Chemistry

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1961

SovietRxiv

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Chemistry

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Investigation of the Mn–Si System in the Silicon-Rich Region

(Presented by Academician N. I. Chernyaev, 12 VI 1961)

In recent years the attention of a number of researchers has been drawn to manganese disilicide ($MnSi_2$), which possesses semiconducting characteristics. At the same time, an analysis of the literature data cited below on the investigation of Mn—Si alloys makes it possible to doubt the complete reliability of the reported phase composition of the part of the system that interests us. All this, together with the results of preliminary microstructural studies, determined the undertaking of work on a thorough study of the Mn—Si system in the silicon-rich region.

a) According to the phase diagram of the Mn—Si system based on early investigations ([1,2]), presented in the monograph by A. S. Berezhnoi ([3]), manganese disilicide is formed by the peritectic reaction: liquid $+Si \rightleftarrows MnSi_2$ at $\sim 1144^\circ$.

The existence of manganese disilicide was confirmed by X-ray diffraction by Boren ([4]). According to his data, $MnSi_2$ crystallizes in a tetragonal structure with constants $a = 5.51$ Å, $c = 17.42$ Å, and $c/a = 3.16$; space group D_4^{18}. A later study by Hansen ([5]) indicates a different scheme for the formation of the disilicide: liquid $+MnSi \rightleftarrows MnSi_2$ at $\sim 1155^\circ$.

According to E. N. Nikitin ([6,7]), manganese disilicide at room temperature has a thermoelectric emf coefficient on the order of 80–120 $\mu V/^\circ C$ (depending on the purity of the starting materials) with an electrical conductivity of 300–400 $\Omega^{-1} \cdot cm^{-1}$. With increasing temperature, the thermoelectric characteristics of $MnSi_2$ change as in metals: the electrical conductivity decreases; the thermoelectric emf increases ([8]). In this work the results are presented of an investigation of the thermoelectric properties of alloys of the Mn—Si system within the range from 20 to 80 at.% Si. On the basis of the dependences obtained, the conclusion was drawn that a new compound, Mn_2Si_3, exists in the MnSi—$MnSi_2$ region. However, this conclusion is not sufficiently justified, since the author did not check the phase composition of the alloys and their equilibrium state.

Summarizing the literature review, it is necessary to repeat the earlier conclusion that the phase composition of the indicated part of the system as reported in the literature is insufficiently substantiated. This is confirmed by the complex

Fig. 1. Microstructures of Mn–Si alloys

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character of the dependence of the thermoelectric properties on composition ([8]), the contradictory data on the nature of disilicide formation ([3,5]), and the absence of original works on X-ray investigation of Mn—Si alloys ([4]) and on the results of microstructural and thermal analyses ([5]) (Hansen refers to his unpublished work).

b) As starting materials, silicon obtained by the Beketov method was used (99.998% Si), as well as electrolytic manganese, preliminarily remelted twice in vacuum and, according to spectral analysis data, containing traces of Al, Si, Cu and less than 0.001% Pb, Mo, Ti, and Co. The alloys were prepared according to the following procedure. Preliminary–

However, in order to carry out the synthesis of the phases corresponding to the phase diagram, the starting components were fused in evacuated and sealed quartz ampoules using high-frequency heating. Subsequently, to prepare specimens of the required dimensions, the resulting alloy was placed in a quartz ampoule of the necessary diameter and remelted in a resistance furnace. After thorough mixing, the melt was cooled in air. The identity of the conditions for preparing the alloys and the slight

Fig. 1. Microstructures of Mn–Si alloys:
a –$MnSi_2$, as-cast, 270×;
b –$MnSi_2$, annealed, 270×;
c –46.4% Mn + 53.5% Si, as-cast, 270×;
d –Mn_3Si_5, annealed, 270×;
e –Mn_3Si_5 + 0.5% Si, annealed, 270×;
zh –Mn_3Si_5 + 0.5% Mn, annealed, 270×;
z –55.5% Mn + 44.5% Si, annealed, 270×;
i –50.5% Mn + 49.5% Si, annealed, 270×

decrease in the weight of the specimens (~0.2%) compared with the weight of the initial charge make it possible to regard the deviation of the composition from the calculated one as insignificant.

To bring the alloys into an equilibrium state, they were annealed in sealed quartz ampoules under argon at a temperature of 1000° for 200 h and cooled with the furnace.

To reveal the structure, the polished surfaces were etched with hydrofluoric acid. Thermal analysis was carried out both by differential recording of heating curves for equilibrium specimens and by recording the cooling of the melt. The specimen and the standard (silicon) were sealed in evacuated Stepanov quartz vessels. The investigation was conducted in the temperature range 600–1200°.

X-ray phase analysis was performed from X-ray diffraction patterns obtained

Fig. 2. Phase diagram of part of the Mn–Si system according to our data

Figure 2: Fig. 2. Phase diagram of part of the Mn–Si system according to our data

by the Debye method using chromium radiation.

The thermoelectric properties at room temperature were measured by a compensation circuit using a potentiometer. The temperature dependence of the electrical conductivity was measured in vacuum up to ~800°.

c) By the procedure described above, a series of alloys with a manganese content from 46 to 55% was prepared.

