

Thermodynamic Assessment of Co-Nb-W System

Liu Xingjun^{1,2}, Niu Zeming¹, Lu Yong¹, Guo Yihui¹, Han Jiajia¹, Chen Yuechao¹,
Wang Cuiping^{1,2}

¹ College of Materials, Xiamen University, Xiamen 361005, China; ² Fujian Key Laboratory of Materials Genome, Xiamen University, Xiamen 361005, China

Abstract: The thermodynamic assessment of the Co-Nb-W ternary system has been carried out by applying the CALPHAD method. A slight modification of the Co-W binary system has been performed to unify the model of μ phase in Co-Nb-W system. The three published isothermal sections at 1273, 1373 and 1473 K have been critically examined and used to optimize the model parameters. The solution phases, including α Co and bcc were modeled as substitutional solutions; the λ , χ , and Co_3Nb phases have been assessed using two-sublattice models. The Co_7W_6 and Co_7Nb_6 phases were described as $(\text{Co},\text{Nb})_1(\text{Co},\text{Nb},\text{W})_2(\text{Co},\text{Nb},\text{W})_4(\text{Co})_6$. Calculated isothermal sections and vertical sections agreed well with the experimental data.

Key words: thermodynamic calculation; CALPHAD; Co-W system; Co-Nb-W system

Co-based alloys have been widely used in many areas such as chemical, energy, and aviation due to their excellent magnetic properties, corrosion resistance, and mechanical properties. In particular, the study on Co-based high-temperature alloys^[1] and Co-W based magnetic recording materials^[2] has obtained remarkable achievements in recent years. Besides, the element Nb is a commonly used cubic carbide forming metal in Co-W based cemented carbides^[3,4]. Therefore, the Co-Nb-W ternary system is a vital constituent system of Co-based alloys. The experimental phase diagram of the Co-Nb-W system was firstly reported by Gerashchenko et al.^[5] Gupta et al.^[6] assessed that their results have several discrepancies in the ternary diagram about the location and extent of phase regions when compared with the binary diagrams. For instance, in the binary diagrams, the regions of Co_7W_6 and Co_7Nb_6 phase occur over slightly different composition regions, and the region of Co_7Nb_6 phase is smaller than that indicated in Gerashchenko's diagram. The χ phase is a stoichiometric compound in the previous binary diagram, but has a range of homogeneity in Gerashchenko's isothermal section. As a result of these discrepancies, Gupta et al. summarized that the binary diagrams need revision or the boundaries of the phase regions in their assessment should be

redetermined. Liu et al.^[7] investigated isothermal sections of the Co-Nb-W system at 1273, 1373 and 1473 K, and observed that the χ phase is stabilized to a higher temperature when Nb is added to Co-W alloys. They also inferred that the melting point of the Nb-stabilized χ phase is between 1373 and 1473 K.

Tao^[8] and Pang^[9] have established thermodynamic models of the Co-Nb-W ternary system. Although their isothermal sections roughly match the experimental data, they incorrectly used different thermodynamic models for Co_7W_6 and Co_7Nb_6 phases. As Co_7W_6 and Co_7Nb_6 phases have the same crystal lattice structure, these phases should be described as one model alone. The purpose of the present work was to evaluate the phase equilibria in the Co-Nb-W system, and the available thermodynamic description for each binary system is reviewed. Two modified μ and χ phase models in binary system were used to assess ternary parameters. These results are contributed to design the related high-temperature structural materials.

1 Literature Reviews

1.1 Binary systems

Several thermodynamic assessments of the Co-Nb system have been performed^[10-13], and the most comprehensive work

Received date: October 25, 2017

Foundation item: National Key Basic Research and Development Program of China ("973" Program) (2016YFB0701401)

Corresponding author: Wang Cuiping, Ph. D., Professor, Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, P. R. China, Tel: 0086-592-2180606, E-mail: wangcp@xmu.edu.cn

Copyright © 2018, Northwest Institute for Nonferrous Metal Research. Published by Elsevier BV. All rights reserved.

was carried out by Kumar et al.^[13] More recently, He et al.^[14,15] applied more reasonable models to describe C14 and C36 Laves phases to fit the homogeneity ranges. However, compared to the Kumar et al.'s assessment, their complicated thermodynamic models of Co₇Nb₆, C14 and C36 phases may introduce more parameters for more high ordered systems. Given lack of C14 phase experimental data in Liu et al.^[7] and simplification of assessment, the thermodynamic parameters for the Co-Nb system were taken from Kumar et al.^[13] in the present study.

The Nb-W system is quite simple with only two condensed stable phases, liquid and bcc. The assessment by Huang et al.^[16] agrees well with the experimental data. In the present study, thermodynamic parameters for the Nb-W system were adopted from Huang et al.^[16].

