THERMODYNAMIC ASSESSMENT OF CR-RARE EARTH SYSTEMS

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Abstract

Early rare earth elements are added to refractory metal based alloys to absorb residual oxygen in the alloy to enhance ductility and form dispersion strengthening oxides to increase creep resistance. In this work, three binary systems, Ce-Cr, Cr-La and Cr-Y, were thermodynamically assessed based on available experimental data in the literature using the CALPHAD method. Self-consistent and reasonable thermodynamic descriptions for all three systems were obtained.

Introduction

Refractory metal based alloys are of great importance due to its usefulness in ultra-high temperature applications. Chromium is of particular interest due to its high melting point (1907°C) [1], "good oxidation resistance, low density (20% less than most nickel-based superalloys) and high thermal conductivity (two to four times higher than most superalloys)" [2]. 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. These disadvantages are high ductile-to-brittle transition temperature (DBTT – 150°C for unalloyed recrystallized chromium of commercial purity [2]) and embrittlement in high-temperature environment due to oxidation and 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 [2]. Alloying with substitutional elements is considered a feasible solution to improving the intrinsic ductility of Cr at low temperature [3] while addition of minor amounts of early rare earth elements including Y, Ce and La can lower the residual oxygen content in the bulk by forming very stable oxides to enhance extrinsic ductility. The slow diffusivities of rare earth elements and dispersion strengthened oxides increase the creep resistance of Cr alloys. Therefore, it is important to understand the Cr-rare earth binary phase diagrams and to obtain their quantitative thermodynamic descriptions for process control, microstructure optimization and kinetics simulations. This work concerns the thermodynamic assessment of three binary systems via CALPHAD (the acronym of calculation of phase diagram) method: Ce-Cr, Cr-La and Cr-Y.

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 equilibrium of chromium-rich end, which is in itself questionable accuracy due to the widely perceived melting point of chromium (1863°C). High vapor pressure of Cr contributes to the major difficulty in determining its melting point with high accuracy. In this report, it is treated as 1907^{o}C based on Ref. [1].

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14. ABSTRACT
Early rare earth elements are added to refractory metal based alloys to absorb residual oxygen in the alloy to enhance ductility and form dispersion strengthening oxides to increase creep resistance. In this work, three binary systems, Ce-Cr, Cr-La and Cr-Y, were thermodynamically assessed based on available experimental data in the literature using the CALPHAD method. Self-consistent and reasonable thermodynamic descriptions for all three systems were obtained.

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There are no compounds formed in all 3 binaries, indicating that the atomic interaction between Cr and rare earth elements are largely repulsive. The terminal solubility in all 3 systems is very limited [4, 5].

Ce-Cr System

The terminal phases are *dhcp*-Ce, *fcc*-Ce, *bcc*-Ce and *bcc*-Cr [4]. This system was experimentally studied by Savitskii *et al.* [6] and Kobzenko *et al.* [7], and the data are largely restricted to Cr-rich solid-liquid equilibrium, the monotectic temperature and composition and eutectic temperature. Data from Kobzenko *et al.* [7] show appreciable scatter for both solidus and liquidus lines with temperatures ranging from 1790 to 1820°C. The monotectic temperature is 1780 ± 10°C and composition approximately 95.18 at.% Cr while extent of solubility of Ce in Cr ranges from 0.56-0.75 at.% to 2.72 at.% [6]. The eutectic temperature was determined to be 780°C based on thermal analysis of cerium-rich alloys [6]. The phase diagram provided by Savitskii *et al.* [6] also includes points corresponding to phase stability values of *bcc*-Cr and the two phase region (*bcc*-Cr + Liquid). The experimental methods reported by Savitskii *et al.* [6] were electronic chromatic pyrometry (for liquidus lines), Pironi's drop method (for solidus lines), photomicroscopy (for solubility) and thermal analysis (for the eutectic point). From 715°C to 785°C, *bcc*-Ce and *bcc*-Cr are relatively immiscible in each other with some solubility of Cr in *bcc*-Ce and little to no solubility of Ce in *bcc*-Cr. According to Massalski *et al.* [4] a eutectic reaction: Liquid ↔ *bcc*-Cr + *bcc*-Ce occurs at 785°C at around 5 at.% Cr and a eutectoid reaction: *bcc*-Ce ↔ *bcc*-Cr + *fcc*-Ce occurs at 715°C at around 1 at.% Cr.

