Stability of Laves Phases in the Ta – V System

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Outline of the presentation

Stability of Laves phases (C14, C15, C36)
- ab initio energetics,
- phase equilibria,
- vibrational stabilisation of phases
C14 Laves Phase
- **hexagonal structure** – prototype MgZn$_2$ (space group 194, P63/mmc)
- 12 atoms per unit cell, lattice parameters a and c
- **3 inequivalent sublattices**

C15 Laves Phase
- **cubic structure** - prototype Cu$_2$Mg (space group 227, Fd-3m)
- 24 atoms per unit cell, lattice parameter a
- **2 inequivalent sublattices**

C36 Laves Phase
- **hexagonal structure** prototype MgNi$_2$ (space group 194 P63/mmc)
- 24 atoms per unit cell, lattice parameters a and c
- **5 inequivalent sublattices**
First-principle Calculations for Modeling of Gibbs Energy of Phases – macroscale level

- Laves-phases Cr$_2$X:

In all mentioned systems: for Cr$_2$X: the most stable structure at 0 K: C15, at high T: C14

Similarly Cr-Hf and Cr-Ti systems: (CALPHAD 34(2) (2010) 215)
Energetics Ta – V: „anomalous system“

(C14 is most stable structure at 0 K, and at high T
C15 is stable at mediate temperatures: $T_{low} – T_{high}$)

(Ta and V belong to the same group of the periodic system.

Studied as prospective superconductors.)

Ab initio calculations results:

\[
\begin{array}{|c|c|c|c|}
\hline
\text{structure} & \text{Cr}_2\text{Hf} & \text{Cr}_2\text{Ti} & \text{V}_2\text{Ta} \\
\hline
\text{C14} & -8,70 & -8,47 & -11,40 \\
\text{C15} & -10,38 & -10,16 & -10,18 \\
\text{C36} & -9,68 & -9,51 & -10,82 \\
\hline
\end{array}
\]

\[\Delta E_{\text{Laves-SER}}^{\text{kJ.mol}^{-1} \text{ of atoms}}\]
Ab initio Calculations – nanoscale level

**CODES**

**VASP** (Vienna Ab initio Simulation Package) with the PAW-PBE (Projector Augmented Wave Perdew-Burke-Ernzerhof) pseudopotential gives us the possibility of the structure relaxation.

**GGA** (Generalized Gradient Approximation) was used to evaluate the exchange-correlation energy.

We used to evaluate the properties (total energies) of:

- Standard element reference (SER) states
- Laves phases with two-sublattice model of occupations of the sublattices:
  - C14,15 - two sublattice model \((A,B)_2(B,A)\) \((A=V, B=Ta)\):
  - \((\text{End-members: } A_2A, A_2B, B_2A, B_2B.)\)

We have calculated **energies of formation** of all configurations:

- starting at experimental lattice parameters
- results based on **equilibrium lattice parameters**
Results: Energetics: Ta – V

\[ \Delta E_{\text{Laves-SER}} \text{(kJ.mol}^{-1} \text{ of atoms)} \]

<table>
<thead>
<tr>
<th>composition</th>
<th>Ta\textsubscript{2}Ta</th>
<th>Ta\textsubscript{5}V</th>
<th>Ta\textsubscript{2}V</th>
<th>TaV</th>
<th>TaV\textsubscript{2}</th>
<th>V\textsubscript{2}V</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14</td>
<td>9.35</td>
<td>5.09</td>
<td>46.69</td>
<td>37.59</td>
<td>-11.40</td>
<td>9.82</td>
</tr>
<tr>
<td>C15</td>
<td>10.94</td>
<td>----</td>
<td>48.11</td>
<td>----</td>
<td>-10.18</td>
<td>11.23</td>
</tr>
<tr>
<td>C36</td>
<td>10.15</td>
<td>5.22</td>
<td>47.38</td>
<td>37.30</td>
<td>-10.82</td>
<td>10.42</td>
</tr>
</tbody>
</table>

(Energies for possible three-sublattice model are also calculated here.)

