Thermodynamic Modeling of Mo-C-N System

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Introduction

Stainless steel with desired properties can be produced by alloying with appropriate amount of known austentie and ferrite formers. Hence, as a part of stainless-steel alloy design purpose, this thermodynamic modeling was conducted on Molybdenum, Nitrogen and Carbon ternary system.

Properties	Austenitic	Ferritic
Toughness	Very high	Moderate
Ductility	Very high	Moderate
Weldability	Good	Limited
Thermal expansion	High	Moderate
Corrosion resistance	Low	Very high

Ferrite formers	Austenite formers
Fe	Ni
Cr	N
Mo	C
Si	Mn
	Cu

Literature Review

Fig 1. Phase Diagram of Mo-C [1]

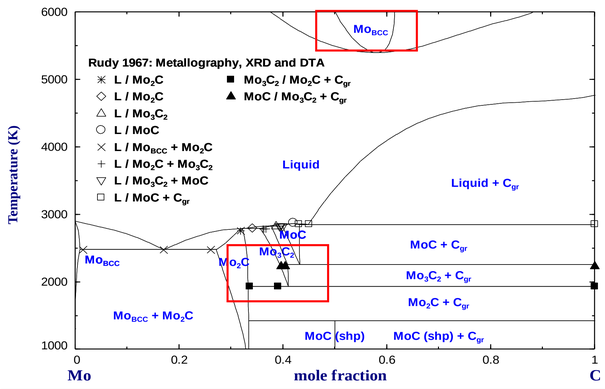
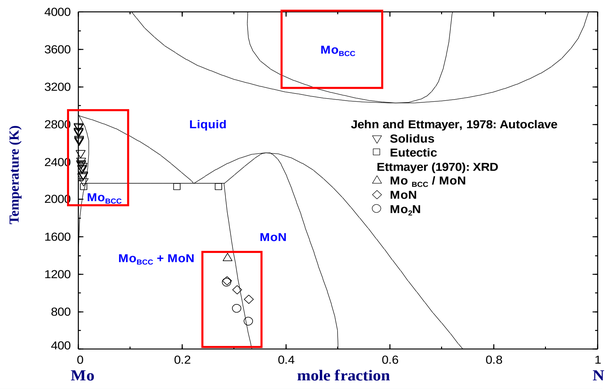


Fig 2. Phase Diagram of Mo-N [2]



Thermodynamic Modeling

Assessments of the FCC Structure

Austenitic (*Cu*)	$(Metal)_1(N, Va)_1$
Carbide and Nitride (*NaCl*)	$(Metal, Va)_1(N, Va)_1$
	$(Metal, Va)_1(C, Va)_1$

Pure Elements and Stoichiometric Compounds :

$$G_T^\circ = H_T^\circ - TS_T^\circ = \Delta H_{298K}^\circ + \int_{298K}^{T} C_P dT - T\left(S_{298K}^\circ + \int_{298K}^{T} \frac{C_P}{T} dT\right)$$

$$where\ C_P = a + bT + cT^{-2} + T\ln T + \cdots$$

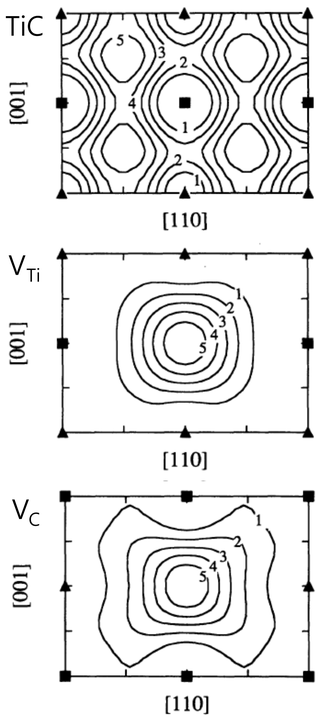
Solid Solution by Compound Energy Formalism [4] :

$$G^{sol} = \gamma_A\gamma_C G_{A:C} + \gamma_A\gamma_D G_{A:D} + \gamma_B\gamma_C G_{B:C} + \gamma_B\gamma_D G_{B:D}$$
$$+pRT(\gamma_A \ln\gamma_A + \gamma_B \ln\gamma_B) + qRT(\gamma_C \ln\gamma_C + \gamma_D \ln\gamma_D)$$
$$+\sum_{i=0,1,2\ldots}\left(\sum_{m=C,D}\gamma_A\gamma_B\gamma_m L_{A,B:m}^i + \sum_{n=A,B}\gamma_n\gamma_C\gamma_D L_{n:,C,D}^i\right)$$

Liquid Solution by Modified Quasi-Chemical Model [5] :

$$G^{liq} = (n_A g_A^\circ + n_B g_B^\circ) + RT[(n_A \ln X_A + n_B \ln X_B)$$
$$+\left[\left(n_{AA}\ln\left(\frac{X_{AA}}{Y_A^2}\right) + n_{BB}\ln\left(\frac{X_{BB}}{Y_B^2}\right) + n_{AA}\ln\left(\frac{X_{AA}}{2Y_AY_B}\right)\right)\right]$$
$$+(n_{AB}/2)[\Delta g_{AB}^\circ + \sum g_{AB}^{i0}X_{AA}^i + \sum g_{AB}^{0j}X_{BB}^j]$$

