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Study of MnSb alloy on the range of 43% to 50% of at.%Sb, revealed an unexpected presence of MN_2SB phase

Abstract

The manganese-antimony (MnSb) alloys with specific stoichiometry, on atomic range from 43% to 50%at.Sb, as cast (with no quenching or annealing), were analyzed using OM, VSM, DSC and XRD characterization methods. The XRD diffractograms were refined using Rietveld method, were possible to identify four different phases: a) Mn_{1}, 09Sb (hexagonal, spatial group P63mmc); a') MnxSb (1.092<x<1.22, hexagonal P63mmc); b) Mn_2Sb (tetragonal P4nmm); and c) Sb (rhombohedral Rm). OM's images helped us to double check the coherence with XRD refined data, and VSM plus DSC helped us to identify the respective magnetic and thermal phase transitions. The $Mn_{1.09}Sb$ phase has proven to be tunable exclusively through its composition, what is a promising property for specific applications, although its second order transition can limit the application to devices where this behavior is desired. The abnormal presence of Mn2Sb in all studied samples suggests the known phase diagrams can contain an extended and not reported Mn2Sb phase region high temperature.

Keywords: magnetic materials, phase transformation, MnSb metals and alloys, manganese-antimony alloys, curie temperature, magnetic transitions

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Introduction

The discovery of nonferrous magnetic alloys was reported by Heusler[1] in 1898 and since then the investigation and application of these alloys on industrial and scientific devices have been growing continuously. Guillaud[2] described a variable Curie Temperature (between 90°C and 314°C) for MnSb alloy, obtained exclusively through the variation of the stoichiometry (from 45% to 49% in atomic percentage of Sb (at.%Sb). At least six different phase diagrams were published, besides the long time from its discovery, they still have some uncertain regions related to minimum/maximum stoichiometry of MnSb phase and its respective Tc. Okamoto's phase diagram[3] defines this region being from 45% and 49% atomic Sb at room temperature up to 314°C, and respective Tc varying from 90°C to 314°C. Crystallographic files from ICSD[4] provide references where the phase is described as $Mn_{1.092}Sb$ or Mn1.1Sb. Eight samples, from 43% to 50% at. Sb was produced, covering the complete range of $Mn_{1.092}Sb$ phase. Guillaud[2] reported a tunable magnetic transition through stoichiometry between 90°C to 314°C, Teramoto & Van Run[5] confirmed the non dependency of annealing temperature between 400°C and 700°C for 49% atomic of Sb, and plotted a partial phase diagram (Figure 1), where MnSb stable phase varies with temperature from 46 to 50%at of Sb at 400°C, and a single point at 41% atomic Sb (%at.Sb) at 840°C describing a non linear behavior. Teramoto & Van Run[5] reported quenching from temperatures between 400°C to 700°C didn't change the Tc, being independent of annealing or quenching temperature, but only related to stoichiometry. Okamoto[3] reported a peritectic transition at 840°C and variable Tc related stoichiometry from 44% to 49% at.Sb. at 400°C. Chen[6] identified the peritectic temperature at 843°C and the stoichiometry between 45% and 49.5% atomic of Sb at 400°C, Vanyarkho[7] reported the peritectic temperature at 841°C and the MnSb phase from 45% to 49% at 400°C, Williams[8] reported the peritectic temperature at 853°C and variable magnetic range from 40% to 50% below 573; and Kainzbauer[9] reported the peritectic temperature at 830°C and limits of MnSb phase from 45.5% to 50.5at% of Sb. Although Guillaud[2] described the reaction at MnSb alloy as a SOMT (Second Order Magnetic Transition), Nwodo[10] reported a FOMT (first order magnetic transition), AFM-FI (Anti- ferromagnetic→Ferrimagnetic) reaction, attributed to a spin reorientation of Mn_2Sb dropped with Sn ($Mn_2Sb_{0.9}Sn_{0.1}$).

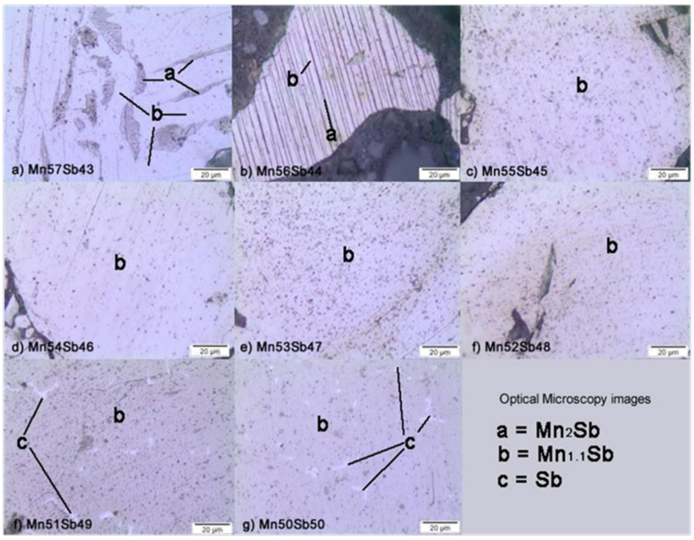

Figure 1 Optical microscopy images (MO) related to as cast samples from 43 %at.Sb to 50 %at.Sb.

