ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Computer Coupling of Phase Diagrams and Thermochemistry 31 (2007) 173–185

www.elsevier.com/locate/calphad

Application of CALPHAD to high pressures

Eli Brosh[a,b,*], Guy Makov[b], Roni Z. Shneck[a]

[a] *Department of Materials Engineering, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel*
[b] *NRCN, P.O. Box 9001, Beer-Sheva 84190, Israel*

Received 10 October 2006; received in revised form 9 December 2006; accepted 21 December 2006

Abstract

The current methods of performing CALPHAD (CALculation of PHAse Diagrams) calculations of high-pressure phase equilibria often lead to spurious predictions of negative thermal expansion or negative heat capacity at high pressures. It is shown that the origin of the problem lies in an incompatibility between the temperature dependence of the widely used SGTE (Scientific Group Thermodata Europe) database and that of typical equations of state of the Mie–Grüneisen type. This inconsistency is also linked to the general problem of describing mechanical instability in CALPHAD. In the present work, a new free energy formulation is developed specifically for inclusion of pressure effects in CALPHAD methodology. It is based on an interpolation between SGTE data at low pressures and the quasiharmonic lattice model at high pressures. The new formulation is constrained to physically credible predictions of the thermophysical properties, while preserving the simplicity of the CALPHAD method. Examples are given of calculations of thermophysical properties and high-pressure phase equilibria in Al, Si, MgO, Fe and the Al–Si binary alloy system.

Keywords: Thermodynamic; Modelling; Pressure; Phase diagram; Equation of state

1. Introduction

The CALPHAD methodology has been very successful in the coupling of thermochemistry and phase equilibria in multicomponent systems at ambient pressure. However, up to now there have been only a few attempts to include pressure effects on condensed phases in CALPHAD calculations. The motivation for such attempts stems mainly from interest in geophysical problems [1] and high-pressure materials physics. In addition there is, in recent years, an interest in extending the CALPHAD method to problems including volume thermal expansion [2,3]. Ideally, it would be best to treat the volumetric data as part of consistent thermodynamic modelling of pressure effects on the Gibbs free energy rather than as a separate database.

In CALPHAD, the Gibbs free energy is written explicitly as a function of temperature and pressure (T, P). Thus, the natural way to extend the formalism to high pressure is to write:

$$G(T, P) = G(T, P_0) + \int_{P_0}^{P} V(T, P')\mathrm{d}P' \tag{1}$$

where G is the Gibbs free energy and P_0 is the reference pressure (usually 1 atm). The first term in Eq. (1) is the Gibbs free energy along the reference isobar, which is the standard CALPHAD data. It should be noted that $G(T, P_0)$ is not a mere tabulation of experimental data since for many calculations, it is necessary to extrapolate $G(T, P_0)$ beyond the measured range. e. g. as done in SGTE (Scientific Group Thermodata Europe) databases [4].

The calculation of the integral in Eq. (1), requires an EOS (Equation Of State): $V(T, P)$. Most of the attempted high-pressure CALPHAD calculations employed for condensed phases the Murnaghan EOS [5,6] with temperature-dependent parameters $V_0(T)$, $B_0(T)$, $B_0'(T)$ that are the volume, the bulk modulus and its first pressure derivative, taken at the reference pressure. Other EOS with similar parameterizations were also considered for application in CALPHAD databases, namely the Birch–Murnaghan EOS [7] and the Jacobs–Oonk EOS [8,9].

---

[*] Corresponding author at: Department of Materials Engineering, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel. Tel.: +972 8 6104887; fax: +972 8 6104887.

E-mail address: ebrosh@nana.co.il (E. Brosh).

0364-5916/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.calphad.2006.12.008

However, up to now the application of CALPHAD at high pressures may be considered as unsuccessful, because the existing models often give manifestly wrong predictions of high-pressure thermophysical properties. For example, negative heat capacities at high pressure have been predicted for MgO and iron [9] as well as for molybdenum [10]. In addition, Jacobs and Oonk [8] have shown that existing models are prone to predicting negative thermal expansion at high pressures,[1] even for close-packed substances, where such phenomena are not expected. It is obvious that the failure of the high-P high-T predictions must arise either from a fault in the structure of the EOS or from some incompatibility between the CALPHAD methodology and the EOS in question.

In the present work, we attempt to resolve this issue and propose a practical formalism for high-pressure calculations in CALPHAD.

First, we try to replace the temperature-dependent Murnaghan EOS by the more established Mie–Grüneisen formulation. As will be seen in Section 2, such a substitution does not resolve the problematics if we retain the usual CALPHAD databases for the ambient pressure caloric properties in $G(T, P_0)$. In Section 3, we propose a new formulation for the inclusion of pressure effects in CALPHAD methodology. In Section 4, this new formulation is applied to the thermodynamic modelling of the elements Al, Si and Fe, the compound MgO and to the Al–Si binary alloy system.

