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Experimental investigation and thermodynamic prediction of the Al–Ge–Zn phase diagram

Ljubiša Balanović · Dragan Manasijević · Dragana Živković · Aleksandra Mitovski · Nadežda Talijan · Duško Minić · Živan Živković

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Abstract The knowledge of the phase diagram of the Al–Ge–Zn ternary system is of importance in the development of high temperature soldering materials. In this study, the phase diagram of the Al–Ge–Zn ternary system was calculated by the calculation of phase diagrams method using binary thermodynamic parameters included in the COST MP0602 thermodynamic database. Chosen alloys with compositions along two vertical sections with molar ratio Al/Ge = 3/1 and 1/3 were measured using DTA (differential thermal analysis). The experimentally determined phase transition temperatures from this work and phase equilibria data from literature were compared with calculation results and good mutual agreement was noticed.

Keywords Al–Ge–Zn ternary system · Phase diagram · Thermal analysis · Thermodynamic prediction

Introduction

Zn–Al based alloys are promising materials for the development of high temperature solders. The main applications for high-temperature (Tm $\geq$ 230 °C) solders within the electronics industry are for advanced packing technologies, e.g. die-attach and ball grid array (BGA) solder spheres, chip scale package (CSP) and multi-chip modelling (MCM).

Knowledge about the phase diagram and the thermodynamic properties of the studied soldering system is required to predict the thermal behaviour, the microstructure evolution of the solder itself and the possible interfacial between solder and substrate.

In this article, the phase equilibria in the Al–Ge–Zn ternary system were predicted using calculation of phase diagrams (CALPHAD) approach and the phase transition temperatures of the Al–Ge–Zn ternary system were measured using DTA. Experimental results from this study and literature were compared with the predicted phase diagram of the Al–Ge–Zn ternary system.

Experimental

The samples were prepared by induction melting of pure metals (purity higher than 99.99%) under an argon atmosphere. The alloys were melted and cooled repeatedly to improve homogeneity. The total mass losses of the prepared ingots were less than 1 mass%.

The DTA measurements were carried out with the Derivatograph (MOM Budapest) apparatus under following conditions: argon atmosphere, sample masses about 50 mg, heating rate 5 °C/min and alumina as the reference material.

The temperatures of invariant transitions were taken from the extrapolated onset on heating. The other phase transition temperatures were taken from the peak temperature.

L. Balanović (✉) · D. Manasijević · D. Živković · A. Mitovski · Ž. Živković
University of Belgrade, Technical Faculty, VJ 12, 19210 Bor, Serbia
e-mail: ljbalanovic@tf.bor.ac.rs

N. Talijan
Institute for Chemistry, Technology and Metallurgy, 11000 Belgrade, Serbia

D. Minić
University of Pristina, Faculty of Technical Sciences, 38220 Kosovska Mitrovica, Serbia

Thermodynamic models and crystallographic data

Phase diagram of the Al–Ge–Zn ternary system was calculated by the CALPHAD method [1, 2], using only optimized thermodynamic parameters for constitutive binary systems. The basic mathematical method used for the calculation of phase equilibria is a constrained minimization of Gibbs energy for a given temperature, pressure and overall composition. This approach is common for all currently available software packages for the modelling of thermodynamic properties and phase diagrams of multicomponent systems.

The pure solid elements in their stable form at 298.15 K and under the pressure of 1 bar were chosen as the reference state for the systems (SER). The Version 4.4 of the Scientific Group Thermo data Europe (SGTE) Unary database of phase stabilities for stable and metastable states of pure elements [3] was used.

Thermodynamic data for the Al–Ge system were taken from Ref. [4], for the Al–Zn system were published in Ref. [5], and thermodynamic data for the system Ge–Zn were taken from Ref. [6]. All this data are included in the COST MP0602 database for high temperature solders [7].

The phases from constitutive binary subsystems considered for thermodynamic binary-based prediction with their crystal structures are listed in Table 1.

Optimized thermodynamic parameters used for calculation are shown in Table 2.