Method

Based on reported and well recognized phase diagram produced by Okamoto & Van Run[3] the samples were prepared with stoichiometry from 43% to 50% at.Sb, producing 8 different samples, nominated as $Mn_{57}Sb_{43}$ (57% atomic of Mn and 43% atomic of Sb), $Mn_{56}Sb_{44}$, $Mn_{55}Sb_{45}$, $Mn_{54}Sb_{46}$, $Mn_{53}Sb_{47}$, $Mn_{52}Sb_{48}$, $Mn_{51}Sb_{49}$ and $Mn_{50}Sb_{50}$. The samples were prepared from pure elements (Sb - Alfa Aesar 99.99% and Mn Alfa Aesar 99.98%), and were weighed at high precision equipment under atmosphere pressure, and then melted under argon atmosphere in an electric arc furnace (100A). Each sample was melted 6 times, inverting its position after each melt. As the intention of this part of the study was to observe the alloy as cast on electric arc furnace, no quenching or annealing treatment was done. The samples were grinded into powder and separated into 4 groups, to be analyzed at XRD (X-Ray Diffraction) and Rietveld refinement using Topas® software, DSC (Differential Scanning Calorimetry), VSM (Vibrating Sample Magnetometer), Optical Microscopy (OM). For metallographic analysis the fourth group was embedded in Bakelite before sanding and polishing processes. The sanding process was done using abrasive discs grades P120, P220, P320, P400, P600, P1200 and P2000, on sequence polishing process was done using synthetic felt discs and alumina paste (1.0µm, 0.3µm and 0.05µm), the samples were etched using HNO_3+CH_3CH_2OH for 20s, and then finally analyzed at Optical Microscope (Olympus BX41M-LED). The XRD parameters were: 2θ from 20 to 100 degrees, step of 0.01 and rotation speed 10omin^{-1}. On DSC: samples were separated and evaluated from 80°C to 370°C, with ramp of 5°Cmin^{-1}. As the alloy can contain metastable phases, only heating curves were considered. VSM samples were analyzed at 200Oe magnetic field from 40°C to 400°C, 5°Cmin^{-1} ramp. The samples $Mn_{57}Sb_{43}$ and $Mn_{50}Sb_{50}$ were evaluated at ED's equipment, using magnification scale of 2,000times, and 10 measures of each phase were done to confirm the coherence of phases described at OM.

Results and discussion

Optical microscopy

The images obtained from Optical Microscope (Figure 1), shows dark stripes (phase a) at Figure 1A $Mn_{57}Sb_{43}$ and Figure 1B $Mn_{56}Sb_{44}$, related to Mn_2Sb phase, the clear phase (phase b) is attributed to Mn_1, 1Sb phase which is dominant in all the samples. At Figure 1, the other samples showed are: c) $Mn_{55}Sb_{45}$, (d) $Mn_{54}Sb_{46}$, (e) $Mn_{53}Sb_{47}$, and (f) $Mn_{52}Sb_{48}$ basically with only one phase (Mn_1,09_2Sb). In accord to EDS lectures the dark dots are reminiscent phase Mn_2Sb or oxides. The images g) $Mn_{51}Sb_{49}$ and h) $Mn_{50}Sb_{50}$ shows an almost white phase, attributed do Sb. The phases were confirmed through EDS probe analysis.

Magnetic analysis using VSM

As the samples were analyzed on "as cast" state, only the heating curve were considered. The data collected were plotted at Origin® software and used the function derivative to determine the transitions temperatures. As the samples were not annealed, the metastable equilibrium was not reached, causing too much noise on magnetic measures. The curves were smoothed and the transition temperatures were defined through derivative function. The magnetic measured data from VSM (MxT) were summarized at Figure 2, it shows a Tc dependence of %at.Sb from 49% to 45%, regressing from 316 °C to 101°C. Two magnetic transitions were observed on samples from 48%at.Sb to 44%at.Sb, the first varying in accord to composition, attributed to Mn1.1Sb phase; the second one, a little above to 310°C, provides evidences there is a second phase. As the samples were not annealed, it is not possible to confirm if this second phase is because of metastable phases or if could be two phase region on phase diagram.

