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A THERMODYNAMIC EVALUATION OF THE Co-Cr AND THE C-Co-Cr SYSTEMS

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ABSTRACT The thermodynamic properties of the systems Co-Cr and C-Co-Cr have been analyzed with the CALPHAD technique using a computerized optimization procedure. The Gibbs Energy of the stable phases have been evaluated applying the compound energy model. A good agreement with a set of selected consistent experimental phase diagram and thermochemical data was obtained.

1 Introduction

The Co-Cr system has been thoroughly investigated experimentally. There is an extensive set of experimental thermochemical and phase diagram data. Previously, Allibert *et al.* [78Al] and Hasebe *et al.* [82Has] investigated the system and calculated phase diagrams. The main features of these two calculated phase diagram are in agreement. However, neither of the two investigations include a treatment of the magnetic separations on the Co-rich side.

The C-Co-Cr system is industrially interesting due to a monovariant eutectic reaction forming an alloy containing a Co-Cr matrix reinforced with carbides. Further more, Cr is an important alloying element for Co-bonded WC tools to inhibit grain coarsening during sintering and to increase corrosion resistance along with mechanical strength of the binder. It is therefore interesting to extend the evaluation of the present ternary system, C-Co-Cr, to the quaternary system, C-Co-Cr-W, in the future. The most thorough experimental determination of the phase diagram for the C-Co-Cr system was performed by Köster and Sperner [55Kos]. They investigated several monovariant reactions and an isothermal section.

2 Experimental Data

2.1 Co-Cr

The binary system Co-Cr has been investigated by several different research teams during this century. There are experimental phase diagram data as well as thermochemical data. In this evaluation the most recent experimental data are used.

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Allibert *et al.* [78All] investigated the system over the whole concentration range at temperatures above 650°C, using several different experimental techniques. Phase separation combined with chemical analysis for liquid + solid equilibria. Liquidus, solidus and transformation temperatures in the solid state were detected using differential thermal analysis. Electron microprobe analysis was used to determine two phase equilibria. The detection of different phases was made by using X-ray technique.

Hasebe *et al.* [82Has], and Chiba [71Chi], have measured tielines in the solid state by electron microprobe analysis of a set of diffusion-couple samples.

Bell *et al.* [73Bel], have measured enthalpies of formation of fcc and bcc alloys at 1350°C and 1450°C, respectively, using a high temperature adiabatic calorimeter. The enthalpies of transformation bcc→sigma were also determined. Bell *et al.* performed solid electrolyte e.m.f. measurements on five alloys in the temperature range 1000-1473K.

Enthalpies of formation at different temperatures were measured by Kubaschewski and Hack [79Kub], Downie and Arslan [83Dow], and also by Zubkov *et al.* [90Zub]. All these enthalpies of formation measured at different temperatures agree well with Bell *et al.* [73Bel], which indicates that the enthalpy of formation can be considered to be temperature independent.

2.2 C-Co-Cr

The only experimental investigation covering the whole system was done by Köster and Sperner [55Kos]. They investigated a set of alloys by several techniques; thermal analysis, optical metallurgy, magnetic, X-ray and hardness measurements. Unfortunately the only primary experimental data presented in the paper is a liquidus surface and an isothermal section at 800°C. An additional complication is that the alloys were prepared from impure Cr, containing significant amounts of iron and nickel.

Thompson *et al.* [70Tho:2], Sahm and Watts [71Sam], Thompson and Lemkey [70Tho:1] studied eutectic alloys that solidify by an eutectic reaction to a composite structure of fcc with M_7C_3 carbides. They used differential thermal analysis combined with electron microprobe measurements. The maximum along the eutectic liquidus line where the monovariant pseudobinary reaction occurs has been determined. Fritscher [79Fri], investigated the same pseudobinary cut using a combined differential thermal analysis and differential scanning calorimetry technique. The maximum solubility of C in the fcc matrix and the heat of fusion were determined.

Tüma and Löbl [71Tum], have measured C activities for alloys containing 12, 20, 28 and 36 weight% Cr in the temperature interval 950-1200°C. Samples of Co-Cr alloys and pure iron were carburized in a controlled gas atmosphere. The iron samples were used as standards for the determination of C activities.

3 Pure Elements

Data for pure elements were taken from the SGTE unary database [91Din]. The magnetic contribution to Gibbs Energy for metastable pure fcc and hcp Cr was assumed to be the same as for pure bcc Cr. This assumption is different from [91Din] but does not affect earlier evaluations within the SGTE solution database. By choosing the the same bohrmagneton number for hcp and fcc Cr as for bcc Cr a better agreement between experimental observations and the calculated phase diagram is obtained.

4 Thermodynamic Models

4.1 Co-Cr

4.1.1 fcc, bcc, hcp and liquid

Five stable phases have been found experimentally in the binary system Co-Cr. Four of these phases, liquid, fcc, bcc and hcp are modelled as substitutional solution phases. The molar Gibbs energy is expressed as follows,

$$G_m = x_{Co}^o G_{Co}^o + x_{Cr}^o G_{Cr}^o + RT(x_{Co} \ln(x_{Co}) + x_{Cr} \ln(x_{Cr})) + {}^E G_m + {}^{magnetic} G_m \quad (1)$$

where x_i denotes the mole-fraction.

