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Thermodynamic assessment of Co−Cr−W ternary system

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Abstract: The Co−Cr−W ternary system was critically assessed using the CALPHAD technique. The solution phases including the liquid, γ-Co, ε-Co and α-Cr were described by a substitutional solution model. The σ, μ and R phases were described by three-sublattice models of $(Co,W)_8(Cr,W)_4(Co,Cr,W)_{18}$, $(Co,Cr,W)_7W_2(Co,Cr,W)_4$ and $(Co,W)_{27}(Cr,W)_{14}(Co,Cr,W)_{12}$, respectively, in order to reproduce their homogeneity ranges. A self-consistent set of thermodynamic parameters for each phase was derived. The calculated isothermal sections at 1 000, 1 200 and 1 350 °C are in good agreement with the experimental data. A eutectoid reaction of $R \Leftrightarrow \mu+\gamma\text{-Co}+\sigma$ in this ternary system was predicted to occur at 1 022 °C.

Key words: Co−Cr−W system; Co-based superalloys; phase diagram; thermodynamics; σ phase; μ phase; R phase

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1 Introduction

Both chromium (Cr) and tungsten (W) are main constituent elements of Co-based superalloys [1−4]. Cr can improve the resistance against high temperature oxidation and corrosion of the alloys [5], while W serves to provide additional strength to the matrix owing to its large atomic size. So the Co−Cr−W system can be regarded as an important subsystem for Co-based superalloys [6−7]. It is also well known that phase diagrams and self-consistent thermodynamic descriptions of alloys are of great value for alloy design and processing [8−13]. Thus, a study on the phase diagram and thermodynamic properties of the Co−Cr−W ternary system is fundamental to develope Co-based superalloys. Until now, several isothermal sections in the Co-rich region in the Co−Cr−W ternary system have been established by experiment [14−16]. However, a precise thermodynamic description for this system, which is crucial for the alloy design of Cr and W in Co-based superalloys, has not been reported. Therefore, in the present study, a thermodynamic assessment of the Co-Cr-W ternary system is carried out by a CALPHAD (CALculation of PHAse Diagram) approach, which is very useful for the development of high quality Co-based superalloys.

2 Available experimental information

The phase equilibria of the Co−Cr−W system, especially in the Co-Cr side, were studied in several works [14−16]. DRAPIER et al [14] first measured the solubility of the γ-Co phase at 1 200 °C and studied the aging characteristic of some Co-Cr-W alloys using optical microscopy (OM), X-ray diffraction (XRD), hardness measurement and transmission electron microscopy (TEM). After that, BARROWS and NEWKIRK [15] investigated the Co−Cr−W system in somewhat more detail by means of OM, microhardness measurement, XRD and electron probe microanalysis (EPMA). In their work, a ternary intermetallic compound R phase was detected around the alloy composition of $Co_{23}Cr_{15}W_{15}$, and the R phase was found to be in equilibrium with the γ-Co, μ and σ phases. The solubility of the γ-Co phase was determined and the μ phase region was detected up to 21% Cr (mass fraction). An isothermal section at 1 350 °C was then established, as the dotted lines shown in Fig. 1. SATO [16] recently investigated the phase equilibria in the Co−Cr−W system from 1 000 °C to 1 350 °C by scanning electron microscopy (SEM) and XRD analysis. A comparison was done for the isothermal section at 1 350 °C determined by BARROWS and NEWKIRK [15] and

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SATO [16]. The phase relations in the Co-rich region and the solid solubility of the γ-Co phase detected in both works are nearly the same. The μ phase in the Co-W side and the σ phase in the Co-Cr side detected by SATO seem to be more stable than in BARROWS' work, which drives the three-phase region of μ+σ+α-Cr towards the higher Cr corner in SATO's work. SATO also studied the isothermal sections at 1 000 °C and 1 200 °C, where nearly the same phase relationships were obtained at 1 200 °C, while the R phase was not stable at 1 000 °C. The solubility of W in the σ phase was determined up to 25% (mole fraction), while the solubility of Cr in the μ phase can be up to about 50% (mole fraction). All these data will be used in the assessments in this work.

