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Thermodynamic assessment of Al–Cu–Dy system

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ABSTRACT

Phase equilibria of ternary Al–Cu–Dy system has been analyzed and a complete thermodynamic description was obtained. The thermodynamic descriptions of its three constituent binary systems were taken from literature. Most of the binary intermetallic phases, except Al_2Dy, Cu_2Dy, and CuDy, were treated to have zero solubility in ternary system. Based on experimental data, seven stable ternary intermetallic phases were taken into consideration in this system. Among them, three were treated as semistoichiometric compounds with large homogeneity ranges for Al and Cu. The rest were treated as stoichiometric compounds. The calculated phase equilibria were in agreement with available experimental data.

1. Introduction

Interest in aluminum alloys is increasing continuously, especially for their potential applications in automotive and aerospace industries. Microalloying has been used to improve the high temperature strength of selected age hardenable Al alloys (such as Al–Cu–Mg–Zn and Al–Cu–Mg–Ag alloys) throughout the years [1–3]. Rare earth elements in conventional aluminum alloys have shown beneficial effects to casting process [4–6]. Addition of these elements helps to reduce the content of gases and impurity and the arm spaces between secondary dendrites. Utilization of Dy as a microalloying element in Al alloys has been studied for years. Not only the rare earth element Dy can benefit the casting process, but also can improve the mechanical properties of Al alloys. It has been reported that the mechanical properties, such as the incubation time and the peak hardness of Al alloys did not change after partial replacement of expensive Sc by Dy [7]. Lantsman et al. [8] have reported that the introduced Dy into Al alloys could raise the recrystallization temperature, reduce grain size, and increase the microhardness of Al–Cu–Mn alloys.

Knowledge of the thermodynamics and phase diagram is vital in the field of materials research and process control, which is especially important for new alloy development. The aims of present work are then to evaluate the Al–Cu–Dy ternary system and develop a self-consistent thermodynamic description by means of calculation of phase diagram (CALPHAD) technique [9].

2. Experiment information

2.1. Binary phases

In addition to solution phases including Liquid, Fcc, Bcc and Hcp, there are 21 intermetallic phases existing in the three binary systems as shown in Figs. 1–3 [10–12]. Experimental data on the ternary solubility for most of the binary compounds are not available. The solubility of Al and Cu in the CuDy, Cu_2Dy and Al_2Dy phases will be discussed below.

2.2. Ternary phases

As summarized by Riani et al. [13], there are eight stable ternary intermetallic compounds being reported in literature. Their structures are listed in Table 1.

Among those, the compound Al_4Cu_8Dy (denoted as τ_1) was first reported by Felner and Nowik [14] and confirmed later by Kuz'ma and Milyan [15]. τ_1 takes $Mn_{12}Th$ type structure.

Prevarskiy and Kuz'ma found a compound with Th_2Zn_{17} type structure and of composition $Al_{10}Cu_7Dy_2$ in Al–Cu–Dy ternary system. However, Kuz'ma and Milyan [15] found this compound had a homogeneity range of Al from 35.2 to 52.6 at.% when determining the Al–Cu–Dy phase diagram. This compound was named as $(Al,Cu)_{17}Dy_2$ (τ_2).

Takeshita et al. [16] found a $CaCu_5$ type compound Al_4CuDy (τ_3). However, Kuz'ma and Milyan [15] determined that this phase

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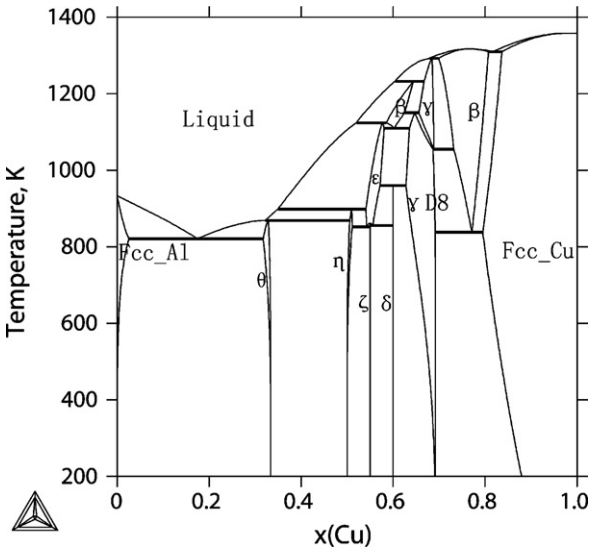

Fig. 1. The calculated Al–Cu phase diagram by Witusiewicz et al. [10].

