

A Revised Thermodynamic Description of the Co-W-C System

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(Submitted January 26, 2004; in revised form October 26, 2004)

A thermodynamic reassessment of the Co-W-C system is presented. New information on the liquid (L) + face-centered cubic (fcc) + graphite + WC and L + fcc + WC + M_6C equilibria has recently been published. Because these equilibria are very important for extrapolation to higher-order systems, the ternary system has been revised. A revision of the Co-W system also has been performed.

1. Introduction

Over the last century, there have been several investigations concerning the Co-W-C system. The investigations have shifted from using only classic metallography toward combining experimental information with theoretical descriptions to define equilibrium phase boundaries.

Fernández Guillermet (Ref 1) has made the most thorough Calphad analysis of the Co-W-C system. The analysis was based on experimental information that was available at the time and has been used extensively to calculate phase equilibria in cemented carbides (Ref 2). For the four-phase equilibrium temperatures liquid (L) + graphite + face-centered cubic (fcc) + WC and L + fcc + WC + M_6C , different experimental values were published, and Fernández Guillermet (Ref 1) selected the values (1548 and 1628 K, respectively) from Åkesson (Ref 3). Recent differential thermal analysis (DTA) of both temperatures by Kruse et al. (Ref 4) showed that the values 1571 and 1641 K, also found in older publications, were the most reliable. Furthermore, the values by Kruse et al. (Ref 4) are in better agreement with measurements in higher-order systems.

To incorporate the new measurements into the thermodynamic description of Co-W-C, it was necessary to perform a complete new optimization, although most of the selection of experimental information could be adopted from the article by Fernández Guillermet (Ref 1).

When performing an optimization on a ternary system, it is important that the binary systems are well described. The selected binary information is presented below.

Fernández Guillermet (Ref 1, 5) performed thermodynamic assessments of the Co-W and Co-C systems, and Gustafson (Ref 6) performed assessments of the W-C system. The Co-W system is revised in the present work. Jonsson (Ref 7) has revised the W-C system. The main difference compared with the previous description by Gustafson (Ref 6) was a new description of the cubic WC phase. This

phase is only stable at very high temperatures (above 2800 K) in the binary W-C system, but the low-temperature properties are important when describing the solubility of W in cubic carbides (for example, TiC, NbC, and TaC). When describing systems Co-W-C-Me, with Me = Ti, Nb, and Ta, the description of W-C by Jonsson (Ref 7) was preferred. The new description of Co-W-C is thus based on the description by Jonsson (Ref 7) of the W-C system and on the description by Fernández Guillermet (Ref 5) of the Co-C system.

2. Selected Experimental Information

2.1 Information on the Co-W System

A full thermodynamic description of the Co-W system has previously been presented by Fernández Guillermet (Ref 1). The description was slightly modified in the present work using the information described below.

From the work of Gabriel (Ref 8), using DTA and a phase-decantation technique, the authors selected the information on the L/L + μ equilibrium boundary, the fcc + L + μ equilibrium and also the equilibrium temperature and L composition of the L + μ + body-centered cubic (bcc) equilibrium. The equilibrium temperature for L + fcc was investigated by incipient melting of Co-W alloys by Åkesson (Ref 3), and these results were used in the present work. From the work by Takayama et al. (Ref 9), using a diffusion couple technique, x-ray, and microprobe measurements, the authors selected the following information: the fcc/fcc + μ equilibrium boundary between 1473 and 1573 K, the fcc/fcc + Co_3W equilibrium boundaries, and phase boundaries for the μ phase. For the μ -phase boundaries, the authors also selected information from Gabriel (Ref 8). The fcc + Co_3W + μ equilibrium temperature was taken from dilatometric measurements from Neumeier and Holman (Ref 10).

The parameters describing the bcc phase and the magnetic contribution to the Gibbs energy were taken directly from Fernández Guillermet (Ref 1).

2.2 Information on the C-Co-W System

The carbon isoactivity compositions from Johansson (Ref 11) and Åkesson (Ref 3) at 1423, 1473, 1548, and 1623

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K were used when defining the thermodynamic properties of the fcc phase and the equilibrium between the fcc and the WC carbide phase. The WC carbide does not dissolve any Co, and the description of this phase was taken directly from Jonsson (Ref 7). The carbon activity in the carburizing atmosphere, used by Johansson (Ref 11) and Åkesson (Ref 3), was defined as an optimization parameter and was optimized together with the other parameters. This was done by using the reported composition of the Co specimens that were carburized simultaneously.

For the M_6C and $M_{12}C$ carbides, the thermodynamic properties were defined by including the experimental tie lines for the fcc + M_6C , fcc + $M_{12}C$, M_6C + $M_{12}C$, and M_6C

+ WC equilibria at different temperatures obtained from studies of Johansson (Ref 11) and Åkesson (Ref 3).

Finally, the properties of the liquid phase were defined. The information used was the four phase equilibrium temperatures, for fcc + L + WC + graphite and fcc + L + WC + M_6C , reported by Kruse et al. (Ref 4), the graphite solubility data in the Co-W liquid at 1873 K reported by Schenck et al. (Ref 12) and the carbon iso-activity compositions from 1623 K presented by Åkesson (Ref 3).

The parameters describing the bcc phase and the magnetic contribution to Gibbs energy were taken directly from the work of Fernández Guillermet (Ref 1).

Table 1 Optimized parameters for the Co-W and Co-W-C systems

Parameter	Present work	Ref 1
${}^0L_{Co,W}^L$	$-57,700 + 22.8T$	$-42,258 + 13.616T$
${}^1L_{Co,W}^L$	2505.9	None
${}^0L_{C,Co,W}^L$	$12,770 - 22.9T$	-70,718
${}^0L_{Co,W:Va}^{fcc}$	$-19,900 + 12.8T$	$-17,267 + 10.878T$
${}^1L_{Co,W:Va}^{fcc}$	$17,970 - 19.3T$	$14,711 - 18.687T$
${}^0L_{Co,W:C}^{fcc}$	87,040	93,868
${}^0G_{Co:W:Co}^\mu - 7^\circ G_{Co:Va}^{fcc} - 2^\circ G_{W:Va}^{bcc} - 4^\circ G_{Co:Va}^{bcc}$	59,040	$-20,534 + 42.774T$
${}^0G_{Co:W:W}^\mu - 7^\circ G_{Co:Va}^{fcc} - 6^\circ G_{W:Va}^{bcc}$	$-32,650 - 14.4T$	$-26,910 - 21.791T$
${}^0G_{Co_3W}^{Co_3W} - 3^\circ G_{Co:Va}^{cph} - 0^\circ G_{W:Va}^{bcc}$	$-17,930 + 2.40T$	$-16,126 + 0.147T$
${}^0G_{Co:W:Co}^{M_{12}C} - 6^\circ G_{Co:Va}^{cph} - 6^\circ G_{W:Va}^{bcc} - 0^\circ G_C^{graph.}$	$-88,450 - 19.1T$	$-82,698 - 28.232T$
${}^0G_{Co:W:Co:C}^{M_6C} - 4^\circ G_{Co:Va}^{cph} - 2^\circ G_{W:Va}^{bcc} - 0^\circ G_C^{graph.}$	$10,203 - 32.3T$	$+2,216 - 29.48T$
${}^0G_{Co:W:W:C}^{M_6C} - 2^\circ G_{Co:Va}^{cph} - 4^\circ G_{W:Va}^{bcc} - 0^\circ G_C^{graph.}$	$-52,019 - 9.36T$	$-27,554 - 29.48T$