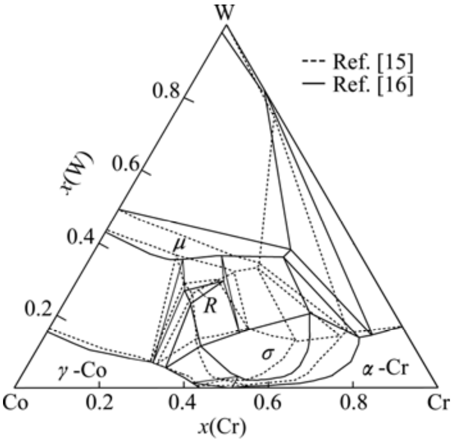

Fig. 1 Isothermal section of Co−Cr−W system at 1 350 °C determined by BARROWS and NEWKIRK [15] and SATO [16]

3 Thermodynamic modeling

3.1 Solution phases

The substitutional solution model is used to describe the solution phases of the liquid and the solid phases of γ-Co, ε-Co and α-Cr, which have the FCC, HCP and BCC structures, respectively. The Gibbs free energy of the phase ϕ (ϕ=liq, FCC, BCC and HCP) is described by the following expression:

$$G_m^{\phi} = x_{\mathrm{Co}}^{\phi} \cdot {}^0G_{\mathrm{Co}}^{\phi} + x_{\mathrm{Cr}}^{\phi} \cdot {}^0G_{\mathrm{Cr}}^{\phi} + x_{\mathrm{W}}^{\phi} \cdot {}^0G_{\mathrm{W}}^{\phi} + RT(x_{\mathrm{Co}}^{\phi} \ln x_{\mathrm{Co}}^{\phi} + x_{\mathrm{Cr}}^{\phi} \ln x_{\mathrm{Cr}}^{\phi} + x_{\mathrm{W}}^{\phi} \ln x_{\mathrm{W}}^{\phi}) + x_{\mathrm{Co}}^{\phi} x_{\mathrm{Cr}}^{\phi} L_{\mathrm{Co,\,Cr}}^{\phi} + x_{\mathrm{Co}}^{\phi} x_{\mathrm{W}}^{\phi} L_{\mathrm{Co,\,W}}^{\phi} + x_{\mathrm{Cr}}^{\phi} x_{\mathrm{W}}^{\phi} L_{\mathrm{Cr,\,W}}^{\phi} + {}^{\mathrm{E}}G_{\mathrm{Co,\,Cr,\,W}}^{\phi} + \Delta G^{mg,\phi} \tag{1}$$

where x_i^{ϕ} (i = Co, Cr, W) is the mole fraction of component i in the ϕ phase; R is the gas constant; T is the thermodynamic temperature; $L_{i,j}^{\phi}$ (i, j = Co, Cr, W, and $i \neq j$) is the binary interaction parameter between the components i and j; ${}^0G_i^{\phi}$ is the molar Gibbs free energy of the pure component i; ${}^{\mathrm{E}}G_{\mathrm{Co,Cr,W}}^{\phi}$ is the ternary excess Gibbs free energy; and $\Delta G^{\mathrm{mg},\phi}$ is the magnetic contribution to the Gibbs free energy. The binary interaction parameter $L_{i,j}^{\phi}$ is written as follows:

$$L_{i,j}^{\phi} = \sum_{n=0}^{m} {}^nL_{i,j}^{\phi}(x_i - x_j)^n \tag{2}$$

The ternary excess Gibbs free energy can be expressed by:

$${}^{\mathrm{E}}G_{\mathrm{Co,Cr,W}}^{\phi} = x_{\mathrm{Co}}^{\phi} x_{\mathrm{Cr}}^{\phi} x_{\mathrm{W}}^{\phi} (x_{\mathrm{Co}}^{\phi} \cdot {}^0L_{\mathrm{Co,Cr,W}}^{\phi} + x_{\mathrm{Cr}}^{\phi} \cdot {}^1L_{\mathrm{Co,Cr,W}}^{\phi} + x_W^{\phi} \cdot {}^2L_{\mathrm{Co,Cr,W}}^{\phi}) \tag{3}$$

The binary interaction parameters ${}^nL_{i,j}^{\phi}$ are taken from the previous thermodynamic calculations [17−19] and the ternary interaction parameters ${}^nL_{i,j,k}^{\phi}$ will be optimized in this work.