Cr-La System

The terminal phases are *bcc*-Cr, *dhcp*-αLa, *fcc*-βLa and *bcc*-γLa [4]. Available experimental data from Savitskii *et al.* [8] include a few points on the Cr-rich solidus equilibrium, monotectic temperature and composition and eutectic temperature. The maximum solubility of Cr in La is 3.91 at.% [8]. The monotectic temperature is reported to be 1710°C and liquid (Cr-rich) phase composition is approximately 3.99 at.% La while the maximum solubility of La in Cr is around 2.54 at.% [8]. This monotectic temperature however differs from the currently accepted phase diagram [4] by more than 100°C and is considered inaccurate. An invariant temperature is observed at 865°C ± 5°C [8] which is confirmed as the eutectic equilibrium by Massalski *et al.* [4]. Another invariant reaction is observed at around 705°C but no reaction is reported by Massalski *et al.* [4] within range of such temperature though Gschneider [9] wrote that this reaction is related to a polymorphic transformation of La at 840°C. The phase diagram provided by Savitskii *et al.* [8] also includes points corresponding to phase stability values of *bcc*-Cr and the two phase region (*bcc*-Cr + liquid). The experimental methods reported by Savitskii *et al.* [8] were optical microscopy (solubility), drop method (solidus) and thermal analysis (invariant). Of particular concern from Massalski et al. [4] is the suggestion of a four phase equilibrium which contradicts the Gibbs phase rule due to the proximity of the invariant line to the polymorphic transformation of La.

Cr-Y System

The terminal phases are *bcc*-Cr, *hcp*-Y and *bcc*-Y [4]. Available experimental data for this system by Terekhova *et al.* [10] is largely restricted to the Cr-rich solidus and liquidus lines, the monotectic temperature and composition and eutectic composition. An investigation of Cr-Y system by Venkatraman and Neumann [11] 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.* [10], the monotectic temperature is 1760°C ± 25°C, monotectic composition is at 23.18 at.% Y, eutectic temperature is 1315°C ± 7°C and eutectic composition is at 91.96 at.% Y. However the phase diagram with a miscibility gap by Venkatraman and Neumann [11] suggests that the eutectic temperature is 1330°C ± 25°C with an eutectic composition of 80 at.% Y. As the article [5] referenced by Venkatraman and Neumann [11] to support the eutectic values is difficult to obtain, it is not possible to confirm the composition or temperature. Citing several literature, Venkatraman and Neumann [11] 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. %. The experimental methods by Terekhova *et al.* [10] were drop method under helium (solidus), optical pyrometry (solidus), photomicroscopy (solubility), microhardness analysis (solubility) and thermo-e.m.f. (solubility).

Thermodynamic Models

The Gibbs energy for each element is defined with respect to its stable state at 298.15 K and 1 atm. In particular, the SGTE-Pure v4 (Cr-La and Cr-Y) and SGTE-SSOL4 v4 (Ce-Cr) databases were used where the Gibbs energy is represented as a power series in terms of temperature in the form

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

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. SGTE-Pure database was not used in the case of the Ce-Cr system because of a discrepancy concerning the polymorphic transformation of *fcc*-Ce to *dhcp*-Ce which according to Massalski et al. [4] is 139°C on heating and -16°C on cooling. An average temperature at 61°C was preferred instead which the SGTE-SSOL4 database provided.