The excess Gibbs energy, ${}^E G_m$, is expressed as a Redlich-Kister polynomial, see eq.2. The term, $G_m^{magnetic}$, gives a magnetic contribution to Gibbs Energy proposed by Inden [81Ind] and modified by Hillert and Jarl [78Hil].

$${}^E G_m = x_{Co} x_{Cr} I_{Co, Cr} \quad I_{Co, Cr} = \sum_{k=0}^k L_{Co, Cr}(x_{Co} - x_{Cr})^k \quad (2)$$

4.1.2 sigma phase

The compound energy model, Andersson *et al.*, [86And], was used to describe the fifth stable phase in the Co-Cr system, the sigma phase. According to Andersson *et al.*, [86And], the sigma phase can be modelled with three sublattices, one sublattice with fcc-like coordination and two sublattices with bcc-like coordination, *i.e.* (Co)₈(Cr)₄(Co,Cr)₁₈. The free energy of an end member is therefore modelled as an energy of formation from appropriate fcc and bcc states. The treatment by Andersson *et al.* was adopted in the present work and the molar Gibbs energy expression yields,

$$G_m^{sigma} = y_{Cr}^{(3)} G_{Co:Cr:Cr} + y_{Co}^{(3)} G_{Co:Cr:Co} + 18RT(y_{Cr}^{(3)} \ln(y_{Cr}^{(3)}) + y_{Co}^{(3)} \ln(y_{Co}^{(3)})) + {}^E G_m \quad (3)$$

where $y_i^{(3)}$ denotes the site fraction of element i on sublattice 3 and

$${}^o G_{Co:Cr:Cr} = 8{}^o G_{Co}^{fcc} + 22{}^o G_{Cr}^{bcc} + \Delta G_{Co:Cr:Cr}^\sigma \quad (4)$$

$${}^o G_{Co:Cr:Co} = 8{}^o G_{Co}^{fcc} + 4{}^o G_{Cr}^{bcc} + 18{}^o G_{Co}^{bcc} + \Delta G_{Co:Cr:Co}^\sigma \quad (5)$$

4.2 C-Co-Cr

In addition to the binary system Co-Cr thermodynamic descriptions of the Co-C and the Cr-C systems are needed to evaluate the ternary C-Co-Cr system. In the present work the assessments of Co-C by Fernández Guillermet [87Fer] and Cr-C by Lee [92Lee] were adopted.

In the ternary system C-Co-Cr there are eight stable phases: fcc, hcp, bcc, liquid, sigma, M₂₃C₆, M₇C₃, M₃C₂ and graphite. No ternary phase has been discovered experimentally. The descriptions for the stable phases in Co-C, *i.e.* fcc, liquid, hcp and graphite, were used together with the description of the bcc phase from the assessment of the ternary system C-Co-Fe by A. Fernández Guillermet [88Fer]. In Cr-C, liquid, bcc, M₂₃C₆, M₇C₃, M₃C₂ and graphite are stable, these thermodynamic descriptions were used. The phases fcc and hcp that are metastable in Cr-C were taken from the assessment of the C-Cr-Fe system by Lee [91Lee].

4.2.1 bcc, hcp and fcc

The phases bcc, fcc and hcp, are treated as solution phases with two sublattices, one sublattice contains substitutional elements and the other sublattice interstitials, (Co,Cr)₁(C,Va)_b. The molar Gibbs energy for each phase is described by the following expression,

$$G_m = y_{Co}^{(1)} y_C^{(2)} {}^o G_{Co:C} + y_{Co}^{(1)} y_{Va}^{(2)} {}^o G_{Co:Va} + y_{Cr}^{(1)} y_C^{(2)} {}^o G_{Cr:C} + y_{Cr}^{(1)} y_{Va}^{(2)} {}^o G_{Cr:Va} + RT(y_{Co}^{(1)} \ln(y_{Co}^{(1)}) + y_{Cr}^{(1)} \ln(y_{Cr}^{(1)})) \\ + RTb(y_C^{(2)} \ln(y_C^{(2)}) + y_{Va}^{(2)} \ln(y_{Va}^{(2)})) + {}^E G_m + {}^{magnetic} G_m \quad (6)$$

$${}^E G_m = y_{Co}^{(1)} y_{Cr}^{(1)} (y_C^{(2)} L_{Co, Cr: C} + y_{Va}^{(2)} L_{Co, Cr: Va}) + y_C^{(2)} y_{Va}^{(2)} (y_{Co}^{(1)} L_{Co: C, Va} + y_{Cr}^{(1)} L_{Cr: C, Va}) \quad (7)$$

where $y_i^{(j)}$ denotes the sitefraction of component i on sublattice j . ${}^o G_{i:Va}$ is the Gibbs energy of pure i whereas ${}^o G_{i:C}$ is the Gibbs energy of a hypothetical state when all interstitial sites are filled with carbon atoms. Since different structures have different number of interstitial sites the parameter b varies, for hcp structure $b=0.5$, for bcc structure $b=3$ and for the fcc structure $b=1$.