The $\Delta G^{\mathrm{mg},\phi}$ in Eq. (1) is a magnetic contribution to the Gibbs free energy [20]. In this work, no ternary magnetic parameters are introduced.

3.2 σ, μ and R phases

The σ phase is D8$_3$ structure with the CrFe type [21]. In the Co−Cr binary system, the σ phase was modeled by $(\mathrm{Co})_8(\mathrm{Cr})_4(\mathrm{Co,Cr})_{18}$ [17]. As shown in Fig. 1, the σ phase can dissolve a large amount of W, where W substitutes partial Co and Cr. Therefore, in this work, we assume that W can enter all the three sublattices, and model the ternary σ phase as $(\mathrm{Co,W})_8(\mathrm{Cr,W})_4(\mathrm{Co,Cr,W})_{18}$.

The μ phase is D8$_5$ structure with the $\mathrm{Fe_7W_6}$ type [22]. In the Co−W binary system, the μ phase was modeled by a three-sublattice model of $(\mathrm{Co,W})_7\mathrm{W}_2(\mathrm{Co,W})_4$ [18]. More than 50% Cr (mole fraction) can dissolve in the μ phase in the ternary system, substituting both Co and W according to its homogeneity range. Therefore, in this work, we assume that Cr can occupy both the first and the third sublattices, and model the ternary μ phase as $(\mathrm{Co,Cr,W})_7\mathrm{W}_2(\mathrm{Co,Cr,W})_4$.

A ternary intermetallic compound, R phase, has been reported in the Co−Cr−W system around the composition of $\mathrm{Co_{23}Cr_{15}W_{15}}$ [15]. It has been known that the R phase has the same structure with that in the Fe−Mo binary system [23], which has been modeled as $(\mathrm{Fe})_{27}(\mathrm{Mo})_{14}(\mathrm{Fe,Mo})_{12}$. As we know, Co and Fe have very similar physical and chemical properties, thus, in the modeling work we assume that Co occupies the sublattices of Fe. Meanwhile, the elements Cr and Mo are in the same group in the periodic table and we assume that Cr occupies the sublattices of Mo. Finally, W atom may occupy all three sublattices. Therefore, the ternary R phase is described by a three-sublattice model of $(\mathrm{Co,W})_{27}(\mathrm{Cr,W})_{14}(\mathrm{Co,Cr,W})_{12}$.

We then describe all the three three-sublattice models for the phases of σ, μ and R as a general formula $(A,B,C)_m(A,B)_p(A,B,C)_q$. The Gibbs energy of the phase φ (φ =σ, μ and R) can be described by the following expression:

$$
\begin{aligned}
G^{\varphi} = {} & \sum_i \sum_j \sum_k y_i^{\mathrm{I}} y_j^{\mathrm{II}} y_k^{\mathrm{III}} \; {}^{0}G_{i:j:k} + mRT \sum_i y_i^{\mathrm{I}} \ln y_i^{\mathrm{I}} + \\
& pRT \sum_j y_j^{\mathrm{II}} \ln y_j^{\mathrm{II}} + qRT \sum_k y_k^{\mathrm{III}} \ln y_k^{\mathrm{III}} + \\
& \sum_{i_1,i_2} \sum_j \sum_k [y_{i_1}^{\mathrm{I}} y_{i_2}^{\mathrm{I}} y_j^{\mathrm{II}} y_k^{\mathrm{III}} (\sum_n {}^{n}L_{i_1,i_2:j:k} (y_{i_1}^{\mathrm{I}} - y_{i_2}^{\mathrm{I}})^n] + \\
& \sum_i \sum_{j_1,j_2} \sum_k [y_i^{\mathrm{I}} y_{j_1}^{\mathrm{II}} y_{j_2}^{\mathrm{II}} y_k^{\mathrm{III}} (\sum_n {}^{n}L_{i:j_1,j_2:k} (y_{j_1}^{\mathrm{II}} - y_{j_2}^{\mathrm{II}})^n] + \\
& \sum_i \sum_j \sum_{k_1,k_2} [y_i^{\mathrm{I}} y_j^{\mathrm{II}} y_{k_1}^{\mathrm{III}} y_{k_2}^{\mathrm{III}} (\sum_n {}^{n}L_{i:j:k_1,k_2} (y_{k_1}^{\mathrm{III}} - y_{k_2}^{\mathrm{III}})^n]
\end{aligned}
\tag{4}
$$

