[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF STOCKHOLM AND THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

x-Ray Analysis of Iron-Tin Alloys

BY W. F. EHRET[1] AND A. F. WESTGREN[2]

The iron–tin system has been the subject of a number of investigations in the past. The first extensive examination of the system was completed by Isaak and Tammann in 1907.[3] Their thermal analysis led them to the following conclusions: (1) the solubility of tin in iron is 19 weight per cent. at all temperatures up to 1140°, (2) at 1140° and between 50-89% tin, a region of incomplete miscibility exists in the liquid state, (3) a compound is formed which undergoes two polymorphic transformations in the solid state. Because of marked segregation in many of their alloys, they were unable to ascribe a definite formula to the compound. In 1926, Wever and Reinecken[4] published the results of a thoroughgoing investigation of the system. They employed the thermal, magnetometric, and microscopic methods of analysis and arrived at an equilibrium diagram which is rather similar to that of Isaak and Tammann. A compound, Fe_3Sn, is supposed to be stable at elevated temperatures and another compound, $FeSn_2$, stable below 890°, is postulated as undergoing three polymorphic transformations as the temperature is varied. It is interesting to note that the diagram of Wever and Reinecken indicates no partial miscibility in the liquid state. According to these experimenters, all that is necessary, to prevent the segregation of alloys of 50–90% Sn into layers of different density, is rapid stirring of the melt followed by quenching. The non-existence of a miscibility gap has, however, been called into question by Ruer and Kuschmann,[5] who examined a 70% Sn alloy and found two distinct layers whose microstructure indicated partial miscibility in the liquid state. More recently, Edwards and Preece,[6] using thermal and microscopic methods, have confirmed the existence of a zone of partial miscibility in the liquid state (see Fig. 1). The equilibrium diagram constructed by these investigators differs from that of Wever and Reinecken in the following additional respects: (1) the compound Fe_3Sn is not found, (2) a compound, Fe_2Sn, is stable between 760–900°, (3) a compound, FeSn, is stable below 800°, (4) the compound $FeSn_2$ exists only below 496°. The x-ray analysis of this system has yielded results which are in fair agreement with those of the last mentioned workers. The latter have apparently overlooked two phases, the γ and β' of Fig. 3.

The number of alloys prepared by the authors may be seen from Table I.

---

(1) Washington Square College, New York University.

(2) Institute of General and Inorganic Chemistry, University of Stockholm.

(3) Isaak and Tammann, *Z. anorg. Chem.*, **53**, 281 (1907).

(4) Wever and Reinecken, *Z. anorg. allgem. Chem.*, **151**, 349 (1926).

(5) Ruer and Kuschmann, *ibid.*, **153**, 260 (1926).

(6) Edwards and Preece, *J. Iron Steel Inst.* (*London*), **124**, 41 (1931).

which gives a summary of the results obtained in this investigation. Electrolytic iron and Kahlbaum tin were used as starting materials and the melts were made in a vacuum furnace constructed by G. Phragmén of the Metallographic Institute, Stockholm. The furnace is essentially a Tammann furnace operating in vacuum. A glass window in the top of the furnace permitted the simultaneous observation of the temperature (optical pyrometer) and condition of the melt. In each case the temperature was raised to 1550–1570° to ensure complete melting of the iron. Although no mechanical means of stirring was provided, the bubbling and spurting which took place in the melt both before and after the last of the solid had disappeared, was apparently very effective in counteracting segregation such as was noticed by previous workers. Even though the melts were cooled slowly—about an hour was required to come to room temperature—a non-uniform regulus was obtained in only one case, that of the 70% Sn alloy. Several attempts to prepare a uniform alloy of this composition resulted in segregation into two layers of approximately equal bulk. The x-ray analysis showed each layer to consist of practically a single intermetallic phase (the β and $FeSn_2$ phases).

