

Supplementary material

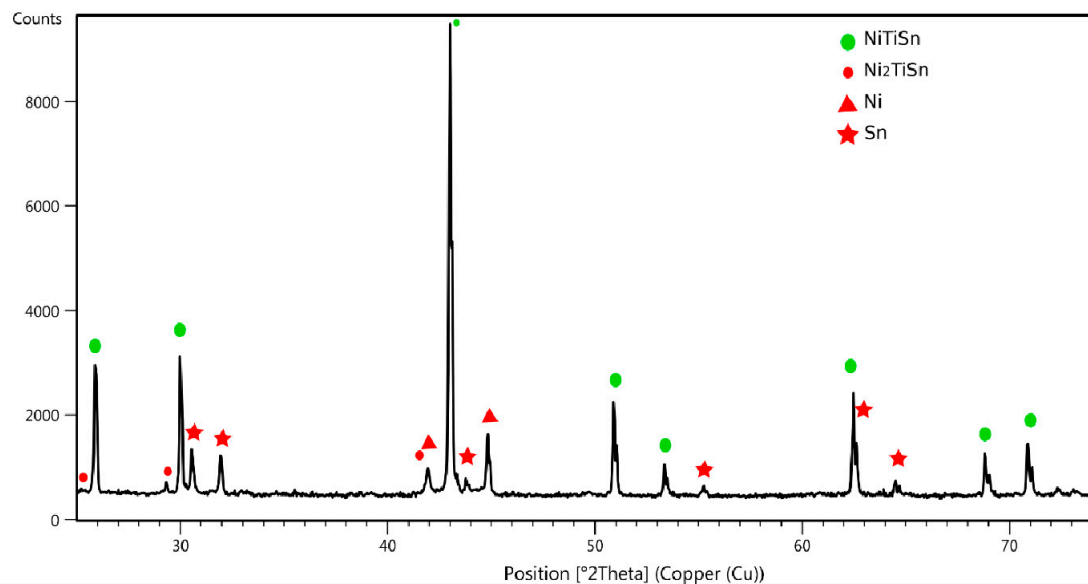


Figure S1. XRD pattern recorded after thermal treatment at 850 °C for 30 days of a mixture of Ni, Ti, Sn powders. NiTiSn has been formed as the major component (about 80 %) but amounts of secondary phases, Ni₂TiSn and unreacted elements, remain very important.

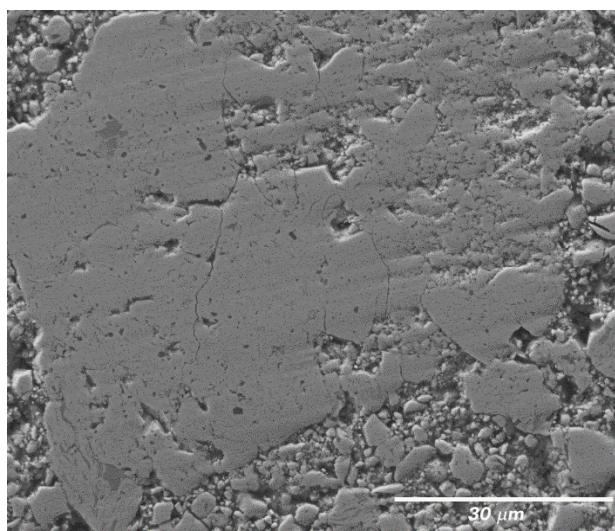


Figure S2. SEM image of a sample obtained at 800 rpm for 5 hours. Prior to observation, the powder was pressed into a pellet and polished. A small amount of dark zones with ternary compositions was observed that almost certainly results from NiTiSn and Ni₃Sn₄ superimposition.

