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Thermodynamic optimization of Co–Ge binary system

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ABSTRACT

Phase diagram of Co–Ge binary system was thermodynamically assessed by using CALPHAD approach in this study. The excess Gibbs energy of the solution phases, liquid, α(Co) and ε(Co), were modeled with Redlich–Kister polynomial. Magnetic contribution to the Gibbs energy was also taken into account for α(Co) and ε(Co). Considering its crystal structure and solubility range, the intermetallic compound βCo_5Ge_3, with $B8_2$-structure, was particularly described with a three-sublattice model, $(Co,Va)_1$:$(Co)_4$:$(Co,Ge)_3$. And the compound CoGe was described with two-sublattice model according to its crystal structure. Other intermetallic compounds were described as stoichiometric phases because of their narrow homogeneity ranges or unknown crystal structure. In order to obtain a reasonable description of several Co–Ge compounds, first-principle calculations were performed before optimization to determine their formation enthalpies. Finally, a set of thermodynamic parameters was finally obtained so that most data of phase boundaries and thermodynamic properties of various phases were reproduced in present optimization.

1. Introduction

A transition metal/semiconductor system is used in spintronics devices. The term "spintronics" requires assembling of suitable structures with desired magnetic properties. The Co/Ge related thin film materials have already been developed to significantly improve the performance of traditional spintronics devices, such as local magnetization of the semiconductor matrix, the redistribution of the electron density in the alloys and so on [1–5]. In order to better understand how the interacted elements diffuse and react and thus to simulate the microstructure evolution of such film materials, knowledge of phase equilibria of the related system is essential.

The Co–Ge system was firstly assessed in 2004 [6]. The detailed assessment and related parameters were not published but a phase diagram, which is shown in Fig. 1. As can be seen, all intermediate phases were treated as stoichiometric compounds in Ref. [6]. However, according to Refs. [7–11], Co_5Ge_3 and CoGe are actually with remarkable homogenous ranges which should be taken into account, especially when extrapolated to higher-order system. Therefore, a reassessment and optimization of Co–Ge system is necessary.

2. Evaluation of literature data

2.1. Phase diagram data

The Co–Ge phase diagram was firstly measured by Pfisterer et al. [12] through thermal analysis, metallographic observation and X-ray diffraction, and the liquidus boundaries were determined. Later, Dayer et al. [9] extensively investigated the phase equilibria using differential thermal analysis, metallographic methods, X-ray diffractography, microhardness and microprobe analysis. Both the liquidus and the solvus were refined, and the temperatures of some invariant reactions were also precisely determined. Phase equilibria up to 40 at.% Ge were further measured by Enoki et al. [10] using diffusion-couple method and an intermetallic compound Co_3Ge was detected. The Co_3Ge was so named due to the existence of M_3Ge type compounds with cubic structure A15, which occurs commonly in binary systems involving Ge and the first transition metals [13]. The intermediate phase βCo_5Ge_3 formed congruently from liquid with a broad homogeneity range determined by X-ray diffraction [7,11] and electron probe microanalysis [8–10], and transformed to αCo_5Ge_3 at low temperature [9]. The compound CoGe, with a narrow homogeneity range, was formed by a peritectic reaction [9]. The compounds Co_5Ge_2, Co_3Ge, Co_5Ge_7 and $CoGe_2$ are with negligible solubility ranges less than ±0.5 at.% Ge and could be considered as stoichiometric phases. The maximum solubility of Co in the terminal phase (Ge) amounts to 4.6×10^{-6} at.% Ge. In addition, Köster and Horn [14] measured the change of Curie

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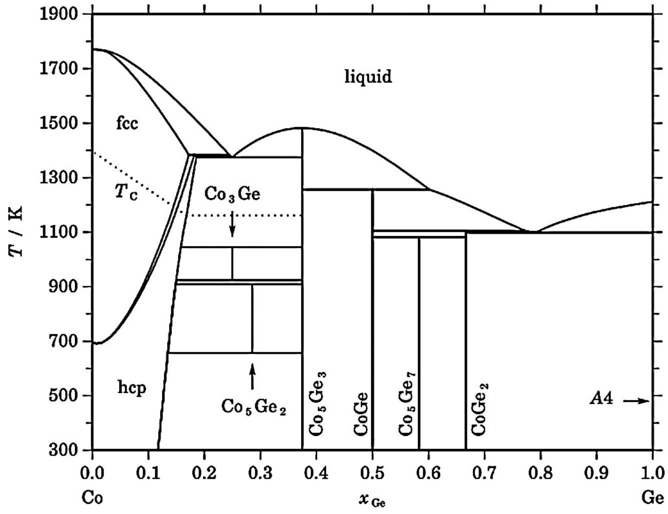

Fig. 1. The phase diagram calculated by Korb [6].

