

Thermodynamic Assessment of Cr-Rare Earth Systems

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

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Addition of light rare earth elements in small amounts to refractory metal based alloys (e.g., Cr) can increase both ductility and creep resistance of an alloy because the additives absorb residual oxygen in the alloy by forming oxides that can serve as dispersion strengtheners. In this work, three binary systems, Cr-Ce, Cr-La and Cr-Y, were thermodynamically assessed based on limited experimental data available in the literature using the CALPHAD method. Self-consistent and reasonable thermodynamic descriptions for all three systems were obtained. More importantly, two predictions are made: a peritectic reaction in the La-rich side of Cr-La system and a catactetic reaction in the Y-rich side of Cr-Y system. These predictions and the developed databases are subject to future experiments that are needed to clarify several discrepancies in these binaries.

Keywords CALPHAD, Cr-Ce, Cr-La, Cr-Y, high temperature alloys

1. Introduction

Refractory metal¹¹ based alloys are of great importance due to their usefulness in ultra-high temperature applications. Chromium is of particular interest due to “good oxidation resistance, low density (20% less than most nickel-based superalloys) and high thermal conductivity (two to four times higher than most superalloys)”.^[1] While efforts were made from the late 1940s to early 1970s to develop chromium-based alloys, two major mechanical disadvantages of chromium have hindered commercial exploitation of Cr alloys as major structural materials at high temperatures. These disadvantages are high ductile-to-brittle transition temperature (DBTT is about 150 °C for unalloyed recrystallized chromium of commercial purity^[1]) and embrittlement in high-temperature environment due to oxidation and subscale nitridation. Creep strength is also of particular concern when chromium is intended for use as vanes or blades in gas-turbine engines especially due to the very low creep resistance of pure chromium.^[1] Theoretical prediction using first principles calculations^[2] showed that alloying with substitutional elements can improve the intrinsic ductility of Cr at low temperatures. On the other

¹Refractory metals commonly refer to V, Cr, Zr, Nb, Mo, Ru, Hf, Ta, W, Re, Os and Ir.

Wren Chan and Anthony D. Rollett, Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15289; Michael C. Gao, Ömer N. Doğan, and Paul King, National Energy Technology Laboratory, 1450 Queen Ave SW, Albany, OR 97321; Michael C. Gao, Parsons, P.O. Box 618, South Park, PA 15129. Contact e-mail: michael.gao@netl.doe.gov.

hand, Cr is very sensitive to oxygen content in the alloy and thus the ductility can be further enhanced by lowering the oxygen content through addition of minor amounts of light rare earth elements including Y, Ce and La.^[3] Such addition results in formation of very stable oxides that also act as dispersion strengtheners. Both the slow diffusivities of rare earth elements due to their large atomic sizes and dispersion strengthening effect from oxides increase the creep resistance of Cr alloys. Therefore, it is important to investigate the Cr-rare earth binary phase diagrams and to obtain their quantitative thermodynamic descriptions that can be used for process control, microstructure optimization and kinetics simulations. In particular, this work concerns the thermodynamic assessment of three binary systems via CALPHAD (the acronym of calculation of phase diagram) method: Cr-Ce, Cr-La and Cr-Y. It constitutes a small part of a large project that concerns developing refractory metal based alloys for advanced fossil energy applications at the National Energy Technology Laboratory.

2. Literature Information

Much of the work done with chromium binary phase diagrams^[4,5] appear to deal extensively with the composition and temperature of the liquidus and solidus equilibria of the chromium-rich end. There are no compounds formed in all three binaries,^[4,5] indicating that the atomic interaction between Cr and rare earth elements are largely repulsive. The terminal solubility in all three systems is either negligible or very limited.^[4,5] One major concern of Cr-related phase diagrams is the accuracy of the melting point of pure Cr. High vapor pressure of Cr contributes to major difficulties in experiments. The widely perceived melting point of chromium is 1863 °C and is reported in most materials handbooks.^[4,5] But, it is assessed as 1907 °C in the Scientific Group Thermodata Europe (SGTE) database^[6] and CRC Handbook of Chemistry and Physics.^[7]

The scattering in data for its melting point was also addressed in earlier reports^[8,9] but remains unresolved even today. For the sake of database compatibility (since most Cr-containing systems adopted SGTE database for CALPHAD type modeling) and the uncertainty in its melting point, the thermodynamic data of pure elements are taken from SGTE database and the melting point of Cr is treated as 1907 °C in the present study.

2.1 Cr-Ce System

The terminal phases of the Cr-Ce system are β Ce (dhcp), γ Ce (fcc), δ Ce (bcc) and Cr (bcc) above room temperature.^[4] This system was experimentally studied by Savitskii et al.^[10] and Kobzenko et al.,^[11] and the data are largely restricted to Cr-rich solid-liquid equilibrium, the monotectic temperature and composition, and the eutectic temperature. The experimental methods reported by Savitskii et al.^[10] were electronic chromatic pyrometry (liquidus equilibria), Pironi's drop method (solidus equilibria), photomicroscopy (solubility) and thermal analysis (eutectic data point). Data from Kobzenko et al.^[11] show appreciable scatter in temperatures of both solidus and liquidus equilibria ranging from 1790 to 1820 °C. The monotectic temperature is 1780 ± 10 °C and the composition approximately 95.15 at.% Cr^[4] while the solubility of Ce in Cr ranges from 0.56-0.75 at.% to 2.72 at.%.^[10] The eutectic temperature was determined to be 780 °C based on thermal analysis of cerium-rich alloys.^[10] The phase diagram provided by Savitskii et al.^[10] also includes points corresponding to phase stability values of Cr and the two phase region (Cr + Liquid). From 715 to 785 °C, δ Ce and Cr are relatively immiscible in each other with some solubility of Cr in δ Ce and little solubility of Ce in Cr. According to Massalski et al.,^[4] a eutectic reaction: Liquid \leftrightarrow Cr + δ Ce occurs at 785 °C at around 5 at.% Cr and a eutectoid reaction: δ Ce \leftrightarrow Cr + γ Ce occurs at 715 °C at around 1 at.% Cr.