4.2.2 liquid

The liquid is modelled assuming random mixing of all components, yielding the following Gibbs molar energy expression.

$$G_m = x_{Co} {}^\circ G_{Co} + x_{Cr} {}^\circ G_{Cr} + x_C {}^\circ G_C + RT(x_{Co} \ln(x_{Co}) + x_{Cr} \ln(x_{Cr}) + x_C \ln(x_C)) + {}^E G_m \quad (8)$$

$${}^E G_m = x_C x_{Co} I_{C,Co} + x_C x_{Cr} I_{C,Cr} + x_{Co} x_{Cr} I_{Co,Cr} + x_C x_{Co} x_{Cr} I_{C,Co,Cr} \quad (9)$$

$$I_{C,Co,Cr} = x_C {}^\circ L_{C,Co,Cr} + x_{Co} {}^I L_{C,Co,Cr} + x_{Cr} {}^2 L_{C,Co,Cr} \quad (10)$$

where eq.10 above allows a composition dependent ternary interaction parameter.

4.2.3 $M_{23}C_6$, M_7C_3 and M_3C_2

Available experimental data shows that there is a solubility range of Co in $M_{23}C_6$ and M_7C_3 . There are two different crystallographic sites for metal atoms on the $M_{23}C_6$ lattice. Larger metal atoms such as Mo and W can only be dissolved on one sublattice. In order to be consistent with other assessments, e.g. the Fe-Cr-W-C system by Gustafson [88Gus], the $M_{23}C_6$ phase is modelled using two metallic sublattices, $(Co,Cr)_{20}(Co,Cr)_3C_6$. The Gibbs molar energy is given below,

$$\begin{aligned} G_m = & y_{Co}^{(1)} y_{Co}^{(2)} {}^\circ G_{Co:Co:C}^{M_{23}C_6} + y_{Co}^{(1)} y_{Cr}^{(2)} {}^\circ G_{Co:Cr:C}^{M_{23}C_6} + y_{Cr}^{(1)} y_{Co}^{(2)} {}^\circ G_{Cr:Co:C}^{M_{23}C_6} + y_{Cr}^{(1)} y_{Cr}^{(2)} {}^\circ G_{Cr:Cr:C}^{M_{23}C_6} \\ & + 20RT[y_{Cr}^{(1)} \ln(y_{Cr}^{(1)}) + y_{Co}^{(1)} \ln(y_{Co}^{(1)})] + 3RT[y_{Cr}^{(2)} \ln(y_{Cr}^{(2)}) + y_{Co}^{(2)} \ln(y_{Co}^{(2)})] + {}^E G_m \end{aligned} \quad (11)$$

where superscript (1) denotes the first sublattice and superscript (2) denotes the second.

According to the model the following compound energies should be defined: ${}^\circ G_{Cr:Cr:C}^{M_{23}C_6}$, ${}^\circ G_{Cr:Co:C}^{M_{23}C_6}$, ${}^\circ G_{Co:Cr:C}^{M_{23}C_6}$ and ${}^\circ G_{Co:Co:C}^{M_{23}C_6}$. The thermodynamic description of the carbide containing only Cr is taken from the binary Cr-C system, while as the carbide containing only Co that is unstable in the Co-C system has to be optimized in this work. Due to lack of experimental data on the ordering on metallic sublattices the compound energies for the mixed carbides are presumed to be linear combinations of the binary carbides, in the present work. These mixed carbides are described below,

$${}^\circ G_{Cr:Co:C}^{M_{23}C_6} = \frac{20}{23} \cdot {}^\circ G_{Cr:Cr:C}^{M_{23}C_6} + \frac{3}{23} \cdot {}^\circ G_{Co:Co:C}^{M_{23}C_6} \quad (12)$$

$${}^\circ G_{Co:Cr:C}^{M_{23}C_6} = \frac{20}{23} \cdot {}^\circ G_{Co:Co:C}^{M_{23}C_6} + \frac{3}{23} \cdot {}^\circ G_{Cr:Cr:C}^{M_{23}C_6} \quad (13)$$

5 Optimization

The optimization was performed using PARROT [84Jan], a program module in Thermo-Calc. PARROT optimizes thermochemical model parameters using least mean square fitting of experimental data.

5.1 Co-Cr

Parameters describing the binary interaction for liquid, bcc, fcc and hcp were evaluated. The binary interactions for the fcc phase is described by a temperature dependent regular solution parameter, whereas the hcp phase is described by a single regular parameter. For the liquid and bcc phases a temperature dependent regular solution parameter and a single subregular parameter had to be used to describe the experimental information. The energy of formation for the sigma phase end-members, $\Delta G_{Co:Cr:Cr}^\sigma$ and $\Delta G_{Co:Cr:Cr}^\sigma$ were assumed to vary linearly with temperature.

5.2 C-Co-Cr

It was assumed that the ternary interaction parameters between Co and Cr with all interstitial sites filled with C for bcc, hcp and fcc are identical to the binary interaction parameters with empty interstitial sites, $L_{Co,Cr,C} = L_{Co,Cr,Va}$. Thus, only the ternary interaction parameters in the liquid and parameters describing the solubility of Co in $M_{23}C_6$ and M_7C_3 were optimized.