Fig 3. Positron annihilation spectroscopy [3]



Phase	Model Parameters	
Liquid	$Z_{MoMo}^{Mo} = Z_{NN}^{N} = Z_{CC}^{C} = Z_{MoN}^{Mo} = Z_{MoN}^{N} = 6,$ $Z_{MoC}^{Mo} = 4, \quad Z_{MoC}^{C} = 6$	$\Delta g_{CN} = 125520$ $\Delta g_{MoN} = (-11715 - 9.20T)X_{MoMo}$ $\Delta g_{MoC} = -61504 + 9.10T - 6401X_{CC}$
Mo_{BCC} $(Mo)_1(C,N,Va)_3$ BCC	$G_{Mo:Va}^{BCC} = G_{Mo(BCC)}^\circ$ $G_{Mo:C}^{BCC} = G_{Mo(BCC)}^\circ + 3G_{C(gr)}^\circ + 292880 - 67.09T$ $G_{Mo:N}^{BCC} = G_{Mo(BCC)}^\circ + 3G_{N(BCC)}^\circ + 235082 - 67.99T$	
Mo_2N $(Mo)_2(N,Va)_1$ Tetragonal	$G_{Mo:Va}^{Mo_2N} = 2\cdot G_{Mo(BCC)}^\circ + 43932$ $G_{Mo:N}^{Mo_2N} = 2\cdot G_{Mo(BCC)}^\circ + G_{N(Tet)}^\circ - 83680 + 9.89T$	$L_{Mo:N,Va}^{Mo_2N} = -54601 + 11.72T$
Mo(C,N) $(Mo)_1(C,N,Va)_1$ Hexagonal	$G_{Mo:Va}^{Mo(C,N)} = G_{Mo(HCP)}^\circ + 25400$ $G_{Mo:C}^{Mo(C,N)} = G_{MoC(SHP)}^\circ$ $G_{Mo:N}^{Mo(C,N)} = G_{Mo(HCP)}^\circ + G_{N(HCP)}^\circ - 46500$	$L_{Mo:C,N}^{Mo(C,N)} = -61532$
$Mo_2(C,N)$ $(Mo)_2(C,N,Va)_1$ Hexagonal	$G_{Mo:Va}^{Mo_2(C,N)} = 2\cdot G_{Mo(HCP)}^\circ$ $G_{Mo:C}^{Mo_2(C,N)} = G_{Mo_2C(HCP)}^\circ$ $G_{Mo:N}^{Mo_2(C,N)} = 2\cdot G_{Mo(HCP)}^\circ + G_{N(HCP)}^\circ + 92466$	$L_{Mo:C,Va}^{Mo_2(C,N)} = 3598.24$
$Mo_3(C,N)_2$ $(Mo)_3(C,N,Va)_2$ Hexagonal	$G_{Mo:Va}^{Mo_3(C,N)_2} = 3\cdot G_{Mo(HCP)}^\circ$ $G_{Mo:C}^{Mo_3(C,N)_2} = G_{Mo_2C(HCP)}^\circ + G_{Mo(HCP)}^\circ + G_{C(gr)}^\circ - 14539 - 14.97T$ $G_{Mo:N}^{Mo_3(C,N)_2} = 3\cdot G_{Mo(HCP)}^\circ + 2\cdot G_{N(HCP)}^\circ$	$L_{Mo:C,Va}^{Mo_3(C,N)_2} = -8368$
Mo(C,N) $(Mo,Va)_1(C,N,Va)_1$ FCC	$G_{Mo:Va}^{Mo(C,N)} = G_{Mo(FCC)}^\circ - 4184$ $G_{Mo:C}^{Mo(C,N)} = G_{Mo(FCC)}^\circ + G_{C(gr)}^\circ - 451.397 - 17.54T$ $G_{Va:C}^{Mo(C,N)} = G_{C(gr)}^\circ + 141840$ $G_{Mo:N}^{Mo(C,N)} = G_{Mo(FCC)}^\circ + G_{N(FCC)}^\circ - 72802 + 16.28T$ $G_{Va:N}^{Mo(C,N)} = G_{N(FCC)}^\circ + 83680$	$L_{Mo:C,Va}^{Mo(C,N)} = -123637 + 31.38T$ $L_{Mo:N,Va}^{Mo(C,N)} = -54392 + 12.55T$ $L_{Mo:C,N}^{Mo(C,N)} = 37656$

