

Thermodynamic Evaluation of the C-Co-W-Hf-Zr System for Cemented Carbides Applications

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Cemented carbides consist of hard carbide particles of hexagonal WC and often also of cubic carbides cemented together in a binder consisting of mainly cobalt (Co). A thermodynamic evaluation of the cubic carbide formers hafnium (Hf) and zirconium (Zr) in cemented carbides has been done. Both thermodynamic evaluations of lower-order systems and experimental investigations have been performed. The new experimental information was necessary for a satisfactory thermodynamic description because there is a lack of earlier experiments of this alloy system. The assessment work with the C-Co-W-Hf-Zr system has resulted in a satisfactory description of the thermodynamic properties compared with the experimental values. This work has been done by combining a new assessment of the CoHf and CoZr systems with already assessed investigations of the Hf-C and Zr-C systems. New experimental information in higher-order systems has been used to improve the thermodynamic descriptions and to verify the reliability of the assessments. The main results of the experimental work are measurements of the composition of the cubic carbide in selected equilibria; measurements of the temperatures of the L + fcc + WC + graphite and L + fcc + WC + M_6C equilibria in the C-Co-Hf, C-Co-Zr, and C-Co-W-X (X=Hf and Zr) systems; and measurements of the solubility of Hf and Zr in liquid cobalt. Detailed comparisons between calculated and experimental data are presented.

Keywords CALPHAD approach, differential thermal analysis (DTA), experimental phase equilibria, invariant equilibria, thermodynamic assessment

1. Introduction

Cemented carbides are produced by liquid phase sintering and consist of grains of hard hexagonal WC embedded in a more ductile binder phase, mainly based on cobalt (Co). Often, other hard phase grains are also presented in the form of carbides and nitrides with a cubic structure. The metal composition of the cubic phase may vary over a wide range but is often a mixture of tungsten (W), titanium (Ti), tantalum (Ta), and niobium (Nb). The hard grains span from submicron size to several micrometers. The content of the binder phase is rather low, typically less than 20 vol%. Zirconium (Zr) and hafnium (Hf) also form cubic carbides and nitrides and are therefore of interest for these applications. Few experimental investigations have been done with Zr and Hf in cemented carbides, and one of the aims was to increase the knowledge about these elements experimentally.

Thermodynamic modeling is a powerful tool in the development of new materials. Within the center for computational thermodynamics (CCT) a thermodynamic database for cemented carbides has been developed.^[1] The present paper describes the addition of the alloying elements Hf and Zr to that database. This work has been done using available

assessments and generating new accurate thermodynamic experimental information on the C-Co-W-Hf-Zr system used for new assessments. A well-established method, the CALPHAD method was adopted.^[2,3] It involves an evaluation of the Gibbs energy functions of the various phases by computer coupling of phase diagram data with thermochemical measurements. The compound energy formalism was selected to describe the Gibbs energy.^[4]

The phases of interest to model are WC, cubic carbide and face-centered cubic (fcc)-Co. In addition, descriptions of the graphite and M_6C are needed to be able to calculate the critical equilibria involving these phases. These phases are important because the carbon (C) content in cemented carbide is adjusted to avoid the formation of graphite or M_6C . During sintering of cemented carbides the binder phase is in the liquid state, thus a description of the liquid phase is also needed.

The approach selected to model the C-Co-W-Hf-Zr system was to assess lower-order systems and combine them with previously available assessments. By this method, a preliminary database is set up. The preliminary database is used to calculate the phase equilibria, which are needed to plan the experimental work. By combining experimental and assessment work, successively improved versions of the database can thus be produced.

2. Models and Methods

2.1 Thermodynamic Models

The solid phases were described by using a two-sublattice version of the compound energy formalism,^[4] $(Co, W, Hf, Zr)_a(C, Va)_c$. The Gibbs energy, as a function of temperature and composition, is described by the expression

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Table 1 Models for the phases

Phase	Model (Co, W, Hf, Zr) _a (C, Va) _c	Comment
bcc	$a = 1, c = 3$...
fcc	$a = c = 1$...
hcp	$a = 1, c = 0.5$...
MC	$a = c = 1$	Cubic carbide
M ₆ C	(Co) ₂ (W) ₂ (Co, W) ₂ C	Ref 8
WC	WC	Simple hexagonal

$$G_m^\phi = \sum_M \sum_I y_M y_I {}^\circ G_{M:I}^\phi + RT \left(a \sum_M y_M \ln y_M + c \sum_I y_I \ln y_I \right) + {}^E G_m^\phi + G_m^{\phi mg} \quad (\text{Eq 1})$$