Note: T refers to the temperature in Kelvin

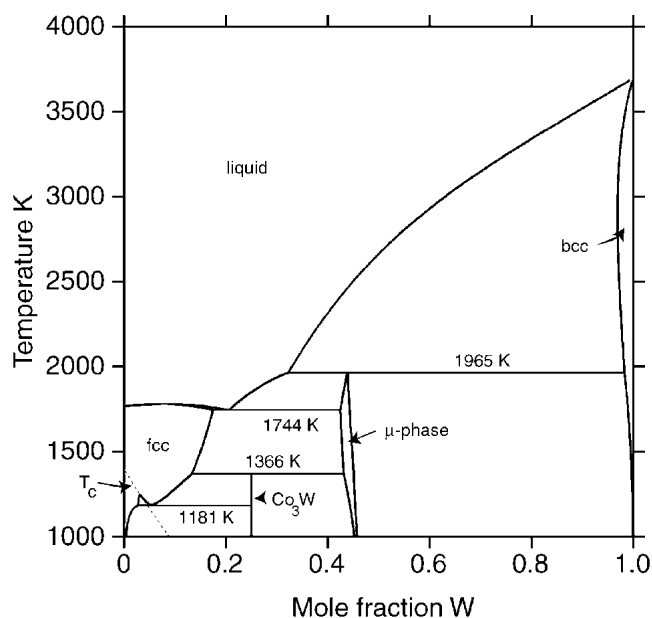


Fig. 1 The Co-W phase diagram using the present description

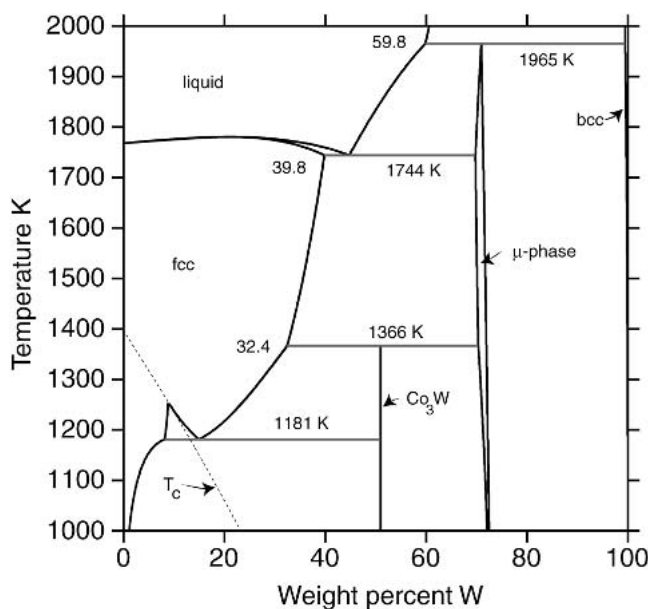


Fig. 2 The Co-W phase diagram using the present description

3. Models and Parameter Optimization

The compound energy model (Ref 13) was used to model the Gibbs energy of the individual phases. The thermodynamic models used in the present work are, without exception, the same as those previously used by Fernández Guillermet, which are described in detail in Ref 1.

The model parameters were evaluated using the selected experimental information described above and were analyzed with a computer optimization program, PARROT (Ref 14). In PARROT, the squared difference between experimental and calculated values are weighted and minimized to determine the parameter values.

4. Results

The parameters that have been optimized with respect to the chosen experimental information are listed in Table 1. Only the revised parameters are listed. The description from the present work is used to recalculate the quantities that have been determined experimentally. In general, the authors have chosen to recalculate the diagrams presented in the work of Fernández Guillermet (Ref 1) to give the reader the opportunity to notice the differences between the two descriptions.

4.1 Co-W

First, the authors present the calculated phase diagrams in Fig. 1 and 2 using the present description. The equilibrium temperatures (1962 and 1744 K, respectively) for fcc + L + μ and L + μ + bcc reported by Gabriel (Ref 8) are reproduced within the experimental errors. As in the Co-V

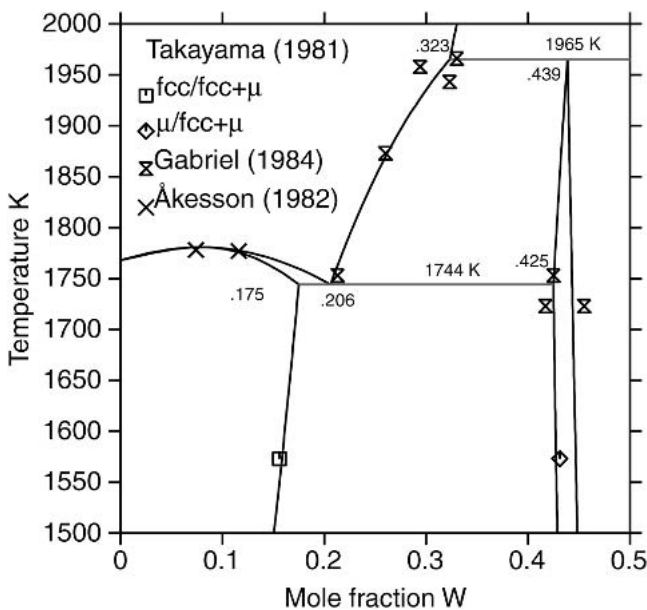


Fig. 3 The liquid-solid equilibrium in the Co-W system according to the present description, compared with experimental data from various sources

system (Ref 15), a so-called tricritical point exists in the fcc phase at 1252 K. The magnetic contribution produces inflection points in the Gibbs energy below this temperature leading to a miscibility gap, which extends on both sides of the Curie temperature (T_C). Within the gap, two phases with the same fcc crystal symmetry, one ferromagnetic and Co-rich, the other paramagnetic and less Co-rich, are in equilibrium. Over 1252 K, the magnetic Gibbs energy contribution is too small to produce inflection points, and here the paramagnetic-to-ferromagnetic transformation along the T_C is second order (i.e., single phase and continuous).

