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New Peritectoid Reaction Identified at the MnSb Alloy

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The tunable Tc region of MnSb alloy (44 - 49 % at. Sb) was analyzed using OM, VSM, DSC, XRD, EDS and XRF characterization techniques. Thermal and magnetic analysis suggests the existence of a non reported irreversible reaction on heating, compatible to a reverse peritectoid transition $Mn_xSb \rightarrow Mn_2Sb + Mn_{x'}Sb$.

Keywords: *Magnetic materials, phase transformation, MnSb metals and alloys, manganese-antimony alloys, Curie Temperature, perictetoid transformation.*

1. Introduction

The MnSb alloy presents an interesting phase, on atomic percentage of Sb (%at.Sb) from 45% to 48%, with Curie Temperature (Tc) varying from 90 °C to 314 °C. The composition limits of the MnSb phase and the corresponding Tc varies significantly at the reported phase diagrams (1-6), these divergences are summarized at Table 1. The minimum limit of the MnSb phase varies from 40.0 to 46.0 %at.Sb, and the maximum limit goes from 49.0 to 50.5 %at.Sb. Also the temperature of peritectic (from 840 to 853 °C) and eutectic (from 568 to 574 °C) reactions are reported at different temperatures. These divergences can be in part related to temperature range evaluated, presence of oxidation, melting and heat treatment methods, and/or chemical composition analysis method.

2. Materials and Method

Eight samples with atomic percentage of Sb (%atSb), from 43% to 50%, were prepared with high purity elements (Sb - Alfa Aesar 99.99% and Mn Alfa Aesar 99.98%), were weighed on precision equipment and melted, under argon atmosphere, at electric arc furnace (EAF). Each sample was melted 6 times, inverting its position after each melt. The ingots were annealed at 500°C for 5 days, slowly cooled (1°C min^{-1}), named as "Rec", a part of the ingots were cut and annealed at 820 °C for 10 days and quenched and named as "TT". The ingots' chemical composition was checked at X-Ray Fluorescence (XRF) equipment, and the phases' stoichiometry at Scanning Electron Microscopy with Energy Dispersive Spectroscopy (EDS) equipment.

Also XRD (X-Ray Difractometer) with Rietveld method analysis, DSC (Differential Scanning Calorimeter), VSM (Vibratory Sample Magnetometer) and OM (Optical Microscope) equipments were used to characterize the samples.

3. Results and Discussion

The samples were identified in accord to its nominal composition, from "1 = 43% at Sb" to 8 = 50% at Sb, and

Table 1. MnSb's phase limits and temperature reactions

	Range (%atSb)	Range Tc (°C)	Peritectic	Eutectic	Temperature evaluation (°C)
Williams	40.0-50.0	? - 328	853	573	100-1240
Teramoto	46.0-49.7	117-319	?	?	400-900
Okamoto	45.0-49.0	90 - 314	840	570	0-940
Chen	45.5-50.0	?	843	574	500-915
Vanyarkho	45.5-49.0	?	841	568	400-920
Kainzbauer	45.5-50.5	?	830	566	300-940

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respective heat treatment (TT or Rec). This study was focused on the region of "tunable" Curie Temperature, the partial phase diagram, Fig. 1., locates the quenched (TT) and annealed (Rec) samples analyzed in this study.

Images obtained from OM, Fig. 1, evidenced a light gray phase named as "a" corresponding to Mn_xSb present on all samples, a dark phase (granular and stripes) named as "b" corresponding to Mn_2Sb present on TT_2, TT_3 and Rec_2 samples, and an almost white phase named as "c" - predominantly Sb, present on TT_8 and Rec_8 samples. EDS analysis nominally confirmed the composition of the phases. The other micrographics' images show basically the same phases.

The reported Curie temperature (Tc) x stoichiometry, on known phase diagrams[1-3], indicates higher Tc as the percentage of Sb increases. The measurement of composition at XRF and precision balance and their respective Tc do not converge to reported data, but do with EDS measures of the individual's phase, this can be explained by the first two are general measurements and the third is specific at MnSb phase. Giving evidences the Tc registered is exclusively related to Mn_xSb phase ("x" is the stoichiometry variation). The chemical composition of Mn_xSb measured at EDS, from 49.4% to 52.3 %at.Sb meaning "x" has a value between 1.02 and 0.91 ($1.02>x>0.91$) are not completely agreeing with phase diagrams [1-3], where Mn_xSb varies from 45.5% to 50.0% at Sb ($1.20>x>1.00$). The samples Rec_1 and Rec_8 presents a secondary phase (Mn_2Sb or Sb), meaning it exceeds the Mn_xSb phase limits. Extrapolating the data Tc x composition as a straight line from closer compositions, the range limit should be 49.5% at Sb for 90 °C, and 53.0 % at Sb for 316 °C, and "x" factor should vary from 0.883 to 1.020 on Rec samples. The Table 2 provides the collected data but is ordered in accord to "x" value of Mn_xSb phase, exclusively where it has only one phase (Rec_1 and Rec_2 presents two phases).