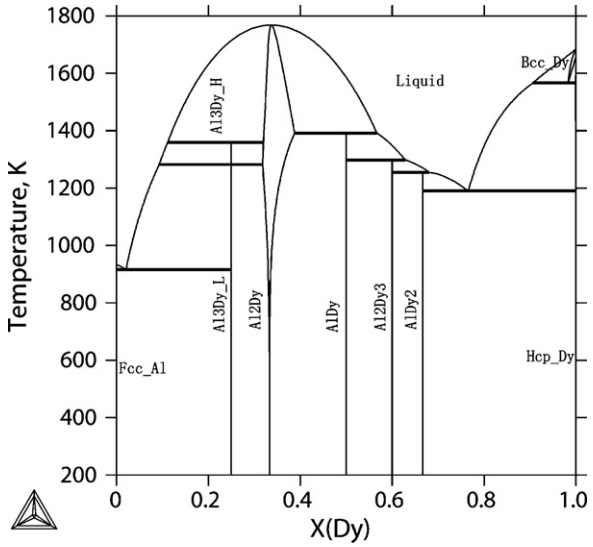

Fig. 2. The calculated Al–Dy phase diagram by Cacciamani et al. [11].

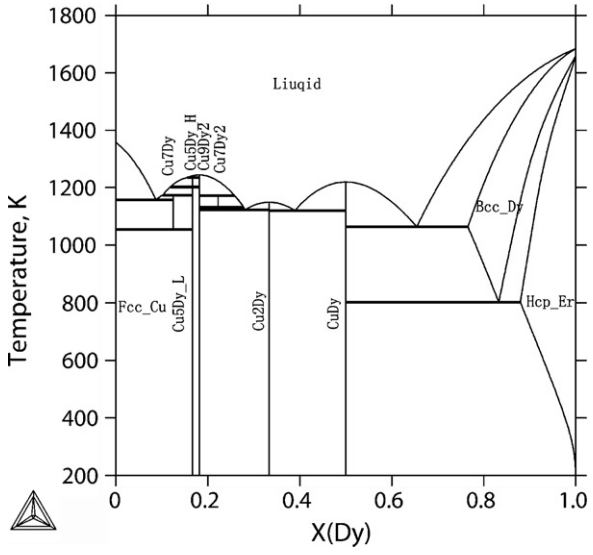

Fig. 3. The calculated Cu–Dy phase diagram by Zhang et al. [12].

Table 1
Crystallographic data of intermetallic phases.

Phase	Lattice parameters			Structure type, Pearson symbol, space group
	a (nm)	*b* (nm)	*c* (nm)	
θ	0.6067		0.4877	Al_2Cu, *tI*12, *I*4/*mcm*
η	1.2066	0.4105	0.6913	AlCu, *mC*20, *C*2/*m*
ζ	0.40972	0.71313	0.99793	$Al_9Cu_{11.5}$, *oI*24, *Imm*2
ε	0.4146		0.5063	In Ni_2,*hP*6,*P*63/*mmc*
γD83	0.87023			Al_4Cu_9, *cP*52, $P\bar{4}3m$
γ				Cu_5Zn_8, *cI*52, $I\bar{4}3m$
β	0.2946			W, *cI*2, $Im\bar{3}m$
Al_3Dy_L	0.6091		0.9533	Ni_3Ti, *hp*16, *P*63/*mmc*
Al_3Dy_H	0.6070		3.594	Al_3Ho, *hR*60, $R\bar{3}m$
Al_2Dy	0.778			Cu_2Mg, *cF*24, $Fd\bar{3}m$
AlDy	0.5570	0.5801	1.1272	AlEr, *oP*16, *Pmma*
Al_2Dy_3	0.817		0.754	Al_2Zr_3, *tP*20, *P*42/*mnm*
$AlDy_2$	0.654	0.508	0.940	Co_2Si, *oP*12, *Pnma*
Cu_7Dy	0.4932		0.4156	Cu_7Tb, *hp*8
Cu_5Dy_L	0.7025			$AuBe_5$, cF_{24}, $F\bar{4}3m$
Cu_5Dy_H	0.502		0.408	$CaCu_5$, *hP*6, *P*6/*mmm*
Cu_9Dy_2				
Cu_7Dy_2				
Cu_2Dy	0.430	0.680	0.729	$CeCu_2$, *oI*12, *Imma*
CuDy	0.357			ClCs, *cP*2, $Pm\bar{3}m$
τ_1-Al_8Cu_4Dy	0.8725		0.5137	$Mn_{12}Th$, *tI*26, *I*4/*mmm*
τ_2-$(Al,Cu)_{17}Dy_2$	0.8812		1.2844	Th_2Zn_{17}, hR_{57}, $R\bar{3}m$
τ_3-$(Al, Cu)_5Dy$	0.5064		0.4152	$CaCu_5$, *hP*6, *P*6/*mmm*
τ_4-Al_3CuDy	0.4184	0.4112	0.9773	Al_4Ba, oI_{10}, *Immm*
τ_5-$Al_{11}Cu_4Dy_4$				
τ_6-$(AlCu)_3Dy$	0.5457		2.5317	Ni_3Pu, *hR*36, $R\bar{3}m$
τ_7-AlCuDy	0.7015		0.4024	AlNiZr, *hP*9, *P*62*m*
$Al_7Cu_{16}Dy_6$				$Mn_{23}Th_6$, *cF*116, $Pm\bar{3}m$

contained a large homogeneity range of Al from 15 to 45 at.%. In this work, this phase was denoted as $(Al,Cu)_5Dy$ (τ_3), which had the same thermodynamic model of the binary phase Cu_5Dy_H due to the same structure.

