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The high-temperature phase equilibria of the Ni–Sn–Zn system: Isothermal sections

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ABSTRACT

In this work three complete isothermal sections of the Ni–Sn–Zn system at 700, 800 and 900 °C are presented. They were constructed based on experimental investigation of more than 60 alloy samples. Powder XRD, single crystal XRD, EPMA, and DTA measurements on selected samples were carried out. Two new ternary compounds, designated as τ2 (Ni_5Sn_4Zn) and τ3 ($Ni_7Sn_9Zn_5$), were identified and their homogeneity ranges and crystal structures could be described. Whereas τ3 is only present at 700 °C, the τ2-phase was found at both 700 and 800 °C. No truly ternary compound could be found in the isothermal section at 900 °C. A seemingly ternary compound at 20 at% Sn in the Ni-rich part of Ni–Sn–Zn was found at 800 and 900 °C. Our XRD results, however, indicate that this phase is a ternary solid solution of Ni_3Sn-HT from constituent binary Ni–Sn. It is stabilized to lower temperatures by additions of Zn. These new experimental results will provide valuable information to the thermodynamic description of alloy systems relevant for high-temperature lead-free soldering.

1. Introduction

Since July 2006 the electronics industry has been forced to replace conventional Pb–Sn solders by lead-free alternatives. While for low temperature soldering suitable materials have been found, e.g. Sn–Ag–Cu and Sn–Cu–Ni, no convenient alloy has so far been found for high-temperature soldering (melting temperature ≥230 °C). At the moment Sn–Zn and Sn–Au containing solders are promising candidates, while Cu and Ni may be used as additions and as contact materials as well. The interfacial reactions between solder and substrate are reflected by the phase diagram.

In general, systems of the type solder + substrate are characterized by huge differences in the melting points of the pure components. The high melting areas cannot be investigated experimentally at the temperatures relevant for soldering, i.e. 200–300 °C, because diffusion is slow and thermodynamic equilibrium will not be reached in reasonable time. Therefore a combination of experiments and thermodynamic modeling is needed. As methods like CALPHAD also strongly depend on experimental data, the subject of the present study is the experimental investigation of the high-temperature (HT) phase equilibria of the ternary Ni–Sn–Zn system. Although not directly related to soldering, these phase relations can be used as a starting point for further work in this system and the expansion to lower temperatures (LT).

2. Literature review

2.1. Binary systems

The binary Sn–Zn system is a simple eutectic system. For the present work the version established by Moser et al. [1] and compiled in Massalski's handbook [2] has been accepted. Within the efforts of COST Action 531 (Lead-free Solder Alloys) to establish a thermodynamic database for the modeling of relevant phase diagrams, this system has also been thermodynamically assessed [3]. The obtained description is in good agreement with Refs. [1,2]. At the investigated temperatures the entire Sn-Zn system is liquid.

The binary Ni–Sn system has recently been substantially modified by Schmetterer et al. [4]. Their version was taken for the present work. The calculated phase diagram in the COST 531 database [5] is based on older data and therefore differs in some points. This new version of Ni–Sn shows that the homogeneity range of LT-Ni_3Sn is comparatively wider than in the previous calculated phase diagrams [6–8] and the assessment of Nash and Nash [9]. Around the Ni_3Sn_2-HT phase, too, a more complex situation with three LT phases was found. Although in the present work the region of our interest is different from the LT phases, lack of basic information about the constituent binary systems can lead to

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the construction of erroneous higher-order phase diagram representations. The Ni_3Sn-HT phase cannot be quenched in the binary system, which is important valuable information for the temperature and composition range of interest in the present study.

Experimental data of the Ni–Zn binary system have been assessed by Nash and Pan [10] and compiled by Massalski et al. [2]. Thermodynamic calculations of Ni–Zn have been published by Su et al. [11] and Vassilev et al. [12]. The latter shows slight differences in transition temperatures for all the phases and in the composition of the δ phase compared to Refs. [2,9].

All unary and binary phases which have been accepted for this work are listed in Table 1.

At the beginning of our investigations only one publication with very little phase diagram information was available [13] for the ternary Ni–Sn–Zn system. At an advanced state of our experiments, Chang et al. published independently isothermal sections of Ni–Sn–Zn at 200, 500 and 800 °C based on their own experimental investigations [8].

3. Experimental

Binary Ni–Zn and ternary Ni–Sn–Zn alloys were prepared from the pure metals: Ni sheet of 1 mm thickness (99.98% Advent Research Materials Ltd., Eynsham – Oxford, UK), Sn ingots (99.999% metal basis, Ventron Alfa Products, Beverly, MA, USA) and Zn (Merck, Germany). Zn was purified before use by filtration of the liquid metal through quartz wool in a quartz tube applying Ar pressure.

The pure elements were cut into smaller pieces and calculated amounts were weighed in order to obtain samples of 1.5–2 g total mass. The metal pieces were sealed into dried and evacuated quartz glass tubes which were checked for vacuum before heating them. The mixtures were slowly heated up to 1180 °C with a rate of 3 K/min where they were kept for 2 days for alloying. The molten samples were shaken repeatedly to ensure homogeneity. Afterwards samples with higher Ni-contents were cooled down to room temperature and powdered using ball mill or mortar, then pressed into 8 mm pellets and sealed again using the same procedure as before for re-melting and alloying. After alloying, the samples were subjected to heat treatment as indicated in Table 2, followed by quenching in water to retain the high-temperature equilibria. Generally, a diamond saw was used to cut the alloys into several pieces for different heat treatments and analyses.

In order to avoid sudden evaporation of Zn, samples were quenched by dipping only the part of the ampoules filled with condensed alloy into the water. Weighing the samples after alloying revealed an acceptable weight loss of ≤0.5 mass%. Thus the real sample compositions should not differ significantly from the nominal compositions given in Table 2.

Powders for powder X-ray diffraction (PXRD) were prepared by grinding, ball milling or filing. In the two latter cases the powder had to be stress annealed for 20 min either at the annealing temperature or below solidification temperature. The diffractograms were recorded by using an Image Plate Guinier camera (Huber GmbH, Rimsting, Germany) on a Siemens Kristalloflex ERL 1000 generator (Siemens AG, Berlin, Germany) with $CuK_{\alpha 1}$ radiation or a Bruker D8 powder diffractometer (Bruker AXS, Karlsruhe, Germany) operating in reflection mode (Cu K_α radiation, Lynxeye Silicon Strip detector). Then the patterns were refined using the TOPAS software provided with the Bruker diffractometer. Single crystal X-ray diffraction (Nonius KappaCCD diffractometer equipped with a monocapillary optics collimator, graphite monochromatized MoK_α radiation) was applied to selected samples. They have been crashed in order to depict appropriate crystals.

For metallographic investigations samples were embedded into a conductive polymer (containing graphite) and ground using discs with SiC 600–1200 mesh size with continuous water flow. Polishing was done using corundum powder (1 μm) in an organic medium (Metadi Fluid). These blocks were rinsed with distilled water and cleaned in an ultrasonic bath with purified ethanol to remove Al_2O_3 from the surface and to avoid surface scratching. The polished samples were investigated by optical microscopy using a Zeiss Axiotech 100 microscope equipped for operations under polarized light. Samples were further analyzed by electron probe microanalysis (EPMA) on a Cameca SX 100 (Wavelength Dispersive Spectroscopy (WDS), 15 kV/20 nA beam current; ZAF matrix correction). The pure metals Ni (K_α-Line), Sn (L_α-line) and Zn (L_α-line) with the above mentioned purity were used for the calibration of the instrument.

Around 50–100 mg of samples, annealed at 700 °C (see Table 2), were sealed in evacuated quartz ampoules for DTA (Difference thermal analysis) measurements which were performed with a DTA 404S (Netzsch Gerätebau Gmbh, Germany) with a heating

Table 1
Crystallographic data of phases in constituent binary systems according to literature.

Phase	Composition [at% Ni]	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
Ni–Sn						
(Ni)	0–10.7	*cF*4	$Fm\bar{3}m$	A1	Cu	[4]
Ni_3Sn-HT	24.1–26.3	*cF*16	$Fm\bar{3}m$	DO_3	BiF_3	[4]
Ni_3Sn-LT	24.8–25.5	*hP*8	$P6_3/mmc$	DO_{19}	Ni_3Sn	[4]
Ni_3Sn_2-HT	36.7–44.0	*hP*6	$P6_3/mmc$	$B8_2$	$InNi_2$	[4]
Ni_3Sn_2-LT"	~38.3–~39.0	…	*Cmcm*[a]	…	…	[4]
Ni_3Sn_2-LT	39.3–41.1	*oP*20	*Pnma*	…	Ni_3Sn_2	[4]
Ni_3Sn_2-LT'	41.25–44.0	…	*Cmcm*[a]	…	…	[4]
Ni_3Sn_4	53.0–57.0	*mC*14	*C*2/*m*	…	Ni_3Sn_4	[4]
(β-Sn)	~100	*tI*4	$I4_1/amd$	A5	α-Sn	[4]
(α-Sn)	~100	*cF*8	*Fd*3*m*	A4	β-Sn	[4]
Metastable phases						
Ni_3Sn martensite	…	*oP*8	*Pmmn*	DO_α	β-Cu_3Ti	[4]
Ni–Zn						
(Ni)	0–39.3	*cF*4	$Fm\bar{3}m$	A1	Cu	[9]
NiZn-HT	47.3–58.3	*cP*2	*Pm*3*m*	B2	CsCl	[9]
NiZn-LT	45.3–51.8	*tP*2	*P*4/*mmm*	$L1_0$	AuCu	[9]
Ni_3Zn_{14}	74–85	*cI*52[b]	$I\bar{4}3m$	$D8_2$	Cu_5Zn_8	[9]
$NiZn_8$	~ 89	*mC*6	*C*2/*m*	…	$CoZn_{13}$	[9]
(Zn)	100	*hP*6	$P6_3/mmc$	A3	Mg	[9]

[a] Symmetry of average cell with modulation vector α.
[b] According to [Nover et al. [19]].

Table 2
Experimental results of the phase analysis in the Ni–Sn–Zn system.