As mentioned before $Cr_{23}C_6$ and Cr_7C_3 dissolve Co on substitutional sites. This caused some trouble during optimization. According to the model these carbides exist on a line between the Cr carbide and the metastable Co carbide. When optimizing the Gibbs energy of formation of the metastable carbides along with the interaction parameter it is difficult to control the minimization procedure, due to meagre experimental information. To avoid this problem a method for predicting thermochemical properties of transition metal carbides by Fernández Guillermet and Grimvall [92Fer] was used. In their work they made an extensive study of the enthalpy of formation and the standard vibrational entropy of metal carbides. Predictions for metastable carbides are made assuming that the bonding properties vary smoothly as a function of the average number of valence electrons per atom. These predictions were applied to the Gibbs energy of formation for the metastable carbides, $Co_{23}C_6$ and Co_7C_3 . Thus, the number of parameters to be evaluated is reduced and the optimization procedure for the interaction parameters converges in a stable way in spite of the scarce quantity of experimental data.

Since the most thoroughly investigated part of this system is the monovariant eutectic reaction $L \Rightarrow fcc + M_7C_3$ these experimental data were allowed to influence the optimization more than other data.

6 Result and discussion

6.1 Co-Cr

The resulting calculated binary phase diagram plotted in Fig. 1 shows good agreement with experimental phase diagram data. In the Co rich region at low temperatures there are no experimental data, this region is an extrapolation from other regions. The resulting separation into ferromagnetic and paramagnetic hcp is in accordance with observations by Maeda *et al.* [86Mae], and predictions by Ishida and Nishizawa [90Ish].

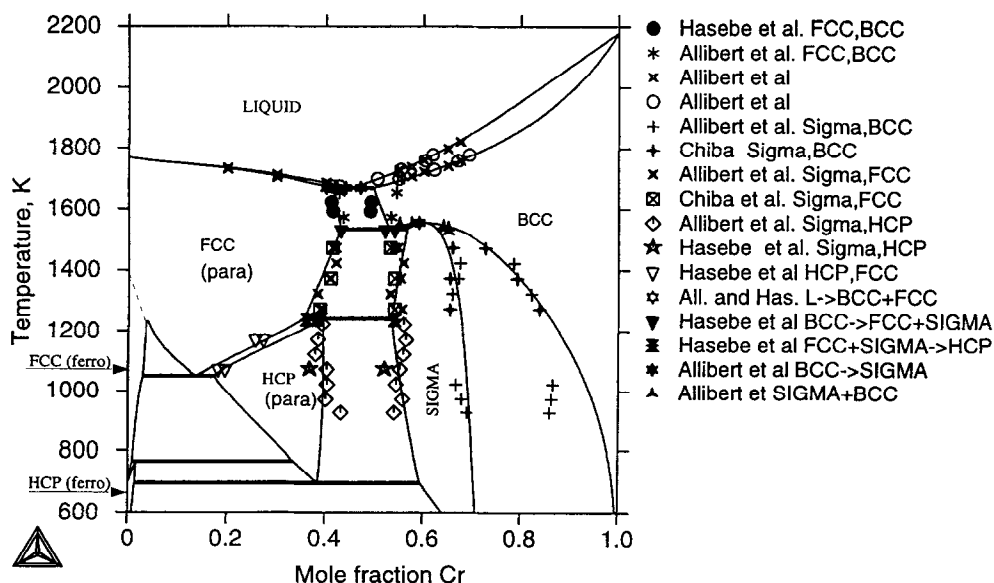


Figure 1: Binary phase diagram Co-Cr

In Fig. 2 the enthalpies of formation at 1623K and 1673K are compared with experimental data from Bell *et al.* [73Bel]. There is a slight discrepancy between experimental and calculated values in the Co-rich side,

remembering the lack of experimental data it may be accepted as reasonable agreement for the time being. In the appendix the optimized parameters are given.

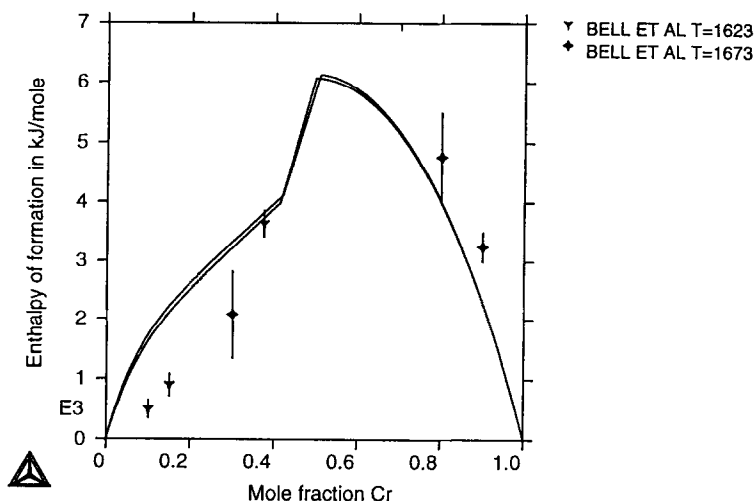


Figure 2: Enthalpies of formation

6.2 C-Co-Cr

As mentioned above, experimental data for the monovariant eutectic reaction, [70Tho:1] [71Sam] [79Fri], [70Tho: were allowed to influence the optimization more than the data by Köster and Sperner [55Kos], the result is shown in Fig.3. The agreement between experimental data and the calculated pseudobinary section is very good.

