Thermodynamic modelling of Al-B-N system

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ABSTRACT

In this work we report the thermodynamic modelling of the Al-N, B-N and Al-B-N systems by the Calphad approach, making use of the \textit{ab initio} calculations and the available experimental thermochemical and phase equilibria data. Gibbs energy description for the Al-B system is taken from the literature, with a modification for the model for the liquid phase. The enthalpy of formation and the heat capacity of various polymorphs of AlN and BN are estimated using the DFT and the phonon calculations, respectively. The enthalpy of mixing of the mixed nitride (Al,B)N in wurtzite and cubic structures are obtained using the SQS method. Gibbs energy of formation of the mixed nitride from the binary nitrides is also computed using the phonon calculations. These quantities along with the critically assessed thermochemical and constitutional data are used for obtaining the Gibbs energy functions of various phases in the Al-N, B-N, and Al-B-N systems. Calculated phase equilibria and thermochemical data are compared with the experimental data.

1. Introduction

Aluminium nitride (AlN) and boron nitride (BN) are important Group 13 nitrides that exhibit polymorphism. Their combination has been explored for tribological and electronic applications. Thin films of cubic BN (cBN) are technologically important because of their high hardness, wear and oxidation resistance. However, the films tend to peel-off from their substrate due to high internal stresses. It was reported by [1] that the addition of Al is effective in preventing delamination as well as improving the oxidation resistance of the BN films. Similarly, the machinability of AlN needs to be improved since it is employed in electronic packaging applications. It has been reported that the machinability of AlN can be improved by incorporation of the soft and lubricating hexagonal BN (hBN) [2]. Hence, the constitutional and thermochemical data concerning Al-B-N system are of significance.

2. Binary systems

2.1. Al-B

The Al-B system was modelled by [3] using a single-lattice random solution model for the liquid phase. This model was converted to the two-sublattice model for ionic melts [4], using the procedure proposed by [5]. This was necessary to ensure compatibility with the thermodynamic descriptions of other binary systems used in this work. The calculated Al-B phase diagram using the converted Gibbs energy description is shown in Fig. 1.

2.2. Al-N

The experimental thermochemical and constitutional data related to Al-N system were reviewed by [6]. The Gibbs energy parameters for Al-N system was optimized by [7], as a part of the thermodynamic assessment of Al-Fe-N system. Another assessment was reported by [8]. In both works, the polymorphism of AlN was not considered, which is required for the Gibbs energy modelling of the Al-B-N system. Hence, the re-optimization of the Al-N system is justified.

Details regarding the solid phases in this system are summarized in Table 1. The polymorphs of AlN with wurtzite and cubic (zincblende) structures are designated as wAlN and cAlN, respectively. Note that wAlN is the most stable polymorph. cAlN is metastable and can be stabilized by epitaxial thin film growth [9]. Sources of experimental thermochemical data available for this system are summarized in Table 2. The enthalpy of formation of wAlN and cAlN structures were computed using \textit{ab initio} calculations by Ref. [10].

The entropy of fusion ($\Delta_{\text{ fus}}S^\circ$) of wAlN was estimated by [15] as + 23 J/mol/K. Subsequently [16], estimated the $\Delta_{\text{ fus}}S^\circ$ for wAlN as + 63.6 J/mol/K, based on a method suggested by [17]. Since these two values are not in agreement with each other, the $\Delta_{\text{ fus}}S^\circ$ of wAlN was estimated here using an alternate procedure outlined by [18]. Using

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2.3. B-N

There are three polymorphs for boron nitride (BN) considered in this work: hexagonal (hBN), cubic (cBN) and wurtzite (wBN). [23] reported that hBN is the most stable polymorph at room temperature and atmospheric pressure, similar to graphite. The thermodynamic assessment of this system by [24,25], however, considered wBN as the most stable polymorph. Based on thermochemical measurements [26] reported that cBN is the most stable polymorph at ambient conditions. This value is used in the present assessment.