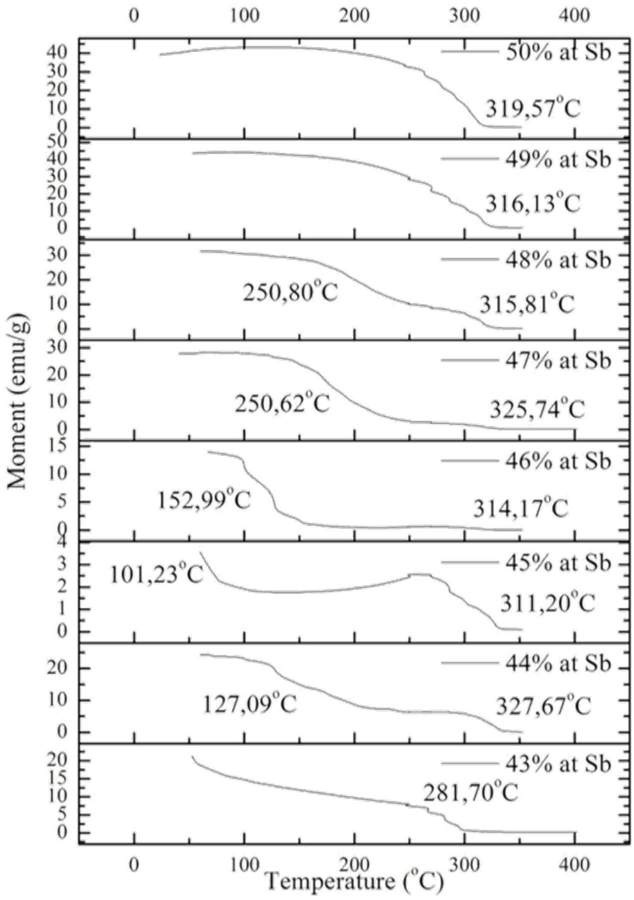

Figure 2 Moment (emu/g) x Temperature diagram – VSM data.

Differential scanning calorimetry

Also on DSC, the data was plotted, smoothed and derivated to reduce the impact of noise caused by metastable phases. Even though, the $Mn_{50}Sb_{50}$ presented only one transition, associated to the richest composition of $Mn_{1.1}Sb$ phase, indicated at phase diagrams[3] as 314°C, but measured at 326°C. Only sample $Mn_{57}Sb_{43}$ presented a secondary transition close to expected transition of Mn_2Sb phase (pointed at 277°C on Okamoto's phase diagram,[3] indicating only this sample would contain this phase. The other samples indicated there is a dependence of Tc in accord to composition, in most cases with at least two transitions temperature, but significantly different from VSM. The probably reason is the non homogeneization of the sample through annealing (Figure 3).

DRX and Rietveld refinement Topas®

The X-ray diffraction (Figure 4) and Rietveld refinement at Topas® software, confirmed the 2θ angles related to "a=$Mn_{1,1}$Sb (hexagonal P63mmc)"; "b=Mn2Sb (tetragonal P4nmm); and "c=Sb (rhombohedral Rm)". All the samples presented predominance of $Mn_{1,1}$Sb. The alpha antimony, peak "c", is only present at Mn52Sb48, $Mn_{51}Sb_{49}$ and $Mn_{50}Sb_{50}$ alloys, and is visible only at OM images Figure 1. (g) and (h) as "white phases". Mn_2Sb phase was identified in all the samples, although in low percentage (below 10.7%), going in opposition to mentioned phase diagrams.

