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Thermodynamic description of phase equilibria in the C–Mo–W–N quaternary system

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ABSTRACT

The Mo–W–N and C–Mo–W ternary systems have been critically evaluated by means of the CALPHAD approach, wherein the C–Mo–W system was reassessed to ensure the model consistency. The Gibbs energies of individual phases in the ternary systems are described with corresponding models, such as substitutional solution model and sublattice model. A set of self-consistent thermodynamic parameters is obtained. Comprehensive comparisons between the calculated and reported phase diagram data show that the reliable information is satisfactorily accounted for by the present modeling. Based on the present work together with the previously reported assessments of C–Mo–N and C–W–N ternary sub-systems, a thermodynamic description of the C–Mo–W–N quaternary system is obtained and used to calculate the phase equilibria and thermodynamic stability of the hexagonal structured (Mo,W)(C,N) carbonitride phase.

1. Introduction

The WC-Co cemented carbides have been widely used in cutting tools, drilling tools and wearing parts, owing to their high strength, hardness and microstructural uniformity at still moderate toughness [1,2]. Due to the increasingly scarce of tungsten resources, the seeking of novel alternatives for hard phases in cemented carbides is inevitable. The ternary (Mo,W)C carbide with a simple hexagonal structure and large solubility of Mo has been recognized as a potential substitute for the WC binary carbide [3]. Moreover, the (Mo,W)C is also the major constituent of ceramic phase in Ti(C,N)-based cermets formed via dissolution-reprecipitation process [4]. Since the grain growth of hard phase can be inhibited by the introduction of nitrogen [5], the phase equilibria involved with (Mo,W)(C,N) carbonitride are therefore important to the phase and microstructure evolution of cemented carbides and Ti(C,N)-based cermets during sintering in N_2 atmosphere.

It is realized that the CALPHAD (CALculation of PHAse Diagrams) approach is a useful tool to establish thermodynamic databases, which are foundation for the predictions of phase diagrams, thermophysical properties, diffusion transformations and phase-field simulations [6–9]. The methods combining both thermodynamic and kinetic calculations have been applied in the design of cemented carbides and Ti(C,N)-based cermets [10–12]. The present work is intended to develop the thermodynamic description and calculate the phase equilibria of the C–Mo–W–N quaternary system, wherein the thermodynamic evaluation of Mo–W–N ternary system is performed. In addition, the C–Mo–W ternary system is reassessed with a desire to construct a self-consistent thermodynamic database for multicomponent cemented carbides [13].

2. Evaluation of experimental information

In the present assessment, the published experimental phase diagram data of Mo–W–N and C–Mo–W–N systems are critically reviewed. To facilitate reading, the symbols to denote stable phases in the quaternary system are summarized in Table 1, in which the crystallographic information is taken from ICSD database [14].

Banik et al. [15] determined the isothermal section of Mo–W–N ternary system by means of X-ray diffraction (XRD) and Kjeldahl methods. Only five Mo–W alloys of different compositions were nitriding with ammonia at 700 °C, and then annealed at 1100 °C under nitrogen pressures of 30 and 300 bars. The nitriding and annealing times were selected to be 2000 and 50 h, respectively. The

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Table 1
List of symbols to denote stable phases in the C–Mo–W–N quaternary system.

Phase	Prototype	Pearson symbol	Space group	Designation	Phase description
(Mo,W)	W	cI2	Im-3m	bcc	Terminal solid solution based on bcc-(Mo,W)
(Mo,W)(C,N)$_{1-x}$	NaCl	cF8	Fm-3m	fcc	Solid solution based on fcc-(Mo,W)(C,N)$_{1-x}$
(Mo,W)$_2$(C,N)	Fe$_2$N	hP3	*P6$_3$/mmc*	hcp	Solid solution based on hcp-(Mo,W)$_2$(C,N)
η-(Mo,W)C	MoC$_{0.67}$	hP12	*P6$_3$/mmc*	(η)	Solid solution based on η-(Mo,W)C
shp-(Mo,W)(C,N)	WC	hP2	P-6m2	MC	Linear compound of shp-(Mo,W)(C,N)
Graphite	C-a	hP4	*P6$_3$/mmc*	Graphite, (C)	Pure graphite
Liquid	–	–	–	Liquid, L	Liquid phase
Gas	–	–	–	N$_2$	Gas phase

substitutional solubility of W in fcc phase at N$_2$ pressure of 300 bar were estimated to be 32 at%, whereas no obvious solubility of fcc phase can be detected at 30 bar N$_2$.

