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Experimental and Theoretical Stability Assessment in Mo-rich Mo-Si-B Ternary System

Sungtae Kim[1], Ridwan Sakidja[2] and John H. Perepezko[2]
[1] Sandia National Laboratories
[2] University of Wisconsin - Madison

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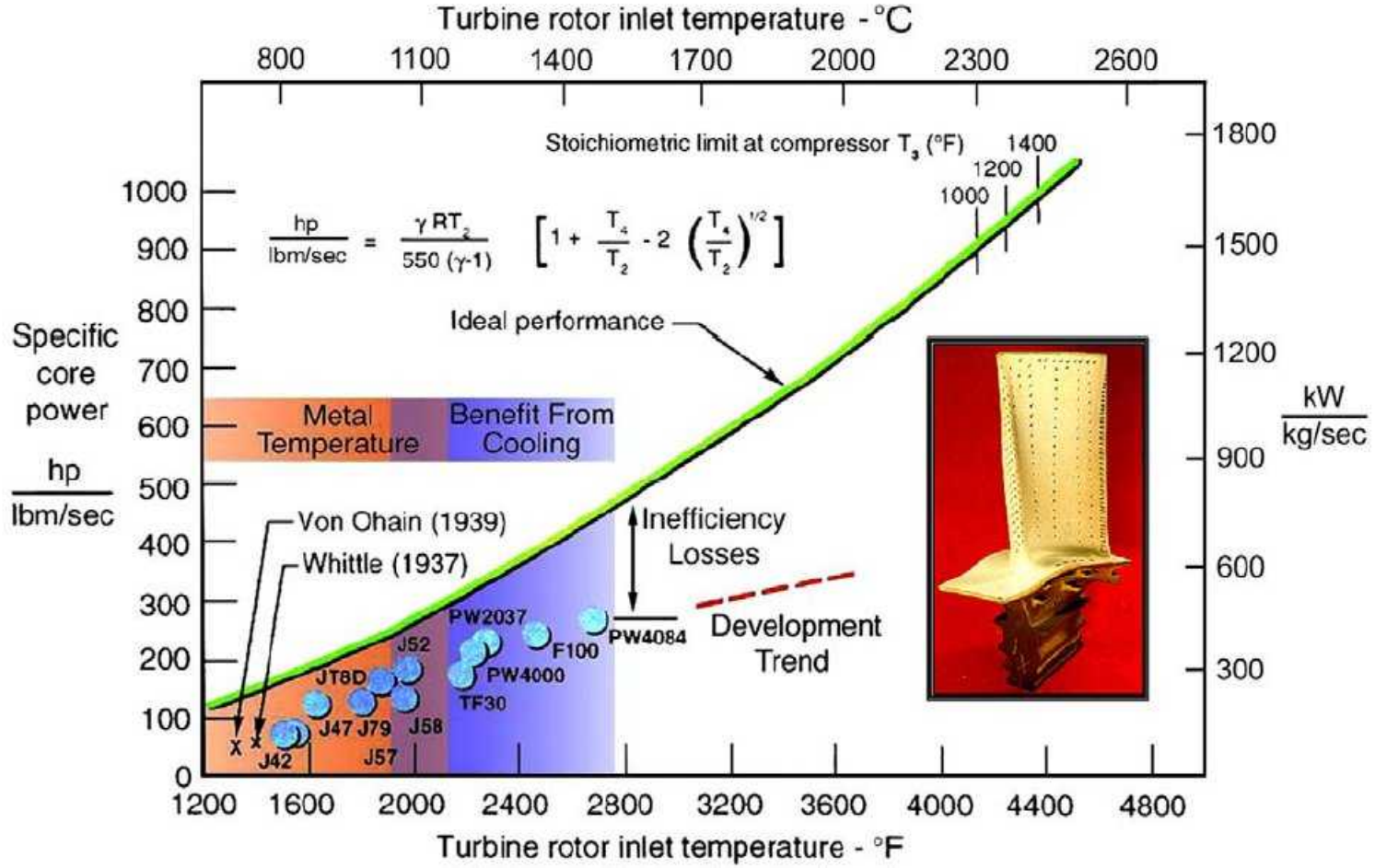
October 7-11, 2012 – Pittsburgh, Pennsylvania

[The Need for High Temperature Structural Materials]



(Dimiduk DM et al. 2003)

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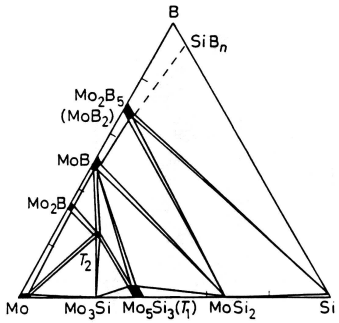
Dimiduk DM, Perepezko JH. MRS Bulletin 2003;28:639

[T_2 stability within the Mo-rich Mo-Si-B region]