Kuz'ma and Stel'makhovich [17] reported a compound $Al_{8.4}Cu_{2.6}Dy_3$ of $Al_{11}La_3$ type structure. However, Stel'makhovych et al. [18] determined this to be a Al_4Ba type structure compound Al_3CuDy (τ_4).

The $Al_{11}Cu_4Dy_4$ compound (τ_5) was reported by Kuz'ma and Milyan [15] without structure analysis.

Kuz'ma and Milyan [15] reported a compound $Al_9Cu_6Dy_5$ (τ_6) without structure, too. Later, Kuz'ma et al. [19] found this phase extended to $Al_{2.1}Cu_{0.9}Dy$ with Ni_3Pu type structure, this phase is treated as $(Al,Cu)_3Dy$ in our work.

The AlCuDy compound (τ_7) was discovered by Dwight et al. [20] and confirmed by Oesterreicher [21].

Kuz'ma and Stel'makhovich [22] reported another ternary compound close to the Al_4CuDy (τ_3) phase. But the stable composition range of this phase is not known to us and we decide not consider it here until there should be more information became available.

2.3. Phase equilibria in the solid state

Only one set of experimental data was available for Al–Cu–Dy ternary phase diagram at 773 K reported by Kuz'ma and Milyan [15]. Their isothermal section is shown in Fig. 4. Riani et al. [13] had assessed the experimental phase diagram. There were seven ternary compounds: τ_1–τ_7, as showed in Fig. 4. Among them, τ_1-Al_8Cu_4Dy, τ_4-Al_3CuDy, τ_5-$Al_{11}Cu_4Dy_4$ and τ_7-AlCuDy are stoichiometric compounds whereas Al and Cu can partial substitute in τ_2-$(Al,Cu)_{17}Dy_2$, τ_3-$(Al,Cu)_5Dy$ and τ_6-$(Al,Cu)_3Dy$ and we call these semi-stoichiometric phases. At 500 °C, Cu_2Dy could dissolve

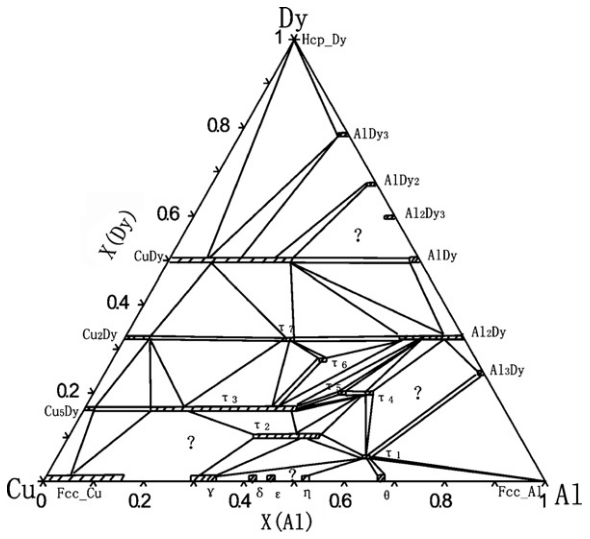

Fig. 4. The measured 773 K isothermal section of Al–Cu–Dy system [15].

up to 5 at.% Al, CuDy up to 25.5 at.% Al, and Al_2Dy up to 12 at.% Cu, respectively [15].

Sokolovskaya et al. [23] determined the Al-rich phase relation in Al–Cu–Dy system at the same temperature. They reported the tie lines of Al-τ_1, Al_3Dy-τ_1 and Al_3Dy-τ_5.

Up to now, there is no experimental or thermodynamic calculation of the Al–Cu–Dy system available in literature. Therefore, the Al–Cu–Dy system has been assessed on the basis of the abovementioned ternary phase diagram information.

3. Thermodynamic model

3.1. Solution phases

The lattice stabilities for element Al, Cu and Dy are referred to Dinsdale [24]. An ordinary substitutional solution model is employed to describe Liquid, Fcc and Hcp terminal solution. The mole Gibbs energy of a solution phase Φ (Φ = Liqiud, Fcc, Hcp) can be represented as a sum of the weighted Gibbs energy for the pure components with the ideal entropy term describing a random mixing of the components and the excess Gibbs energy describing the degree of deviation from ideal mixing, i.e.

$$G^{\phi} = \sum_{i=\mathrm{Al,Cu,Dy}} x_i^0 G_i^{\phi} + RT \sum_{i=\mathrm{Al,Cu,Dy}} x_i \ln(x_i) + {}^{ex}G^{\phi} \quad (1)$$

where

$$\begin{aligned} {}^{ex}G^{\phi} &= x_{\mathrm{Al}}x_{\mathrm{Cu}} \sum_{j=0,1\ldots}^{N} (x_{\mathrm{Al}}-x_{\mathrm{Cu}})^{j(j)}L^{\phi}_{\mathrm{Al,Cu}} + x_{\mathrm{Al}}x_{\mathrm{Dy}} \sum_{j=0,1\ldots}^{N} (x_{\mathrm{Al}}-x_{\mathrm{Dy}})^{j(j)}L^{\phi}_{\mathrm{Al,Dy}} \\ &\quad + x_{\mathrm{Cu}}x_{\mathrm{Dy}} \sum_{j=0,1\ldots}^{N} (x_{\mathrm{Cu}}-x_{\mathrm{Dy}})^{j(j)}L^{\phi}_{\mathrm{Cu,Dy}} + x_{\mathrm{Al}}x_{\mathrm{Cu}}x_{\mathrm{Dy}}L^{\phi}_{\mathrm{Al,Cu,Dy}} \end{aligned} \quad (2)$$