Kaufman and Nesor^[17] firstly assessed the Co-W binary phase diagram. Gabriel et al.^[18] reassessed this system by considering additional experimental results. However, the Co₇W₆ phase was modeled as a stoichiometric compound, and the magnetic contribution to the Gibbs energy was not considered. Guillermet et al.^[19] reassessed the Co-W system by considering the solubility range and magnetic contribution of Co₇W₆. Until recently, Sato et al.^[20] applied a more reasonable model to describe Co₇W₆ to fit the solubility range. Markström et al.^[21] optimized parameters for equilibrium boundaries based on the reassessment of Guillermet et al. Data from previous experimental studies^[20,22-24] suggest that χ phase has a little solubility at 1500~1900 K. Hence, Zhu et al.^[25] gave a slight modification of χ phase (i.e., treat Co₃W as Co_{0.75}(Co, W)_{0.25}).

However, since Co₇W₆ and Co₇Nb₆ phases have the same crystal lattice structure, it is supposed to have the same thermodynamic model^[26]. The Co₇Nb₆ phase was used by the 4-sublattice model^[13], and several studies^[13,27,28] suggest that 4-sublattice model is more accurate to describe the homogeneity range of μ phase. Therefore, a new 4-sublattice model for Co₇W₆ phase should be used to assess the ternary Co-Nb-W system in the present assessment.

1.2 Ternary system

The isothermal sections at 1273, 1373 and 1473 K in the Co-Nb-W system were experimentally investigated by Liu et al.^[7], which is more reasonable than Gerashchenko's ones. Therefore, the present work used the experimental data by Liu et al.^[7] and took Gerashchenko's work as a reference.

2 Thermodynamic Models

In the present work, the Gibbs energy functions for Co, Nb and W were taken from the SGTE compilation by Dinsdale^[29]. The readjusted Co-W models compared to Markström et al.^[21] are listed in Table 1. There are seven stable phases in the Co-Nb-W system at 1273, 1373 and 1473 K. In the following section, the analytical expressions for those phases will be briefly presented.

Table 1 Models used for the phases of the Co-W system in the present work compared to those used in Markström

Names	Structure	bericht	Present model	Ref.[21]
fcc(α Co)	A1		(Co,W)	(Co,W)
bcc	A2		(Co,W)	(Co,W)
LIQUID	-		(Co,W)	(Co,W)
hcp	A3		(Co,W)	(Co,W)
χ (Co ₃ W)	DO ₁₉		(Co) _{0.75} (Co,W) _{0.25}	Co ₃ W
μ (Co ₇ W ₆)	D8 ₅		Co ₁ W ₂ (Co,W) ₄ Co ₆	Co ₇ W ₂ (Co,W) ₄

2.1 Solution phases

The molar Gibbs free energy for the liquid, α Co, bcc and hcp phases, modeled as a substitutional solution, is defined as:

$$G_m^\phi = \sum_{i=\text{Co,Nb,W}} x_i^0 G_i^\phi + RT \sum_{i=\text{Co,Nb,W}} x_i \ln x_i^\phi + {}^{\text{ex}}G^\phi + {}^{\text{mag}}G^\phi \quad (1)$$

where G_i^ϕ is the molar Gibbs free energy of pure element i in the structure ϕ phase; x_i is the mole fraction of the components i ; and ${}^{\text{ex}}G^\phi$ is the excess free energy, which is expressed by the Redlich-Kister polynomials as:

$${}^{\text{ex}}G^\phi = \sum_i \sum_j x_i x_j L_{i,j}^\phi + x_{\text{Co}} x_{\text{Nb}} x_{\text{W}} (x_{\text{Co}}^0 L_{\text{Co,Nb,W}}^\phi + x_{\text{Nb}}^1 L_{\text{Co,Nb,W}}^\phi + x_{\text{W}}^2 L_{\text{Co,Nb,W}}^\phi) \quad (2)$$

$$L_{i,j}^\phi = \sum_{m=0}^n L_{i,j}^m (x_i - x_j)^m \quad (i, j = \text{Co, Nb or W and } i \neq j) \quad (3)$$

$${}^n L_{\text{Co,Nb,W}}^\phi = a + bT \quad (n = 0, 1, 2) \quad (4)$$

The magnetic contribution to the Co-Nb-W ternary system is considered for the bcc, α Co and hcp phases due to the presence of Co. The term ${}^{\text{mag}}G^\phi$ is expressed by the following formula:

$${}^{\text{mag}}G^\phi = RT \ln(\beta^\phi + 1) f(\tau^\phi) \quad (5)$$

where τ is defined as T/T_C with T_C being the Curie temperature, β^ϕ is the Bohr magneton number, and $f(\tau^\phi)$ is the integral of a function describing the magnetic contribution to the heat capacity. A more detailed explanation for ${}^{\text{mag}}G^\phi$ can be found in Ref.[30].