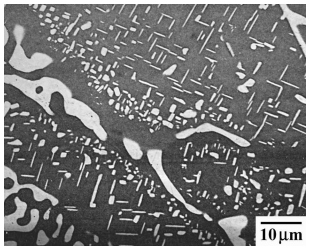
Phase equilibria observations

T_2 phase stability

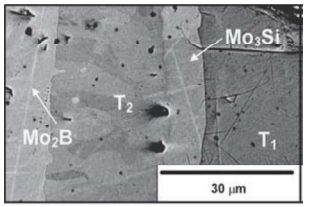
Thermodynamics calculations



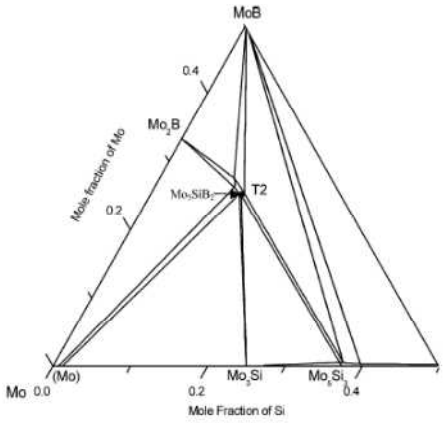
(*Nowotny et al., 1957*)



(*Sakidja et al., 2008*)



(*Kim et al., 2006*)



(*Yang et al., 2005*)

- **Use 2 sub lattice model**
  $(Mo)_{0.625}(B,Si,Va)_{0.375}$
- **Cannot describe at $X_{Mo} < 0.625$**

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Kim S, Perepezko JH. J. Phase Equilibria and Diffusion 2006;27:605

Nowotny H, Dimakopoulou E, Kudielka H. Monatsh Chem 1957;88:180

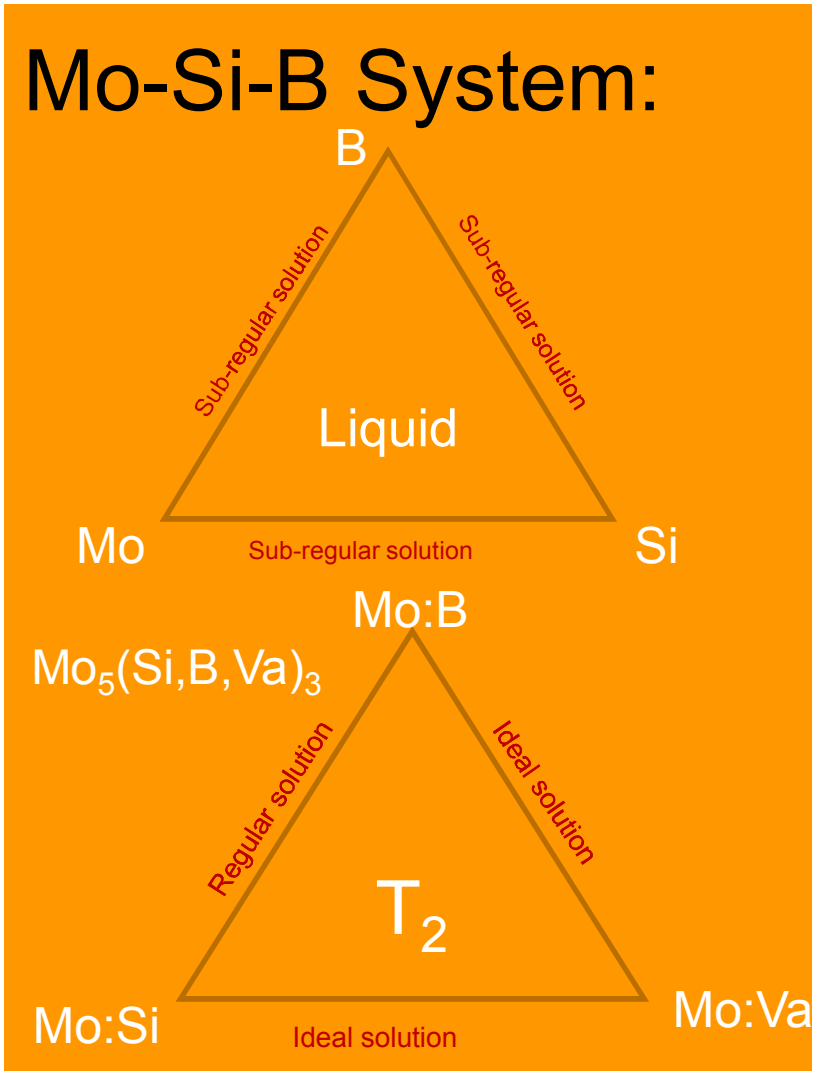
Sakidja R, Perepezko JH, Kim S, Sekido N. Acta Materialia 2008;56:5223

Yang Y, Chang YA. Intermetallics 2005;13:121

OUTLINES

- Current Status of T_2 Phase Stability Presented by Thermodynamic Modeling
- Experimental Determination of T_2 Stability
- Defect-Structure and Thermodynamic Modeling
- Conclusions