In Fig. 3, a comparison of the calculated and experimentally determined phase boundaries for the liquid phase is made, and the calculated boundaries fit the experimental values well. The experimental information from Takayama et al. (Ref 9) describing the phase boundaries for the fcc phase is very well reproduced by the present work, as seen in Fig. 4. The experimental information on the μ phase is reproduced by the calculations.

Figures 5 and 6 compare the present work with the work by Fernández Guillermet (Ref 1) and show a similar description, except for an improvement of the description of the μ phase at low temperatures and a slight shift of the L/L + bcc phase boundary toward higher W contents.

4.2 Co-W-C

Experimental information about the effect on the activity coefficient when carburizing Co-W alloys with varying W content at various C activities was determined by Johansson (Ref 11) and Åkesson (Ref 3). Figures 7 to 10, present the composition of the fcc phase obtained in experiments at temperatures of 1423, 1473, 1548, and 1623 K,

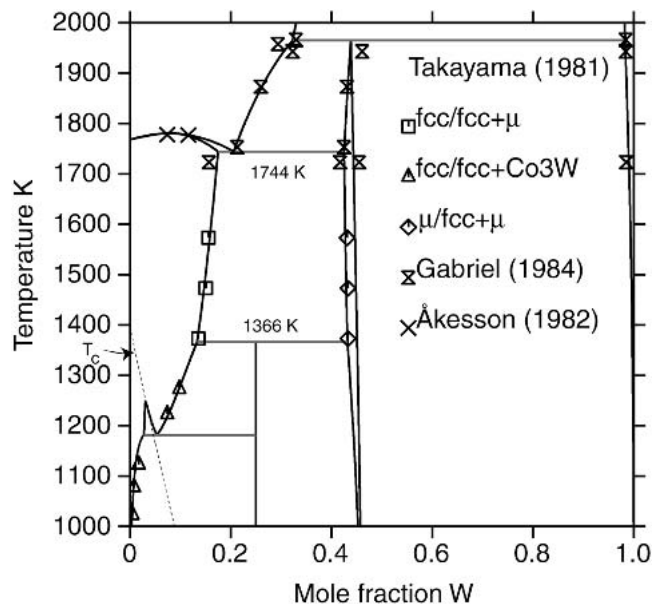


Fig. 4 The Co-W phase diagram according to the present description, compared with experimental data from various sources

respectively. The compositions are given in μ -fractions of W and C, which are defined as:

$$u_W = \frac{x_W}{1 - x_C}$$

$$u_C = \frac{x_C}{1 - x_C}$$

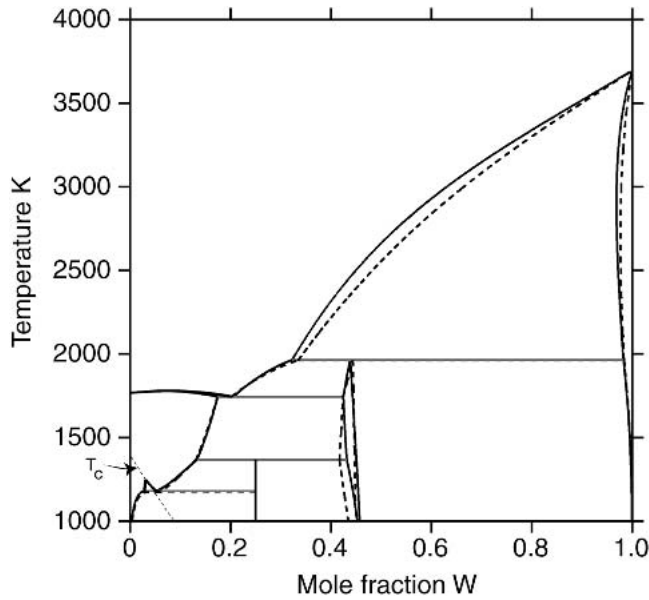


Fig. 5 The Co-W phase diagram according to the present description (solid lines) compared with the description by Fernández Guillermet (Ref 1)

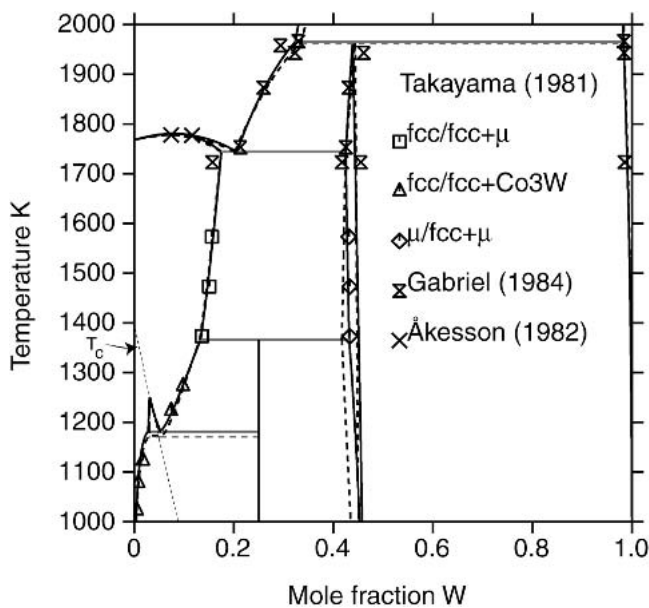


Fig. 6 The Co-W phase diagram according to the present description (solid lines) compared with the description by Fernández Guillermet (Ref 1) and experimental data from various sources

where x_C and x_W are the atomic fractions. The compositions that were obtained in the same carburization experiment are represented with the same symbols. Isoactivity lines calculated with the present description of the fcc phase are also presented. One sees that the positive slope of the isoactivity