2.2 Binary phases with ternary solubilities

As discussed in section 2.1, the phases of Co₇W₆ and Co₇Nb₆ have the same thermodynamic model. Hence, the two phases' models will combine to form a unified model under the name of μ phase, described as (Co, Nb)₁(Co, Nb, W)₂(Co, Nb, W)₄(Co)₆ in the present assessment. According to this model, the molar Gibbs free energy of the phase in the Co-Nb-W ternary system is expressed as follows:

$$G^\mu = \sum_i \sum_j \sum_k y_i^I y_j^{II} y_k^{III} G_{i,j,k;\text{Co}}^\mu + RT \left(\sum_i y_i^I \ln y_i^I + 2 \sum_j y_j^{II} \ln y_j^{II} + 4 \sum_k y_k^{III} \ln y_k^{III} \right) + \sum_j \sum_k \left[y_{\text{Co}}^I y_{\text{Nb}}^I y_j^{II} y_k^{III} \sum_{(i=\text{Co,Nb}; j=\text{Co,Nb,W}; k=\text{Co,Nb,W})} {}^n L_{\text{Co,Nb};j,k;\text{Co}} \left(y_{\text{Co}}^I - y_{\text{Nb}}^I \right)^n \right] + \sum_i \sum_j \sum_k \left[y_i^I y_j^{II} y_l^{III} \sum_{(i=\text{Co,Nb}; j,l=\text{Co,Nb,W}, \text{ and } j \neq l; k=\text{Co,Nb,W})} {}^n L_{i,j,l;k;\text{Co}} \left(y_j^{II} - y_l^{III} \right)^n \right] + \sum_i \sum_j \sum_k \left[y_i^I y_j^{II} y_k^{III} y_l^{III} \sum_{(i=\text{Co,Nb}; j=\text{Co,Nb,W}; k,j=\text{Co,Nb,W}, \text{ and } k \neq l)} {}^n L_{i,j,k,l;\text{Co}} \left(y_k^{III} - y_l^{III} \right)^n \right] \quad (6)$$

where $G_{i,j,k;Co}^{\mu}$ is the Gibbs free energy of the phase. ${}^nL_{Co,Nb,j;k;Co}$ is the interaction energy when the second one is occupied by the element j ($j=Co, Nb$ or W), and the third one is occupied by the element k ($k=Co, Nb$ or W). The ${}^nL_{i,j,l;k;Co}$ is the interaction energy between Co, Nb and W in the second sublattice. The first one is occupied by the element i ($i=Co$ or Nb), the third one is occupied by the element k ($k=Co, Nb$ or W). The parameters ${}^nL_{i,j,k;l;Co}$ is described in the same way.

The λ phase is C15 Laves structure with the Cu_2Mg type. In the $Co-Nb$ binary system, the λ phase is formulated as $(Co, Nb)_2(Co, Nb)_1$. The λ phase is extended from the binary phase with W substitution for partial Nb . Therefore, the λ phase is described as a two-sublattice model of $(Co, Nb, W)_2(Co, Nb, W)_1$. The Co_3Nb phase is C36 Laves structure with the $MgNi_2$ type. In the $Co-Nb$ binary system, the Co_3Nb phase was modeled by $(Co)_3(Nb)_1$. Hence, its binary model extended to a two-sublattice model of $(Co)_3(Nb, W)_1$. The χ phase is DO_{19} structure with the Ni_3Sn type. In the $Co-W$ binary system, the χ phase was formulated as $(Co)_3(Co, W)_1$. The χ phase in the $Co-Nb-W$ ternary system has a narrow solubility of Nb . Therefore, the ternary χ phase is described as a two-sublattice model of $(Co)_3(Co, Nb, W)_1$.

The present study described all the two-sublattice models for the phases of λ, χ and Co_3Nb as a general formula $(Co, Nb, W)_p(Co, Nb, W)_q$. The Gibbs energy of the phase φ ($\varphi=\lambda, \chi$ and Co_3Nb) can be described by the following expression:

$$G^{\varphi} = \sum_i \sum_j y_i^I y_j^{II} G_{i,j}^{\varphi} + pRT \sum_i y_i^I \ln y_i^I + qRT \sum_j y_j^{II} \ln y_j^{II} + \sum_{i,j} \sum_j \left[y_i^I y_j^{II} y_j^{II} \left(\sum^n L_{i,l,j} (y_i^I - y_l^I)^n \right) \right] + \sum_i \sum_j \left[y_i^I y_j^{II} y_i^{II} \left(\sum^n L_{i,j,l} (y_j^{II} - y_l^{II})^n \right) \right] \quad (7)$$

where $G_{i,j}^{\varphi}$ is the Gibbs free energy of the phase. ${}^nL_{i,l,j}$ is the interaction energy between i and l ($l=Co, Nb, W$ and $l \neq i$) in the first sublattice when the second one is occupied by the element j ($j=Co, Nb, W$). ${}^nL_{i,j,l}$ is described in the same way.

2.3 Stoichiometric compounds

The binary phases of $Co_{16}Nb_9$ (C14 Laves structure), and Co_7Nb_2 were treated as pure binary stoichiometric compounds due to the lack of experimental data on its solubility of the third component.

2.4 Optimization

The interaction parameters of the $Co-W$ and $Co-Nb-W$ system were thermodynamically optimized by using the CALPHAD technique with the aid of the PARROT module in the Thermo-Calc package^[31]. In the assessment procedure, each piece of experimental information was given a certain weight. The optimization was conducted until the sum of the squares of the errors between the calculated and the experimental thermodynamic properties were minimized. The optimized binary parameters were systematically extrapolated to the ternary $Co-Nb-W$ system to ensure consistency and agreement with experimental data^[7]. All the optimized thermodynamic

parameters are listed in Table 2.