The magnetic analysis (MxT) of TT and Rec samples, plotted at Fig. 2"a-e", evidenced hysteresis from heating/cooling curves, compatible to a reverse peritectoid reaction (Mn_xSb ➔ MnSb + Mn_2Sb) on heating. When comparing the results to the Okamoto's phase diagram, the magnetic event: M_1 is probably related to Mn_2Sb's spin rotation (alignment with external magnetic field), M_2 converges to variable Tc of Mn_xSb ($0.883<x<1.013$), M_3 to $Mn_{0.883}Sb$, and M_4 is probably

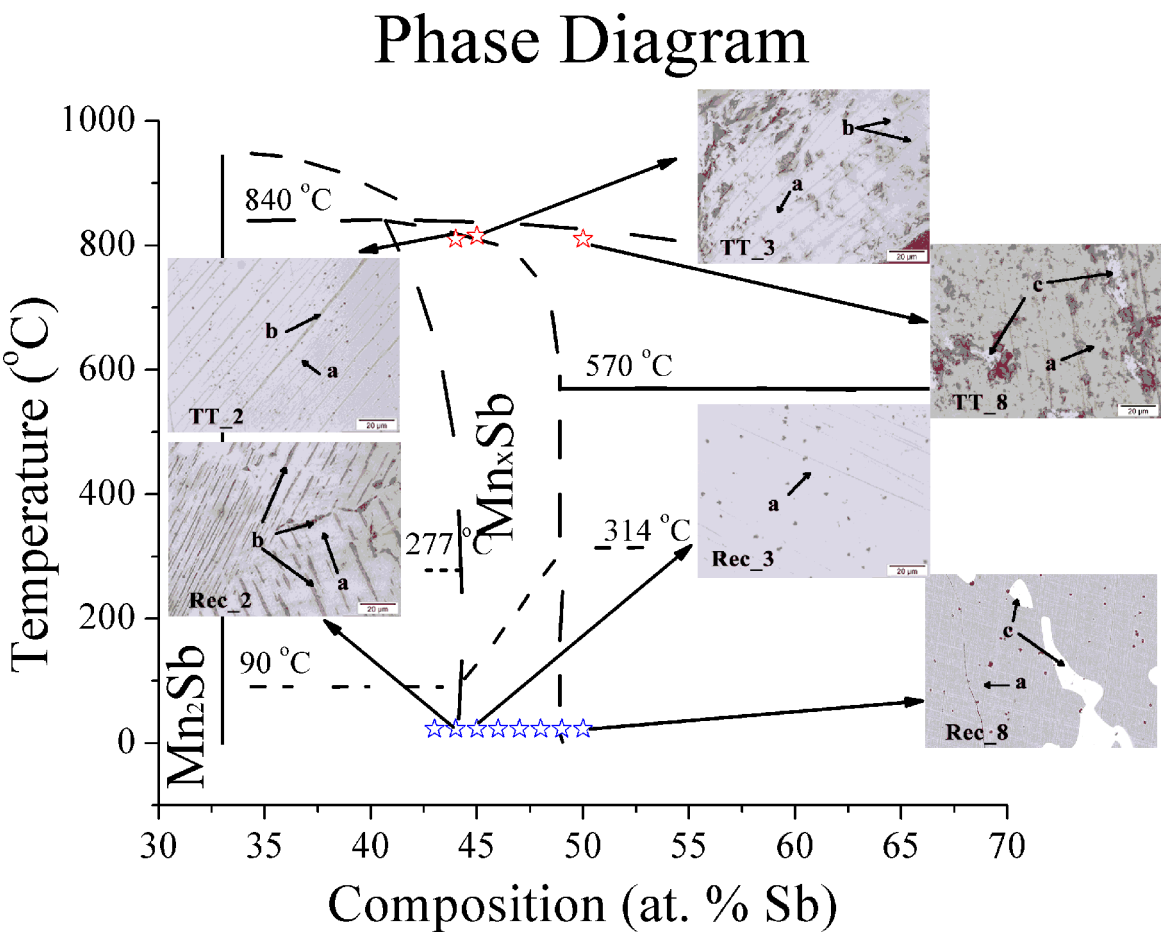

Figure 1. MnSb partial phase diagrams, from diverse authors, and the corresponding images, where: "a" = Mn_xSb phase, "b" = Mn_2Sb phase, and "c" is predominantly Sb phase; Dark gray spots at TT_3 and TT_8 are holes caused at manipulation by fragility of material.

