

Thermodynamic Assessment of Mo-Ce and Mo-Y Systems

Wren Chan, Michael C. Gao, Ömer N. Doğan, and Paul King

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Molybdenum is a refractory metal that is typically used for high-temperature applications due to its high melting point (2615 °C), high-temperature strength, low thermal-expansion coefficient, and high thermal conductivity. The alloying of rare earth elements to molybdenum can help improve oxidation resistance as well as strengthening the alloy via dispersion strengthening due to formation of rare earth oxides. In this study, two binary systems, Mo-Ce and Mo-Y, were thermodynamically assessed based on limited phase equilibria information available in the literature. Self-consistent thermodynamic descriptions for both systems were obtained using the CALPHAD method.

Keywords CALPHAD, Mo-Ce, Mo-Y, refractory metals

1. Introduction

Refractory metal based alloys are important materials primarily due to their mechanical properties in high-temperature applications. Molybdenum and its alloys (e.g., Mo-Si-B alloys^[1]) are used for high-temperature structural parts because of their high melting point, high-temperature strength, and low thermal-expansion coefficient.^[2] Other applications are “power semi-conductor components and glass-melting electrodes” due to its high thermal/electrical conductivity.^[2] Molybdenum is also widely utilized “as an alloying agent in cast iron, steel, and superalloys to enhance hardenability, strength, toughness, wear- and corrosion-resistance.”^[3] Although further application of molybdenum and its alloys are limited due to brittleness, molybdenum and its alloys with improved ductility have been developed by doping with rare earth oxide (ceria CeO₂, lanthanum oxide La₂O₃ and yttria Y₂O₃).^[2] Therefore, it is important to obtain quantitative thermodynamic descriptions that can be used to assist developing Mo-based alloys for high-temperature applications. In particular, this work provides a thermodynamic assessment for Mo-Ce and Mo-Y binary systems via the CALPHAD (the acronym of calculation of phase diagrams) method. Some analogous systems including Mo-La^[4] and Cr-X^[5] (X = Ce, La, Y) binaries were thermodynamically assessed previously using the CALPHAD approach.

Wren Chan, Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA; **Michael C. Gao**, **Ömer N. Doğan**, and **Paul King**, National Energy Technology Laboratory, 1450 Queen Ave. SW, Albany, OR 97321-2198, USA; **Michael C. Gao**, URS, P.O. Box 618 South Park, PA 15129, USA. Contact e-mail: michael.gao@netl.doe.gov.

2. Literature Information

There is limited literature information available on molybdenum-RE binary phase diagrams. There are no intermetallic compounds in either Mo-Ce or Mo-Y system. The terminal solubilities for both systems are negligible. The lack of terminal solubility and the absence of compound phases indicate repulsive atomic interaction between Mo and the RE elements.

2.1 Mo-Ce System

The terminal phases of the Mo-Ce system are Mo (bcc), βCe (dhcp), γCe (fcc), and δCe (bcc) above room temperature. The currently accepted Mo-Ce phase diagram^[6] (see Fig. 1a) was assessed by Palenzona and Cirafici.^[7] The Mo-Ce system was studied by Savitskii et al.^[8] and Gaume-Mahn and coworkers^[9,10] with brief reviews of the system done by Gschneidner^[11] and Brewer et al.^[12] Gschneidner^[11] quoted a study by Daane and Spedding^[13] that: (1) there are no intermediate phases formed in the system; (2) the solubility of Mo in liquid Ce at 1300 °C is less than 0.2 wt.%. Additional solubility data were determined for temperatures between 800 and 1200 °C for Mo in liquid Ce from 0.0016 at.% to 0.0256 at.% by Gaume-Mahn and coworkers.^[9,10] Both Brewer et al.^[12] and Palenzona and Cirafici^[7] cited a study by Savitskii et al.^[8] who estimated the solubility of Ce in Mo to be between 0.10 and 0.15 at.% at 1450 °C. The phase diagram calculated by Brewer et al.^[12] is based on “thermodynamic equations derived from bonding considerations and consistent with the valence state, promotion energy, enthalpy of vaporization, and molar volume of Ce.”^[7] Utilizing the calculated invariant (monotectic and eutectic) temperature and composition from Brewer et al.,^[12] Palenzona and Cirafici^[7] assessed the currently accepted phase diagram.^[6]