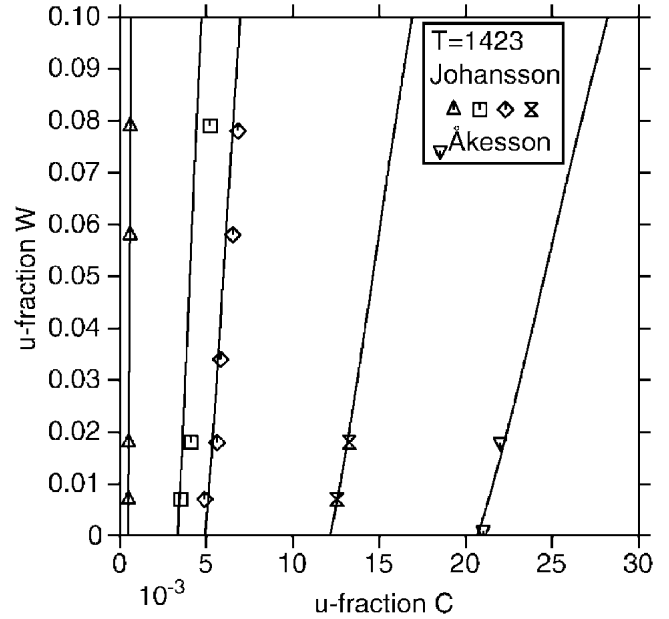


Fig. 7 Isoactivity lines from the present work at 1423 K, compared with experimental data from Johansson (Ref 11) and Åkesson (Ref 3). Isoactivity lines are calculated at C activities of 0.01862, 0.1331, 0.1968, 0.4846, and 0.8222, respectively.

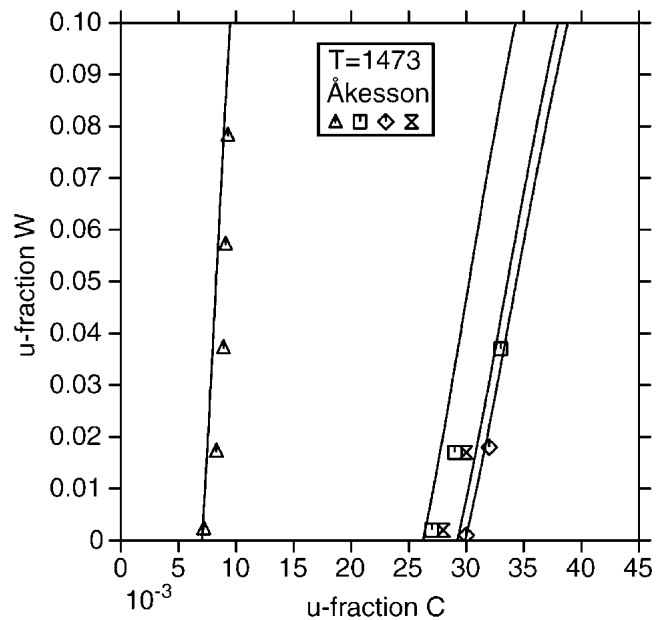


Fig. 8 Isoactivity lines from the present work at 1473 K, compared with experimental data from Åkesson (Ref 3). Isoactivity lines are calculated at 0.2340, 0.8766, 0.9767, and 1.000, respectively.

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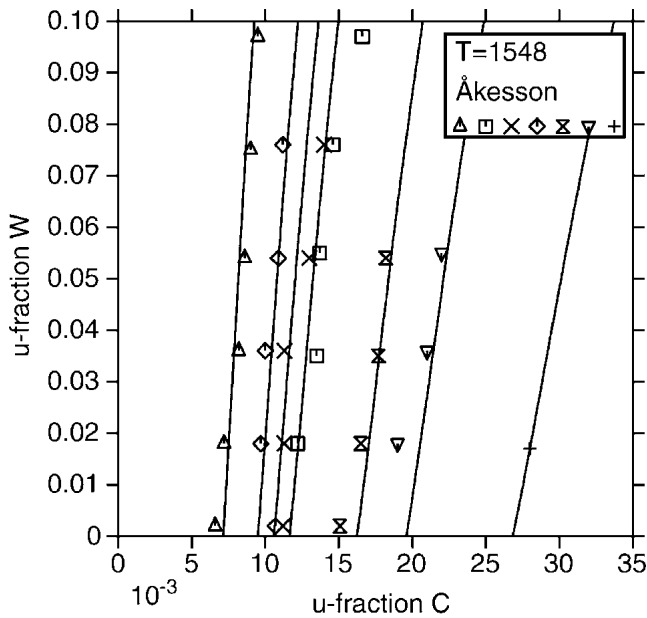


Fig. 9 Isoactivity lines from the present work at 1548 K, compared with experimental data from Åkesson (Ref 3). Isoactivity lines are calculated at 0.1888, 0.2495, 0.2784, 0.3068, 0.4282, 0.5175, and 0.7108, respectively.

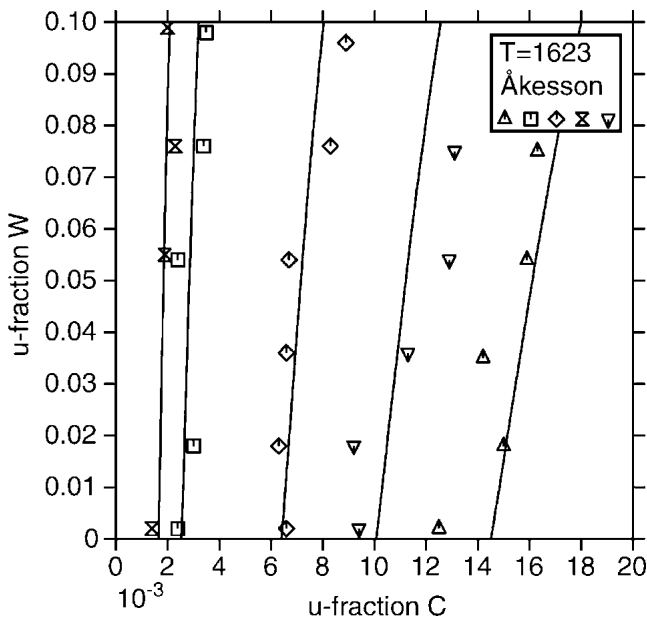


Fig. 10 Isoactivity lines from the present description at 1623 K, compared with experimental data from Åkesson (Ref 3). Isoactivity lines are calculated at 0.03515, 0.05419, 0.1359, 0.2154, and 0.3111, respectively.

line is reproduced within the experimental error by the calculated lines.