2.2 Cr-La System

The terminal phases of the Cr-La system are Cr, α La (dhcp), β La (fcc) and γ La (bcc).^[4] Available experimental data from Savitskii et al.^[12] include a few points on the Cr-rich solidus equilibria, the monotectic temperature and composition, the eutectic temperature, and the eutectoid temperature. The experimental methods reported by Savitskii et al.^[12] were optical microscopy (solubility), drop method (solidus equilibria) and thermal analysis (invariant equilibrium). Savitskii et al.^[12] reported that the monotectic temperature is 1710 °C, but it is considered inaccurate by the currently accepted phase diagram^[4] that uses 1830 °C instead. Therefore, the latter is adopted in this study. Savitskii et al.^[12,13] also reported that the maximum solubility of La in Cr is around 2.54 at.%^[12] and the maximum solubility of Cr in La is 0.57 at.%.^[12]

On the La-rich side, the handbook^[4] presents a four-phase equilibrium at 865 °C (i.e., liquid, Cr, γ La, and β La) which contradicts the Gibbs phase rule (see Fig. 1). The polymorphic transformation of pure La (i.e. γ La \leftrightarrow β La)

occurs at 865 °C.^[4] A eutectic reaction is reported by Savitskii et al.^[12] that occurs at $865 \text{ °C} \pm 5 \text{ °C}$,^[12] and it is presumed to be $L \leftrightarrow Cr + \gamma La$, while Gschneider^[13] assessed it at 900 °C instead. However, the handbook^[4] assessed this eutectic reaction as $L \leftrightarrow Cr + \beta La$ at 865 °C. Another invariant reaction is reported at around 705 °C by Savitskii et al.^[12] whose reaction type is presumed to be eutectoid ($\gamma La \leftrightarrow Cr + \beta La$), while Gschneider^[13] assessed it at 730 °C instead. However, this eutectoid reaction is not accepted in the handbook.^[4] Clearly there must be an invariant reaction that involves γLa and βLa in Cr-La system whose reaction type could be eutectoid, peritectic or others, but there is a lack of convincing experiments to confirm the type, temperature and compositions. Based on current thermodynamic calculations (see the results section), we think it is likely peritectic. For a clear presentation, two schematic equilibrium configurations in the La rich side are shown in Fig. 1. The first one involves a eutectic reaction ($L \leftrightarrow Cr + \gamma La$) and a eutectoid reaction ($\gamma La \leftrightarrow Cr + \beta La$). The other involves a peritectic reaction ($L + \gamma La \leftrightarrow \beta La$) and a eutectic reaction ($L \leftrightarrow Cr + \beta La$).

2.3 Cr-Y System

The terminal phases of the Cr-Y system are Cr, α Y (hcp) and β Y (bcc).^[4] Available experimental data for this system by Terekhova et al.^[14] is largely restricted to the Cr-rich solidus and liquidus equilibrium, the monotectic temperature and composition and eutectic composition. The experimental methods by Terekhova et al.^[14] were drop method under helium (solidus), optical pyrometry (solidus), photomicroscopy (solubility), microhardness analysis (solubility) and thermo-e.m.f. (solubility). An investigation of Cr-Y system by Venkatraman and Neumann^[15] proposed two possible phase diagrams: one without a miscibility gap and one with a miscibility gap in addition to reviewing and citing some experimental literature that are at present difficult to retrieve. According to Terekhova et al.,^[14] the monotectic temperature is $1760 \text{ °C} \pm 25 \text{ °C}$, monotectic composition is at 9.36 at.% Y, eutectic temperature is $1315 \text{ °C} \pm 7 \text{ °C}$ and eutectic composition is at 79.65 at.% Y.

They further determined the solidus of β Y solid solution using the drop method under helium, and the maximum Cr solubility in β Y is about 0.59 at.%. However, the phase diagram with a miscibility gap by Venkatraman and Neumann^[15] suggests that the eutectic temperature is $1330 \text{ °C} \pm 25 \text{ °C}$ with a eutectic composition of 80 at.% Y. As the article^[5] referenced by Venkatraman and Neumann^[15] to support the eutectic values is difficult to obtain, it is not possible to confirm the composition or temperature. Citing several literature references, Venkatraman and Neumann^[15] suggest the extent of maximum solubility of Cr in Y to be 0.7 at.% Cr and maximum solubility of Y in Cr to be less than 1 at. %. However, Taylor et al.^[16] measured the lattice constants of Cr and Cr₇₅Y₂₅ alloys using x-ray diffraction and they concluded that the Y solubility in Cr is less than 1 ppm. The same conclusion was drawn as to Y solubility in other refractory metals they studied (i.e. W, Ta, Mo and Nb).^[16]

