Phase Diagram of Manganese-Zinc System

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The constitution of binary alloys of Mn and Zn has been investigated mainly by X-ray and magnetic examinations. A revised phase diagram is presented, which differs from the so-called Hansen's phase diagram in the following points. (1) There is a new ferromagnetic phase, named the \( \beta_1 \) phase, extending from 50 to 56 at\% Mn at temperatures below 180\(^\circ\)C, and (2) the \( \beta_{Mn} \)-phase field is much wider, the Mn-poor boundaries being located at 53, 56 and 69 at\% Mn at temperatures 250\(^\circ\), 300\(^\circ\) and 400\(^\circ\)C, respectively. The cubic-tetragonal transformation of the \( \alpha' \) phase and the existence of the metastable \( \varepsilon' \) phase are also mentioned briefly.

(Received September 4, 1971)

I. Introduction

The constitution of the Mn–Zn system was investigated by Schramm\(^{(1)}\) and by Potter and Huber\(^{(2)}\) who dealt with the ranges 0 to 50 and 50 to 100 wt\% Mn, respectively. The results are summarized in Hansen's book\(^{(3)}\), as shown in Fig. 1. The First Supplement of this book written by Elliott\(^{(4)}\) in 1965 gave no reference to the Mn–Zn system except a preliminary report by the present authors and their collaborators\(^{(5)}\) who studied this system with a particular interest in its magnetic properties. The present authors made it clear that the ferromagnetism of the alloy containing about 25 at\% Mn, firstly observed by Nowotny and Bittner\(^{(6)}\), was due to the existence of a metastable phase having an ordered hcp structure of the Ni\(_3\)Sn type. This phase was named the \( \varepsilon' \) phase because a disordered hcp phase in the Mn–Zn system had been known as the \( \varepsilon \) phase.

The present authors also found that the \( \alpha' \) phase near 25 at\% Mn has an ordered fcc structure of the Cu\(_3\)Au type\(^{(7)}\) and exhibits antiferromagnetism\(^{(7)}\) below -150 \(^\circ\)C, where the lattice is transformed to a tetragonal structure simultaneously. These facts were confirmed later by neutron diffraction\(^{(8)}\) and specific heat measurements\(^{(9)}\). The tetragonal phase was named the \( \alpha'_t \) phase.

In 1964 a new ferromagnetic phase was found in a composition range near 50 at\% Mn at temperatures below 180\(^\circ\)C\(^{(10)}\). This range corresponds to a portion of the \( \alpha' + \beta_{Mn} \) field in Hansen's diagram. The crystal structure of the new phase is an ordered bcc structure of the CsCl type which is identical to that of the well-known \( \beta \) phase containing about 60 at\% Mn. The \( \beta \) phase is stable only above 600\(^\circ\)C and also exhibits ferromagnetism if quenched to room temperature\(^{(11)}\). The new phase near 50 at\% Mn was named the \( \beta_1 \) phase because of its similarity to the \( \beta \) phase. Magnetic properties of both \( \beta \) and \( \beta_1 \) phases are interesting in view of the fact that they have a canted spin structure\(^{(8,11)}\).

The Second Supplement of Hansen's book written by Shunk\(^{(12)}\) has briefly referred to the existence of \( \alpha'_t \) and \( \beta_1 \) phases. The homogeneity range of the \( \beta_1 \) phase has been reported later, together with the effect of the addition of third elements on this phase\(^{(13)}\).

In the present paper, a revised phase diagram of the Mn–Zn system is presented for the first time since the

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publication of Hansen's book. In addition to the insertion of the new $\beta_1$ phase, a marked revision of the boundary of the $\beta_{\text{Mn}}$ phase is made.

II. Experimental Procedures

1. Preparation of alloys

Desired amounts of 99.9% pure electrolytic Mn and 99.9% pure Zn were sealed together in an evacuated quartz tube and heated up to a temperature sufficiently higher than the liquidus line. The preparation of Murrich alloys was rather difficult because the quartz tube was attacked by Mn and often exploded on account of the high vapour pressure of Zn.

