

COMPUTATION OF METASTABLE PHASES IN TUNGSTEN-CARBON SYSTEM

Marios D. Demetriou, Nasr M. Ghoniem, Adrienne S. Lavine

Mechanical & Aerospace Engineering Department

University of California, Los Angeles

Los Angeles, CA 90095-1597

ABSTRACT

Metastable phase equilibria in the W-C system are presented in the vicinity of the metastable reactions involving W_2C , WC_{1-x} , and WC. Metastable phase boundaries were obtained by reproducing the stable boundaries using optimized Gibbs energy formulations and extrapolating them into regions of metastability. Four metastable reactions were obtained: a metastable congruent melting reaction of WC at 3106 K, a metastable eutectic reaction between WC_{1-x} and graphite at 2995 K, a metastable eutectic reaction between W_2C and WC at 2976 K, and a metastable eutectic reaction between W_2C and graphite at 2925 K. The reaction enthalpies and entropies associated with these transitions are also computed using the available Gibbs energy data. Furthermore, possible kinetic paths that could lead to metastability are discussed.

1. INTRODUCTION

The tungsten-carbon system is a refractory, compound-forming binary system. According to the constitution W-C phase diagram investigated by Rudy [1], three different carbides are reported to form: a simple hexagonal carbide WC which melts incongruently and is almost stoichiometric, a cubic carbide which is referred to as WC_{1-x} , and a second hexagonal carbide W_2C , both of which are shown to have a slightly varying carbon content and melt congruently.

Uhrenius [2] and Gustafson [3] have previously modeled the stable binary W-C system. Their results compare well with the experimental phase diagram presented by Rudy [1]. Several others have modeled the stable ternary systems of W-C-Co [4,5], W-C-Ti [2], W-C-Nb [6], and W-C-Ta [7].

A number of authors have previously reported metastability in the W-C system, and have reported that in both concentration-driven and temperature-driven non-equilibrium transitions metastable compounds turn out to be the most kinetically favorable products. Upon annealing of W-C multilayer thin films, metastable W_2C forms as a kinetic product of solid-state reaction driven by interfacial mixing [8,9,10,11]. Upon rapid cooling experiments, several authors attributed the formation of W_2C and WC_{1-x} solely to the decarburization of WC at high temperatures [12,13,14,15], however Demetriou et al. [16] demonstrated that phase selection and consequently microstructural evolution in the W-C system is primarily limited by metastability regardless of whether decarburization occurs.

The kinetic analysis of metastability requires information about metastable thermodynamic equilibrium. According to Perepezko and Boettinger [17], metastable phase diagrams may be constructed by extrapolating equilibrium phase boundaries into regions of metastability. In compound-forming systems, metastable equilibria of incongruently melting compounds form a

congruent melting point that is masked by the equilibrium phase diagram while metastable equilibria of congruently melting compounds usually form metastable eutectics with non-neighboring phases.

In the present investigation, the stable W-C phase equilibria were reproduced using Gibbs energy data obtained from Gustafson's optimization [3]. Metastable phase equilibria were then obtained by extrapolating the stable equilibrium boundaries into regions of metastability. The computed metastable reactions temperatures and compositions are reported, along with the associated reaction enthalpies and entropies as computed from the available free energy data. The following section discusses the computational model, while the computed phase diagram is presented in section 3. Finally, a general discussion regarding metastability in the W-C system is given in section 4.

