THERMODYNAMIC, THERMAL AND ELASTIC PROPERTIES OF TITANIUM NITRIDE TiN: COMPARISON OF VARIOUS DATA AND DETERMINATION OF THE MOST RELIABLE VALUES

Anton Kozma
PhD, Associate Professor
Department of Physical and Colloid Chemistry
Uzhhorod National University
46 Pidhirna str., Uzhhorod, Ukraine, 88000
Anton_Kozma@yahoo.com

Abstract: The analysis of literary data on thermodynamic, thermal and elastic properties of titanium nitride TiN which included values Debye temperature θ_D, volume coefficient of thermal expansion α_V and bulk modulus B under standard conditions is carried out. It has been shown that the known data have a significant spread of values from 20 to 43 %. The 8 most rational variants of optimizing calculations are proposed, which make it possible to reveal the most reliable values of some TiN parameters. At the same time, the minimum and maximum values of θ_D and α_V were used from literary sources, as well as the least contradictory data on isobaric heat capacity C_p, melting temperature $T_{m.p}$ and density d of TiN. To improve the calculated results, the values of θ_D(TiN) determined using the methods of Magnus – Lindeman and Debye were also used. The Mayer's relation was the basic test expression. The obtained values of the bulk modulus were compared with the literature data. This made it possible to distinguish the least and most reliable values of α_V and θ_D, as well as make a refinement correction for the last value. As a result, it was found that under standard conditions, the value of θ_D(TiN) close to the optimal should be within 746–769 K, and for its isochoric heat capacity C_V – in the range 36.55–37.19 J/(mol×K). The range of values, after optimization, does not exceed 3 %, unlike the 20 % available in the literature. A more accurate definition of Debye temperature for TiN needs to radically refine the values of its α_V and B.

Keywords: titanium nitride, thermodynamic properties, heat capacity, thermal indicators, thermal expansion, mechanical parameters, bulk modulus, calculation methods.

1. Introduction

Titanium nitride TiN, due to a number of valuable physicochemical properties, refers to promising polyfunctional materials [1]. At the same time, numerous studies of its physicochemical properties are quite controversial. For example, thermodynamic, thermal and mechanical parameters of TiN [2–21] are characterized by a significant spread of values (**Table 1**).

It follows from **Table 1** that the differences between the minimum and maximum values of Debye temperature θ_D are about 20 %, for volume coefficient of thermal expansion α_V exceed 32 %, and for bulk modulus B are within 30–43 %. Such differences in the properties of TiN established by different authors [2–21] can be explained by using various methods of its synthesis and determination of physicochemical parameters. From this it follows that the properties of titanium nitride are more correctly represented not by specific values, but by rather wide ranges of values. However, this approach has some drawbacks. After all, modern materials science needs high-precision data. At the same time, the maximum deviations in the value of a certain parameter should not exceed one or several percent. Based on this, the task of this work was formulated – to carry out optimizing calculations that would minimize existing contradictions in the properties of TiN and could reveal the most reliable values of its physicochemical parameters.

Table 1

Values of Debye temperature, volume coefficient of thermal expansion and bulk modulus of TiN at standard conditions established in the works [2–21]

θ_D, K	$\alpha_V \times 10^{-6}$, K^{-1}	B, GPa		
700 [2]	19 * [4]	245* [4]	272* [4]	294 [18]
780* [3]	22 [5]	257* [9]	275 [14]	296 [5]
799* [4]	23 * [4]	263 [10]	280 [5, 15]	302* [9]
809* [3]	~25 [3]	264 [11]	283* [4]	311–315* [6]
841* [4]	27 [4, 6, 7]	265 [12]	289 [16]	318 [19, 20]
870 [5]	28 [4, 8]	267 [13]	290 [17]	352 [21]

*Note: * – the difference in the values obtained in one work is due to the use of different research methods.*

2. Methods

This work used the methods of Magnus – Lindeman and Debye [22–25]. Basic expressions were [22, 23]:

$$C_V = C_p - \omega T^{3/2}, \quad (1)$$

$$D(T/\theta_D) = 3(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx, \quad (2)$$

$$C_V / 3R = 4D(T/\theta_D) - \left((3\theta_D/T)/\left(e^{\theta_D/T} - 1\right)\right), \quad (3)$$

where C_V and C_p – isochoric and isobaric heat capacity respectively; ω – design factor; T – absolute temperature; $D(T/\theta_D)$ – Debye function; R – universal gas constant.