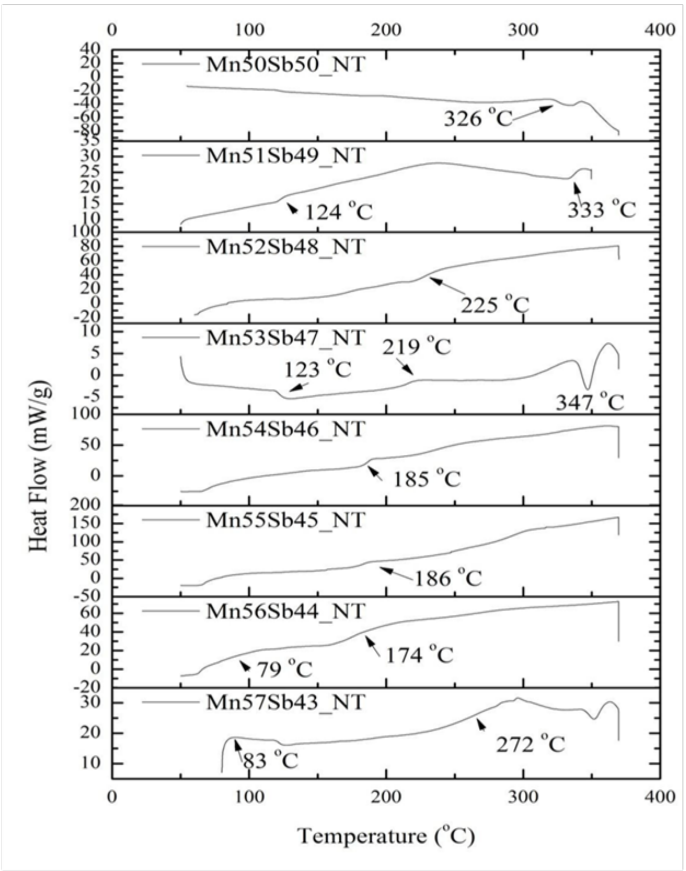

Figure 3 Heat flow x Temperature diagram – DSC data.

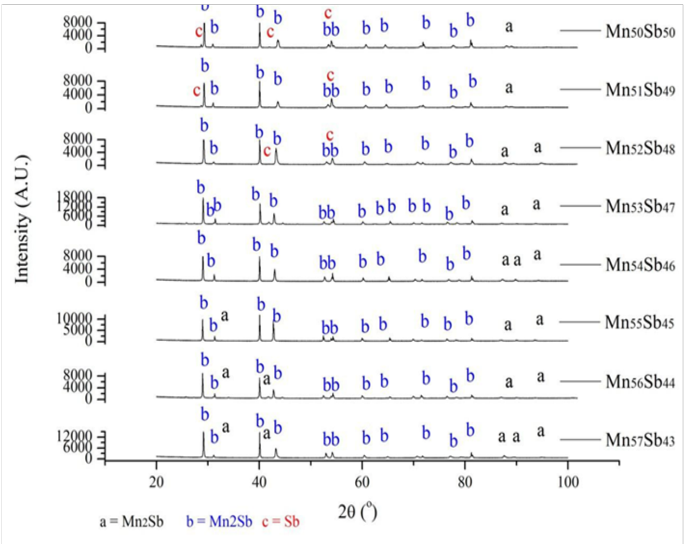

Figure 4 XRD – 2θ angles.

Conclusion

The $Mn_{1.1}Sb$ phase has proven to be tunable exclusively through its composition, what is a promising property for specific applications, although it is a second order transition, what can limit frequency of devices, what could be compensated increasing the mass of them. The abnormal presence of Mn_2Sb in all studied samples suggests the known phase diagrams can contain an extended and not reported double phase region (Mn_2Sb +$Mn_{1.1}Sb$) at high temperatures, indicating the reported "phase precipitation" by Teramoto[1] can be a perithectoid reaction.[11]

Perspective

Further studies are in progress to investigate the region of tunable Tc with stoichiometry from 43%at.Sb to 50%at.Sb with objective to better understand the "precipitation effect of Mn_2Sb from $Mn_{1.1}Sb$ phase".

Acknowledgments

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Conflicts of interest

Authors declare that there is no conflict of interest.

References

1. Heusler F, Take E. The nature of the Heusler alloys. *Trans Faraday Soc*. 1912;8:169–184.
2. Guillaud C. Ferromagnetic properties of manganese-antimony and manganese-arsenic alloys. *Annales de Physique*. 1949;12:671–703.
3. Okamoto H. Manganese-Antimony Binary Phase Diagram (based on 1990 Okamoto H.). 1990.
4. Bergerhoff G, Brown ID. Inorganic Crystal Structure Database. *Acta Crystallogr Sect A Found Crystallogr*. 1981.
5. Teramoto I, Van Run AMJG. The existence region and the magnetic and electrical properties of MnSb. *J Phys Chem Solids*. 1968;29(2):347–55.
6. Chen T, Charlan GB, Keezer RC. Growth of MnSb Single Crystals by Pulling With a Seed From non Stoichiometric Molten Solution. *J Cryst Growth*. 1977;29–36.
7. Vanyarkho VG, Moshchalkova NA, Gunchenko VM, et al. On the existence of the compound MnSb. *Inorg Mater*. 1988.
8. Williams RS. LI. Über die Legierungen des Antimons mit Mangan, Chrom, Silicium und Zinn; des Wismuts mit Chrom und Silicium und des Mangans mit Zinn und Blei. *ZAAC*. 1907;55:1–33.
9. https://matdata.asminternational.org/apd/index.aspx
10. Kainzbauer P, Richter KW, Ipser H. Experimental Investigation of the Binary Mn-Sb Phase Diagram. *J Phase Equilibria Diffus*. 2016;37(4):459–468.
11. Nwodo AN, Kobayashi R, Wakamori T, et al. Quasi-First Order Magnetic Transition in Mn1.9Fe0.1Sb0.9Sn0.1. *Mater Trans*. 2018;59(3):348–52.

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