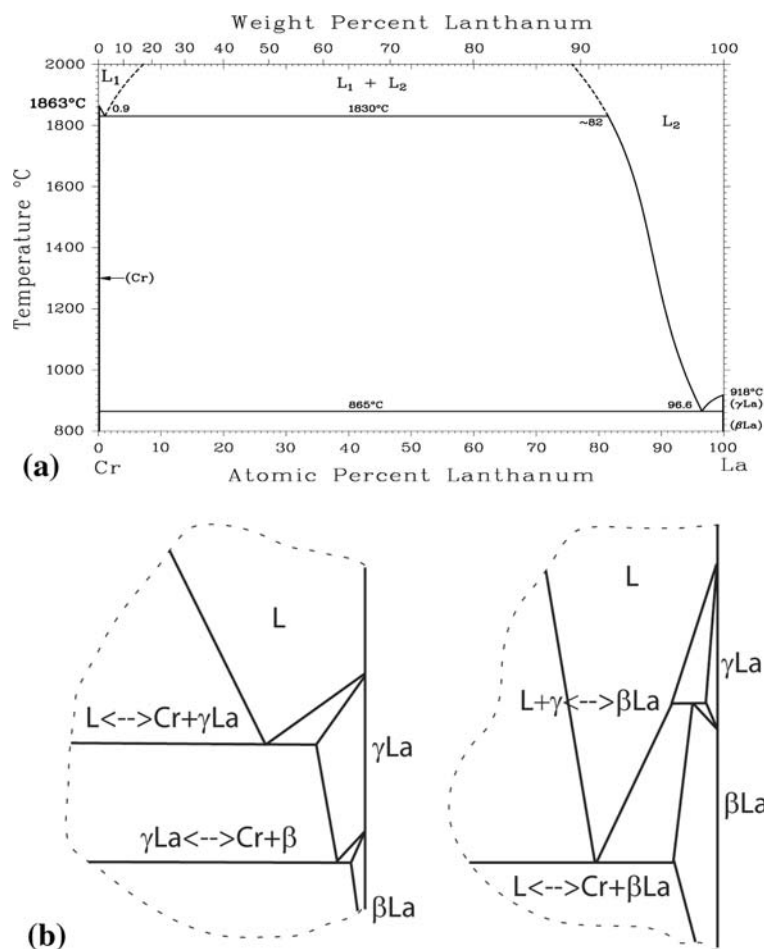


Fig. 1 (a) The Cr-La phase diagram assessed in the handbook.^[4] (b) Two possible phase equilibrium configurations in the La-rich side

3. Thermodynamic Models

The Gibbs energy for each element is defined with respect to its stable state at 298.15 K and 1 atm. In the CALPHAD method, the Gibbs energy of pure elements is 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^[6] for database compatibility purpose. The authors noticed that SGTE-Pure v4^[6] treats the polymorphic transformation temperature of $\gamma\text{Ce} \leftrightarrow \beta\text{Ce}$ at 10 °C, which is based on a 20-year experimental study by Gschneider and Pecharsky^[17] who discovered that γCe is the true standard state of elemental Ce. On the other hand, SGTE-SSOL4 v4 estimates the $\gamma\text{Ce} \leftrightarrow \beta\text{Ce}$ equilibrium temperature to be 61 °C and treats βCe as the standard state. According to Massalski et al.,^[4] the $\gamma\text{Ce} \leftrightarrow \beta\text{Ce}$ transformation temperature is 139 °C on heating and -16 °C on cooling. It appears that the SGTE-SSOL4 database takes the average

Table 1 Thermodynamic parameters of the Cr-X (X = Ce, La, Y) systems (J/mol of atoms) optimized in the present study

Cr-Ce system	Cr-La system	Cr-Y system
Liquid	Liquid	Liquid
${}^0L_{\text{Ce,Cr}} = 33900$	${}^0L_{\text{Cr,La}} = 39000$	${}^0L_{\text{Cr,Y}} = 32000$
${}^1L_{\text{Ce,Cr}} = -10646$	${}^1L_{\text{Cr,La}} = 14000$	${}^1L_{\text{Cr,Y}} = 8500$
${}^2L_{\text{Ce,Cr}} = -3549$	${}^2L_{\text{Cr,La}} = -5000$	
BCC-A2	BCC-A2	BCC-A2
${}^0L_{\text{Ce,Cr}} = 29434$	${}^0L_{\text{Cr,La}} = 40000$	${}^0L_{\text{Cr,Y}} = 69000$
${}^1L_{\text{Ce,Cr}} = -11304$	${}^2L_{\text{Cr,La}} = 25000$	${}^1L_{\text{Cr,Y}} = -14000$
${}^2L_{\text{Ce,Cr}} = 20351$		
FCC-A1	FCC-A1	HCP-A3
${}^0L_{\text{Ce,Cr}} = 52594$	${}^0L_{\text{Cr,La}} = 20000$	${}^0L_{\text{Cr,Y}} = 63000$
${}^1L_{\text{Ce,Cr}} = -18794$	${}^2L_{\text{Cr,La}} = 25000$	

temperature at 61 °C. Therefore, the data for Ce from SGTE-Pure v4^[6] is more accurate and thus is used for optimizing Ce-Cr system.