3 Results and Discussion

3.1 Co-W system

The calculated phase diagram compared to the experimental data and the assessment by Markström et al.^[20] is shown in Fig.1. Fig.2 shows the calculated Gibbs energy of formation of several phases compared with the experimental data and previous assessment^[32] at 1250 K. Table 3 lists the calculated temperatures and compositions of all invariant reactions compared with the reported experimental data^[7] in the $Co-W$ system.

As shown in Fig.1, Fig.2 and Table 3, all the experimental values used in the optimization were well reproduced. The calculated results suggest that an eutectoid reaction, $\alpha Co_{para} \leftrightarrow \chi + \alpha Co_{ferro}$ is located at 911 °C. From Table 3, the calculated temperatures for the invariant reactions are in good agreement with the experimental data, and the difference is only 1 K. The present assessment was improved on the two following points:

(1) The models for Co_7W_6 were readjusted by using a 4-sublattice model to improve the capability of being extrapolated to the $Co-Nb-W$ system.

(2) χ phase was readjusted by giving a slight solubility in the composition range 23.1 at% ~23.6 at% W at 910~1093 °C. This reassessment made the calculated region of χ phase accord closely with experimental data.

3.2 Co-Nb-W system

Fig.3a~3c show the comparison between the experimental data and our calculated results on the isothermal sections at 1273, 1373, 1473 K, respectively. The calculated results are in reasonable agreement with most of the experimental data. In the Co -rich corner, the αCo phase agrees fairly well with the experimental data. Data on single-phase αCo , two-phase $\alpha Co + \chi$ and two-phase $\alpha Co + Co_3Nb$ equilibrated at corresponding temperature by Liu et al.^[7] match the present results.

In the W -rich corner, the bcc phase field is narrower than the experimentally determined one. In the Nb -rich corner, the bcc phase behaves as predicted by the experimental isothermal sections. In Fig.3a and 3b, the reported maximum solubility of Nb in the χ phases are 13.3 at% and 8.9 at%, while the calculated ones are 13.7 at% and 10.2 at%, respectively. It can be seen that the calculation can reproduce the ternary solid solubility of χ phases determined by experiments.

The Co_3Nb phase exist in the calculated 1273 K isothermal section which has not been determined by relevant experimental points. The μ phase region extended from the $Co-W$ binary at 1073, 1273, 1373 K is smaller than that of Liu et al.^[7].

The μ phase is stabilized to fit the experimental data at 1373 K results in a much too vast and unreasonable single-phase region at above 1600 K. Moreover, the experimental points of μ phase are quiet scatter and cannot be accurately fitted. Thus, a detail investigation on the phase equilibria of Co_3Nb and μ phase at 1073, 1273 and 1373 K is required in the future.