where ϕ denotes the solution phases, x_i(i = Al, Cu and Dy) denotes mole fraction of component i, and ${}^0G_i^{\phi}$ is the molar Gibbs energy of pure element i in the structural state of ϕ. ${}^{(j)}L^{\phi}_{\mathrm{Al,Cu}}$, ${}^{(j)}L^{\phi}_{\mathrm{Al,Dy}}$ and ${}^{(j)}L^{\phi}_{\mathrm{Cu,Dy}}$ are taken from Refs. [10–12], respectively.

$L^{\phi}_{\mathrm{Al,Cu,Dy}}$ is ternary interaction parameters in the structural state of ϕ. Due to the lack of experiment data, they are set to be zero.

3.2. Binary intermetallic phases

According to Kuz'ma and Milyan [15], the Al_2Dy, CuDy and Cu_2Dy phases have the homogeneity regions in Al–Cu–Dy ternary system. The Gibbs energy expression of CuDy and Cu_2Dy phases are formalized as

$$\begin{aligned} G^{(\mathrm{Al,Cu})_x\mathrm{Dy}_y} &= Y^I_{\mathrm{Al}}G_{\mathrm{Al:Dy}} + Y^I_{\mathrm{Cu}}G_{\mathrm{Cu:Dy}} + \frac{x}{x+y}RT(Y^I_{\mathrm{Al}} \ln Y^I_{\mathrm{Al}} + Y^I_{\mathrm{Cu}} \ln Y^I_{\mathrm{Cu}}) \\ &\quad + Y^I_{\mathrm{Al}}Y^I_{\mathrm{Cu}}L_{\mathrm{Al,Cu:Dy}} \end{aligned} \quad (3)$$

where x and y are the stoichiometry ratios. The superscript I denotes the first sublattice. Y^I_{Al} and Y^I_{Cu} stand for the site fractions of Al, Cu in the first sublattices, respectively. And the term $L_{\mathrm{Al,Cu:Dy}}$ represents the interaction between the Al and Cu in the first sublattice, expressed in Redlich–Kister polynomials. The parameter $G_{\mathrm{Cu:Dy}}$ is the Gibbs energy of formation of the compound Cu_xDy_y, which can be taken from binary system. And $G_{\mathrm{Al:Dy}}$ is expressed as

$$G_{\mathrm{Al:Dy}} = \frac{x}{x+y}{}^0G^{\mathrm{Fcc}}_{\mathrm{Al}} + \frac{y}{x+y}{}^0G^{\mathrm{Hcp}}_{\mathrm{Dy}} + A + BT \quad (4)$$

which represents the Gibbs energy of the assumed Al_xDy_y compound with Cu_xDy_y structure.

A and B are the adjusted parameters to be optimized in the present work.

The Gibbs energy expression of Al_2Dy phase is formalized as

$$\begin{aligned} &G^{(\mathrm{Al,Cu,Dy})_2(\mathrm{Al,Cu,Dy})_1} \\ &= \sum_i\sum_j Y^I_i Y^{II}_j G_{i:j} + 2RT(Y^I_{\mathrm{Al}} \ln Y^I_{\mathrm{Al}} + Y^I_{\mathrm{Cu}} \ln Y^I_{\mathrm{Cu}} + Y^I_{\mathrm{Dy}} \ln Y^I_{\mathrm{Dy}}) \\ &\quad + RT(Y^{II}_{\mathrm{Al}} \ln Y^{II}_{\mathrm{Al}} + Y^{II}_{\mathrm{Cu}} \ln Y^{II}_{\mathrm{Cu}} + Y^{II}_{\mathrm{Dy}} \ln Y^{II}_{\mathrm{Dy}}) \\ &\quad + \sum_i\sum_j\sum_k Y^I_i Y^I_j Y^{II}_k \sum_{v=0,1\ldots} {}^vL_{i,j:k}(Y^I_i - Y^I_j)^v \\ &\quad + \sum_i\sum_j\sum_k Y^I_k Y^I_i Y^{II}_j \sum_{v=0,1\ldots} {}^vL_{k:i,j}(Y^{II}_i - Y^{II}_j)^v \end{aligned} \quad (5)$$

where i, j, k denote Al, Cu, Dy, and $L_{i,j:k}$ stands for the interaction between the i and j in the first sublattice while the second sublattice is fully occupied by the element k. $G_{\mathrm{Al:Al}}$, $G_{\mathrm{Al:Dy}}$, $G_{\mathrm{Dy:Al}}$ and $G_{\mathrm{Dy:Dy}}$ are taken from corresponding binary systems. Other parameters are to be optimized in this work.