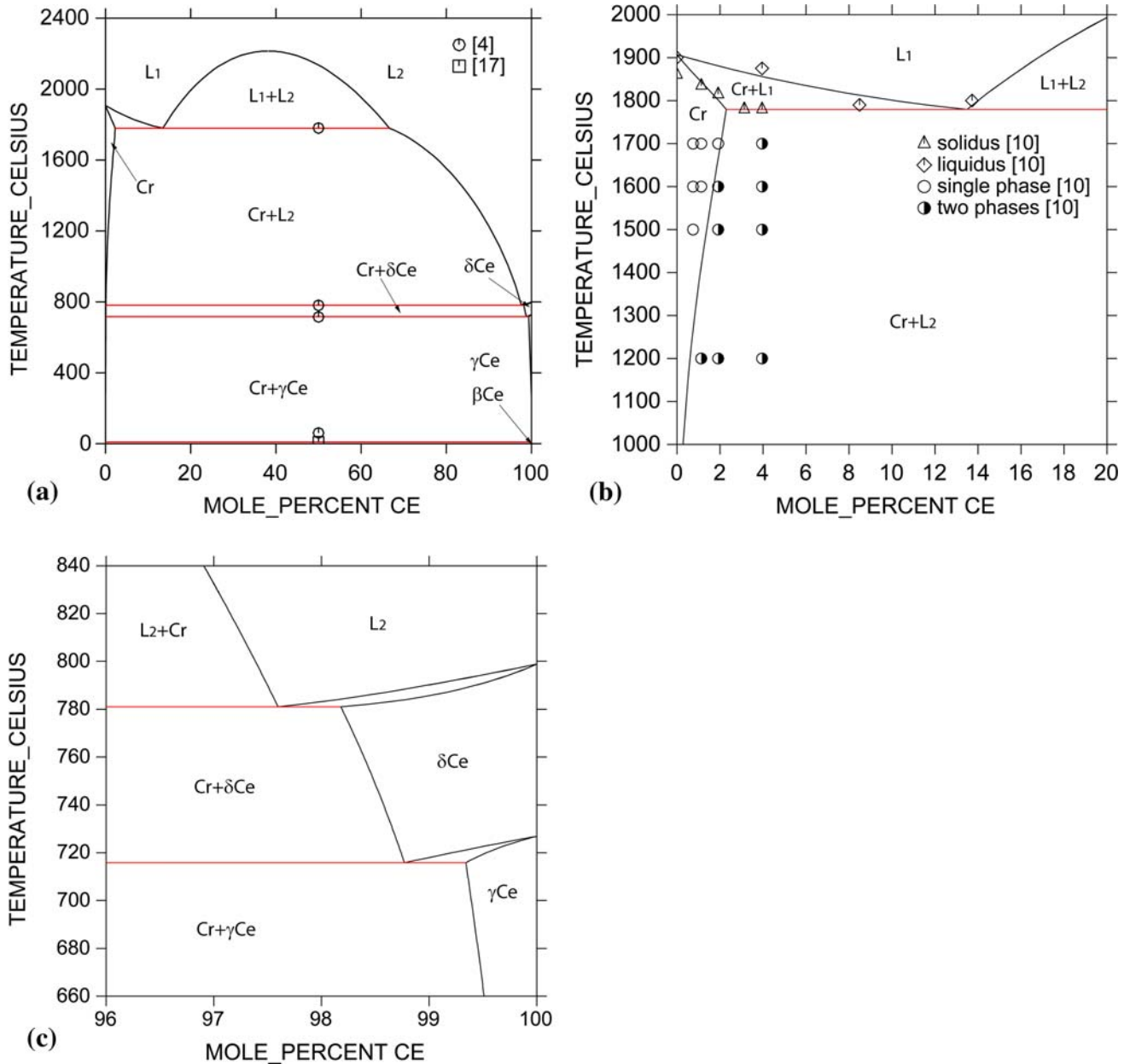


Fig. 2 (a) Calculated phase diagram of the Cr-Ce system and experimental points. (b) Enlarged Cr-rich side of the Cr-Ce phase diagram. (c) Enlarged Ce-rich side of the Cr-Ce phase diagram

The Gibbs energy of individual solid solution phases (e.g. liquid, bcc, fcc, hcp and dhcp) was modeled using the sublattice solution model:

$$G^\Phi = x_{Cr} \overline{G}_{Cr}^\Phi + x_{RE} \overline{G}_{RE}^\Phi + G^{id} + G_m^{ex} + G_m^{mag} \quad (\text{Eq 2})$$

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

$$G_m^{ex} = x_{Cr} x_{RE} \cdot \sum_{\nu=0}^n {}^\nu L_{Cr,RE} (x_{Cr} - x_{RE})^\nu \quad (\text{Eq 4})$$

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

where RE stands for elements Ce, La or Y; \overline{G}_{Cr}^Φ and \overline{G}_{RE}^Φ are the Gibbs energy of the pure elements in the solution phase Φ ; G^{id} is the ideal mixing energy; G_m^{ex} is the excess energy of the phase using the Redlich-Kister polynomial form^[18]; x_{Cr} and x_{RE} are the mole fractions of the constituents; ${}^\nu L_{Cr,RE}$ is the binary interaction parameter of Cr and RE of an order ν , R is the gas constant and T is the absolute temperature (K). G_m^{mag} is the Gibbs energy due to magnetic ordering, but it was set to zero in this study because of lack of

Table 2 Invariant reactions in the Cr-Ce system

Invariant reactions	T , °C	Ce concentration, at.%			Reference
$L_1 \leftrightarrow L_2 + Cr$	1780 ± 10	4.82 (a)	n/a	2.72 (a)	Savitskii et al. ^[10]
	1790	1.85	71	1.25	Massalski et al. ^[4]
	1819.4	3.9	96.1	n/a	Ray and Neumann ^[21]
	1779	13.5	66.7	2.3	This study
$L_2 \leftrightarrow Cr + \delta Ce$	780	n/a	n/a	n/a	Savitskii et al. ^[10]
	785	~95	~0	~98.5	Massalski et al. ^[4]
	771	98.26	n/a	n/a	Terekhova and Korzun ^[20]
	797.5	99.98	n/a	n/a	Ray and Neumann ^[21]
	781	97.6	0.1	98.2	This study
$\delta Ce \leftrightarrow Cr + \gamma Ce$	715	~99	~0	~99.5	Massalski et al. ^[4]
	716	98.8	0.06	99.3	This study
$\gamma Ce \leftrightarrow Cr + \alpha Ce$	61	n/a	n/a	n/a	Massalski et al. ^[4]
	61	100	0	100	This study

(a) Estimated from diagram^[10]

experimental data and the fact that terminal solid solutions in all three binaries are truly negligible.