2. ANALYSIS

In this study, the W-C phase equilibria were computed by means of an algorithm derived from first principles (i.e. chemical potential equality). The Gibbs energy formulations that characterize W-C phases were obtained from Gustafson thermodynamic optimization [3]. In Gustafson's model, the liquid phase was treated as a single-lattice random solution using the ordinary regular solution model. The WC_{1-x} phase was modeled as an interstitial solution of carbon in fcc tungsten matrix using the two-sublattice model. The W_2C phase appears in three allotropic forms [1]: ordered hexagonal between 1500 and 2450 K, orthorhombic between 2450 and 2750 K, and hcp between 2750 and 3050 K. Gustafson treated W_2C compound as a single hcp phase throughout its stability range for the sake of simplicity. However, since all metastable

reactions of concern are anticipated to occur above 2750 K, treating W_2C as a single hcp phase in the temperature vicinity of metastability appears to be a justifiable assumption. Thus W_2C was modeled as an interstitial solution of carbon in hcp tungsten matrix using the two-sublattice model. The WC and graphite phases were treated as perfectly stoichiometric at 50% and 100% carbon compositions respectively.

Principles of phase equilibria dictate that for a phase α in a binary system with components W and C having molar Gibbs energy G_m^α , the W and C partial Gibbs energies (chemical potentials) at temperature T_o and composition x_{C_o} are given by [18]:

$$\bar{G}_W^\alpha(T_o, x_{C_o}) = G_m^\alpha(T_o, x_{C_o}) - x_{C_o} \left(\frac{\partial G_m^\alpha}{\partial x_C} \right)_{(T_o, x_{C_o})} \quad (1a)$$

$$\bar{G}_C^\alpha(T_o, x_{C_o}) = G_m^\alpha(T_o, x_{C_o}) + (1 - x_{C_o}) \left(\frac{\partial G_m^\alpha}{\partial x_C} \right)_{(T_o, x_{C_o})} \quad (1b)$$

In the case of a perfectly stoichiometric compound $W_{\nu_W}C_{\nu_C}$, where ν_W and ν_C are the stoichiometric coefficients, the chemical potential can be defined in terms of the formula unit of the compound composition rather than in terms of a pure component, as follows [18]:

$$\bar{G}^{W_{\nu_W}C_{\nu_C}}(T_o) \equiv G_m^{W_{\nu_W}C_{\nu_C}}(T_o) \quad (2)$$

In a multi-component system, two or more phases are in equilibrium when their components' chemical potentials are equal. For the equilibrium between two phases α and β in a binary W-C system at temperature T_o and carbon compositions $x_{C,\alpha}$ and $x_{C,\beta}$ respectively, the following relation holds:

$$\bar{G}_C^\alpha(T_o, x_{C,\alpha}) = \bar{G}_C^\beta(T_o, x_{C,\beta}) \quad (3a)$$

$$\bar{G}_W^\alpha(T_o, x_{C,\alpha}) = \bar{G}_W^\beta(T_o, x_{C,\beta}) \quad (3b)$$

Equation (3) represents a system of two non-linear equations in two unknowns, namely $x_{C,\alpha}$ and $x_{C,\beta}$. For a phase α in equilibrium with a stoichiometric compound $W_{\nu_W}C_{\nu_C}$, the equilibrium condition is modified as follows:

$$\bar{G}_{W_{\nu_W}C_{\nu_C}}^\alpha(T_o, x_{C,\alpha}) = \bar{G}^{W_{\nu_W}C_{\nu_C}}(T_o) \quad (4)$$

where $\bar{G}_{W_{\nu_W}C_{\nu_C}}^\alpha \equiv (\nu_C \bar{G}_C^\alpha + \nu_W \bar{G}_W^\alpha) / (\nu_C + \nu_W)$ is the hypothetical chemical potential of $W_{\nu_W}C_{\nu_C}$ in the α phase. Since the composition of the stoichiometric compound is fixed and known, only one unknown is left to represent the equilibrium at T_o , that is $x_{C,\alpha}$ and is given by Eq. (4).

3. RESULTS

The phase equilibria as a function of temperature, which constitute the phase boundaries, are obtained by solving the equilibrium conditions Eq. (3) and (4) in the temperature range of interest. These non-linear equations were solved iteratively using Newton's method [19] by means of an algorithm implemented in MATLAB. Regions of metastability were distinguished from regions of stability by identifying local vs. global Gibbs energy minima. The stable phase diagram is then constructed by the superposition of all stable phase boundaries, and the metastable one by the superposition of the extrapolated metastable phase boundaries.