where ${}^{0}G_{i:j:k}$ is the Gibbs free energy of the φ phase when the first sublattice is occupied by the element i (i = Co, Cr or W), the second by the element j (j = Cr, W), and the third by the element k (k = Co, Cr or W); ${}^{n}L_{i_1,i_2:j:k}$ is the interaction parameter between element i_1 and i_2 (i_1, i_2 = Co, Cr or W and $i_1 \neq i_2$) when the second sublattice is occupied by the element j (j = Cr, W), and the third by the element k (k = Co, Cr or W); the parameters ${}^{n}L_{i:j_1,j_2:k}$ and ${}^{n}L_{i:j:k_1,k_2}$ are described in the same way.

4 Optimization

The thermodynamic parameters of the binary Co−Cr, Co−W and Cr−W systems were taken from the work of OIKAWA et al [17], SATO et al [18] and GUSTAFSON [19], respectively. The ternary interaction parameters were thermodynamically optimized in this work by using the CALPHAD technique with the aid of the PARROT module of the Thermo-Calc package [24]. The optimization began with the γ-Co phase. The determined solid solubility data of the γ-Co phase by BARROWS and NEWKIRK [15] and SATO [16] were used to optimize the parameters of ${}^{n}L^{\gamma\text{Co}}_{\text{Co,Cr,W:Va}}$. The model parameters of the σ and μ phases were then considered based on the phase relationships claimed by both BARROWS and NEWKIRK [15] and SATO [16], with a larger weight factor on the data of SATO. The parameter ${}^{0}G^{\sigma}_{\text{W:Cr:Cr}}$ was specially evaluated in order to reproduce the σ phase boundary in the Cr-rich region. For the μ phase, the parameters ${}^{0}G^{\mu}_{\text{Co:W:Cr}}$ and ${}^{0}G^{\mu}_{\text{Cr:W:Co}}$ were adjusted in order to reproduce the homogeneity range extending to the high Cr region. Finally, the model parameters of the R phase were considered according to the determined phase compositions and the phase stability in Refs. [15] and [16]. The ternary model parameters obtained in this work together with those in the constituent binary systems are listed in Table 1.