4. Thermodynamic Assessment and Discussion

The binary interaction parameters for Cr-Ce system was obtained via the least-square optimization PARROT module of Thermo-CalcTM^[19] since there are relatively sufficient experimental data available. The Cr-La and Cr-Y binaries were manually optimized due to the fact that the experimental data are scarce. All the binary interaction parameters for three systems are listed in Table 1. In the PARROT module, the difference between the experimental input and the calculated value multiplied by the optimization weight of the experiment is called “error”. To achieve best fit, the reduced sum of squares of these “errors” should be less than 1. The optimization weights of the experiments are adjusted during the optimization and may vary depending on the accuracy or importance of the experiments in question.

To start the manual optimization of the Cr-La and Cr-Y systems, a temperature-independent positive interaction parameter ${}^0L_{Cr,RE}^{liq} = a_0$ is used to reproduce the miscibility gap in the liquid phase. The resulting phase diagrams generally have a wide range of solubility for the solid phases which is reduced by destabilizing such phases with a temperature-independent positive interaction parameter ${}^0L_{Cr,RE}^{solid} = a_0$. From there, higher-order temperature-independent interaction parameters are added and adjusted to obtain the desired asymmetry, invariant temperature and composition and solubility. Emphasis is placed on ensuring the invariant temperature is within reasonable range of the experimental data with 10 °C for the monotectic invariant equilibrium and 5 °C for the other invariant equilibrium. The rationale behind the ranges is linked to the accuracy of measuring the monotectic equilibrium as opposed to the

other invariant equilibrium. The accuracy of the measurements related to the monotectic equilibrium is questionable due to the high temperature of the monotectic (typically close to the melting point of Cr).

The calculated Cr-Ce binary phase diagram is shown in Fig. 2 with experimental data from solidus and liquidus points.^[10] The invariant reactions are listed in Table 2. The Cr-rich liquidus and solidus were determined over a relatively narrow range of temperatures from around the reported melting point ($T = 1900$ °C) to the monotectic ($T = 1780$ °C).^[10,11] The calculated compositions of phases at the eutectic and monotectic equilibrium are largely in disagreement with the existing phase diagram^[4] though the invariant temperatures are consistent. The calculated values show that the liquid at the monotectic point contains around 15 at.% less Cr than reported.^[10] The discrepancy between the calculated liquid composition at the eutectic point and the accepted composition^[4] differs by around 4 at.%. A consistent thermodynamic assessment of the Cr-Ce could not be obtained to agree with both temperature and composition at both monotectic and eutectic reaction. However a good fit is obtained with the phase stability data points and liquidus and solidus values on the Cr-rich end as reported.^[10] As experimental data that led to the accepted composition^[4] is irretrievable, the optimized eutectic composition can be considered an acceptable estimate. Although the monotectic composition is significantly off the reported value,^[10] considering the difficulty of high temperature measurement and the difficulty of measuring the monotectic composition directly, the estimate is reasonable as the solidus and liquidus^[10] suggest a reasonable fit.

The Cr-La system is optimized primarily based on the handbook^[4] and the solidus data is taken from Ref 12. The optimized diagram is shown in Fig. 3, and the invariant reactions are listed in Table 3. The manual assessment reproduced the general shape and temperatures of the invariant reactions. However, the calculated solidus and the monotectic composition remain unsatisfactory if compared