where M represents the elements on the first sublattice and I the elements on the second sublattice. The y parameters denote the fraction of lattice sites occupied by a given component. The quantity ${}^\circ G_{M:I}^\phi$ represents the Gibbs energy of the compound $M_a I_c$ and is referred to the enthalpy of the stable element reference (SER), which is defined as the stable state of the respective element at 298.15 K and 0.1 MPa. The parameter ${}^\circ G_{M:Va}^\phi$ is the Gibbs energy of pure element M ($M = \text{Co, W, Hf, Zr}$) with the structure ϕ in a hypothetical nonmagnetic state, and ${}^\circ G_{M:C}^\phi$ is the Gibbs energy of a hypothetical nonmagnetic state where all the interstitial sites are filled with carbon. The excess Gibbs energy in Eq 1, ${}^E G_m^\phi$ represents the nonideal contributions to mixing and it was expressed as shown in Eq 2, where all the L^ϕ parameters can be composition and temperature dependent. The composition dependence of the L^ϕ parameters is expressed by the so-called Redlich-Kister polynomial.^[5] The term $G_m^{\phi mg}$ in Eq 1 gives a magnetic contribution to the Gibbs energy proposed by Inden^[6] and modified by Hillert and Jarl.^[7] However, the M₆C phase was modeled utilizing a four sublattice model. The metallic sites are divided into three separate sublattices based on crystallographic information.^[8]

$${}^E G_m^\phi = \sum_i \sum_j y_i y_j (y_C L_{i,j:C}^\phi + y_{Va} L_{i,j:Va}^\phi) + y_C y_{Va} \sum_i y_i L_{i:C,Va}^\phi + \sum_i \sum_j \sum_k y_i y_j y_k (y_C L_{i,j,k:C}^\phi + y_{Va} L_{i,j,k:Va}^\phi) \quad (\text{Eq 2})$$

$i \neq j \neq k$

2.2 Phases and Structures

The phases that have been studied in detail are the liquid, body-centered cubic (bcc), face-centered cubic (fcc) and hexagonal close-packed (hcp) states of the metallic elements. The cubic carbide has been treated as a C-rich solution of the fcc state of the metal, and the hexagonal carbide as a C-rich solution of the hcp state of the metal. The models for the different phases are summarized in Table 1.

2.3 Evaluation of Thermodynamic Parameters

The evaluation of thermodynamic parameters was carried out using the PARROT^[9] module of the Thermo-Calc^[10] data-bank system. This module works by minimizing an error sum where each piece of information is given a certain weight according to its estimated accuracy and allows the simultaneous consideration of various types of thermodynamic and phase diagram data. The best-fit criterion follows the maximum likelihood principle and that principle as a criterion for best fit is most efficient when the amount of data is large. The last has been shown in many different works within the Calphad society.

3. Experimental information

3.1 Background

The experimental information used to evaluate the thermodynamic parameters in the models is very important; as accurate thermodynamic calculations as possible must be reached for multicomponent equilibria. Also important is the reliability and consistency of the experimental information. Because there is a lack of this kind of information for a cemented carbides system with Hf and Zr, a new critical experiment was performed as part of the present work. The critical equilibria to investigate were identified to be the temperature at which the Co phase (fcc) melts in various alloys, the solubility of W in the cubic carbide, and the solubility of Hf and Zr in the Co-rich liquid phase.

3.2 Differential Thermal Analysis Experiments

Differential thermal analysis (DTA) experiments have been performed to determine the temperature of the invariant melting in the Co-Me-C pseudobinaries (Me = Hf or Zr) at carbon activity unity. For the C-Co-W-Hf/Zr systems, the corresponding invariant equilibria will also include the cubic carbide phase. The chemical compositions for the latter alloys were chosen so that either free graphite or M₆C phase was present at the invariant equilibrium $L + \text{fcc-Co} + \text{WC} + \text{cubic carbide} + \text{graphite/M}_6\text{C}$ phase. This was done using the CN2000 database^[11] calculating the C-Co-W-Ti system so approximately 32% liquid, 32% WC, 32% cubic carbide, and 4% graphite/M₆C by volume phase existed at 1450 °C and atmospheric pressure. Then the mole fraction of Ti was replaced by Hf or Zr. From these calculations, around 100 g powder was produced for each alloy, and the raw materials used in the experiment were the same as in cemented carbides production. The samples were prepared in 0.25 L ball mills running 485 min together with 900 g milling bodies and 50 ml milling fluid. From these mixtures, a sample of approximately 90-150 mg was taken out for DTA runs.