Table 2 Optimized parameters of the Co-W and Co-Nb-W system in this work

System	Phase and model	Thermodynamic parameters /J·mol ⁻¹	Reference
Co-W	Liquid (Co, W)	${}^0L_{Co,W}^{Liq} = -57700+22.8T$	[21]
		${}^1L_{Co,W}^{Liq} = +2500$	
	bcc (Co, W)	${}^0L_{Co,W}^{bcc} = +56517$	[21]
		${}^0T_{CCo,W}^{bcc} = -3379$	
		${}^0\beta_{Co,W}^{bcc} = -3.146$	
	α Co (Co, W)	${}^0L_{Co,W}^{\alpha Co} = -19900+12.8T$	[21]
		${}^1L_{Co,W}^{\alpha Co} = +17970-19.3T$	
${}^0T_{CCo,W}^{\alpha Co} = -3379$			
hcp (Co, W)	${}^0L_{Co,W}^{hcp} = +63000$	[21]	
	${}^0T_{CCo,W}^{hcp} = -3379$		
	${}^0\beta_{Co,W}^{hcp} = -3.268$		
μ Co ₁ W ₂ (Co, W) ₄ Co ₆	${}^0G_{Co:W:Co:Co}^{\mu} = 59994.9 - 7.0T + 7G_{Co}^{fcc} + 2G_W^{bcc} + 4G_{Co}^{bcc}$	This work	
	${}^0G_{Co:W:Co}^{\mu} = -36011.1 - 12.6T + 7G_{Co}^{fcc} + 6G_W^{bcc}$		
	${}^0L_{Co:W:Co,W:Co}^{\mu} = 24058.9 - 4.52726T$		
χ (Co) _{0.75} (Co, W) _{0.25}	${}^0G_{Co:Co}^{\chi} = 13910.6 + 5.06542T + G_{Co}^{hcp}$	This work	
	${}^0G_{Co,W}^{\chi} = -4500.48 + 0.82T + 0.75G_{Co}^{hcp} + 0.25G_W^{bcc}$		
	${}^0L_{Co:Co,W}^{\chi} = -14414.5 - 2.74407T$		
Co-Nb-W	α Co(Co, Nb, W)	${}^0L_{Co,Nb,W}^{\alpha Co} = -317315 + 100T$	This work
	bcc (Co, Nb, W)	${}^0L_{Co,Nb,W:Va}^{bcc} = +2000000$	This work
${}^0L_{Co,Nb,W:Va}^{bcc} = -56019 - 100T$			
${}^0L_{Co,Nb,W:Va}^{bcc} = -886575 + 500T$			
μ (Co, Nb) ₁ (Co, Nb, W) ₂ - (Co, Nb, W) ₄ (Co) ₆	${}^0G_{Co:Co:Co:Co}^{\mu} = 100000 + 7G_{Co}^{fcc} + 6G_{Co}^{bcc}$	This work	
	${}^0G_{Co:Co:W:Co}^{\mu} = 200000 + 7G_{Co}^{fcc} + 2G_{Co}^{fcc} + 4G_W^{bcc}$		
	${}^0G_{Co:Nb:Co:Co}^{\mu} = -287019 + 260T + 7G_{Co}^{fcc} + 2G_{Nb}^{bcc} + 4G_{Co}^{bcc}$		
	${}^0G_{Co:Nb:W:Co}^{\mu} = 20000 + 7G_{Co}^{fcc} + 2G_{Nb}^{bcc} + 4G_W^{bcc}$		
	${}^0G_{Co:W:Nb:Co}^{\mu} = -44630 + 200T + 7G_{Co}^{fcc} + 2G_W^{bcc} + 4G_{Nb}^{bcc}$		
	${}^0G_{Nb:Co:Co:Co}^{\mu} = +1G_{Nb}^{fcc} + 6G_{Co}^{bcc} + 6G_{Co}^{fcc}$		
	${}^0G_{Nb:Co:W:Co}^{\mu} = +1G_{Nb}^{fcc} + 2G_{Co}^{bcc} + 4G_W^{bcc} + 6G_{Co}^{fcc}$		
	${}^0G_{Nb:Nb:Co:Co}^{\mu} = +1G_{Nb}^{fcc} + 2G_{Nb}^{bcc} + 4G_{Co}^{bcc} + 6G_{Co}^{fcc}$		
	${}^0G_{Nb:Nb:W:Co}^{\mu} = +1G_{Nb}^{fcc} + 2G_{Nb}^{bcc} + 4G_W^{bcc} + 6G_{Co}^{fcc}$		
	${}^0G_{Nb:W:Co:Co}^{\mu} = +1G_{Nb}^{fcc} + 2G_W^{bcc} + 4G_{Co}^{bcc} + 6G_{Co}^{fcc}$		
	${}^0G_{Nb:W:Nb:Co}^{\mu} = +1G_{Nb}^{fcc} + 2G_W^{bcc} + 4G_{Nb}^{bcc} + 6G_{Co}^{fcc}$		
	${}^0G_{Nb:W:W:Co}^{\mu} = +1G_{Nb}^{fcc} + 6G_W^{bcc} + 6G_{Co}^{fcc}$		
	${}^0L_{Co:Nb:Nb,W:Co}^{\mu} = -206343 - 50T$		
	${}^0L_{Nb:Nb:Nb,W:Co}^{\mu} = +44630 - 200T$		
	${}^0L_{Co:Nb,W:W:Co}^{\mu} = +160603 - 350T$		
	${}^1L_{Co:Nb,W:W:Co}^{\mu} = -55370 - 200T$		
	${}^2L_{Co:Nb,W:W:Co}^{\mu} = -495973 + 150T$		
${}^0L_{Co:Nb,W:Co:Co}^{\mu} = -310000$			
${}^0L_{Co:Nb,W:Co,W:Co}^{\mu} = -300000$			

Co_3Nb $(\text{Co})_3(\text{Nb}, \text{W})_1$	${}^0G_{\text{Co:Nb}}^{\text{Co}_3\text{Nb}} = -14600 + 3G_{\text{Co}}^{\text{hcp}} + G_{\text{W}}^{\text{bcc}}$ ${}^0L_{\text{Co:Nb,W}}^{\text{Co}_3\text{Nb}} = +45699 - 41T$ ${}^1L_{\text{Co:Nb,W}}^{\text{Co}_3\text{Nb}} = -13732 + 10T$	This work
χ $(\text{Co})_{0.75}(\text{Co}, \text{Nb}, \text{W})_{0.25}$	${}^0G_{\text{Co:Nb}}^{\chi} = -22865.75 + 5T + 0.75G_{\text{Co}}^{\text{hcp}} + 0.25G_{\text{Nb}}^{\text{bcc}}$ ${}^0G_{\text{Co:Nb,W}}^{\chi} = 5000$ ${}^1G_{\text{Co:Nb,W}}^{\chi} = +4365.75 - 5T$ ${}^0L_{\text{Co:Co,Nb,W}}^{\chi} = -50000$	This work
λ $(\text{Co}, \text{Nb}, \text{W})_2(\text{Co}, \text{Nb}, \text{W})_1$	${}^0G_{\text{Co:W}}^{\lambda} = -12333 + 2.5T + 2G_{\text{Co}}^{\text{hcp}} + G_{\text{W}}^{\text{bcc}}$ ${}^0G_{\text{Nb:W}}^{\lambda} = +2G_{\text{Nb}}^{\text{bcc}} + G_{\text{W}}^{\text{bcc}}$ ${}^0G_{\text{W:Co}}^{\lambda} = 100000 + 2G_{\text{W}}^{\text{bcc}} + G_{\text{Co}}^{\text{hcp}}$ ${}^0G_{\text{W:Nb}}^{\lambda} = 60000 + 2G_{\text{W}}^{\text{bcc}} + G_{\text{Nb}}^{\text{bcc}}$ ${}^0G_{\text{W:W}}^{\lambda} = 60000 + 3G_{\text{W}}^{\text{bcc}}$ ${}^0L_{\text{Co:Nb,W}}^{\lambda} = +75389 - 60T$ ${}^1L_{\text{Co:Nb,W}}^{\lambda} = -66658 + 50T$ ${}^0L_{\text{Co:Co,Nb,W}}^{\lambda} = -250973 + 150T$ ${}^0L_{\text{Co,W:Nb,W}}^{\lambda} = 130000$	This work

