Experimental investigation and thermodynamic assessment of the V–W–C system

Shuigen Huang[a,b], Jef Vleugels[a,*], Lin Li[b], Omer Van der Biest[a]

[a] *Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44, B-3001 Heverlee, Belgium*
[b] *School of Material Science and Engineering, Shanghai University, 149 Yanchang Road, Shanghai 200072, China*

Abstract

Phase equilibrium information of the V–C, W–C and V–W systems are reviewed and the V–W phase diagram was optimized by the substitutional solution model for liquid and bcc phases. A set of self-consistent thermodynamic parameters on the interaction of W and V atoms in the fcc (V,W)C and hcp (V,W)$_2$C phases was established by CALPHAD techniques. The calculated isothermal section at 1500 °C was consistent with the available experimental literature data of the V–W–C system. To validate the thermodynamic calculations, V$_8$C$_7$/WC interaction couples were annealed at 1400 °C for 196 h and WC powder mixtures with 20, 40 and 70 wt.% V$_8$C$_7$ were sintered at 1400 °C for 15 h. The obtained materials were investigated by scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray diffraction (XRD). The composition of the single phase fcc (V,W)C reaction product in the interaction couple and the constituent phases of the sintered materials were consistent with the calculated phase diagram at 1400 °C.
© 2004 Elsevier B.V. All rights reserved.

Keywords: V–W–C; Phase diagram; Carbides; Thermodynamics; Interaction couple

1. Introduction

Progress in powder processing techniques allows superfine WC powders to be used in WC–Co materials. The challenge in sintering superfine grade WC–Co is to retain the fine structure. One of the effective methods to control the WC grain size is the addition of small amounts of refractory carbides such as VC, Cr$_3$C$_2$, TaC and NbC. Among these carbides, VC is the most effective inhibitor due to its high solubility in the Co binder, thereby decreasing the solution of W atoms in the binder phase [1,2]. Moreover, the existence of a stable (V,W)C carbide at the WC/Co interface retards the dissolution and precipitation of W and C atoms on the WC grains. By using TEM–EDS, Egami et al. found that (V,W)C precipitations were formed periodically along the WC/Co boundaries of VC-doped WC–Co alloy [3]. Taniuchi et al. pointed out the presence of sparsely and homogeneously dispersed 0.1 μm sized (V,W)C carbides in a WC–12% Co–0.5% VC alloy [4]. Despite the importance of VC in inhibiting WC grain growth, the solubility of W in VC has hardly been investigated.

As one of the key systems in VC-doped WC–Co cemented carbides, knowledge of the V–W–C phase diagram and thermodynamic data are essential. In this work, a thermodynamic description of the V–W–C system was performed by a computer-aided optimization technique, CALPHAD. On the other hand, it is possible to examine the equilibrium phase diagram from annealed interaction couples based on the local equilibrium. It is not only suitable for the investigation of interfacial reactions and diffusivity of atoms, but also contributes to map the equilibrium phase diagram of binary and ternary systems [5–7]. Moreover, investigating of carefully selected annealed powder mixtures by XRD is useful to investigate the crystal structure of the constituent phases. Therefore, V$_8$C$_7$/WC interaction couples and annealed WC–V$_8$C$_7$ powder compacts were used to verify the thermodynamic calculations.

* Corresponding author. Tel.: +32 16 321244; fax: +32 16 321992.
E-mail address: jozef.vleugels@mtm.kuleuven.ac.be (J. Vleugels).

2. State-of-the-art on the binary V–C, W–C and V–W systems

A critical review of the phase equilibrium diagram, crystal structures, lattice parameters and thermodynamic properties of the V–C system was presented by Carlson et al. [8]. With the available thermochemical and experimental data, Lee and Lee [9] and Huang [10] optimized this system by the CALPHAD technique. The optimizations were in good agreement with the corresponding experimental data. However, their thermodynamic calculations were based on different reference state values for the pure elements. In the work of Huang [10], the V and C reference state were taken from the SGTE database [11], allowing extrapolation of the low-order to high-order systems with the same reference state. In the optimization of Lee and Lee [9], however, the lattice stability of bcc-V is set as a reference, which is not consistent with the other thermodynamic calculations. The calculated V–C phase diagram using the thermodynamic description by Huang [10] is presented in Fig. 1, which shows three intermediate carbides: V_2C_x, V_3C_2 and VC_x. The V_2C_x and VC_x carbides exhibit a wide homogeneity range due to the carbon deficiency at high temperature.