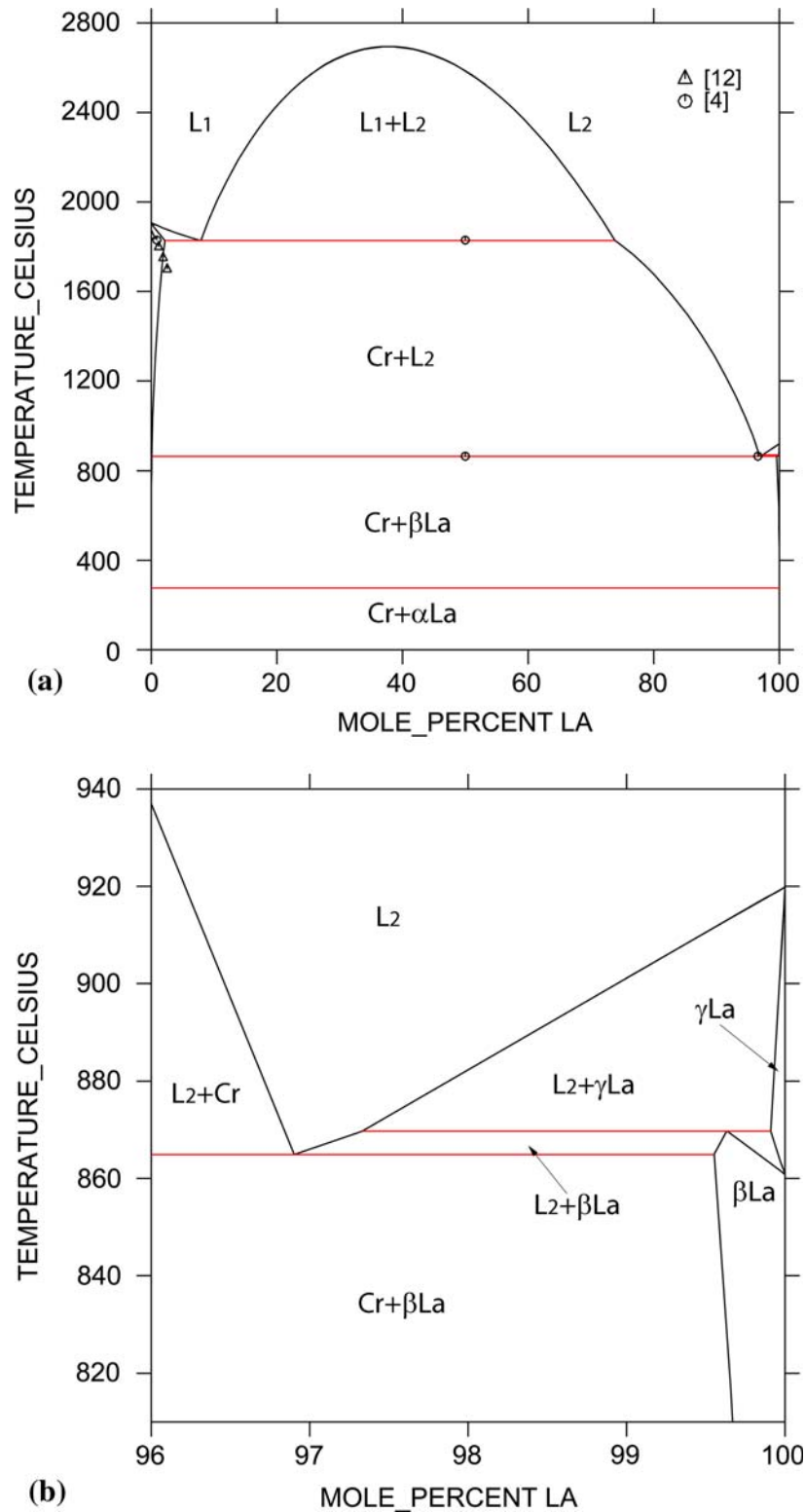


Fig. 3 (a) Calculated phase diagram of the Cr-La system and experimental points. (b) Enlarged La-rich side of the Cr-La phase diagram

with experiment data.^[4] The uncertainty in the melting point of Cr and lack of liquidus data mainly contribute to the discrepancy. On the La-rich side, the present optimization

predicts a eutectic reaction ($L \leftrightarrow Cr + \beta La$) and a peritectic reaction ($L_2 + \gamma La \leftrightarrow \beta La$). The peritectic reaction occurs over a very narrow composition range and the temperature

Table 3 Invariant reactions in the Cr-La system

Invariant reactions	T , °C	La concentration, at. %		Reference	
$L_1 \leftrightarrow L_2 + Cr$	1710	3.99 (a)	n/a	2.46 (a)	Savitskii et al. ^[12]
	1830	0.9	82	~0	Massalski et al. ^[4]
	1835.1	2.4	97.6	n/a	Ray and Neumann ^[21]
	1829	7.87	73.9	2.15	This study
$L_2 + \gamma La \leftrightarrow \beta La$	870	97.3	99.9	99.6	This study
$L_2 \leftrightarrow Cr + \beta La$	865 ± 5	n/a	n/a	n/a	Savitskii et al. ^[12]
	865	96.6	~0	~100	Massalski et al. ^[4]
	867.6	97.026	n/a	n/a	Terekhova and Korzun ^[20]
	917.3	99.97	n/a	n/a	Ray and Neumann ^[21]
	865	96.9	0.11	99.6	This study
$\beta La \leftrightarrow Cr + \alpha La$	277	100	0	100	This study

(a) Estimated from diagram^[12]

is so close to that of the eutectic reaction, therefore, it may not be easily detected in common experiments such as microstructure analysis and thermal analysis depending on the compositions. This perhaps explains why a four-phase equilibrium appears in the handbook.^[4]

On the other hand, in order to examine other equilibrium possibility on the La-rich side, we attempted to optimize the Cr-La system assuming a eutectic reaction ($L \leftrightarrow Cr + \gamma La$) and a eutectoid reaction ($\gamma La \leftrightarrow Cr + \beta La$), based on Ref 12, 13. The optimization predicts a Cr solubility in γLa of ~7 at.% in order to reach a eutectic temperature of 703 °C (not shown). This is unlikely because Cr is 31.7% smaller than La^[13] and one would expect small terminal solubility.^[13] In fact, according to the handbook,^[4] the terminal solubility between all 3d transition metals (except Ti) and La are all negligible. Although we believe that a peritectic reaction is most likely, future experiment to verify this prediction is important.

The calculated Cr-Y phase diagram is shown in Fig. 4. The invariant reactions are listed in Table 4. The manual assessment reproduced the general shape and temperatures of the invariant reactions where the composition of the phases is relatively close to the experimental data.^[14] The calculated Cr-Y phase diagram is largely in agreement with the currently accepted diagram by Okamoto.^[5] However, Okamoto^[5] did not address the reaction type involving L, βY and αY on the Y-rich side. There are only a few points that denote the βY -rich solidus and liquidus over a range from around 1440 to 1500 °C by Terekhova.^[14] Terekhova et al.^[14] showed that the lowest solidus temperature is 1460 °C, therefore, we took 1460 °C as the invariant temperature. This differs from the early assessment by Venkatraman and Neumann^[15] and Okamoto^[5] who used 1478 °C, which is the allotropic transformation temperature of pure Y ($\beta Y \leftrightarrow \alpha Y$). Based on the limited experimental information from Ref 4, 14, 15, Cr solubility in (α, β)Y and Y solubility in Cr were kept low during optimization. The solidus line^[14] of βY is well reproduced and the present calculation predicts a catatectic reaction ($\beta Y \leftrightarrow L_2 + \alpha Y$) assuming that Cr solubility in αY is much smaller than that

in βY . A similar catatectic reaction was also suggested in the Nb-Y system.^[4] But, on the other hand, a peritectic reaction ($\beta Y \leftrightarrow L_2 + \alpha Y$) is also possible if Cr solubility in αY is much larger than that in βY , such as the case of V-Y system.^[4] Therefore, future experiments on the Cr-Y system are needed to determine the terminal solubility and the corresponding invariant reactions.

