

Table S1 Crystallographic data of unary and binary phases pertinent to the system Ti-Ni-Sn

Phase, Temperature range (°C)	Space group, Prototype	Lattice parameters (nm)			Comments/References
		a	b	c	
α -Ti, rt $\leq 882^\circ\text{C}$ ²¹	$P6_3/mmc$ Mg $\bar{3}m$	0.29506	-	0.46853	Ref.21
β -Ti, ht 882-1670°C ²¹	$Im\bar{3}m$ W	0.33065	-	-	Ref.21
ω -Ti, hp	$P6_3/mmm$ ω -Ti	0.4625	-	0.2813	Ref.21
Ni $\leq 1455^\circ\text{C}$ ²¹	$Fm\bar{3}m$ Cu	0.35241	-	-	Ref.21
α -Sn $\leq 13^\circ\text{C}$ ²¹	$Fd\bar{3}m$ C(diamond)	0.64892	-	-	Ref.21
β -Sn 13-232°C ²¹	$I4_1/amd$ β Sn	0.58318	-	0.31818	Ref.21
Ti ₃ Sn, hp	$Pm\bar{3}m$ Cu ₃ Au	0.4176(1)	-	-	Ref.28
Ti ₃ Sn $\leq 1670^\circ\text{C}$ ²¹	$P6_3/mmc$ Mg ₃ Cd	0.5921	-	0.4762	Ref.28
Ti ₂ Sn $\leq 1550^\circ\text{C}$ ²¹	$P6_3/mmc$ Ni ₂ In	0.4658	-	0.57	Ref.29
Ti ₂ Ni ₃ Sn ₃ $\leq 1510^\circ\text{C}$ ²¹	$P6_3/mcm$ Mn ₅ Si ₃	0.8049	-	0.5454	x = 0 ³⁰
	$P6_3/mcm$ Hf ₅ CuSn ₃	0.81440(1) 0.81389(9) 0.8128(2) 0.8135(4)	- - - -	0.555922(9) 0.55677(3) 0.5552(4) 0.5551(2)	x = 0.96 [*] SC x = 1 [*] XPD x=1 ³¹ x=1, 1073K ⁴
Ti ₆ Sn ₅ , ht 790-1490°C ²¹	$P6_3/mmc$ Ti ₆ Sn ₅	0.9248	-	0.569	Ref.32
Ti ₆ Sn ₅ ,rt $\leq 790^\circ\text{C}$ ²¹	$Immm$ Ti ₆ Sn ₅	0.5735	0.9144	1.6930	Ref.33
Ti ₂ Sn ₃ $\leq 751^\circ\text{C}$ ²¹	$Cmca$ Ti ₂ Sn ₃	0.59556(4)	1.9964(2)	0.70281(5)	Ref.34
Ti ₂ Ni $\leq 984^\circ\text{C}$ ²¹	$Fd\bar{3}m$ Ti ₂ Ni	1.1307	-	-	Ref.35
TiNi, ht 630-1310 °C ²¹	$Pm\bar{3}m$ CsCl	0.3015	-	-	Ref.36
(Ti _{1-x} Ni _x) _{1-y} Sn _y TiNi martensite	$P12_1/m1$ TiNi	0.30258(6) 0.2884(2)	- 0.4110(2)	- 0.4665(3)	x = 0.532, y = 0.06 [*] Ref.37
TiNi ₃ $\leq 1380^\circ\text{C}$ ²¹	$P6_3/mmc$ TiNi ₃	0.5101(2)	-	0.8322(2)	[38]
(Ti _{1-x} Sn _x)Ni ₃ Ni ₃ Sn, ht 850-1170°C ²¹	$Fm\bar{3}m$ BiF ₃	0.5144(2) 0.598(1)	- -	0.8393(3) -	x = 0.27 [*] Ref.39
Ni ₃ Sn, rt $\leq 975^\circ\text{C}$ ²¹	$P6_3/mmc$ Mg ₃ Cd	0.5305	-	0.4254	Ref.40
Ni ₃ Sn, hp	$Pm\bar{3}m$ Cu ₃ Au	0.3738(1)	-	-	Ref.28
Ni _{1.5} Sn, ht 600-1250°C ²¹	$P6_3/mmc$ Ni ₂ In	0.40781	-	0.5197	Ref.37
Ni ₃ Sn ₂ , rt $\leq 600^\circ\text{C}$ ²¹	$Pnma$ Ni ₃ Sn ₂	0.71240(9)	0.51970(4)	0.81562(7)	Ref.41
Ni ₃ Sn ₄ $\leq 795^\circ\text{C}$ ²¹	$C12/m1$ Ni ₃ Sn ₄	1.2214(6)	0.4060(2)	0.5219(3)	Ref.42
NiSn ^a	$Pbam$ NiSn	2.4452(8)	0.5200(2)	0.4091(2)	Ref.43