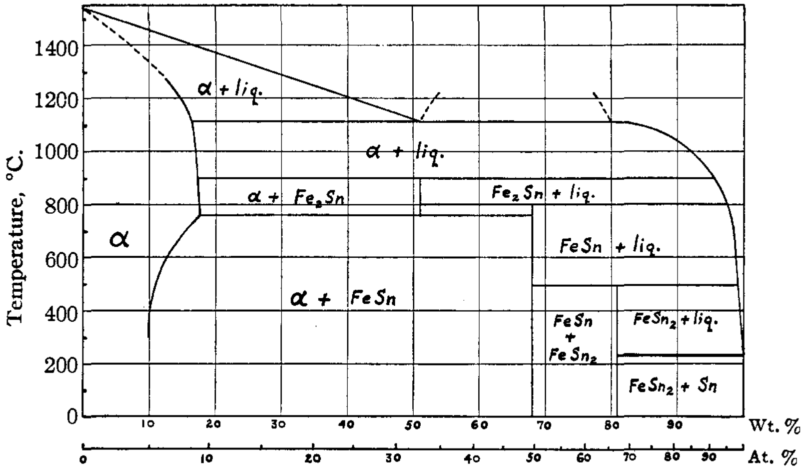

Fig. 1.—Equilibrium diagram of the system Fe–Sn drawn in accordance with the data of Edwards and Preece.

The several alloys were subjected to different heat treatments as is indicated in Table I. The annealing was always carried out upon filings of the original melts sealed in evacuated glass or quartz tubes. That equilibrium was not always established, even after long annealing, follows from the fact that a number of our photograms indicate the presence of three and even four phases. This may be laid in large measure to the tendency toward sintering which is especially pronounced at high temperatures and in alloys of high tin content. Since the powder method of x-ray analysis was to be employed it was necessary to counteract the sintering. The admixture of powdered glass or quartz with the metal filings was found quite effective for this purpose. The glass or quartz was removed subsequent to the annealing by means of a sieve, or the alloy powder was isolated by means of a magnet.

TABLE I

SUMMARY OF X-RAY STUDIES OF IRON–TIN ALLOYS

% Sn	At. % Sn	Heat treatment	Phases	Lattice dimensions
1.0	0.5	Annealed 900°, 1 week Recryst. 650°, 3 min. Air cooled	α	2.864 Å. (pure α-Fe = 2.861 Å.)
3.0	1.5	Ann. 900°, 1 wk. Recryst. 600°, 10 min.	α	2.871 Å.
7.6	3.7	Ann. 900°, 1 wk. Recryst. 700°	α	2.887 Å.
12.1	6.0	Ann. 900°, 1 wk. Recryst. 650°, 10 min.	α	2.903 Å.
17.6	9.0	Ann. 900°, 1 wk. Recryst. 650°, 10 min.	α	2.921 Å.
27.7[a]	15.5[a]	Ann. 900°, 1 wk. Recryst. 600°, 10 min.[a]	β + α (trace)	β: a_1 = 5.293 Å. a_3 = 4.443 a_3/a_1 = 0.839
27.7	15.5	Ann. 680°, 4 days Quenched	α + β'	α: a_1 = 2.894 Å.
27.7	15.5	Ann. 860°, 2 days Quenched	α + β″ + γ (Sn?)	α: a_1 = 2.922 Å. β″: a_1=5.449 Å. a_3 = 4.353 a_3/a_1 = 0.80 γ: a_1 = 4.179 Å. a_3 = 5.201 a_3/a_1 = 1.245
27.7	15.5	Ann. 950°, 10 min. Quenched	α + β″ + Sn	α: a_1 = 2.92 Å. β″: a_1= 5.449 Å. a_3 = 4.353 a_3/a_1 = 0.779
39.3	23.5	Ann. 450°, 75 min. Quenched	α + β	α: a_1 = 2.91 Å.[b] β: a_1 = 5.293 Å. a_3 = 4.442 a_3/a_1 = 0.839
39.3	23.5	Ann. 680°, 4 days Quenched	α + β′	α: a_1 = 2.896 Å.
39.3	23.5	Ann. 850°, 15 min. Quenched	α + β″ + γ	
39.3	23.5	Ann. 860°, 2 days Quenched	α + β″ + γ + Sn	α: a_1 = 2.925 Å. γ: a_1 = 4.179 Å. a_3 = 5.201 a_3/a_1 = 1.245
39.3	23.5	Ann. 910°, quenched	α + Sn	α: a_1 = 2.924 Å.