Sample name	Nominal composition, at%	Heat treatment, °C & days	Phases	Space group	Structure type	Unit cell parameter (pm)	WDS analysis			
							Ni, at%	Sn, at%	Zn, at%	Σ wt%
900 °C										
A1	$Ni_{80}Sn_5Zn_{15}$	900, 12d	(Ni)	Fm-3m	Cu	$a = 359.956(6)$	77.4	5.4	17.2	99.8
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.31(10)$ $c = 424.1(2)$	70.7	22.6	6.7	101.6
A2	$Ni_{80}Sn_{10}Zn_{10}$	900, 12d	(Ni)	Fm-3m	Cu	$a = 360.698(2)$	80.5	6.2	13.3	99.8
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.298(4)$ $c = 423.119(4)$	73.5	22.6	3.9	100.7
A3	$Ni_{80}Sn_{15}Zn_5$	900, 12d	(Ni)	Fm-3m	Cu	a = 359.868(1)	84.5	6.9	8.7	100.3
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 528.121(3)$ $c = 423.618(3)$	74.2	23.5	2.3	101.5
B1	$Ni_{65}Sn_5Zn_{30}$	900, 11d	(Ni)	Fm-3m	Cu	$a = 361.83(6)$	68.5	2.8	28.7	99.8
			NiZn-LT	P4/mmm	AuCu	$a = 390.85(4)$ $c = 322.44(5)$	60.0	9.5	30.5	100.6
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 365.23(3)$	Phase not found			
B2	$Ni_{65}Sn_{10}Zn_{25}$	900, 35d	(Ni)	Fm-3m	Cu	$a = 344.6(1)$	69.9	3.6	26.5	99.2
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 363.31(2)$	Phase not found			
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 585.18(2)$	62.7	14.5	22.8	100.8
B3	$Ni_{65}Sn_{20}Zn_{15}$	900, 12d	Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.229(6)$	64.9	20.5	14.6	100.5
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.9(1)$ $c = 515.2(2)$	61.4	30.4	8.2	100.6
B4	$Ni_{65}Sn_{25}Zn_{10}$	900, 11d	Ni_3Sn-HT	Fm-3m	BiF_3	$a = 588.14(2)$	66.5	22.2	11.3	100.4
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.200(6)$ $c = 516.441(9)$	61.3	31.4	7.3	100.4
B5	$Ni_{65}Sn_{30}Zn_5$	900, 12d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 531.18(8)$ $c = 426.6(1)$	70.0	24.5	5.5	100.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.664(3)$ $c = 518.030(6)$	61.9	33.5	4.6	100.7
B6	$Ni_{65}Sn_7Zn_{28}$	900, 8d	(Ni)	…	…	Not measured	68.5	3.3	28.3	100.1
			NiZn-HT	…	…		60.2	10.6	28.3	100.2
C1	$Ni_{50}Sn_{45}Zn_5$	900, 12d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 408.252(5)$ $c = 514.761(10)$	52.5	43.6	3.8	101.3
			Ni_3Sn_4	C2/m	Ni_3Sn_4	$a = 1241.6(6)$ $b = 418.7(2)$ $c = 521.8(3)$ $\beta = 106.54(4)$	42.1	57.6	0.3	101.4
			(Sn)	I41/amd	β-Sn	$a = 582.81(6)$ $c = 318.05(4)$	0.3	99.2	0.6	99.5
C2	$Ni_{50}Sn_{35}Zn_{15}$	900, 12d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.11(3)$ $c = 517.56(7)$	49.6	36.9	13.5	101.3
			τ2	Cmcm	Ni_2GaGe	$a = 414.60(1)$ $b = 1256.09(4)$ $c = 1165.47(4)$	Phase not found			
			τ3	…	…	Phase not found	39.7	27.9	32.4	101.5
			Ni_3Zn_{14}	…	…	Phase not found	24.5	6.0	69.5	100.1
C3	$Ni_{50}Sn_{25}Zn_{25}$	900, 12d	NiZn-HT	Pm-3m	CsCl	$a = 294.309(9)$	47.1	19.4	33.5	100.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.90(2)$ $c = 516.58(4)$	52.4	33.4	14.2	101.2
			τ2	Cmcm	Ni_2GaGe	$a = 416.0(1)$ $b = 1252.1(3)$ $c = 1168.1(3)$	Phase not found			
C4	$Ni_{50}Sn_{15}Zn_{35}$	900, 11d	NiZn-HT	Pm-3m	CsCl	$a = 293.892(3)$	50.2	15.7	34.1	100.8
G1	$Ni_{67}Sn_{26}Zn_7$	900, 13d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 569.5(2)$ $c = 429.9(3)$	68.7	23.7	7.7	99.7
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 584.89(3)$	Phase not found			
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.87(4)$ $c = 517.24(5)$	61.8	32.4	5.8	99.8
G2	$Ni_{73}Sn_{15}Zn_{12}$	900, 13d	(Ni)	Fm-3m	Cu	$a = 361.419(8)$	76.7	5.1	18.2	100.1
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 521.06(9)$ $c = 427.6(1)$	70.3	22.0	7.7	101.0
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 584.26(5)$	Phase not found			
G3	$Ni_{57}Sn_{29}Zn_{14}$	900, 13d	NiZn-HT	Pm-3m	CsCl	$a = 294.11(4)$	51.1	15.9	33.0	100.4
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.90(2)$ $c = 516.48(3)$	56.3	31.8	11.9	100.8
G4	$Ni_{57}Sn_{22}Zn_{21}$	900, 13d	NiZn-HT	Pm-3m	CsCl	$a = 293.10(2)$	55.1	14.4	30.5	100.9
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.14(2)$ $c = 516.19(4)$	59.0	30.6	10.4	100.9
G5	$Ni_{69}Sn_{12}Zn_{19}$	900, 13d	(Ni)	Fm-3m	Cu	$a = 361.769(7)$	72.1	4.1	23.8	100.3
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 586.57(1)$	66.6	18.7	14.7	100.8
G6	$Ni_{39}Sn_{31}Zn_{30}$	900, 13d	Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 889.27(7)$	22.3	4.7	73.0	97.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 410.42(2)$ $c = 517.50(7)$	50.9	37.9	11.2	100.6
			τ2	Cmcm	Ni_2GaGe	$a = 414.08(2)$ $b = 1257.8(1)$ $c = 1165.88(7)$	47.9	37.5	14.6	101.5
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.21(2)$	39.1	32.4	28.5	101.0
			(Sn)	I41/amd	β-Sn	$a = 583.44(2)$ $c = 318.29(2)$	Phase not found			
G7	$Ni_{42}Sn_{28}Zn_{30}$	900, 13d	Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 890.2(1)$	23.9	5.3	70.8	97.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 410.76(3)$ $c = 516.98(6)$	51.0	35.9	13.1	101.5
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 882.63(5)$	41.8	23.7	34.5	100.6
			τ2	Cmcm	Ni_2GaGe	$a = 420.22(4)$ $b = 1231.8(1)$ $c = 1190.0(1)$	49.0	34.8	16.2	101.1
			(Sn)	I41/amd	β-Sn	$a = 582.8(2)$ $c = 317.7(1)$	Phase not found			
G9	$Ni_{66.5}Sn_{24.5}Zn_9$	900, 8d	NiZn-HT	Pm-3m	CsCl	$a = 294.19(2)$	61.9	31.8	6.6	100.5
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.73(1)$	Phase not found			
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.28(1)$ $c = 516.71(2)$	67.6	22.6	10.0	101.1
G12	$Ni_{70}Sn_{17}Zn_{13}$	900, 8d	(Ni)	Fm-3m	Cu	$a = 361.08(1)$	73.6	4.3	22.3	100.3
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 574.241(0)$ $b = 414.921(0)$	Phase not found			
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 582.77(9)$	68.6	20.9	10.6	100.1
G15	$Ni_{68}Sn_{10}Zn_{22}$	900, 8d	(Ni)	Fm-3m	Cu	$a = 361.67(2)$	70.2	3.5	26.4	100.1
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 572.2(8)$	64.9	16.8	18.4	100.1
G17	$Ni_{59}Sn_{21}Zn_{20}$	900, 8d	NiZn-HT	Pm-3m	CsCl	$a = 293.08(2)$	57.3	14.4	28.4	…
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 585.20(1)$	Phase not found			
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.377(7)$ $c = 516.10(1)$	60.2	30.7	9.4	…

(*continued on next page*)

Table 2 (*continued*)

Sample name	Nominal composition, at%	Heat treatment, °C & days	Phases	Space group	Structure type	Unit cell parameter (pm)	WDS analysis			
							Ni, at%	Sn, at%	Zn, at%	Σ wt%
G21	$Ni_{63}Sn_{21}Zn_{16}$	900, 8d	NiZn-HT	Pm-3m	CsCl	$a = 293.298(7)$	Phase not found			
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 586.45(2)$	63.0	19.0	18.1	100.1
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.793(10)$ $c = 515.81(2)$	61.3	30.3	8.5	100.1
H10	$Ni_{61}Sn_{21}Zn_{18}$	900, 8d	NiZn-HT	Pm-3m	CsCl	$a = 292.848(9)$	Phase not found			
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 588.7(2)$	60.4	17.1	22.5	100.5
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.77(2)$ $c = 516.04(3)$	60.7	30.0	9.3	100.7
H11	$Ni_{62}Sn_{21}Zn_{17}$	900, 8d	NiZn-HT	Pm-3m	CsCl	$a = 292.543(9)$	56.8	13.7	29.5	98.9
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.5(2)$	Phase not found			
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.068(9)$ $c = 517.47(1)$	60.0	30.2	9.8	100.7
H13	$Ni_{66}Sn_{11.5}Zn_{22.5}$	900, 8d	(Ni)	Fm-3m	Cu	$a = 360.90(2)$	70.0	3.7	26.3	101.2
			NiZn-HT	Pm-3m	CsCl	$a = 292.830(0)$	64.8	9.3	25.9	104.5
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 570.0(3)$	63.5	15.5	21.0	102.2
H14	$Ni_{67}Sn_{25}Zn_8$	900, 8d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.510(8)$ $b = 517.24(1)$	61.9	32.0	6.0	101.5
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.95(2)$	68.3	23.1	8.6	101.1
H15	$Ni_{71}Sn_{17}Zn_{12}$	900, 8d	(Ni)	Fm-3m	Cu	$a = 361.35(6)$	72.7	4.6	22.7	99.9
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 548.5(4)$ $b = 409.5(6)$	Phase not found			
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 586.39(9)$	68.1	20.4	11.5	100.8
H16	$Ni_{40}Sn_{44}Zn_{16}$	900, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 410.54(2)$ $c = 517.07(3)$	Not measured			
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 884.02(3)$				
			(Sn)	I41/amd	β-Sn	$a = 583.56(2)$ $c = 318.22(1)$				
800 °C										
A1	$Ni_{80}Sn_5Zn_{15}$	800, 16d	(Ni)	Fm-3m	Cu	$a = 359.924(5)$	79.2	3.6	17.2	99.2
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.04(6)$ $c = 423.2(1)$	73.7	21.9	4.4	100.9
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 600.08(2)$	Phase not found			
A2	$Ni_{80}Sn_{10}Zn_{10}$	800, 16d	(Ni)	Fm-3m	Cu	$a = 358.941(2)$	81.8	3.9	14.3	100.2
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.337(6)$ $c = 422.967(7)$	74.0	22.4	3.6	100.0
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 368.121(6)$	Phase not found			
A3	$Ni_{80}Sn_{15}Zn_5$	800, 16d	(Ni)	Fm-3m	Cu	$a = 358.87(2)$	85.6	4.6	9.8	101.1
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 528.03(2)$ $c = 423.93(3)$	74.2	23.5	2.3	101.1
B1	$Ni_{65}Sn_5Zn_{30}$	800, 16d	(Ni)	Fm-3m	Cu	$a = 361.262(8)$	70.3	2.6	27.1	99.7
			NiZn-LT	P4/mmm	AuCu	$a = 388.20(3)$ $c = 324.81(4)$	59.9	8.5	31.6	100.2
			Ni_3Zn	Fm-3m	$AuCu_3$	$a = 365.72(2)$	Phase not found			
B2	$Ni_{65}Sn_{10}Zn_{25}$	800, 16d	(Ni)	…	…	Phase not found	70.6	3.2	26.2	99.8
			NiZn-LT	P4/mmm	AuCu	$a = 393.80(2)$ $c = 320.39(3)$	63.0	14.4	22.6	100.6
B3	$Ni_{65}Sn_{20}Zn_{15}$	800, 16d	Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.49(8)$	64.6	20.6	14.8	100.3
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 415.37(3)$ $c = 508.81(8)$	61.2	31.7	7.1	101.1
B4	$Ni_{65}Sn_{25}Zn_{10}$	800, 16d	Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.750(8)$	66.3	21.9	11.8	100.8
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.133(5)$ $c = 516.900(10)$	61.5	32.1	6.4	100.8
B5	$Ni_{65}Sn_{30}Zn_5$	800, 16d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.98(2)$ $c = 423.68(2)$	72.8	23.0	4.2	100.8
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.417(5)$ $c = 517.723(8)$	61.5	33.3	5.2	100.7
B6	$Ni_{65}Sn_7Zn_{28}$	800, 25d	(Ni)	Fm-3m	Cu	$a = 363.334(0)$	69.5	3.0	27.7	102.2
			NiZn-LT	P4/mmm	AuCu	$a = 390.249(2)$ $c = 322.59(9)$	60.9	10.8	28.3	102.4
C1	$Ni_{50}Sn_{45}Zn_5$	800, 15d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 407.91(1)$ $c = 514.26(2)$	51.6	44.4	4.0	100.9
			Ni_3Sn_4	…	…	Phase not found	44.1	55.8	0.1	100.6
			(Sn)	…	…	Phase not found	0.2	99.7	0.1	100.8
C2	$Ni_{50}Sn_{35}Zn_{15}$	800, 15d	τ2	Cmcm	Ni_2GaGe	$a = 414.646(7)$ $b = 1256.31(2)$ $c = 1164.02(2)$	51.0	33.9	15.1	96.5
			NiZn-HT	…	…	Phase not found	45.8	19.3	34.9	96.6
C3	$Ni_{50}Sn_{25}Zn_{25}$	800, 15d	τ2	Cmcm	Ni_2GaGe	$a = 414.02(4)$ $b = 1252.5(2)$ $c = 1175.6(2)$	53.2	35.9	10.9	100.9
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 410.97(2)$ $c = 516.67(3)$	Phase not found			
			NiZn-HT	Pm-3m	CsCl	$a = 294.378(6)$	47.2	18.2	34.6	100.6
C4	$Ni_{50}Sn_{15}Zn_{35}$	800, 15d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 419.29(8)$ $c = 499.7(1)$	56.1	34.7	9.2	101.9
			NiZn-HT	Pm-3m	CsCl	$a = 293.903(5)$	49.9	14.4	35.7	100.5
C5	$Ni_{50}Sn_5Zn_{45}$	800, 15d	NiZn-LT	P4/mmm	AuCu	$a = 396.35(1)$ $c = 314.37(2)$	Phase not found			
			NiZn-HT	…	…	Phase not found	51.7	5.6	42.6	100.1
D1	$Ni_{35}Sn_{60}Zn_5$	800, 15d	τ2	Cmcm	Ni_2GaGe	$a = 419.64(5)$ $b = 1252.4(2)$ $c = 1178.4(2)$	46.7	44.2	9.1	101.0
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 408.195(2)$ $c = 514.365(5)$	51.6	44.2	4.2	101.5
			(Sn)	I41/amd	β-Sn	$a = 583.44(7)$ $c = 318.11(4)$	0.0	99.8	0.2	99.6
D2	$Ni_{35}Sn_{50}Zn_{15}$	800, 15d	τ2	Cmcm	Ni_2GaGe	$a = 414.144(5)$ $b = 1260.18(2)$ $c = 1163.94(2)$	47.1	42.0	10.9	101.3
			τ1	…	…	…	35.6	42.4	22.0	101.2
			(Sn)	I41/amd	β-Sn	$a = 583.07(4)$ $c = 318.15(3)$	0.4	98.9	0.8	100.9
D3	$Ni_{35}Sn_{40}Zn_{25}$	800, 15d	τ2	Cmcm	Ni_2GaGe	$a = 414.90(1)$ $b = 1257.83(4)$ $c = 1164.19(3)$	46.7	38.8	14.5	101.1
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 882.73(7)$	37.4	37.1	25.5	101.0
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.19(7)$	17.1	4.0	79.0	97.8
			(Sn)	I41/amd	β-Sn	$a = 583.191(0)$ $c = 318.231(0)$	0.2	98.5	1.3	101.0
D4	$Ni_{35}Sn_{30}Zn_{35}$	800, 15d	τ2	Cmcm	Ni_2GaGe	$a = 415.94(8)$ $b = 1255.4(2)$ $c = 1176.4(2)$	47.0	38.2	14.7	101.5
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 882.89(2)$	38.7	32.6	28.7	101.4
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.80(4)$	21.1	3.7	75.2	98.6
			(Sn)	I41/amd	β-Sn	$a = 583.18$ $c = 318.24(3)$	1.0	96.4	2.6	101.4