A B24 Setaram instrument equipped with symmetrical thermal analyzer, TAG 24, was used. For equilibria with M₆C phase alumina crucibles were used and graphite crucibles for equilibria with graphite. The crucible containing the sample was closed with a lid to reduce any interaction between sample and furnace atmosphere. Samples were cycled three times between 1250 and 1450 °C at a rate of

Table 2 Comparison between measured and calculated melting temperatures for the Co-rich fcc phase (solidus temperatures)

Alloy system	Equilibrium	Freezing point depression		
		Measured <i>T</i> , °C	Calculated <i>T</i> , °C	ΔT , °C
C-Co-Hf	Graphite	1310	1310	-11/-11
C-Co-Zr	Graphite	1295	1295	-26/-26
C-Co-W-Hf	Graphite	1290	1291	-8/-7
C-Co-W-Hf	M ₆ C	1360	1358	-8/-10
C-Co-W-Zr	Graphite	1283	1284	-15/-14
C-Co-W-Zr	M ₆ C	1358	1354	-10/-14

2 °C/min in an atmosphere of slowly flowing argon. After the last cycling, the sample was allowed to rapidly cool down to room temperature. The temperature readings were calibrated by comparing the eutectic temperature for the C-Co system, using both an alumina and a graphite crucible, with the assessed value of Fernández Guillermet.^[12] This calibrating procedure resulted in an adjustment of the experimental values by -3 °C. To measure the freezing point depression caused by Hf and Zr additions, the temperature 1298 °C for L+ fcc-Co + WC + graphite and 1368 ° for L+ fcc-Co + WC + M₆C in the C-Co-W system from earlier experiment^[13] were used. Samples were picked out of the crucible after each experiment. Polished sections were prepared and phases were identified by light optical microscope (LOM) to secure the expected phase assembly. A summary of the experimental DTA results compared with calculations using the assessed thermodynamic description in the present work can be found in Table 2.

3.3 Measurements of the W Solubility in the Cubic Carbide

Measurements of the W solubility in the cubic carbide have been performed for the C-Co-W-Hf and C-Co-W-Zr systems in equilibria with WC and graphite. The composition for the two different alloys has been prepared as described in Sec. 3.2, but in this case also 2 vol% of an organic binder has been added to facilitate the manufacturing of green bodies. The samples were then sintered with a standardized sintering cycling up to 1450 °C followed immediately by heat treatment of 4 h under 40 mbar argon at two different temperatures, 1600 and 1800 °C. The samples were then cooled down to room temperature in the oven. The W solubility in the cubic carbide was measured with the electron microprobe analysis (EPMA) technique. In the present work, a JEOL model JXA-8900R was used. The microstructure was investigated by LOM to ensure the correct phase assembly. A summary of the experimental electron probe microanalysis (EPMA) results compared with calculations using the assessed thermodynamic description in the present work can be found in Table 3.

3.4 Measurements of the Solubility of Hf and Zr in the Co-Rich Liquid Phase

The solubility of Hf and Zr in liquid Co in equilibrium with the MC, WC, and graphite/M₆C phase was recently

Table 3 Comparison between measured and calculated solubility of W in the cubic carbide

Alloy system	Equilibrium	Temperature, °C	Measured W, wt. %	Calculated W, wt. %
C-Co-W-Hf	Graphite	1600	14.42	13.77
C-Co-W-Hf	Graphite	1800	19.33	19.44
C-Co-W-Zr	Graphite	1600	23.61	20.00
C-Co-W-Zr	Graphite	1800	24.64	28.09

measured by Andersson and Jansson^[14] using a diffusion couple technique. A mean value of several measurements is given in Table 4 as the molar ratio of Hf and Zr to Co present in the liquid. These values were not used for an adjustment of the thermodynamic parameters. The corresponding value taken from the calculations is also given in Table 4.

4. Assessments of the Lower Order Systems

4.1 Introduction

The alloy system thermodynamically modeled in the present work is the C-Co-W-Hf-Zr system. Assessments of all the binary subsystems except of Co-Hf and Co-Zr are available from earlier work. The two missing binary systems were assessed in the present work with the goal of obtaining a reasonable description of the liquid only. The binary systems Hf-C and Zr-C were taken from earlier work by Bitterman and Rogl^[15] and by Fernández Guillermet,^[16] respectively. Shao recently assessed the Hf-W system,^[17] and the thermodynamics for the liquid phase in the W-Zr system were taken from theoretical based estimations by Miedema et al.^[18] The remaining binary systems have been taken from the database for cemented carbides CN2000, which were developed within the Swedish material consortium CAMPADA.^[11]

The ternary systems C-Co-Hf and C-Co-Zr were first investigated when all the binary systems had been added together. After that, the work continued to the quaternary systems C-Co-W-Hf and C-Co-W-Zr. The experimental information according to Sec. 3 was used to verify the information generated from the added binary system but most importantly to improve the thermodynamic description of the ternaries and quaternaries. In Table 5, all the thermodynamic parameters optimized in the present work are summarized.