TABLE I (*Concluded*)

% Sn	At. % Sn	Heat treatment	Phases	Lattice dimensions
39.3	23.5	Ann. 920–930°, 5 min. Quenched	α + γ	
48.2	30.4	Ann. 450°, 1 wk. Quenched	β + very little α	
48.2	30.4	Ann. 680°, 2.5 days Quenched	α + β'	α: a_1 = 2.898 Å.
48.2	30.4	Ann. 860°, 1 day Quenched	β" + little Sn	β": a_1 = 5.449 Å. a_3 = 4.353 a_3/a_1 = 0.799
48.2	30.4	Ann. 950°, 1.5 hrs. Quenched	α + Sn + β"	α: a_1 = 2.924 Å. β": same as at 860°
59.4	40.7	Ann. 450°, 5 days Quenched	β + α (trace)	β: a_1 = 5.292 Å. a_3 = 4.440 a_3/a_1 = 0.839
59.4	40.7	Ann. 660–680°, 2 days Quenched	β'	
[c]				
81.7	67.7	Ann. 330°, 40 hrs. Air cooled	$FeSn_2$	$FeSn_2$: a_1 = 5.317 Å. a_3 = 9.236 a_3/a_1 = 1.737
81.7	67.7	Ann. 450°, 1 wk. Quenched	$FeSn_2$	
81.7	67.7	Ann. 600°, 2 days Quenched	β + Sn	
81.7	67.7	Ann. 680°, 4 days Quenched	β + Sn	β: a_1 = 5.291 Å. a_3 = 4.437 a_3/a_1 = 0.839
81.7	67.7	Ann. 760–780°	Sn + γ	
81.7	67.7	Ann. 850–870°, 30 min. Quenched	Sn + γ	γ: a_1 = 4.231 Å. a_3 = 5.211 a_3/a_1 = 1.232
90.1	80.0	Ann. 400°, 15 hrs.	Sn + $FeSn_2$	[d]
97.7	95.0	Ann. 400°, 15 hrs.	Sn + $FeSn_2$	[d]

[a] It is probable that the ten minutes at 600° were sufficient to bring about not only a recrystallization but also to establish a new equilibrium characteristic of the lower temperature. A sample of this alloy was annealed at 600° thirty minutes and quenched, whereupon photograms were obtained which indicated the presence of the β and α phases. The positions of the diffraction lines were practically identical with those for the alloy sample which had been annealed at 900° and recrystallized at 600°.

[b] Probably no real equilibrium.

[c] An alloy containing 71.8% Sn separated into two layers upon cooling. It was probably not in a state of equilibrium. The upper layer, containing 78.9% Sn, produced the diffraction pattern of $FeSn_2$. The lower layer (54.9% Sn) gave the pattern of the β phase.

[d] The constants calculated for Sn were identical with those reported for pure Sn by Westgren and Phragmén [*Z. anorg. allgem. Chem.*, 175, 80 (1928)]. Iron is therefore practically insoluble in tin.

x-Radiation was obtained from an iron anode in a Siegbahn–Hadding type of tube. The cameras were of the focusing type and constructed according to the specifications of G. Phragmén. The mean error of the parameter values given is estimated at 0.002 Å.

The Alpha Phase

From Table I and Fig. 2 it is apparent that α-iron dissolves increasing amounts of tin as the temperature is raised. The value of a_1, the length of the cube edge in the body-centered α-Fe lattice, increases linearly with the concentration of tin. At 680° the solubility of tin in iron is 9.8%, corresponding to $a_1 = 2.896$ Å. At about 900° the solubility has increased to 18.8%, corresponding to $a_1 = 2.925$ Å.[7] At higher temperatures the solid solubility is very likely even greater.

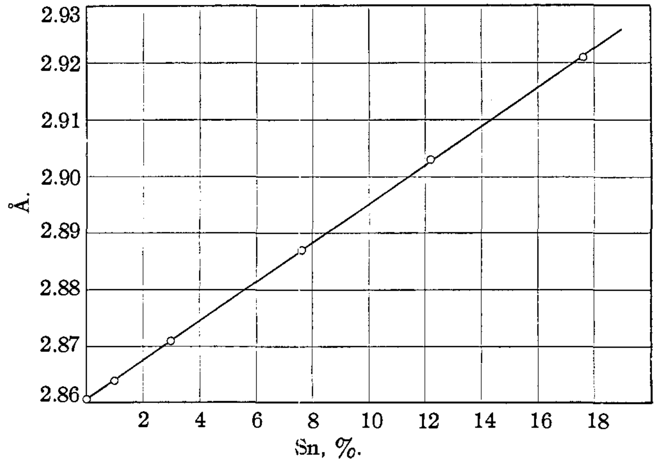

Fig. 2.—Expansion of α–Fe lattice as tin is dissolved.