Table 2 (*continued*)

Sample name	Nominal composition, at%	Heat treatment, °C & days	Phases	Space group	Structure type	Unit cell parameter (pm)	WDS analysis			
							Ni, at%	Sn, at%	Zn, at%	Σ wt%
D5	$Ni_{35}Sn_{20}Zn_{45}$	800, 15d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 889.55(4)$	36.3	32.3	31.4	101.5
			NiZn-HT	Pm-3m	CsCl	$a = 294.29(2)$	40.4	23.3	36.3	101.1
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 887.29(6)$	19.0	3.9	77.1	98.2
			(Sn)	I41/amd	β-Sn	$a = 583.5(1)$ $b = 318.2(1)$	3.0	91.3	5.7	103.0
D6	$Ni_{35}Sn_{10}Zn_{55}$	800, 15d	NiZn-HT	Pm-3m	CsCl	$a = 294.398(5)$	42.2	16.1	41.7	100.4
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.18(2)$	28.4	4.0	67.6	99.2
D7	$Ni_{35}Sn_5Zn_{60}$	800, 15d	NiZn-HT	Pm-3m	CsCl	$a = 292.802(9)$	43.5	8.4	48.1	100.3
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 886.48(3)$	28.7	2.4	68.9	99.6
F1	$Ni_{58}Sn_{40}Zn_2$	800, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 409.305(4)$ $c = 517.440(7)$	Not measured			
F2	$Ni_{55}Sn_{39}Zn_6$	800, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 409.165(4)$ $c = 516.271(6)$	Not measured			
F3	$Ni_{50}Sn_{39}Zn_{11}$	800, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 409.275(6)$ $c = 516.21(1)$	55.0	42.0	3.0	100.5
F4	$Ni_{48}Sn_{38}Zn_{14}$	800, 18d	τ2	Cmcm	Ni_2GaGe	$a = 414.739(6)$ $b = 1258.25(2)$ $c = 1164.22(2)$	47.3	38.8	13.9	100.6
F5	$Ni_{42}Sn_{38}Zn_{20}$	800, 18d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.758(0)$	36.9	37.6	25.5	100.6
			τ2	Cmcm	Ni_2GaGe	$a = 414.594(0)$ $b = 1258.884(0)$ $c = 1164.389(0)$	47.3	39.5	13.1	101.0
			Ni_3Zn_{14}	…	…	Phase not found	19.4	3.6	77.0	97.7
			(Sn)	I41/amd	β-Sn	$a = 589.736(0)$ $c = 317.471(0)$	0.6	97.5	2.0	101.1
F6	$Ni_{37}Sn_{37}Zn_{26}$	800, 18d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.37(1)$	37.2	36.6	26.3	100.8
			τ2	Cmcm	Ni_2GaGe	$a = 414.783(5)$ $b = 1258.86(2)$ $c = 1164.34(2)$	47.2	39.5	13.3	100.6
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.31(5)$	18.7	3.7	77.6	97.1
			(Sn)	I41/amd	β-Sn	$a = 583.26(1)$ $c = 318.225(8)$	Phase not found			
F7	$Ni_{36}Sn_{37}Zn_{27}$	800, 18d	Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 887.043(0)$	18.7	3.4	77.9	…
			(Sn)	I41/amd	β-Sn	$a = 583.315(0)$ $c = 318.231(0)$	Phase not found			
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.258(0)$	Phase not found			
			τ2	Cmcm	Ni_2GaGe	$a = 414.683(0)$ $b = 1258.875(0)$ $c = 1164.311(0)$	45.8	39.1	15.1	…
G1	$Ni_{67}Sn_{26}Zn_7$	800, 27d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.72(4)$ $c = 423.55(6)$	72.4	22.4	5.2	100.0
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 588.53(3)$	67.0	2.4	10.6	100.1
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.15(2)$ $c = 517.03(2)$	61.5	2.3	6.2	101.0
G2	$Ni_{73}Sn_{15}Zn_{12}$	800, 27d	(Ni)	Fm-3m	Cu	$a = 360.054(5)$	73.1	3.3	23.6	100.0
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 526.916(8)$ $c = 422.675(10)$	72.8	20.3	6.9	101.3
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 597.93(5)$	Phase not found			
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 368.17(2)$	Phase not found			
G3	$Ni_{57}Sn_{29}Zn_{14}$	800, 27d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.82(10)$ $c = 516.6(1)$	57.0	34.4	8.6	101.0
			NiZn-HT	Pm-3m	CsCl	$a = 293.79(7)$	50.4	14.0	35.6	100.4
G4	$Ni_{57}Sn_{22}Zn_{21}$	800, 27d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.29(1)$ $c = 516.59(2)$	59.1	33.0	7.9	…
			NiZn-HT	Pm-3m	CsCl	$a = 292.85(1)$	54.0	11.6	34.4	100.5
G5	$Ni_{69}Sn_{12}Zn_{19}$	800, 27d	(Ni)	Fm-3m	Cu	$a = 361.342(4)$	72.2	3.3	24.5	101.0
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 586.804(10)$	66.0	18.4	15.6	101.2
			NiZn-LT	P4/mmm	AuCu	$a = 391.70(4)$ $c = 329.37(6)$	Phase not found			
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 526.09(5)$ $c = 424.02(10)$	Phase not found			
			τ2	Cmcm	Ni_2GaGe	$a = 414.971(8)$ $b = 1257.26(2)$ $c = 1164.06(2)$	47.1	37.1	15.8	98.1
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 882.95(4)$	40.9	25.5	33.6	…
G6	$Ni_{39}Sn_{31}Zn_{30}$	800, 27d	NiZn-HT	Pm-3m	CsCl	$a = 297.54(4)$	40.2	30.2	29.6	98.6
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 889.89(4)$	24.4	4.9	70.7	94.9
			(Sn)	I41/amd	β-Sn	$a = 588.720(0)$ $c = 314.269(0)$	Phase not found			
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 884.53(6)$	39.5	31.8	28.7	101.2
			τ2	Cmcm	Ni_2GaGe	$a = 414.958(9)$ $b = 1256.71(3)$ $c = 1163.90(3)$	47.5	37.4	15.1	101.1
G7	$Ni_{42}Sn_{28}Zn_{30}$	800, 27d	Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.6(1)$	23.2	5.0	71.8	98.9
			NiZn-HT	Pm-3m	CsCl	$a = 297.02(3)$	Phase not found			
			(Sn)	I41/amd	β-Sn	$a = 583.28(9)$ $c = 318.13(7)$	Phase not found			
G9	$Ni_{66.5}Sn_{24.5}Zn_9$	800, 25d	Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.979(0)$	67.5	22.5	10.0	101.8
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.244(8)$ $c = 516.98(2)$	62.0	32.0	6.2	102.0
G12	$Ni_{70}Sn_{17}Zn_{13}$	800, 25d	(Ni)	Fm-3m	Cu	$a = 361.32(4)$	72.1	3.8	24.3	102.4
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 586.13(5)$	67.5	20.2	10.0	102.1
			Ni_3Sn-LT	P63/mmc	Mg3Cd	$a = 525.45(7)$ $c = 422.47(8)$	72.4	20.3	6.2	102.0
G15	$Ni_{68}Sn_{10}Zn_{22}$	800, 25d	(Ni)	Fm-3m	Cu	$a = 355.2(3)$	70.4	3.3	26.5	102.9
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.38(8)$	64.9	17.0	18.3	102.6
G17	$Ni_{59}Sn_{21}Zn_{20}$	800, 25d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.434(9)$ $c = 516.56(2)$	60.3	31.5	8.3	101.9
			NiZn-HT	Pm-3m	CsCl	$a = 292.72(1)$	56.5	12.8	30.8	101.8
G21	$Ni_{63}Sn_{21}Zn_{16}$	800, 25d	Ni_3Sn-HT	Fm-3m	BiF_3	$a = 586.939(0)$	62.6	18.4	18.1	102.2
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.896(9)$ $c = 516.31(2)$	61.2	31.2	7.7	101.6
H1	$Ni_{52}Sn_{24.5}Zn_{23.5}$	800, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.278(8)$ $c = 516.35(2)$	55.3	35.4	9.3	101.2
			NiZn-HT	Pm-3m	BiF_3	$a = 294.064(3)$	48.2	15.6	36.2	100.6
H7	$Ni_{49}Sn_{26}Zn_{25}$	800, 18d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 887.48(4)$	38.7	30.7	31.2	100.1
			NiZn-HT	Pm-3m	CsCl	$a = 294.822(9)$	40.7	20.0	39.3	99.6
			(Sn)	…	…	Phase not found	4.9	90.4	4.7	98.0
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 593.28(2)$	Phase not found			
			τ2	Cmcm	Ni_2GaGe	$a = 418.1(2)$ $b = 1249.8(6)$ $c = 1176.4(5)$	54.6	34.4	11.0	97.7