2.2 Mo-Y System

The terminal phases of the Mo-Y system are Mo, αY (hcp), and βY (bcc) above room temperature. The currently

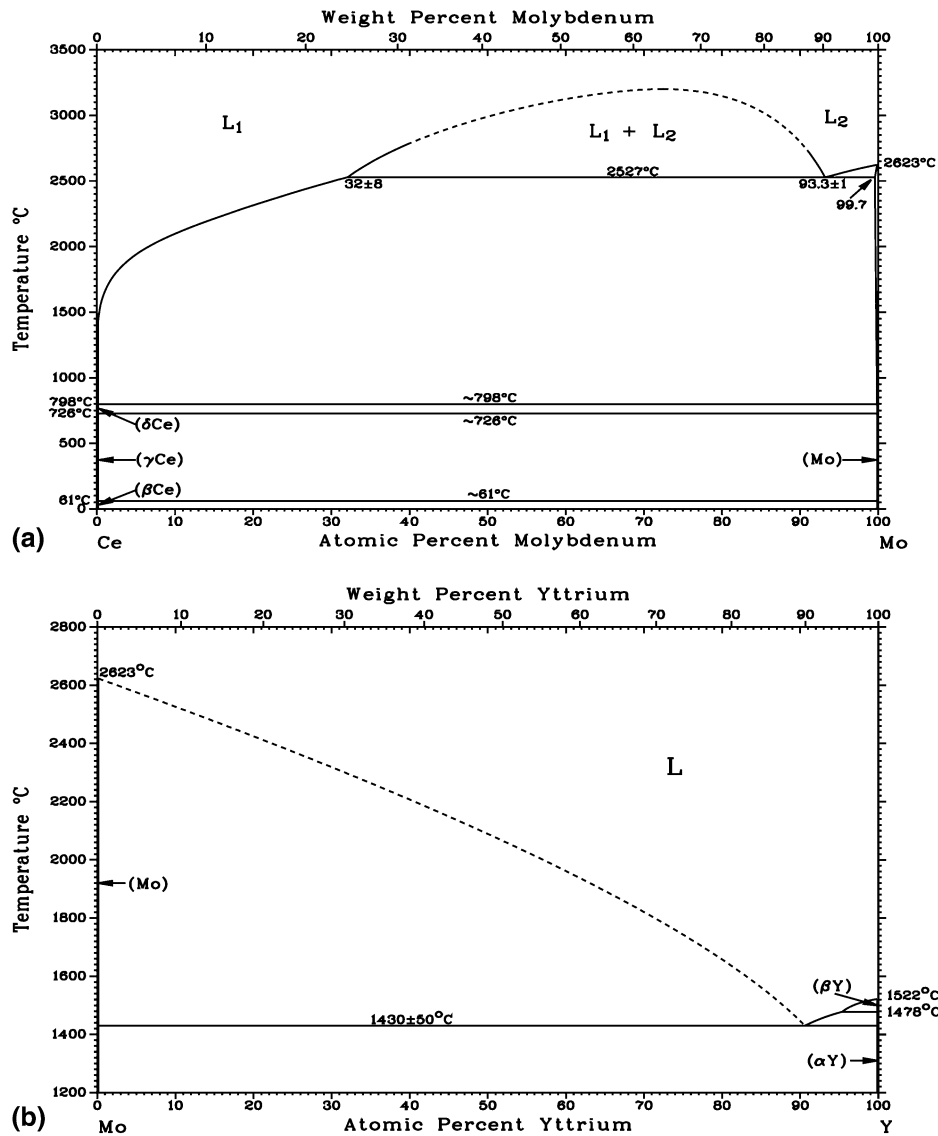


Fig. 1 (a) The Ce-Mo binary phase diagram reviewed by Palenzona and Cirafici,^[6,7] (b) The Mo-Y binary phase diagram reviewed by Brewer and Lamoreaux^[6]

accepted Mo-Y phase diagram^[6] (see Fig. 1b) was calculated by Brewer et al.^[12] The Mo-Y system was studied by Savitskii et al.^[8] and Lundin^[14] with reviews of the system done by Gschneidner^[11] and Brewer et al.^[12] According to Brewer et al.,^[12] Savitskii et al.^[8] determined the solubility of Y in Mo to be between 0.03 and 0.065 at.% at 1450 °C. Another reference by Brewer et al.^[12] reported a solubility of 10^{-4} at.% Y in Mo at 1585 °C. Gschneidner^[11] assessed a diagram determined by Lundin^[14] based on the eutectic invariant equilibrium determined in an experiment with 99.9% pure yttrium (oxygen and nitrogen as major impurities). The purity of the molybdenum was not specified but the eutectic temperature given by Lundin^[14] was 1498 °C which was 4 °C below the adjusted melting