4.2 Binary Co-Hf System

The assessment of the binary Co-Hf system is based on the phase diagram from the literature^[19] and of theoretically calculated enthalpy of formation values for different phases from Miedema et al.^[18] The temperatures for all the different phase equilibria are taken from the phase diagram according to Massalski^[19] and the phases Co₂Hf, CoHf, and CoHf₂ have been approximated to be stoichiometric. After all thermodynamic parameters have been optimized (Table 5) a phase diagram can be created (Fig. 1).

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Table 4 The solubility of Hf and Zr in liquid Co at three different temperatures given as the molar ratio of Hf and Zr (M) to Co in the liquid phase

Alloy system	Experiment		Calculated	
	Graphite, % n_M/n_{Co}	M_6C , % n_M/n_{Co}	Graphite, % n_M/n_{Co}	M_6C , % n_M/n_{Co}
C-Co-W-Hf	1500 °C	1.04	1.59	1.23
	1450 °C	0.89	1.30	1.07
	1400 °C	0.73	0.41	1.05
C-Co-W-Zr	1500 °C	2.38	2.71	1.64
	1450 °C	2.37	2.29	1.53
	1400 °C	1.96	1.91	1.41

Table 5 Optimized thermodynamic parameters in this present work

Phase	Parameter	Value
bcc	${}^0L_{Co,Hf:Va}^{bcc}$	-91,154
fcc	${}^0L_{Co,Hf:Va}^{fcc}$	-83,611
hcp	${}^0L_{Co,Hf:Va}^{hcp}$	-44,605
Liquid	${}^0L_{Co,Hf}^{Liquid}$	-127,000
Co_2Hf	${}^0G_{Co,Hf}^{Co_2Hf} - 2H_{Co}^{SER} - H_{Hf}^{SER}$	-161,982 + 20.1T
CoHf	${}^0G_{Co,Hf}^{CoHf} - H_{Co}^{SER} - H_{Hf}^{SER}$	-112,776 + 13.5T
$CoHf_2$	${}^0G_{Co,Hf}^{CoHf_2} - H_{Co}^{SER} - 2H_{Hf}^{SER}$	-137,644 + 24.6T
bcc	${}^0L_{Co,Zr:Va}^{bcc}$	-93,690
fcc	${}^0L_{Co,Zr:Va}^{fcc}$	-88,100
hcp	${}^0L_{Co,Zr:Va}^{hcp}$	-87,600
Liquid	${}^0L_{Co,Zr}^{Liquid}$	-131,500
Co_2Zr	${}^0G_{Co,Zr}^{Co_2Zr} - 2H_{Co}^{SER} - H_{Zr}^{SER}$	-187,000 + 28.1T
CoZr	${}^0G_{Co,Zr}^{CoZr} - H_{Co}^{SER} - H_{Zr}^{SER}$	-128,600 + 23.0T
$CoZr_2$	${}^0G_{Co,Zr}^{CoZr_2} - H_{Co}^{SER} - 2H_{Zr}^{SER}$	-141,600 + 23.2T
Liquid	${}^0L_{W,Zr}^{Liquid}$	-36,000
fcc	${}^0L_{Hf,W:C}^{fcc}$	4,000
fcc	${}^0L_{W,Zr:C}^{fcc}$	6,000
Liquid	${}^0L_{Co,W,Zr}^{Liquid}$	110,000

Note: J/mol; element for pure data was taken from the SGTE unary database^[23]; functions valid in the temperature range 298.15-6000 K

4.3 Binary Co-Zr System

The same approach and assumptions have been taken for the binary Co-Zr system, as for the Co-Hf system. The calculated phase diagram can be seen in Fig. 2.

Compared with the phase diagram from Massalski,^[19] some intermetallic phases are missing and some invariant temperatures show some deviation. Because the main aim of the present work was to experimentally investigate how Hf or Zr influences cemented carbides, the rough assessments here are accepted. In the case of cemented carbides, only extrapolations from the Co side of the binary system are important.