Current Status: Limited MoSiB Thermo model



The currently obtained model parameters for the Mo–Si–B system

Phase name	Parameters
Liq	${}^0L^{Liq}_{B,Mo} = -148828.2 + 10.9T$
	${}^1L^{Liq}_{B,Mo} = -17793.3$
	${}^2L^{Liq}_{B,Mo} = 21053.3$
	${}^0L^{Liq}_{B,Mo,Si} = -101753$
	${}^1L^{Liq}_{B,Mo,Si} = -98747.9$
	${}^2L^{Liq}_{B,Mo,Si} = 230563$
Mo_5Si_3 or T1	${}^0G^{Mo_5Si_3}_{Mo:B} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Beta\_rhomb\_B}_{B} = -21678.8 + 0.89T$
	${}^0G^{Mo_5Si_3}_{Si:B} - 0.625\,{}^0G^{Diamond}_{Si} - 0.375\,{}^0G^{Beta\_rhomb\_B}_{B} = 0$
MoB	${}^0G^{\beta MoB}_{Mo:B} - 0.5\,{}^0G^{Bcc\_a2}_{Mo} - 0.5\,{}^0G^{Beta\_rhomb\_B}_{B} = -52017 + 0.21T$
MoB_2	${}^0G^{MoB_2}_{Mo:B} - {}^0G^{Bcc\_a2}_{Mo} - 2\,{}^0G^{Beta\_rhomb\_B}_{B} = -123803 - 1.25T$
	${}^0G^{MoB_2}_{Mo:Va} - {}^0G^{Bcc\_a2}_{Mo} = 13106$
Mo_2B_5	${}^0G^{Mo_2B_5}_{Mo:B} - 2\,{}^0G^{Bcc\_a2}_{Mo} - 5\,{}^0G^{Beta\_rhomb\_B}_{B} = -309004 + 21.36T$
	${}^0G^{Mo_2B_5}_{Mo:Va} - 2\,{}^0G^{Bcc\_a2}_{Mo} = 14545$
MoB_4	${}^0G^{MoB_4}_{Mo:B} - 0.2\,{}^0G^{Bcc\_a2}_{Mo} - 0.8\,{}^0G^{Beta\_rhomb\_B}_{B} = -32984 + 2.97T$
Mo_2B	${}^0G^{Mo_2B}_{Mo:B} - 0.667\,{}^0G^{Bcc\_a2}_{Mo} - 0.333\,{}^0G^{Beta\_rhomb\_B}_{B} = -42176 + 2T$
T2 or (Mo_5SiB_2)	${}^0G^{T2}_{Mo:B} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Beta\_rhomb\_B}_{B} = -34999$
	${}^0G^{T2}_{Mo:Si} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Diamond}_{Si} = -1417$
	${}^0G^{T2}_{Mo:Va} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} = 3827 + T$
	${}^0L^{T2}_{Mo:B,Si} = -103553 + 16T$

(Yang et al., 2005)

Yang Y, Chang YA. Intermetallics 2005;13:121

Current Two Sub-lattice Thermodynamic Model for T_2 Phase

$(Mo,)_{0.625}(B,Si)_{0.375}$

$${}^0G^{T_2}_{Mo:B} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Beta\_rhomb\_B}_{B} = -34999$$

$${}^0G^{T_2}_{Mo:Si} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Diamond}_{Si} = -1417$$

$${}^0L^{T_2}_{Mo:B,Si} = -103552.8 + 16.3T$$

"Mo-poor, B-rich" **"Mo-rich"**

$(B,Mo)_{0.625}(B,Si,Va)_{0.375}$

$${}^0G^{T_2}_{Mo:B} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Beta\_rhomb\_B}_{B} = -34999$$

$${}^0G^{T_2}_{Mo:Si} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} - 0.375\,{}^0G^{Diamond}_{Si} = -1417$$

$${}^0G^{T_2}_{Mo:Va} - 0.625\,{}^0G^{Bcc\_a2}_{Mo} = 1654 + 2T$$

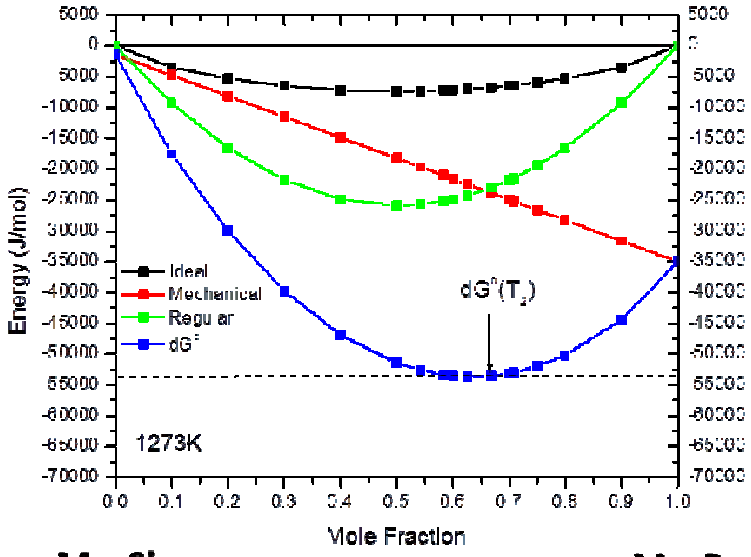
$${}^0G^{T_2}_{B:B} - {}^0G^{Beta\_rhomb\_B}_{B} = 0$$

$${}^0G^{T_2}_{B:Si} - 0.625\,{}^0G^{Beta\_rhomb\_B}_{B} - 0.375\,{}^0G^{Diamond}_{Si} = 0$$