There are at least two modeling attempts^[20,21] associated with each of the three systems. An early attempt^[20] utilized the generalized lattice model which yield Cr-Ce, Cr-La and Cr-Y phase diagrams but lacked the liquid miscibility gap expected in the three systems. Nevertheless, the calculated eutectic temperature and compositions for the Cr-Ce and Cr-La systems^[20] (see Table 2 and 3) are comparable to the calculated values obtained in the present study. A later attempt by Ray and Neumann^[21] which coupled the Miedema and regular solution models for Cr-Ce and Cr-La produced very simple phase diagrams with the expected miscibility gap. Although the monotectic and eutectic reaction temperatures are fairly consistent with our values, the compositions are considerably off due to their assumption of negligible terminal solubility for the solid state.^[21] The currently accepted Cr-Y phase diagram^[4,5] is calculated from the subregular solution model which has been largely replicated in our current assessment.

Present thermodynamic modeling on Cr-Ce, Cr-La and Cr-Y systems predict that a miscibility gap exists in liquid for all three binaries. The gap is broadest for Cr-La system and the critical point is about 2694 °C. It is the smallest for Cr-Y system and the critical point is about 1897 °C. It is worth noting that Y has 2 polymorphs, while both Ce and La have 3 in the solid state above room temperature. Further, the eutectic point is highest for Cr-Y (about 1329 °C), while it is lowest for Cr-Ce (about 781 °C). A low temperature eutectic point can induce liquid film formation at grain boundaries at high temperatures during service and generally should be avoided. From this point of view, Y appears to be superior to Ce or La in developing Cr alloys for high temperatures applications.

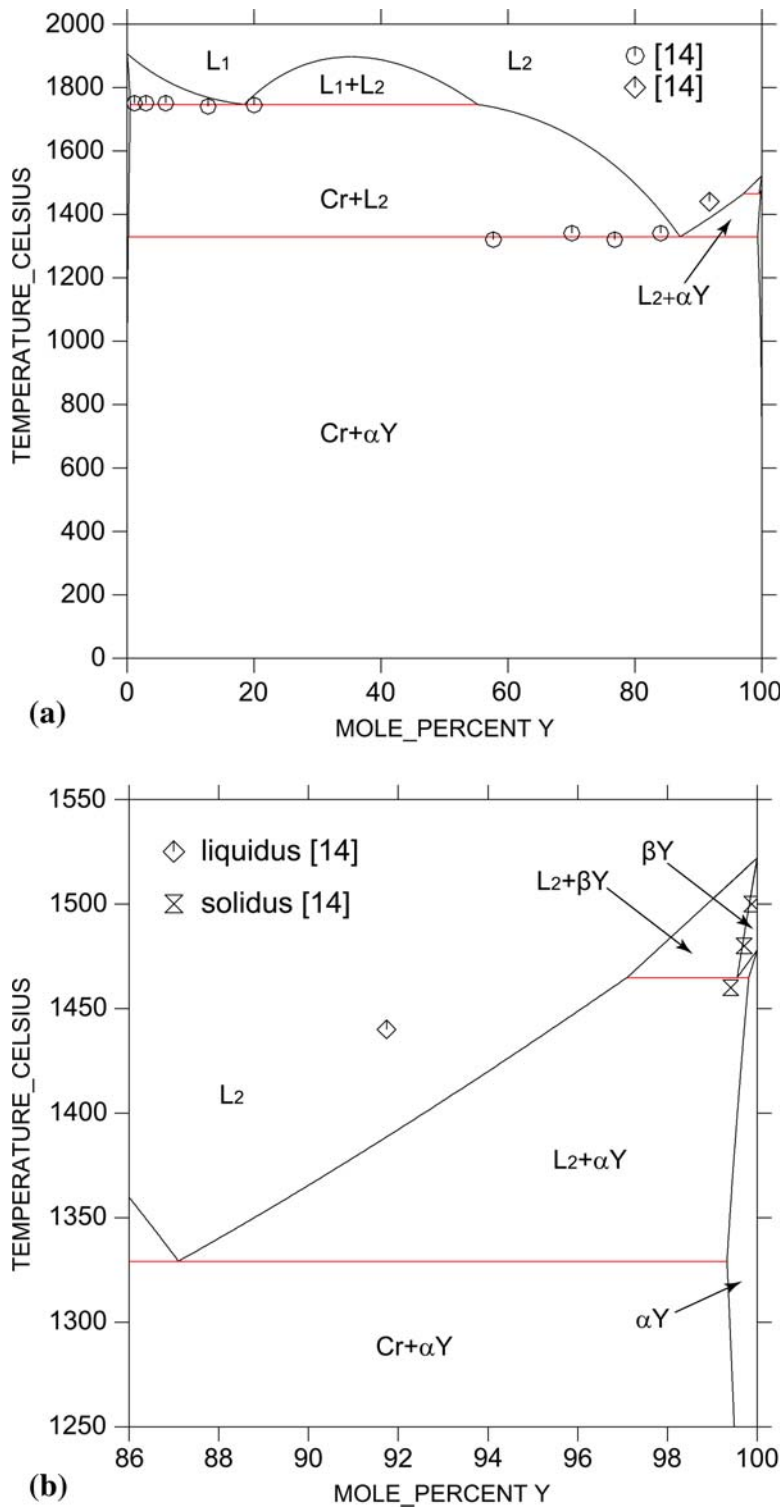


Fig. 4 (a) Calculated phase diagram of the Cr-Y system and experimental points. (b) Enlarged Y-rich side of the Cr-Y phase diagram

5. Conclusions

With limited amount of experimental information, consistent thermodynamic descriptions of the binary systems

Cr-Ce, Cr-La and Cr-Y were obtained. These thermodynamic descriptions were used to calculate the corresponding phase diagrams which are generally of reasonable agreement with available literature data. The present assessment