Literature review

The phase diagrams of the constitutive binary systems are well known. The assessed phase diagram of the Al–Ge system [4], shown in Fig. 1a, is a simple eutectic comprising the liquid, the fcc (Al) solid solution (FCC_A1) and the diamond cubic (Ge) solid solution (DIAMOND_A4). The calculated eutectic occurs at 423 °C and 28.4 at.% Ge. The calculated maximum solubility is 2.4 at.% Ge in FCC_A1. The solubility of Al in DIAMOND_A4 is negligible. The assessed Al–Zn phase diagram [5] is shown in Fig. 1b. It contains no intermediate phases. A miscibility gap occurs in the fcc (A1) solid solution (FCC_A1) below 351 °C, where the fcc phase splits into FCC_A1′ and FCC_A1″. The monotectoid reaction FCC_A1″ ↔ FCC_A1′ + HCP_Zn follows at 277 °C. The assessed equilibrium phase diagram of the Ge–Zn system [6] is shown in Fig. 1c. It shows a eutectic transformation at 392 °C and 94.9 at.% Zn. The mutual solid solubilities of Ge and Zn are negligible.

There are few researches done in order to study Al–Ge–Zn system phase equilibria [8–13]. Tyapkin et al. [8] investigated metastable phase with a regular structure in the alloys 40Al–59Zn–1Ge and 20Al–70Zn–1Ge. Tadjbakhche [9] experimentally investigated Al–Ge–Zn system using thermal and microstructural analysis, while Storokin et al. [10] determined the liquidus projection of the mentioned system. Further, Chattopadhyay et al. [11] evaluated Al–Ge–Zn system and some isothermal sections at several temperatures above the ternary eutectic. The most complete work on thermodynamic calculation of phase equilibria in the Al–Ge–Zn system is given by Srikanth et al. [13], calculated at 600, 500 and 385 °C according to quasi/regular solution and shortest distance path equations.

The newest results on Al–Ge–Zn phase equilibria, including experimental thermal and microstructural investigations, calculation according to CALPHAD method, and

Table 1 Phases with their crystal structures

Phase name	Common name	Space group	Pearson symbol
LIQUID	Liquid		
FCC_A1	(Al)	*Fm3 m*	*cF4*
DIAMOND_A4	(Ge)	*Fd3 m*	*cF8*
HCP_ZN	(Zn)	$P6_3/mmc$	*hP2*

Table 2 Optimized thermodynamic parameters for constitutive binaries used in this study

Phase and thermodynamic model	Thermodynamic parameter	References
LIQUID (Al, Ge, Zn)	${}^0L^{\mathrm{LIQUID}}_{\mathrm{Al,Ge}} = -13000 - 3.954T$	[4]
	${}^1L^{\mathrm{LIQUID}}_{\mathrm{Al,Ge}} = -418 + 0.0335T$	[4]
	${}^2L^{\mathrm{LIQUID}}_{\mathrm{Al,Ge}} = 4552 - 2.335T$	[4]
	${}^0L^{\mathrm{LIQUID}}_{\mathrm{Al,Zn}} = 10465.55 - 3.39259T$	[5]
	${}^0L^{\mathrm{LIQUID}}_{\mathrm{Ge,Zn}} = 4940.9 - 6.50965T$	[6]
	${}^1L^{\mathrm{LIQUID}}_{\mathrm{Ge,Zn}} = 1119$	[6]
FCC_A1 (Al, Ge, Zn)$_1$(Va)$_1$	${}^0L^{\mathrm{FCC\_A1}}_{\mathrm{Al,Ge}} = 600$	[4]
	${}^0L^{\mathrm{FCC\_A1}}_{\mathrm{Al,Zn:Va}} = 7297.48 + 0.47512T$	[5]
	${}^1L^{\mathrm{FCC\_A1}}_{\mathrm{Al,Zn:Va}} = 6612.88 - 4.5911T$	[5]
	${}^2L^{\mathrm{FCC\_A1}}_{\mathrm{Al,Zn:Va}} = -3097.19 + 3.30635T$	[5]
DIAMOND_A4 (Al, Ge, Zn)	${}^0L^{\mathrm{DIAMOND\_A4}}_{\mathrm{Al,Ge}} = 80T$	[4]
	${}^0L^{\mathrm{DIAMOND\_A4}}_{\mathrm{Al,Zn}} = 80T$	[5]
	${}^0L^{\mathrm{DIAMOND\_A4}}_{\mathrm{Ge,Zn}} = 80T$	[6]
HCP_ZN (Al, Zn)$_1$(Va)$_1$	${}^0L^{\mathrm{HCP\_ZN}}_{\mathrm{Al,Zn:Va}} = 18820.95 - 8.95255T$	[5]
	${}^1L^{\mathrm{HCP\_ZN}}_{\mathrm{Al,Zn:Va}} = 0$	[5]
	${}^2L^{\mathrm{HCP\_ZN}}_{\mathrm{Al,Zn:Va}} = 0$	[5]
	${}^3L^{\mathrm{HCP\_ZN}}_{\mathrm{Al,Zn:Va}} = -702.79$	[5]