2. Use of the Mie–Grüneisen EOS in CALPHAD

One of the possible sources of the problematics in the current modelling of pressure effects in CALPHAD is the use of completely empirical EOS formulations. Thus, it may seem that an improvement can be achieved if an EOS based on physical considerations is invoked instead. For example, consider the MG (Mie–Grüneisen) EOS [11], which is commonly used to describe the thermal contribution to the high-pressure behaviour of condensed matter:

$$P = P_c(V) + \frac{\gamma}{V} \cdot [E(T, \Theta_D) - E(T_0, \Theta_D)] \qquad (2)$$

where $P_c(V)$ is the cold compression curve (the T_0 isotherm) and the second term is the thermal pressure [11]. γ is the Grüneisen parameter, $E(T, \Theta_D)$ is the internal energy, evaluated from the standard expression in the Debye model and Θ_D is the Debye temperature that is a function of volume. The MG EOS has several advantages over the more empirical approach that was previously tried in CALPHAD. For example, if the γ parameter is kept positive, negative thermal expansion is avoided at any pressure.

Hänström and Lazor [12] fitted an MG type EOS to wide-ranging experimental data for aluminium. While Hänström and Lazor treated only the P–V–T relation, here, we use their fitted EOS to examine the effect of pressure also on "caloric" properties. Hence, using their fitted EOS, the Gibbs free energy of solid aluminium can be calculated by Eq. (1), with the $G(T, P_0)$ term taken from the SGTE database [4] and the pressure-dependent term is calculated (numerically) using Eq. (2). In particular, let us consider the effect of pressure on the isobaric heat capacity calculated in this manner.

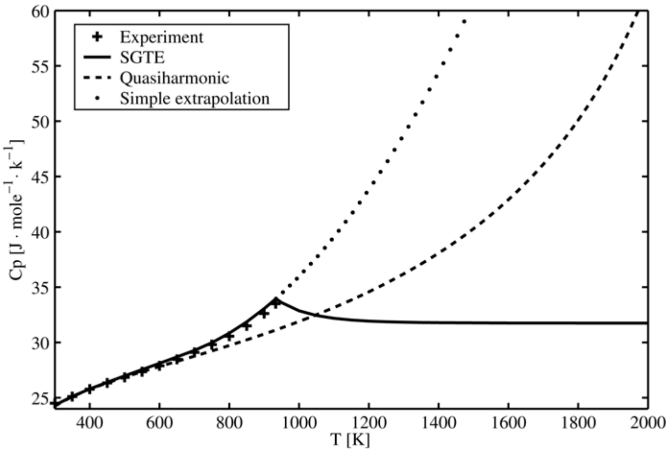

Fig. 1. The calculated isobaric heat capacity of fcc-Al at ambient pressure. The solid curve corresponds to the SGTE database. The broken curve corresponds to a calculation made with the quasiharmonic model for C_v and the Mie–Grüneisen EOS. The dotted curve corresponds to a simple polynomial extrapolation of the solid heat capacity beyond the melting point. Measured heat capacity is indicated by crosses.

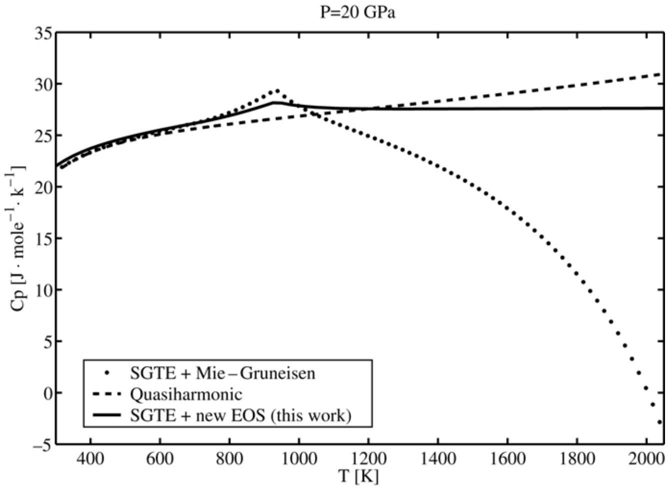

Fig. 2. The calculated isobaric heat capacity of fcc-Al at 20 GPa. The dotted curve corresponds to a combination of the SGTE data for ambient-pressure heat capacity and the Mie–Grüneisen EOS (2). The broken curve corresponds to a calculation made with the quasiharmonic model for C_v and the Mie–Grüneisen EOS. The solid curve corresponds to the new EOS developed in the present work.

The heat capacity at ambient pressure as given in the SGTE database, is shown in Fig. 1, where it is seen to match the experimental data [13] below the melting point. However, at $P = 20$ GPa, the heat capacity calculated by combining the SGTE database for ambient pressure and the MG EOS (2) is manifestly unphysical. As seen in Fig. 2, this combination yields a negative heat capacity above $T = 2000$ K, a temperature that is below the melting point at $P = 20$ GPa [12].

---

[1] This spurious anomaly is equivalent to anomalous pressure-dependence of the entropy [8].