$${}^0G^{T_2}_{B:Va} - 0.625\,{}^0G^{Beta\_rhomb\_B}_{B} = 0$$

$${}^0L^{T_2}_{Mo:B,Si} = 103553 + 16.3T$$

Current Two Sub-lattice Thermodynamic Model for T_2 Phase

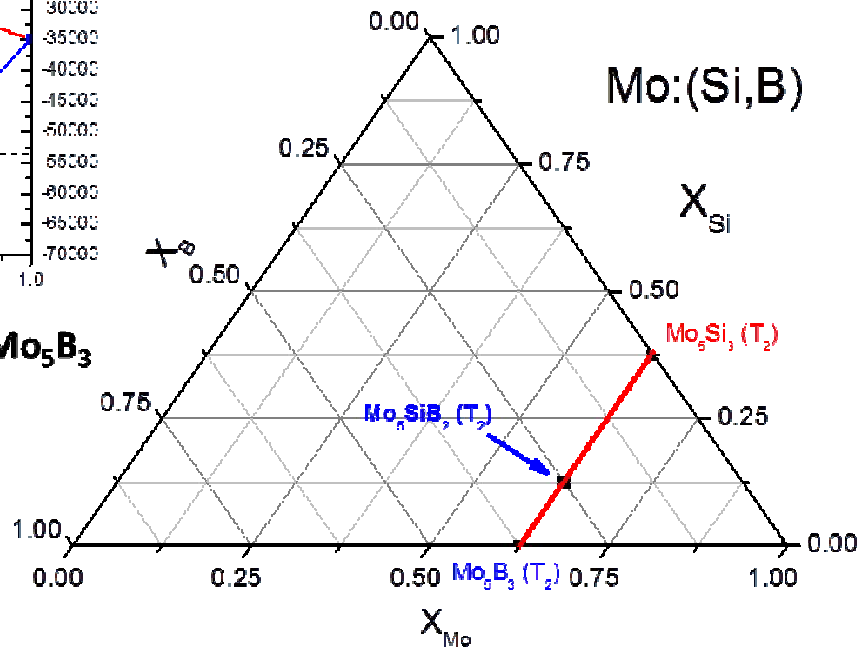


$(Mo,)_{0.625}(B,Si)_{0.375}$

$^{0}G^{T_2}_{Mo:B} - 0.625\,^{0}G^{Bcc\_a2}_{Mo} - 0.375\,^{0}G^{Beta\_rhomb\_B}_{B} = -34999$

$^{0}G^{T_2}_{Mo:Si} - 0.625\,^{0}G^{Bcc\_a2}_{Mo} - 0.375\,^{0}G^{Diamond}_{Si} = -1417$

$^{0}L^{T_2}_{Mo:B,Si} = -103552.8 + 16.3T$



T = 1000 K

$$dG^0(Mo{:}Si,B) = x_{Mo_5Si_3}\,dG^0(Mo_5Si_3) + x_{Mo_5B_3}\,dG^0(Mo_5B_3) + RT\left[x_{Mo_5Si_3}\ln\left(x_{Mo_5Si_3}\right) + x_{Mo_5B_3}\ln\left(x_{Mo_5B_3}\right)\right] + dG^{ex}$$

$$dG^{ex} = x_{Mo_5Si_3}.x_{Mo_5B_3}.(-103552.8 + 16.3T)$$

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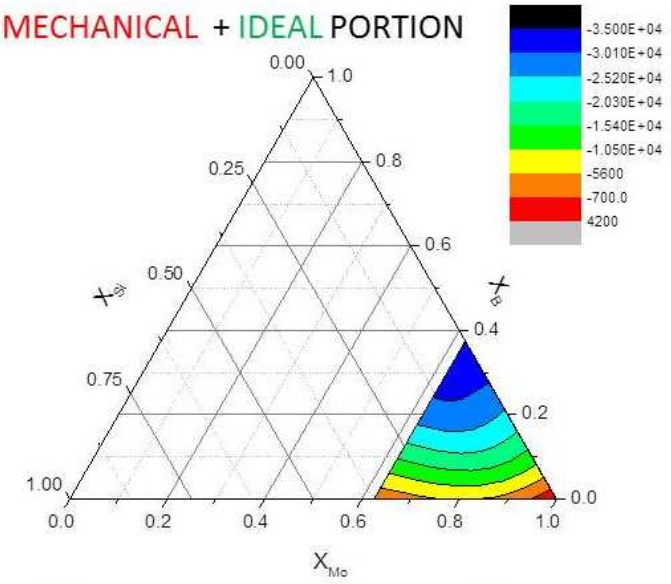
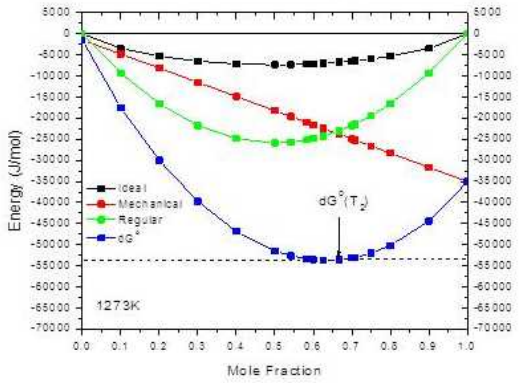
Current Two Sub-lattice Thermodynamic Model for T_2 Phase