3. Al-B-N

A critical review of the system can be found in [39]. There are no ternary phases reported in this system. The mutual solid solubilities of AlN and BN are limited [40]. A thermodynamic assessment of Al-B-N system was presented by Ref. [24]. It is revised here using improved thermodynamic descriptions of the binaries Al-N and B-N.

4. Thermodynamic models

The sublattice formulations used for various phases are listed in Table 4 (underline denotes the major constituent in the sublattice). A

Table 1
Details regarding solid phases in the constituent binary systems of Al-B-N.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pearson symbol</th>
<th>Prototype</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>cF8</td>
<td>Cu</td>
<td>Fm3m</td>
</tr>
<tr>
<td>B</td>
<td>hR105</td>
<td>βB</td>
<td>R3m</td>
</tr>
<tr>
<td>cB</td>
<td>hR12</td>
<td>αB</td>
<td>R3m</td>
</tr>
<tr>
<td>AlB6</td>
<td>hP3</td>
<td>AlB6</td>
<td>P6/mmm</td>
</tr>
<tr>
<td>AlB12</td>
<td>hP216</td>
<td>AlB12</td>
<td>P42 1 2</td>
</tr>
<tr>
<td>wAlN</td>
<td>hP4</td>
<td>ZnO</td>
<td>P6 3 mc</td>
</tr>
<tr>
<td>cAlN</td>
<td>hP6</td>
<td>ZnS</td>
<td>Fd3m</td>
</tr>
<tr>
<td>cBN</td>
<td>hP6</td>
<td>ZnS</td>
<td>Fd3m</td>
</tr>
<tr>
<td>wBN</td>
<td>hP4</td>
<td>BN</td>
<td>P6 3/mmc</td>
</tr>
</tbody>
</table>

Table 2
Sources of experimental thermochemical data for Al-N system.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Quantity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>wAlN</td>
<td>ΔH_{fus}</td>
<td>[11-14]</td>
</tr>
<tr>
<td></td>
<td>S_{BN}</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>H_{f} - H_{BN}</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>C_{p,T}</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>P_{S}</td>
<td>[13]</td>
</tr>
</tbody>
</table>

Thermodynamic calculations show that it transforms to hBN at 1640 K [26]. Further, they showed that in the temperature range 0–4000 K, the wBN is not thermodynamically stable, at least to pressures up to 10 GPa. Subsequently, using in situ diffraction experiments [27], confirmed that cBN is the most stable polymorph at ambient conditions. Taking into consideration of this new information, B-N system is re-assessed here.

The crystallographic data for the solid phases in B-N system are listed in Table 1. Sources of the thermochemical data for cBN, wBN and hBN are summarized in Table 3. ΔH_{fus} of cBN was reported as +25 J/mol/K by [28]. It was also calculated using the method proposed by [18] and the value is +26.4 J/mol/K. This value is used in the present assessment. There are only limited constitutional data available for this system. The decomposition and melting temperature of hBN at atmospheric pressure were reported as 2600 ± 100 K [20] and 3240 ± 200 K [28], respectively. The congruent melting temperature of hBN was estimated by [22] to be 3800 ± 50 K.

3. Al-B-N

A critical review of the system can be found in [39]. There are no ternary phases reported in this system. The mutual solid solubilities of AlN and BN are limited [40–43]. [44] established an isothermal section at 1173 K under 0.1 MPa argon (in the absence of external nitrogen) from X-ray powder diffractogram data. The partial isothermal section at 1773 K was obtained using X-ray powder diffractograms of 21 samples [45]. The AlN-BN phase diagram was deduced by Ref. [46] using ab initio methods and the critical temperature for miscibility gap was found to be approximately 9500 K. A thermodynamic assessment of Al-B-N system was presented by Ref. [24]. It is revised here using improved thermodynamic descriptions of the binaries Al-N and B-N.
two-sublattice ionic model proposed by [4] was used for modelling the liquid phase in this work. AlN and BN were included as the constituents in the second sublattice rather than the anionic species in order to have compatibility with the Ionic Solutions (ION2) database from Ref. [47].