The alloys containing 50~70 at% Mn could be prepared by means of double quartz tube sealing. Although the reaction between the sample and the inner quartz tube was unavoidable, no appreciable amount of silicon was permeated in the sample. Chemical analysis showed that the composition of alloys was not different from the mixing ratio by more than 0.5%, and that there were no appreciable impurities. Therefore, only the mixing ratio of the alloys is shown in the present paper.

The quartz tube containing the molten alloy was quenched into water so as to reduce the size of segregation domains as small as possible. An ingot thus obtained was sealed in an evacuated quartz tube again, and heated to a temperature at which a single phase was stable. The small segregation domains were easily eliminated by annealing for a short time. For example, a homogeneous $\varepsilon$-phase alloy containing 50 at% Mn was obtained by annealing at 600°C for a few hours.

Since the present work is mainly concerned with the equilibrium state at fairly low temperatures, it is essential to accelerate the rate of transformation from a high-temperature phase to a low-temperature phase. The internal stress imposed by filing was found to be most effective for this purpose. Therefore, the ingot was filed down and then annealed at a required temperature. For example, if the $\varepsilon$-phase ingot containing 50 at% Mn was powdered by filing and annealed at 150°C for 24 hours, it was completely transformed to the $\beta_1$ phase.*

On the other hand, no appreciable transformation occurred if the same heat treatment was applied to the bulk ingot. It is to be mentioned here that the process of homogenization of the $\varepsilon$-phase ingot can be omitted in order to obtain the $\beta_1$-phase alloy. The inhomogeneity of the specimen can be removed by the heat treatment at 150°C, since the size of the segregation domains is much less than that of the filed powders. Thus the present method for the preparation of the low-temperature phase alloys is also applicable to the alloys having no single-phase field at high temperatures.

2. X-ray diffraction experiments

Not only the phase identification but also the determination of phase boundaries were made by X-ray diffraction experiments using a conventional diffractometer of the Geiger-counter type. Powder diffraction patterns were taken by CuKα radiation throughout the present work.

The phase boundaries can be determined from the composition dependence of lattice parameters and/or relative intensities of diffraction lines of the two coexisting phases. In general the lattice parameters are dependent on the composition in a single-phase field but independent of the average composition of a two-phase field, so that the phase boundary corresponds to an angle point on the lattice parameter vs. composition curve. In some cases, however, the angle point is not so distinct that an erroneous conclusion may be derived as will be pointed out later.

The determination of phase boundaries from the diffraction intensities is based on the following principle. For the alloys consisting of the two phases $\alpha + \beta$, the intensity $I_\alpha$ or $I_\beta$ of a diffraction line of $\alpha$ or $\beta$ should be proportional to the amount of $\alpha$ or $\beta$, respectively, if the conditions of the powder samples and of the incident X-ray beams would be the same. The composition dependence of $I_\alpha$ and $I_\beta$ is shown in Fig. 2 schematically, where $I_\alpha$ and $I_\beta$ correspond to the intensities for the single-phase samples of $\alpha$ and $\beta$, respectively. However, it is difficult to take the diffraction patterns for the different samples under the same conditions. On the other hand, the relative intensity $I_\alpha/I_\beta$, which varies from 0 to infinity in the $\alpha + \beta$ field, can easily be determined by usual experiments. A quantity $P$, defined as

$$P = \frac{k I_\alpha/I_\beta - 1}{k I_\alpha/I_\beta + 1},$$

where $k$ is a constant, will vary from $-1$ to $+1$, corresponding to $I_\alpha/I_\beta$.

If it is chosen that $k = I_{\alpha \beta}/I_{\alpha \beta}$, a
linear relationship between \( P \) and composition is expected, as shown in the lower part of Fig. 2. However, the value of \( k \) cannot be determined directly, and so it is chosen by trial and error so as to obtain a straight line for \( P \) vs. composition. The phase boundaries are thus determined by extrapolations of the straight line to the positions \( P = \pm 1 \).