Table 4 Invariant reactions in the Cr-Y system

Invariant reactions	T, °C	Y concentration, at. %			Reference
$L_1 \leftrightarrow L_2 + Cr$	1760 ± 25	9.36	57.71	n/a	Terekhova et al. ^[14]
	1760 ± 25	9	58	n/a	Venkatraman and Neumann ^[15]
	1740	10.9	61.1	n/a	Okamoto ^[5]
	1747	18.5	55.2	0.05	This study
$\beta Y \leftrightarrow L_2 + \alpha Y$	1478	n/a	98.1	n/a	Okamoto ^[5]
	1465	99.8	97.1	99.6	This study
$L_2 \leftrightarrow Cr + \alpha Y$	1315 ± 7	79.65	n/a	n/a	Terekhova et al. ^[14]
	1330 ± 25	80	n/a	n/a	Venkatraman and Neumann ^[15]
	1237	84.633	n/a	n/a	Terekhova and Korzun ^[20]
	1300	85.9	n/a	n/a	Okamoto ^[5]
	1329	87.1	0.02	99.3	This study

predicts a likely peritectic reaction ($L_2 + \gamma La \leftrightarrow \beta La$) in the La-rich side of the Cr-La system which resolves the ambiguity of the currently accepted phase diagram. It also predicts a possible catatectic reaction ($\beta Y \leftrightarrow L_2 + \alpha Y$) in the Y-rich side of the Cr-Y system. However, in order to verify the predictions made in the present study and also clarify some known discrepancies for these binaries, the authors suggest several future experiments:

1. Accurate measurement of melting point of high-purity Cr at 1 atm.
2. Investigation of the La-rich side Cr-La phase diagram.
3. Investigation of the Y-rich side of Cr-Y phase diagram.

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References

1. Y.F. Gu, H. Haruda, and Y. Ro, Chromium and Chromium-Based Alloys: Problems and Possibilities for High-Temperature Service, *JOM*, 2004, **56**, p 28-33
2. M.C. Gao, Ö.N. Doğan, P. King, A.D. Rollett, and M. Widom, The First-Principles Design of Ductile Refractory Alloys, *JOM*, 2008, **60**, p 61-65
3. H. Kurishita, T. Kuwabara, and M. Hasegawa, Development of Fine-Grained V-28Cr-2.3Y and V-52Cr-1.8Y Alloys with Superior Mechanical Properties, *Mater. Sci. Eng. A*, 2006, **433**, p 32-38
4. T.B. Massalski, P.R. Subramanian, H. Okamoto, and L. Kacprzak, *Binary Alloy Phase Diagrams*, 2nd ed., Vol 1-3, ASM International, Materials Park, OH, 1990
5. H. Okamoto, Cr-Y (Chromium-Yttrium), *J. Phase Equilib.*, 1992, **13**, p 100-101
6. A. Dinsdale, SGTE Data for Pure Elements, *CALPHAD*, 1991, **15**, p 317-425
7. D.R. Lide, *CRC Handbook of Chemistry and Physics*, 88th ed. (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL, 2008
8. W. Zhuang, J. Shen, Y. Liu, L. Ling, S. Shang, Y. Du, and J.C. Schuster, Thermodynamic Optimization of the Cr-Ti System, *Z. Metallkd.*, 2000, **91**, p 121-127
9. G. Ghosh, Thermodynamic and Kinetic Modeling of the Cr-Ti-V System, *J. Phase Equilib.*, 2002, **23**, p 310-328
10. E.M. Savitskii, V.F. Terekhova, and A.V. Kholopov, The Phase Diagram for the Chromium-Cerium System, *Russ. J. Inorg. Chem.*, 1959, **4**, p 195-198
11. G.F. Kobzenko, A.G. Kholodov, V.G. Ivanchenko, E.L. Martinchuk, and O.N. Kashevskaya, Solubility of Cerium, Praseodymium, and Neodymium in Chromium Containing Oxygen, *Metallofizika*, 1971, **33**, p 95-99 (in Russian)
12. E.M. Savitskii, V.F. Terekhova, and A.V. Kholopov, Phase Diagram for Alloys in the Chromium-Lanthanum System, *Russ. J. Inorg. Chem.*, 1960, **5**, p 362-363
13. K.A. Gschneidner, Jr., *Rare Earth Alloys*, D. Van Nostrand Company, Inc., Princeton, NJ, 1961, p 144-148
14. V.F. Terekhova, I.A. Markova, and E.M. Savitskii, Equilibrium Diagram of the Chromium-Yttrium System, *Russ. J. Inorg. Chem.*, 1961, **6**, p 641-642
15. M. Venkatraman and J.P. Neumann, The Cr-Y (Chromium-Yttrium) System, *Bull. Alloy Phase Diagr.*, 1985, **6**, p 429-431
16. A. Taylor, W.M. Hickman, and N.J. Doyle, Solid Solubility Limits of Y and Sc in the Elements W, Ta, Mo, Nb, and Cr, *J. Less-Common Met.*, 1965, **9**, p 214-232
17. K.A. Gschneidner, Jr. and V.K. Pecharsky, The Standard State of Cerium, *J. Phase Equilib.*, 1999, **20**, p 612-614
18. O. Redlich and A.T. Kister, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, *Ind. Eng. Chem.*, 1948, **40**, p 345
19. B. Sundman, B. Jansson, and J.O. Andersson, The Thermo-Calc Databank System, *CALPHAD*, 1985, **9**, p 153-190
20. S.V. Terekhova and E.L. Korzun, The Thermodynamic Description of Lanthanide-Chromium Binary Condensed Solution, *Russ. J. Phys. Chem.*, 1990, **64**, p 643-646
21. S. Ray and J.P. Neumann, Calculation of the Binary Chromium-Lanthanide Phase Diagrams, *J. Phase Equilib.*, 1996, **17**, p 179-185