5. Ab initio calculations

Vienna Ab initio Simulation Package (VASP) [48,49] with projector augmented wave (PAW) potentials [50,51] was used for estimating the total energies of the stable and metastable nitrides. GGA-PW91 [52] was used as the exchange-correlation functional since it gave better agreement with the measured enthalpy of formation and the lattice parameters. Monkhorst-Pack scheme [53] was used for sampling the k-points in the Brillouin zone. An energy cut-off of 600 eV was used and the number of k-points was chosen such that the total energy converged within $1 \times 10^{-3}$ eV/atom. Tetrahedron method with Blöchl corrections [54] was used as the integration scheme in these calculations. The volume, shape and atomic positions of the input structures were relaxed until the energy converged to $10^{-7}$ eV/atom in each electronic step and the force converged to $2 \times 10^{-5}$ eV/Å in each ionic step. The enthalpy of formation was estimated using Equation (1).

$$\Delta H_{\text{f}298}^\text{MN}(\text{MN}) \approx E_0(\text{MN}) - E_0(\text{M}) - \frac{1}{2}E_0(\text{N}_2),$$  

where $E_0$ is the total energy obtained from VASP and M corresponds to either Al or B. The total energy of N$_2$ molecule was calculated according to the procedure outlined in [10]. The $\Delta H_{\text{f}298}^\text{MN}$ values calculated with respect to Al(Fe), $\beta$B and N$_2$(g) are listed in Table 5.

The calculated values of $\Delta H_{\text{f}298}^\text{MN}$ are in reasonable agreement with the values computed by [10] for the polymorphs of AlN. Results show that wAlN is thermodynamically more stable than cAlN. Similarly, cBN is more stable than wBN as already suggested by [26]. The $\Delta H_{\text{f}298}^\text{MN}$ for hBN has to be estimated using DFT calculations that include Van der Waals forces (vdW-DFT) due to its layered structure. However, the values obtained using vdW-DFT for hBN was not in agreement with the experimental measurement ($-250300$ J/mol) by [35]. The Gibbs energy functions for hBN are, therefore, taken from the SGTE Substance database (Version 5.1) [55].

Finite temperature thermodynamic properties of the polymorphs of AlN and BN were obtained using quasiharmonic approximation (QHA) as implemented in Phonopy [56]. A $4 \times 4 \times 1$ and $2 \times 2 \times 2$ supercells were used for the wurtzite and cubic structures, respectively. The volume of the structure was varied by changing the lattice parameters by ±5% (in steps of 1%) about the equilibrium volume. The shape and atomic positions of the strained structures were relaxed. Subsequently, supercells with a finite displacement of ± 0.01 Å were created and the forces were calculated using VASP. Finally, the phonon frequencies obtained from the computed forces were collected from each volume and post-processed using Phonopy to obtain the finite temperature properties. The calculated $C_p^V$ as a function of temperature for the polymorphs of AlN and BN are shown in Figs. 2 and 3, respectively.

The heat capacities calculated using QHA were fitted to appropriate expressions and integrated to obtain Gibbs energy functions valid down to 0 K. More details about the fitting procedure can be found in [57]. The fitted Gibbs energy functions (with respect to SER) are represented by functions given in Equation (2).

$$C_p^V = \sum_i \nu_i H_i^{\text{SER}} = \begin{cases} \text{a} + \text{b}T + y T^2 \text{(low temperature)} \\
\text{a} + \text{b}T + c T \ln T + d T^2 + e T^{-1} + f T^3 + g T^{0.5} \text{(high temperature)}
\end{cases}$$

(2)