The phase diagram of the W–C system is largely based on the experimental investigation of Rudy et al. [12–14]. Kaufman and Nesor calculated the W–C system according to which WC melts congruently instead of being formed by the observed peritectic reaction [15]. Using a subregular solution model for the liquid and bcc phases and a multi-sublattice model for W_2C_x and WC_x, Uhrenius assessed this system well, except for the peritectic formation of WC_x [16]. More recently, Gustafson reassessed the W–C system by a subregular solution model (W,C) for the liquid phase and a sublattice model $(W)_1(C,Va)_3$, $(W)_1(C,Va)_1$, $(W)_1(C,Va)_{0.5}$ for the bcc, fcc and hcp phases [17]. The W–C phase diagram assessed by Gustafson is presented in Fig. 2. The calculated phase diagram consists of two intermediate phases, W_2C_x and WC_x, and WC. The W_2C_x and WC_x phases have an extensive composition range at elevated temperature.
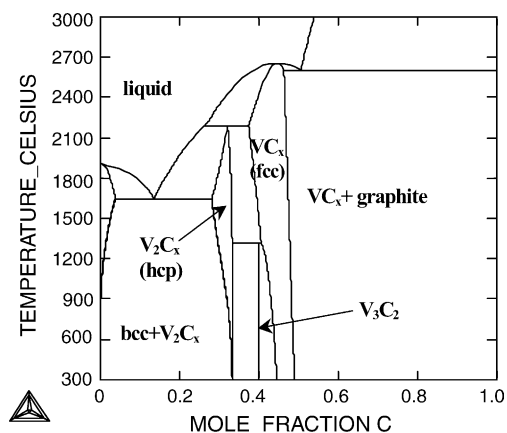

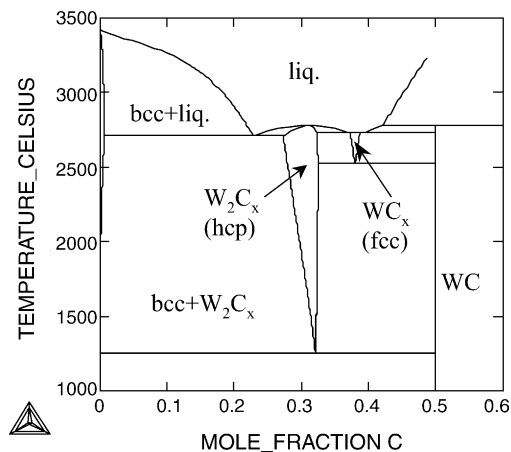Fig. 1. Calculated V–C phase diagram according to Huang [10].

Fig. 2. Calculated W–C phase diagram according to Gustafson [17].

In the V–W system, both V and W have a bcc-cI2-type crystal structure and form a continuous solid solution with bcc structure. Nagender Naidu et al. [18] determined the V–W phase diagram by metallographic techniques, microhardness, thermal and X-ray spectroscopy analysis. In the present work, the V–W system was optimized with the stable elements as reference state and a solution model (V,W) for liquid and bcc phases.

Until now, the only experimental phase diagram of the W–V–C system is available from Rudy and Benesovsky [19]. By analysis of the lattice parameters of different phases using XRD, isothermal sections at 1500–1800 °C were presented. At these temperatures, V and W atoms in the bcc phase as well as the V2C and W2C carbides are completely miscible. An amount of 43 mol% WC was dissolved into vanadium carbide at 1800 °C, whereas no solubility of VC was observed in WC.

3. Thermodynamic calculations

The properties of the pure elements W (bcc), V (bcc) and C (graphite) referred to their standard state are taken from the SGTE (Scientific Group Thermodate Europe) database [11].

The liquid phase is described by a substitutional solution model (W,V,C). The molar Gibbs energy is given by:

$$G_m^{liquid} = \sum_{i=W,V,C} x_i\, {}^0G_i^{liquid} + RT \sum_{i=W,V,C} x_i \ln x_i$$
$$+ x_W x_C L_{W,C} + x_W x_V L_{W,V} + x_V x_C L_{V,C}$$
$$+ x_W x_V x_C L_{W,V,C} \qquad (1)$$

where x_i is the mole fraction of element i and ${}^0G_i^{liquid}$ the Gibbs energy of liquid V, W and C. The binary $L_{i,j}$ parameters are obtained from the evaluation of the binary systems, whereas the ternary L parameter is set to zero since no experimental data are available to verify the ternary liquidus.

The Gibbs free energy of the solid solution phases was described by the compound energy model [20]. The VC_x and WC_x phases in the V–C and W–C systems both have