[*] - this work

Table S2. EPMA data for the samples annealed at different temperatures (SEM images are shown on Figures 6-8).

Figure 6					Figure 7					Figure 8				
Phase ^a	at%			SEM (Δ^b) HT ^c	Phase ^a	at%			SEM (Δ), °C	Phase ^a	at%			SEM (Δ), °C
	Ti	Ni	Sn			Ti	Ni	Sn			Ti	Ni	Sn	
τ_2	25.2	49.7	25.1	Fig. 6a	τ_2	24.7	50.5	24.8	Fig. 7a	τ_2	24.4	46.8	28.8	Fig. 8a
τ_2'	18.2	58.1	23.7	(-)	Ni_3Sn_2	0.9	59.2	39.9	(-)	Ni_3Sn_4	0.1	44.7	55.2	(-)
Ni_3Sn_2	2.0	62.4	35.6	as-cast					950°C	(Sn)	0.2	0.6	99.2	as-cast
τ_1	31.2	37.3	31.5	Fig. 6b	τ_1	32.8	34.0	33.2	Fig. 7b	τ_2	24.5	50.2	25.3	Fig. 8b
$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.0	7.3	37.7	(-)	Ti_6Sn_5	54.0	2.2	43.8	(u)	Ni_3Sn_2	0.5	57.9	41.6	(-)
(Sn)	1.1	0.8	98.1	as-cast	(Sn)	0.4	0.5	99.1	950°C	Ni_3Sn_4	-0.1	43.9	56.2	as-cast
										(Sn)	0.1	31.5	68.4	
τ_1	32.1	35.6	32.3	Fig. 6c	τ_1	33.1	33.6	33.3	Fig. 7c	τ_2	24.9	49.6	25.5	Fig. 8c
$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	56.3	6.2	37.5	(-)	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	57.9	5.9	36.2	(f)	Ni_3Sn_2	0	56.2	43.8	(b)
Ti_6Sn_5	52.8	4.4	42.8	as-cast	Ti_6Sn_5	54.3	2.3	43.4	950°C	Ni_3Sn_4	0	46.8	53.2	700°C
(Sn)	0.5	0.8	98.7											
τ_4	8.3	79.8	11.9	Fig. 6d	τ_4	6.2	77.4	16.4	Fig. 7d	τ_2	25.8	48.2	26.0	Fig. 8d
Ni_3Sn	1.1	75.1	23.8	(-)	Ni_3Sn	1.0	75.8	23.2	(g)	Ni_3Sn_4	0.1	45.2	54.7	(-)
(Ni)	6.5	85.0	8.5	as-cast	(Ni)	4.2	86.8	9.0	950°C	(Sn)	0.4	1.9	97.7	as-cast
Ni_3Sn_2	1.3	63.8	34.9	Fig. 6e	τ_4	8.1	75.5	16.4	Fig. 7e	τ_1	32.6	34.1	33.3	Fig. 8e
Ni_3Sn	3.9	71.9	24.2	(-)	Ni_3Sn_2	0.4	63.4	36.2	(h)	τ_2	25.2	49.2	25.6	(c)
e	7.5	71.7	20.8	as-cast	Ni_3Sn	1.2	73.3	25.5	950°C	Ni_3Sn_4	0	46.5	53.5	600°C
τ_2	23.3	52.3	24.4	Fig. 6f	τ_2	23.0	52.3	24.7	Fig. 7f	τ_2	18.9	57.0	24.1	Fig. 8f
Ni_3Sn_2	2.1	62.4	35.5	(-)	Ni_3Sn_2	0.8	61.5	37.7	(i)	Ni_3Sn_2	1.8	62.5	35.7	(i)
e	10.1	68.9	21.0	as-cast	TiNi_3	21.3	75.1	3.6	950°C	TiNi_3	19.6	75.3	5.1	1100°C
τ_2	33.3	51.6	15.1	Fig. 6g	τ_2	37.3	51.5	11.2	Fig. 7g	τ_1	31.4	37.3	31.3	Fig. 8g
TiNi	39.8	54.7	5.5	(-)	TiNi_3	25.1	74.8	0.1	(j)	Ti_6Sn_5	53.0	4.4	42.6	
e	36.0	61.1	2.9	as-cast	TiNi	41.9	52.6	5.5	950°C	(Sn)	0.7	0.1	99.2	as-cast
τ_2	29.4	49.4	21.2	Fig. 6h	τ_2	40.3	50.2	9.5	Fig. 7h	τ_1	32.6	34.5	32.9	Fig. 8h
τ_2'	41.6	49.9	8.5	(-)	τ_3	41.5	40.4	18.1	(k)	Ti_2Sn_3	39.9	0.5	59.6	(-)
τ_3	44.3	40.1	15.6	as-cast	TiNi	44.4	50.0	5.6	950°C	(Sn)	1.3	0.6	98.1	700°C