Table 2. chemical composition of samples (weighed and XRF) and EDS for Mn_xSb phase correlated to Tc.

Sample	Weighed (%atSb)	XRF (%atSb)	EDS - MnSb (%atSb)	Tc (°C)	Mn_xSb x =
Rec_1	43.1%	40.1%	48.9%	140.35	-
Rec_4	46.1%	48.1%	49.7%	102.06	1.013
Rec_2	44.1%	44.5%	50.5%	143.00	0.980
Rec_3	45.0%	47.1%	50.6%	177.22	0.977
Rec_5	47.1%	48.3%	51.2%	217.85	0.952
Rec_6	48.1%	48.7%	52.2%	246.04	0.915
Rec_7	49.1%	49.3%	53.1%	316.11	0.883
Rec_8	50.0%	52.8%	54.1%	316.90	-

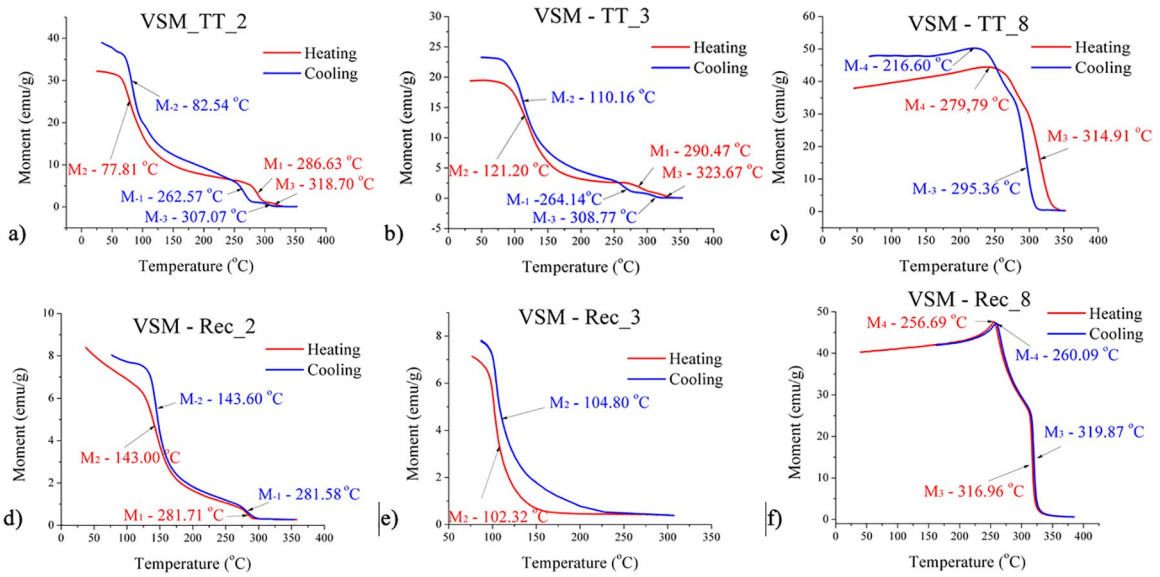

Figure 2. Magnetic analysis. a) TT_2; b) TT_3; c) TT_3; d) Rec_2; e) Rec_3; and f) Rec_8.

an AFM-FM (Anti-ferromagnetic - Ferromagnetic) reaction of Sb predominant phase ($Mn_{0.05}Sb_{0.95}$).

Teramoto[1] reported an irreversible reaction when analyzing a 46 %at.Sb quenched sample, after each measurement of five cicles, the susceptibility curve moved to upper temperatures, he attributed this behavior to the "precipitation of Mn_2Sb phase from MnSb". Chen[2] also mentioned the precipitation of Mn_2Sb phase.

Only the sample Rec_8 didn't present this hysteresis, suggesting, at this stoichiometry and temperature range, probably the peritectoid transition does not occur anymore. On the other hand, the events M_4 and M_{-4} were not expected. A similar event was reported by Nwodo[3] as a FOMT (first order magnetic transition) AFM-FI (Anti-ferromagnetic ➔Ferrimagnetic) reaction, attributed to a spin reorientation of Mn_2Sb dopped with Sn ($Mn_2Sb_{0.9}Sn_{0.1}$). At Rec_8 and TT_8 the present phases are "Mn_xSb + Sb", where "Sb" is apparently providing an AFM behavior to the alloy up to 256.69 °C on heating, when a FOMT occurs (event M_4 - AFM ➔ FM), followed by an M_3 event at 316.96 °C, a SOMT (second order magnetic transition) "FM ➔ PM" reaction (ferromagnetic ➔ paramagnetic).