Gue and Kleppa^[20] measured the enthalpy of formation for the intermetallic phases in the Co-Hf and Co-Zr systems using high-temperature direct synthesis calorimetry. In this work, the values theoretically calculated by Miedemas et

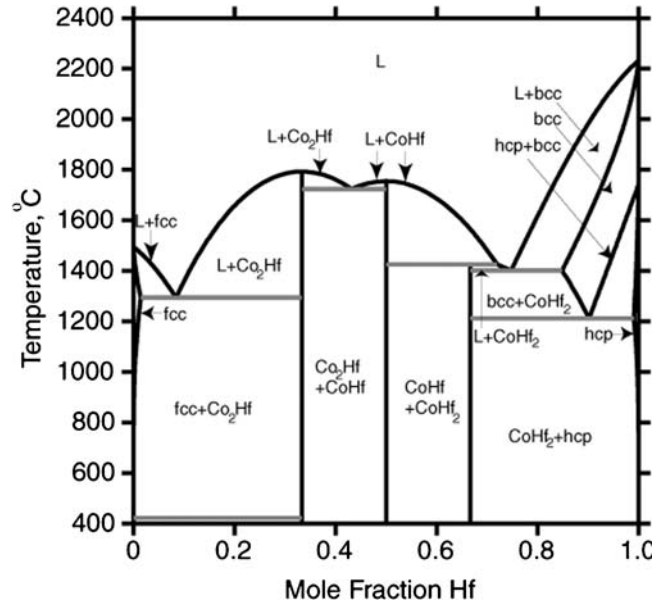


Fig. 1 Calculated Co-Hf system with the present work thermodynamic parameters

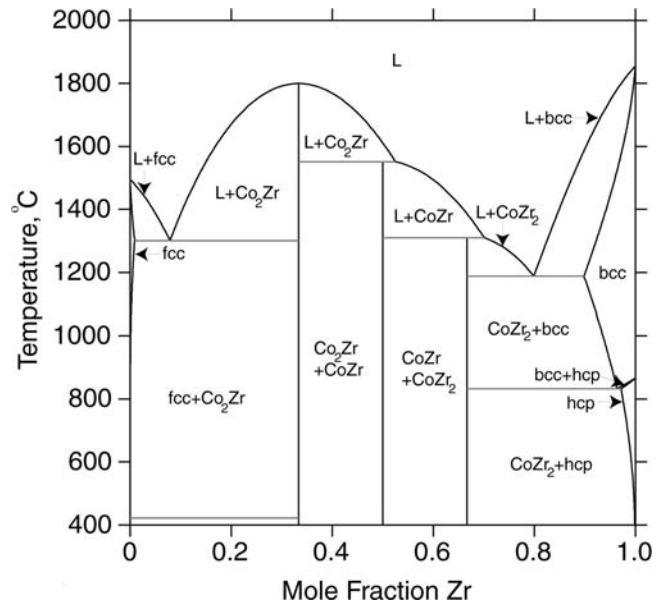


Fig. 2 Calculated Co-Zr system with the present work thermodynamic parameters

al.^[18] were used both for the solid compounds as for the liquid because Gue and Kleppa^[20] did not present any measurements in the liquid. In Table 6, a comparison between the values measured by Gue and Kleppa^[20] and those calculated here is shown. In general, the calculated values based on Miedema's predictions are 10-20 kJ/mol higher than the values from Gue and Kleppa.^[20]

4.4 Ternary C-Co-Hf System

Simple extrapolations from the binary systems gave some lower calculated invariant melting temperatures in

Table 6 Comparison of the calculated enthalpies of formation in the present work (at 298 K) to reported values in the work by Guo and Kleppa^[19] and Miedema et al.^[18]

Compound	Guo and Kleppa ^[19]	Miedema et al. ^[18]	Present work
CoZr	-35.8	-60	-60
Co ₂ Zr	-35.8	-56	-57
CoZr ₂	-26.4	-44	-44
CoHf	-42.8	-51	-52
Co ₂ Hf	-39.4	-48	-48
CoHf ₂	Not measured	-38	-43

All values in kJ/mol

comparison with the results from the DTA experiment in Sec. 3.2. Instead of assessing a ternary interaction parameter in the liquid, ${}^0L_{C,Co,Hf}^{Liquid}$, it was decided to adjust the description of the liquid in the binary Co-Hf system. To use a ternary interaction parameter with a relatively high value to counteract the effect of a badly assessed binary interaction parameter was considered to be a worse alternative. This resulted in the binary interaction parameter in the liquid, ${}^0L_{Co,Hf}^{Liquid}$, changing from -140 kJ/mol as predicted by Miedema et al.^[18] to -127 kJ/mol when the ternary interaction parameter was put to zero. The change of Miedema's theoretical value is probably within the accuracy of prediction and was therefore accepted in the present work. This adjustment resulted in marginal changes in the description of the binary Co-Hf system, but a very good agreement between the calculated invariant temperatures compared with experimental DTA values for the C-Co-Hf system is reached (Table 2). A calculated section at a carbon activity of unity can be seen in Fig. 3.