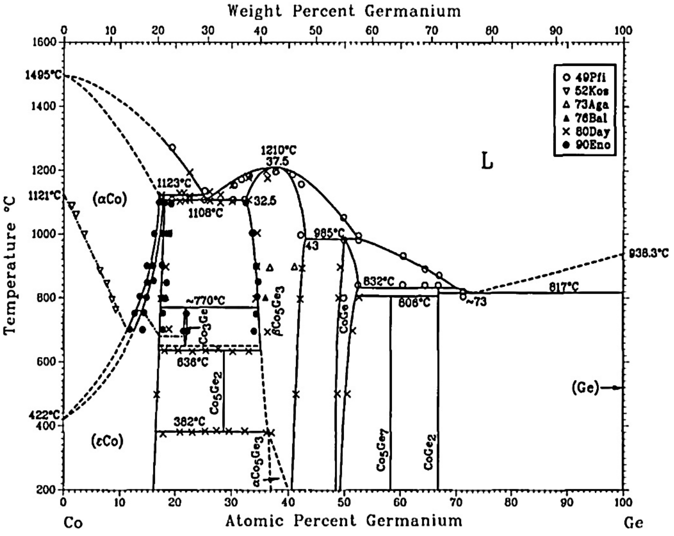

Fig. 2. The phase diagram evaluated by Ishida and Nishizawa [15].

temperature of α(Co) at different compositions and that of ε(Co) at the composition of 12.5 at.% Ge. All the magnetism transition data was used as input to the optimization in the present assessment to fit the T_C concentration dependence.

By evaluating the early reported boundary data [7–10,12,14], Ishida and Nishizawa [15] constructed the Co–Ge phase diagram as shown in Fig. 2. The measured boundaries of phases and their crystal structure information are summarized in Tables 1 and 2, respectively. All the phase boundary data were adopted for the present assessment.

2.2. Thermodynamic information

Measured and/or estimated thermodynamic data including enthalpy of mixing of liquid Co–Ge alloys, activities of Co and Ge in liquid and formation enthalpy for the intermetallic compounds are summarized in Table 3.

Through high-temperature calorimetry, enthalpy of mixing of liquid Co–Ge alloys at 1823 K was measured by Shlopak et al. [19]. According to Shlopak et al. [19], enthalpy of mixing of liquid alloys takes the minimum at about 50 at.% Ge.

Table 1
Summary of experimental data for the Co–Ge system.

Type of experimental data	Composition (at.% Ge)	Temp. range (K)	Experimental method	Refs.
Solvus (α(Co))	11.1–16.3	973–1373	EPMA[a]	[10]
Solvus (ε(Co))	13.3–18.0	973–1373	EPMA[a]	[10]
	17.4 ± 0.6	1073	EPMA[a]	[8]
	16.1–17.8	773–1273	EPMA[a]	[9]
Solvus (CoGe)	49.5	1073	TA[b]	[12]
	48.3–52.0	773–1173	EPMA[a]	[9]
Solvus (Co_3Ge)	21.7–22.0	773–823	EPMA[a]	[10]
Solvus (βCo_5Ge_3)	36.0–40.5	1173	XRD[c]	[7]
	35.0 ± 1.0	1073	EPMA[a]	[8]
	36.0–40.5	1173	XRDc	[11]
	33.5–41.9	773–1273	EPMA[a]	[9]
	32.5–34.3	973–1373	EPMA[a]	[10]
Liquidus (α(Co), β-Co_5Ge_3, CoGe, $CoGe_2$) noninvariants	18.3–71.0	1093–1553	TA[b]	[12]
Liquidus (α(Co), β-Co_5Ge_3) noninvariants	22.5–37.0	1404–1482	EPMA[a]	[9]
Solidus (βCo5Ge3)	41.5	1268	TA[b]	[12]
T_C (α(Co))	0	1394	MG[d]	[16]
T_C (α(Co))	0.8–9.1	1044–1362	MG[d]	[14]
T_C (ε(Co))	12.5	1033	MG[d]	[14]

[a] Electron probe microanalysis.
[b] Thermal analysis.
[c] X-ray diffraction.
[d] Magnetic measurements.

Activities of Co and Ge in liquid Co–Ge alloys at 1723 K and 1870 K were measured by using distribution method [20] and mass spectrometry approach [21], respectively.

Enthalpies of formation for the phase βCo_5Ge_3, CoGe and $CoGe_2$ at 1060 K were measured by using solution calorimeter [22]. These data show an unreasonable tendency (See later in Fig. 4), especially around 40 at.% Ge. Thus, these data were given lower weight during optimization.

The heat of formation of βCo_5Ge_3 at 298 K was measured by Kleppa and Jung [23] using high temperature synthesis calorimetry, and calculated by Niessen et al. [24] using Miedema's empirical theory [25,26]. The measured and calculated enthalpy of formation of βCo_5Ge_3 at 298 K reported in Refs. [23,24] were in good agreement with each other. Therefore, larger weight was assigned to them when the phase equilibria involving βCo_5Ge_3 were optimized.

All the above information of thermodynamics was included in the present optimization.

Table 2
Crystallographic data of the compounds in Co–Ge system reported.

Phase	Pearson symbol	Space group	Prototype	Ref.
α(Co)	*cF4*	*Fm$\bar{3}$m*	Cu	[16]
ε(Co)	*hP2*	*P6$_3$/mmc*	Mg	[16]
(Ge)	*cF8*	*Fd$\bar{3}$m*	C	[17]
Co_3Ge	*cP8*	*Pm$\bar{3}$n*	Cr_3Si	[10]
Co_5Ge_2	*hP*	–	–	[9]
Co_5Ge_7	*tI24*	*I4* mm	Co_5Ge_7	[17]
$CoGe_2$	*oC24*	*Aba2*	$PdSn_2$	[17]
CoGe	*mC16*	*C2/m*	CoGe	[17]
αCo_5Ge_3	*oP*	*Pbnm*	–	[9,11,18]
βCo_5Ge_3	*hP6*	*P6$_3$/mmc*	Ni_2In	[9,11,17]