The Beta Phase

Figure 3 represents roughly the results obtained in this investigation. The broken lines are simply indications of probable phase boundaries. As the Sn concentration is increased at low temperatures, the α phase is followed by a two-phase range in which α appears along with a phase we have called β (corresponds to FeSn of Edwards and Preece). The crystal lattice of the latter possesses hexagonal symmetry. The dimensions of the unit cell show practically no change with temperature or composition and this may be taken to mean that the β phase has a very narrow homogeneity range. Confirmation of this point is obtained from an examination of the diffraction pattern of the lower layer of the 71.8% Sn alloy, annealed at 480°. The pattern shows that the diffraction lines of the β phase correspond, within the limits of error, with those found on photograms of alloys

---

(7) Compare A. F. Westgren, *Trans. Am. Inst. Min. Met. Eng., Inst. Metals Division*, **14** (1931).

in which β is in equilibrium with α. The cell constants of the β phase as calculated from the photograms of the 59.4% Sn alloy, are: a_1 = 5.292 Å., a_3 = 4.440 Å., a_3/a_1 = 0.839. The volume of the unit cell is therefore 107.6 Å.^{3} Since the aforementioned alloy still contains traces of the α-phase, it is probable that the composition of the β-phase corresponds to FeSn (68% Sn). The density of the 59.4% Sn alloy, after tempering for a week at 370°, was 7.54 g. per cc. If the alloy is considered homogeneous, calculation gives 6.04 atoms per unit cell. In view of this it seems most probable that there are six atoms (three groups of FeSn) in the elementary prism of the β phase. Table II is typical of the results obtained in this investigation. In it the observed $\sin^2 \Theta/2$ values for the

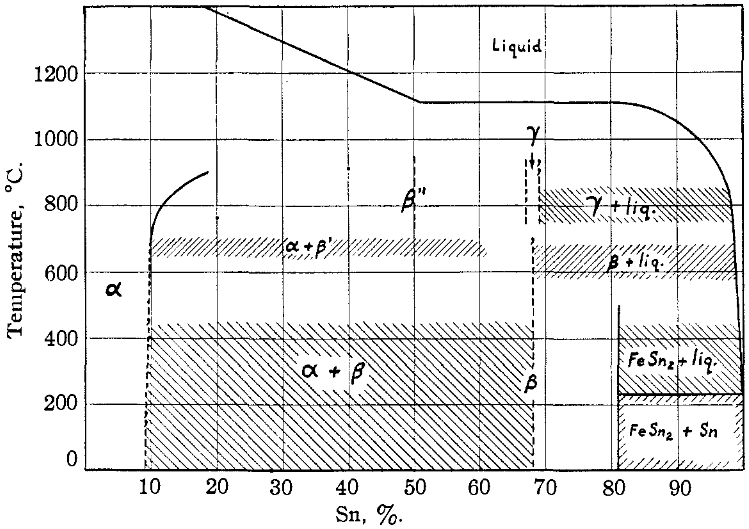

Fig. 3.—Schematic phase diagram of the system Fe–Sn.

TABLE II

DATA TAKEN FROM PHOTOGRAMS OF THE 59.4% SN ALLOY (β PHASE) ANNEALED AT 450° FOR FIVE DAYS AND QUENCHED

Intensity	FeK radiation	$h_1h_2h_3$	$\sin^2 \Theta/2$ observed	$\sin^2 \Theta/2$ calculated
s.	α	101	0.0917	0.0918
w.	β	110	.1092	.1098
s.	α	110	.1332	.1335
v. w.	β	111	.1486	.1488
w.	β	002	.1559	.1562
w.	α	200	.1780	.1780
w.	α	111	.1808	.1808
w.	β	201	.1855	.1855
m.	α	002	.1892	.1892
v. w.	α	110 (αFe)	.2200	.2200
v. s.	α	201	.2251	.2253