4.5 Ternary C-Co-Zr System

In the same way as that used for the ternary C-Co-Hf system, the binary interaction parameter in liquid for the Co-Zr system, ${}^0L_{Co,Zr}^{Liquid}$, was adjusted to fit the ternary invariant temperature for the ternary C-Co-Zr system. This resulted in the value predicted by Miedema et al.^[18] changing from -164 to -131.5 kJ/mol. The ternary interaction parameter in liquid, ${}^0L_{C,Co,Zr}^{Liquid}$, was also put to zero, which led to a good agreement compared with the experimental DTA values (Table 2). A calculated section at a carbon activity of unity can be seen in Fig. 4.

Dmitrieva and Shurin^[21] have also measured the invariant melting temperature for the C-Co-Hf and C-Co-Zr systems. They found much higher temperatures, 1400 °C for the C-Co-Hf system and 1370 °C for the C-Co-Zr system, which are probably caused by inhomogeneous samples because they were cast.

4.6 Quaternary C-Co-W-Hf System

At the assessment of the quaternary C-Co-W-Hf system, both the experimental invariant temperatures and the W solubility in the cubic carbide have been taken into consid-

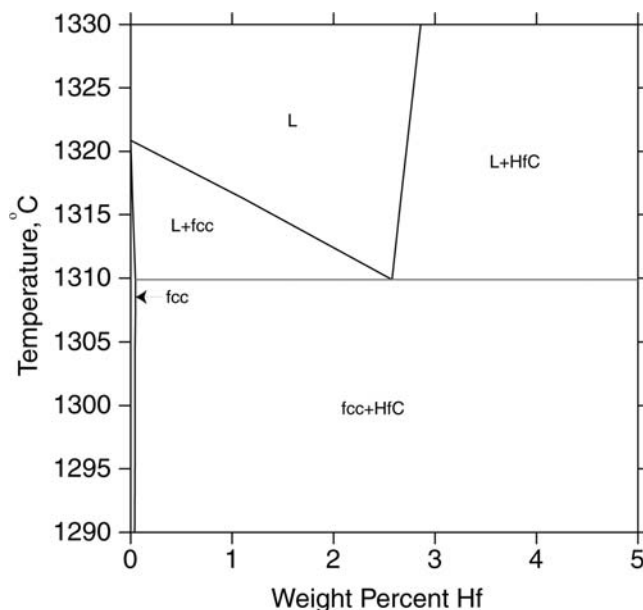


Fig. 3 Calculated section of the ternary C-Co-Hf system in equilibrium with graphite

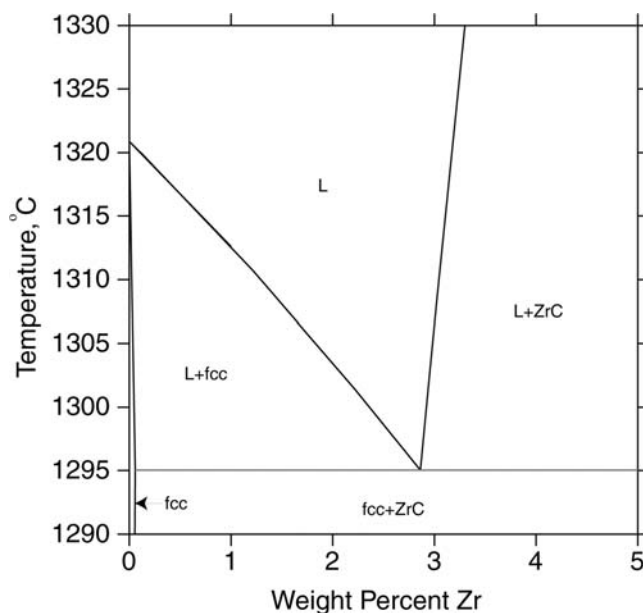


Fig. 4 Calculated section of the ternary C-Co-Zr system in equilibrium with graphite

eration. To fit the experimental result on the W solubility in the cubic carbide, an interaction parameter between Hf and W in the fcc phase with C on the interstitial sites was necessary. It was optimized to the value, ${}^0L_{Hf,W:C}^{fcc} = 4000$ J/mol. With this small interaction parameter, the ternary C-Hf-W system was comparable to the one drawn by Holleck.^[22] The calculated solubility of W in the cubic carbide in equilibrium with WC at carbon activity of unity has been compared with experimental data in Fig. 5 and Table 3.