"Mo-rich" T_2 Phase

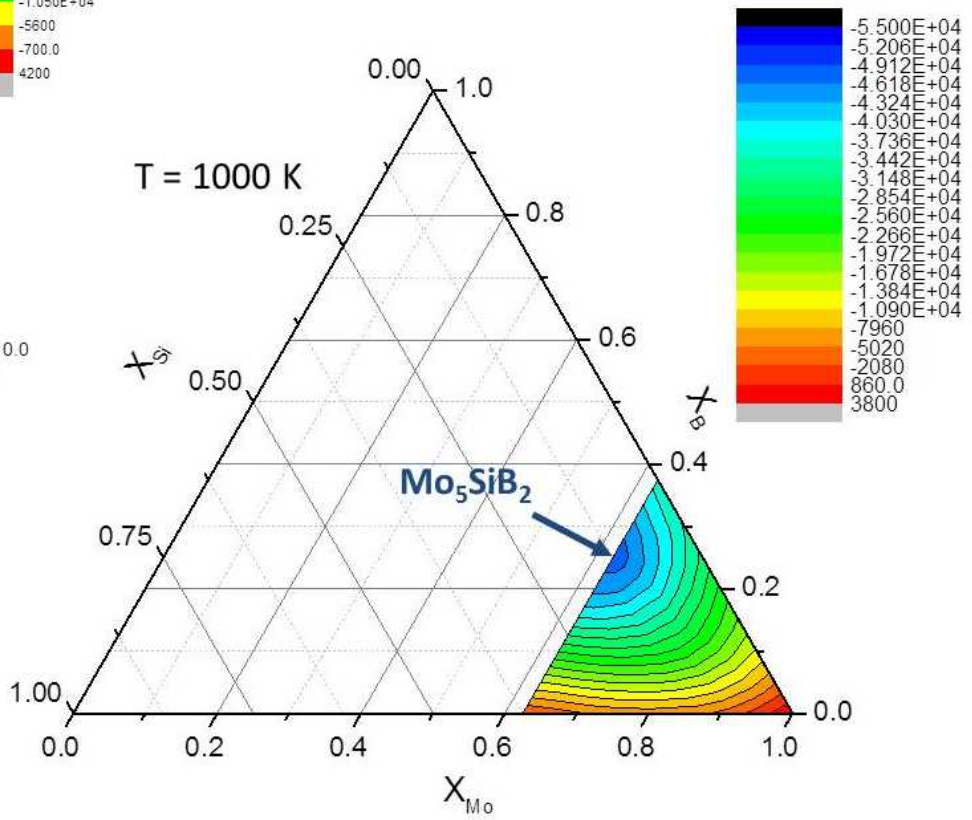
MECHANICAL + IDEAL PORTION





Mo: (B,Si,Va)

MECHANICAL + IDEAL + REGULAR PORTION



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Experimental Determination of T_2 Stability within the Mo-rich Mo-Si-B region

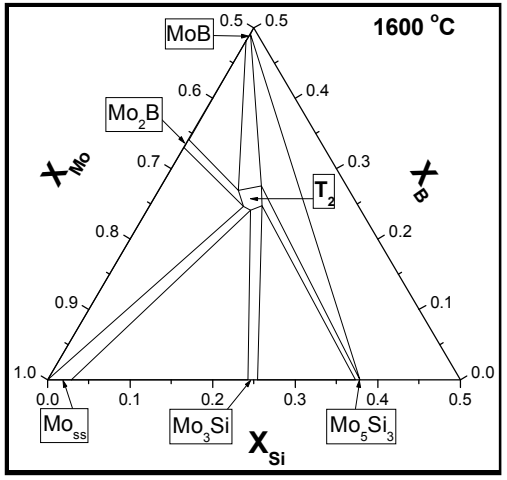
High Temperature Furnace & EPMA

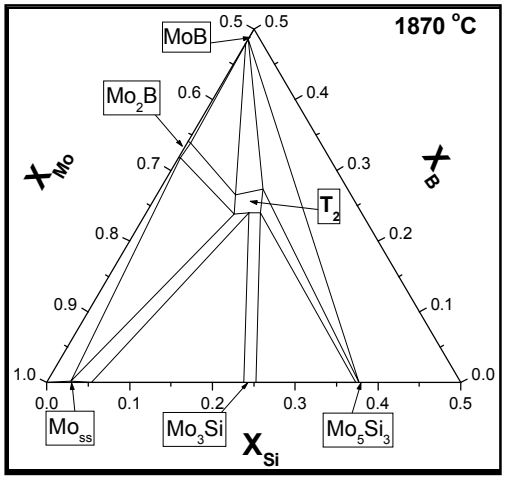
Ultra-high Temperature Furnace with Rapid Quenching Facility (up to 2400°C) (UW-Madison)

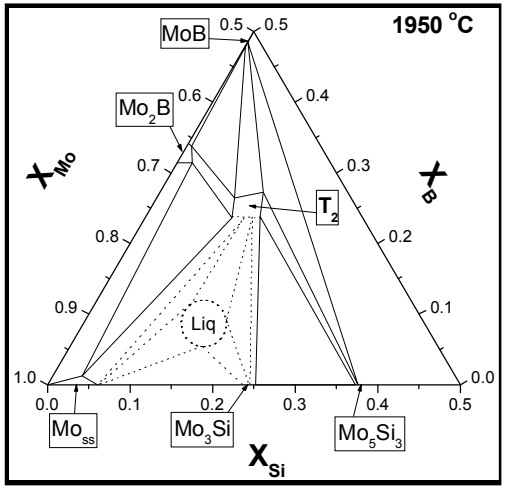
CAMECA SX50 EPMA (UW-Madison)