TABLE II (*Concluded*)

Intensity	FeK Radiation	$h_1h_2h_3$	$\text{Sin}^2\ \theta/2$ observed	$\text{Sin}^2\ \theta/2$ calculated
m.	β	112	0.2685	0.2660
w.	β	121	.2972	.2953
v. w.	β	202	.3040	.3026
v. w.	α	210	.3128	.3115
v. s.	α	112	.3248	.3227
v. w.	β	300	.3309	.3294
s.	α	121	.3607	.3588
m.	α	202	.3693	.3672
w.	β	103	.3901	.3881
m.	α	300	.4027	.4005
w.	β	220	.4411	.4391
m.	α	301	.4494	.4478
v. w.	β	113	.4623	.4613
m.	α	103	.4723	.4702
w.	β	302	.4871	.4856
w.	β	203	.4986	.4979
w.	β	311	.5165	.5148
s.	α	220	.5354	.5340
m.	α	113	.5615	.5592
m.	α	302	.5908	.5897
w.	β	222	.5965	.5953
v. s.	α	203	.6062	.6037
s.	α	311	.6274	.6258
m.	α_1	311	.6253	.6258
m.	α_2	311	.6281	.6275
s.	α_1	222	.7235	.7232
s.	α_2	222	.7266	.7258
m.	α_1	213	.7376	.7372
w.	α_2	213	.7407	.7411
s.	α_1	401 004	.7592	.7568 .7573
m.	α_2	401 004	.7628	.7613 .7624
v. w.	β	204 or 410?	.7693	.7712 .7685
w.	α_1	303	.8269	.8262
v. w.	α_2	303	.8303	.8303
s. (diff.)	α_1	114 321	.8912	.8903 .8928
m. (diff.)	α_2	114 321	.8952	.8962 .8951
v. w.	α_1	402	.9014	.9012
v. w.	α_2	402	.9053	.9042
w.	β	412	.9259	.9247
m.	α_1	204 or 410?	.9348	.9348 .9345

s. = strong. v. s. = very strong. m. = medium. w. = weak. diff. = diffuse.

β phase are compared with those calculated from the following quadratic form characteristic of the hexagonal system.

$$(\mathrm{K}_{\alpha_1}) \qquad \sin^2\frac{\Theta}{2} = 0.0445(h_1^2 + h_1h_2 + h_2^2) + 0.0473h_3^2$$

For K_{α_2} the corresponding constants in the equation are: 0.0446, 0.04765, and for K_β: 0.0366 and 0.03905. In Fig. 4 may be seen the photograms of the most deviated diffraction lines of this as well as the other phases encountered in the system.