The Gibbs energy of individual solid solution phases was modeled on the sublattice solution model which uses the Redlich-Kister polynomials for the excess Gibbs free energy. The liquid, *bcc*, *fcc*, *hcp* and *dhcp* phases are described by a substitutional model with their Gibbs energy defined as

$$G^{\Phi} = x_{Cr}\overline{G}^{\Phi}_{Cr} + x_{RE}\overline{G}^{\Phi}_{RE} + G^{ideal} + G^{ex}_m + G^{magn}_m \qquad \text{(Eq. 2)}$$

$$G^{id} = \mathrm{R}T \cdot \left[x_{Cr}\ln(x_{Cr}) + x_{RE}\ln(x_{RE})\right] \qquad \text{(Eq. 3)}$$

$$G^{ex}_m = x_{Cr}x_{RE} \cdot \sum_{v=0}^{n} {}^{v}L_{Cr,RE}(x_{Cr} - x_{RE})^{v} \qquad \text{(Eq. 4)}$$

$${}^{v}L_{Cr,RE} = a_v + b_v T + c_v T\ln(T) \qquad \text{(Eq. 5)}$$

where RE stands for elements Ce, La or Y; $\overline{G}^{\Phi}_{Cr}$ and $\overline{G}^{\Phi}_{RE}$ are the Gibbs energy of the pure elements in the solution phase Φ; G^{id} is the ideal mixing energy; G^{ex}_m is the excess energy of the phase; x_{Cr} and x_{RE} are the mole fractions of the constituents; ${}^{v}L_{Cr,RE}$ is the binary interaction paramseter of Cr and RE of an order v, R is the gas constant and T is the absolute temperature (K). The Gibbs free energy of the phases may include magnetic ordering, G^{magn}_m due to ferromagnetism, ferrimagnetism, antiferromagnetism or paramagnetism.

Thermodynamic Assessment and Results

The binary interaction parameters for Ce-Cr system was obtained via least-squares optimization PARROT module of Thermo-Calc, and Cr-La and Cr-Y binaries were manually optimized. 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 the Ce-Cr, Cr-La and Cr-Y systems, a temperature-independent positive interaction parameter ${}^0L^{liq}_{Cr,RE} = a_0$ 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 ${}^0L^{solid}_{Cr,RE} = a_0$. 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).

For the Ce-Cr system, 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) [6, 7]. For the Cr-La system, the Cr-rich solidus were determined from over a range from the melting point (T = 1850°C) to the monotectic (T = 1700°C) [8]. Although the data is of questionable accuracy, Gschneider [9] confirms the eutectic reaction reported [8] as Liquid ↔ Cr (*bcc*-Cr) + γ-La (*fcc*-La) rather than Liquid ↔ *bcc*-Cr + *bcc*-La. This suggests a peritectic reaction (Liquid + γ-La (*fcc*-La) ↔bcc-La) within the vicinity (± 5°C) of the eutectic invariant. However as mentioned earlier, the data is insufficient for an effective computer optimization hence the manually assessed interaction parameters are used as the final interaction parameters. For the Cr-Y system, a few points denote the Y-rich solidus and liquidus over a range from around 1440°C to 1500°C [10]. The invariant equilibrium, the monotectic and eutectic are given at 1760°C ± 25°C and 1315°C ± 7°C. Like the Cr-La system, the manually assessed interaction parameters are used as the final interaction parameters because the data is insufficient for an effective computer optimization.

The calculated Ce-Cr binary phase diagram is shown in Fig. 1 with experimental data from solidus and liquidus points [6]. 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 [6]. 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 Ce-Cr 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 [6]. 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 [6], 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 [6] suggest a reasonable fit.

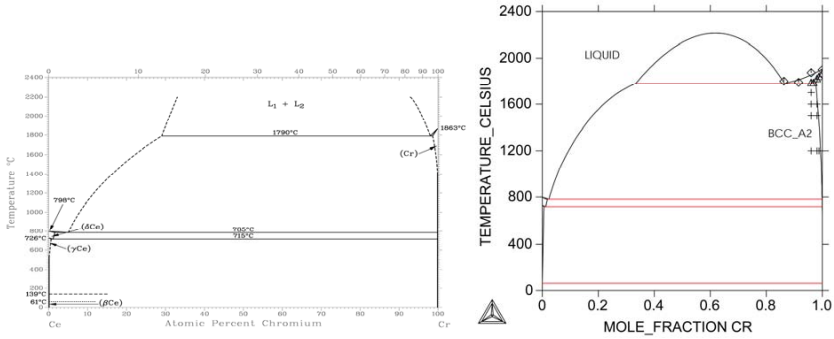

Fig. 1: Ce-Cr system: from the handbook [4] (left) and from the current assessment (right).