The thermal analysis (DSC), Fig. 3, of Rec samples evidenced two endothermic peaks, the first identified as E1 from 65.98 to 79.77 °C, which is compatible to the reported precipitation of Mn_2Sb from Mn_xSb, probably related to a crystaline structure change from Mn_xSb (hexagonal) to form Mn_2Sb (tetragonal). And the second, E2, near 573 °C, compatible to a reverse peritectic reaction "Mn_xSb ➔ Mn_xSb + Liquid", reported by Okamoto[4] at 570 °C, and by Kainzbauer at 566 °C, but in disagreement with lower levels of Sb (Rec_3 to Rec_8), where it was expected to be near to 840 °C.

The refinement of XRD data revealed 3 main phases "a = Mn_xSb (hexagonal-$P6_{3mmc}$)"; "b = Mn_2Sb (tetragonal-$P4nmm$); "c = predominantly Sb (rhombohedral-R$\bar{3}$m)". All the samples presented the "a" phase, while "b" was identified at Rec_1 and Rec_2, and from TT_1 to TT_6. The presence of "b" on samples TT_3 to TT_6 conflicts to published phase diagrams[1,2,4-7], but agrees with the expected "precipitation"

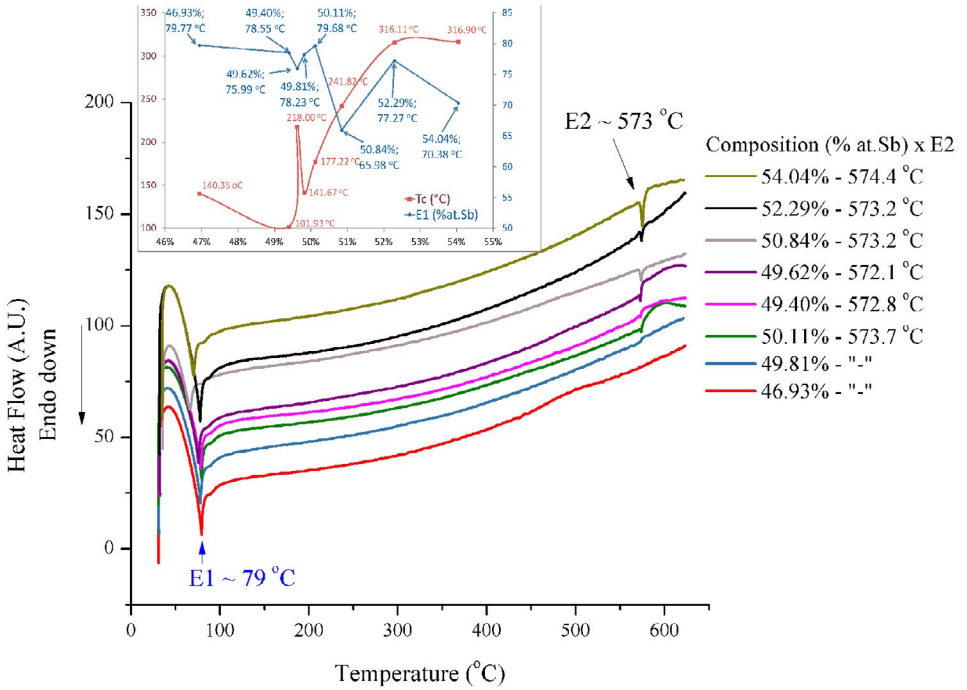

Figure 3. Heat flow x Temperature diagram - DSC data.