Åkesson (Ref 3) and Johansson (Ref 11) also gave information concerning the fcc + carbide and carbide + carbide phase equilibria. Figures 11 to 14 compare the experimental data concerning these equilibria with the cal-

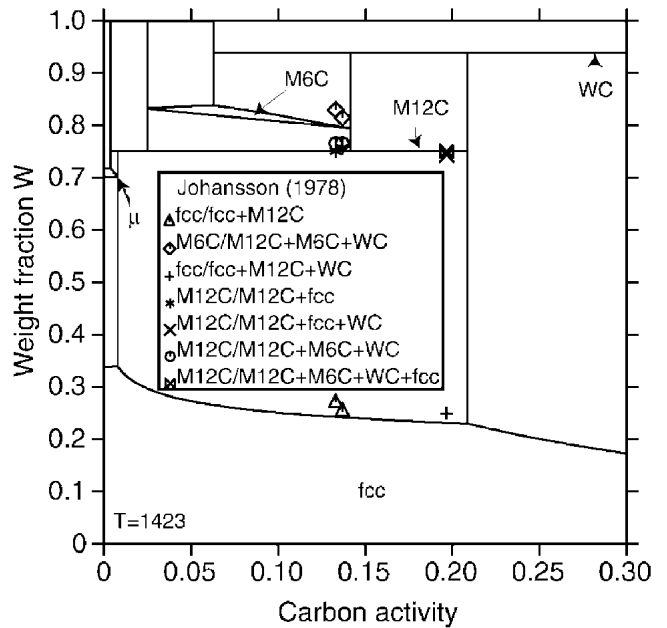


Fig. 11 The Co-W-C phase diagram at 1423 K, according to the present description, compared with experimental data from Johansson (Ref 11)

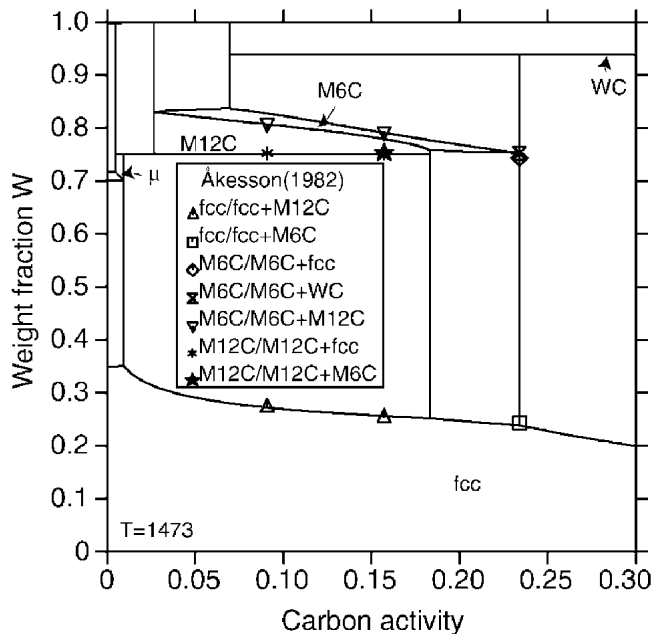


Fig. 12 The Co-W-C phase diagram at 1473 K, according to the present description, compared with experimental data from Åkesson (Ref 3)

culations from the present work. As seen in Fig. 11 to 14, the three phase equilibria are very well described in most cases. The phase boundaries are also fitted within experimental errors for most data.

At a carbon activity near 0.2, Johansson (Ref 11) found a four-phase equilibrium between fcc, $M_{12}C$, M_6C , and WC at 1423 K. This four-phase equilibrium is predicted at 1425

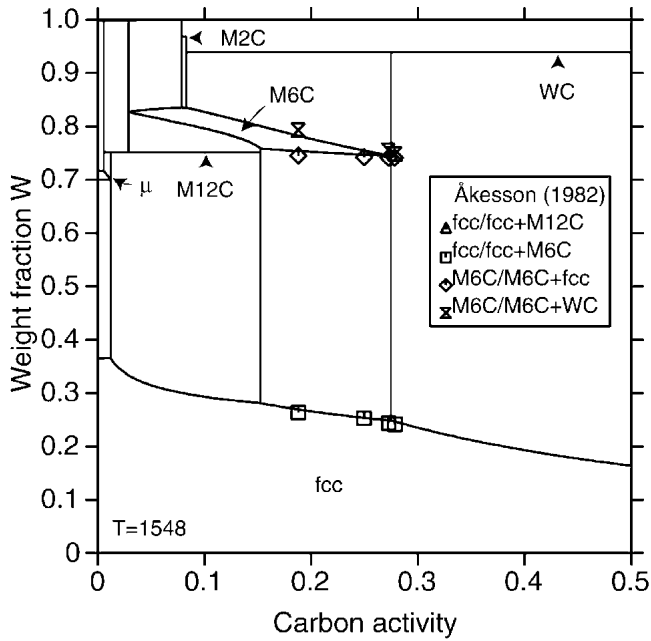


Fig. 13 The Co-W-C phase diagram at 1548 K, according to the present description, compared with experimental data from Åkesson (Ref 3)

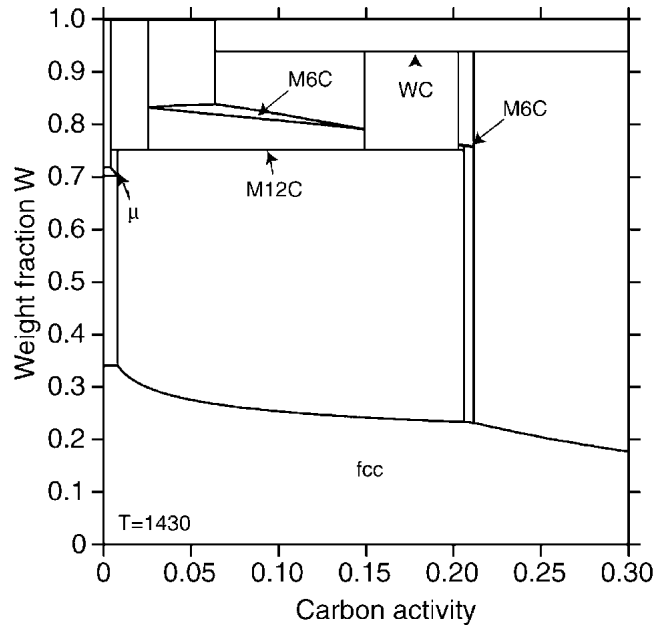


Fig. 15 The Co-W-C phase diagram at 1430 K, according to the present description. Note the presence of Co-rich M_6C carbide

