New Peritectoid Reaction Identified at the MnSb Alloy

Gerson Yoshinobu Iwamoto* , Christiane de Arruda Rodrigues, Luciana Aparecida de Sousa Iwamoto, Rogerio de Almeida Vieira

*Laboratório de Materiais e Manufatura Mecânica - LMMM, Universidade Federal de São Paulo - UNIFESP, Av. Manoel da Nóbrega, 1535, 09910720, Centro, Diadema, SP, Brasil

Laboratório de Engenharia e Controle Ambiental - LENCA, Departamento de Engenharia Química, Universidade Federal de São Paulo - UNIFESP, Rua São Nicolau, 210, 09913-030, Centro, Diadema, SP, Brasil

Centro de Terapia Celular e Molecular - CTCMOL, Universidade Federal de São Paulo - UNIFESP, São Paulo, SP, Brasil

Received: October 02, 2018; Accepted: March 09, 2019

The tunable $T_c$ 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 $\text{Mn}_x\text{Sb} \rightarrow \text{Mn}_2\text{Sb} + \text{Mn}_x'\text{Sb}$.

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

1. Introduction

The MnSb alloy presents an interesting phase, on atomic percentage of Sb (%at.Sb) from 45% to 48%, with Curie Temperature ($T_c$) varying from 90 °C to 314 °C. The composition limits of the MnSb phase and the corresponding $T_c$ 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 $T_c$ (°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                     |

*e-mail: gyiwamoto@hotmail.com
Iwamoto et al. 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$_x$Sb present on all samples, a dark phase (granular and stripes) named as “b” corresponding to Mn$_2$Sb 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$_x$Sb phase (“x” is the stoichiometry variation).

The chemical composition of Mn$_x$Sb 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$_x$Sb 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$_x$Sb or Sb), meaning it exceeds the Mn$_x$Sb phase limits. Extrapalating 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$_x$Sb 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$_x$Sb $\rightarrow$ MnSb + Mn$_x$Sb) on heating. When comparing the results to the Okamoto’s phase diagram, the magnetic event: M$_1$ is probably related to Mn$_x$Sb’s spin rotation (alignment with external magnetic field), M$_2$ converges to variable Tc of Mn$_{0.883}$Sb (0.883<x<1.013), M$_3$ to Mn$_{0.883}$Sb, and M$_4$ is probably

![Phase Diagram](image_url)

**Figure 1.** MnSb partial phase diagrams, from diverse authors, and the corresponding images, where: "a" = Mn$_x$Sb phase, "b" = Mn$_2$Sb 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.
New Peritectoid Reaction Identified at the MnSb Alloy

Teramoto reported an irreversible reaction when analyzing a 46% at Sb quenched sample, after each measurement of five cycles, the susceptibility curve moved to upper temperatures, he attributed this behavior to the "precipitation of Mn2Sb phase from MnSb". Chen also mentioned the precipitation of Mn2Sb 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_x and M_y were not expected. A similar event was reported by Nwodo as a FOMT (first order magnetic transition) AFM-FI (Anti-ferromagnetic Ferromagnetic) reaction, attributed to a spin reorientation of Mn2Sb dopped with Sn (Mn2Sb0.9Sn0.1). At Rec_8 and TT_8 the present phases are "MnxSb + 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_x - AFM ➔ FM), followed by an M_y event at 316.96 °C, a SOMT (second order magnetic transition) "FM ➔ PM" reaction (ferromagnetic ➔ paramagnetic).

The refinement of XRD data revealed 3 main phases "a = MnSb (hexagonal-P6_3mmc)"; "b = MnSb (tetragonal-P4nmm)"; "c = predominantly Sb (rhombohedral-R3m)". All the samples presented the "a" phase, while "b" was identified at Rec_8 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 diagrams1,2,4-7, but agrees with the expected "precipitation" event at 316.96 °C, a SOMT (second order magnetic transition) "FM ➔ PM" reaction (ferromagnetic ➔ paramagnetic).

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

| Sample | Weighed (%atSb) | XRF (%atSb) | EDS - MnSb (%atSb) | Tc (°C) | Mn_Sb 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.