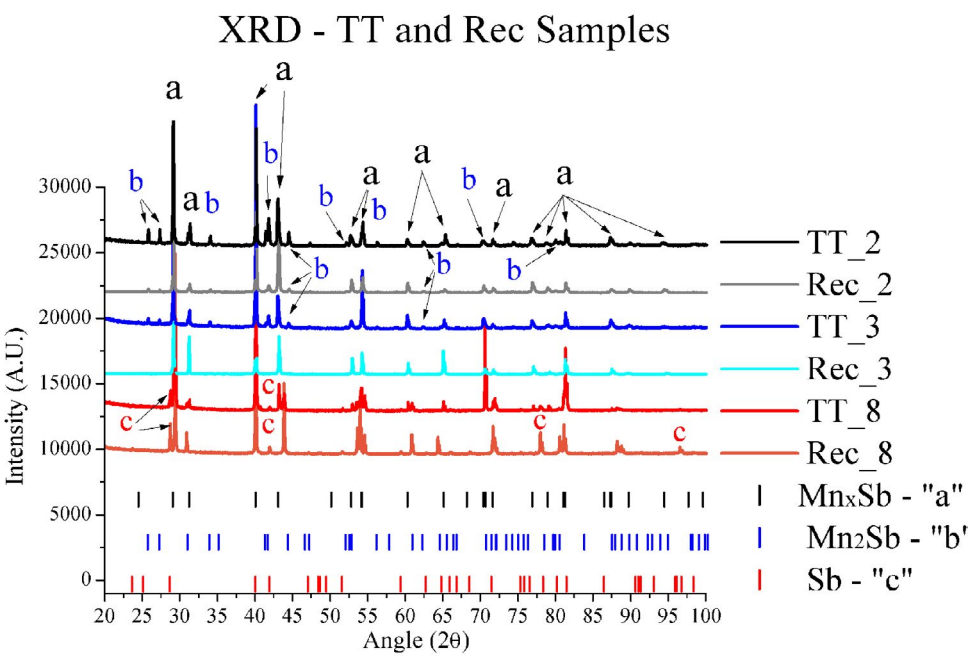

Figure 4. XRD Analysis, where 2 = 44%atSb, 3 = 45%atSb, 8 = 50%atSb on nominal stoichiometry.

of Mn_2Sb phase at high temperatures. The "c" phase is only present at TT_7, TT_8, Rec_7 and Rec_8. At Fig. 4, the "b" phase detected on sample TT_ 3 at the angles 25.82°, 27.33°, 34.11°, 41.93°, 44.51° and 62.43° reinforce the hypothesis of existence of the peritectoid reaction, as they were not detected at Rec_3 sample.

The volume of unit cells is larger as higher is the percentage of Sb (larger atomic ratio). The precipitation of Mn_2Sb reduces the value of "x" due to the diffusion of Mn atoms on TT samples x Rec samples. The absence of Mn_2Sb phase on Rec_8 and TT_8, and absence of Sb phase on Rec_3, TT_3, Rec_2 and TT_2 confirms they are out of

Table 3. cell's lattice parameters

Cell's net parameters							
Fase	Parameter	**Rec_8**	**TT_8**	**Rec_3**	**TT_3**	**Rec_2**	**TT_2**
	a (Å)	4.130	4.191	4.190	4.201	4.200	4.214
	c (Å)	5.790	5.731	5.734	5.728	5.724	5.716
Mn_xSb (P6)	Volume	85.546	87.163	87.181	87.534	87.433	87.880
	R-Bragg	4.331	3.036	4.379	3.997	3.324	3.242
	X	1.00	1.00	1.09	1.00	1.22	1.09
	a (Å)			4.056	4.078	4.075	4.077
	c (Å)			6.110	6.546	6.543	6.546
Mn_2Sb (P4)	Volume			100.536	108.846	108.655	108.777
	R-Bragg			1.584	1.770	2.519	2.620
	a (Å)	4.309	4.307				
	c (Å)	5.635	5.633				
Sb (R3)	Volume	90.595	90.509				
	R-Bragg	1.399	2.350				
GOF		1.83	1.88	1.68	1.89	1.49	1.45
RWP		8.74	7.68	14.71	7.42	12.24	5.67

the limits of respective solid solution. Details of parameters are plotted on the Table 3.

4. Conclusions

The magnetic hysteresis between heating and cooling suggests a reaction with compositional change. The thermal analysis revealed two endothermic peaks E1 ~ 80 °C compatible to the Mn_2Sb precipitation mentioned previously, and E2 ~ 573 °C on samples Rec_3 to Rec_8 samples agreeing to peritectic reaction at the limit border of $Mn_{0.883}Sb$ phase and "$Mn_{0.883}Sb$ + Sb" solid solution. The absence of E2 on samples Rec_1 and Rec_2, a two phase region of "Mn_2Sb + Mn_xSb" is probably because at this stoichiometry there are no more exceeding Mn atoms to diffuse and permit the precipitation of Mn_2Sb phase from MnSb.

The results suggests the existence of a reverse peritectoid reaction (Mn_xSb ➔ Mn_2Sb + $Mn_{0.883}Sb$) on heating at samples Rec_3 to Rec_6 (or more precisely $1.020 \geq x > 0.883$), also the existence of the two phase solid (Mn_2Sb + Mn_xSb) at high temperature region (above E1 ~ 79 °C) from 33% to near 53 %at.Sb, but limited from 33% to 49.7 %at.Sb under this temperature.

5. Acknoledgements

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