Table 1 Thermodynamic parameters of the Mo-Ce and Mo-Y systems (J/mol of atoms) obtained from the present CALPHAD modeling

Mo-Ce system	Mo-Y system
<i>Liquid</i>	<i>Liquid</i>
${}^0L_{Ce,Mo} = 104,000-20.3T$	${}^0L_{Mo,Y} = 29,700$
${}^1L_{Ce,Mo} = 26,000-17.2T$	${}^1L_{Mo,Y} = -1,500$
${}^2L_{Ce,Mo} = 18,700-7.9T$	
<i>BCC-A2</i>	<i>BCC-A2</i>
${}^0L_{Ce,Mo} = 118,000$	${}^0L_{Mo,Y} = 100,000$
<i>FCC-A1</i>	<i>HCP-A3</i>
${}^0L_{Ce,Mo} = 99,500$	${}^0L_{Mo,Y} = 100,000$

point of yttrium in the study. Gschneidner^[11] believes that the impurities in Y might have affected the eutectic temperature in the same manner as it had affected the melting point (1522 °C). Brewer et al.^[12] calculated a phase diagram with an adjusted eutectic temperature of 1430 °C ± 50 °C from thermodynamic equations similar to those used for the Mo-Ce system.

3. Thermodynamic Models

The Gibbs energy for each element is defined with respect to the enthalpies of its stable state at 298.15 K and 1 atm, referred as standard element reference (SER). In the CALPHAD method, the Gibbs energy of pure elements is