An initial study of the microstructure of a specimen of composition $MnSi_2$ in the cast and annealed states (Fig. 1, a, b) showed that it is not single-phase and contains appreciable silicon precipitates (the differences in the structure of the cast and annealed alloy, mainly in the outlines of the silicon precipitates, are apparently connected with the features of crystallization of the eutectic, to which, as will be seen below, the indicated composition is close). A detailed study of the microstructure of specimens richer in silicon confirmed the correctness of the conclusion that there is no phase of composition $MnSi_2$ in the Mn –Si system and, secondly, no phase transformations whatever in the region of primary crystallization of silicon. Confirmation of the latter conclusion may be provided by the structure of the alloy containing 53% Si in the cast state (Fig. 1, c). Study of the structure of alloys richer in manganese (Fig. 1, d–h) gave grounds to suppose the presence in this part of the system of a transformation whose result is the appearance of homogeneity in the specimen containing 46% Si (Fig. 1, g, d). This composition corresponds to a stoichiometric ratio between the components of 3 : 5.

Fig. 2. Phase diagram of part of the Mn–Si system according to our data

A detailed study of alloys near the indicated composition made it possible to establish that the compound Mn_3Si_5 has a narrow homogeneity range, corresponding to solution in the compound of about 0.5% excess silicon and manganese atoms (Fig. 1, e, zh).

The results of differential thermal analysis of the heating of equilibrium specimens and the cooling of melts, together with the microstructural data, made it possible to construct a phase diagram for part of the Mn–Si system (Fig. 2). Crosses mark the thermal effects obtained by Hansen ([5]), which, as is seen from Fig. 2, agree well with our results. From the diagram presented it follows that the compound Mn_3Si_5 is formed by a peritectic reaction from manganese monosilicide and liquid:

$$\text{liquid} + \text{MnSi} \rightleftarrows Mn_3Si_5,$$

Fig. 3. Isotherms of thermoelectric properties of Mn–Si alloys in the cast (a) and annealed (b) states in the region of the Mn_3Si_5 compound

Figure 3: Fig. 3. Isotherms of thermoelectric properties of Mn–Si alloys in the cast (a) and annealed (b) states in the region of the Mn_3Si_5 compound

Fig. 4. Temperature dependences of the electrical conductivity of alloys in the solid-solution region based on Mn_3Si_5. 1 –53.99% Mn; 2 –54.51% Mn; 3 – 53.45% Mn

Figure 4: Fig. 4. Temperature dependences of the electrical conductivity of alloys in the solid-solution region based on Mn_3Si_5. 1 –53.99% Mn; 2 –54.51% Mn; 3 –53.45% Mn

at 1159°. The eutectic of this compound with silicon corresponds to a content of 49% Si (Fig. 1, i) and melts at a temperature 10° lower (1149°). The composition of the compound is very close to the composition of the liquid phase corresponding to the nonvariant peritectic transformation. This determines the fact, evident from the analysis of the microstructures, that the process of formation of the compound Mn_3Si_5 occurs mainly during crystallization

Fig. 3. Isotherms of thermoelectric properties of Mn–Si alloys in the cast (a) and annealed (b) states in the region of the Mn_3Si_5 compound

(compare photograph 2, d in Fig. 1), and in cast specimens no patterns characteristic of quenched peritectic transformations are observed.

The principal conclusion of the microstructural studies and thermal analysis –that the compound $MnSi_2$ is absent in the Mn–Si system and that a more manganese-rich phase, Mn_3Si_5, exists–is confirmed by X-ray phase-analysis data: additional reflection lines appear on the X-ray patterns at those points where, according to the microstructural studies, separation of secondary phases (MnSi and silicon) occurs.

In all prepared alloys, in the cast and annealed state, the specific electrical conductivity and the coefficient of thermoe.m.f. were measured. The obtained values were plotted as functions of composition (Fig. 3). From the graphs presented it becomes clear that the complex character of the dependences of thermoelectric properties in this part of the system ([8]) is determined by the presence of a homogeneity range based on the compound Mn_3Si_5. Dissolution of manganese and silicon atoms in excess relative to the stoichiometric composition, probably associated with the formation of a defective lattice by subtraction of atoms of the other kind, is accompanied by the appearance of additional current carriers. Evidence of this is the considerable increase in electrical conductivity within the limits of the solid solution. At the same time there is some increase in the thermoelectromotive force.

Fig. 4. Temperature dependences of the electrical conductivity of alloys in the

solid-solution region based on Mn_3Si_5.
1 –53.99% Mn; 2 –54.51% Mn; 3 –53.45% Mn

The change in thermoelectric characteristics in two-phase regions is determined by the influence of secondary phases of different nature. For three specimens in the solid-solution region of the compound Mn_3Si_5, the temperature dependences of electrical conductivity were measured. The results obtained were plotted (Fig. 4). Up to a temperature of about 500° all three specimens show a metallic dependence $\ln \sigma$ $(1/T)$; at higher temperatures the measured values fall well on a single straight line. The activation energy of the current carriers calculated from its slope is ~ 0.2 eV.

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Academy of Sciences of the USSR

Received
8 VI 1961

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Note: Figure translations are in progress. See original paper for figures.