(*continued on next page*)

Table 2 (*continued*)

Sample name	Nominal composition, at%	Heat treatment, °C & days	Phases	Space group	Structure type	Unit cell parameter (pm)	WDS analysis			
							Ni, at%	Sn, at%	Zn, at%	Σ wt%
H8	$Ni_{51}Sn_{25}Zn_{24}$	800, 18d	NiZn-HT	Pm-3m	CsCl	$a = 294.6(1)$	47.4	17.6	35.0	100.9
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.159(2)$ $b = 516.760(2)$	Phase not found			
H12	$Ni_{64}Sn_{20}Zn_{16}$	800, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 414.18(4)$ $c = 516.00(6)$	61.4	31.3	7.4	100.6
			Ni_3Sn-HT	Fm-3m	BiF_3	$a = 587.06(1)$	63.9	19.3	16.9	99.9
			NiZn-LT	P4/mmm	AuCu	$a = 412.19(5)$ $c = 297.82(7)$	Phase not found			
H13	$Ni_{66}Sn_{11.5}Zn_{22.5}$	800, 18d	(Ni)	Fm-3m	Cu	$a = 361.58(2)$	70.2	3.2	26.7	101.8
			NiZn-LT	P4/mmm	AuCu	$a = 398.71(3)$ $c = 314.49(3)$	63.5	15.7	20.8	101.3
H16	$Ni_{40}Sn_{44}Zn_{16}$	800, 18d	τ2	Cmcm	Ni_2GaGe	$a = 414.323(6)$ $b = 1260.13(2)$ $c = 1164.18(2)$	Not measured			
			(Sn)	I41/amd	β-Sn	$a = 583.33(4)$ $c = 31.18(3)$				
700 °C										
A1	$Ni_{80}Sn_5Zn_{15}$	700, 20d	(Ni)	Fm-3m	Cu	$a = 358.445(5)$	76.9	2.2	20.9	99.2
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 367.59(1)$	Phase not found			
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.34(3)$ $c = 423.16(4)$	73.5	21.8	4.7	100.6
A2	$Ni_{80}Sn_{10}Zn_{10}$	700, 20d	(Ni)	Fm-3m	Cu	$a = 358.063(4)$	83.5	2.6	13.9	99.4
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.322(9)$ $c = 423.04(1)$	74.1	22.7	3.2	101.3
A3	$Ni_{80}Sn_{15}Zn_5$	700, 20d	(Ni)	Fm-3m	Cu	$a = 357.07(7)$	88.2	3.3	8.5	98.7
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.9(1)$ $c = 423.9(2)$	74.3	23.7	2.0	101.1
B2	$Ni_{65}Sn_{10}Zn_{25}$	700, 20d	NiZn-LT	P4/mmm	AuCu	$a = 382.8(1)$ $c = 332.2(2)$	59.3	7.3	33.4	100.0
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 526.7(1)$ $c = 423.6(2)$	72.0	21.1	6.9	101.9
B3	$Ni_{65}Sn_{20}Zn_{15}$	700, 20d	NiZn-LT	P4/mmm	AuCu	$a = 384.30(7)$ $c = 320.1(1)$	61.0	15.3	23.7	99.8
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.7(8)$ $c = 418.6(7)$	72.4	21.7	5.9	100.8
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.21(5)$ $c = 517.13(8)$	61.1	32.6	6.3	100.9
B4	$Ni_{65}Sn_{25}Zn_{10}$	700, 20d	NiZn-LT	…	…	Phase not found	61.7	16.7	21.6	100.8
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.98(4)$ $c = 423.98(4)$	71.4	21.2	7.4	100.2
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.39(3)$ $c = 517.28(4)$	61.1	32.5	6.4	100.9
B5	$Ni_{65}Sn_{30}Zn_5$	700, 20d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 528.22(2)$ $c = 423.87(3)$	71.4	23.3	5.3	101.1
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.203(6)$ $c = 517.98(1)$	60.9	33.8	5.3	101.1
B6	$Ni_{65}Sn_7Zn_{28}$	700, 25d	(Ni)	Fm-3m	Cu	$a = 364.5(1)$	69.8	2.5	27.8	102.3
			NiZn-LT	P4/mmm	AuCu	$a = 385.41(4)$ $c = 330.60(6)$	59.7	4.6	35.9	101.9
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.03(6)$ $c = 421.7(1)$	71.6	20.2	8.3	102.2
C1	$Ni_{50}Sn_{45}Zn_5$	700, 17d	Ni_3Sn_2-HT	P63/mmc	BiF_3	$a = 407.94(9)$ $c = 513.96(2)$	51.2	44.5	4.3	101.1
			τ2	Cmcm	Ni_2GaGe	$a = 418.43(3)$ $b = 1233.1(1)$ $c = 1183.7(1)$	48.5	43.8	7.7	101.3
			Ni_3Sn_4	C2/m	Ni_3Sn_4	$a = 1233.0(7)$ $b = 407.58(3)$ $c = 511.73(3)$ $\beta = 105.98(5)$	44.8	55.0	0.2	101.3
			(Sn)	I41/amd	β-Sn	$a = 592.44(5)$ $c = 326.99(3)$	Phase not found			
C2	$Ni_{50}Sn_{35}Zn_{15}$	700, 17d	NiZn-HT	Pm-3m	CsCl	$a = 309.7(1)$	45.7	17.3	37.0	100.0
			τ2	Cmcm	Ni_2GaGe	$a = 414.866(4)$ $b = 1257.19(1)$ $c = 1164.93(1)$	49.3	36.7	13.9	100.6
C3	$Ni_{50}Sn_{25}Zn_{25}$	700, 17d	NiZn-HT	Pm-3m	CsCl	$a = 294.04(4)$	48.2	14.7	37.1	100.0
			τ2	Cmcm	Ni_2GaGe	$a = 414.61(5)$ $b = 1256.64(2)$ $c = 1166.21(2)$	50.6	35.5	13.8	102.3
C4	$Ni_{50}Sn_{15}Zn_{35}$	700, 17d	NiZn-HT	Pm-3m	CsCl	$a = 293.674(3)$	49.3	12.7	37.9	100.4
			τ2	Cmcm	Ni_2GaGe	$a = 415.41(8)$ $b = 1244.2(3)$ $c = 1173.8$	Phase not found			
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.48(1)$ $c = 517.03(2)$	55.5	35.2	9.3	101.7
C5	$Ni_{50}Sn_5Zn_{45}$	700, 17d	NiZn-LT	P4/mmm	AuCu	$a = 394.79(1)$ $c = 316.411(0)$	51.6	5.2	43.2	99.8
D1	$Ni_{35}Sn_{60}Zn_5$	700, 15d	τ2	Cmcm	Ni_2GaGe	$a = 413.2(2)$ $b = 1241.8(5)$ $c = 1169.8(6)$	47.3	43.6	9.1	100.8
			Ni_3Sn_4	C2/m	Ni_3Sn_4	$a = 1244.3(4)$ $b = 408.32(1)$ $c = 521.49(2)$ $\beta = 105.37(1)$	42.4	56.5	1.2	101.1
			τ1	…	…	…	34.8	46.6	18.5	100.0
			(Sn)	I41/amd	β-Sn	$a = 583.8(2)$ $c = 318.41(10)$	0.3	99.0	0.7	101.2
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.25(1)$ $c = 518.1(2)$	Phase not found			
D2	$Ni_{35}Sn_{50}Zn_{15}$	700, 15d	τ2	Cmcm	Ni_2GaGe	$a = 414.320(7)$ $b = 1260.56(2)$ $c = 1163.63(2)$	44.5	43.5	12.0	101.7
			τ1	…	…	…	39.5	44.7	15.8	101.4
			τ3	…	…	Phase not found	37.2	40.7	22.1	101.1
			(Sn)	I41/amd	β-Sn	$a = 582.73(8)$ $c = 318.35(5)$	0.6	96.5	2.9	100.2
D3	$Ni_{35}Sn_{40}Zn_{25}$	700, 15d	τ2	Cmcm	Ni_2GaGe	$a = 413.9(1)$ $b = 1254.1(5)$ $c = 1187.0(5)$	45.9	42.6	11.4	101.1
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.59(2)$	34.7	42.8	22.5	100.2
			Ni_3Zn_{14}	…	…	Phase not found	15.9	4.2	79.9	96.9
			(Sn)	…	…	Phase not found	0.0	99.2	0.8	100.4
D4	$Ni_{35}Sn_{30}Zn_{35}$	700, 15d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.43(2)$	37.6	34.9	27.4	100.8
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 891.21(2)$	22.2	3.1	74.7	99.4
			(Sn)	…	…	Phase not found	0.9	96.0	3.1	101.3
			τ2	Cmcm	Ni_2GaGe	$a = 418.93(4)$ $b = 1244.3(2)$ $c = 1167.2(1)$	Phase not found			
D5	$Ni_{35}Sn_{20}Zn_{45}$	700, 15d	τ2	Cmcm	Ni_2GaGe	$a = 417.39(9)$ $b = 1247.6(3)$ $c = 1184.2(3)$	46.6	38.1	15.3	102.1
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 890.56(3)$	24.7	3.6	71.7	99.1
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.383(9)$	Phase not found			

Table 2 (*continued*)