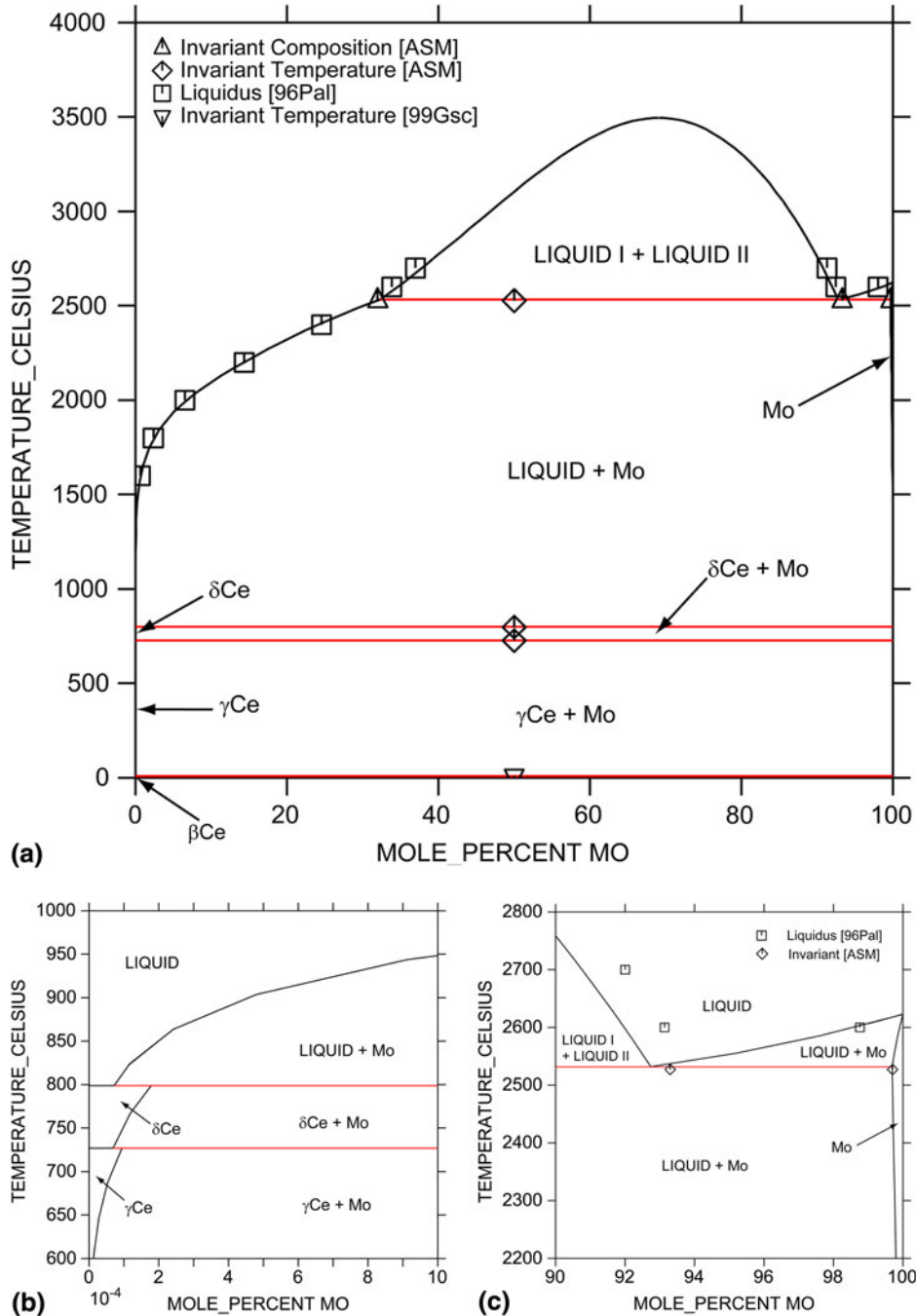


Fig. 2 (a) Calculated Ce-Mo binary phase diagram from the present study in comparison with available experimental points. (b) Enlarged Ce-rich side. (c) Enlarged Mo-rich side

represented as a power series in terms of temperature in the form:

$$G = a + bT + cT \ln(T) + \sum_n d_n T^n, \quad (\text{Eq 1})$$

where a , b , c , and d_n are coefficients and n represents a set of integers typically of the values of 2, 3, and -1 . The thermodynamic data for pure elements are taken from SGTE-PURE-v4^[15] for database compatibility purpose.

The Gibbs energy of individual random substitutional solution phases (e.g., liquid, *bcc*, *fcc*, *hcp*, and *dhcp*) was modeled using a single substitutional sublattice model:

$$G^\Phi = x_{\text{Mo}} {}^\circ G_{\text{Mo}}^\Phi + x_{\text{RE}} {}^\circ G_{\text{RE}}^\Phi + G^{\text{id}} + G_{\text{m}}^{\text{ex}} + G_{\text{m}}^{\text{mag}} \quad (\text{Eq 2})$$

$$G^{\text{id}} = RT[x_{\text{Mo}} \ln x_{\text{Mo}} + x_{\text{RE}} \ln x_{\text{RE}}] \quad (\text{Eq 3})$$

$$G_{\text{m}}^{\text{ex}} = x_{\text{Ce}} x_{\text{Mo}} \sum_{\nu=0}^n {}^\nu L_{\text{Ce,Mo}} (x_{\text{Ce}} - x_{\text{Mo}})^\nu \quad (\text{Eq 4a})$$

$$G_{\text{m}}^{\text{ex}} = x_{\text{Mo}} x_{\text{Y}} \sum_{\nu=0}^n {}^\nu L_{\text{Mo,Y}} (x_{\text{Mo}} - x_{\text{Y}})^\nu \quad (\text{Eq 4b})$$

$${}^\nu L_{\text{Ce,Mo}} = a_\nu + b_\nu T + c_\nu T \ln(T) \quad (\text{Eq 5a})$$

$${}^\nu L_{\text{Mo,Y}} = a_\nu + b_\nu T + c_\nu T \ln(T) \quad (\text{Eq 5b})$$