Table 1 Thermodynamic parameters of ternary Co-Cr-W system

Phase	Parameter	Source
γ-Co (Co,Cr, W)$_1$(Va)$_1$	${}^{0}L^{\gamma\text{-Co}}_{\text{Co,Cr:Va}}=-24\,052.09+8.188\,4\,T$, ${}^{1}L^{\gamma\text{-Co}}_{\text{Co,Cr:Va}}=5\,331.825\,2-6.905\,9T$	Ref. [17]
	${}^{0}Tc^{\gamma\text{-Co}}_{\text{Co,Cr:Va}}=-9\,392.525\,9$, ${}^{1}Tc^{\gamma\text{-Co}}_{\text{Co,Cr:Va}}=8\,383.042\,4$	Ref. [17]
	${}^{0}L^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-15\,626.162+8.112\,646\,4\,T$, ${}^{1}L^{\gamma\text{-Co}}_{\text{Co,W:Va}}=1\,571.693\,6-5.965\,389\,T$	Ref. [18]
	${}^{2}L^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-9\,909.888\,6+3.124\,381\,3\,\mathrm{T}$, ${}^{0}Tc^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-3\,520.31$, ${}^{0}\beta^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-2.926\,62$	Ref. [18]
	${}^{1}Tc^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-4\,796.2$, ${}^{1}\beta^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-4.769\,58$, ${}^{2}Tc^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-813.657$	Ref. [18]
	${}^{2}\beta^{\gamma\text{-Co}}_{\text{Co,W:Va}}=-4.548\,64$, ${}^{3}Tc^{\gamma\text{-Co}}_{\text{Co,W:Va}}=569\,9.827$, ${}^{3}\beta^{\gamma\text{-Co}}_{\text{Co,W:Va}}=10.143\,96$	Ref. [18]
	${}^{0}L^{\gamma\text{-Co}}_{\text{Cr,W:Va}}=3\,1520$, ${}^{1}L^{\gamma\text{-Co}}_{\text{Cr,W:Va}}=-1\,320$	Ref. [19]
	${}^{0}L^{\gamma\text{-Co}}_{\text{Co,Cr,W:Va}}=5\,000$	This work
α-Cr (Co, Cr, Va, W)$_1$(Va)$_3$	${}^{0}L^{\alpha\text{-Cr}}_{\text{Co,Cr:Va}}=1\,033.282\,9-1.480\,8\,T$, ${}^{1}L^{\alpha\text{-Cr}}_{\text{Co,Cr:Va}}=11\,971.500\,8-13.374\,1\,T$	Ref. [17]
	${}^{0}L^{\alpha\text{-Cr}}_{\text{Co,Va:Va}}=151\,000-28.873\,338\,T$	This work
	${}^{0}L^{\alpha\text{-Cr}}_{\text{Co,W:Va}}=45\,663.27-4.677\,220\,8\,T$, ${}^{1}L^{\alpha\text{-Cr}}_{\text{Co,W:Va}}=-15\,241.606$	Ref. [18]
	${}^{0}Tc^{\alpha\text{-Cr}}_{\text{Co,W:Va}}=-3\,379$, ${}^{0}\beta^{\alpha\text{-Cr}}_{\text{Co,W:Va}}=-3.146$	Ref. [18]
	${}^{0}L^{\alpha\text{-Cr}}_{\text{Cr,Va:Va}}=100\,000$	Ref. [26]
	${}^{0}L^{\alpha\text{-Cr}}_{\text{Cr,W:Va}}=31\,250$, ${}^{1}L^{\alpha\text{-Cr}}_{\text{Cr,W:Va}}=-1\,320$	Ref. [19]
	${}^{0}L^{\alpha\text{-Cr}}_{\text{Va,W:Va}}=150\,000$, ${}^{0}L^{\alpha\text{-Cr}}_{\text{Co,Cr,W:Va}}=70\,000+30\,T$	This work
	${}^{1}L^{\alpha\text{-Cr}}_{\text{Co,Cr,W:Va}}=50\,000-30\,T$ ${}^{2}L^{\alpha\text{-Cr}}_{\text{Co,Cr,W:Va}}=50\,000$	This work

(to be continue)