Tables of the Debye functions [24] were used to determine C_V to $D(\theta_D/T)$.

The Mayer's relation [26] was used as the test formula:

$$C_p - C_V = \alpha_V^2 VTB^T, \quad (4)$$

where V – molar volume; B^T – isothermal bulk modulus.

The extreme parameter is directly related to the heat capacities [26]:

$$C_p / C_V = B^S / B^T, \quad (5)$$

where B^S – isentropic bulk modulus.

When calculating, it was assumed that most of the values B obtained in works [4, 5, 9–21] belong to the isentropic bulk modulus. This is argued by the fact that in studies of elastic properties priority is given to acoustic and acoustooptic methods [19, 20], in which B^S is directly determined [26, 27].

In this work, C_p(TiN)=37.50 J/(mol×K) was taken. This is the average among data [28] and [29] at 298.15 K, which differ only by 2 %. Differences between density d of titanium nitride given in different works [6, 30], are within 1 %. The value of d from [30] was used in this paper. Values of molar mass of TiN and its melting point $T_{m.p.}$ also borrowed from [30].

3. Results

As a result of the analysis, the calculation operations were minimized as much as possible. Their optimized number was reduced to the eight most rational variants, which are grouped in **Table 2.**

Consider some calculation options in more detail.

Variant I: minimum values of θ_D (780 K [3]) and α_V (19×$\times 10^{-6}$ K^{-1} [4]). For this option, the difference between C_p and C_V is 1.25 J/(mol×K), and the values of B^T and B^S exceed the sizes 950 GPa (**Table 2**). As can be seen from **Table 1**, the resulting of bulks modulus exceeds the maximum values from known sources [4, 5, 9–21]. It follows that the suggested option is unlikely.

It should also be noted that if to use [2] as the minimum value of θ_D (700 K) from the operation, then come to a neg-

ative size of α_V. In such a case, the TiN should taper upon heating rather than expand. However, this is contrary to all known publications [3–8] on the thermal expansion of titanium nitride.

Table 2

The results of the calculations (obtained using the minimum and maximum values of θ_D and α_V from [3–5, 8])

Variant calculation	θ_D, K	C_V, J/(mol×K)	α_V, $\times 10^{-6}$ K^{-1}	B^T, GPa	B^S, GPa
I	780 [3]	36.25	19 [4]	950<	1000<
II	780 [3]	36.25	28 [8]	450	466
III	870 [5]	33.75	19 [4]	1000<	1000<
IV	870 [5]	33.75	28 [8]	1000<	1000<
V	747	37.16	19 [4]	266	268
VI	747	37.16	28 [8]	122	124
VII	792	35.92	19 [4]	1000<	1000<
VIII	792	35.92	28 [8]	569	594

Variant II: minimum value of θ_D (780 K [3]) and maximum value of α_V (28×10^{-6} K^{-1} [4, 8]). In this case, the difference C_p–C_V is also 1.25 J/(mol×K), but the values of B^T and B^S take sizes 450 and 466 GPa, respectively. As it is possible to see from **Table 1**, these values are already approaching those presented in the literature [21].

Similarly, calculations were implemented for variants III and IV. At the same time, overestimated values of B^T and B^S were recorded (**Table 2**), which makes these variants unlikely. Let's note that the known data on Debye temperature for TiN [2–5] does not allow to significantly optimize the range of its most likely values. It can only be stated that a more reliable value θ_D should exceed 700 K, but not exceed 780 K. In this regard, let's consider an additional 4 variants that can be reached using the methods of Magnus – Lindeman [22] and Debye [22–24]. Consider them below.

Variant V: the value of C_V set according to the Magnus – Lindeman method at 298.15 K, and the minimum coefficient α_V (19×10^{-6} K^{-1} from [4]). For this case, the difference between C_p and C_V is 0.34 J/(mol×K). Herewith B^T=266 and B^S=268 GPa. The values obtained are well consistent with the literature data 257–275 GPa [4, 9–14] (**Table 1**). Calculated size C_V(TiN)= =37.16 J/(mol×K) corresponds to Debye temperature equal to 747 K. This indicator can be considered as one of the minimum in determining the optimal interval of the values of θ_D(TiN).

The remaining variants VI-VIII have lower accuracy of results (**Table 2**).