The enthalpy of mixing of Al in cBN and B in wAlN were computed using the SQS approach. 32-atom and 48-atom supercells were generated using the mcsqs code [58] of Alloy Theoretic Automated Toolkit (ATAT) [59] to mimic the random distribution of metal atoms in cubic and wurtzite structures, respectively. The structures generated using this code belong to the triclinic crystal system. The calculated correlation functions mimic the correlation function corresponding to a random alloy for the first few nearest neighbours. The structures generated using the mcsqs code neglects the possible effects of short-range order in these solid solutions. The SQS structures for cubic were completely relaxed, whereas for wurtzite a constrained relaxation (volume and atomic position) was performed in order to maintain the symmetry. The $\Delta_{\text{mix}} H$ was calculated with respect to the binary nitrides using Equation (3).

$$\Delta_{\text{mix}} H \approx E_0(\text{Al}, \text{B}_{1-x}, \text{N}) - x E_0(\text{AlN}) - (1 - x) E_0(\text{BN})$$

(3)

![Fig. 2. $C_p^V$ as a function of temperature for the polymorphs of AlN obtained using QHA.](image)

![Fig. 3. $C_p^V$ as a function of temperature for the polymorphs of BN obtained using QHA.](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\Delta H_{\text{f}298}^\text{MN}$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>wAlN</td>
<td>$-286578$</td>
</tr>
<tr>
<td>cAlN</td>
<td>$-284347$</td>
</tr>
<tr>
<td>cBN</td>
<td>$-243352$</td>
</tr>
<tr>
<td>wBN</td>
<td>$-239937$</td>
</tr>
</tbody>
</table>

Table 5: Enthalpy of formation of the stable and metastable end-members obtained using ab initio calculations.
The calculated $\Delta_{mix}H$ of Al in cBN and B in wAlN is shown in Fig. 4. The positive values indicate that a miscibility gap is expected.

The Gibbs energy of reaction ($\Delta_r G^f$) for the formation of wurtzite and cubic polymorphs from the corresponding binary nitrides were calculated using the harmonic approximation implemented by Phonopy [56]. The harmonic approximation was used for these structures since QHA calculations would be computationally intensive. $1 \times 1 \times 2$ supercells were created from the relaxed SQS structures for both the polymorphic structures. The Gibbs energy of reaction was calculated using the following equation.

$$\Delta r G^f \approx G_f^r (A_l B_{1-x} N) - x G_f^r (A l N) - (1-x) G_f^r (B N)$$  \hspace{1cm} (4)

The calculated $\Delta r G^f$ as a function of temperature for the mixed nitride is shown in Fig. 5. The phonon calculations for the other SQS structures failed due to the presence of imaginary frequencies.

### 6. Optimization

The Gibbs energy model parameter optimization was done using the PARROT module [60] of Thermo-Calc software [61]. Al-N and B-N systems were optimized with the experimental as well as ab initio thermochemical data and constitutional data as input. The coefficients “a” and “b” in the Gibbs energy function for wAlN (Equation (2)) were further refined using the experimental thermochemical and constitutional data. Similarly, the “a” term was further refined for cBN and wBN using the experimental thermochemical data.

![Fig. 4. Calculated enthalpy of mixing of AlN and BN using SQS.](image)