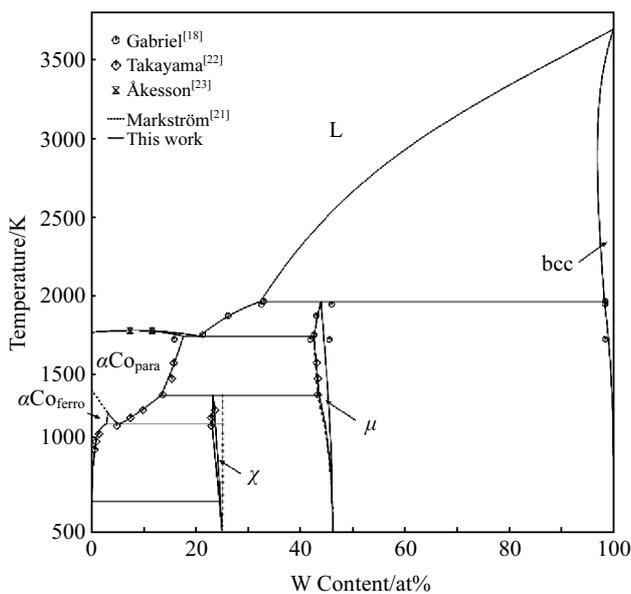


Fig.1 Re-calculated Co-W phase diagram compared with the previous assessment^[20] and phase equilibria data^[18,21,22]

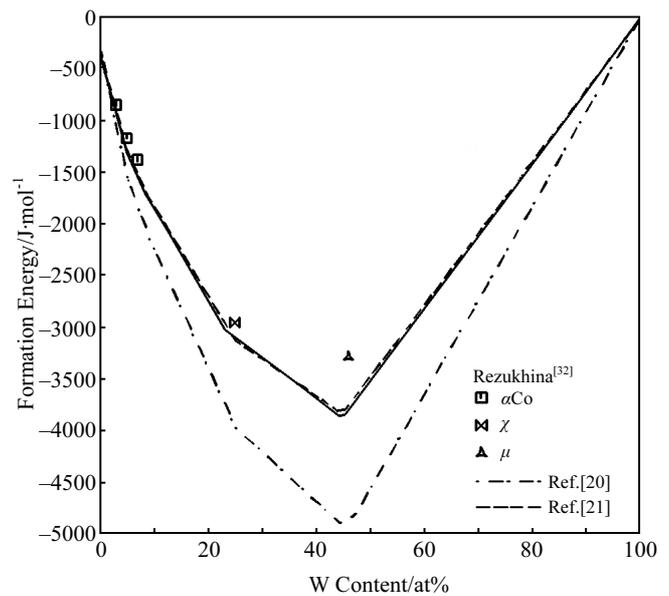


Fig.2 Calculated Gibbs energy of formation compared with the experimental data and previous assessment at 1250 K in the Co-W system

The present calculation did not correctly describe the λ phase at 1373, 1473 K, especially several two-phase tie-lines are located in the calculated three phase regions. Attempts at fitting this phase boundary resulted in λ phase becoming too stable at 1373 K which disagrees with results from the experimental data. The slight discrepancies may be explained by the fact that the λ phase should enlarge with increasing temperature, but the solubility for λ phase is quite similar at 1273 and 1373 K in

experimental isothermal sections.

Fig.4a~4c show the calculated Co-Nb-W phase diagram vertical sections with 60 at% Co, 5 at% and 15 at% W, respectively. The calculated results for the phase relations and phase boundaries are in good agreement with the experimental ones. Since there are limited experimental data for the invariant reactions and liquidus reactions, further experimental investigations are required to check the calculated results.

