Contents lists available at ScienceDirect

CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

journal homepage: www.elsevier.com/locate/calphad

A thermodynamic assessment of the Cr–Mo system using CE-CVM

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ARTICLE INFO

Article history:
Received 25 May 2013
Received in revised form
5 September 2013
Accepted 1 October 2013

Keywords:
Cr–Mo system
Phase diagram
Thermodynamic assessment
Cluster variation method
CALPHAD method

ABSTRACT

A thermodynamic assessment of the condensed phase region of the Cr–Mo system has been carried out on the basis of available experimental thermodynamic and phase equilibria data. The Gibbs energy of the BCC_A2 solid phase was described by using octahedron–rhombohedron–cube (ORC) approximation of the Cluster Expansion and Cluster Variation Methods (CE-CVM), while a sub-regular solution model was used for describing Gibbs energy of the liquid phase. An optimal set of parameters has been obtained for describing the Gibbs energies of the liquid and solid phases in the Cr–Mo binary system by simultaneous optimization of all experimental data. The calculated phase diagram and thermodynamic properties are in good agreement with experimental data. The relevance of CE-CVM has been demonstrated in the present case by computing first to fifth neighbor short range order (sro) parameters of the solid phase as a function of composition at various temperatures.

1. Introduction

The phase diagram of the Cr–Mo system consists of liquid (*l*) and BCC_A2 (*β*) solid phases in the condensed phase region. The system is characterized by a miscibility gap in the solid phase at low temperatures, complete mutual solubility of Cr and Mo in this phase at higher temperatures and presence of a congruent minimum in the liquidus and solidus boundaries. Several efforts were made earlier to combine all available experimental information to achieve a consistent description of the phase equilibria and thermodynamics of the phases involved [1–7]. In all these efforts, the Gibbs energy of the solid phase (as well as liquid phase) was modeled using Redlich–Kister polynomials [8]. One of the drawbacks of this model is the lack of physical basis to describe short range order (sro), which is often present in real systems. This issue is addressed in the present work by using the cluster variation method (CVM) [9] to model the mixing entropy of the solid phase. This method is currently the method of choice to account for sro. The basic clusters in the CVM approximation used here are the octahedron, rhombohedron and cube (ORC). A comparison of the accuracy of this approximation and the more frequently used irregular tetrahedron (T) approximation as well as a modification of the latter for improving its accuracy will be published separately.

2. Review of experimental data

The liquidus and solidus in the Cr–Mo system have been experimentally determined by several investigators [10–17]. The currently accepted melting points of Cr and Mo are 2180 K and 2896 K respectively [18] and have been adopted by us. The data of Trzebiatowski et al. [12] are not used for optimization due to their inconsistency with these melting points. Similarly, the measurements of Svechnikov and Kobzenko [15] near the Cr-rich end are inconsistent with these values and hence their measurements for alloy compositions up to 25 at% Mo have not been considered. Their solidus data are also not consistent with other measurements and have therefore not been considered. All investigators except Rudy [16] have found a congruent minimum in the liquidus/solidus curves near 12.5 at% Mo. Consequently, the solidus data of Rudy for alloy compositions up to 45 at% Mo have not been considered.

Thermodynamic measurements have been carried out on solid Cr–Mo alloys between 1471 and 1773 K [2,19–21]. The data of Dickson et al. [21] are inconsistent with those of all others and thus have not been considered. In addition to thermodynamic data, Kubaschewski and Chart [20] have reported the equilibrium phases at different temperatures on the basis of X-ray diffraction studies. They have observed a single equilibrium phase at 923 K for 44.2 and 61.3 at% Mo alloys. Since these observations are made on samples homogenized in the single-phase field at high temperature and then equilibrated at the lower temperature of interest, it is possible that equilibrium is not attained if the latter temperature is too low or the equilibration time is not sufficient for diffusion and the single phase is retained in a metastable state. The authors [20] state their estimate of the equilibration time as 250 years at this temperature. A similar reason for lack of equilibrium may be applicable to the presence of a single-phase in the 61.3 at% Mo alloy equilibrated at 1123 K, owing to the higher concentration of Mo in this alloy and the lower diffusion coefficient of Mo. Thus these data have not been considered. Consequently the miscibility gap boundary is expected to pass between

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0364-5916/$ - see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.calphad.2013.10.003

the points (44.2 at% Mo, 1173 K) and (44.2 at% Mo, 1223 K) as well as between the points (44.2 at% Mo, 1173 K) and (61.3 at% Mo, 1173 K).