where RE stands for elements Ce, or Y; ${}^\circ G_{\text{Mo}}^\Phi$ and ${}^\circ G_{\text{RE}}^\Phi$ are the Gibbs energy of the pure elements in the solution phase; G^{id} is the ideal mixing energy; G_{m}^{ex} is the excess energy of the phase using the Redlich–Kister polynomial form^[16]; x_{Ce} , x_{Mo} , x_{Y} , and x_{RE} are the mole fractions of Ce, Mo, Y, and RE; ${}^\nu L_{\text{Ce,Mo}}$ or ${}^\nu L_{\text{Mo,Y}}$ is the binary interaction parameter of Mo and RE elements of an order ν with the coefficients a_ν , b_ν , c_ν to be optimized; R is the gas constant and T is the absolute temperature (K). $G_{\text{m}}^{\text{mag}}$ is the Gibbs energy due to magnetic ordering, but it is set to zero in this study because

of lack of experimental data. In fact, elements Ce, Mo, and Y are all nonmagnetic in the SER states.

4. Thermodynamic Assessment and Discussion

Due to the scarcity of experimental data, the Mo-Ce and Mo-Y binaries were manually optimized mainly based on the currently accepted phase diagrams.^[6] The binary interaction parameters are listed in Table 1. To start the manual optimization for the Mo-Ce, a positive temperature-independent interaction parameter was chosen to reproduce the miscibility gap in the liquid phase. While Mo-Y does not have a miscibility gap in the currently accepted phase diagram,^[6] a smaller positive temperature-independent interaction parameter was found to reproduce the desired liquidus shape. A similar miscibility gap was also applied to the solid phases as Mo and Ce are negligibly soluble in one another even when they are both in the *bcc* phase. Higher-order temperature-independent interaction parameters are added to adjust the symmetry, invariant temperature and composition, and terminal solubility. Emphasis was placed on ensuring that the invariant temperatures were within reasonable range of the accepted phase diagram temperatures (10 °C for monotectic and 5 °C for the other invariant equilibrium unless specified by the diagram). Temperature-dependent interaction parameters (namely b_ν in Eq 5a and 5b) were introduced when using temperature-independent parameters alone (namely a_ν in Eq 5a and 5b) was unsatisfactory in reproducing the phase diagrams.

The calculated Mo-Ce diagram is shown in Fig. 2a, and the calculated composition and temperature for the invariant reactions are listed in Table 2. A reasonable agreement between the currently accepted phase diagram,^[6] and the present study is obtained. Further comparisons between the experimental solubilities of Mo in liquid Ce as given by Gaume-Mahn and coworkers^[9,10] and Daane and Spedding^[13] with presently calculated solubilities are listed in Table 3. The agreement is not satisfactory for the liquidus line in this extremely low Mo concentration region that also has an extremely sharp slope. Optimization attempts were made to gain better agreement in the liquidus for this region by introducing more interaction parameters and assigning more weight to these data sets,^[9,10,13] but it was not possible to fit this region simultaneously and satisfactorily with other

Table 2 Calculated invariant reactions in the Mo-Ce system compared with available literature data

Invariant reactions	T , °C	Mo Concentration, at.%			Reference
$L_2 \leftrightarrow L_1 + \text{Mo}$	2527 ± 10	93.3	32	99.7	[12]
	2527	90.5 ± 1	24 ± 8	99.6	[7]
	2527	90.5 ± 1	32 ± 8	99.6	[6,7]
	2532	92.74	32.35	99.69	This study
$L + \text{Mo} \leftrightarrow \delta\text{Ce}$	798	0.07 ± 0.01	n/a	n/a	[12]
	798	n/a	n/a	n/a	[6,7]
	799	~0	~100	~0	This study
$\delta\text{Ce} + \text{Mo} \leftrightarrow \gamma\text{Ce}$	726	~0	~100	~0	[6]
	727	~0	~100	~0	This study
$\gamma\text{Ce} \leftrightarrow \text{Mo} + \beta\text{Ce}$	61	~0	~100	~0	[6]
	10	n/a	n/a	n/a	[17]
	10	~0	~100	~0	This study

Table 3 Calculated solubility of Mo in liquid Ce for the Mo-Ce system compared with available literature data

Mo concentration, at.%	T , °C	Reference	Calculated Mo concentration, at.%
1.61E-03	800	[9,10]	7.302E-05
3.65E-03	900	[9,10]	4.513E-04
2.19E-02	1100	[9,10]	7.783E-03
2.56E-02	1200	[9,10]	2.423E-02
2.92E-01	1300	[13]	6.548E-02