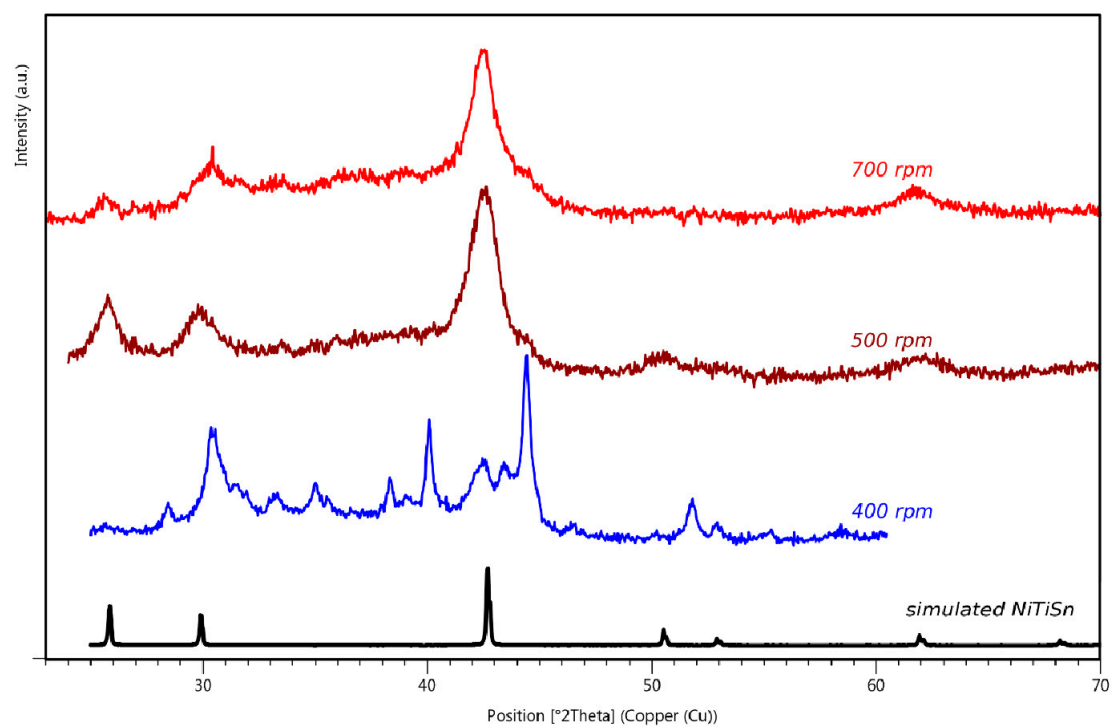


Figure S3. XRD patterns recorded for samples prepared by mechanical alloying for 14 hours.

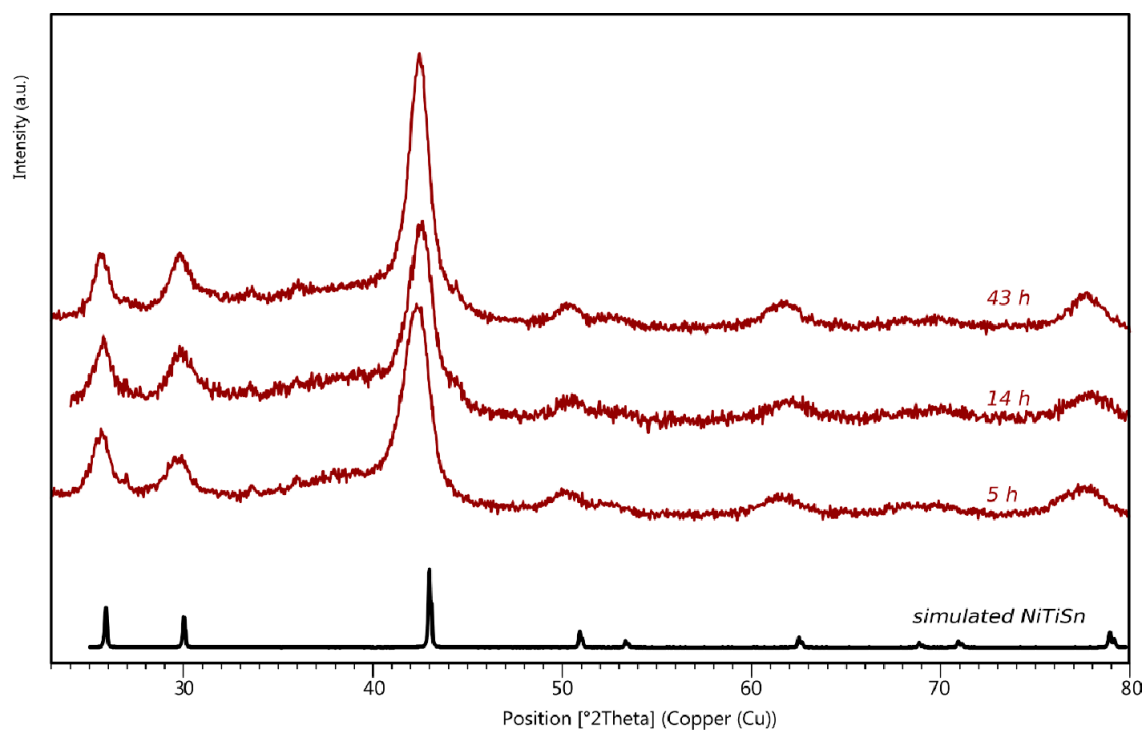


Figure S4. XRD patterns recorded for samples prepared by mechanical alloying at 500 rpm.

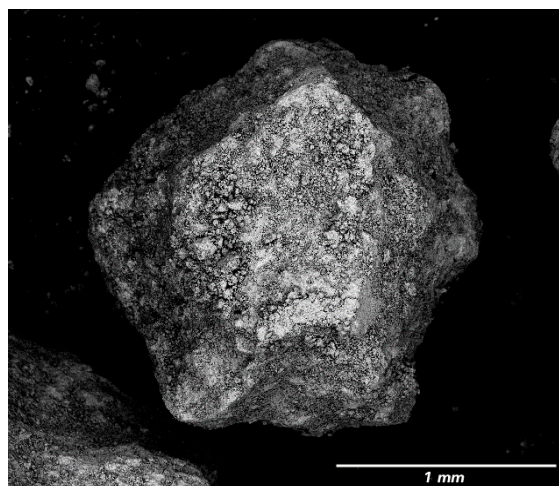


Figure S5. SEM image of a typical aggregate recovered in samples alloyed at 400 rpm.