Continued

Co_3W $(Co)_3(W)_1$	${}^{0}G^{\mathrm{Co_3W}}_{\mathrm{Co:W}}=-31\ 976.631+10.940\ 883\ T+3\,{}^{0}G^{\varepsilon}_{\mathrm{Co}}+{}^{0}G^{\alpha}_{\mathrm{W}}$	Ref. [18]
σ $(Co,W)_8$ $(Cr, W)_4$ $(Co, Cr,W)_{18}$	${}^{0}G^{\sigma}_{\mathrm{Co:Cr:Co}}=8\,{}^{0}G^{\gamma}_{\mathrm{Co}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+18\,{}^{0}G^{\alpha}_{\mathrm{Co}}-16\ 898.717\ 8-29.814\ 0\ T$	Ref. [17]
	${}^{0}G^{\sigma}_{\mathrm{Co:Cr:Cr}}=8\,{}^{0}G^{\gamma}_{\mathrm{Co}}+22\,{}^{0}G^{\alpha}_{\mathrm{Cr}}-259\ 935.807+85.096\ 6\ T$	Ref. [17]
	${}^{0}G^{\sigma}_{\mathrm{Co:Cr:W}}=8\,{}^{0}G^{\gamma}_{\mathrm{Co}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+18\,{}^{0}G^{\alpha}_{\mathrm{W}}+100\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{Co:W:Co}}=8\,{}^{0}G^{\gamma}_{\mathrm{Co}}+4\,{}^{0}G^{\alpha}_{\mathrm{W}}+18\,{}^{0}G^{\alpha}_{\mathrm{Co}}+50\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{Co:W:Cr}}=8\,{}^{0}G^{\gamma}_{\mathrm{Co}}+4\,{}^{0}G^{\alpha}_{\mathrm{W}}+18\,{}^{0}G^{\alpha}_{\mathrm{Cr}}$	This work
	${}^{0}G^{\sigma}_{\mathrm{Co:W:W}}=8\,{}^{0}G^{\gamma}_{\mathrm{Co}}+22\,{}^{0}G^{\alpha}_{\mathrm{W}}+500\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{W:Cr:Co}}=8\,{}^{0}G^{\gamma}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+18\,{}^{0}G^{\alpha}_{\mathrm{Co}}+400\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{W:Cr:Cr}}=8\,{}^{0}G^{\gamma}_{\mathrm{W}}+22\,{}^{0}G^{\alpha}_{\mathrm{Cr}}-100\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{W:Cr:W}}=8\,{}^{0}G^{\gamma}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+18\,{}^{0}G^{\alpha}_{\mathrm{W}}+600\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{W:W:Cr}}=8\,{}^{0}G^{\gamma}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{W}}+18\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+150\ 000$	This work
	${}^{0}G^{\sigma}_{\mathrm{W:W:W}}=8\,{}^{0}G^{\gamma}_{\mathrm{W}}+22\,{}^{0}G^{\alpha}_{\mathrm{W}}+750\ 000$	This work
μ $(Co, Cr, W)_7$ W_2 $(Co, Cr, W)_4$	${}^{0}G^{\mu}_{\mathrm{Co:W:Co}}=7\,{}^{0}G^{\gamma}_{\mathrm{Co}}+2\,{}^{0}G^{\alpha}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Co}}+477\ 746.37-123.282\ 1\ T$	Ref. [18]
	${}^{0}G^{\mu}_{\mathrm{Co:W:Cr}}=7\,{}^{0}G^{\gamma}_{\mathrm{Co}}+2\,{}^{0}G^{\alpha}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}-230\ 000+126.565\ T$	This work
	${}^{0}G^{\mu}_{\mathrm{Co:W:W}}=7\,{}^{0}G^{\gamma}_{\mathrm{Co}}+6\,{}^{0}G^{\alpha}_{\mathrm{W}}-96\ 587.924+27.840\ 609\ T$	Ref. [18]
	${}^{0}G^{\mu}_{\mathrm{Cr:W:Co}}=7\,{}^{0}G^{\gamma}_{\mathrm{Cr}}+2\,{}^{0}G^{\alpha}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Co}}-326\ 587.924+154.405\ 609\ T$	This work