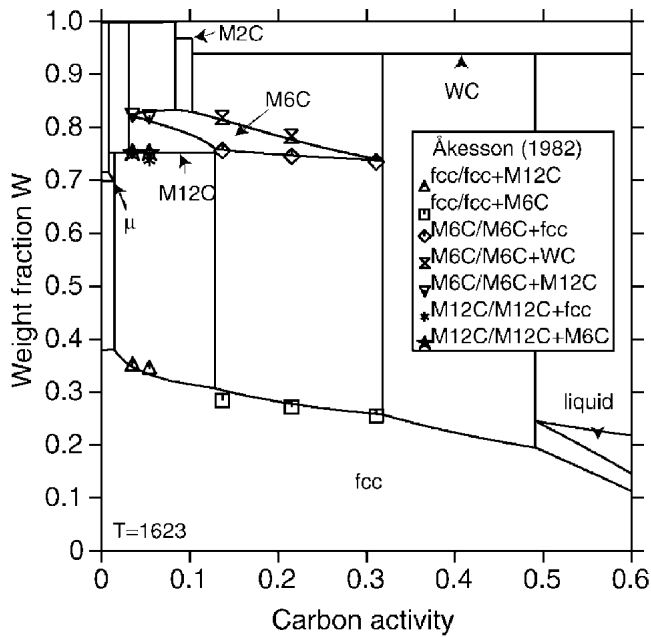


Fig. 14 The Co-W-C phase diagram at 1623 K, according to the present description, compared with experimental data from Åkesson (Ref 3)

K by the present description in which Co-rich M_6C carbide, $Co_{2.89}W_{3.11}C$, is in equilibrium with $M_{12}C$, WC, and fcc. In Fig. 15, the M_6C carbide is shown to be stable both at low- and high-C activities. The L + fcc + MC + M_6C four-phase equilibrium is predicted at 1641 K, as shown in Fig. 16.

The previous figures made comparisons with experimen-

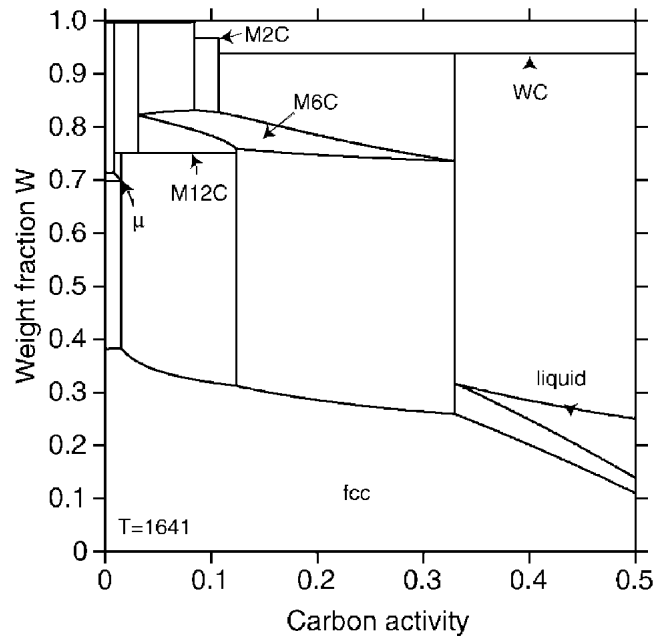


Fig. 16 The Co-W-C phase diagram at 1641 K, according to the present description. Note the four-phase equilibrium.

tal information that was used in the optimization procedure. Figures 17 to 22 compare the present work with other experimental data not used in the optimization. Figures 17 and 19 compare the present work with experimental data from Pollock and Stadelmaier (Ref 16), who have investigated the $M_{12}C$ and M_6C carbides at 1273 and 1673 K. The experiment conducted at 1273 K shows $M_6C + M_2C + bcc$, $M_6C + M_{12}C$, and $M_{12}C + \mu$ -phase + fcc equilibria, which

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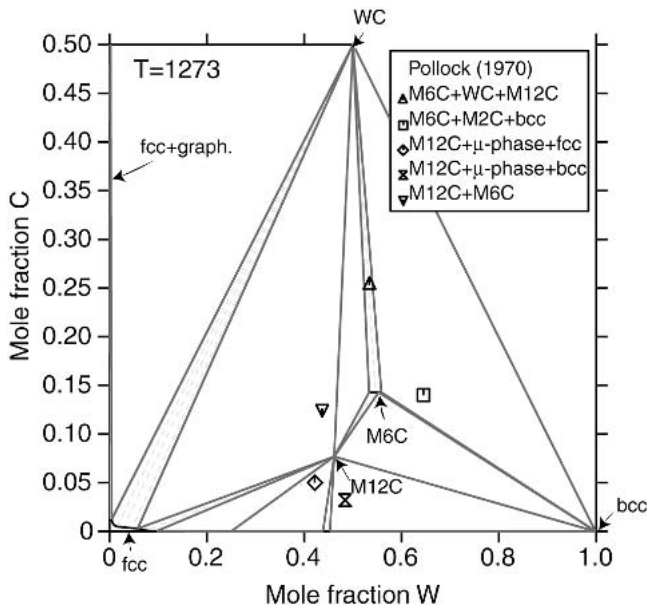


Fig. 17 The Co-W-C phase diagram at 1273 K, according to the present description, compared with the constitution of the experimental alloys studied by Pollock and Stadelmaier (Ref 16). The dashed lines are calculated tie-lines.

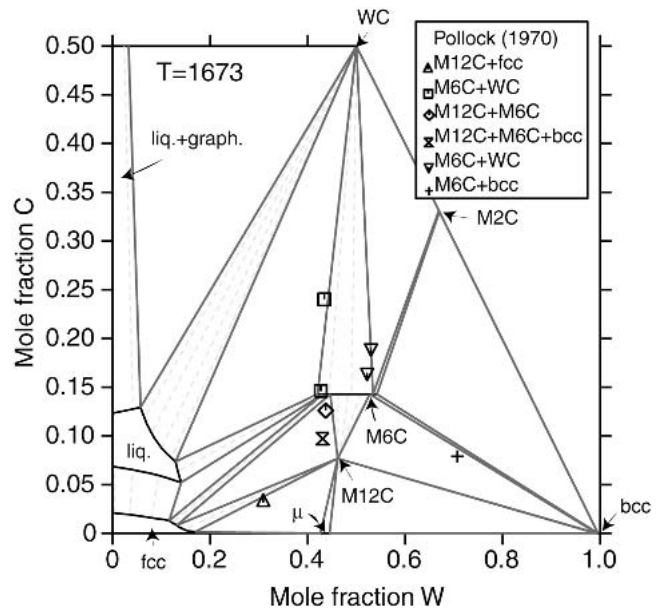


Fig. 19 The Co-W-C phase diagram at 1673 K, according to the present description, compared with the constitution of the experimental alloys studied by Pollock and Stadelmaier (Ref 16). The dashed lines are calculated tie-lines.