With the above and earlier shown parameters from the lower-order system, it was not necessary to use any more

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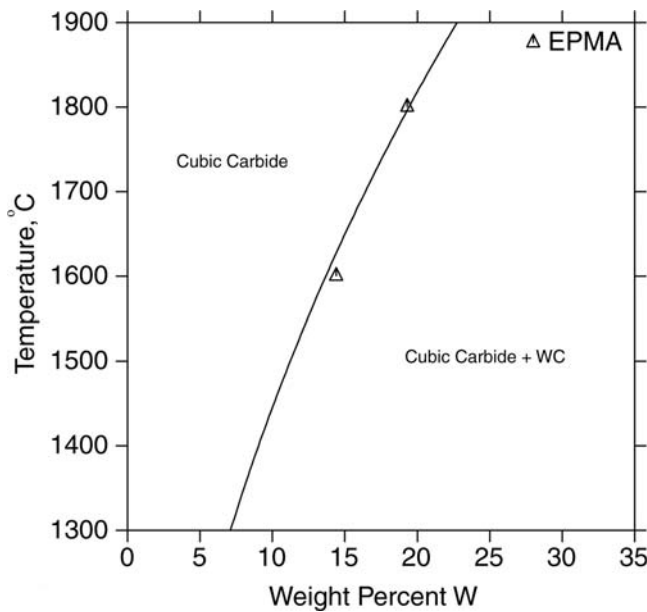


Fig. 5 W solubility in the cubic carbide at equilibria with graphite and WC for the C-Hf-W system compared against EPMA measurements

parameters to be able to describe the invariant temperatures for the C-Co-W-Hf system in equilibrium with the graphite or M_6C phase (Table 2). The result was the ternary interaction parameter, ${}^0L_{Co,Hf,W}^{Liquid}$, was set to zero in this case. Figure 6 shows the interesting part of the C-Co-W-Hf system where one can see clearly that the agreement with DTA measurements is satisfactory.

4.7 Quaternary C-Co-W-Zr System

For the assessment of the quaternary C-Co-W-Zr system, both the experimental invariant temperatures and the W solubility in the cubic carbide have been taken into consideration. The added interaction between Zr and W in liquid from Miedema et al.^[18] is in this case, ${}^0L_{W,Zr}^{Liquid} = -36000$ J/mol. To fit the result on the W solubility in the cubic carbide, an interaction parameter between Zr and W in the fcc phase with C on the interstitial sites was necessary. This interaction parameter was optimized to the value, ${}^0L_{W,Zr:C}^{fcc} = 6000$ J/mol. With this small interaction parameter the ternary C-W-Zr system was comparable with the one drawn by Holleck.^[22] The calculated solubility of W in the cubic carbide in equilibrium with WC at carbon activity of unity has been compared with experimental data in Fig. 7 and Table 3.

The above and earlier shown parameters from lower-order systems did not give a satisfactory description of the invariant temperatures for the C-Co-W-Zr system in equilibrium with graphite respectively M_6C phase. To fit these temperatures satisfactorily, a ternary interaction parameter between Co, W, and Zr in liquid, ${}^0L_{Co,W,Zr}^{Liquid}$, was necessary. This parameter ended up with the value 110,000 J/mol, which gave a good description of the invariant temperatures (Table 2). Figure 8 shows the interesting part of the C-Co-W-Zr system, and one can clearly see that the agreement with DTA measurements is satisfactory.

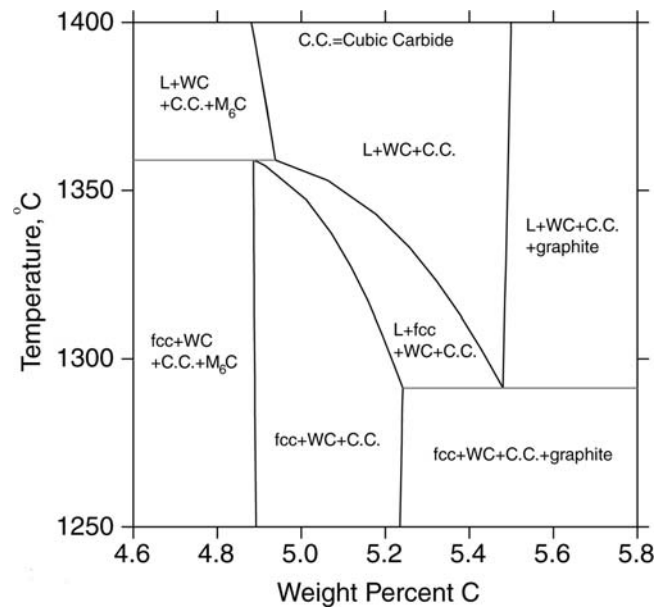


Fig. 6 Interesting part of the C-Co-W-Hf system, calculated at 20 wt.% Hf and 16 wt.% Co, shows the invariant temperatures in equilibria with graphite or M_6C