Table 3 Calculated invariant reactions in the Co-W system compared with the previous assessment and experimental data

Reaction type	Reaction	Composition of the respective phases, W content/at%			T/°C	Reference
Eutectoid	$\alpha\text{Co} \leftrightarrow \text{hcp} + \chi$	-	-	-	422	Expt. [22]
		~0	~0	25.0	421	Calc. [21]
		~0	~0	25.0	446	Calc. [20]
		~0	~0	24.5	421	This work
Eutectoid	$\alpha\text{Co}_{\text{par}} \leftrightarrow \chi + \alpha\text{Co}_{\text{ferro}}$	4.2*	-	2.6*	910*	Expt. [20]
		5.3	25.0	2.8	908	Calc. [21]
		5.3	25.0	2.4	898	Calc. [20]
		5.2	23.1	2.8	911	This work
Peritectoid	$\alpha\text{Co} + \mu \leftrightarrow \chi$	13.0	43.3	-	1093	Expt. [22]
		13.3	43.2	25.0	1093	Calc. [21]
		13.5	43.6	25.0	1093	Calc. [20]
		13.3	43.4	23.3	1093	This work
Eutectic	$\text{L} \leftrightarrow \alpha\text{Co} + \mu$	21.0	17.5	43.1	1471	Expt. [18]
		20.6	17.5	42.5	1471	Calc. [21]
		20.6	17.3	42.9	1470	Calc. [20]
		20.6	17.5	42.6	1471	This work
Peritectic	$\text{L} + \text{bcc} \leftrightarrow \mu$	32.0	99.1	~45.7	1689	Expt. [18]
		32.3	98.2	43.9	1692	Calc. [21]
		32.2	97.6	48.5	1689	Calc. [20]
		32.3	98.2	43.9	1689	This work

* Experimental results suggested that the eutectoid reaction is located between 900 °C and 910 °C

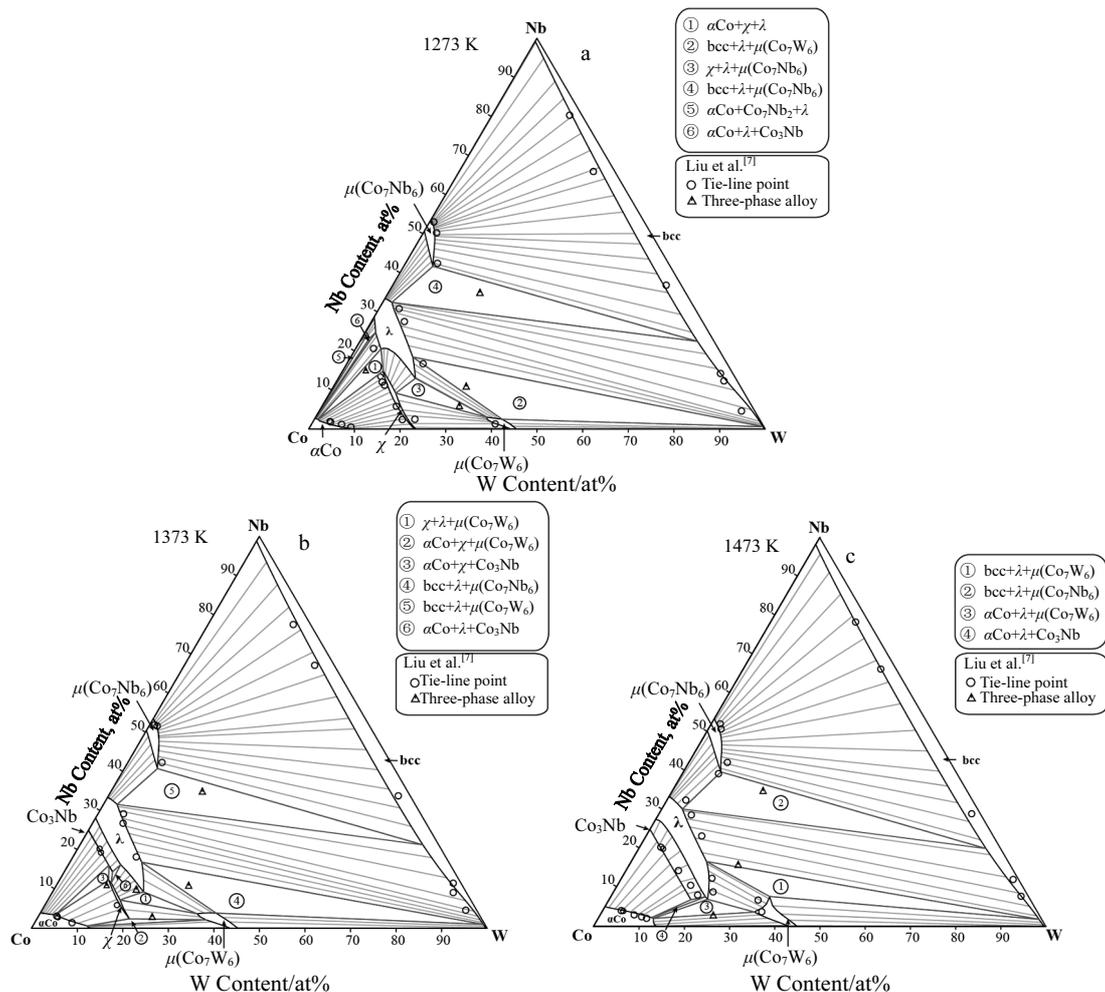


Fig. 3 Calculated Co-Nb-W isothermal sections at 1273 K (a), 1373 K (b), and 1473 K (c) compared with the experimental data