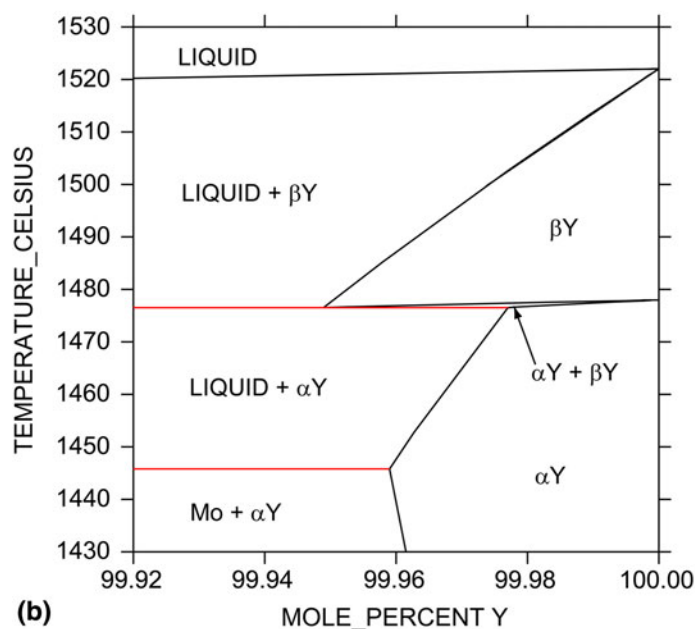
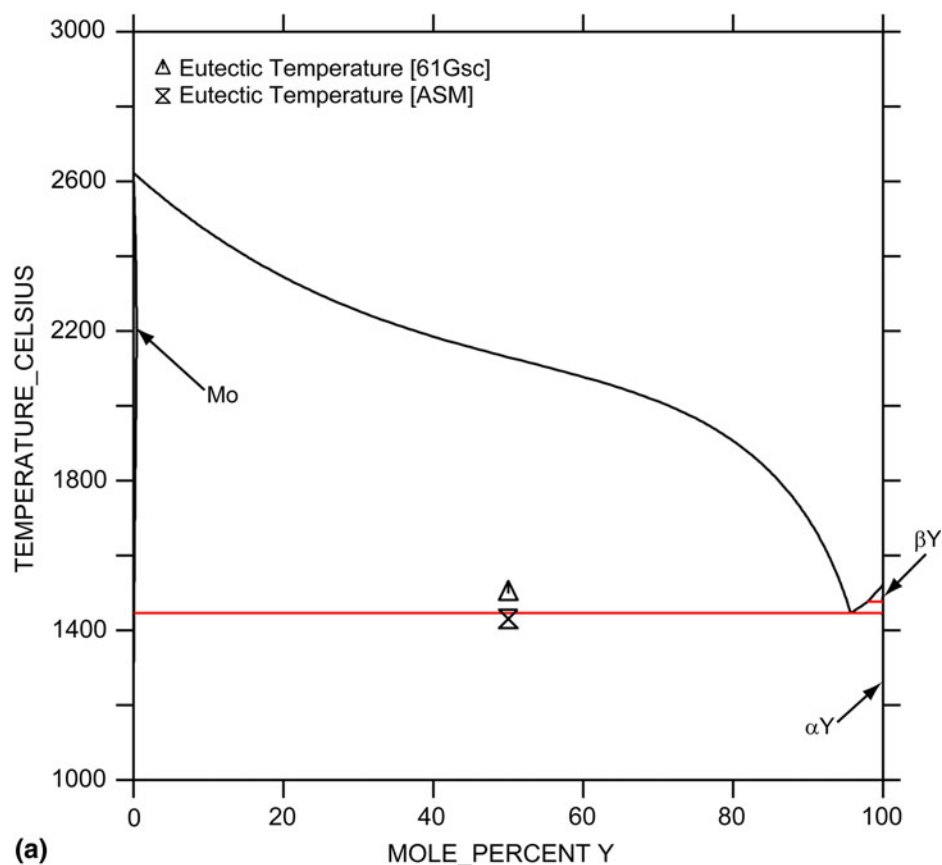