3.3. Ternary intermetallic compounds

In the ternary system, τ_1-Al_8Cu_4Dy, τ_4-Al_3CuDy, τ_5-$Al_{11}Cu_4Dy_4$ and τ_7-AlCuDy are modeled as stoichiometric phases ($Al_xCu_yDy_z$), i.e. Al, Cu, and Dy cannot substitute each other in any sublattice. τ_2-$(Al,Cu)_{17}Dy_2$, τ_3-$(Al, Cu)_5Dy$ and τ_6-$(Al, Cu)_3Dy$ are treated as semi-stoichiometric phases ($(Al,Cu)_xDy_y$), i.e. Al and Cu can partially substitute each other in the first sublattice, but Al and Cu cannot substitute Dy atoms in the second sublattice. The Gibbs energy expression for each one of these stoichiometric compounds is written as

$$\begin{aligned} G_{\mathrm{Al}_x\mathrm{Cu}_y\mathrm{Dy}_z} &= \frac{x}{x+y+z}{}^0G^{\mathrm{Fcc}}_{\mathrm{Al}} + \frac{y}{x+y+z}{}^0G^{\mathrm{Fcc}}_{\mathrm{Cu}} \\ &\quad + \frac{z}{x+y+z}{}^0G^{\mathrm{Hcp}}_{\mathrm{Dy}} + A + BT \end{aligned} \quad (8)$$

where x, y and z are the stoichiometry ratios of the sublattices. And for each one of the semi-stoichometric compounds, it becomes

$$\begin{aligned} G^{(\mathrm{Al,Cu})_x\mathrm{Dy}_y} &= Y^I_{\mathrm{Al}}G_{\mathrm{Al:Dy}} + Y^I_{\mathrm{Cu}}G_{\mathrm{Cu:Dy}} + \frac{x}{x+y}RT(Y^I_{\mathrm{Al}} \ln Y^I_{\mathrm{Al}} + Y^I_{\mathrm{Cu}} \ln Y^I_{\mathrm{Cu}}) \\ &\quad + Y^I_{\mathrm{Al}}Y^I_{\mathrm{Cu}}L_{\mathrm{Al,Cu:Dy}} \end{aligned} \quad (9)$$

Table 2
Thermodynamic parameters of Al–Cu–Dy system.

Phase	Thermodynamic parameters	Ref.
Al_2Dy Model: $(Al,Cu,Dy)_2(Al,Cu,Dy)_1$	$G^{Al_2Dy}_{Al:Al} = 15000 + 3GHSERAL$	[11]
	$G^{Al_2Dy}_{Dy:Dy} = 15000 + 3GHSERDY$	[11]
	$G^{Al_2Dy}_{Cu:Cu} = 15000 + 3GHSERCU$	This work
	$G^{Al_2Dy}_{Al:Dy} = -162000 + 40.24T + 2GHSERAL + GHSERDY$	[11]
	$G^{Al_2Dy}_{Dy:Al} = +192000 - 40.24T + GHSERAL + 2GHSERDY$	[11]
	$G^{Al_2Dy}_{Al:Cu} = +30000 + 2GHSERAL + GHSERCU$	This work
	$G^{Al_2Dy}_{Cu:Al} = +30000 + GHSERAL + 2GHSERCU$	This work
	$G^{Al_2Dy}_{Cu:Dy} = -66000 + 4.24T + 2GHSERCU + GHSERDY$	This work
	$G^{Al_2Dy}_{Dy:Cu} = +96000 - 4.24T + GHSERCU + 2GHSERDY$	This work
	${}^0L^{Al_2Dy}_{Al,Cu:Dy} = -55000$	This work
Cu_2Dy Model: $(Al,Cu)_{0.6667}(Dy)_{0.3333}$	$G^{Cu_2Dy}_{Al:Dy} = -26409.4524 + 3.9279T + 0.6667GHSERAL + 0.3333GHSERDY$	This work
	$G^{Cu_2Dy}_{Cu:Dy} = -24409.4524 + 0.9279T + 0.6667GHSERCU + 0.3333GHSERDY$	[12]
	${}^0L^{Cu_2Dy}_{Al,Cu:Dy} = -35009.4524$	This work
CuDy Model: $(Al,Cu)_{0.5}(Dy)_{0.5}$	$G^{CuDy}_{Al:Dy} = -27500 + 0.2T + 0.5GHSERAl + 0.5GHSERDY$	This work
	$G^{CuEr}_{Cu:Er} = -25910.8476 + 0.5347T + 0.5GHSERCU + 0.5GHSERDY$	[12]
	${}^0L^{CuDy}_{Al,Cu:Dy} = -31000$	This work
τ_1 Model: $(Al)_{0.615385}(Cu)_{0.307692}(Dy)_{0.076923}$	$G^{\tau1}_{Al:Cu:Er} = -34920 + 3.3T + 0.615385GHSERAl + 0.307692GHSERCU + 0.076923GHSERDY$	This work
τ_2 model: $(Al,Cu)_{0.894737}(Dy)_{0.105263}$	$G^{\tau2}_{Al:Dy} = -8850 + 1.7T + 0.894737GHSERAl + 0.105263GHSERDY$	This work
	$G^{\tau2}_{Cu:Dy} = +3350 - 1.9T + 0.894737GHSERCU + 0.105263GHSERDY$	This work
	${}^0L^{\tau2}_{Al,Cu:Dy} = -110100 + 2T$	This work
Cu_5Dy_H (τ_3) Model: $(Al,Cu)_{0.8333}(Dy)_{0.1667}$	$G^{Cu_5Dy\_H}_{Al:Dy} = -20000.3656 + 3T + 0.8333GHSERAL + 0.1667GHSERDY$	This work
	$G^{Cu_5Dy\_H}_{Cu:Dy} = -16506.3656 + 0.13T + 0.8333GHSERCU + 0.1667GHSERDY$	[12]
	${}^0L^{Cu_5Dy\_H}_{Al,Cu:Dy} = -70990.5756$	This work
	${}^1L^{Cu_5Dy\_H}_{Al,Cu:Dy} = -10000$	This work
τ_4 Model: $(Al)_{0.6}(Cu)_{0.2}(Dy)_{0.2}$	$G^{\tau4}_{Al:Cu:Dy} = -42500 + 1T + 0.6GHSERAl + 0.2GHSERCU + 0.2GHSERER$	This work
τ_5 Model: $(Al)_{0.578948}(Cu)_{0.210526}(Dy)_{0.210526}$	$G^{\tau5}_{Al:Cu:Dy} = -43050 + 1.01T + 0.578948GHSERAl + 0.210526GHSERCU + 0.210526GHSERDY$	This work
τ_6 Model: $(Al,Cu)_{0.75}(Dy)_{0.25}$	$G^{\tau6}_{Cu:Dy} = -25850 + 1.7T + 0.75GHSERAl + 0.25GHSERDY$	This work
	$G^{\tau6}_{Cu:Dy} = -11350 + 1.9T + 0.75GHSERCu + 0.25GHSERDY$	This work
	${}^0L^{\tau6}_{Al,Cu:Dy} = -75100 + 2T$	This work
	${}^1L^{\tau6}_{Al,Cu:Dy} = -50100 + 2T$	This work
τ_7 Model: $(Al)_{0.333333}(Cu)_{0.333333}(Dy)_{0.333334}$	$G^{\tau7}_{Al:Cu:Er} = -41150 + 0.05T + 0.333333GHSERAl + 0.333333GHSERCU + 0.333334GHSERDY$	This work