Thus, the best agreement between the various literature data was achieved with the calculated variants II and V. They were used for subsequent optimization. From variant V, it is possible to reach the following result. If in the expression (5) let's substitute the smallest value of B^S equal to 245 GPa [4] (**Table 1**), then let's obtain C_V(TiN)=37.19 J/(mol×K), which corresponds to θ_D(TiN)=746 K. It is this value of Debye temperature that is most rational to consider the lower bound of optimal values θ_D(TiN). Of variants II and VIII (**Table 2**), the upper bound of the most probable value θ_D(TiN) was determined. By optimizing calculations, let's came to the value C_V(TiN)=36.55 J/(mol×K), which corresponds to θ_D(TiN)=769 K. If to use it with the value α_V = 28×10^{-6} K^{-1} from [4, 8], then obtain B^T=342 and B^S=351 GPa. The latter value is in good agreement with the maximum size of parameter B set in [21].

Let's note that 3 of the 4 considered variants (with numbers I, III, VII) with a minimum value of α_V (19×10^{-6} K^{-1} [4]) lead to significantly overestimated values of B (**Tables 1**, **2**). At the same time, when calculating using the maximum value α_V (28×10^{-6} K^{-1} [8]), only 1 of the 4 variants (variant of number IV) gives significant deviations from the known quantities of B. From this it follows that the most reliable value of thermal expansion TiN is closer to the size 28×10^{-6} K^{-1} [8] than to 19×10^{-6} K^{-1} [4]. It is also noted that for 6 of the 8 variants considered (**Table 2**), the values of B^T and B^S are obtained, which are closer to the maximum sizes of [21] than to the minimum of [4, 9]. It follows that the TiN should have a higher resistance to external pressure than was thought in the works [4, 9].

4. Discussion

The results obtained can be explained by the integrated approach applied in this work. The use in Mayer's relation (4) of most of the known values of θ_D and α_V leads to both significantly overestimated and in some cases underestimated values of the bulk modulus B. Many calculated values are significantly outside the known range B=245–352 GPa (**Tables 1**, **2**). Thanks to the analysis of literary data [2–21] and the use of the methods of Magnus – Lindeman and Debye, it was possible to significantly optimize the values of θ_D(TiN) from 700–870 K to 746–769 K. This led to a decrease in the existing scatter of literary data from 20 % to 3 %. The carried-out clarification of sizes θ_D(TiN) also allowed to reveal the most probable intervals of values α_V(TiN) and B(TiN) which don't contradict Mayer's relation (4). So, for titanium nitride, the most reliable are the values $\alpha_V\approx(25–28)\times10^{-6}$ K^{-1} and $B\approx$310–350 GPa obtained in works [3, 4, 6–8] and [6, 19–21] respectively. A disadvantage of this work is the impossibility of determining the true θ_D(TiN) to one degree. Achieving such high accuracy is possible only after radical refinement of the values α_V and B.

The results obtained, together with the previously known [1–21, 28], serve as an additional confirmation of the practical importance of the TiN as a weakly expandable material when heated that can be used at high external pressures. The established range of optimal values of θ_D(TiN) is important for subsequent thermodynamic and thermophysical studies and allows in the future to more accurately determine its thermal and elastic properties.

The approach proposed in this work to identify the most reliable parameters of titanium nitride can be used for many similar compounds. These include nitrides of the composition XN, where X – Boron, Aluminum, Scandium, Vanadium, Yttrium, Zirconium, Niobium, Lanthanum, Hafnium, Tantalum and others. Also in the future, it is planned to significantly develop the approach used and identify the most accurate values of θ_D, C_V, α_V and B for XN in a wide temperature range of 300–3200 K.

5. Conclusions

Analysis of literature data regarding thermodynamic, thermal and elastic properties of titanium nitride TiN was carried out, which included values of its θ_D, α_V and B under standard conditions. It was shown that the previous results are characterized by a significant spread of values from 20 to 43 %. There are 8 basic variants of optimizing calculations, which made it possible to identify the most reliable values of some parameters of TiN. It has been established that under

standard conditions, the size of θ_D(TiN) close to the optimal should be within 746–769 K, and for C_V(TiN) – in the range of 36.55–37.19 J/(mol×K). The spread of values for optimized parameters does not exceed 3 %.

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Received date 23.09.2020
Accepted date 02.11.2020
Published date 30.11.2020