Sample name	Nominal composition, at%	Heat treatment, °C & days	Phases	Space group	Structure type	Unit cell parameter (pm)	WDS analysis			
							Ni, at%	Sn, at%	Zn, at%	Σ wt%
D6	$Ni_{35}Sn_{10}Zn_{55}$	700, 15d	NiZn-HT	Pm-3m	CsCl	$a = 294.537(3)$	43.0	18.6	38.4	100.3
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 887.99(2)$	26.9	3.2	69.9	99.4
D7	$Ni_{35}Sn_5Zn_{60}$	700, 15d	NiZn-HT	Pm-3m	CsCl	$a = 292.630(4)$	44.5	12.2	43.3	100.6
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 885.46(1)$	28.4	2.8	68.8	98.0
E1	$Ni_{15}Sn_5Zn_{80}$	700, 17d	Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.42(1)$	17.0	1.8	81.2	99.2
			Sn	I41/amd	β-Sn	$a = 582.96(5)$ $c = 317.98(5)$	0.3	90.2	9.4	103.1
E2	$Ni_{15}Sn_{25}Zn_{60}$	700, 17d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 884.38(7)$	34.8	40.2	25.0	100.0
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 889.92(1)$	19.8	3.0	77.2	99.4
			(Sn)	I41/amd	β-Sn	$a = 583.29(1)$ $c = 318.24(1)$	0.4	97.0	2.6	101.0
E3	$Ni_{15}Sn_{45}Zn_{40}$	700, 17d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 882.77(2)$	35.6	39.3	25.1	101.0
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 887.44(2)$	15.6	3.8	80.6	96.1
			(Sn)	I41/amd	β-Sn	$a = 583.31(1)$ $c = 318.24(9)$	0.6	98.1	1.3	100.4
E4	$Ni_{15}Sn_{65}Zn_{20}$	700, 17d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.7(2)$	36.5	42.2	21.3	101.4
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 887.9(2)$	15.8	3.8	80.4	96.5
			(Sn)	I41/amd	β-Sn	$a = 583.13(1)$ $c = 318.21(6)$	0.1	99.0	0.9	100.7
			τ2	Cmcm	Ni_2GaGe	$a = 414.25(8)$ $b = 1260.4(2)$ $c = 1163.47(2)$	Phase not found			
E5	$Ni_{15}Sn_{75}Zn_{10}$	700, 17d	τ1	…	…	…	37.1	47.6	15.3	100.2
			Ni_3Zn_{14}	…	…	Phase not found	15.8	9.5	74.7	97.3
			(Sn)	I41/amd	β-Sn	$a = 583.49(2)$ $c = 318.34(2)$	0.1	99.2	0.7	100.1
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.2(1)$	Phase not found			
F1	$Ni_{58}Sn_{40}Zn_2$	700, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 408.14(1)$ $c = 515.94(3)$	Not measured			
F2	$Ni_{55}Sn_{39}Zn_6$	700, 18d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 409.676(7)$ $c = 517.28(1)$	57.0	42.2	0.8	101.0
F3	$Ni_{50}Sn_{39}Zn_{11}$	700, 18d	Ni_3Sn_4	C2/m	Ni_3Sn_4	$a = 1259.4(2)$ $b = 407.59(5)$ $c = 513.98(6)$ $ß = 105.1(1)$	45.3	54.6	0.1	101.7
			τ2	Cmcm	Ni_2GaGe	$a = 407.67(4)$ $b = 1247.2(2)$ $c = 1170.5(2)$	48.9	43.2	7.9	100.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 410.06(2)$ $c = 517.14(4)$	51.3	44.3	4.4	100.7
F4	$Ni_{48}Sn_{38}Zn_{14}$	700, 18d	τ2	Cmcm	Ni_2GaGe	$a = 414.88(5)$ $b = 1258.9(2)$ $c = 1164.88(1)$	47.5	38.7	13.7	100.9
F5	$Ni_{42}Sn_{38}Zn_{20}$	700, 18d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.628(9)$	38.0	38.0	24.0	100.8
			τ2	Cmcm	Ni_2GaGe	$a = 414.68(1)$ $b = 1259.31(4)$ $c = 1164.18(4)$	46.6	40.8	12.6	100.7
F6	$Ni_{37}Sn_{37}Zn_{26}$	700, 18d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.87(1)$	37.7	37.3	25.0	100.7
			τ1	…	…	…	41.1	44.3	14.6	101.0
F7	$Ni_{36}Sn_{37}Zn_{27}$	700, 18d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 884.3(1)$	37.6	37.6	24.9	94.6
			τ1	…	…	…	40.5	44.7	14.8	100.6
			(Sn)	I41/amd	β-Sn	$a = 583.9(1)$ $c = 318.42(10)$	0.4	97.7	2.0	100.5
G1	$Ni_{67}Sn_{26}Zn_7$	700, 27d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.67(3)$ $c = 423.67(3)$	72.5	22.0	5.5	101.0
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.78(2)$ $c = 517.06(3)$	61.2	32.7	6.1	100.5
G2	$Ni_{73}Sn_{15}Zn_{12}$	700, 27d	(Ni)	Fm-3m	Cu	$a = 360.161(0)$	72.1	2.5	25.4	99.3
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 366.67(0)$	72.6	5.7	21.7	100.6
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 526.663(0)$ $c = 422.603(0)$	72.7	20.8	6.5	100.7
G3	$Ni_{57}Sn_{29}Zn_{14}$	700, 27d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.6(1)$ $c = 517.4(1)$	57.6	36.3	6.1	101.0
			NiZn-HT	Pm-3m	CsCl	$a = 293.54(9)$	50.1	10.5	39.4	99.4
G4	$Ni_{57}Sn_{22}Zn_{21}$	700, 27d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.05(2)$ $c = 517.56(2)$	59.7	34.6	5.7	101.6
			NiZn-LT	P4/mmm	AuCu	$a = 394.46(6)$ $c = 317.16(10)$	52.0	7.6	40.4	99.4
G5	$Ni_{69}Sn_{12}Zn_{19}$	700, 27d	(Ni)	Fm-3m	Cu	$a = 360.33(6)$	71.6	2.2	26.2	101.0
			Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 526.46(9)$ $c = 422.48(7)$	72.4	19.7	7.9	101.8
			NiZn-LT	P4/mmm	AuCu	$a = 383.42(6)$ $c = 329.07(6)$	61.1	4.5	34.4	100.0
			Ni_3Zn	Pm-3m	$AuCu_3$	$a = 367.06(6)$	Phase not found			
G6	$Ni_{39}Sn_{31}Zn_{30}$	700, 27d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.07(1)$	36.8	36.7	26.4	101.6
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 888.0(2)$	20.7	3.1	76.2	99.6
			τ2	Cmcm	Ni_2GaGe	$a = 414.970(9)$ $b = 1258.45(3)$ $c = 1164.55(3)$	Phase not found			
G7	$Ni_{42}Sn_{28}Zn_{30}$	700, 27d	τ2	Cmcm	Ni_2GaGe	$a = 414.924(7)$ $b = 1257.80(2)$ $c = 1164.77(2)$	47.1	38.0	14.9	101.3
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 889.88(4)$	24.6	3.5	71.9	99.7
G9	$Ni_{66.5}Sn_{24.5}Zn_9$	700, 25d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.65(4)$ $c = 423.86(4)$	72.6	21.5	6.1	98.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 413.29(2)$ $c = 516.85(3)$	61.8	31.5	6.7	98.9
G12	$Ni_{70}Sn_{17}Zn_{13}$	700, 25d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 526.7(3)$ $c = 422.9(2)$	71.3	20.8	7.9	101.7
			NiZn-LT	P4/mmm	AuCu	$a = 400.3(2)$ $c = 315.7(2)$	61.1	8.9	30.0	102.2
			(Ni)	Fm-3m	Cu	$a = 338.3(3)$	Phase not found			
			(Ni)	Fm-3m	Cu	$a = 337.6(4)$	70.7	3.6	25.8	102.5
G15	$Ni_{68}Sn_{10}Zn_{22}$	700, 25d	Ni_3Sn-LT	P63/mmc	Mg_3Cd	$a = 527.05(3)$ $c = 423.03(2)$	72.0	19.9	8.3	101.1
			NiZn-LT	P4/mmm	AuCu	$a = 418.45(4)$ $c = 288.10(4)$	60.0	4.9	35.2	102.4
G17	$Ni_{59}Sn_{21}Zn_{20}$	700, 25d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.66(5)$ $c = 517.06(6)$	61.1	32.8	6.4	102.4
			NiZn-LT	P4/mmm	AuCu	$a = 395.92(6)$ $c = 315.67(6)$	55.4	10.3	34.4	101.7
			NiZn-LT	P4/mmm	AuCu	$a = 415.5(2)$ $c = 292.3(1)$	62.9	17.7	19.5	101.4
G21	$Ni_{63}Sn_{21}Zn_{16}$	700, 25d	Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 412.98(2)$ $c = 516.65(2)$	61.6	32.1	6.4	102.0
			Ni_3Sn-LT	P4/mmm	Mg_3Cd	$a = 567.39(2)$ $c = 404.4(2)$	Phase not found			
			τ2	Cmcm	Ni_2GaGe	$a = 414.60(1)$ $b = 1255.5(3)$ $c = 1167.2(3)$	52.0	35.3	12.7	101.0

(*continued on next page*)

Table 2 (*continued*)

Sample name	Nominal composition, at%	Heat treatment, °C & days	Phases	Space group	Structure type	Unit cell parameter (pm)	WDS analysis			
							Ni, at%	Sn, at%	Zn, at%	Σ wt%
H1	$Ni_{52}Sn_{24,5}Zn_{23,5}$	700, 30d	NiZn-HT	Pm-3m	CsCl	$a = 293.88(6)$	48.3	13.8	37.9	100.7
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.42(8)$ $c = 517.17(1)$	Phase not found			
			Ni_3Sn_4	C2/m	Ni_3Sn_4	$a = 1239.80(0)$ $b = 407.09(0)$ $c = 521.48(0)$ $\beta = 104.2(0)$	43.0	56.7	0.3	99.5
H2	$Ni_{40}Sn_{55}Zn_5$	700, 30d	(Sn)	I41/amd	β-Sn	$a = 583.069(0)$ $c = 318.106(0)$	0.2	98.8	1.0	99.5
			τ2	…	…	Phase not found	48.2	43.3	8.5	100.7
			τ1	…	…	…	33.8	47.7	18.5	99.9
H3	$Ni_{40}Sn_{50}Zn_{10}$	700, 30d	τ2	Cmcm	Ni_2GaGe	$a = 414.162(7)$ $b = 1261.02(2)$ $c = 1163.75(2)$	47.7	42.6	9.7	100.3
			(Sn)	I41/amd	β-Sn	$a = 583.39(5)$ $c = 318.16(4)$	0.1	98.2	1.6	99.6
			τ2	Cmcm	Ni_2GaGe	$a = 414.447(5)$ $b = 1260.21(2)$ $c = 1163.70(1)$	46.6	41.6	11.7	100.6
H4	$Ni_{40}Sn_{45}Zn_{15}$	700, 30d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.78(7)$	35.0	41.6	23.4	100.2
			(Sn)	I41/amd	β-Sn	$a = 583.30(3)$ $c = 318.25(2)$	0.1	97.8	2.1	99.9
			τ2	Cmcm	Ni_2GaGe	$a = 414.547(6)$ $b = 1259.81(2)$ $c = 1163.67(2)$	46.2	41.3	12.5	101.1
H5	$Ni_{40}Sn_{42}Zn_{18}$	700, 30d	τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.16(8)$	37.9	39.8	22.3	100.3
			(Sn)	I41/amd	β-Sn	$a = 581.90(3)$ $c = 318.70(2)$	0.3	97.4	2.4	100.2
			τ2	Cmcm	Ni_2GaGe	$a = 415.1(1)$ $b = 1256.0(4)$ $c = 1164.7(4)$	48.1	36.0	15.9	101.7
H6	$Ni_{40}Sn_{20}Zn_{40}$	700, 30d	NiZn-HT	Pm-3m	CsCl	$a = 293.763(4)$	42.5	21.9	35.7	101.5
			Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 889.5(3)$	25.4	3.1	71.5	101.3
			Ni_3Sn_2-HT	P63/mmc	$InNi_2$	$a = 411.08(1)$ $c = 517.09(3)$	56.2	37.0	6.8	100.6
H8	$Ni_{51}Sn_{25}Zn_{24}$	700, 30d	τ2	Cmcm	Ni_2GaGe	$a = 414.22(1)$ $b = 1255.30(3)$ $c = 1165.60(3)$	51.9	35.0	13.2	100.8
			NiZn-HT	Pm-3m	CsCl	$a = 294.437(3)$	48.2	14.2	37.6	100.3
			τ3	Pm-3m	$Ni_7Sn_9Zn_5$	$a = 883.7(1)$	36.7	36.5	26.8	100.9
H9	$Ni_{26}Sn_{22}Zn_{52}$	700, 30d	Ni_3Zn_{14}	I-43m	Cu_5Zn_8	$a = 891.1(1)$	22.5	3.5	74.0	102.1
			(Sn)	I41/amd	β-Sn	$a = 583.37(8)$ $b = 318.34(4)$	0.5	96.5	3.0	100.8

rate of 5 K/min. The Pt/Pt10Rh thermocouples (S-type) were calibrated with pure metals (Au, Ag, Sn and In) under the same conditions as described above.