Effect of magnetic order: C15(Cr\textsubscript{2}Cr): \( E_{\text{FM}} - E_{\text{NM}} = -3.01 \text{ kJ.mol}^{-1} \text{ of atoms}, \) (for V\textsubscript{2}V not tested)
(At 0 K – FM - Laves phase is more stable, at room temperature – it is nonmagnetic)

Equilibrium lattice parameters correspond to the experimental ones – nonmagnetic state
Energy differences, between the total energy of Laves phases of various types and SER states (bcc-Ta, bcc-V) calculated in this work and compared with literature data

<table>
<thead>
<tr>
<th>Composition</th>
<th>Energy differences (kJ.mol$^{-1}$of atoms) (vrt. SER)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ta$_2$Ta</td>
</tr>
<tr>
<td>C14 this work</td>
<td>9.35</td>
</tr>
<tr>
<td>C15 this work</td>
<td>10.94</td>
</tr>
<tr>
<td>C36 Ref.</td>
<td>-----</td>
</tr>
<tr>
<td>C36 this work</td>
<td>10.15</td>
</tr>
</tbody>
</table>

Ta-V phase diagram calculation – macroscale level


- Two sublattice model for Laves phases C14 and C15, (C15 most stable at 0 K).

Every Laves phase – 6 assessed (free) parameters
(5 kJ.mol⁻¹ of atoms – guess for Gibbs energy of hypothetical compositions)

Phase equilibrium data:
- Savitskij E.M., Efimov J.V.: Monatsh.Chem. 103 (1972) 270

Thermodynamic data: low temperature heat capacity data only
Thermodynamic models of phases-macroscopic level

BCC: 2 \ 1 \ 3
Liquid: 1 \ 1

Laves_C14: 2 \ 2 \ 1
Laves_C15: 2 \ 2 \ 1

Assignment of lattice sites in models

Sublattice 1 2
Laves_C14 2a 6h (V) 4f
Laves_C15 16d (V) 8a (two sublattice model)

Ab initio values (NEW) for $\Delta H^\circ(T = 0 \text{ K})$ for Ta – V Laves phases C14, C15, (C36) vs. SER phases (all combinations) – not changed in assessment – taken as thermodynamic data!
(Instead of infamous 5 kJ.mol$^{-1}$ !!!)
Parameter values of solution phases: Ta - V (in J.mol⁻¹ of atoms) – adjusted to experimental data

**Ta-V**

[Danon, Servant 2004]

**BCC**

\[ L^0 = 5476.65 \]
\[ L^1 = -16527.68 \]

**Liquid**

\[ L^0 = -3707.72 + 0.285 \times T \]

(Tanaka´s rule for liquid is not fulfilled, but no new experimental data exist.)
Contribution of vibrational heat capacity and vibrational entropy to the Gibbs energy – influence of temperature

\[ G_{L-SER} = \Delta H_o + \int_0^T \Delta C_p \,dT - T \int_0^T (\Delta C_p /dT) \,dT \]

\[ \Delta H_o = E_o^L - E_o^{SER} \quad (0 \text{ K}) \]

\[ \Delta C_p = C_p^L - C_p^{SER} = a + bT \]

\[ G_{L-SER} = \Delta H_o + T(a - b - a \ln T) + (b/2)T^2 \]

(assumption: \( b = 0, \Delta C_p = a \))

\[ G_{L-SER} \approx \Delta H_o + Ta(1 - \ln T) \]

New: ---------------------------------------------

( \( a(T - T \ln T) \) – adjusted for C14)

(\( (a-b)T - aT \ln T + (b/2)T^2 \) – adjusted for C15)
\[ G = \Delta H_0 + T(a - b - a \ln(T)) + (b/2)T^2 \]

\[ G = \Delta H_0 + Ta(1 - \ln(T)) \]

C15 \[ b \neq 0 \]

C14 \[ b = 0 \]
Parameter values of Laves phases (in J.mol$^{-1}$ of comp.)

