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## *The magnetic properties of $Mn_2Sb$ modified with vanadium*

Swoboda *et al.* [1] found that the addition of chromium can induce $Mn_2Sb$ to show, on cooling, an abrupt transition from its normal ferrimagnetic state [2] to an antiferromagnetic one (the type of behaviour shown in Fig. 1). This phenomenon is found in a limited number of other materials [3]. Bither *et al.* [4] later reported further elements which modify the magnetic properties of $Mn_2Sb$ in the same way. Vanadium additions [4] seem particularly interesting because, in the region of ambient temperature, the magnetic transition is relatively insensitive to composition (Fig. 2). The present work was designed to supplement the data given by Bither *et al.*, particularly at higher vanadium levels.

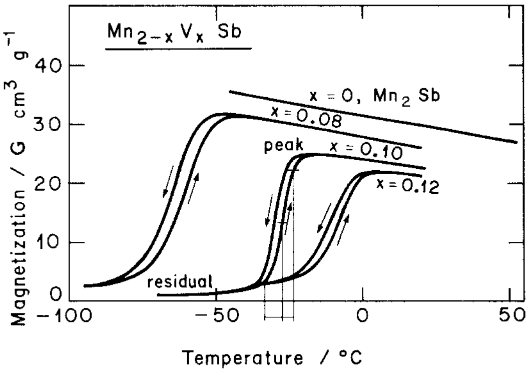

*Figure 1* The magnetic transition in some vanadium-modified $Mn_2Sb$ alloys on heating and cooling. The range of temperature used in Fig. 2 to describe the transition on heating, corresponding to 0.1, 0.5 and 0.9 of the magnetization between the residual and peak values, is also indicated.

The alloys studied here were made by melting the components together under argon in a pyrolytic boron nitride crucible using intermediate frequency heating. The compositions $Mn_{2-x}V_xSb$ were in the range $x = 0.08$ to 0.25. The alloys were annealed in vacuum at 700° C for 2 weeks. Polycrystalline spheres (~ 2 mm diameter) were subsequently ground out and tested in a vibrating sample magnetometer with a heating rate of 5° C $min^{-1}$. The applied field was 17 kOe which is well beyond the anisotropy field (as calculated from the date of Darnell *et al.* [5] for chromium-modified $Mn_2Sb$) so that the samples were completely saturated magnetically.

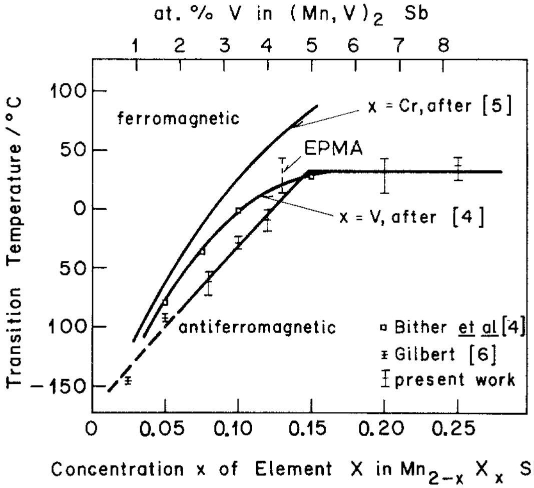

*Figure 2* The transition temperature of vanadium- and chromium-modified $Mn_2Sb$ [4–6] as a function of concentration together with the results from the present study. Also shown is the location of the vanadium solid solution limit in terms of the transition temperature observed in high vanadium alloys following EPMA analysis.

Typical magnetization curves as a function of temperature are shown in Fig. 1. Both the thermal hysteresis and the residual magnetization in the antiferromagnetic condition are apparent. The magnetization above the transition in the ferrimagnetic condition falls with increasing vanadium level.