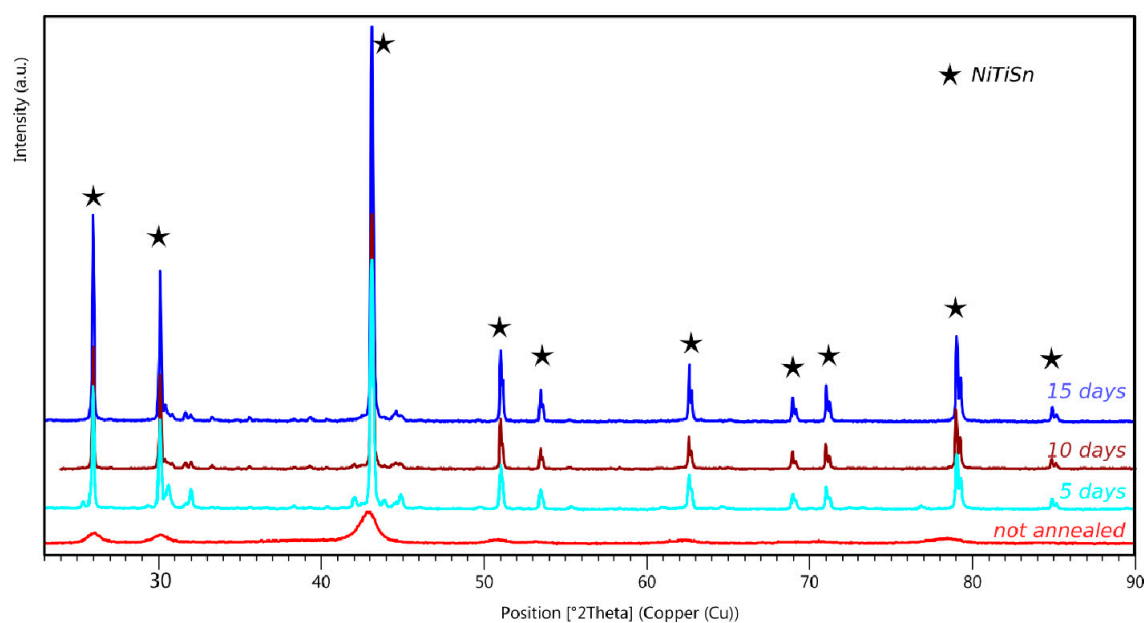


Figure S6. XRD patterns recorded for samples prepared by mechanical alloying at 700 rpm for 5 hours and submitted to subsequent annealing at 800 $^{\circ}\text{C}$.

Table S1. Indexation of diffraction peaks, 2θ angular positions and relative intensities for cubic compounds NiTiSn ($a = 5.93 \text{ \AA}$, $F\bar{4}3m$) and Ni₂TiSn ($a = 6.10 \text{ \AA}$, $Fm\bar{3}m$).

h	k	l	NiTiSn		Ni ₂ TiSn	
			2θ	Int.	2θ	Int.
1	1	1	26.0	34	25.3	17
0	0	2	30.1	46	29.3	5
0	2	2	43.1	100	41.9	100
1	1	3	51.1	16	49.5	8
2	2	2	53.5	11	51.9	2
0	0	4	62.6	15	60.7	15
1	3	3	69.0	6	66.8	3
0	2	4	71.1	13	68.8	2
2	2	4	79.1	27	76.4	26

Table S2. Enthalpies calculated for compounds in the NiTiSn system.

Phase	$\Delta_f H$ (kJ/mol of atom)				
	GGA-CASTEP	GGA VASP	GGA+U [61]	GGA+U [62]	Exp [67-75]
Ni ₃ Sn	-22.48	-20.12	-20.14	-23.83	-22.5 to -26.3
Ni ₃ Sn ₂	-30.31	-28.10	-29.52	-31.16	-28.1 to -38.5
NiSn	-28.18	-28.03	-28.03		
Ni ₃ Sn ₄	-27.77	-24.61	-25.43	-26.92	-24.0 to -31.4
Ni ₃ Ti	-49.59	-47.00	-41.90	-46.12	-42.2 to -46.5
Ni ₄ Ti ₃	-42.19				
NiTi	-40.68	-38.78	-30.91	-39.66	-33.1
NiTi ₂	-28.83	-27.05	-22.16	-27.79	
Ti ₂ Sn ₃	-32.88	-31.92	-31.92	-	
Ti ₆ Sn ₅	-37.82	-37.32	-37.32	-36.76	-43.4
Ti ₅ Sn ₃	-35.17	-34.90	-34.90	-33.58	
Ti ₂ Sn	-33.55	-32.77	-32.77	-32.61	
Ti ₃ Sn	-29.44	-29.25	-29.25	-29.04	
Ni ₂ Ti ₂ Sn	-49.89	-45.60	-42.80	-46.80	
Ni ₂ TiSn	-45.47	-43.21	-44.58	-60.01	-46.8
NiTiSn	-54.31	-52.79	-50.24	-68.99	-52.6
NiTi ₅ Sn ₃	-38.78	-36.96	-37.53	-37.44	

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