where

$$G_{Al:Dy} = \frac{x}{x+y}{}^0G^{Fcc}_{Al} + \frac{y}{x+y}{}^0G^{Hcp}_{Dy} + A + BT \quad (10)$$

$$G_{Cu:Dy} = \frac{x}{x+y}{}^0G^{Fcc}_{Cu} + \frac{y}{x+y}{}^0G^{Hcp}_{Dy} + A + BT \quad (11)$$

where the $L_{Al,Cu:Dy}$ represents the interaction between Al and Cu in the first sublattice, expressed in Redlich–Kister polynomials. A and B are the adjusted parameters to be optimized in the present work.

4. Results and discussion

On the basis of lattice stabilities cited from Dinsdale [24], the optimization of the Al–Cu–Dy system is carried out using the Parrot modules in the Thermo_Calc program developed by Sundman et al. [25]. Since we do not have thermochemical and liquid projection information in ternary, the ternary interaction parameters of liquid are then considered as zero. Based on the phase relations by Kuz'ma and Milyan [15], seven ternary compounds are assessed. Because there are seven ternary compounds, their relative stability across the entire temperature range is somewhat difficult to control. Care is taken to ensure that all ternary compounds are stable to room temperature. All the evaluated parameters are listed in Table 2. Also, we have close checked the database with Pandat software [26], and found that the calculation by Pandat software is in good agreement with the result by Thermo_Calc.

The calculated 773 K isothermal section for Al–Cu–Dy system is shown in Fig. 5. Comparing our calculated results with the experimental data, it can be found that the intermetallic phases in the calculated three boundary binary systems are not the same as those shown in the diagrams by Kuz'ma and Milyan [15]. According to the calculated Al–Cu binary phase diagram, as shown in Fig. 1, the ε phase is not stable at 773K, while it is stable in the isothermal section reported by Kuz'ma and Milyan [15]. Therefore, this phase is omitted in our assessment. Similarly, the $AlDy_3$ phase suggested by Kuz'ma and Milyan [15] is not a stable phase in the calculated binary Al–Dy phase diagram [11], too. As a result, this phase is also omitted in our calculation. Moreover, the Cu_9Dy_2 phase which is not observed in the work of Kuz'ma and Milyan [15] is a stable

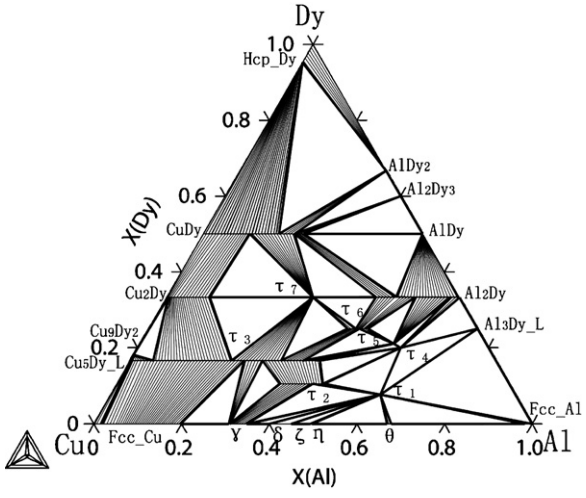

Fig. 5. The calculated 773 K isotherm section of Al–Cu–Dy system.