Results

Fig 4. Mo-C Phase Diagram Comparison

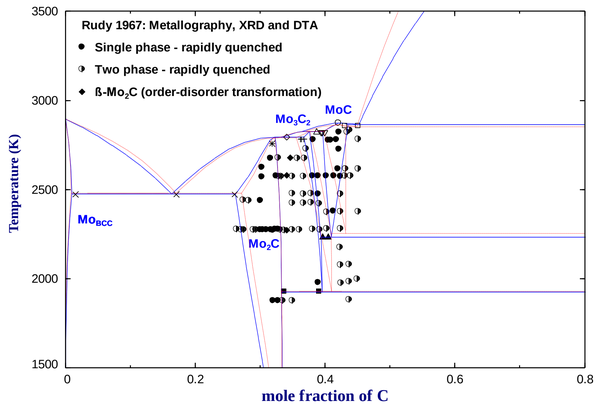


Fig 5. Mo-C Phase Diagram

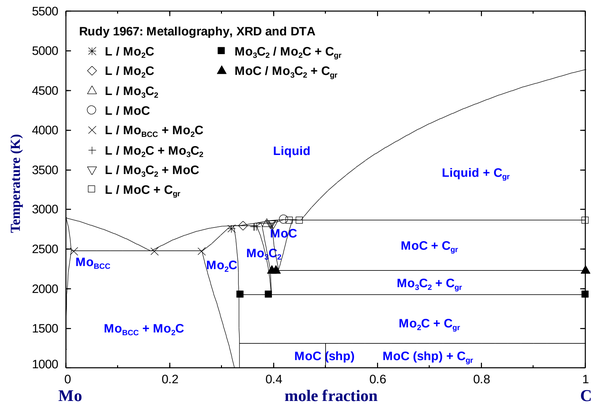


Fig 6. Liquid-BCC-MoN

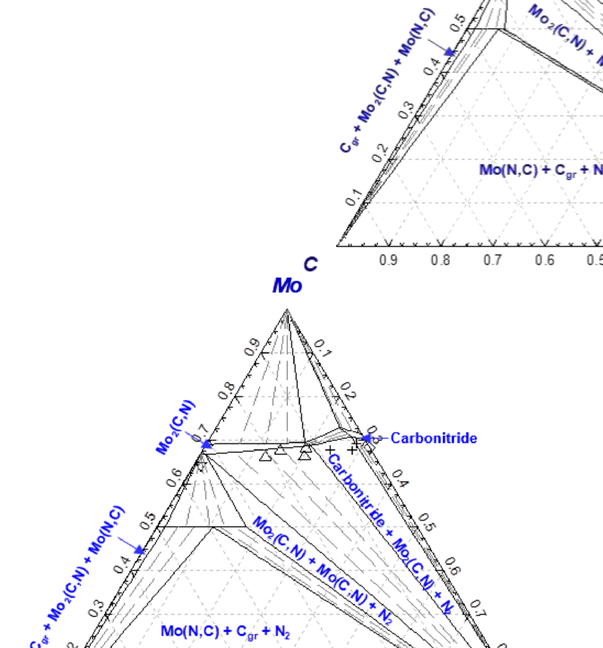
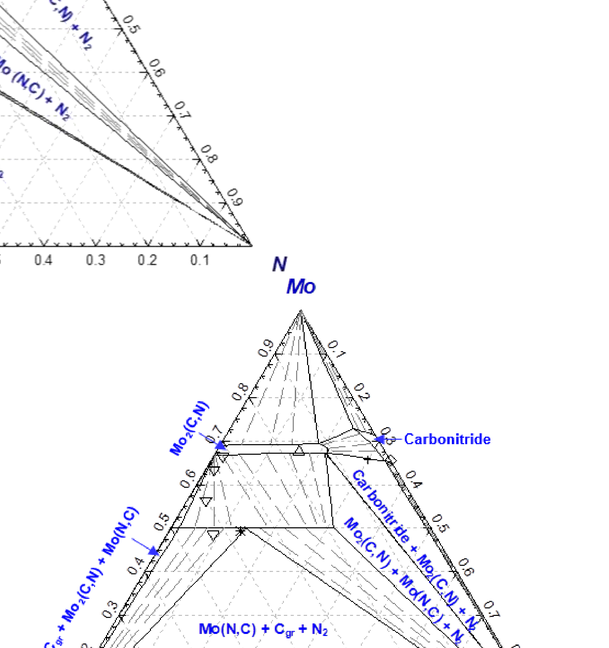


Fig 7. Mo-N Phase Diagram



Conclusion

Thermodynamic assessment of Mo-C, Mo-N and Mo-C-N system based on critical evaluation of the existing experimental results is completed. In future, this study will be integrated into the stainless-steel database which is currently being developed.

Mo-C-N Phase Diagram at 1373 K [6]
1 (top), 30 (left bottom) and 300 (right bottom) atm

References & Acknowledgement

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HYUNDAI STEEL, TATA STEEL, voestalpine, NUCOR, SeAH Besteel, posco, RHI, NIPPON STEEL & SUMITOMO METAL, JFE, DOOSAN Doosan Heavy Industries & Construction, RioTinto, SCHOTT glass made of ideas