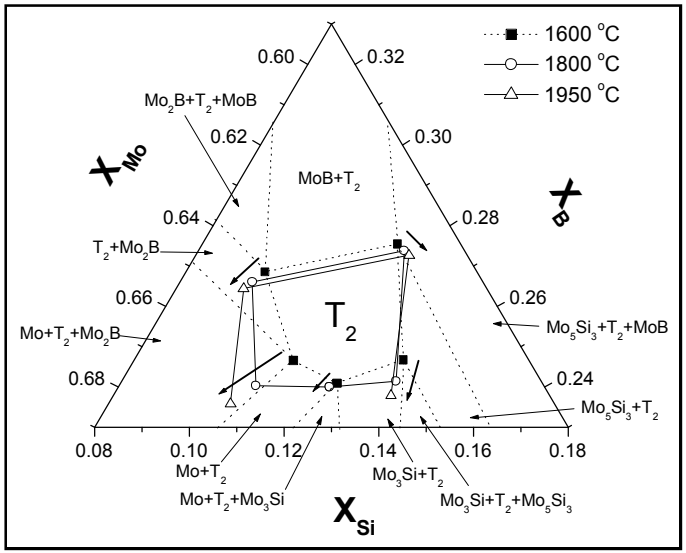
Condition: 7 kV and 20 nA

Experimentally Determined T_2 Stability



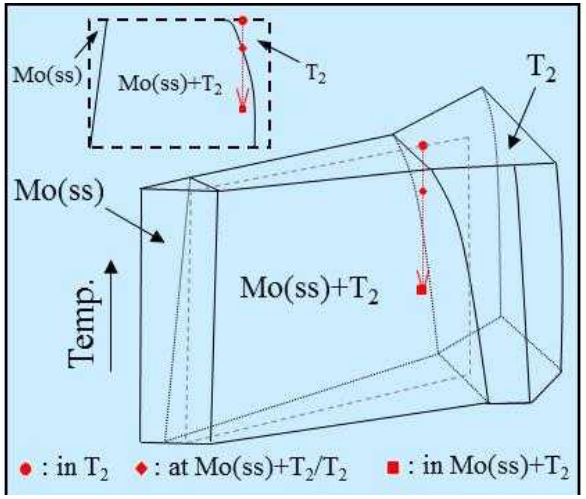


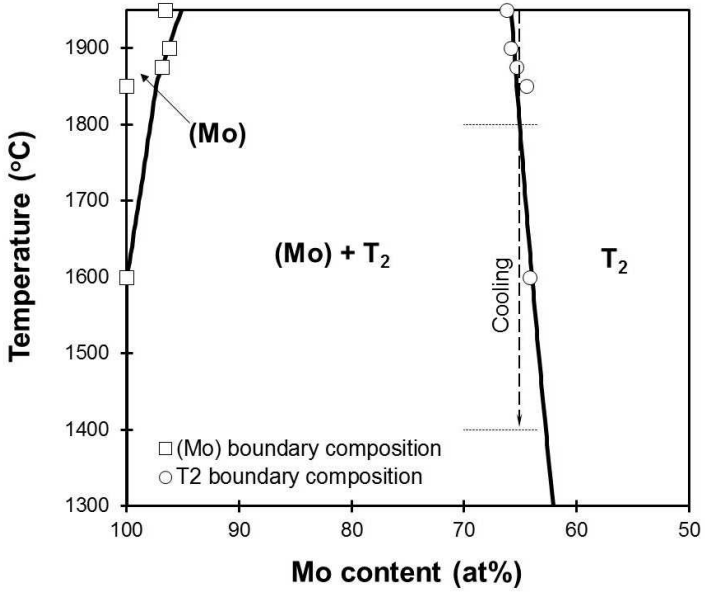




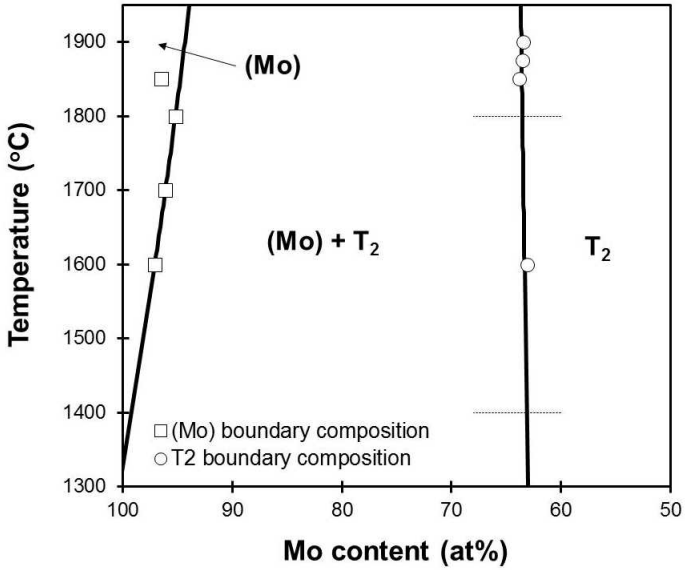
Mo(ss)/T_2+Mo(ss)/T_2 phase boundary

Plethal sections of Mo(ss)+T_2 two phase equilibrium regions are projected. They are projections of sides of (a) the Mo(ss)+T_2+Mo_2B and (b) the Mo(ss)+T_2+Mo_3Si ternary equilibria.