TiNi	~46	50	4											
e	50.6	34.5	14.9											
τ_2	27.7	48.2	24.1	Fig. 6i	τ_2	27.5	48.6	23.9	Fig. 7i	τ_2	28.9	48.9	22.2	Fig. 8i
τ_3	43.7	40.1	16.2	(-)	τ_3	41.8	40.0	18.2	(l)	τ_3	41.2	40	18.8	(l)
$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.4	11.7	32.9	as-cast	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.5	10.9	33.6	950°C	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.6	11.1	33.3	1050°C
TiNi	43.1	49.5	7.4											
e	49.2	37.0	13.8											
$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.7	9.7	34.6	Fig. 6j	τ_1	32.8	34.7	32.5	Fig. 7j	τ_2	37.8	49.5	12.7	Fig. 8j
e	41.0	29.6	29.4	(-)	τ_2	28.1	46.3	25.6	(m)	τ_3	43.8	40.1	16.1	(-)
τ_2	27.8	46.5	25.7	as-cast	Ti_5NiSn_3	55.2	11.2	33.6	950°C	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.6	11.4	33.0	as-cast
										TiNi	44.8	49.2	6.0	
										e	49.1	38.0	12.9	
$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	56.2	10.7	33.1	Fig. 6k	τ_3	43.8	40.1	16.1	Fig. 7k	τ_1	30.9	38.0	31.1	Fig. 8k
e	48.8	38.2	13.0	(-)	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	56.6	10.6	32.8	(n)	τ_2	27.5	45.3	27.2	(-)
				as-cast	TiNi	47.5	49.9	2.6	950°C	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	55.8	10.1	34.1	as-cast
										(Sn)	0.5	1.4	98.1	
$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	56.5	11.0	32.5	Fig. 6l	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	56.2	11	32.8	Fig. 7l	τ_3	45.0	40.3	14.7	Fig. 8l
Ti_3Sn	72.9	2.4	24.7	(-)	Ti_3Sn	73.8	1.2	25.0	(o)	$\text{Ti}_5\text{Ni}_x\text{Sn}_3$	57.0	7.2	35.8	(-)
e	57.4	33.0	9.6	as-cast	TiNi	49.6	48.3	2.1	950°C	e	49.9	36.2	13.9	as-cast
Ti_3Sn	74.2	1.6	24.2	Fig. 6m	TiNi	50	50	0	Fig. 7m	τ_2	23.7	51.3	25.0	Fig. 8m
Ti_2Ni	64.8	33.4	1.8	(-)	Ti_2Ni	65.4	33.6	1.0	(p)	Ni_3Sn_2	0.6	59.1	40.3	(-)
TiNi	50.1	49.6	0.3	as-cast	Ti_3Sn	74.4	1.5	24.1	950°C	e	6.3	57.6	36.1	as-cast
Ti_3Sn	79.1	1.0	19.9	Fig. 6n	Ti_3Sn	77.7	1.0	21.3	Fig. 7n	τ_1	30.8	38.1	31.1	Fig. 8n
Ti_2Ni	66.0	33.1	0.9	(-)	Ti_2Ni	66.3	33.1	0.6	(q)	τ_2	26.8	46.3	26.9	(c)
(Ti)	83.6	5.8	10.6	as-cast	(Ti)	86.4	5.5	8.1	950°C	Ni_3Sn_4	1.3	28.5	70.2	1100°C
τ_2	25.1	49.4	25.5	Fig. 6o	τ_2	24.9	49.9	25.2	Fig. 7o	τ_2	29.5	49.9	20.6	Fig. 8o
Ni_3Sn_2	0.4	56.8	42.8	(-)	Ni_3Sn_2	0.2	56.9	42.9	(s)	TiNi	41.3	50.8	7.9	(-)
Ni_3Sn_4	0.4	46.1	53.5	as-cast	(Sn)	0.07	0.95	98.98	950°C					as-cast
(Sn)	0.2	0.1	99.7											