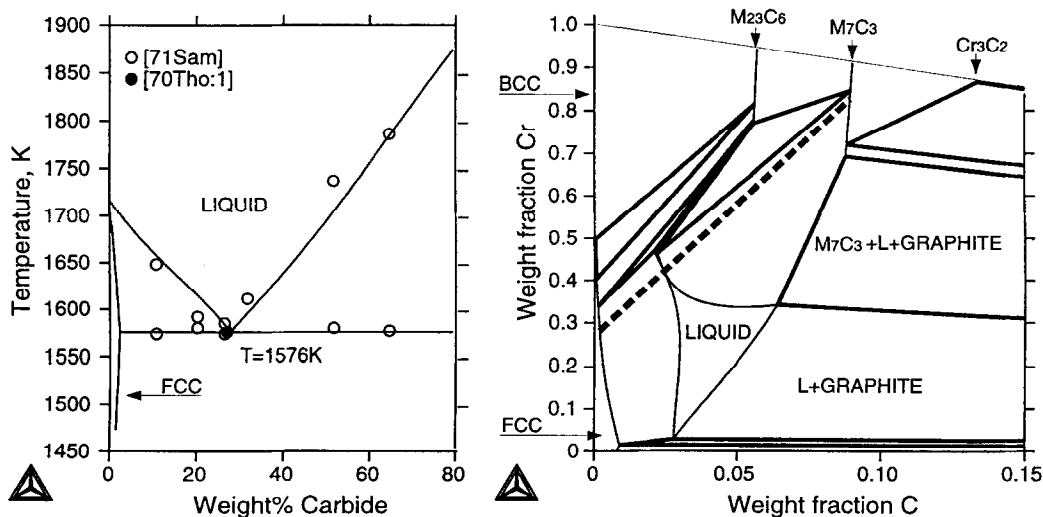


Figure 3: To the left, the pseudobinary section and to the right the isothermal section at $T=1576\text{K}$. In the isothermal section the pseudobinary section is indicated by a dashed line

When Köster and Sperner [55Kos] examined an isothermal section at 800°C in 1955 they did not see the hcp phase form, also the fcc phase was regarded as one phase, *i.e.* no phase separation into ferromagnetic and paramagnetic fcc was investigated. Therefore a metastable isothermal section at 800°C is calculated without hcp phases and with only one fcc phase. As can be seen in Fig.4 there is some disagreement which is mainly caused by the different descriptions of Co-Cr. However the solubility range of Co in the $M_{23}C_6$ and the M_7C_3 carbide is in good agreement with experimental observations

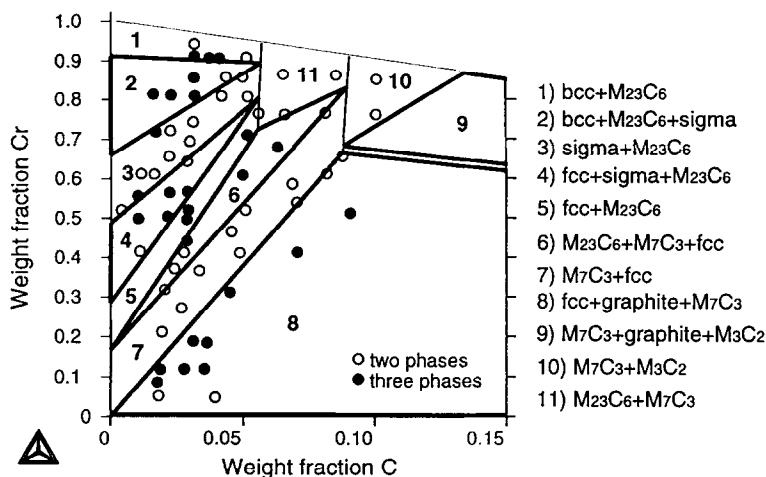


Figure 4: Metastable isothermal section at 800°C compared with experimental data by Köster and Sperner.

In Fig.5 carbon activity measurements by Tüma an Löbl [71Tum], are compared with calculated values. Note that the kinks in the curve in Fig.5 are in fairly good agreement with the experimental data. This indicates that the carbon content in the fcc phase at the solubility limit of the carbides is well described. The set of optimized parameters is given in the appendix.

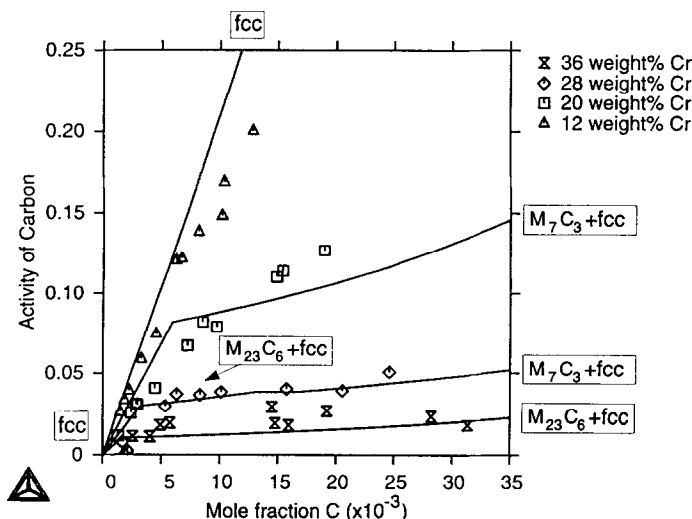


Figure 5: Comparison between calculated carbon activities at 1100°C at different compositions and experimental data by Tüma an Löbl.

7 Summary

The thermodynamic properties of the Co-Cr and C-Co-Cr systems have been analyzed by adopting the CALPHAD technique.