	${}^{0}G^{\mu}_{\mathrm{Cr:W:Cr}}=7\,{}^{0}G^{\gamma}_{\mathrm{Cr}}+2\,{}^{0}G^{\alpha}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+10\ 000$	This work
	${}^{0}G^{\mu}_{\mathrm{Cr:W:W}}=7\,{}^{0}G^{\gamma}_{\mathrm{Cr}}+6\,{}^{0}G^{\alpha}_{\mathrm{W}}+10\ 000$	This work
	${}^{0}G^{\mu}_{\mathrm{W:W:Co}}=7\,{}^{0}G^{\gamma}_{\mathrm{W}}+2\,{}^{0}G^{\alpha}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Co}}+639\ 334.294-151.123\ 309\ T$	This work
	${}^{0}G^{\mu}_{\mathrm{W:W:Cr}}=7\,{}^{0}G^{\gamma}_{\mathrm{W}}+2\,{}^{0}G^{\alpha}_{\mathrm{W}}+4\,{}^{0}G^{\alpha}_{\mathrm{Cr}}$	This work
	${}^{0}L^{\mu}_{\mathrm{Co,W:W:Co}}=-1\ 220.000\ 9+24.595\ 098T$	Ref. [18]
	${}^{0}L^{\mu}_{\mathrm{Co:W:Co,W}}=-323\ 795.62-2.622\ 129\ 7\ T$	Ref. [18]
	${}^{0}L^{\mu}_{\mathrm{W:W:Co,W}}=-323\ 795.62-2.622\ 129\ 7\ T$	Ref. [18]
	${}^{0}L^{\mu}_{\mathrm{Co,W:W:W}}=-1\ 220.000\ 9+24.595\ 098\ T$	Ref. [18]
R $(Co,W)_{27}(Cr,W)_{14}(Co,Cr,W)_{12}$	${}^{0}G^{R}_{\mathrm{Co:Cr:Co}}=27\,{}^{0}G^{\gamma}_{\mathrm{Co}}+14\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+12\,{}^{0}G^{\alpha}_{\mathrm{Co}}$	This work
	${}^{0}G^{R}_{\mathrm{Co:Cr:Cr}}=27\,{}^{0}G^{\gamma}_{\mathrm{Co}}+26\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+50\ 000$	This work
	${}^{0}G^{R}_{\mathrm{Co:Cr:W}}=27\,{}^{0}G^{\gamma}_{\mathrm{Co}}+14\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+12\,{}^{0}G^{\alpha}_{\mathrm{W}}-700\ 000$	This work
	${}^{0}G^{R}_{\mathrm{Co:W:Co}}=27\,{}^{0}G^{\gamma}_{\mathrm{Co}}+14\,{}^{0}G^{\alpha}_{\mathrm{W}}+12\,{}^{0}G^{\alpha}_{\mathrm{Co}}+400\ 000$	This work
	${}^{0}G^{R}_{\mathrm{Co:W:Cr}}=27\,{}^{0}G^{\gamma}_{\mathrm{Co}}+14\,{}^{0}G^{\alpha}_{\mathrm{W}}+12\,{}^{0}G^{\alpha}_{\mathrm{Cr}}-700\ 000$	This work
	${}^{0}G^{R}_{\mathrm{Co:W:W}}=27\,{}^{0}G^{\gamma}_{\mathrm{Co}}+26\,{}^{0}G^{\alpha}_{\mathrm{W}}+500\ 000$	This work
	${}^{0}G^{R}_{\mathrm{W:Cr:Co}}=27\,{}^{0}G^{\gamma}_{\mathrm{W}}+14\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+12\,{}^{0}G^{\alpha}_{\mathrm{Co}}-850\ 000$	This work
	${}^{0}G^{R}_{\mathrm{W:Cr:Cr}}=27\,{}^{0}G^{\gamma}_{\mathrm{W}}+26\,{}^{0}G^{\alpha}_{\mathrm{Cr}}$	This work
	${}^{0}G^{R}_{\mathrm{W:Cr:W}}=27\,{}^{0}G^{\gamma}_{\mathrm{W}}+14\,{}^{0}G^{\alpha}_{\mathrm{Cr}}+12\,{}^{0}G^{\alpha}_{\mathrm{W}}+50\ 000$	This work
	${}^{0}G^{R}_{\mathrm{W:W:Co}}=27\,{}^{0}G^{\gamma}_{\mathrm{W}}+14\,{}^{0}G^{\alpha}_{\mathrm{W}}+12\,{}^{0}G^{\alpha}_{\mathrm{Co}}+500\ 000$	This work
	${}^{0}G^{R}_{\mathrm{W:W:Cr}}=27\,{}^{0}G^{\gamma}_{\mathrm{W}}+14\,{}^{0}G^{\alpha}_{\mathrm{W}}+12\,{}^{0}G^{\alpha}_{\mathrm{Cr}}$	This work
	${}^{0}G^{R}_{\mathrm{W:W:W}}=27\,{}^{0}G^{\gamma}_{\mathrm{W}}+26\,{}^{0}G^{\alpha}_{\mathrm{W}}+500\ 000$	This work