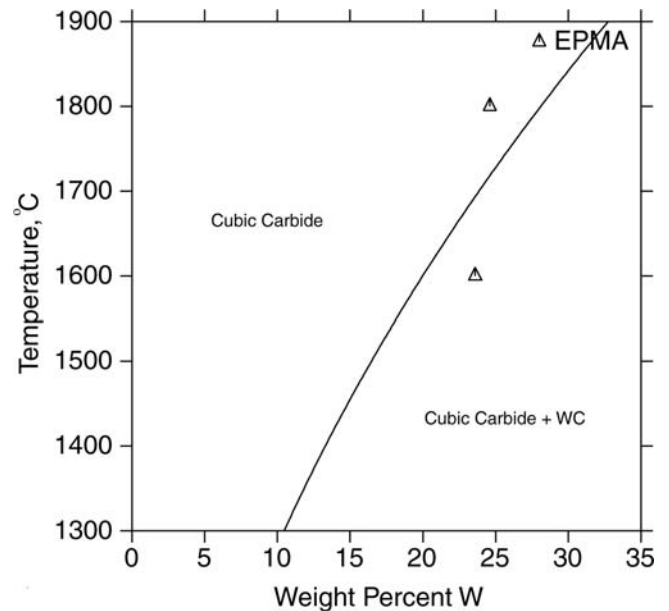


Fig. 7 W solubility in the cubic carbide at equilibria with graphite and WC for the C-Zr-W system compared against EPMA measurements

5. Summary and Conclusions

The already existing database for cemented carbides CN2000 has been expanding through the addition of the elements Hf and Zr. New assessments of the binary Co-Hf and Co-Zr systems were necessary due to lack of earlier information. These new assessments have been performed and added to already existing assessments on the C-Hf and

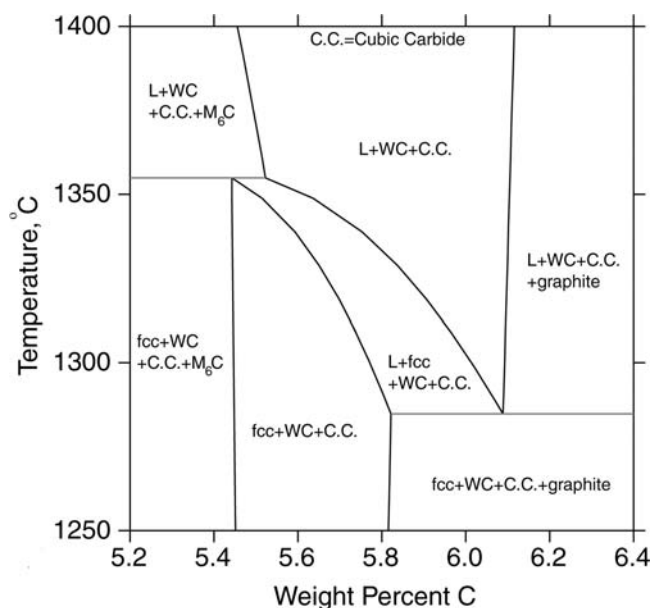


Fig. 8 The interesting part of the C-Co-W-Zr system, calculated at 11.5 wt.% Zr and 18 wt.% Co, shows the invariant temperatures in equilibria with graphite or M_6C

C-Zr systems. It should be pointed out that the new assessments are simplified but show that a practically useful description can be obtained with a preliminary database for cemented carbides. In the future, more accurate assessments must be done for these systems.

Thermodynamic information has been produced in the present work for both Hf and Zr in ternary and quaternary systems with C, Co, and W. All the experimental information presented in this work has been used to adjust the database and increase the precision of calculated predictions. These adjustments have resulted in a thermodynamic database that describes the experimental information well. All thermodynamic model parameters assessed in the present work are given in Table 5. To create an even more accurate database for cemented carbides, more critical experimental information must be produced and fitted to verify the reliability. Another area that must be investigated in the future is the multicomponent calculations that are based on extrapolations from lower-order systems, which in some cases may lead to errors or deviations. Trends are often correct, but absolute values tend to deviate for systems such as commercial cemented carbides, which often contain many alloying elements in high concentrations.

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