3. Thermodynamic models

3.1. Pure elements

The Gibbs energy of pure element i (i=Cr, Mo) in a particular phase, with reference to the enthalpy H_i^{SER} of their respective stable states at 298.15 K, is described as a function of temperature by [18]

$$\begin{aligned} G_{\mathrm{Cr}}^{\beta,0}(T)-H_{\mathrm{Cr}}^{\mathrm{SER}} &= -8856.94+157.48T-26.908T\ln T \\ &\quad +1.89435E-3T^2-1.47721E-6T^3 \\ &\quad +139250T^{-1}(298.15<T<2180) \\ &= -34869.344+344.18T-50T\ln T \\ &\quad -2885.26E29T^{-9}(2180<T<6000) \end{aligned} \tag{1a}$$

$$\begin{aligned} G_{\mathrm{Cr}}^{l,0}(T)-H_{\mathrm{Cr}}^{\mathrm{SER}} &= 15483.015+146.059775T \\ &\quad -26.908T\ln T+1.89435E-3T^2-1.47721E \\ &\quad -6T^3+139250T^{-1}+237.615E-23T^7(298.15<T<2180) \\ &= -16459.984+335.616316T-50T\ln T(2180<T<6000) \end{aligned} \tag{1b}$$

$$\begin{aligned} G_{\mathrm{Mo}}^{\beta,0}(T)-H_{\mathrm{Mo}}^{\mathrm{SER}} &= -7746.302+131.9197T-23.56414T\ln T \\ &\quad -3.443396E-3T^2+0.566283E-6T^3+65812T^{-1}-0.130927E \\ &\quad -9T^4(298.15<T<2896) = -30556.41+283.559746T \\ &\quad -42.63829T\ln T-4849.315E30T^{-9}(2896<T<6000) \end{aligned} \tag{1c}$$

$$\begin{aligned} G_{\mathrm{Mo}}^{l,0}(T)-H_{\mathrm{Mo}}^{\mathrm{SER}} &= 34085.045+117.224788T \\ &\quad -23.56414T\ln T-3.443396E-3T^2+0.566283E \\ &\quad -6T^3+65812T^{-1}-0.130927E-9T^4+424.519E \\ &\quad -24T^7(298.15<T<2896) = 3538.963+271.6697T \\ &\quad -42.63829T\ln T(2896<T<5000) \end{aligned} \tag{1d}$$

The pressure terms and those representing magnetic contributions to $G_{\mathrm{Cr}}^{\beta,0}$ are not included because the contributions from those are negligibly small at the temperatures of our interest. As such, these contributions are not included even for solution phases.

3.2. Solution phases

The Gibbs energy of 1 mol of formula unit of phase φ can be expressed as the sum of a reference term $G^{\varphi,\mathrm{ref}}$ and a mixing term $G^{\varphi,\mathrm{mix}}$.

$$G^{\varphi} = G^{\varphi,\mathrm{ref}} + G^{\varphi,\mathrm{mix}} \tag{2a}$$

The reference term is given in terms of the Gibbs energies of the pure elements by

$$G^{\varphi,\mathrm{ref}} = x_{\mathrm{Cr}} G_{\mathrm{Cr}}^{\varphi,0} + x_{\mathrm{Mo}} G_{\mathrm{Mo}}^{\varphi,0} \tag{2b}$$

The mixing term can be expressed as a sum of the ideal $G^{\varphi,\mathrm{id}}$ and excess $G^{\varphi,\mathrm{xs}}$ contributions.

$$G^{\varphi,\mathrm{mix}} = G^{\varphi,\mathrm{id}} + G^{\varphi,\mathrm{xs}} \tag{2c}$$

The ideal Gibbs energy of mixing is given by

$$G^{\varphi,\mathrm{id}} = RT(x_{\mathrm{Cr}} \ln x_{\mathrm{Cr}} + x_{\mathrm{Mo}} \ln x_{\mathrm{Mo}}) \tag{2d}$$

Here x_{Cr} and x_{Mo} represent the mole fractions of Cr and Mo respectively. There are two solution phases in the system: liquid and solid. Excess Gibbs energy for the liquid phase has been modeled by using Redlich–Kister polynomial expansion [8] as follows

$$G^{l,\mathrm{xs}} = x_{\mathrm{Cr}} x_{\mathrm{Mo}} [L_0^l(T) + L_1^l(T)(x_{\mathrm{Cr}} - x_{\mathrm{Mo}}) + L_2^l(T)(x_{\mathrm{Cr}} - x_{\mathrm{Mo}})^2 + \ldots] \tag{3a}$$

and

$$L_i^l = L_{i0}^l + L_{i1}^l T \tag{3b}$$

where $L_i^l(T)$ is the ith interaction parameter.