4. Results and discussion

All phases occurring in Ni–Sn–Zn hitherto described in literature are summarized in Table 1. More than 60 alloy samples were prepared and annealed at different temperatures, i.e. at 700, 800 and 900 °C, respectively; for more information see Table 2. Samples were placed at compositions up to 75 at% Sn and 80 at% Zn according to the formation of the liquid phase close to the Sn–Zn binary system at the respective temperatures. Accordingly, the phase relationships of the Ni–Sn–Zn system were deduced for three isothermal sections at 700, 800 and 900 °C; the sections were constructed based on EPMA and XRD results and are shown in Figs. 1–3, respectively. In the diagrams, single-phase regions are shaded and three-phase fields are designated with roman numbers for which the legends can be found in Table 3. Tie lines evaluated by EPMA are indicated by solid lines whereas tie-lines deduced from XRD results only are indicated with dashed lines. DTA measurements served for the rough estimation of liquidus phase boundaries; the respective results are given in Table 4.

Fig. 1 shows the phase relations in Ni–Sn–Zn at 700 °C as an isothermal section. Six ternary solid solutions were found along with the Ni(Sn, Zn) solid solution. Additionally, two new ternary compounds, designated as τ2 and τ3 have been included. The stable ternary solid solutions Ni_3Sn-LT, Ni_3Sn_2-HT, Ni_3Sn_4, NiZn-LT, NiZn-HT, Ni_3Zn_{14} and Ni(Sn, Zn) are in good agreement with the constituent binary systems Ni–Sn [4] and Ni–Zn [2]. The Ni(Sn, Zn) solid solution is much wider along the Ni–Zn side than along Ni–Sn side. Considering the much closer chemical relationship of Ni and Zn compared to Ni and Sn this is not astonishing. All binary phases show a significant ternary solubility. While the monoclinic phase Ni_3Sn_4 dissolves a rather low amount of Zn (1–2 at%), the solubility of Sn in both, NiZn-LT and NiZn-HT, is noticeably high (up to 22 at% Sn). It is noteworthy that NiZn-HT containing dissolved Sn can be stabilized at lower temperatures by quenching. This is not possible with the pure binary phase NiZn-HT as reported by Murakami et al. [14].

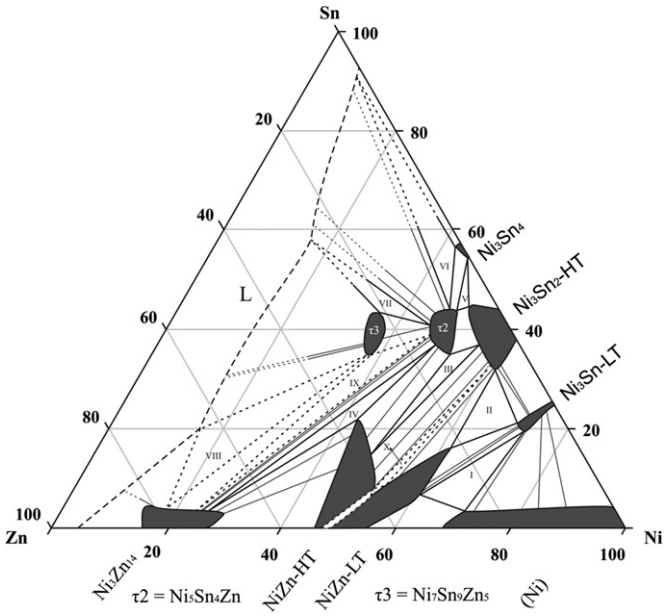

Fig. 1. Isothermal section at 700 °C; (1) ternary solid solutions and ternary compounds are shown shaded in gray; (2) measured tie-lines are shown by solid lines and estimated phase field boundaries and liquidus are shown by dashed lines.

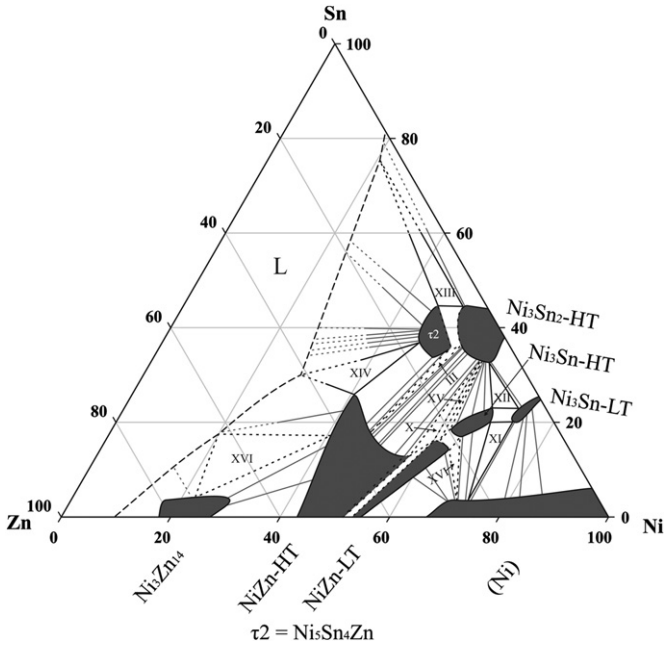

Fig. 2. Isothermal section at 800 °C; (1) ternary solid solutions and ternary compounds are shown shaded in gray; (2) measured tie-lines are shown by solid lines and estimated phase field boundaries and liquidus are shown by dashed lines.

Tie-lines and three-phase fields connecting the equilibrium phases are experimentally determined (for more details see Table 2) and drawn accordingly. In order to construct the full isothermal section at 700 °C, eight three-phase fields could be exactly determined by EPMA and two three-phase fields were estimated from XRD analyses only. The extension of the two-phase field between NiZn-LT and NiZn-HT from Ni–Zn into the ternary

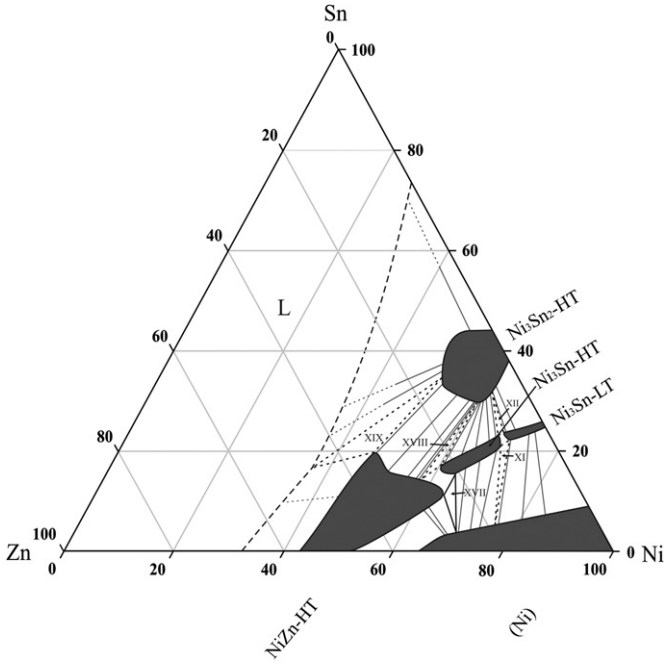

Fig. 3. Isothermal sections at 900 °C; (1) ternary solid solutions are shown shaded in gray; (2) measured tie-lines are shown by solid lines and estimated phase field boundaries and liquidus are shown by dashed lines.

Table 3
Legends of Phase field designation.

No.	Phase field designation
I	(Ni) + Ni_3Sn-LT + NiZn-LT
II	Ni_3Sn-LT + Ni_3Sn_2-HT + NiZn-LT
III	Ni_3Sn_2-HT + τ2 + NiZn-HT
IV	NiZn-HT + Ni_3Zn_{14} + τ2
V	Ni_3Sn_2-HT + Ni_3Sn_4 + τ2
VI	L + Ni_3Sn_4 + τ2
VII	L + τ2 + τ3
VIII	L + Ni_3Zn_{14} + τ3
IX	Ni_3Zn_{14} + τ2 + τ3
X	Ni_3Sn_2-HT + NiZn-HT + NiZn-LT
XI	(Ni) + Ni_3Sn-HT + Ni_3Sn-LT
XII	Ni_3Sn-HT + Ni_3Sn-LT + Ni_3Sn_2-HT
XIII	L + Ni_3Sn_2-HT + τ2
XIV	L + Ni_3Zn_{14} + τ2
XV	Ni_3Sn-HT + Ni_3Sn_2-HT + NiZn-LT
XVI	(Ni) + Ni_3Sn-HT + NiZn-LT
XVII	(Ni) + Ni_3Sn-HT + NiZn-HT
XVIII	Ni_3Sn-HT + Ni_3Sn_2-HT + NiZn-HT
XIX	L + Ni_3Sn_2-HT + NiZn-HT

system is only estimated from other phase relations such as [Ni_3Sn-LT + Ni_3Sn_2-HT + NiZn-LT] and [Ni_3Sn_2-HT + τ2 + NiZn-HT]. There is no direct experimental evidence because a sample placed at $Ni_{50}Sn_5Zn_{45}$ did not show two-phases, neither in XRD nor in EPMA. However, NiZn-HT can undergo a martensitic transformation to the LT-modification [14] during quenching and the contrast in an SEM-BSE image is expected to be very low. Also the three-phase field [Ni_3Sn_2-HT + NiZn-HT + NiZn-LT] is a rough estimate along with the consideration of other phase relations.

Our most important result, however, is the discovery of two new ternary compounds in the ternary Ni–Sn–Zn system. The first one, designated τ2, was observed at 700 °C within composition ranges given by $Ni_{44-49}Sn_{37-44}Zn_{9-14}$. We decided to designate it shortly as Ni_5Sn_4Zn. The diffraction pattern of the τ2 phase is shown in Fig. 4. It represents the PXRD diagram of the sample $Ni_{40}Sn_{44}Zn_{16}$ together with the calculated patterns and the error from the Rietveld refinement. Additionally, small amounts of Sn could be observed in this sample. Moreover, small single crystals were picked from this sample in order to perform crystallographic studies on a single crystal diffractometer. The τ2 phase exhibits an orthorhombic crystal structure with $a = 415.2$ pm, $b = 1260.3$ pm, $c = 1165.7$ pm, space group *Cmcm*, Pearson symbol oC40; see also Table 2. The results will be published in detail [15], the ICSD CSD No. 421611 was already allocated. A very similar crystal structure was already described before by Bhargava and Schubert [16] for the compound Ni_2GaGe. It could be considered as the parent structure type. There are also structural similarities between the τ2 phase and the neighboring Ni_3Sn_2-HT solid solution although there is no

Table 4
DTA results of selected samples of Ni–Sn–Zn.