### 3. Magnetic measurements

Since the \( \beta_1 \) phase is ferromagnetic at room temperature while the neighbouring phases are not, phase boundaries around the \( \beta_1 \) phase can be determined from angle points on the magnetization vs. composition curve at room temperature. The magnetization was measured by Faraday's method using an automatic chemical balance and an electromagnet. A pure nickel sample was used as a standard of the intensity of magnetization.

### III. Results and Discussion

#### 1. Homogeneity range of the \( \beta_1 \) phase

The alloys containing 30–60 at% Mn were studied by X-ray and magnetic examinations after they reached equilibrium at 150°C. Composition dependences of the magnetization and the lattice constant of the \( \beta_1 \) phase are shown in Fig. 3 (a) and 3 (b), respectively. Values of \( P \) calculated from relative intensities of the (111) line of the \( \alpha' \) phase and (110) line of the \( \beta_1 \) phase are shown in Fig. 3 (c), where the value of \( k \) in eq. (1) is chosen to be 3.0. It is concluded from these data that the homogeneity range of the \( \beta_1 \) phase at 150°C extends from 50.0 to 56.5 at% Mn and also that the \( \alpha' \) phase contains at most 30 at% Mn and the \( \beta_{\text{Mn}} \) phase contains at least 60 at% Mn at 150°C.

Similar but less detailed studies were made on the alloys in equilibrium at temperatures lower than 150°C. When the filed specimens of \( \alpha' \)-phase alloys containing 50–56 at% Mn were annealed at a temperature as low as 100°C for 24 hours, they were almost completely transformed to the \( \beta_1 \) phase, whereas those containing 36–44 at% Mn could not easily reach equilibrium at 100°C so that \( \varepsilon \) was still found together with \( \alpha' \) and \( \beta_1 \) even after a prolonged annealing.

The \( \beta_1 \) phase becomes unstable at 200°C, undergoing the transformation \( \beta_1 \to \alpha' + \beta_{\text{Mn}} \) or \( \beta_1 \to \beta_{\text{Mn}} \) at the composition of 50 or 56 at% Mn, respectively. The lower the temperature, the slower becomes the rate of transformation. At 175°C, however, the transformation does not occur, the equilibrium state being the same as that at 150°C. It is likely that the transformation temperature is around 180°C.

Now, some questions may arise as to the intrinsic stability of the \( \beta_1 \) phase, which exists only at temperatures as low as 150°C. The possibility of the existence of more stable states cannot absolutely be excluded, since the approach to equilibrium is, in general, extremely sluggish at these temperatures. It might be considered, for example, that the \( \beta_{\text{Mn}} \) phase or the \( \alpha' + \beta_{\text{Mn}} \) phase is more stable than the \( \beta_1 \) phase even at 150°C. At the present stage, however, the \( \beta_1 \) phase has to be regarded as the stable phase, because no further transformation has been observed below 180°C at all.

#### 2. Boundary of the \( \beta_{\text{Mn}} \) phase

According to Hansen's phase diagram(3) the boundary of the \( \beta_{\text{Mn}} \) phase is located at the composition of 80 at% Mn, while the \( \beta_{\text{Mn}} \) field at 150°C seems to extend to 60 at% Mn, as can be seen in Fig. 3. Thus the equilibrium phase relationship was studied at higher temperatures, 250°C, 300°C and 400°C, for the alloys containing 42–66 at% Mn. Since most samples were found to be in the two-phase field, \( \varepsilon + \beta_{\text{Mn}} \), the phase boundaries could be determined by the relative intensities of the diffraction lines. The \( P \) values in eq. (1) for the (10.1) line of the \( \varepsilon \) phase and the (221+300) line of the \( \beta_{\text{Mn}} \) phase are plotted against the composition, as shown in Fig. 4, where \( k = 1.2 \) was chosen. The phase boundaries are indicated by arrows in the figure. The boundaries between the \( \varepsilon \) field and the \( \varepsilon + \beta_{\text{Mn}} \) field at 250°C, 300°C and 400°C are located at 39, 41 and 48 at% Mn, respectively, in good agreement with Hansen's diagram, whereas those between the \( \varepsilon + \beta_{\text{Mn}} \) field and the \( \beta_{\text{Mn}} \) field are located at 53, 56 and 69 at% Mn, respectively, and are greatly different from Hansen's diagram based on Potter and Huber's work(5).