Fig. 3 (a) Calculated Mo-Y binary phase diagram from the present study in comparison with available experimental points. (b) Enlarged Y-rich side

liquidus lines having higher Mo contents, and the invariant temperatures and compositions (i.e., the monotectic reaction and the peritectic reaction on the Ce-rich side). Based on our optimization effort and considering the difficulty and

uncertainty in measuring solubility in the impurity level in liquid such as in this case (0.0016-0.0256 at.% Mo), the data sets^[9,10,13] were assigned low weight during optimization. Nonetheless, the calculated phase diagram in the very

Table 4 Calculated invariant reactions in the Mo-Y system compared with available literature data

Invariant reactions	T, C°	Y concentration, at.%			Reference
$\beta Y \leftrightarrow L + \alpha Y$	1478	n/a	n/a	n/a	[6,12]
	1477	99.95	97.92	99.98	This study
$L \leftrightarrow \alpha Y + Mo$	1498 ± 50	89.72	99.81	< 1.08	[11,14]
	1430 ± 50	~90	~100	~0	[6,12]
	1446	95.69	99.96	0.09	This study

Ce-rich side shown in Fig. 2b appears to be reasonable given the arguments stated above and the fact that there is a lack of experimental data on Mo solubility in γ Ce and δ Ce. However, careful experiments will be helpful in confirming the peritectic reaction ($L + Mo \leftrightarrow \delta$ Ce) and the eutectoid reaction (δ Ce + Mo \leftrightarrow γ Ce) in the very Ce-rich side predicted from the present modeling.

The calculated Mo-rich portion of the Ce-Mo diagram is shown in Fig. 2c. The monotectic temperature and compositions are well reproduced. The calculated solubility of Ce in Mo at 1450 °C from the present study is ~0.021 at.% which is much smaller than the experimental data of ~0.10-0.15 at.%.[8] Attempts were made during the computer optimization process to fit both the invariant reaction and the solubility data set but it was not successful. One possible reason for the inconsistency between the calculations and the experiment is that the samples studied by Savitskii et al.[8] did not reach equilibrium at 1450 °C. Savitskii et al.[8] studied the mechanical effects of the alloying of rare earth metals to cast molybdenum. The samples were vacuum-annealed at 1450 °C for 1 h, and then the microstructure was examined microscopically. They observed a coarsely grained phase with composition of 0.10 at.% Ce and a second phase of 0.15 at.% Ce. It is our opinion that coring might have occurred during synthesis when cooling from the melt and that annealing for 1 h may be too short to homogenize the sample. As a result, Savitskii et al.'s data[8] were assigned a low weight during optimization, and this led to a reasonable number of interaction parameters and a calculated phase diagram that fitted well with the invariant reaction data set and liquidus boundaries.

The calculated Mo-Y diagram as shown in Fig. 3a is a reasonable phase diagram given the uncertainties of the eutectic experiments.[6] As shown in the calculated diagram, the liquidus equilibria behave remarkably similar to the Mo-Sc system,[6] namely lack of a liquid miscibility gap. The composition and temperatures for the invariant reactions are compared in Table 4. The very Y-rich side of the diagram is shown in Fig. 3b. A catatectic reaction of $\beta Y \leftrightarrow L + \alpha Y$ was predicted from the present modeling at 1477 °C. While other types of invariant reaction might be possible (e.g., $L + \beta Y \leftrightarrow \alpha Y$), but there lacks experimental data in the literature. The exact type of this reaction involving L, βY , and αY depends on the reaction temperature with respect to the allotropic transformation temperature of pure Y (1478 °C.[6]) and Mo solubilities in both βY and αY . Future experiments in this regard are very important to confirm the

catatectic reaction predicted in this study. The present modeling predicts that a maximum Y solubility of ~0.43 at.% in Mo occurs at ~2200 °C, and it decreases rapidly as the temperature is lowered. The calculated solubility of Y in Mo at 1450 °C is ~0.087 at.% which disagrees with the reported experimental solubility values of 0.03-0.065 at.%.[8] Similar to the case of Ce-Mo system studied by Savitskii et al.,[8] the sample was only annealed for 1 h, thus equilibrium may not be reached, and the sample remained inhomogeneous. Therefore, their data were assigned a low weight during optimization, and the disagreement is understandable.