Sample Name	Nominal composition, at%	Heat treatment, °C & days	Rate of Heating K/min	Liquidus	
				Heating °C	Cooling °C
E1	$Ni_{15}Sn_5Zn_{80}$	700, 17 d	5	801	788
E2	$Ni_{15}Sn_{25}Zn_{60}$	700, 17 d	5	675	668
E3	$Ni_{15}Sn_{45}Zn_{40}$	700, 17 d	5	668	658
E4	$Ni_{15}Sn_{65}Zn_{20}$	700, 17 d	5	724	697
E5	$Ni_{15}Sn_{75}Zn_{10}$	700, 17 d	5	–*	689
D2	$Ni_{35}Sn_{50}Zn_{15}$	700, 15 d	5	977	955
D7	$Ni_{35}Sn_5Zn_{60}$	700, 15 d	5	936	936
H9	$Ni_{26}Sn_{22}Zn_{52}$	700, 30d	5	858	841

*Melting effect could not be observed.

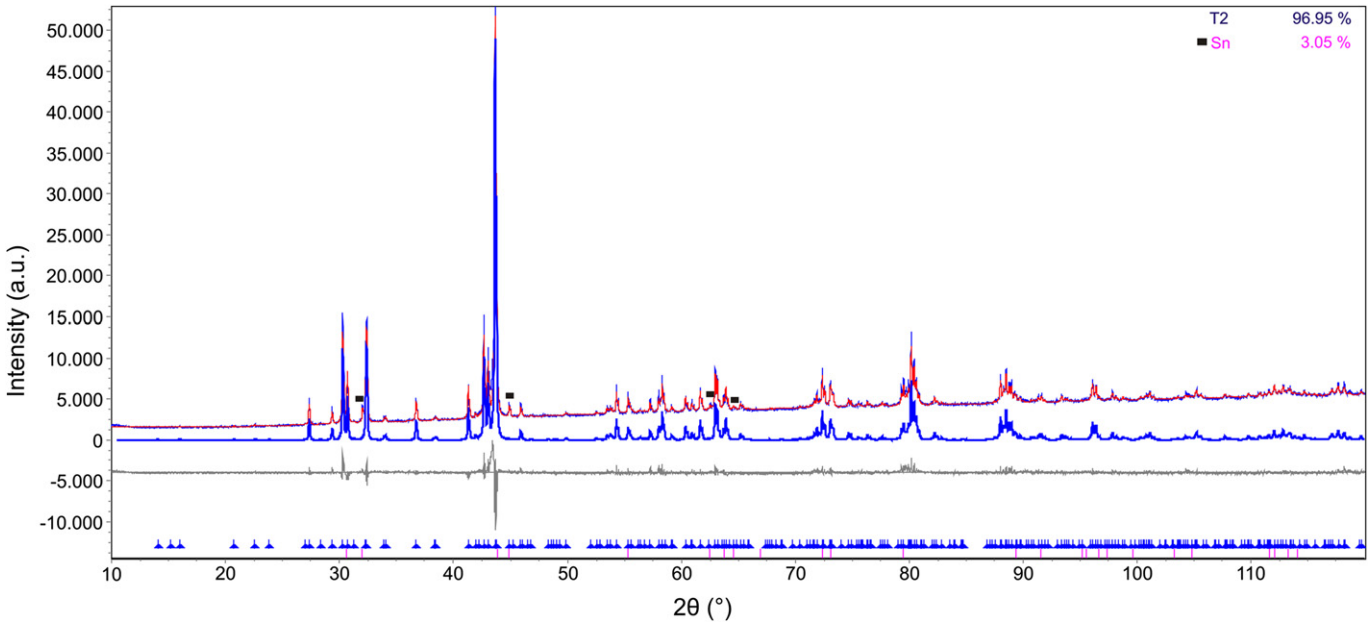

Fig. 4. Diffraction pattern (red-observed) for sample $Ni_{40}Sn_{44}Zn_{16}$ along with the refinement (blue-calculated) for τ2 phase. Sn positions are marked with filled rectangles.

direct structure/superstructure relation (for more details see Ref. [15]).

As can be seen from Fig. 1, the three-phase fields III, IV, V, VI, VII and IX contain τ2 as an equilibrium phase. Most of the equilibrium concentrations involved could be explicitly determined by EPMA measurements. From a metallographic point of view, primary crystallization of τ2 additionally proves it to be a stable phase at 700 °C; see as an example the BSE micrograph of $Ni_{40}Sn_{45}Zn_{15}$ in Fig. 5.

The second ternary compound found was designated τ3 or $Ni_7Sn_9Zn_5$. The homogeneity range at 700 °C can be given as $Ni_{35-38}Sn_{35-43}Zn_{23-27}$. The diffraction pattern of the τ3 phase, together with τ1 is shown in Fig. 6, representing the PXRD diagram of the sample $Ni_{37}Sn_{37}Zn_{26}$. Small single crystals were picked also from this sample to perform crystallographic studies on a single crystal diffractometer. The τ3 phase shows a cubic crystal structure with

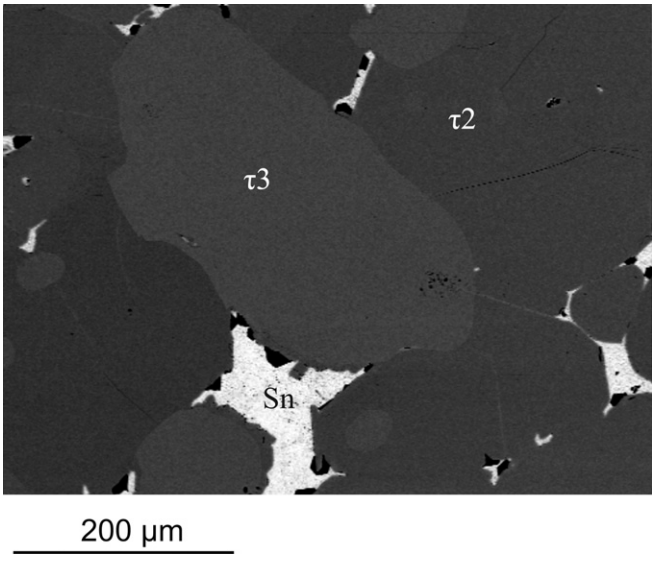

Fig. 5. Microstructure of $Ni_{40}Sn_{45}Zn_{15}$ alloy annealed at 700 °C for 30 days exhibiting primary crystallization of τ2 (dark), and secondary crystallization of τ3 (gray).

$a = 883.87$ pm, space group *Pm-3 m*, Pearson symbol cP74; see also Table 2. The results will be published in detail [17], the ICSD CSD No. 422044 was already allocated. An isotypic structure was not found in literature but a very similar crystal structure was already described before by Larsson et al. [18] for the quaternary compound $Sn_{8.7}(Ni_{0.5},Zn_{0.4}Cu_{0.1})_{10.4}$. The structure described in Ref. [18] contains additional Sn atom sites compared to τ3 and the exact distribution of the other atoms over the atomic sites was not given.

The PXRD pattern shown in Fig. 6 indicates the presence of an additional phase, designated τ1. It is a ternary phase found as well by metallographic investigations, e.g. in the sample $Ni_{37}Sn_{37}Zn_{26}$ shown in Fig. 7. Single crystal refinements resulted in a monoclinic structure which served as a model in order to describe the PXRD pattern shown in Fig. 6. However, low crystal quality and unsatisfactory results of the single crystal refinements did not allow a full crystallographic description yet. In addition, this ternary phase τ1 is not an equilibrium phase at 700 °C but probably at lower temperatures. A ternary compound was reported by Chang et al. [8] at 500 °C which may be identical to our τ1 phase. In the present work, it never appears in micrographs of corresponding alloys as direct crystallization but as formed during quenching from 700 °C or higher; see e.g. the crystallization of τ1 within τ3 shown in Fig. 7. Thus τ1 was not included in the isothermal section at 700 °C although it was found in several alloy samples by EPMA and XRD analysis, see also Table 2.

The isothermal section at 800 °C is shown in Fig. 2. An important change compared to the 700 °C isotherm is the disappearance of τ3 which is not anymore an equilibrium phase. As it can be seen in Table 2 the phase τ3 was found in several alloys annealed at 800 °C. However, it is only present in samples which had a liquid equilibrium phase at 800 °C. Two examples, $Ni_{35}Sn_{30}Zn_{35}$ and $Ni_{39}Sn_{31}Zn_{30}$, are shown in Fig. 8 and Fig. 9, respectively. It can be clearly seen that τ3 crystallized from the liquid phase present at the annealing temperature. The phase τ2 is still present at 800 °C but its homogeneity range is slightly changed and can be expressed as $Ni_{46-55}Sn_{34-44}Zn_{11-16}$. The micrographs in Figs. 8,9 both show the crystallization of τ2 phase from liquid at annealing temperature.

The mutual solubility of Sn and Zn in the respective binary phases is very similar to that described for the isothermal section at

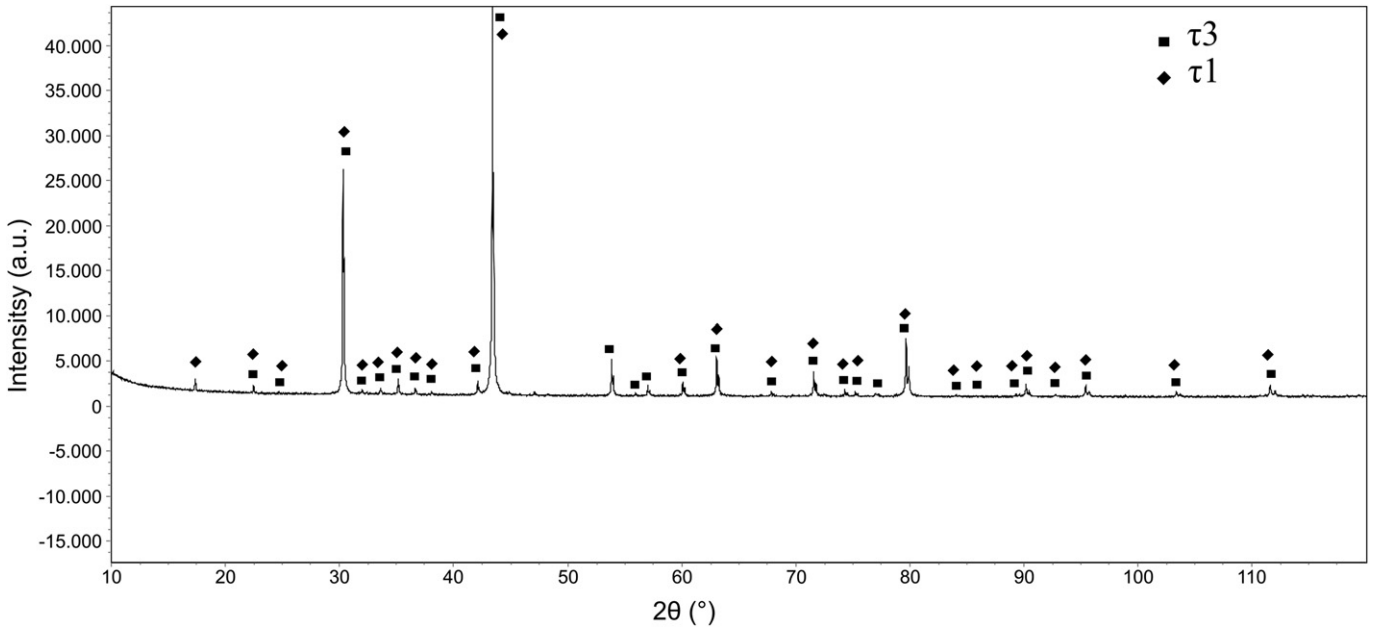

Fig. 6. Diffraction pattern for sample $Ni_{37}Sn_{37}Zn_{26}$ which exhibits τ3 and τ1 phase.