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 MnSb from Mn$_2$Sb, probably related to a crystalline structure change from Mn$_2$Sb (hexagonal) to form Mn$_2$Sb (tetragonal). And the second, E2, near 573 °C, compatible to a reverse peritectic reaction "Mn$_x$Sb ➔ Mn$_x$'Sb + Liquid", reported by Okamoto 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 = MnSb (hexagonal-P6_3mmc)"; "b = MnSb (tetragonal-P4nmm)"; "c = predominantly Sb (rhombohedral-R3m)". 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 diagrams1,2,4-7, but agrees with the expected "precipitation"
of Mn$_2$Sb 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 25.8°, 27.3°, 34.1°, 41.9°, 44.5° and 62.4° 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$_2$Sb reduces the value of "x" due to the diffusion of Mn atoms on TT samples x Rec samples. The absence of Mn$_2$Sb 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
New Peritectoid Reaction Identified at the MnSb Alloy

4. Conclusions

The magnetic hysteresis between heating and cooling suggests a reaction with compositional change. The thermal analysis revealed two endothermic peaks $E_1 \sim 80^\circ C$ compatible to the Mn$_2$Sb precipitation mentioned previously, and $E_2 \sim 573^\circ C$ 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 $E_2$ on samples Rec$_1$ and Rec$_2$, a two phase region of "Mn$_2$Sb + MnxSb" is probably because at this stoichiometry there are no more exceeding Mn atoms to diffuse and permit the precipitation of Mn$_2$Sb phase from MnSb. The results suggest the existence of a reverse peritectoid reaction (Mn$_2$Sb $\rightarrow$ Mn$_{2-x}$Sb + Mn$_x$Sb) on heating at samples Rec$_3$ to Rec$_6$ (or more precisely $1.020 \leq x \leq 0.883$), also the existence of the two phase solid (Mn$_{2-x}$Sb + Mn$_x$Sb) at high temperature region (above $E_1 \sim 79^\circ C$) from 33% to near 53 %at.Sb, but limited from 33% to 49.7 %at.Sb under this temperature.

5. Acknowledgements

Prof. Dr. Davinson M. Silva and prof. dr. Silvano L. Santos, LPCM, FATEC.

6. References

1. Teramoto I, Van Run AMJG. The existence region and the magnetic and electrical properties of MnSb. Journal of Physics and Chemistry of Solids. 1968;29(2):347-355. DOI: 10.1016/0022-3697(68)90080-2
2. Chen T. Growth of MnBi single crystals by pulling with a seed from nonstoichiometric molten solution. Journal of Crystal Growth. 1974;24-25:454-460. DOI: 10.1016/0022-0248(74)90357-1
3. Nwodo AN, Kobayashi R, Wakamori T, Matsumoto Y, Mitsui Y, Hiroi M, et al. Quasi-First Order Magnetic Transition in Mn$_{1.9}$Fe$_{0.1}$Sb$_{0.9}$Sn$_{0.1}$. Materials Transactions. 2018;59(3):348-352. DOI: 10.2320/matertrans.M2017291
4. Okamoto H. Manganese-Antimony Binary Phase Diagram. In: Massalski TB, ed. Binary Alloy Phase Diagrams. 2nd ed. Materials Park: ASM International; 1990.
5. Williams RS. Über die Legierungen des Antimons mit Mangan, Chrom, Silicium und Zinn; des Wismuts mit Chrom und Silicium und des Mangans mit Zinn und Blei. Zeitschrift für anorganische Chemie. 1907;55(1):1-33. DOI: 10.1002/zaac.19070550102
6. Vanyarkho VG, Moshchalkova NA, Gunchenko VM, Fadeeva NV. On the existence of the compound MnSb. Inorganic Materials. 1988;24(6):762-765.
7. Kainzbauer P, Richter KW, Ipser H. Experimental Investigation of the Binary Mn-Sb Phase Diagram. Journal of Phase Equilibria and Diffusion. 2016;37(4):459-468. DOI: 10.1007/s11669-016-0470-2

Table 3. cell's lattice parameters

| Cell's net parameters | Parameter | Rec_8 | TT_8 | Rec_3 | TT_3 | Rec_2 | TT_2 |
|-----------------------|-----------|-------|------|-------|------|-------|------|
| Phase                 |           |       |      |       |      |       |      |
| Mn$_2$Sb (P6)         |           |       |      |       |      |       |      |
| 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 |
| 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  |
| Mn$_2$Sb (P4)         |           |       |      |       |      |       |      |
| Volume                | 100.536   | 108.846| 108.655| 108.777|       |       |
| R-Bragg               | 1.584     | 1.770 | 2.519| 2.620 |      |       |
| Sb (R3)               |           |       |      |       |      |       |      |
| a (Å)                 | 4.309     | 4.307 |      |       |      |       |
| c (Å)                 | 5.635     | 5.633 |      |       |      |       |
| 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  |