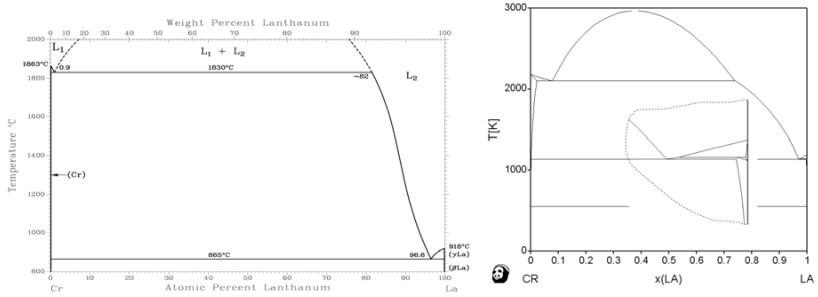

Fig. 2: Cr-La system: from the handbook [4] (left) and from the current assessment (right).

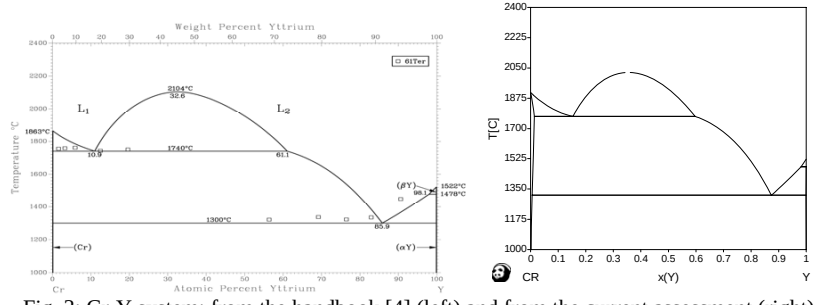

Fig. 3: Cr-Y system: from the handbook [4] (left) and from the current assessment (right).

The Cr-La phase diagram was plotted using the PANDAT^{TM} demo version (shown in Fig. 2). The manual assessment reproduced the general shape and temperatures of the invariant reactions though some difference with the composition of the monotectic equilibrium remained. The inset shows the enlarged portion of the La-rich side that contains a possible peritectic reaction. The peritectic reaction is presumably undetected experimentally because the transformation temperature between La allotropes and the eutectic invariant are reported to be the same [4] which violates the Gibbs phase rule. A reasonable fit is still obtained even though the composition of the monotectic equilibrium is significantly off from the reported composition [8] which may be accounted for similarly to the Ce-Cr monotectic in addition to the loss of lanthanum by evaporation reported by Savitskii *et al.* [8] to not exceed 25%.

The calculated Cr-Y phase diagram is shown in Fig. 3 using the PANDAT^{TM} demo version. The manual assessment like the Cr-Y assessment reproduced the general shape and temperatures of the invariant reactions where the composition of the phases is relatively close to the experimental data [10]. The calculated Cr-Y assessment is largely in agreement with the currently accepted phase diagram by Okamoto [5].

There are at least two modeling attempts associated with each of the three systems which are generally successful in reproducing the shape of the diagrams. An early attempt [12] utilized the generalized lattice model which yield binary phase diagrams for Ce-Cr, Cr-La and Cr-Y but lacked the liquid miscibility gap expected in the three systems. Another attempt with the Miedema model [13] produced very simple phase diagrams for the chromium-lanthanide metal systems which include Ce-Cr and Cr-La that contained calculated temperature and compositions for the monotectic and eutectic equilibrium. The currently accepted phase diagram for the Cr-Y system ([4, 5]) is calculated from the subregular solution model [5].

Conclusions

With limited amount of experimental information, consistent thermodynamic descriptions of the binary systems Ce-Cr, 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 although more experiments would be needed to further refine the diagrams. The present assessment predicted a likely peritectic invariant reaction in the La-rich Cr-La system which resolves the ambiguity of the currently accepted phase diagram.

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