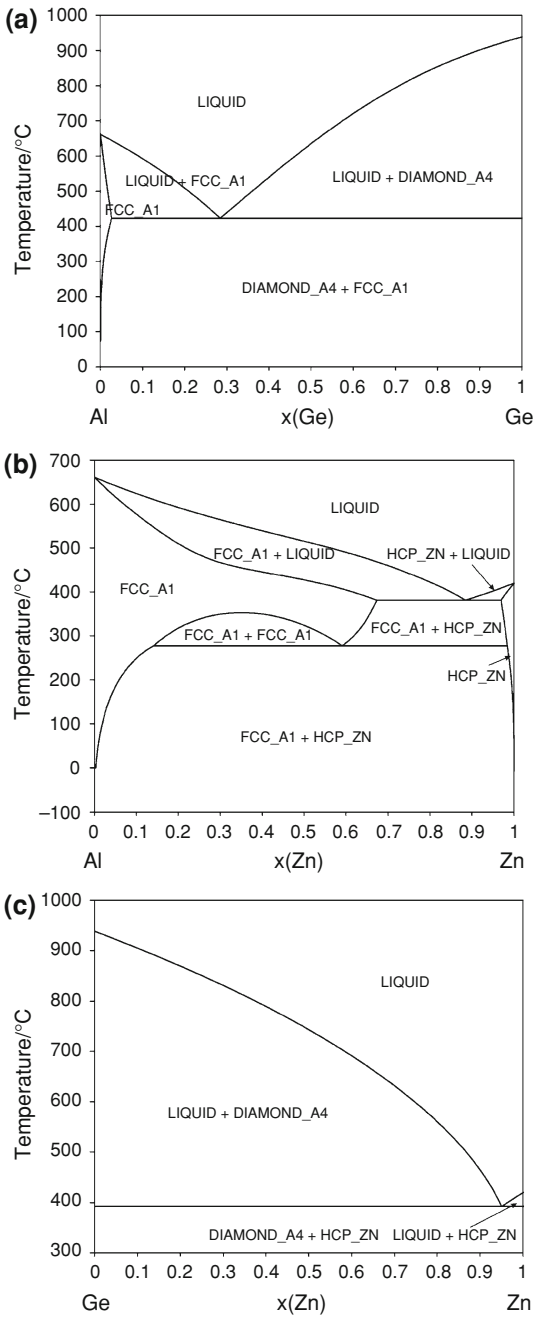

Fig. 1 Calculated phase diagrams of constitutive binary systems **a** Al–Ge **b** Al–Zn **c** Ge–Zn

thermodynamic predicting using GSM (general solution model), were done in the frame of project COST MP0602—HISOLD [14, 15].

Results and discussion

Based on thermodynamic parameter values given in Table 2, the liquidus projection of the Al–Ge–Zn ternary system is calculated and plotted in Fig. 2. One invariant reaction involving liquid phase: ternary eutectic and three primary crystallization areas (FCC_A1 (Al-based solid solution), DIAMOND_A4 (Ge-based solid solution), HCP_ZN (Zn-based solid solution)) are predicted in this ternary system.

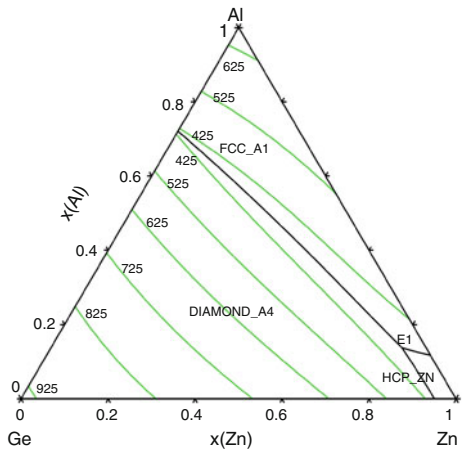

Fig. 2 The predicted liquidus projection of the Al–Ge–Zn ternary system

The predicted temperature of ternary eutectic reaction and the compositions of the corresponding phases are listed in Table 3.