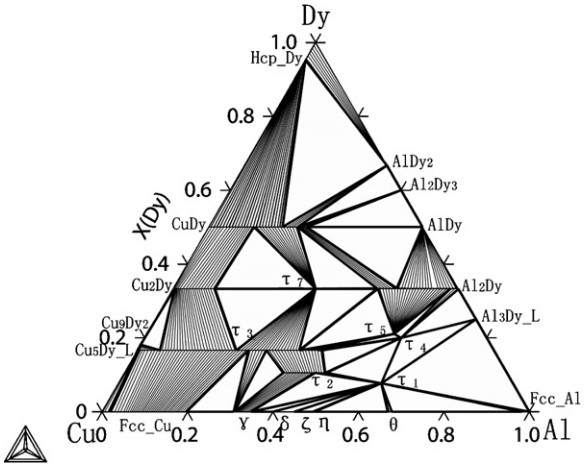

Fig. 6. The calculated 773 K meta-stable isotherm section of Al–Cu–Dy system.

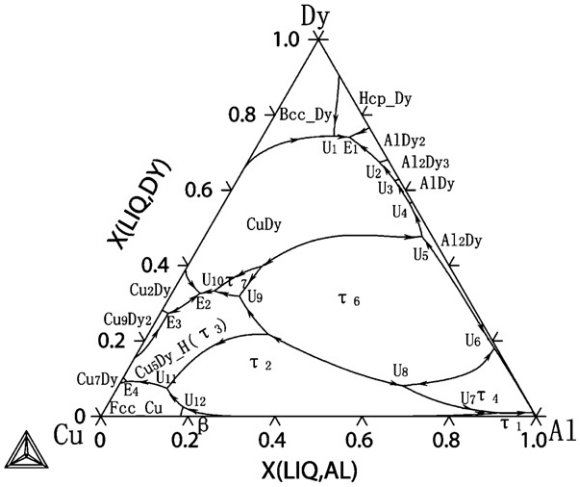

Fig. 9. The calculated liquidus projection of Al–Cu–Dy system.

phase in Cu–Dy system [12]. So in our assessment, this phase is calculated.

In Ref. [15], the τ_3-$(Al,Cu)_5Dy$ phase was reported to contain about 15–45 at.% Al at 773 K, but our calculated result showed the composition range of Al is 1–44 at.%. Actually, in our assessment, we found it was very difficult to fit the result of Kuz'ma and Milyan [15]. Moreover, comparing with the other isothermal sections of Al–Cu–Gd, Al–Cu–Tb and Al–Cu–Yb systems [27–29] at 773 K, we found the homogeneity range of all the τ_3-$(Al,Cu)_5RE$ (RE = Gd,Tb,Yb) phase are more close to our calculation result and therefore we think our calculation is reasonable. Further experimental verification is still needed.

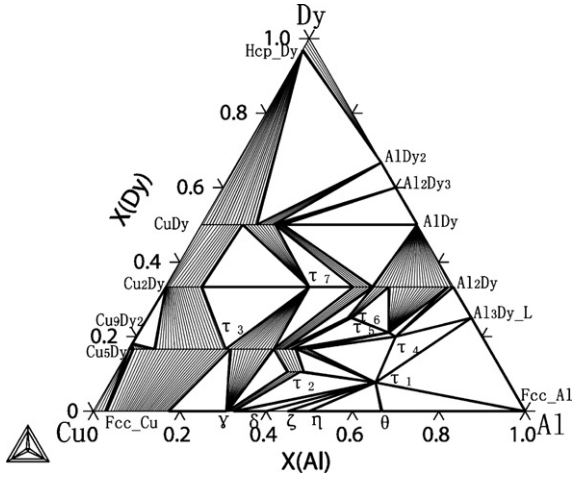

Fig. 7. The calculated 573 K isotherm section of Al–Cu–Dy system.

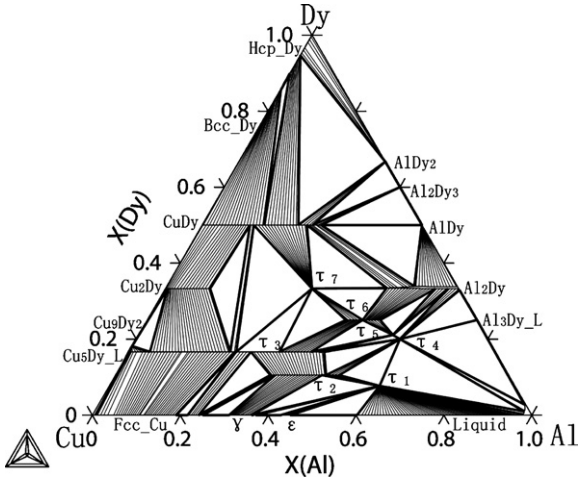

Fig. 8. The calculated 973 K isotherm section of Al–Cu–Dy system.