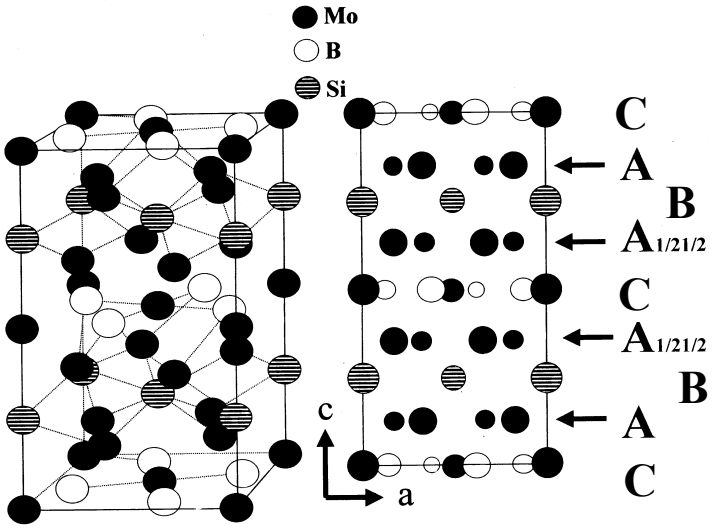


(a) Side of the Mo(ss)+T_2+Mo_2B ternary equilibrium

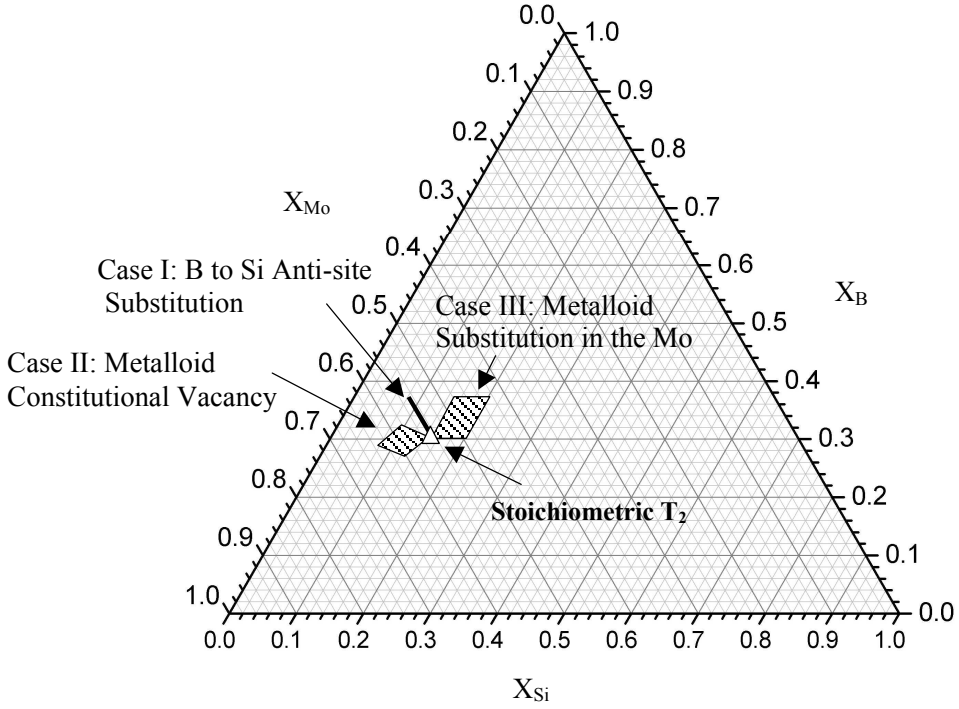


(b) Side of the Mo(ss)+T_2+Mo_3Si ternary equilibrium

Ternary Mo_5SiB_2 (T_2) Defect Structure



	Nearest Neighbors	
Mo1 (A or A1/21/2 layer)	2 B (2.34 Å), 2 Si (2.56 Å), 2 Mo1 (2.72 Å) and 9 Mo2 (2.82-3.18 Å)	
Mo1 (C layer)	4 B (2.38 Å), 2 Si (2.77 Å) and 8 Mo1 (2.72 Å)	
Si (B layer)	2 Mo1 (2.77 Å) and 8 Mo1 (2.56 Å)	
B (C layer)	2 Mo1 (2.38 Å), 6 Mo1 (2.34 Å) and 1 B (2.13 Å)	



Ref.) Aronsson, B. , Acta Chemica Scandinavica, 1958, 12: 31

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Defect-Structure and Thermodynamic Modeling

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Ab initio calculations:

Use of 4 sublattice model:

$$(Mo)_{0.5}(Mo,Si,Va)_{0.125}(Si,B)_{0.125}(B,Si,Va)_{0.25}$$

metastable phases in this model:

$(Mo)_{0.5}(Mo)_{0.125}(Si)_{0.125}(B)_{0.25}$, $(Mo)_{0.5}(Mo)_{0.125}(Si)_{0.125}(Si)_{0.25}$, $(Mo)_{0.5}(Mo)_{0.125}(Si)_{0.125}(Va)_{0.25}$,
$(Mo)_{0.5}(Mo)_{0.125}(B)_{0.125}(B)_{0.25}$, $(Mo)_{0.5}(Mo)_{0.125}(B)_{0.125}(Si)_{0.25}$, $(Mo)_{0.5}(Mo)_{0.125}(B)_{0.125}(Va)_{0.25}$,
$(Mo)_{0.5}(Si)_{0.125}(Si)_{0.125}(B)_{0.25}$, $(Mo)_{0.5}(Si)_{0.125}(Si)_{0.125}(Si)_{0.25}$, $(Mo)_{0.5}(Si)_{0.125}(Si)_{0.125}(Va)_{0.25}$,
$(Mo)_{0.5}(Si)_{0.125}(B)_{0.125}(B)_{0.25}$, $(Mo)_{0.5}(Si)_{0.125}(B)_{0.125}(Si)_{0.25}$, $(Mo)_{0.5}(Si)_{0.125}(B)_{0.125}(Va)_{0.25}$,
$(Mo)_{0.5}(Va)_{0.125}(Si)_{0.125}(B)_{0.25}$, $(Mo)_{0.5}(Va)_{0.125}(Si)_{0.125}(Si)_{0.25}$, $(Mo)_{0.5}(Va)_{0.125}(Si)_{0.125}(Va)_{0.25}$,
$(Mo)_{0.5}(Va)_{0.125}(B)_{0.125}(B)_{0.25}$, $(Mo)_{0.5}(Va)_{0.125}(B)_{0.125}(Si)_{0.25}$, $(Mo)_{0.5}(Va)_{0.125}(B)_{0.125}(Va)_{0.25}$,

ABINIT calculation condition:

GGA pseudopotentials, 4x4x4 k-point

Total energies of Mo(bcc), Si(diamond) and B(β-rhombohedral) were calculated. They were used as the reference states for calculating the formation energies

Ab initio calculations:

Metastable phases	Formation E (J/site mole)	Metastable phases	Formation E (J/site mole)
$(Mo)_{0.5}(Mo)_{0.125}(Si)_{0.125}(B)_{0.25}$	-43017.93	$(Mo)_{0.5}(Si)_{0.125}(B)_{0.125}(B)_{0.25}$	-24205.19
$(Mo)_{0.5}(Mo)_{0.125}(Si)_{0.125}(Si)_{0.25}$	-31423.32	$(Mo)_{0.5}(Si)_{0.125}(B)_{0.125}(Va)_{0.25}$	-2510.52
$(Mo)_{0.5}(Mo)_{0.125}(Si)_{0.125}(Va)_{0.25}$	14128.06	$(Mo)_{0.5}(Va)_{0.125}(Si)_{0.125}(B)_{0.25}$	-14751.03
$(Mo)_{0.5}(Mo)_{0.125}(B)_{0.125}(B)_{0.25}$	-35734.57	$(Mo)_{0.5}(Va)_{0.125}(Si)_{0.125}(Si)_{0.25}$	-15421.23
$(Mo)_{0.5}(Mo)_{0.125}(B)_{0.125}(Si)_{0.25}$	-14599.72	$(Mo)_{0.5}(Va)_{0.125}(Si)_{0.125}(Va)_{0.25}$	28753.62
$(Mo)_{0.5}(Mo)_{0.125}(B)_{0.125}(Va)_{0.25}$	18487.31	$(Mo)_{0.5}(Va)_{0.125}(B)_{0.125}(B)_{0.25}$	-11690.10
$(Mo)_{0.5}(Si)_{0.125}(Si)_{0.125}(B)_{0.25}$	-29041.72	$(Mo)_{0.5}(Va)_{0.125}(B)_{0.125}(Si)_{0.25}$	223.06
$(Mo)_{0.5}(Si)_{0.125}(Si)_{0.125}(Va)_{0.25}$	-3102.03	$(Mo)_{0.5}(Va)_{0.125}(B)_{0.125}(Va)_{0.25}$	22120.65

Up-to-date results table shows that energetically Va is not favored to occupy the B sublattice sites (orange colored cells). Also Mo_{II} sublattice sites are likely to be occupied by Si defect atom rather than Va.

Va

$$(Mo)_{0.5}(Mo,Si,\cancel{Va})_{0.125}(Si,B)_{0.125}(B,Si,\cancel{Va})_{0.25}$$

Conclusions

- T_2 stability within the Mo-rich Mo-Si-B ternary region has been investigated. There have been endeavors to produce the T_2 stability diagram using thermodynamic modeling.
- Several reported thermodynamic models of T_2 use a two sublattice model.
- Crystallographic structure of the T_2 phase presents that it consists of FOUR sublattices: Mo_I, Mo_{II}, Si and B sublattices.
- Four sublattice model has been suggested. Use of ab initio calculations provides the formation energies of metastable phases that are constituent phases inside this model.
- Ab initio calculations also provides the likeliness of atom occupancy on sublattice sites.
- Currently, it is discovered that Vacancy is unlikely to occupy the Mo_{II} and B sublattice sites.