The computed phase diagram in the vicinity of the three compounds is shown in Fig. 1. The stable equilibrium phase boundaries are shown as solid lines while the metastable ones as dotted. The stable invariant points from Gustafson's optimization [3] and Rudy's experiment [1] are displayed on the phase diagram and are tabulated in Table 1 for comparison with the current model. From Fig. 1 and Table 1 it appears that the equilibria computed by the algorithm developed in this study are in excellent agreement with those computed in Gustafson's work by means of a Thermo-Calc computer program [20], hence verifying the accuracy of the current computational algorithm. Moreover the computed equilibria from the two models appear to closely resemble Rudy's experimental equilibria at most invariant points (with the exception of W_2C eutectic composition and WC_{1-x} congruent melting temperature). The computed metastable reactions include a congruent melting reaction of WC, a eutectic reaction between WC_{1-x} and graphite, a eutectic reaction between W_2C and WC, and a eutectic reaction between W_2C and graphite. These metastable reactions along with their corresponding equilibrium temperatures and compositions are tabulated in Table 2.

Thermal analysis of phase transformations requires knowledge of the enthalpy of fusion, ΔH_f , which constitutes the latent heat, while kinetic analysis of phase transformations requires knowledge of the entropy of fusion, ΔS_f , as it determines the liquid-crystal interfacial energy. For a congruent transition $liq \rightleftharpoons \alpha$ at equilibrium temperature T_m , the enthalpy and entropy of fusion, ΔH_f and ΔS_f , are given by:

$$\Delta M_f = M^{liq}(T_m) - M^\alpha(T_m) \quad (5)$$

where M stands for H or S . For a eutectic transition $liq \rightleftharpoons \alpha + \beta$ at equilibrium temperature T_m and equilibrium compositions $x_{C,liq}$, $x_{C,\alpha}$, $x_{C,\beta}$, the enthalpy and entropy of fusion are given by:

$$\Delta M_f = M^{liq}(T_m, x_{C,liq}) - f^\alpha M^\alpha(T_m, x_{C,\alpha}) - f^\beta M^\beta(T_m, x_{C,\beta}) \quad (6)$$

The enthalpy and entropy of a phase is obtained from the temperature-dependent Gibbs energy as $H = \partial(G/T)/\partial(1/T)$ and $S = -\partial G/\partial T$ respectively, and the phase fractions are given by the lever rule as $f^\alpha = 1 - f^\beta = (x_{C,liq} - x_{C,\beta}) / (x_{C,\alpha} - x_{C,\beta})$. The enthalpies and entropies of fusion associated with the metastable reactions are computed from Eqs. (5) and (6) and are tabulated in Table 3.

4. DISCUSSION

The metastable phase diagram presented in Fig. 1 unmasks the phase equilibria that do not correspond to global Gibbs energy minima, hence are not thermodynamically stable. Under highly non-equilibrium processing conditions, the induced deviations from equilibrium may occur at a rate that would favor a kinetic path that leads to metastability rather than the thermodynamic path that leads to the stable state. Consequently, thermodynamic equilibration may be bypassed and conditions of metastability would prevail. Such kinetically controlled phase selection processes form the basis for non-equilibrium processing of materials.

In compositionally induced transitions encountered in solid-state reaction processes such as solid-state amorphization or ion implantation, the metastable W-C phase diagram elucidates the possibility of forming a phase at annealing temperatures outside the stability region associated with that phase, or at compositions other than those dictated by the stable solidus. Consider for instance the solid-state reaction driven by interfacial mixing in W-C diffusion couples. The *liq*-WC metastable equilibria suggest that WC may be formed kinetically at annealing temperatures between 3047-3107 K, i.e. above its upper stability bound of 3047K. Moreover, W_2C or WC_{1-x} may be formed kinetically along compositions that are dictated by the metastable *gra*- W_2C and *gra*- WC_{1-x} solidus rather than the stable WC- W_2C and WC- WC_{1-x} solidus, respectively.