Despite the sparse data in the literature, the Mo-Ce and Mo-Y systems were thermodynamically assessed and reasonable agreement with the currently accepted diagrams is obtained.[6] However, additional work would be needed specifically for experimentally confirming the Mo-Ce invariant reactions as they were derived from a thermodynamic model.[12] A more accurate measurement of the Mo-Y eutectic invariant temperature and composition would be extremely beneficial in verifying the calculated invariant reaction.

5. Summary

The available experimental phase equilibria data of Mo-Ce and Mo-Y binary systems are reviewed. Based on limited available experimental data and ASM handbook, a self-consistent thermodynamic description of both systems is obtained by modeling the Gibbs energy of individual phases in the system using the CALPHAD approach. For the Ce-Mo system, a peritectic reaction ($L + Mo \leftrightarrow \delta$ Ce) and a eutectoid reaction (δ Ce + Mo \leftrightarrow γ Ce) in the very Ce-rich side was predicted from the present modeling. For the Mo-Y system, a catatectic reaction of $\beta Y \leftrightarrow L + \alpha Y$ was predicted in the very Y-rich side. Future experiments will be very helpful to confirm these predicted invariant reactions.

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References

1. D.M. Dimiduk and J.H. Perepezko, Mo-Si-B alloys: Developing a Revolutionary Turbine-Engine Material, *MRS Bull.*, 2003, **28**, p 639-645

Section I: Basic and Applied Research

- G.J. Zhang, Y.J. Sun, C. Zuo, J.F. Wei, and J. Sun, Microstructure and Mechanical Properties of Multi-Components Rare Earth Oxide-Doped Molybdenum Alloys, *Mater. Sci. Eng. A*, 2008, **483**, p 350-352
- D.E. Polyak, 2007 Minerals Yearbook—Molybdenum, U.S. Geological Survey, 2009
- C.P. Wang, J. Wang, X.J. Liu, I. Ohnuma, R. Kainuma, and K. Ishida, Thermodynamic Assessment of the Co-La and Mo-La Systems, *J. Alloy Compd.*, 2008, **453**, p 174-179
- W. Chan, M.C. Gao, Ö.N. Doğan, P. King, and A.D. Rollett, Thermodynamic Assessment of Cr-Rare Earth Systems, *J. Phase Equil. Diff.*, 2009, **30**, p 578-586
- T.B. Massalski, P.R. Subramanian, H. Okamoto, and L. Kacprzak, *Binary Alloy Phase Diagrams*, Vol 1–3, 2nd ed., ASM International, Materials Park, OH, 1990
- A. Palenzona and S. Cirafici, The Ce-Mo (Cerium-Molybdenum) System, *J. Phase Equilib.*, 1996, **17**, p 57-59
- E.M. Savitskii, V.V. Baron, and T.T. Tao, Effect of Rare Earth Metals on the Ductility of Cast Molybdenum, *Izv. Akad. Nauk. SSSR. Otd. Tekhn. Nauk, Met. Toplivo*, 1962, **1**, p 156-159
- F. Gaume-Mahn and M. Blanchard, Chimie Minerale—Attaque Du Molybdene Par Le Cerium Liquide, *Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences*, 1962, **254**, p 1082
- F. Gaume-Mahn and C. Madéj, The Rare Earth Metal-Refractory Metal Systems and Their Applications, *Progr. Sci. Technol. Rare Earth*, 1968, **3**, p 515-537
- K.A. Gschneidner, Jr., *Binary Alloy Systems: Rare Earth Alloys*, Nostrand Company, Princeton, NJ, 1961
- L. Brewer, R.H. Lamoreaux, R. Ferro, R. Marazza, and K. Girgis, *Molybdenum: Physico-Chemical Properties of its Compounds and Alloys*, International Atomic Energy Agency, Vienna, 1980
- A.H. Daane and F.H. Spedding, Quarterly Summary Research Report in Chemistry for July, August and September 1954, U.S. At. Energy Comm. ISC-530, 1954
- C.E. Lundin, Rare Earth Metal Phase Diagrams, *Rare Earth Symposium, Annual Meeting*, Am. Soc. Metals, Chicago, 1959
- A. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, 1991, **15**, p 317-425
- O. Redlich and A.T. Kister, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, *Ind. Eng. Chem.*, 1948, **40**, p 345-348
- K.A. Gschneidner, Jr, and V.K. Pecharsky, The Standard State of Cerium, *J. Phase Equilib.*, 1999, **20**, p 612-614