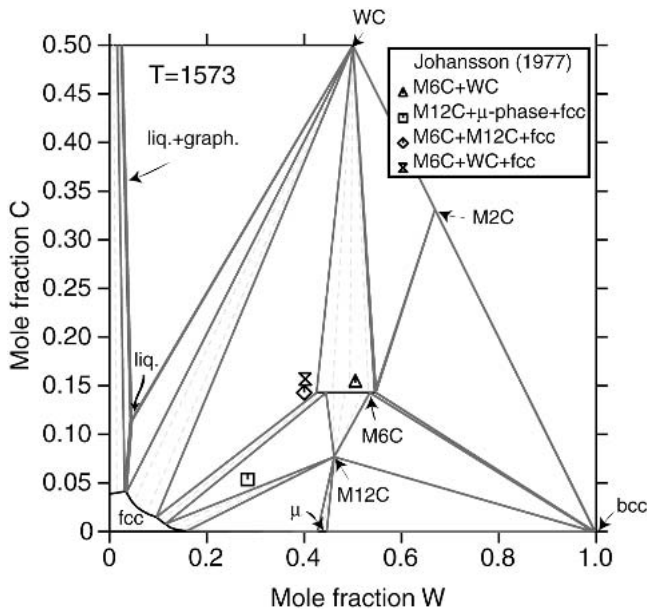


Fig. 18 The Co-W-C phase diagram at 1573 K, according to the present description, compared with the constitution of the experimental alloys studied by Johansson (Ref 11). The dashed lines are calculated tie-lines.

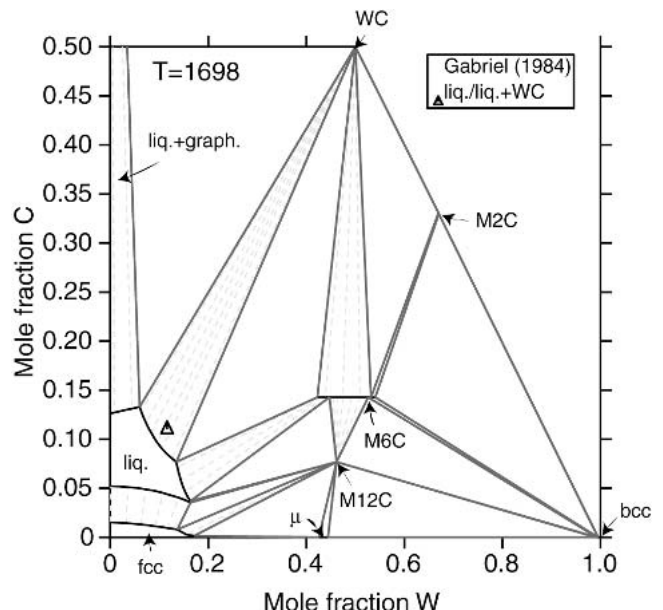


Fig. 20 The Co-W-C phase diagram at 1698 K, according to the present description, compared with the constitution of the experimental alloys studied by Gabriel (Ref 8). The dashed lines are calculated tie-lines.

are not predicted by the present work. One explanation for the discrepancy could be, as mentioned by Pollock and Stadelmaier (Ref 16), that the heat treatment times were too short, leading to metastable phases (e.g., M_2C and Co-rich M_6C).

In Fig. 18, the constitutions of the experimental alloys

studied by Johansson at 1573 K are compared with the present description. The agreement is good for most of the alloys. The different symbols for the $WC + M_6C$ equilibrium in Fig. 19 represent the W-rich (triangles) and Co-rich (squares) M_6C carbide. These equilibrium points are reasonably accounted for in the present description. The other

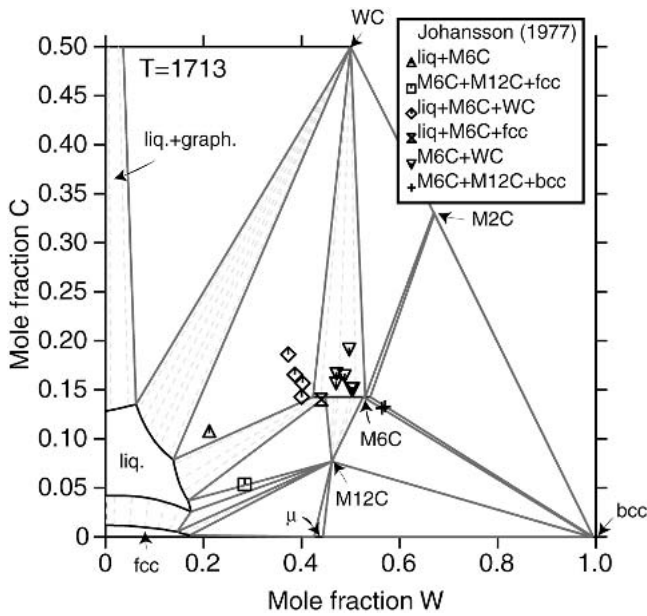


Fig. 21 The Co-W-C phase diagram at 1713 K, according to the present description, compared with the constitution of the experimental alloys studied by Johansson (Ref 11). The dashed lines are calculated tie-lines.

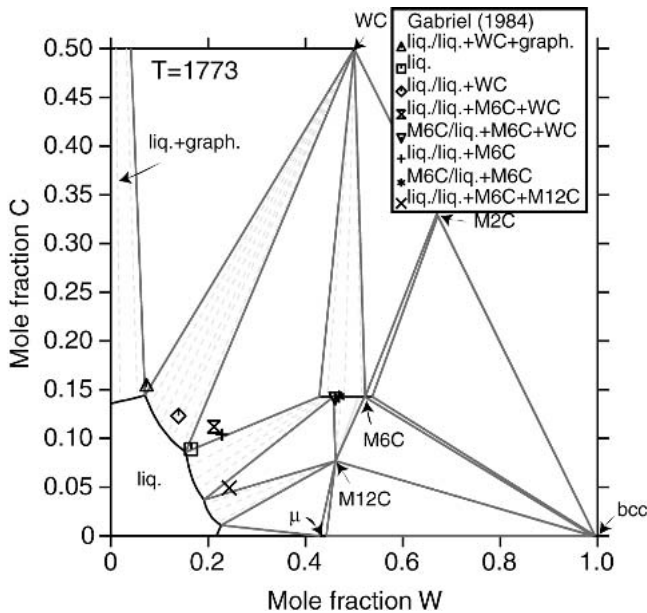


Fig. 22 The Co-W-C phase diagram at 1773 K, according to the present description, compared with the constitution of the experimental alloys studied by Gabriel (Ref 8). The dashed lines are calculated tie-lines.