In thermally induced transitions encountered in rapid thermal processes, such as rapid heating or quenching, the metastable W-C phase diagram reveals the possibility of kinetically bypassing a stable phase in favor of a metastable one. Consider for instance rapid thermal processing at 50%-C, which corresponds to the WC composition. Upon rapid heating, the peritectic melting reaction at 3047 K may be kinetically bypassed due to the frustration in the kinetics of graphitization, and as a result metastable congruent melting of WC at 3107 K would

ensue. Upon rapid cooling from temperatures above the peritectic point, the thermodynamically stable WC, which crystallizes via the peritectic reaction at 3047 K provided that liquid has established an equilibrium interface with graphite, may be suppressed by the metastable WC_{1-x} or W_2C , which crystallize via eutectic reactions at 2995 K and 2925 K respectively.

This study can be further utilized towards computing key thermodynamic variables required in thermal and kinetic modeling of non-equilibrium phase transitions. The degree of supersaturation along a metastable reaction path, which constitutes the thermodynamic driving force for a phase transition, can be obtained from the difference in chemical potentials that can be computed from Eqs. (1) or (2). Based on Spaepen's model [21], the liquid-crystal interfacial energy can be related to the entropy of fusion that can be computed from Eqs. (5) or (6). Moreover, modeling the phenomenon of recalescence, which is caused by the evolution of latent heat, requires knowledge of the enthalpy of fusion, which can also be computed from Eqs. (5) or (6). Demetriou [22] developed a computational model to dynamically simulate thermally induced non-equilibrium reactions in a compound-forming binary system. He applied the model in the W-C system at 50%-C, and concluded that under sufficiently high heating and cooling rates metastability along the aforementioned reaction paths prevails, hence quantifying the importance of metastability during rapid thermal processing.

REFERENCES

1. E. Rudy, Compendium of Phase Diagram Data, Air Force Materials Laboratory, Wright-Patterson Air Force Base, OH. Rep. No. AFML-TR-65-2, Part V, 1969, pp. 192-197.
2. B. Uhrenius, *Calphad*, Vol. 8, No. 2, 1984, pp. 101-119.

3. P. Gustafson, *Mater. Sci. Tech.*, Vol. 2, 1986, pp. 653-658.
4. T. Johansson, and B. Uhrenius, *Metal Sci.*, Feb. 1978, pp. 83-94.
5. A. F. Guillermet, *Metall. Trans. A*, Vol. 20A, 1989, pp. 935-956.
6. W. Huang, and M. Selleby, *Z. Metallkd.*, Vol. 88, No. 1, 1997, pp. 55-62.
7. K. Frisk, *Z. Metallkd.*, Vol. 90, No. 9, 1999, pp. 704-711.
8. G. M. Lamble, S. M. Heald, D. E. Sayers, E. Ziegler, and P. J. Viccaro, *Physica B*, Vol. 158, 1989, pp. 672-673.
9. T. Oshino, D. Shindo, M. Hirabayashi, E. Aoyagi, and H. Nikaido, *Jpn. J. Appl. Phys.*, Vol. 28, No. 10, 1989, pp. 1909-1914.
10. J. Gonzalez-Hernandez, B. S. Chao, and D. A. Pawlik, *J. Vac. Sci. Technol. A*, Vol. 10, No. 1, 1992, pp. 145-151.
11. J. Luthin, and Ch. Linsmeier, *Surf. Sci.*, Vol. 454-456, 2000, pp. 78-79.
12. D. Tu, S. Chang, C. Chao, and C. Lin, *J. Vac. Sci. Technol. A*, Vol. 3, No. 6, 1985, pp. 2479-2482.
13. C. Verdon, A. Karimi, and J.-L. Martin, *Mater. Sci. Eng. A*, Vol. A246, 1998, pp. 11-24.
14. Y. Suda, T. Nakazono, K. Ebihara, K. Baba, and R. Hatada, *Mater. Chem. Phys.*, Vol. 54, 1998, pp. 177-180.
15. S. Sharafat, A. Kobayashi, S. Chen, N. M. Ghoniem, *Surf. Coat. Tech.*, Vol. 130, 2000, pp. 164-172.
16. M. D. Demetriou, N. M. Ghoniem, and A. S. Lavine, *Acta Mater.*, in press, 2002.
17. J. H. Perepezko, and W. J. Boettinger, *Mat. Res. Soc. Symp. Proc.*, Vol. 19, 1983, pp. 223-240.