In the work of Kuz'ma and Milyan [15], there existed a two-phase region ($Al_2Dy + \tau_3$), as shown in Fig. 4. But in our calculation (Fig. 5), the τ_6 phase separates this two-phase region to be two two-phase regions ($Al_2Dy + \tau_6$ and $\tau_6 + \tau_3$). That's because the τ_6 phase was suggested to be a stoichiometric compound ($Al_9Cu_6Dy_5$) by Kuz'ma and Milyan [15] at 773 K. While a homogeneity range (about 45–52.5 at.% Al) was reported later by Kuz'ma et al. [19]. In order to simulate this homogeneity range, a semi-stoichiometric phase (τ_6-$(Al,Cu)_3Dy$) model is used in this work. And the calculated homogeneity range is 45.2–51.5 at.% Al which is good agreement with the experimental data [19], If a stable two-phase region ($Al_2Dy + \tau_3$) existed, the homogeneity range could not be

Table 3
Calculated invariant reactions and temperatures of Al–Cu–Dy ternary system.

Type	Reaction	T/K
E_1	Liquid ⇔ CuDy + Al_2Dy + Hcp_Dy	1145.97
E_2	Liquid ⇔ CuDy + Cu_2Dy + Cu_5Dy_H	1105.38
E_3	Liquid ⇔ Cu_2Dy + Cu_9Dy_2 + Cu_5Dy_H	1108.96
E_4	Liquid ⇔ Cu_5Dy_H + Fcc_Cu + Cu_7Dy	1153.16
E_5	Liquid ⇔ Fcc_Al + τ_4 + Al_3Dy_L	915.53
U_1	Liquid + Bcc_Dy ⇔ CuDy + Hcp_Dy	1202.52
U_2	Liquid + Al_2Dy_3 ⇔ Al_2Dy + CuDy	1236.42
U_3	Liquid + AlDy ⇔ Al_2Dy_3 + CuDy	1288.07
U_4	Liquid + Al_2Dy ⇔ CuDy + AlDy	1382.39
U_5	Liquid + τ_6 ⇔ Al_2Dy + CuDy	1611.20
U_6	Liquid + τ_6 ⇔ τ_4 + Al_2Dy	1366.41
U_7	Liquid + τ_2 ⇔ τ_4 + τ_1	1399.27
U_8	Liquid + τ_6 ⇔ τ_4 + τ_2	2158.72
U_9	Liquid + τ_6 ⇔ τ_7 + Cu_5Dy_H	1494.74
U_{10}	Liquid + τ_7 ⇔ Cu_5Dy_H + CuDy	1191.62
U_{11}	Liquid + τ_2 ⇔ Cu_5Dy_H + Fcc_Cu	1185.08
U_{12}	Liquid + β ⇔ τ_2 + Fcc_Cu	1270.07
U_{13}	Liquid + Al_2Dy ⇔ Al_3Dy_H + τ_4	1348.72
U_{14}	Liquid + Al_3Dy_H ⇔ τ_4 + Al_3Dy_L	1281.23
U_{15}	Liquid + τ_1 ⇔ τ_4 + Fcc_Al	924.35
U_{16}	Liquid + Cu_5Dy_L ⇔ Cu_7Dy + Cu_5Dy_H	1173.31
U_{17}	Liquid + τ_2 ⇔ τ_1 + β	1183.89
U_{18}	Liquid + γ ⇔ β + τ_2	1232.11
U_{19}	Liquid + β ⇔ γ + τ_2	1291.38
P_1	Liquid + τ_6 + τ_2 ⇔ Cu_5Dy_H	2025.69
P_2	Liquid + τ_6 + CuDy ⇔ τ_7	1614.38
P_3	Liquid + β + τ_1 ⇔ ε	1124.24

well reproduced. Furthermore, the meta-stable isothermal section at 773 K is also calculated in this work; it is found that without the τ_6 phase, a two-phase region ($Al_2Dy + \tau_3$) existed in this temperature, as shown in Fig. 6. This calculated meta-stable isothermal section is in agreement with the result by Kuz'ma and Milyan [15]. Except from the differences mentioned above, our calculated results are in agreement with the experimental data.

Moreover, we have calculated the isothermal sections at 573 and 973 K and the results are showed in Figs. 7 and 8, respectively. The liquidus projection is calculated and showed in Fig. 9. Note here the invariant equilibria involving the Al–Cu binary phases are not visible in Fig. 9 because they are very close to the Al–Cu binary subsystem. The calculated invariant reactions and temperatures involved liquid in the Al–Cu–Dy ternary system are summarized in Table 3. Further experimental data are needed to verify the liquidus projection.

5. Conclusions

The Al–Cu–Dy ternary system has been assessed thermodynamically based on reported experimental data of phase diagrams and thermodynamic properties. Reasonable agreement between calculation and experimental data has been reached and thermodynamic parameters for various phases in this ternary system have been obtained.

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