![Fig. 5. Calculated Gibbs energy of reaction for the formation of Al$_{0.75}$B$_{0.25}$N from the binary nitrides obtained using harmonic approximation.](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Function</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase name: Liquid; Sublattice formulation: $(A_l^+)^3, (B^+)^3 (N_{3a},A_{15}N,B_{45}N)_{0}$</td>
<td>$G_f^r (A_{15}N,B_{45}N)_{0}$ + GHIQLG</td>
<td>[63]</td>
</tr>
<tr>
<td>Phase name: AlN; Sublattice formulation: $(A_l)<em>{1}$ $(B,N,Va)</em>{1}$</td>
<td>$G_f^r (A_l)<em>{1}$ $(B,N,Va)</em>{1}$</td>
<td>[56]</td>
</tr>
<tr>
<td>Phase name: AlB$^+$; Sublattice formulation: $(Al)<em>{1}$ $(B)</em>{12}$</td>
<td>$G_f^r (Al)<em>{1}$ $(B)</em>{12}$</td>
<td>[63]</td>
</tr>
<tr>
<td>Phase name: AlB$^+$; Sublattice formulation: $(Al)<em>{1}$ $(B)</em>{2}$</td>
<td>$G_f^r (Al)<em>{1}$ $(B)</em>{2}$</td>
<td>[63]</td>
</tr>
<tr>
<td>Phase name: AlB$^+$; Sublattice formulation: $(Al)<em>{1}$ $(B)</em>{12}$</td>
<td>$G_f^r (Al)<em>{1}$ $(B)</em>{12}$</td>
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<td>$G_f^r (Al)<em>{1}$ $(B)</em>{2}$</td>
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<td>$G_f^r (Al)<em>{1}$ $(B)</em>{12}$</td>
<td>[56]</td>
</tr>
<tr>
<td>Phase name: Liquid; Sublattice formulation: $(A_{0.75}B_{0.25})<em>{1}$ $(N)</em>{0.75}$ $cBN$</td>
<td>$G_f^r (A_{0.75}B_{0.25})<em>{1}$ $(N)</em>{0.75}$ $cBN$</td>
<td>[63]</td>
</tr>
<tr>
<td>Phase name: Liquid; Sublattice formulation: $(A_{0.75}B_{0.25})<em>{1}$ $(N)</em>{0.75}$ $wBN$</td>
<td>$G_f^r (A_{0.75}B_{0.25})<em>{1}$ $(N)</em>{0.75}$ $wBN$</td>
<td>[63]</td>
</tr>
</tbody>
</table>

(continued on next page)
Table 6 (continued)

<table>
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<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_{GHBN}^\text{AlN}$</td>
<td>$+ , G_{HBN} = -261040.389 + 126.499602T$</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>$- , 18.7341T \ln(T) - 0.019441475T^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ , 2.07714 \times 10^{-6}T^3 + 422878.4T^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(298.15 &lt; T &lt; 1200)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$- , 284729.181 + 357.047504T - 51.636367 \ln(T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$- , 3.9540955 \times 10^{-7}T^2 - 1.98643167 \times 10^{-11}T^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$+ , 3437095T^{-1}$</td>
<td>$(1200 &lt; T &lt; 3240)$</td>
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<td></td>
<td>$- , 33288.511 + 496.275015T - 67T \ln(T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$- , 2.701375 \times 10^{-11}T^2 + 9.95781 \times 10^{-29}T^5$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$- , 1.313297 \times 10^{-15}T^{-1}$</td>
<td>$(3240 &lt; T &lt; 6000)$</td>
</tr>
</tbody>
</table>

Fig. 6. Calculated Al-N phase diagram.

Fig. 7. Comparison of calculated heat content of wAlN with experimental data from [12].

Fig. 8. Comparison of calculated dissociation pressure of wAlN with experimental data from [13].

Fig. 9. Comparison of calculated solubility of nitrogen in liquid Al with experimental data from [19].
The parameters for liquid were optimized using the constitutional data as input for both the systems. In the last stage of optimization, all the model parameters and data were included and optimized, simultaneously. The parameters obtained from the final run were rounded off according to the procedure outlined in [62].

A preliminary description of the ternary system is obtained by combining the optimized Gibbs energy parameters of Al-N and B-N from the present work and Al-B from [3] (modified). The ab initio thermochemical data was used for optimizing the Gibbs energy functions of wAlN and cBN. The optimized Gibbs energy parameters for Al-B-N system are listed in Table 6.

