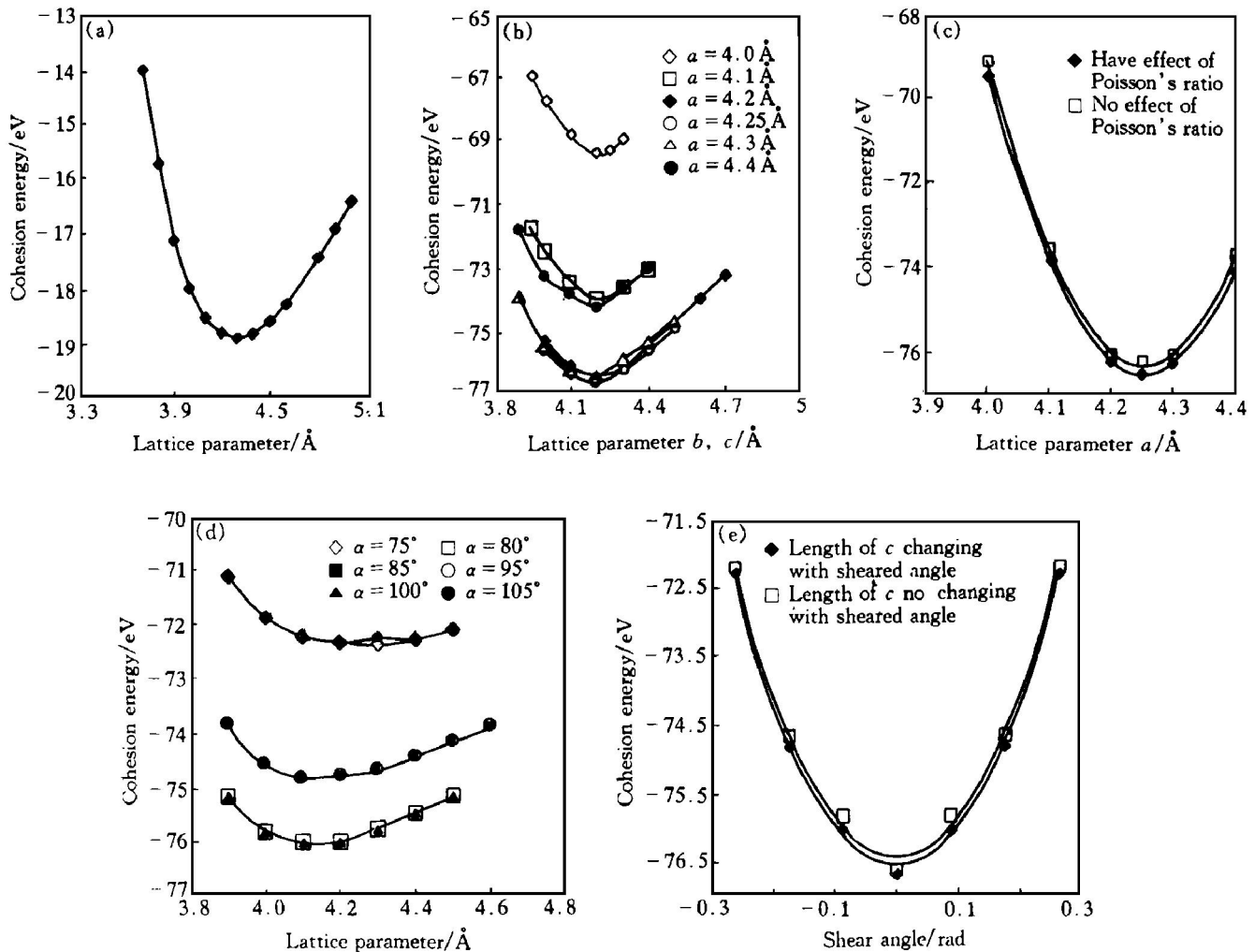
The calculated bulk modulus, lattice parameter are 260.57 GPa, 4.22 Å and 0.205. They are close to 236.4 GPa, 4.25 Å and 0.201 in Ref. [15, 16].

**Table 3** Elastic constants of TiN single crystal

	$c_{11}$ /GPa	$c_{12}$ /GPa	$c_{44}$ /GPa	$K$ /GPa	$a_0$ /Å	$\nu$
A	516.19	128.67	131.52	260.57	4.22	0.205
B	601.40	75.60	119.80	260.57	4.22	0.111
C	497.80	105.70	168.10	236.40	4.25	0.201

**Table 4** Elastic constants of TiN polycrystalline (GPa)

	Calculated result			Literature result		
	$c_{11}$	$c_{12}$	$c_{44}$	$c_{11}$	$c_{12}$	$c_{44}$
Voigt	467.90	136.70	155.60	475.44	116.88	179.28
Reuss	461.22	130.02	150.61	475.34	119.47	178.57
Kroner	465.02	134.11	153.77	475.41	118.37	179.09

**Fig. 2** Cohesion energy curves of TiN calculated by CASTEP software

- (a) —Expanding along three axes simultaneously; (b) —Stretching along  $a$  axis only and  $a$ ,  $b$  and  $c$  are three lattice parameters; (c) —Stretching along  $a$  axis only; (d) —Shearing parallel to  $XOY$  plane,  $\alpha$  is shearing angle and  $c$  is the lattice parameter; (e) —Shearing parallel to  $XOY$  plane

The deviation is about 13% and is larger than that for Al. The reason is that the software CASTEP shall induce error when other species of atoms are involved. In this case, the difference between Ti and N atoms is not so large, thus the error of the calculated elastic constants is not large. The error of single crystal calculation will result in the error of the calculated elastic constant of polycrystal. Though the error exists, the result is still acceptable.

#### 4 CONCLUSIONS

Using *ab initio* method, the elastic constants of the single cubic crystal can be calculated. Three deformation directions are selected in order to obtain the different constants of  $c_{11}$ ,  $c_{12}$  and  $c_{44}$ . The cohesion energy curves in the three deformation directions are calculated and the effects of Poisson's ratio and the lattice distortion must be taken into consideration to obtain the real lowest cohesion energy curves. The results of the second order partial differential at the  $\epsilon$ -equilibrium point of the cohesion energy curve provide the elastic constants of the single crystal. The pure Al is selected to check the method, its result is very close to that in the literature and convinces that this method is appreciable. Then this method is applied to calculate the elastic constant of TiN and the results are also acceptable. The elastic constants of the polycrystalline material can be obtained with the Kroner model. The calculated results are in good agreement with that in the literature. This theoretical calculation method is important in calculating the elastic constants that cannot be obtained either from handbook or from experiment.

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