The phase equilibria regarding the (Mo,W)(C,N) carbonitride phase with a WC-type hexagonal structure were investigated by Schreiner et al. [16] using chemical analysis (CA) and XRD techniques. The specimens were prepared by reacting pre-alloyed powders of Mo and W with carbon in the presence of nitrogen. The carbonitriding process was carried out at 1000, 1200 and 1450 °C for 10 h with N$_2$ pressure of 700 mbar. Chemical analysis indicated that the nitrogen content of (Mo,W)(C,N) carbonitride increases with increasing Mo content. Results of the carbonitriding experiments revealed that only hexagonal (Mo,W)(C,N) single-phase, with up to 50 at% substitutional exchange by W, can be detected at 1000 and 1200 °C. As the temperature raised to 1450 °C, the phase equilibria passing through hcp + (C), MC + hcp + (C) and MC regions with the increasing substitutional exchange of Mo (C,N) by tungsten.

3. Thermodynamic models

In this work, the Gibbs energy functions for C, Mo, W and N pure elements were extracted from the SGTE compilation by Dinsdale [17]. The thermodynamic descriptions of C–Mo, C–W, Mo–W, Mo–N and W–N binary sub-systems in the C–Mo–W–N quaternary framework were taken from Andersson [18], Jonsson [19], Gustafson [20], Frisk [21] and Fernández Guillermet and Jonsson [22], respectively. The C–N system was directly extrapolated based on unary data.

In the present modeling, the C–Mo–W system was reassessed considering the incompatibility of C–W binary parameters between an earlier work by Gustafson [23] and the self-consistent multicomponent thermodynamic database (CSUTDCC) [13]. The C–Mo–N and C–W–N ternary systems evaluated by Frisk and Uhrenius [24] and Jonsson [25] were reliable and applied in this work. The thermodynamic optimization of Mo–W–N system is still unavailable and therefore performed here to obtain the final fragment of the C–Mo–W–N quaternary system. The thermodynamic models are described here with C–Mo–W system as an example.

3.1. Liquid phase

The liquid is modeled as substitutional solution phase, and its Gibbs energy is expressed by the Redlich-Kister-Muggianu polynomial [26,27]:

$$G_m^L = x_C\cdot G_C^L + x_{Mo}\cdot G_{Mo}^L + x_W\cdot G_W^L + RT\cdot(x_C\cdot \ln x_C + x_{Mo}\cdot \ln x_{Mo} + x_W \cdot \ln x_W) + x_C\cdot x_{Mo}\cdot L_{C,Mo}^L + x_C\cdot x_W\cdot L_{C,W}^L + x_{Mo}\cdot x_W\cdot L_{Mo,W}^L + {}^{ex}G_{C,Mo,W}^L \tag{1}$$

where R is the gas constant, and x_C, x_{Mo} and x_W are the molar fractions of elements C, Mo and W, respectively. The standard element reference (SER) state, i.e. the stable structure of the element at 25 °C and 1 bar, is used as the reference state of Gibbs energy. The ternary excess Gibbs energy ${}^{ex}G_{C,Mo,W}^L$ is expressed as:

$$ {}^{ex}G_{C,Mo,W}^L = x_C\cdot x_{Mo}\cdot x_W\cdot(x_C\cdot{}^0L_{C,Mo,W}^L + x_{Mo}\cdot{}^1L_{C,Mo,W}^L + x_W\cdot{}^2L_{C,Mo,W}^L) \tag{2}$$

in which the interaction parameters ${}^0L_{C,Mo,W}^L$, ${}^1L_{C,Mo,W}^L$ and ${}^2L_{C,Mo,W}^L$ will be evaluated in the present work.

