Preparation of Manganise Bismuthide by the Solid Diffusion Method and Its Thermal and Magnetic Properties

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A new procedure for the preparation of the MnBi was established by utilizing the solid diffusion. The sample heat treated for 1070 hr at 520 K was indexed roentgenographically as the NiAs type crystal structure of \( c = 1.164 \text{ Å} \) and \( a = 4.135 \text{ Å} \), which agrees well with previous data. The total excess specific heat for the magnetic transition at 640 K was estimated as \( (13.5 \pm 1.5) \times 10^2 \text{cal/mol} \), which exceeds distinctly that expected by the molecular field theory. Besides the experiments of the low-temperature phase MnBi, roentgenographic, calorimetric and magnetic experiments for the high temperature phase proposed by Heikes were carried out.

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I. Introduction

A ferromagnetic compound MnBi is noted to have a transition at about 640 K on heating, where the spontaneous magnetization disappears abruptly. Structural investigations concerning the transition have hitherto been reported by several authors.

The intermetallic compound MnBi is usually alloyed by the peritectic reaction. However, by this method, neither single phase nor nearly single phase samples can easily be formed due to the reduction in the surface area contacting with the reacting solid during the peritectic reaction. Owing to such a difficulty of preparing the single phase specimen, quite few thermodynamic data for the present compound are available up to the present. In this paper a new method for the preparation of nearly single phase samples of this compound by utilizing solid diffusion is proposed. Results of thermal and magnetic measurements is reported for the present samples, together with those for the high temperature phase proposed by Heikes, are also reported.

II. Preparation of the Compound

The phase diagram of the Mn–Bi binary system shows an eutectic reaction at 535 K and a peritectic reaction to form the compound MnBi occurs at 715 K. The conventional alloying procedure of the compound MnBi was to keep a mixture of manganese and bismuth just below the peritectic temperature. However, the reaction in the present method is found not to proceed effectively except for the initial stage of the reaction. Hence, in this case the magnetic separation technique is usually applied and the final yield of the bonded compound MnBi by the above-mentioned procedure is about 90 per cent. The present author made an attempt to expedite the reaction by solid diffusion just below the eutectic temperature.

Electrolytic manganese and bismuth of high purity were ground into fine powders, mixed in equi-atomic ratio, pressed at about 2 t/cm² to mold into small lumps and kept for a specified time just below 535 K in an evacuated hard glass capsule. Then the solid reaction between the two ingredients proceeded, and the reaction product was examined by the roentgenographic, calorimetric and magnetic techniques. In the present experiments, the setting temperatures of the furnace controller were about 525 K for 120, 200 and 300 hr of heat treatment and about 520 K for 1070 hr.

A chart of X-ray diffraction for the reaction product obtained by heat treatment for 1070 hr at 520 K heat treatment confirms the lines diffracted by the NiAs type crystal structure (low temperature MnBi phase) with \( c = 1.164 \text{ Å} \) and \( a = 4.135 \text{ Å} \), in agreement with the results obtained previously. In addition the lines given by bismuth, manganese and traces of manganese monoxide are found in the same diffractogram. With increasing reaction time, the intensity of the diffracted lines of the compound becomes stronger.

The high-temperature phase of MnBi, detected by Heikes was prepared as follows. Lumps of MnBi were ground into powder and sealed in an evacuated glass capsule. The capsule was first heated to 700 K and then plunged into iced water. The glass capsule was cracked by a shock of sudden cooling and the specimen was quenched. X-ray diffraction lines of this quenched material were indexed as a hexagonal crystal structure with lattice constants of \( c = 5.980 \text{ Å} \) and \( a = 4.338 \text{ Å} \), which was coincident with the high-temperature phase of Heikes. The crystal structure of the high-temperature phase differs definitely from the complete NiAs type structure, because the (003) line which must become extinct in the NiAs type structure has clearly been observed in the X-ray diffractogram.

III. Experimental Results

First, the result of magnetic measurement for the low-temperature phase MnBi will be mentioned here. Figure 1 shows the saturation magnetization versus temperature relation for the specimen treated for 1070 hr at 520 K. The saturation magnetization decreases rapidly with increasing temperature.

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Fig. 1 Saturation magnetization of the low temperature phase versus temperature.

below the eutectic point. As can be seen in the figure, the spontaneous magnetization disappears suddenly at 660 K, which coincides well with the results of previous experiments. As will be described later, the yield in this case is 93 per cent and consequently the saturation magnetization per gram extrapolated to 0 K is 3.64 μB, which coincides with the value 3.52 μB by Guillaud(1) rather than 3.95 μB by Heikes(2).