The range of temperature over which the transition occurs during heating (at 0.1, 0.5 and 0.9 of the magnetization between residual and peak values, Fig. 1) is recorded in Fig. 2. The transition temperature range becomes independent of vanadium level at higher concentrations. This is associated with the solubility limit of vanadium in $Mn_2Sb$ and a new primary phase appears in the microstructure (Fig. 3). This phase is of variable composition $(V_{1-Y}Mn_Y)_3Sb$, where electron probe micro-analysis (EPMA) data give $Y$ mainly in the region of 0.17 for the results given in Fig. 2 (occasionally values as high as 0.48 were recorded) and is presumably based on the $V_3Sb$ phase [7]. The light-etching fine structure in the $(Mn, V)_2Sb$ matrix is ferrimagnetic MnSb precipitate on {1 0 1} habit planes [8] and is responsible for the residual magnetization below the transition temperature [1].

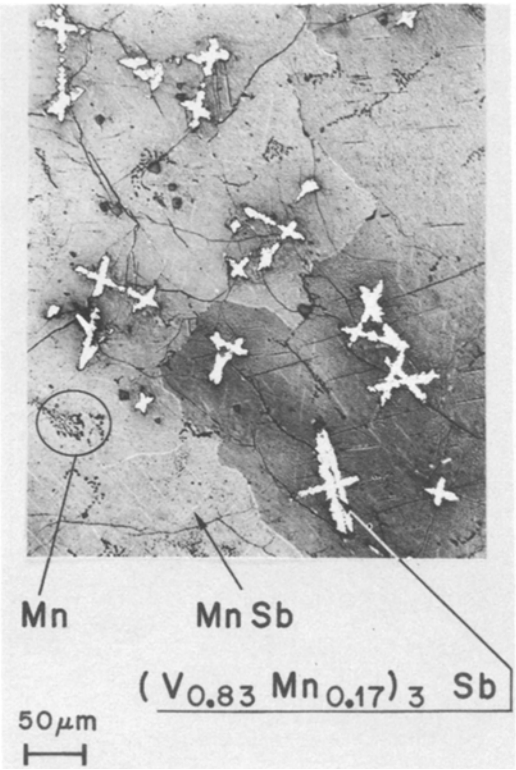

*Figure 3* Optical microstructure, etched with 1 to 2% brominal [8], of the alloy $Mn_{1.80}V_{0.20}Sb$ after annealing for 2 weeks at 700° C showing (EPMA) primary $(V_{0.63}Mn_{0.17})_3Sb$ in a matrix of $Mn_{1.87}V_{0.13}Sb$. The eutectic Mn phase and fine MnSb precipitates are also apparent.

Combining the electron microprobe analyses of matrix composition of the $x = 0.20$ and 0.25 samples with the data in Fig. 2, the variation of the transition temperature with vanadium level can be drawn in as shown.

The present results are somewhat at variance with the earlier data [4], showing a lower transition temperature and a sensitivity to vanadium level which is similar to that of chromium-modified material. It was confirmed by EMPA that the different transition temperature is not due to a different matrix composition, the measured and nominal values being in excellent agreement.

The materials studied here show a limiting transition temperature slightly above ambient temperatures, the limit being associated with the first appearance of the $(V, Mn)_3Sb$ phase. A similar effect with copper-modified material has been reported [4]. The results of Gilbert [6] and those of the present study fall on a single curve whereas those of Bither *et al.* [4] might be regarded as corresponding effectively to a lower vanadium level. This difference could be accounted for by loss of manganese by evaporation on melting increasing the actual vanadium level above the nominal value. Their alloy [4] $x = 0.15$ would then be beyond the solubility limit, lying on the plateau observed in the present study; its transition temperature is in good agreement with our results, supporting the argument of composition deviation.

The properties shown by the vanadium-modified material do not compare well with the chromium-modified one [1, 5]: The transition covers a far wider temperature range in spite of the extended annealing, indeed the range is little narrower than in as-melted material. Also the peak magnetization for material with any given transition temperature is lower and is more sensitive to the level of the modifying element. It is concluded, therefore, that vanadium-modified $Mn_2Sb$ is less advantageous than chromium-modified material for practical applications.

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