Ta-V system - 2 sublattices (1:2) for C14 and C15 Laves phases

*adjusted values are in red* - correspond to the contribution of vibrational entropy and vibrational heat capacity

*ab initio calculated values are in blue* – not changed during optimization

C14

\[
\begin{align*}
G(V:V) &= 29448 + 3 \cdot \text{GHSERV} \\
G(Ta:V) &= -34219 -1.57*T + 1.57*T*\ln(T) + 2 \cdot \text{GHSERV} + \text{GHSERTA} \\
G(V:Ta) &= 140061 + 2 \cdot \text{GHSERTA} + \text{GHSERV} \\
G(Ta:Ta) &= 28038 + 3 \cdot \text{GHSERTA} \\
L(Ta:Ta,V;0) &= 14800 \\
L(Ta,V:V;0) &= -4200 \\
\end{align*}
\]

C14 (3-subl.)

\[
\begin{align*}
G(V:V) &= 117792 + 12 \cdot \text{GHSERV} \\
G(V:Ta) &= -136876 -6.19*T +6.19*T*\ln(T) + 4 \cdot \text{GHSERTA} + 8 \cdot \text{GHSERV} \\
G(V:V:Ta) &= 451080 + 6 \cdot \text{GHSERV} + 6 \cdot \text{GHSERTA} \\
G(V:V:Ta) &= 61080 + 10 \cdot \text{GHSERTA} + 2 \cdot \text{GHSERV} \\
L(V:Ta:Ta,V;0) &= 31000 \\
L(V:V, Ta:V;0) &= -9000 \\
\end{align*}
\]

C15

\[
\begin{align*}
G(V:V) &= 33703 + 3 \cdot \text{GHSERV} \\
G(Ta:V) &= -30525 +0.1782*T -0.190*T*\ln(T) +0.0059*T^{**2} + 2 \cdot \text{GHSERV} + \text{GHSERTA} \\
G(V:Ta) &= 144334 + 2 \cdot \text{GHSERTA} + \text{GHSERV} \\
G(Ta:Ta) &= 32815 + 3 \cdot \text{GHSERTA} \\
L(Ta:Ta,V;0) &= 1011 \\
L(Ta,V:V;0) &= -6124 \\
\end{align*}
\]
Assessment results
Ta - V

(Predicted lower limit of C15 stability is about 600 K. C14 – three sublattice model = dashed lines)


Results - calculated thermodynamic data
- prediction

**Ta - V**

\[ E_{\text{form}} = E_{\text{tot}}^{\text{Lav}} - 2E_{\text{tot}}^{\text{V}} - E_{\text{tot}}^{\text{Ta}} \]

C15 (cub.) \(-30.52\) kJ.mol\(^{-1}\)
C14 (hex.) \(-34.22\)

**Ta - V**

\[ \Delta C_{p}^{\text{L-SER}} = C_{p}^{\text{Lav}} - 2C_{p}^{\text{V}} - C_{p}^{\text{Ta}} \]

C15 (cub.) \(-1.57\) J.(mol.K)\(^{-1}\)
C14 (hex.) \(+0.190 + 0.0118*T\)
Conclusions

Energetics

• Ab initio calculations are able to predict the relative stability of the C14 and C15 Laves phases in metallic materials

Phase diagram

Only 3 (4) assessed parameters for Laves phase C14 (C15) type are necessary in reassessed phase diagram

• New: Contribution of heat capacity
  - Term $\Delta C_p^{L-SER}$ at higher temperature stabilises respective structures.
  - C15 is stable at mediate temperatures: $T_{low} - T_{high}$
  - Temperature dependence of $\Delta C_p^{L-SER}$ term is necessary to consider here!!!
  - The origin of this heat capacity is more probably vibrational (not configurational) (adjusted parameters may be calculated from vibrational data)
Thank you for your attention

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