Potter and Huber determined the phase boundary on the basis of the composition dependence of the lattice
parameter of the $\beta_{Mn}$ phase. Their experimental results are plotted in Fig. 5*, together with those obtained by the present authors. For the alloys containing less than 85 at% Mn, the specimens were quenched from 427°C by Potter and Huber's and from 250°C by the present authors. For the Mn-richer alloys, however, the specimens were quenched from higher temperatures at which the single $\beta_{Mn}$ phase is stable. Potter and Huber's results seem to fall on two straight lines, shown by broken lines in Fig. 5, which intersect with each other at 80 at% Mn. Based on a prejudice that the lattice parameter of the $\beta_{Mn}$ phase is a linear function of the composition, they might have concluded that the boundary of $\beta_{Mn}$ phase is located at 80 at% Mn. The results of the present authors, on the other hand, reveals clearly that the lattice parameter vs. composition curve is concave downwards, as illustrated by a solid line in Fig. 5, suggesting that the boundary at 250°C is located at less than 60 at% Mn. Moreover, this curve intersects with the horizontal broken line at the composition of about 70 at% Mn, indicating that the phase boundary of the $\beta_{Mn}$ phase at 427°C is located at 70 at% Mn, in agreement with that determined by the diffraction intensity measurement. It is to be emphasized that Potter and Huber's experimental results are quite consistent with the present ones although the conclusions are quite different from each other.

3. Temperature of eutectoid $\varepsilon \Rightarrow \alpha' + \beta_{Mn}$

In the composition range between 30 and 50 at% Mn, the eutectoid reaction $\varepsilon \Rightarrow \alpha' + \beta_{Mn}$ was found at around 220°C**. In order to determine the precise temperature, some trials were made to obtain the equilibrium state at 200°C~260°C, but ended in failure even though use was made of the filing technique mentioned above. For example, when the $\varepsilon$-phase alloy with 42 at% Mn was filed down and annealed at 220°C for over a week, there still existed the three phases $\varepsilon + \alpha' + \beta_{Mn}$. The internal stress imposed by filing had possibly been relaxed before the transformation $\varepsilon \Rightarrow \alpha' + \beta_{Mn}$ was accomplished, so that the acceleration of the rate of transformation was interrupted. This was in marked contrast to the fact that the 42 at% Mn alloy reached equilibrium in a short time at 150°C and transformed to the two phases $\alpha' + \beta_1$ completely.

4. Phase diagram

The results obtained by the present work are summarized in a revised phase diagram shown in Fig. 6. Reliable and uncertain boundaries are indicated by solid and broken lines, respectively. Heavy lines are due to the present work as distinguished from light lines based on Hansen's diagram. Small circles on the heavy lines indicate the locations of the boundaries determined with high certainty.

Main differences between Fig. 1 and Fig. 6 are as follows: (1) the existence of the $\beta_1$ phase, and (2) the extension of the $\beta_{Mn}$ field. The present work is not so inconsistent with the previous works by Schramm(1) and by Potter and Huber(2), whose studies were restricted in the temperature range above 200°C.

The existence of the $\alpha'_1$ phase and the $\varepsilon'$ phase, found in the present authors as described in the introduction, is omitted in Fig. 6, because the $\alpha'_1$ field exists at excessively low temperatures and the $\varepsilon'$ phase is merely metastable.

Acknowledgments

The authors are indebted to many students in their laboratory for co-operation in the experiments, and especially to Mr. Shunsuke Matsuyama for the preparation and the X-ray measurements of the $\beta_{Mn}$-phase alloys.

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* The unit of lattice parameters in Potter and Huber's paper seems to be the $\times 10^2$ unit, although they used the term 'Å unit'. In this figure their values were multiplied by 1.002 to convert into the true Å unit.

** According to Hansen's phase diagram, the eutectoid temperature is around 250°C.