The lattice stabilities of pure Co, Cr and W were taken from the SGTE unary database [25].

5 Results and discussion

With the thermodynamic parameters in Table 1, the phase diagrams of the Co−Cr−W system can be calculated. Figure 2 shows the calculated isothermal sections at 1 000, 1 200 and 1 350 °C compared with the experimental data. It can be seen that the calculation can reproduce the ternary solid solubility of the *γ*-Co and *α*-Cr determined by experiments. The phase relationships derived by the calculation agree well with the work in Refs. [15] and [16]. The very large solubilities of the *μ* and *σ* phases determined by experiments have been satisfied in the calculation. The *R* phase is stable at high temperatures of 1 200 and 1 350 °C, and is not stable below 1 000 °C. A eutectoid reaction of $R \Leftrightarrow \mu+\gamma\text{-Co}+\sigma$ is predicted to occur at 1 022 °C, and at a higher temperature of 1 444 °C, the *R* phase disappears due to a reaction of $L+R \Leftrightarrow \gamma\text{-Co}+\sigma$ by our calculation.

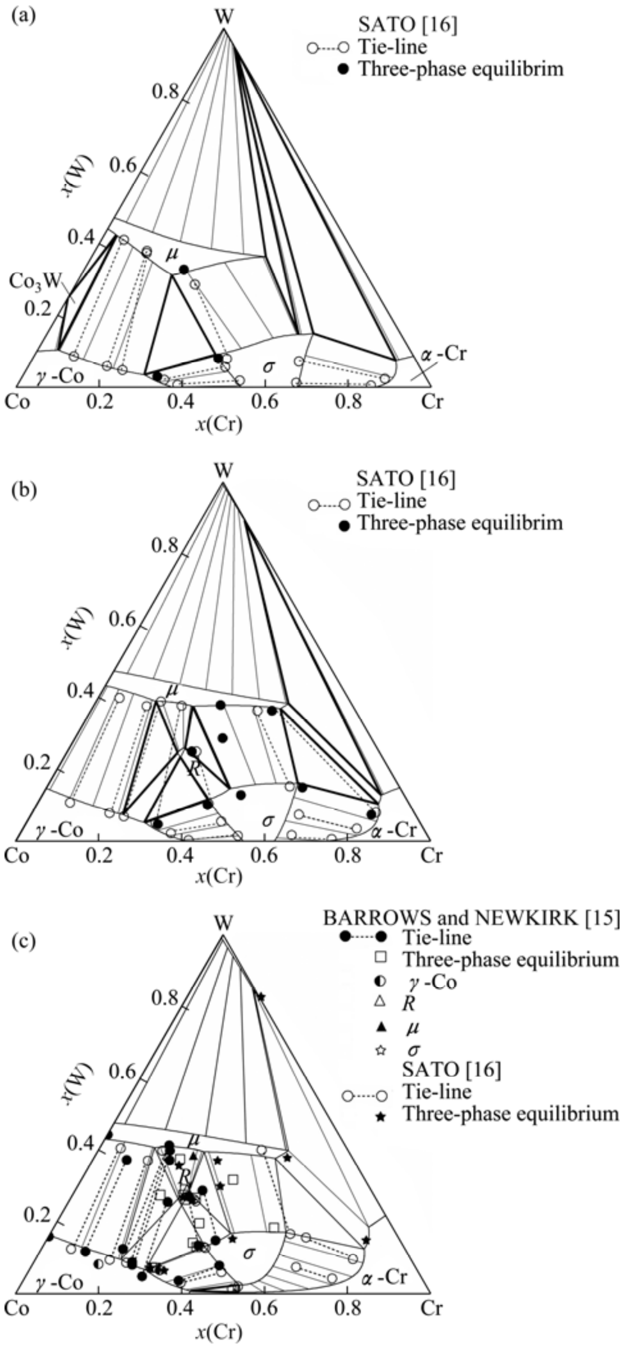

Fig. 2 Calculated isothermal sections at 1 000 °C (a), 1 200 °C (b) and 1 350 °C (c) compared with experimental data by BARROWS and NEWKIRK [15] and SATO [16]

6 Conclusions

1) A thermodynamic analysis of the Co−Cr−W system was carried out and a self-consistent set of thermodynamic parameters was obtained. The calculated isothermal sections are in good agreement with the available experimental data.

2) The phase relationships and the solid solubilities of the *γ*-Co, *α*-Cr, *μ* and *σ* phases determined by experiments have all been reproduced reasonably.

3) The ternary *R* phase is stable from 1 022 °C to 1 444 °C in the Co−Cr−W system by the present calculation. All these provide useful information for the alloying of Cr and W in Co-based superalloys design.

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Co−Cr−W 三元系相平衡的热力学计算

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摘 要：用 CALPHAD 方法评估了 Co−Cr−W 三元系，计算了 1 000， 1 200 和 1 350 °C 的相平衡。采用亚正规溶体模型描述了液相，fcc 相，bcc 相和 hcp 相。σ 相，μ 相，*R* 相分别用模型$(Co,W)_8(Cr,W)_4(Co,Cr,W)_{18}$，$(Co,Cr,W)_7W_2(Co,Cr,W)_4$ 和$(Co,W)_{27}(Cr,W)_{14}(Co,Cr,W)_{12}$来表示；得到了自洽的热力学相互作用参数。计算的 1 000, 1 200 和 1 350 °C 的相图与实验数据吻合。

关键词：Co−Cr−W 三元系；Co 基高温合金；相图；热力学；σ 相；μ 相；*R* 相

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