The BCC phase is treated using phenomenological cluster expansion (CE) for configurational enthalpy of mixing and using CVM for configurational entropy of mixing [22]. The octahedron–rhombohedron–cube (ORC) [23] approximation of the CE-CVM has been used here. The basic clusters used in this approximation are shown in Fig. 1. This model takes into account interactions up to fifth nearest neighbor pairs. Sanchez et al. [23] have used this approximation to extract effective pair interactions in alloys from experimental sro diffuse intensities and shown its accuracy in their analysis. The Gibbs energy of mixing for the BCC phase is expressed as

$$G^{\beta,\mathrm{mix}} = H^{\beta,\mathrm{mix}} - TS^{\beta,\mathrm{mix}} \tag{4a}$$

where $H^{\beta,\mathrm{mix}}$ and $S^{\beta,\mathrm{mix}}$ respectively denote the enthalpy and entropy of mixing.

$$H^{\beta,\mathrm{mix}} = \sum_i C_i^{\beta} m_i^{\beta} u_i^{\beta,\mathrm{mix}} \tag{4b}$$

$$S^{\beta,\mathrm{mix}} = -\mathrm{R} \sum_i \gamma_i^{\beta} m_i^{\beta} \sum_j w_{i,j} \rho_{i,j} \ln \rho_{i,j} \tag{4c}$$

$$C_i^{\beta} = C_{i0}^{\beta} + C_{i1}^{\beta} T \tag{4d}$$

The C_i^{β} are phenomenological cluster expansion coefficients (CECs) or effective cluster interactions (ECIs) which may be temperature dependent. The subscript i refers to one of the 69 crystallographically distinct clusters (details of the clusters are given as e-component) for the ORC approximation. The multiplicity m_i^{β} is equal to the number of clusters of type i per atomic site in the structure and $u_i^{\beta,\mathrm{mix}} = u_i^{\beta} - x_{\mathrm{Cr}} u_{i,\mathrm{Cr}}^{\beta} - x_{\mathrm{Mo}} u_{i,\mathrm{Mo}}^{\beta}$. Here u_i^{β}, $u_{i,\mathrm{Cr}}^{\beta}$ and $u_{i,\mathrm{Mo}}^{\beta}$ represent the correlation functions corresponding to cluster type i for the alloy and those for pure Cr and Mo respectively. These correlation functions are the average values of site operators or their products. In the orthogonal basis used by us, the site operator takes the value -1 or $+1$ respectively when an atom of component A or B occupies the site [24]. Further, γ_i^{β} is the Kikuchi–Barker overlap correction coefficient for cluster type i. The cluster variable $\rho_{i,j}$ represents the probability of occurrence of cluster configuration j

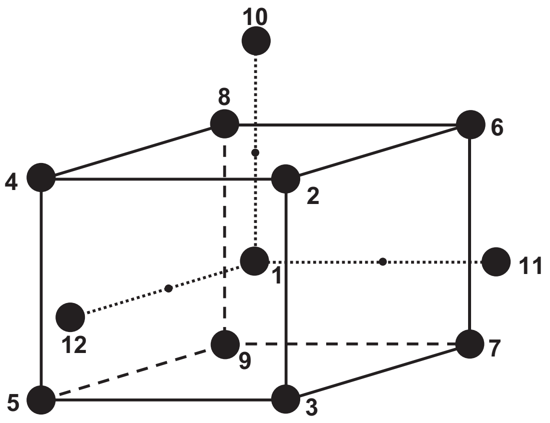

Fig. 1. Basic clusters used in ORC approximation: octahedron (sites 1–2–3–4–5–12), rhombohedron (sites 1–2–3–4–6–10–11–12) and body-centered cube (sites 1–2–3–4–5–6–7–8–9).

Please cite this article as: V. Jindal, et al., A thermodynamic assessment of the Cr–Mo system using CE-CVM, Calphad (2013), http://dx.doi.org/10.1016/j.calphad.2013.10.003