18. C. H. P. Lupis, *Chemical Thermodynamics of Materials*, Elsevier, New York, 1983, pp. 56, 332.
19. R. L. Burden and J. D. Fairs, *Numerical Analysis*, 5th Edition, PWS, Boston, 1993, pp. 56, 553.
20. B. Sundman, B. Jansson, and J-O. Anderson, *Calphad*, Vol. 9, 1985, pp. 153-190.
21. F. Spaepen, *Acta Metall.*, Vol. 23, 1975, pp. 729-743.
22. M. D. Demetriou, Ph.D. Dissertation, University of California, Los Angeles, 2001.

Reaction	Reaction type	Study	Composition			Temperature T (K)
			x_C			
$liq = W_2C$	Congruent	Rudy [1]	-	0.310	-	3049 ± 12
		Gustafson [3]	-	0.312	-	3052
		Current	-	0.312	-	3051
$liq = W_2C + WC_{1-x}$	Eutectic	Rudy [1]	0.345	0.365	0.375	3008 ± 12
		Gustafson [3]	0.324	0.370	0.373	3004
		Current	0.324	0.370	0.373	3004
$liq = WC_{1-x}$	Congruent	Rudy [1]	-	0.390	-	3020 ± 12
		Gustafson [3]	-	0.376	-	3005
		Current	-	0.376	-	3005
$liq = WC_{1-x} + WC$	Eutectic	Rudy [1]	0.395	0.415	0.495	2993 ± 12
		Gustafson [3]	0.387	0.396	0.500	3002
		Current	0.387	0.396	0.500	3002
$liq + gra = WC$	Peritectic	Rudy [1]	0.420	0.500	1.00	3049 ± 4
		Gustafson [3]	0.421	0.500	1.00	3047
		Current	0.421	0.500	1.00	3047

Table 1: Stable invariant equilibria between W-C compounds.

Reaction	Reaction type	Composition			Temperature T (K)
		x_C			
$liq \rightleftharpoons WC$	Congruent	-	0.500	-	3107
$liq \rightleftharpoons WC_{1-x} + gra$	Eutectic	0.396	0.414	1.00	2995
$liq \rightleftharpoons W_2C + WC$	Eutectic	0.326	0.384	0.500	2976
$liq \rightleftharpoons W_2C + gra$	Eutectic	0.328	0.406	1.00	2925

Table 2: Metastable invariant equilibria between W-C compounds.

Reaction	Enthalpy of fusion	Entropy of fusion
	ΔH_f (KJ/mol)	ΔS_f (J/mol-K)
$liq \rightleftharpoons WC$	77.72	25.03
$liq \rightleftharpoons WC_{1-x} + gra$	49.23	16.45
$liq \rightleftharpoons W_2C + WC$	52.16	17.53
$liq \rightleftharpoons W_2C + gra$	48.81	16.69

Table 3: Enthalpies and entropies of fusion associated with metastable reactions.