To study the agreement between experimental and predicted phase transition temperatures samples with chosen compositions along two vertical sections with molar ratio Al/Ge = 3/1 and 1/3 were investigated using DTA. The thermal analysis was performed on curves obtained during the heating of the samples. Examples of DTA heating curves for samples along two investigated vertical section are given in Fig. 3. Every heating run was performed two times to test the reproducibility of results. The thermal analysis results are shown in Table 4. The temperatures reported in Table 4 represent the average values of the thermal effects detected during first and second heating. The total experimental error of the method has been estimated to be ± 2 °C.

Calculated vertical sections with determined phase transition temperatures from the present DTA measurements are

Table 3 Predicted invariant reaction in the Al–Ge–Zn ternary system

T/°C	Type	Phase	Composition	
Reaction			xAl	xGe
356.8	E_1	LIQUID	0.132	0.056
LIQUID ↔ FCC_A1+		FCC_A1	0.320	0.018
DIAMOND_A4+		DIAMOND_A4	0	1
HCP_ZN		HCP_ZN	0.025	0

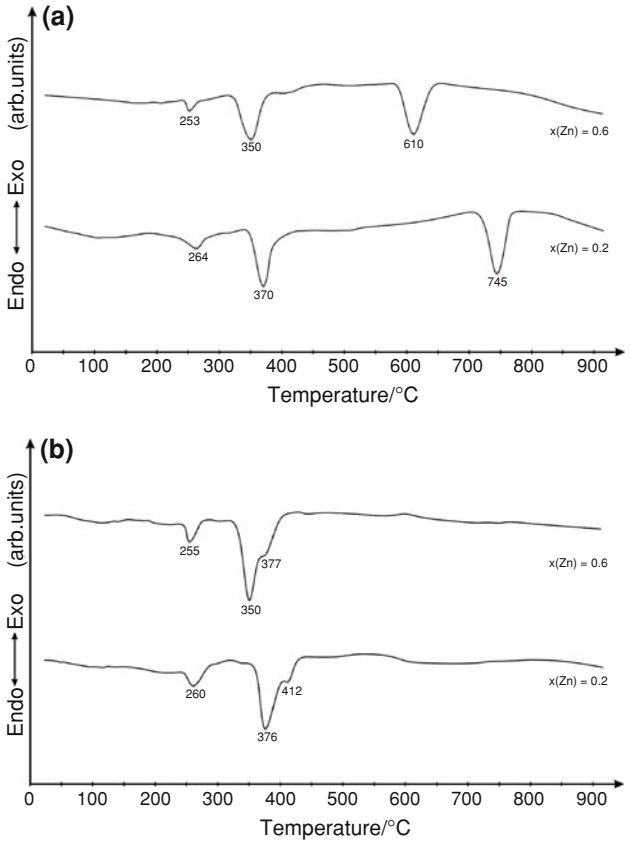

Fig. 3 DTA heating curves for some investigated samples from **a** Al/Ge = 1/3 section **b** Al/Ge = 3/1 section

Table 4 DTA results for the investigated alloys of the Al–Ge–Zn ternary system

Sample composition/at.%	Thermal effect/°C	
	Liquidus temperature	Other peak temperature
Al:Ge = 1:3		
0.2	745	264, 370
0.4	654	262, 340
0.6	610	253, 350
0.8	487	349
Al:Ge = 1:3		
0.2	412	260, 376
0.4	380	263
0.6	377	255, 350
0.8	–	260, 351

plotted in Fig. 4 a and b for mutual comparison. Liquidus temperatures obtained by DTA are in good agreement with the corresponding calculated values. Experimentally measured temperature of ternary eutectic reaction (350 °C) is somewhat lower than predicted value (356.8 °C). According