The assessment of the Co-Cr system is based on an extensive amount of experimental data and calculated data are in good agreement with selected experimental information. However, in order to obtain a more complete assessment more accurate thermochemical data and phase diagram information in the Co rich corner at low temperatures are needed.

The experimental data on the C-Co-Cr system is mainly concerning the eutectic reaction forming an alloy containing a fcc matrix reinforced with M_7C_3 carbides. In addition some uncertain phase diagram information and carbon activity data are available. The assessment provides a good description of most experimental data. Considerable amounts of phase diagram data are needed to validate the thermodynamic models.

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APPENDIX

The thermodynamic properties of the C-Co-Cr system. Parameters marked by * were optimized in this work.

The magnetic contribution:

$$G_m^{mo} = RT \ln(\beta+1)f(\tau), \quad \tau = T/T_c$$

for $\tau < 1$

$$f(\tau) = 1 - \left[\frac{79\tau^{-1}}{140p} + \frac{474}{497p} \left(-\frac{1}{6} + \frac{\tau^3}{135} + \frac{\tau^9}{600} \right) \right] / A$$

and for $\tau > 1$

$$f(\tau) = - \left(\frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{518} + \frac{\tau^{-25}}{1500} \right) / A$$

$$\text{where } A = \left(\frac{1}{1125} \right) + \left(\frac{1}{15975} \right) \left[\left(-\frac{1}{p} \right) - 1 \right] \text{ and } p \text{ depends on the structure.}$$

Pure element data

Element for pure data is taken from the SGTE unary database ref. [23]. The functions are valid in the temperature range 298.15 K to 6000 K.

$$\text{GHSERCC} = -17368.441 + 170.73 \cdot T - 24.3 \cdot T \cdot \ln(T) - 4.723 \cdot 10^{-4} \cdot T^2 + 2562600 \cdot T^{-1} - 2.643 \cdot 10^8 \cdot T^{-2} + 1.2 \cdot 10^9 \cdot T^{-3}$$

$$\text{GHSERCO} =$$

$$298.15 < T < 1768 : +310.241 + 133.36601 \cdot T - 25.0861 \cdot T \cdot \ln(T) - 0.002654739 \cdot T^2 - 1.7348 \cdot 10^7 \cdot T^3 + 72527 \cdot T^{-1}$$

$$1768 < T < 6000 : -17197.666 + 253.28374 \cdot T - 40.5 \cdot T \cdot \ln(T) + 9.3488 \cdot 10^3 \cdot T^{-9}$$

$$\text{GHSERCR} =$$

$$298.15 < T < 2180 : -8856.94 + 157.48 \cdot T - 26.908 \cdot T \cdot \ln(T) + 0.00189435 \cdot T^2 - 1.47721 \cdot 10^6 \cdot T^3 + 139250 \cdot T^{-1}$$

$$2180 < T < 6000 : -34869.344 + 344.18 \cdot T - 50 \cdot T \cdot \ln(T) - 2.88526 \cdot 10^3 \cdot T^{-9}$$

$$\text{GCOBCC} = +2938 - 7138 \cdot T + \text{GHSERCO}$$

$$\text{GCOFCC} = +427.59 - 615248 \cdot T + \text{GHSERCO}$$

$$\text{GCRFCC} = +7284 + 163 \cdot T + \text{GHSERCR}$$

$$\text{GCRM23C6} = -521983 + 3622.24 \cdot T - 620.965 \cdot T \cdot \ln(T) - 126431 \cdot T^2$$

$$\text{GCRM7C3} = -201690 + 1103.128 \cdot T - 190.177 \cdot T \cdot \ln(T) - 0.578207 \cdot T^2$$

$$\text{GCRM3C2} = -100823.8 + 530.66989 \cdot T - 89.6694 \cdot T \cdot \ln(T) - 0.301188 \cdot T^2$$

GRAPHITE

$$^{\circ}G_C^{\text{GRAPHITE}} - H_C^{\text{SER}} = +\text{GHSERCC}$$

LIQUID

$$^{\circ}G_C^{\text{LIQUID}} - H_C^{\text{SER}} = +117369 - 24.63 \cdot T + \text{GHSERCC}$$

$$^{\circ}G_{\text{Co}}^{\text{LIQUID}} - H_{\text{Co}}^{\text{SER}} =$$

$$298.15 < T < 1768 : +15085.037 - 8.931932 \cdot T - 2.19801 \cdot 10^{-21} \cdot T^{**7} + \text{GHSERCO}$$

$$1768 < T < 6000 : +16351.056 - 9.683796 * T - 9.3488E+30 * T^{**(-9)} + \text{GHSERCO}$$

$$\begin{aligned} {}^0G_{\text{Cr}}^{\text{LIQUID}} - H_{\text{Cr}}^{\text{SER}} = \\ 298.15 < T < 2180 : +24339.955 - 11.420225 * T + 2.37615E-21 * T^{**7} + \text{GHSERCR} \\ 2180 < T < 6000 : +18409.36 - 8.563683 * T + 2.88526E+32 * T^{**(-9)} + \text{GHSERCR} \end{aligned}$$

