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Thermodynamic description and unidirectional solidification of eutectic organic alloys: IV. Binary systems neopentylglycol–succinonitrile and amino-methyl-propanediol–succinonitrile

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Abstract

The temperature and enthalpy of transformations of organic alloys from the binary systems neopentylglycol–succinonitrile (NPG–SCN) and 2-amino-2-methyl-1,3-propanediol–succinonitrile (AMPD–SCN) were measured by means of differential scanning calorimetry (DSC). The phase diagrams of these binary systems were assessed via the CALPHAD approach using Thermo-Calc by simultaneously optimizing the thermodynamic and phase equilibrium data measured in the present work. Proper agreements between the experimental and calculated data for the phase diagrams as well as for the thermochemical properties were achieved. Experiments and calculations show that both the NPG–SCN and the AMPD–SCN systems exhibit a non-variant eutectic reaction with the eutectic point at 90.45 mol% SCN (318.0 K) and at 97.39 mol% SCN (325.7 K), respectively. In the NPG–SCN system the temperature of the eutectic reaction is about 3 K higher than the temperature of the transformation from the ordered crystals (OCs) to the orientationally disordered crystals (ODICs), whereas the eutectic reaction in the AMPD–SCN involves the OCs of AMPD and the ODICs of SCN.

Unidirectional solidification experiments were performed with selected NPG–SCN and AMPD–SCN alloys in order to verify phases involved in solid–liquid equilibria and the nature of eutectic growth in these systems. We find that eutectic growth in NPG–SCN eutectic alloy occurs with both solid phases being non-facetted and with a rod-like eutectic structure. The eutectic as well as some hypo-eutectic alloys from the AMPD–SCN system show irregular eutectic growth with a non-facetted BCC_A2 phase of SCN and a facetted monoclinic phase of AMPD.

Keywords: Neopentylglycol–succinonitrile; Amino-methyl-propanediol–succinonitrile; Binary system; Thermodynamic description; Bridgman solidification; Eutectic growth

1. Introduction

In the previous parts of our work addressing the thermodynamic description of binary organic alloy systems we published experimental measurements, the CALPHAD description of the phase equilibria and unidirectional solidification experiments of the eutectic alloys in the binary systems succinonitrile (SCN) [1]–(D)camphor (DC) [2] [1], neopentylglycol (NPG) [3]–amino-methyl-propanediol (AMPD) [4] [2], NPG–DC [3] and

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[1] Butanedinitrile, CAS No. [110-61-2].
[2] (1*R*)-1,7,7-Trimethylbicyclo[2,2,1]heptan-2-one, CAS No. [464-49-3].
[3] 2,2-Dimethyl-1,3-propanediol, CAS No. [126-30-7].
[4] 2-Amino-2-methyl-1,3-propanediol, CAS No. [115-69-5].

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Table 1
DSC data on temperature and enthalpy of transformations of NPG–SCN alloys

SCN (mole fraction)	Transformation temperatures (K)			Enthalpy of transformation (J mol^{-1})			
	OCs/ODICs	Solidus	Liquidus	OCs/ODICs	Melting	Eutectic	Primary phase
0.000	314.5 [8]	–	403.3 [7]	12,520 [7]	4440 [7]	–	4440 [7]
0.000	315.0 [2]	–	403.2 [2]	12,061 [2]	4431 [2]	–	4431 [2]
0.039	315.9	317.3	399.8	12,106	4287	136	4151
0.146	316.1	320.3	381.5	10,811	4613	801	3811
0.254	315.8	317.9	368.8	9559	4829	1397	3432
0.294	314.1	316.6	364.9	8832	4696	1099	3597
0.313	314.2	319.0	366.1	8961	4448	1470	2978
0.418	313.5	318.0	361.3	7182	4667	1773	2894
0.418	313.5	318.2	361.3	7380	4755	1817	2938
0.499	313.4	318.8	359.7	6661	4964	2334	2630
0.503	314.3	316.9	356.0	5789	4819	2443	2376
0.560	313.9	317.3	353.3	5250	4688	2629	2058
0.607	314.4	318.5	353.7	4596	4810	2938	1872
0.665	315.9	318.4	352.6	3844	4725	3064	1661
0.699	314.3	317.2	347.9	3947	4766	3466	1301
0.713	315.6	317.8	347.0	3623	4531	3395	1136
0.754	314.1	316.9	340.9	3260	4888	3598	1290
0.817	314.1	317.7	338.5	2171	4666	3993	673
0.857	315.0	317.9	332.6	1870	4660	4133	527
0.898	314.6	318.5	321.0	1287	4611	4207	405
0.898	314.4	318.3	319.9	1077	4576	4282	294
0.899	313.9	317.3	320.4	1210	4270	4270	0
0.900	315.9	318.1	321.8	1207	4279	4265	14
0.905	312.7	317.1	317.1	1008	4658	4658	0
0.906	315.1	317.6	317.6	998	4515	4308	0
0.913	312.9	317.3	320.7	778	4230	4045	186
0.946	314.7	318.2	324.2	668	4302	3013	1289
0.949	314.0	317.4	325.4	303	3903	2536	1366
0.963	313.3	316.7	326.4	244	3937	1484	2454
0.974	314.0	318.3	329.4	296	4396	1086	3013
1.000	–	–	331.7	–	3693	–	3693
1.000	–	–	331.3 [1]	–	3610 [1]	–	3610 [1]
1.000	233.1 [5]	–	331.23 [6]	–	3703 [5]	–	3703 [5]

AMPD–DC [3]. All these investigations aimed to achieve a thermodynamic description of the quaternary organic alloy system AMPD–NPG–DC–SCN [4] intended to be used for in situ observation and numerical modelling of multicomponent eutectic growth in univariant and non-variant reactions.

The present work addresses investigations by means of experiments and computational thermodynamics with the last two constituent binary systems of the above named quaternary system, namely NPG–SCN and AMPD–SCN. To our best knowledge, for both systems no phase diagram and thermochemical data have been reported in literature.

In the present paper the NPG–SCN and AMPD–SCN phase diagrams, the enthalpy of transformation from the ordered crystals (OCs) to the orientationally disordered crystals (ODICs) and the enthalpy of fusion of different alloys were determined by differential scanning calorimetry (DSC). The obtained thermodynamic and phase equilibria data for both systems were consistently described via the CALPHAD approach. The model parameters have been evaluated using a computer optimisation technique based on the descriptions of the Gibbs energy of all individual phases of the pure AMPD, NPG and SCN substances proposed in the previous parts of the work [1,2]. Moreover, selected alloys of the NPG–SCN and AMPD–SCN systems were investigated by unidirectional solidification using the Bridgman technique in order to verify phases involved in solid–liquid equilibria and the nature of eutectic growth in these systems.

The purification and characterisation of pure substances, the procedures for preparation and alloying of the samples, the DSC and unidirectional solidification techniques and measuring procedures were the same as previously described in [1,4].

2. Results

2.1. DSC-measurements

Tables 1 and 2 summarise the results of the DSC measurements for different alloys of the NPG–SCN and the AMPD–SCN systems, respectively. The tables