^a binary solid solutions ($\text{Ti}_{1-x}\text{Ni}_x$)_{1-y} Sn_y and $\text{Ti}_{1-x}\text{Sn}_x\text{Ni}_3$ are denoted as TiNi and TiNi_3 , respectively; ^b three-phase equilibria; ^c heat treatment.

Table S3. X-ray Rietveld refinement for τ_1 -TiNiSn and τ_2 -Ti_{1+y}Ni_{2-x}Sn_{1-y}

Parameter/compound	τ_1 -TiNiSn	τ_2 -Ti _{1+y} Ni _{2-x} Sn _{1-y}		
Space group, Prototype	$F\bar{4}3m$, MgAgAs	$Fm\bar{3}m$, MnCu ₂ Al -		
Composition:				
EPMA, at%	Ti _{32.55} Ni _{34.90} Sn _{32.55}	Ti _{25.2} Ni _{49.7} Sn _{25.1}	Ti _{38.6} Ni _{50.7} Sn _{10.7}	Ti _{21.8} Ni _{53.7} Sn _{24.5}
x; y	0.928; 0.000	0.024; 0.002	-0.057; 0.566	-0.320; -0.058
Refinement; at%	Ti _{33.3} Ni _{33.3} Sn _{33.3}	Ti _{25.0} Ni _{50.0} Sn _{25.0}	Ti _{39.2} Ni _{50.0} Sn _{10.8}	Ti _{21.5} Ni _{53.5} Sn _{25.0}
x; y	1.000; 0.000	0.000; 0.000	0.000; 0.568	-0.301; -0.075
a [nm], Rietveld	0.593633(3)	0.60834(2)	0.60642(2)	0.607634(6)
a [nm], Ge standard	0.59349(1)	0.60854(3)	0.60605(5)	-
Reflections measured	15	15	18	16
R _i	3.61	2.14	4.05	3.91
R _F	1.80	2.35	5.32	3.21
R _{wp}	5.19	3.91	2.98	3.31
R _p	3.14	2.25	1.90	1.94
R _{exp}	2.38	2.09	2.44	2.25
Chi ²	4.75	3.51	1.49	2.17
Atom parameters:				
4a (0,0,0), occ ^a	4 Sn	4 Sn	1.73 Sn + 2.27 Ti	4 Sn
occ ^b	4.04(1) Sn	4.05(1) Sn	1.49(1) Sn+2.51 Ti	4.06(6) Sn
B _{iso}	0.71	0.28	0.49	0.42
4b (½,½,½), occ ^a	4.0 Ti	4 Ti	4 Ti	3.44 Ti+ 0.56 Ni
occ ^b	3.99(1)	4.02(1)	4.05(1)	3.48(3) Ti+0.52 Ni
B _{iso}	0.36	0.36	0.48	0.51
4c/8c (¼,¼,¼), occ ^a	4 Ni	8 Ni	8 Ni	8 Ni
occ ^b	4.00(1) Ni	7.96(2) Ni	7.85(7) Ni	8.03(8) Ni
B _{iso}	0.41	0.95	1.25	0.68
Secondary phases	Ni ₃ Sn ₄	-	-	Ni ₃ Sn ₂ +TiNi ₃

^a fixed after EPMA for final refinement; ^b refined occupancy