$${}^0L_{\text{C,Co}}^{\text{LIQUID}} = -107940.6 + 24.956 T$$

$${}^1L_{\text{C,Co}}^{\text{LIQUID}} = -9805.5$$

$${}^0L_{\text{C,Co,Cr}}^{\text{LIQUID}} = -302180^*$$

$${}^1L_{\text{C,Co,Cr}}^{\text{LIQUID}} = +35575^*$$

$${}^2L_{\text{C,Co,Cr}}^{\text{LIQUID}} = +35575^*$$

$${}^0L_{\text{C,Cr}}^{\text{LIQUID}} = -90526 - 25.9116 T$$

$${}^1L_{\text{C,Cr}}^{\text{LIQUID}} = 80000$$

$${}^2L_{\text{C,Cr}}^{\text{LIQUID}} = 80000$$

$${}^0L_{\text{Co,Cr}}^{\text{LIQUID}} = -3034 - 5.624 T^*$$

$${}^1L_{\text{Co,Cr}}^{\text{LIQUID}} = 909^*$$

BCC_A2

$${}^0G_{\text{Co,C}}^{\text{BCC}_A2} - H_{\text{Co}}^{\text{SER}} - 3 H_{\text{C}}^{\text{SER}} = +\text{GHSERCO} + 3 \text{GHSERCC} + 248204 - 31.271 T$$

$${}^0G_{\text{Cr,C}}^{\text{BCC}_A2} - H_{\text{Cr}}^{\text{SER}} - 3 H_{\text{C}}^{\text{SER}} = +\text{GHSERCR} + 3 \text{GHSERCC} + 416000$$

$${}^0G_{\text{Co,VA}}^{\text{BCC}_A2} - H_{\text{Co}}^{\text{SER}} = +\text{GCOBCC}$$

$${}^0G_{\text{Cr,VA}}^{\text{BCC}_A2} - H_{\text{Cr}}^{\text{SER}} = +\text{GHSERCR}$$

$${}^0L_{\text{Co,Cr,C}}^{\text{BCC}_A2} = +17208 - 13.519 T^*$$

$${}^1L_{\text{Co,Cr,C}}^{\text{BCC}_A2} = -5470^*$$

$${}^0L_{\text{Cr,C,VA}}^{\text{BCC}_A2} = -190 T$$

$${}^0L_{\text{Co,Cr,VA}}^{\text{BCC}_A2} = +17208 - 13.519 T^*$$

$${}^1L_{\text{Co,Cr,VA}}^{\text{BCC}_A2} = -5470^*$$

p is 0.4 for BCC_A2

$${}^0T_{\text{Cr,C}}^{\text{BCC}_A2} = -311.5$$

$${}^0T_{\text{Co,VA}}^{\text{BCC}_A2} = 1450$$

$${}^0T_{\text{Cr,VA}}^{\text{BCC}_A2} = -311.5$$

$${}^0P_{\text{Cr,C}}^{\text{BCC}_A2} = -.008$$

$${}^0P_{\text{Co,VA}}^{\text{BCC}_A2} = 1.35$$

$${}^0P_{\text{Cr,VA}}^{\text{BCC}_A2} = -.008$$

FCC_A1

2 sublattices, sites 1: 1

Constituents Co,Cr : C,VA

$${}^0G_{\text{Co:C}}^{\text{FCC_A1}} - H_{\text{Co}}^{\text{SER}} - H_{\text{C}}^{\text{SER}} = +\text{GHSERCO} + \text{GHSERCO} + 50463.8 - 6.849 \text{ T}$$

$${}^0G_{\text{Cr:C}}^{\text{FCC_A1}} - H_{\text{Cr}}^{\text{SER}} - H_{\text{C}}^{\text{SER}} = +\text{GHSERCR} + \text{GHSERCO} + 1200 - 1.94 \text{ T}$$

$${}^0G_{\text{Co:VA}}^{\text{FCC_A1}} - H_{\text{Co}}^{\text{SER}} = +\text{GCOFCC}$$

$${}^0G_{\text{Cr:VA}}^{\text{FCC_A1}} - H_{\text{Cr}}^{\text{SER}} = +\text{GCRFCC}$$

$${}^0L_{\text{Co,Cr:C}}^{\text{FCC_A1}} = +1500 - 9.592 \text{ T}^*$$

$${}^0L_{\text{Cr:C,VA}}^{\text{FCC_A1}} = -11977 + 6.8194 \text{ T}$$

$${}^0L_{\text{Co,Cr:VA}}^{\text{FCC_A1}} = +1500 - 9.592 \text{ T}^*$$

p is 0.28 for FCC_A1

$${}^0T_{\text{Co:VA}}^{\text{FCC_A1}} = 1396$$

$${}^0T_{\text{Cr:VA}}^{\text{FCC_A1}} = -1109$$

$${}^0T_{\text{Co,Cr:VA}}^{\text{FCC_A1}} = -1795$$

$${}^0P_{\text{Co:VA}}^{\text{FCC_A1}} = 1.35$$

$${}^0P_{\text{Cr:VA}}^{\text{FCC_A1}} = -.008$$

HCP_A3

2 sublattices, sites 1: .5

Constituents Co,Cr : C,VA

$${}^0G_{\text{Co:C}}^{\text{HHCP_A3}} - H_{\text{Co}}^{\text{SER}} - .5 H_{\text{C}}^{\text{SER}} = +\text{GHSERCO} + .5 \text{ GHSERCO} + 22916.5 - 2.855 \text{ T}$$