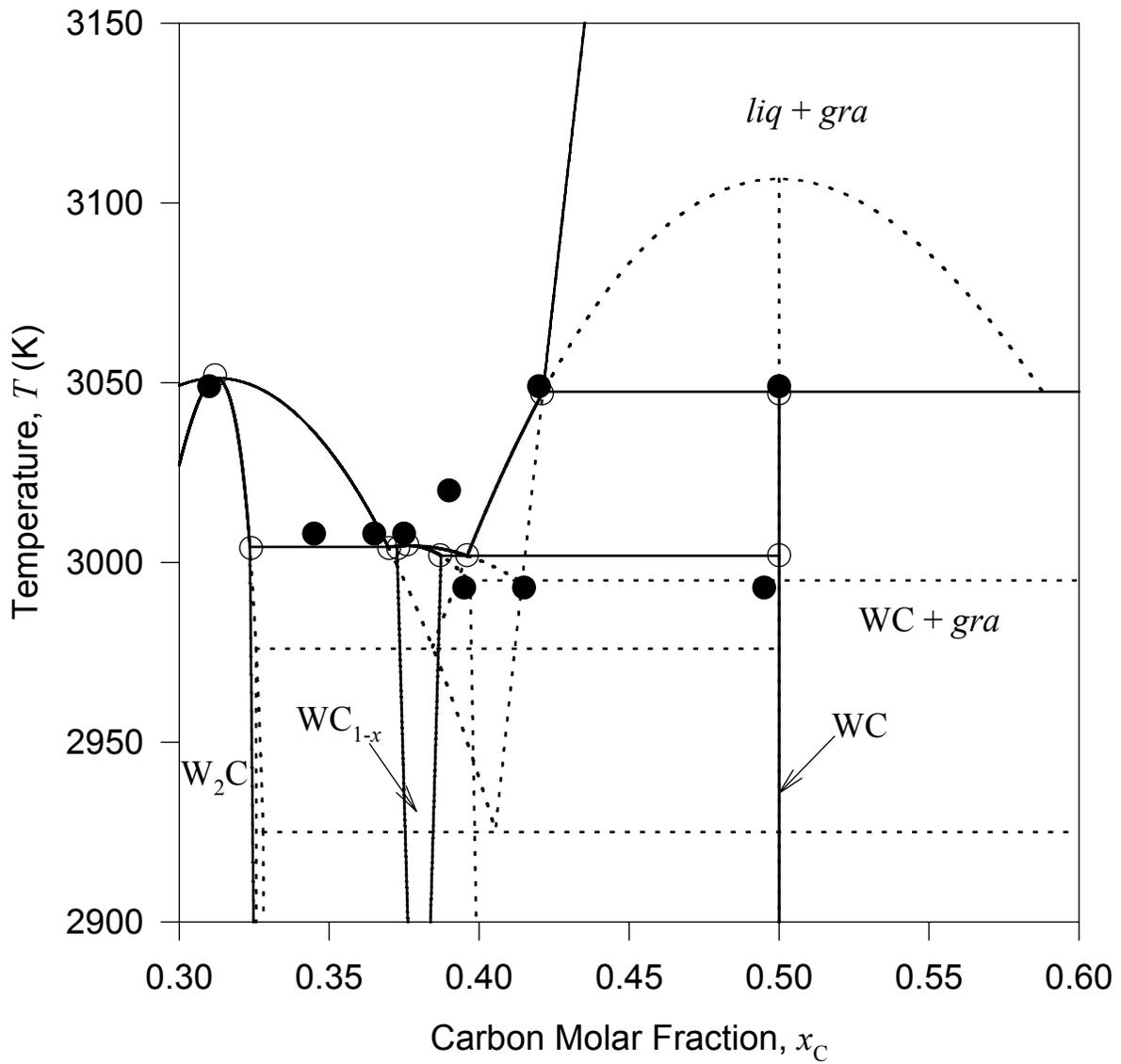


Figure 1: Tungsten-Carbon phase diagram.

- Stable phase boundaries (current computational model)
- - - Metastable phase boundaries (current computational model)
- Stable invariant points (Gustafson's model [3,20])
- Stable invariant points (Rudy's experiment [1])