- Xiamen University, 2014 (in Chinese)
- 9 Pang Mengde. Thermodynamic Modeling of Be-Sr, Be-Mg and C-Co-W-Nb Systems, *Thesis for Master*[D]. Changsha: Central South University, 2014 (in Chinese)
 - 10 Kaufman L, Nesor H. *Metallurgical Transactions A*[J], 1975, 6(11): 2115
 - 11 Kaufman L, Nesor H. *Calphad*[J], 1978, 2(1): 35
 - 12 Bormann R, Busch R. *Journal of Non-Crystalline Solids*[J], 1990, 117: 539
 - 13 Kumar K C H, Ansara I, Wollants P et al. *Journal of Alloys and Compounds*[J], 1998, 267(1-2): 105
 - 14 He C, Stein F, Raabe D et al. *MRS Proceedings*[J], 2009, 506: 239
 - 15 He C, Stein F, Palm M. *Journal of Alloys and Compounds*[J], 2015, 637: 361
 - 16 Huang W. *Metallurgical and Materials Transactions A*[J], 1996, 27(11): 3591
 - 17 Kaufman L, Nesor H. *Calphad*[J], 1978, 2(1): 81
 - 18 Gabriel A, Allibert C, Ansara I et al. *Zeitschrift für Metallkunde*[J], 1985, 76(9): 589
 - 19 Guillet A F. *Metallurgical Transactions A*[J], 1989, 20(5): 935
 - 20 Sato J, Oikawa K, Kainuma R et al. *Journal of the Japan Institute of Metals and Materials*[J], 2004, 68(12): 992
 - 21 Markström A, Sundman B, Frisk K. *Journal of Phase Equilibria & Diffusion*[J], 2005, 26(2): 152
 - 22 Takayama T, Wey M Y, Nishizawa T. *Transactions of the Japan Institute of Metals*[J], 1981, 22(5): 315
 - 23 Akesson L. *Science of Hard Materials*[M]. Boston: Springer, 1983: 71
 - 24 Gabriel A. *Mécanismes de Dissolution et de Précipitation Dans les Carbures Cémentés WC/Co*[D]. Grenoble: INPG, 1984
 - 25 Zhu J, Titus M S, Pollock T M. *Journal of Phase Equilibria and Diffusion*[J], 2014, 35(5): 595
 - 26 Huron E S, Reed R C, Hardy M C et al. *Superalloys 2012*[M]. New Jersey: Wiley, 2012: 813
 - 27 Davydov A, Kattner U R. *Journal of Phase Equilibria*[J], 1999, 20(1): 5
 - 28 Joubert J M, Dupin N. *Intermetallics*[J], 2004, 12(12): 1373
 - 29 Dinsdale A T. *Calphad*[J], 1991, 15(4): 317
 - 30 Hillert M, Jarl M. *Calphad*[J], 1978, 2(3): 227
 - 31 Saunders N, Miodownik A P. *The Application of CALPHAD Methods*[M]. Amsterdam: Elsevier Science, 1998: 299
 - 32 Rezhukhina T N, Kashina T A. *The Journal of Chemical Thermodynamics*[J], 1976, 8(6): 513

Co-Nb-W 三元系的热力学评估

刘兴军^{1,2}, 牛泽明¹, 卢勇¹, 郭毅慧¹, 韩佳甲¹, 陈悦超¹, 王翠萍^{1,2}

(1. 厦门大学 材料学院, 福建 厦门 361005)

(2. 厦门大学 福建省材料基因工程重点实验室, 福建 厦门 361005)

摘要: 采用 CALPHAD 方法对 Co-Nb-W 三元系合金开展了热力学评估。为了统一 Co-Nb-W 三元系中 μ 相的热力学模型, 首先对 Co-W 二元系的热力学进行了优化, 并采用文献报道的 1273、1373 和 1473 K 3 个等温截面的相平衡实验数据开展了模型参数的优化。优化过程中采用亚正规溶体模型描述 α Co 和 bcc 等固溶体相, 而 λ 、 χ 和 Co_3Nb 相则采用双亚点阵模型来描述, Co_7W_6 和 Co_7Nb_6 相所用的点阵模型为 $(\text{Co}, \text{Nb})_i(\text{Co}, \text{Nb}, \text{W})_2(\text{Co}, \text{Nb}, \text{W})_4(\text{Co})_6$ 。计算的等温截面和纵截面相图与实验结果取得了很好的一致性。

关键词: 热力学计算; CALPHAD; Co-W 合金; Co-Nb-W 合金

作者简介: 刘兴军, 男, 1962 年生, 博士, 教授, 厦门大学材料学院, 福建 厦门 361005, 电话: 0592-2187888, E-mail: lxj@xmu.edu.cn