3.2. Solid solution phase

The Gibbs energies of solid solution phases in the C–Mo–W system, such as fcc, bcc, hcp and (η) are described by a two-sublattice model developed by Hillert and Staffansson as (Mo,W)$_a$(C,Va)$_c$ [28]. In this model, the first sublattice is substitutional type and occupied by Mo and W atoms, while the second sublattice is an interstitial one filled with C atoms and vacancies. The symbols a and c denote the numbers of sites on each sublattice, and have values of $a = 1$ and $c = 1$ for fcc and (η) phases; $a = 1$ and $c = 3$ for bcc phase; $a = 1$ and $c = 0.5$ for hcp phase. For one formula unit of φ phase (Mo,W)$_a$(C,Va)$_c$, the Gibbs energy is expressed as follows:

$$G_m^\varphi = y'_{Mo}\cdot y''_C\cdot{}^0G_{Mo:C}^\varphi + y'_W\cdot y''_C\cdot{}^0G_{W:C}^\varphi + y'_{Mo}\cdot y''_{Va}\cdot{}^0G_{Mo:Va}^\varphi + y'_W\cdot y''_{Va}\cdot{}^0G_{W:Va}^\varphi + a \cdot RT\cdot(y'_{Mo}\cdot \ln y'_{Mo} + y'_W\cdot \ln y'_W) + c\cdot RT\cdot(y''_C\cdot \ln y''_C + y''_{Va}\cdot \ln y''_{Va}) + y'_{Mo} \cdot y'_W\cdot y''_C\cdot L_{Mo,W:C}^\varphi + y'_{Mo}\cdot y'_W\cdot y''_{Va}\cdot L_{Mo,W:Va}^\varphi + y'_{Mo}\cdot y''_C\cdot y''_{Va}\cdot L_{Mo:C,Va}^\varphi + y'_W\cdot y''_C \cdot y''_{Va}\cdot L_{W:C,Va}^\varphi + y'_{Mo}\cdot y'_W\cdot y''_C\cdot y''_{Va}\cdot L_{Mo,W:C,Va}^\varphi \tag{3}$$

where y'_{Mo} and y'_W are the site fractions of Mo and W in the first sublattice, while y''_C and y''_{Va} are the site fractions of carbon and vacancy in the second one. The parameter ${}^0G_{i:Va}^\varphi(i = MoorW)$ is the Gibbs energy of pure element i, and the parameter ${}^0G_{i:C}^\varphi(i = MoorW)$ is the Gibbs energy of a hypothetical state where all the interstitial sites are completely occupied by C atoms. The $L_{Mo:C,Va}^\varphi$, $L_{W:C,Va}^\varphi$ and $L_{Mo,W:Va}^\varphi$ are binary parameters from the sub-systems, $L_{Mo,W:C}^\varphi$ and $L_{Mo,W:C,Va}^\varphi$ are the ternary parameters which will be optimized in the present assessment. Based on the experimental information, the MC phase is a linear compound and should be modeled as (Mo,W)$_1$(C,N)$_1$ in the quaternary system. Graphite shows negligible solubility for the other elements, it can be regarded as pure carbon.

3.3. Gas phase

The gas phase is described as an ideal gas mixture of the species C, C$_1$N$_1$, C$_2$, C$_2$N$_1$, C$_2$N$_2$, C$_3$, C$_4$, C$_4$N$_2$, C$_5$, Mo, Mo$_1$N$_1$, Mo$_2$, N, N$_2$ and N$_3$. The Gibbs energy functions of individual gas species were taken from the SGTE substances database.

The thermodynamic models in Mo–W–N, C–Mo–N and C–W–N systems are analogous and thus not described to avoid redundancy of this section.

4. Results and discussion

The evaluations of model parameters in the C–Mo–W and Mo–W–N systems have been carried out by recurrent runs of the PARROT module of Thermo-Calc software [29], which works by minimizing the square sum of the differences between experimental and computed values. Each piece of experimental information was given a certain weight, and