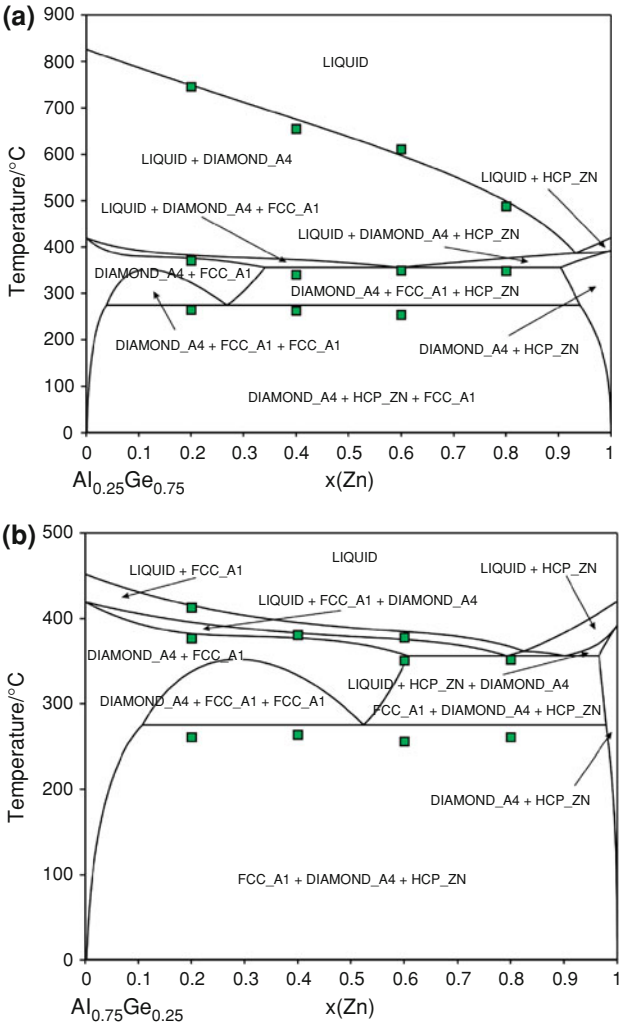

Fig. 4 Calculated vertical sections of the Al–Ge–Zn ternary system compared with DTA results (*triangle*) from the present study **a** Al/Ge = 1/3 **b** Al/Ge = 3/1

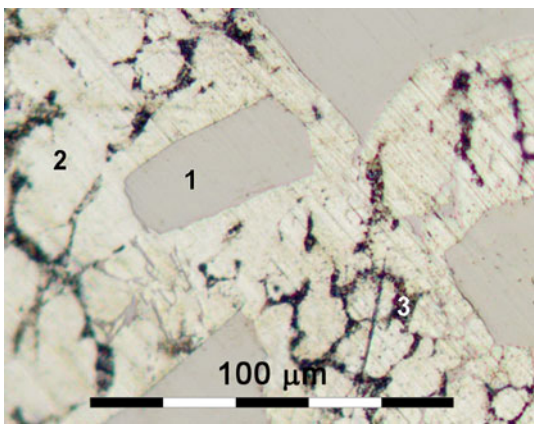

Fig. 5 Optical microphotograph of the sample with 80 at.%Zn in investigated section with molar ratio Al/Ge = 1/3

to thermodynamic prediction there is invariant reaction in solid state at 273 °C of the eutectoid (E-type) reaction:

$$\text{FCC\_Al} \leftrightarrow \text{HCP\_ZN} + \text{FCC\_Al}$$

DTA results also indicate the existence of thermal effect close to the calculated temperature of eutectoid reaction but the measured temperatures are dispersed and considerably lower in comparison with calculation.

After DTA measurements, samples microstructures were investigated using light optical microscopy (LOM). Fig. 5. represents microstructure of sample from Al/Ge = 1/3 section with 80at%Zn. As can be seen from Fig. 5 three phases were detected in the microstructure of investigated sample: 1—gray phase, responding to germanium-based solid solution (DIAMOND_A4); 2—light phase, responding to zinc-based solid solution (HCP_ZN); and 3—dark phase, responding to aluminium-based solid solution (FCC_A1). Such obtained microscopic results are in agreement with calculated phase diagram.

The calculated isothermal sections of the Al–Ge–Zn ternary system at 600, 500 and 385 °C are shown in Fig. 6a, b and c together with corresponding assessed isotheral sections reported by Chattopadhyay et al. [11] for comparison.