700 °C. Also at the higher temperature both, NiZn-HT and NiZn-LT show extended solid solubility into the ternary system. The NiZn-LT phase field becomes more narrow with rising temperature and the two-phase field between NiZn-LT and NiZn-HT could again only be estimated (see above). Fig. 9 shows the primary crystallization of NiZn-HT phase which is in equilibrium with τ2 and solidified liquid phase. In agreement with the binary phase diagram of Ni–Sn [4], the phase Ni_3Sn_4 is not present anymore at 800 °C. In the Ni-rich corner a seemingly ternary phase appears, designated Ni_3Sn-HT. A BSE micrograph of the sample $Ni_{67}Sn_{26}Zn_7$ shown in Fig. 10 represents the three-phase equilibrium XII [Ni_3Sn-HT + Ni_3Sn-LT + Ni_3Sn_2-HT]. In fact it is not a real ternary phase but the solid solution of Zn in the binary phase Ni_3Sn-HT which is thereby stabilized to lower temperatures.

Chang et al. [8] recently proposed an isothermal section at 800 °C for Ni-contents below 60 at%. Phase triangulation, ternary solid solubility of binary compounds and extension of the liquid phase are rather similar. However, there is no ternary τ2 phase but the homogeneity range of Ni_3Sn_2-HT into the ternary is shown much wider. This indicates that the change in crystal structure from Ni_3Sn_2-HT to τ2 was not recognized by the authors. It has to be mentioned that the main intensities of the PXRD diffraction patterns of both phases are actually coincident. Furthermore, the NiZn-LT phase is not indicated at all in the 800 °C isothermal section of Chang et al. [8] although they had calculated a binary Ni–Zn phase diagram which shows both, NiZn-HT and NiZn-LT, in equilibrium at 800 °C.

In their low temperature isotherms at 200 °C and 500 °C, two new phases τ1 and τ2, were included. No crystallographic information was provided for the readers; the authors identified them only as "un-indexed phases" in multiphase PXRD patterns shown in their Fig. 15 [7]. Comparing the peak patterns with the present results, the main diffraction peaks in τ2 of Chang et al. [8] may correspond to those of our τ3 phase.

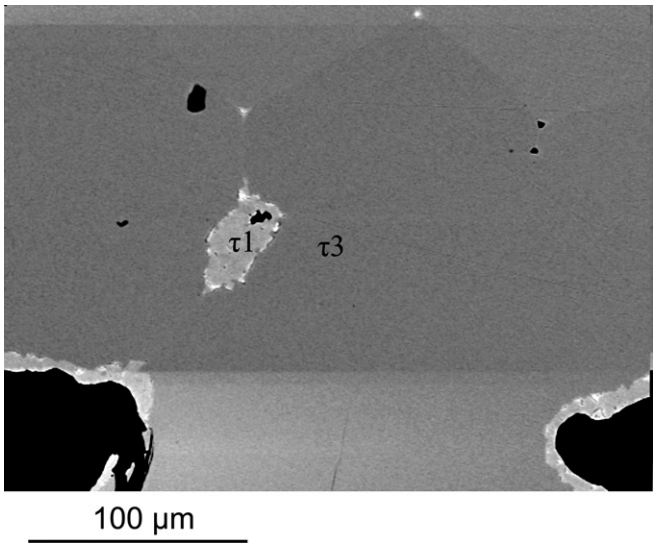

Fig. 7. Microstructure of $Ni_{37}Sn_{37}Zn_{26}$, annealed at 700 °C for 18 days, showing primary phase τ3 (gray), and intergrown τ1 (light gray).

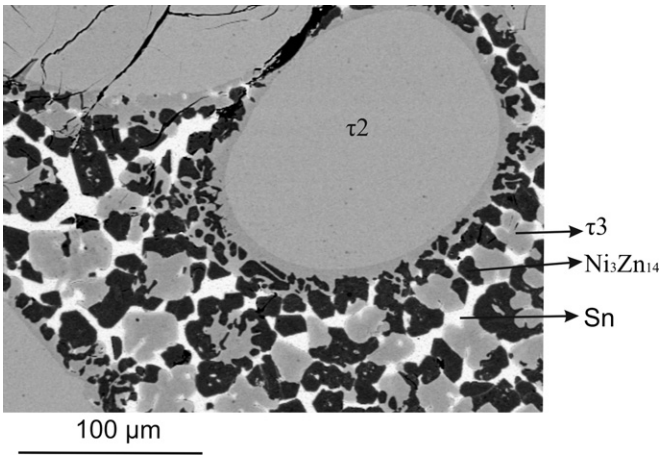

Fig. 8. Microstructure of $Ni_{35}Sn_{30}Zn_{35}$, annealed at 800 °C for 15 days, showing primary τ2 phase (primary crystal) and Ni_3Zn_{14} (dark), τ3 phase (light gray), and Sn (white) from the liquid.

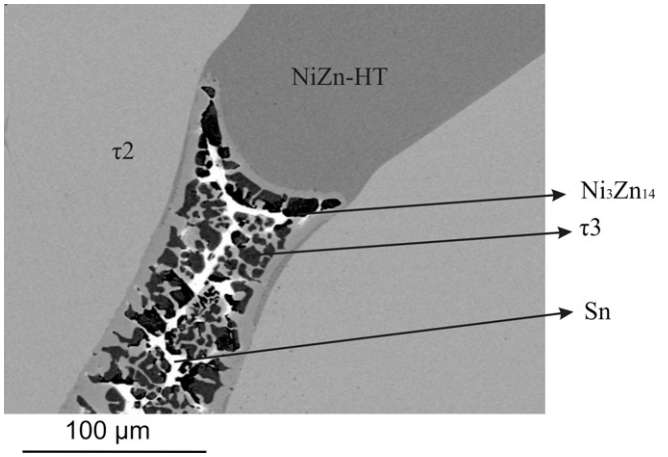

Fig. 9. Microstructure of $Ni_{39}Sn_{31}Zn_{30}$, annealed at 800 °C for 13 days, showing NiZn-HT (primary crystal, dark gray), τ2 phase (secondary crystal, light gray), and τ3 phase (light gray), Ni_3Zn_{14} (dark), and Sn (white), all three from the liquid.

The isothermal section at 900 °C is shown in Fig. 3; all XRD and EPMA results are listed in Table 2. The phase diagram includes four ternary solid solutions based on binary phases in agreement with the Ni–Sn [4] and Ni–Zn [2] binary phase diagrams. The ternary solid solution Ni(Sn, Zn) has a lower solubility for Sn (5.4 at%) while it has a comparatively high solubility for Zn (28.7 at%). NiZn-HT extends far into the ternary system, it dissolves up to 20 at% Sn. The Ni_3Sn_2-HT phase dissolves up to 14.6 at% Zn. As already described for the 800 °C isothermal section, Ni_3Sn-HT appears as a virtually ternary phase; it is, however, a binary phase stabilized to lower temperatures by dissolving Zn. NiZn-LT, Ni_3Zn_{14} and the phase τ2 obviously decompose below 900 °C and are not present anymore. Nevertheless, these phases were found by EPMA and XRD in samples annealed at 900 °C (see Table 2) since they crystallized during quenching from the liquid equilibrium phase. As an example, Fig. 11 shows a BSE micrograph of a sample with the nominal composition $Ni_{42}Sn_{28}Zn_{30}$. It reveals that τ2, Ni_3Zn_{14} and τ3 were formed during quenching from the liquid phase. Only Ni_3Sn_2-HT was present at the annealing temperature of 900 °C. Thus this sample is on a tie-line in the two-phase field Ni_3Sn_2-HT + Liquid. Only the three-phase field XVII, [(Ni) + Ni_3Sn-HT + NiZn-HT], could be explicitly determined by XRD and EPMA experiments. Other three-phase fields were estimated from results of samples placed at surrounding compositions; they are shown by dotted lines.

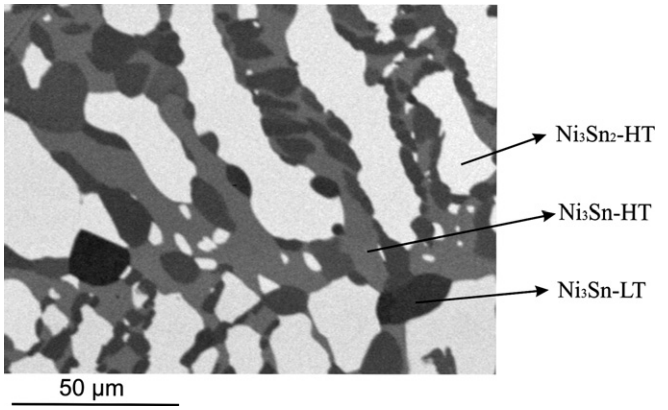

Fig. 10. Microstructure of $Ni_{67}Sn_{26}Zn_7$, annealed at 800 °C for 18 days, exhibiting Ni_3Sn-HT (light gray), Ni_3Sn_2-HT (white), and Ni_3Sn-LT (gray) ternary solutions.

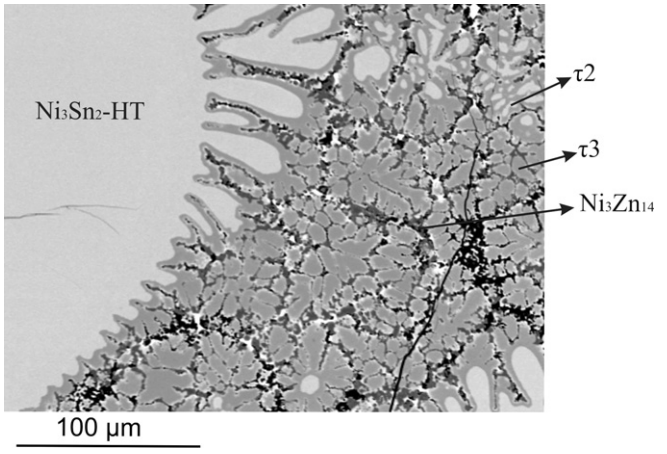

Fig. 11. Micrograph of sample with nominal composition $Ni_{42}Sn_{28}Zn_{30}$, annealed at 900 °C for 13 days, showing primary Ni_3Sn_2-HT (grain) and τ2 phase (light gray), Ni_3Zn_{14} (dark), and τ3 (gray) phase from the liquid.

5. Conclusions

Based on careful experimental investigation of 65 Ni–Sn–Zn alloy samples, annealed at 700, 800 and 900 °C, by means of XRD and EPMA it was possible to establish reliable isothermal sections at the respective temperatures. Additionally, a few samples were investigated by DTA in order to estimate the liquid phase regions. Two new ternary compounds, designated as τ2 and τ3, were found in the Zn-poor part of the 700 °C isothermal section. Their crystal structures could be established, and more detailed reports are currently in preparation for publication. Only τ2 is still present at 800 °C whereas no ternary compound could be found at 900 °C. The Ni_3Sn-HT phase can be obviously stabilized at lower temperatures by additions of Zn. This is indicated by the appearance of this phase in the ternary isotherms at 800 and 900 °C, respectively. As it has naturally no direct connection to the binary Ni–Sn at both temperatures it seems to be a ternary phase, however, its PXRD pattern could be fully described by the BiF_3 (DO_3) structure type and thus we rather consider it as a ternary solubility of the binary Ni_3Sn-HT phase.

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