experimental points agree fairly well with the present work except for the $M_{12}C + M_6C + bcc$ equilibrium, which is inconsistent with the other experimental points. Most of the experimental points from Johansson at 1713 K (Fig. 21) are accounted for by the present work. The experimental points concerning the $L + M_6C + fcc$ and $M_{12}C + M_6C + fcc$

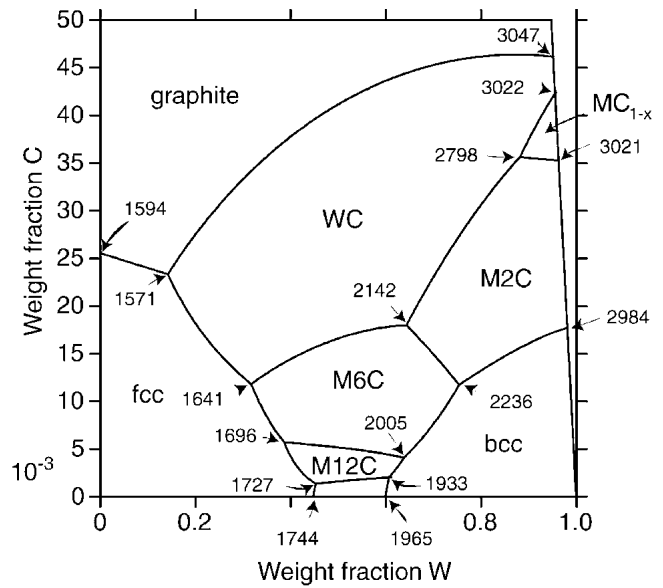


Fig. 23 The projection of the liquidus surface of the Co-W-C system calculated using the present description. Temperatures for the various invariant equilibria are given in degrees Kelvin.

equilibria are not reproduced by the authors' calculations, which could indicate too low a temperature for the $L + M_{12}C + M_6C + fcc$ equilibrium in the present work. The experimental information on this four-phase equilibrium is too scarce to draw any conclusions, and no attempt was made to improve the agreement.

In Fig. 20 and 22, comparisons between the present work and experimental data from Gabriel (Ref 8), at 1698 and 1773 K, respectively, are made. With the selected model and optimization parameters, it was not possible to fit these experiments together with the four-phase equilibrium temperatures determined by Kruse et al. (Ref 4). The information about the four-phase equilibrium temperature was judged to be more important to fit than the liquid phase boundaries at higher temperatures. These boundaries were not satisfactorily described in the previous description by Fernández Guillermet (Ref 1) either.

The calculated projection of the liquidus surface is presented in Fig. 23. The lines show the composition of the L phase in equilibrium with two phases. In Table 2, various data concerning liquid four-phase equilibria are compared. The experimental data from Kruse et al. (Ref 4) were used in the present optimization. The metastable $fcc + M_6C + graphite + L$ equilibrium temperature from the present work agrees with the equilibrium temperatures for $fcc + WC + graphite + L$ by Åkesson (Ref 3) determined from rapid solidification. This could indicate that they measured a metastable equilibrium if the WC carbide was dissolved in the liquid in their experiment. The nucleation of WC carbide from liquid could be difficult to achieve.

5. Conclusions

In the present work, reassessments of the Co-W and Co-W-C systems have been made. The reason for the reassess-

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Table 2 The four-phase equilibria temperatures in the C-Co-W system, according to present description, compared with experimental data from various sources

Equilibrium	Rautala and Norton (Ref 17) (DTA)	Uhrenius et al. (Ref 18) (solidification)	Johansson (Ref 11) (solidification)	Åkesson (Ref 3) (solidification)	Fernández Guillermet (Ref 1) (modeling)	Kruse et al. (Ref 4) (DTA)	Present work (modeling)
fcc + WC + graph. + L	1573	1528	1518-1573	1548	1548	1571	1571
fcc + WC + M ₆ C + L	1632	~1593	1573-1673	1628	1599	1641	1641
fcc + M ₆ C + M ₁₂ C + L	...	1643	1713-1743	1688	1667	...	1696
fcc + μ + M ₁₂ C + L	~1743	...	1716	...	1727
bcc + μ + M ₁₂ C + L	~1873	...	1911	...	1933
bcc + M ₆ C + M ₁₂ C + L	1873-1973	...	1934	...	2005
bcc + M ₆ C + M ₂ C + L	2211	...	2236
WC + M ₆ C + M ₂ C + L	2108	...	2142
WC + M ₂ C + MC _{1-x} + L	~2773	...	2792	...	2798
fcc + M ₆ C + graph. + L (metastable)	...	1518	1497	...	1546

Note: The fcc + WC + graph. + L and fcc + WC + M₆C + L equilibrium temperatures from Kruse et al. (Ref 4) were used in present optimization. All values are in degrees Kelvin. DTA, differential thermal analysis

ments is that new DTA measurements of the equilibrium temperatures have been published by Kruse et al. (Ref 4). In the Co-W system, improvements in the description of the μ-phase boundaries have been achieved. The Co-W-C system shows improvements in the description of the liquid four-phase equilibria temperatures determined by Kruse et al. (Ref 4). The effect on the C activity when adding W to Co-C agrees well with the experimental information. Finally, the fcc + carbide and carbide + carbide phase equilibria were determined within the uncertainty of most of the experimental information. There are some improvements when fitting to C activity (Fig. 11 to 14). These improvements are partly due to improvements in the optimization software.

Acknowledgments

The project committee members Bo Jansson and Susanne Norgren from Sandvik Coromant, and Jenni Zachrisson and Jan Qvick from Seco Tools, are gratefully acknowledged for their comments on the present work. The project was financed by the Centre of Computational Thermodynamics (CCT). CCT is funded by Stiftelsen for Strategisk Forskning (SSF), Sandvik Coromant, Sandvik Hard Materials, Seco Tools, SSAB Tunnpå, SSAB Oxelösund, Uddeholm Tooling, Höganäs, Ovako Steel, AvestaPolarit, Sandvik Materials Technology, Åkers Sweden, Erasteel Kloster, and Thermo-Calc Software AB (TCSAB).

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