Experimentally based isothermal sections and those predicted by the CALPHAD method show mutual agreement with following exceptions:

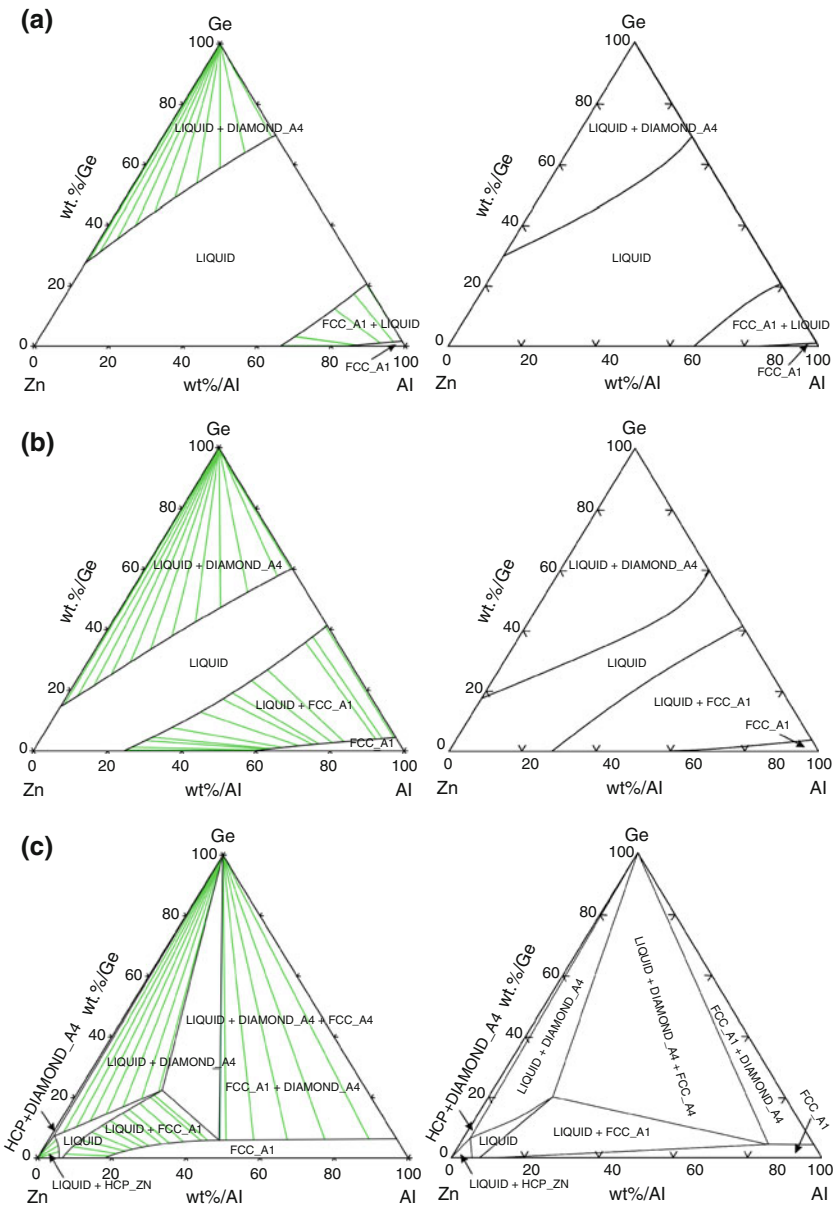

Fig. 6 Comparison between predicted and experimentally based isotheral section of the Al–Ge–Zn ternary system at **a** 600 °C **b** 500 °C **c** 385 °C

– Predicted isothermal sections at 600 and 500 °C show somewhat larger composition ranges of stability of the liquid phase then corresponding assessed diagrams.
– Predicted isothermal section at 385 °C exhibits considerably smaller stability field of (Liquid + DIAMOND_A4 + FCC_A1) three-phase equilibrium.

Conclusions

The phase diagram of the Al–Ge–Zn ternary system was calculated using only binary thermodynamic parameters included in the COST MP0602 thermodynamic database. Predicted phase transition temperatures are in reasonable agreement with the experimental results from this work. Ternary eutectic reaction at 350 °C was determined by DTA measurements. This temperature is somewhat lower than thermodynamically predicted temperature of ternary eutectic reaction (356.8 °C). Also, predicted isothermal sections at 600 and 500 °C are in general agreement with related assessed isotheral sections from the literature [11]. Predicted isothermal section at 385 °C shows partial agreement with the assessed isotheral section due to observed difference in the composition range of stability of three-phase field (Liquid + DIAMOND_A4 + FCC_A1).

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