7. Results

7.1. Al-N

The calculated Al-N phase diagram using the Gibbs energy functions obtained in the present work is shown in Fig. 6. The calculated congruent decomposition temperature of wAlN (2709 K) matches quite well with the value reported by [20] (2708 K). From the calculated condensed phase diagram (i.e. without the gas phase) (Fig. 6(b)), it can be seen that wAlN undergoes syntectic melting at 4714 K, which is very close to the value deduced by [22] (4800 ± 100 K). From Table 7, it is evident that the optimized value for enthalpy of formation of wAlN is in reasonable agreement with the experimental and ab initio values. The

![Figure 10. Calculated B-N phase diagram.](image1)

![Figure 11. Calculated Gibbs energy for various polymorphs of BN using the thermodynamic description obtained with ab initio and experimental data as inputs.](image2)

![Figure 12. Calculated cBN-wAlN section.](image3)

![Figure 13. Calculated isothermal section of Al-B-N system at 1173 K.](image4)

![Figure 14. Calculated isothermal section of Al-B-N system at 1773 K.](image5)
comparison of calculated heat content and dissociation pressure of wAlN with experimental data show that they are in good agreement (Figs. 7 and 8). Fig. 9 shows the calculated solubility of nitrogen in molten aluminium, which is in close agreement with the experimental data from [19].

7.2. B-N

The computed B-N phase diagram using the parameters obtained in the present work is shown in Fig. 10. As seen in Fig. 10(a), the calculated decomposition temperature of hBN (hBN = L + G) is 2774 K. This is somewhat lower than the value recommended by [20] (2600 ± 100 K). The computed phase diagram of B-N without the gas phase is given in Fig. 10(b). The calculated congruent melting point of hBN (3794 K) matches well with the value estimated by [22] (3800 ± 50 K). According to [26], since the melting and decomposition temperatures of cBN and wBN are not known experimentally, it can be conjectured that these dense polymorphs transform to hBN before they melt or decompose. According to present calculations, cBN → hBN transformation takes place at 1856 K, whereas wBN → hBN transformation is at 1742 K. The order of stability of the polymorphs can also be inferred from the Gibbs energy vs. temperature plot, as shown in Fig. 11. It is seen that at room temperature cBN is the most stable polymorph, followed by wBN and hBN. Even though the current assessment is quite thorough in considering polymorphs of compounds, it is not thorough in considering polymorphs of pure Boron.

7.3. Al-B-N

The calculated pseudobinary section BN-AlN and using the parameters listed in Table 6 is shown in Fig. 12. It is seen from the diagram that the mutual solid solubility between these nitrides is limited. Besides, a four-phase reaction involving liquid, gas, hBN and wAlN (L + G + hBN + wAlN) is seen to occur at 2632 K.

The calculated isothermal sections at 1173 K (without the gas phase) and 1773 K are shown in Figs. 13 and 14, respectively. At 1173 K, it is seen that wAlN is in equilibrium with AlB2. Whereas in the isothermal section proposed by [44], the equilibrium is between cBN and AlB2. The isothermal section at 1773 K agrees with the partial isothermal section given by [45], but includes the tie-triangle involving the liquid phase. This was missing in the isothermal section given by [45].

8. Conclusions

Thermodynamic description for Al-N, B-N and Al-B-N were obtained using the Calphad method, including metastable polymorphs of AlN and BN. Extensive use of ab initio calculations have resulted in the improved thermodynamic functions for these systems. Calculated phase diagrams and thermochemical quantities were compared with available information, wherever possible. Good agreement is seen between both in most cases. Measurement of the temperature and enthalpy of decomposition of the binary nitrides can further improve the thermochemical functions, although it may be quite difficult to accomplish due to the high temperatures involved. It will also be useful to conduct experiments to establish phase relations in the ternary, especially in the temperature range 1173–1773 K.

Data availability

The raw data required to reproduce these findings are available to download from Supplementary material section. The processed data required to reproduce these findings are available to download from Supplementary material section.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.calphad.2019.03.008.

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