The specific heat of the compound was measured by an adiabatic calorimeter. Samples of about 10 grams were stowed in evacuated silica capsules. Observed curves of specific heat versus temperature under a heating rate of 5°/min are shown in Fig. 2. In the figure (a) represents the result for a sample processed for 200 hr, (b) for 1070 hr, and (c) for the high temperature phase prepared by quenching of the sample (b). The peak on the lowest temperature side or the peak in the range from 520° to 540°K in Fig. 2 is due to the melting of bismuth and the eutectic reaction in the Mn–Bi system. However, since no change in magnetization occurred during heating (heating rate: 2°/min) in the present experiment as shown in Fig. 1, the first peak should be due exclusively to the melting of bismuth. The middle peak at about 630°K is due to the magnetic transition temperature of MnBi, and the peak at the highest temperature, 710°K, can be ascribed to the peritectic reaction of MnBi. The samples heated up above the peritectic temperature no longer exhibited ferromagnetism.

From the quantity of heat of the first peak, the amount of residual raw bismuth is calculated using the heat of melting of bismuth, 2.8 kcal/mol. From this calculated amount of residual bismuth, the percentage or yield of bonded MnBi is calculated and plotted as a function of the reaction time, as indicated with small circles in Fig. 3. As shown in the figure, about 93 per cent yield is attained by the present method. The yield calculated from the quantity of heat for the transformation of the bonded compound is also plotted with cross marks in the same figure.

The specific heat of the second peak from the low temperature side in Fig. 2, peaks 630°~650°K, correspond to the magnetic transformation. From them it can be estimated that the total amount of heat for the transformation is \((13.5 \pm 1.5) \times 10^2\) cal/g atoms of the bonded compound.

Magnetization of the high-temperature phase versus temperature is shown by the solid curve in Fig. 4. The extrapolation of this curve leads to a value 2.70 μB at 0 K, which is almost 60 per cent larger than the value given by Heikes. Above 400°K the quenched high-

Fig. 3 Yield of bonded compound MnBi versus time of heat treatment at 520°K.

Fig. 4 Magnetization of the high temperature phase versus temperature.
temperature phase begins to transform into a low-temperature phase. In the present experiment the magnetization of the high-temperature phase was measured with an automatic magnetic balance under a high heating speed of about 100°C/min. The result of measurement is shown by the broken curve in the same figure. The spontaneous magnetization disappears completely at 450°C, reappears at 490°C, and again disappears somewhat abruptly at 630°C. A part of the high-temperature phase may be dissociated by selective oxidation of Mn during quenching, as evidenced in the calorimetric data that the relative amount of bonded element was found to decrease to 64 per cent. It was also noted that some lines of manganese monoxide and bismuth appeared newly on the X-ray diffractogram.

IV. Conclusions

Several bonding procedures of MnBi in the temperature range from 540°C to 1520°C have been reported previously\(^6\)\(^\text{--}^8\). But, none of them have established the reacting temperature to be below the eutectic point of the Mn–Bi binary system. In the bonding reaction above the eutectic point, the coexistence of the liquid and solid phases should bring about the reduction of the contacting surface area whereby the bonding reaction ceases to proceed effectively.

From the present result of magnetic measurement, it can be seen that by the transformation of the compound into the high-temperature phase, about 26 per cent of total manganese atoms lose the ferromagnetic exchange. According to the disordered model for the high-temperature phase by Roberts\(^4\), some manganese atoms on the simple hexagonal site of the NiAs structure intrude into the interstices of bismuth layers situated on the close-packed hexagonal site, and consequently the ferromagnetic interaction between the nearest neighbours in the direction parallel to the c axis must be lost partially. Nearly 4.3 per cent of total manganese atoms are required to jump into the interstices to reduce the magnetization of the high-temperature phase from that of low-temperature phase, which is a smaller value than that in a previous report\(^5\). Random intrusion of 4.3 per cent of manganese atoms leads to the nearly 26 per cent decrease of magnetization. The value of anomalous specific heat at the magnetic transition temperature, \((13.5 \pm 1.5) \times 10^2 \text{cal/mol})\), exceeds distinctly that expected from the known formula for the total excess specific heat at the magnetic transition by molecular field theory,

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Q = \frac{3s}{2(s+1)} RT = 6.3 \times 10^2 \text{cal/mol},
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where \(s\) is the total spin quantum number of the magnetic element, \(R\) the gas constant and \(T\) the transition temperature. So, at least the same level of energy should be required for the structural transformation at the magnetic transition temperature by the random intrusion of manganese atoms into the interstices of bismuth layers accompanied by the extension of the a axis and the contraction of the c axis.

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