$${}^0G_{\text{Cr:C}}^{\text{HHCP_A3}} - H_{\text{Cr}}^{\text{SER}} - .5 H_{\text{C}}^{\text{SER}} = +\text{GHSERCR} + .5 \text{ GHSERCO} - 18504 + 9.4173 \text{ T} - 2.4997 \text{ T} \ln \text{ T} + .001386 \text{ T}^2$$

$${}^0G_{\text{Co:VA}}^{\text{HHCP_A3}} - H_{\text{Co}}^{\text{SER}} = +\text{GHSERCO}$$

$${}^0G_{\text{Cr:VA}}^{\text{HHCP_A3}} - H_{\text{Cr}}^{\text{SER}} = +4438 + \text{GHSERCR}$$

$${}^0L_{\text{Co,Cr:C}}^{\text{HCP_A3}} = -6436^*$$

$${}^0L_{\text{Cr:C,VA}}^{\text{HCP_A3}} = 4165$$

$${}^0L_{\text{Co,Cr:VA}}^{\text{HCP_A3}} = -6436^*$$

p is 0.28 for HCP_A3

$${}^0T_{\text{Co:VA}}^{\text{HCP_A3}} = 1396$$

$${}^0T_{\text{Cr:VA}}^{\text{HCP_A3}} = -1109$$

$${}^0T_{\text{Co,Cr:VA}}^{\text{HCP_A3}} = -1795$$

$${}^0p_{\text{Co:VA}}^{\text{HCP}_A3} = 1.35$$

$${}^0p_{\text{Cr:VA}}^{\text{HCP}_A3} = -.008$$

M23C6

3 sublattices, sites 20: 3: 6

Constituents Co,Cr : Co,Cr : C

$${}^0G_{\text{Co:Co:C}}^{\text{M23C6}} - 20 H_{\text{Co}}^{\text{SER}} - 3 H_{\text{Co}}^{\text{SER}} - 6 H_{\text{C}}^{\text{SER}} = +23 \text{ GHSERCO} + 6 \text{ GHSERCC} + 145000 + 116\text{T}^*$$

$${}^0G_{\text{Cr:Co:C}}^{\text{M23C6}} - 20 H_{\text{Cr}}^{\text{SER}} - 3 H_{\text{Co}}^{\text{SER}} - 6 H_{\text{C}}^{\text{SER}} = +.8695652 \text{ GCRM23C6} + .1304348 \text{ GCOM23C6}$$

$${}^0G_{\text{Co:Cr:C}}^{\text{M23C6}} - 20 H_{\text{Co}}^{\text{SER}} - 3 H_{\text{Cr}}^{\text{SER}} - 6 H_{\text{C}}^{\text{SER}} = +.8695652 \text{ GCOM23C6} + .1304348 \text{ GCRM23C6}$$

$${}^0G_{\text{Cr:Cr:C}}^{\text{M23C6}} - 20 H_{\text{Cr}}^{\text{SER}} - 3 H_{\text{Cr}}^{\text{SER}} - 6 H_{\text{C}}^{\text{SER}} = + \text{ GCRM23C6}$$

$${}^0L_{\text{Co,Cr:Co:C}}^{\text{M23C6}} = {}^0L_{\text{Co:Co,Cr:C}}^{\text{M23C6}} = {}^0L_{\text{Cr:Co,Cr:C}}^{\text{M23C6}} = {}^0L_{\text{Co,Cr:Cr:C}}^{\text{M23C6}} = -182237^*$$

M3C2

2 sublattices, sites 3: 2

Constituents Cr : C

$${}^0G_{\text{Cr:C}}^{\text{M3C2}} - 3 H_{\text{Cr}}^{\text{SER}} - 2 H_{\text{C}}^{\text{SER}} = + \text{ GCRM3C2}$$

M7C3

2 sublattices, sites 7: 3

Constituents Co,Cr : C

$${}^0G_{\text{Co:C}}^{\text{M7C3}} - 7 H_{\text{Co}}^{\text{SER}} - 3 H_{\text{C}}^{\text{SER}} = +7 \text{ GHSERCO} + 3 \text{ GHSERCC} + 75000 + 50\text{T}^*$$

$${}^0G_{\text{Cr:C}}^{\text{M7C3}} - 7 H_{\text{Cr}}^{\text{SER}} - 3 H_{\text{C}}^{\text{SER}} = + \text{ GCRM7C3}$$

$${}^0L_{\text{Co,Cr:C}}^{\text{M7C3}} = -96092^*$$

SIGMA

3 sublattices, sites 8: 4: 18

Constituents Co : Cr : Co,Cr

$${}^0G_{\text{Co:Cr:Co}}^{\text{SIGMA}} - 8 H_{\text{Co}}^{\text{SER}} - 4 H_{\text{Cr}}^{\text{SER}} - 18 H_{\text{Co}}^{\text{SER}} = +8 \text{ GCOFCC} + 4 \text{ GHSERCR} + 18 \text{ GCOBCC} + 17077 - 30.518\text{T}^*$$

$${}^0G_{\text{Co:Cr:Cr}}^{\text{SIGMA}} - 8 H_{\text{Co}}^{\text{SER}} - 4 H_{\text{Cr}}^{\text{SER}} - 18 H_{\text{Cr}}^{\text{SER}} = +8 \text{ GCOFCC} + 22 \text{ GHSERCR} - 7466 - 104.215\text{T}^*$$