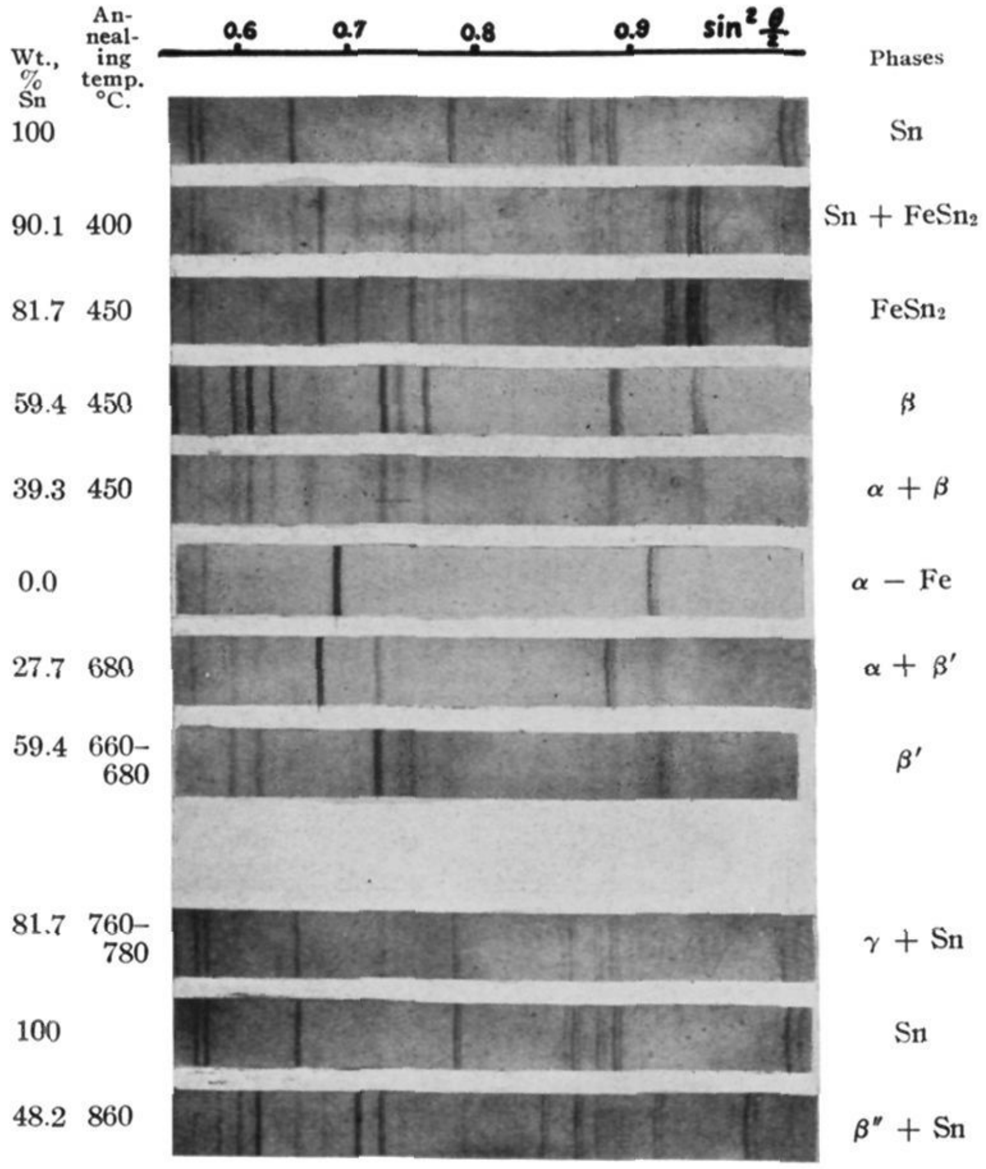

Fig. 4.—Powder photograms of Fe–Sn alloys annealed at various temperatures.

The $FeSn_2$ Phase

The alloy containing 81.7% Sn yielded the diffraction pattern of a single phase after annealing at 330 or 450°. The same pattern was found, together with Sn, for alloys containing 90.1 and 97.7% Sn, when annealed at

400°. The upper layer of the 71.8% alloy, when annealed at 450°, also produced diffraction lines identical with those of the 81.7% alloy. All of these facts indicate that a phase possessing a very narrow homogeneity interval is stable at a composition corresponding almost exactly to $FeSn_2$ (81.0% Sn). This phase, like the β phase, belongs to the hexagonal system. The dimensions of the unit prism are: $a_1 = 5.317$ Å., $a_3 = 9.236$ Å., $a_3/a_1 = 1.737$, and the volume is 226.1 Å^3. The density of the unannealed alloy was 7.60 g./cc. which gives, by calculation, 10.7 atoms per unit cell. It is likely that this is low, since the alloy in this condition contained considerable tin (density 7.31 g./cc.). Annealing produced a very brittle and porous structure whose density was difficult to determine. The authors are of the opinion that the unit cell of the $FeSn_2$ phase contains twelve atoms (4 $FeSn_2$).

The quadratic equation reproducing the observed $\sin^2 \Theta/2$ values and leading to the constants given for the unit cell size, is:

$$(K_{\alpha_1}) \qquad \sin^2\frac{\Theta}{2} = 0.04402(h_1^2 + h_1h_2 + h_2^2) + 0.01094h_3^2$$

The corresponding constants for K_{α_2} are: 0.04419, 0.01101, and for K_β, 0.03628, 0.00900.

The Beta′ Phase (or Phases)

Alloys containing 27, 39, 48 or 59% Sn, when annealed at 680°, all gave rise to a diffraction pattern which characterizes the β' phase. From the powder data alone, the authors have not been able to discover the symmetry and dimensions of the unit cell of this phase. The well-known graphical methods of Hull and Davey and the more recent graphical method of Bjurström have not given any clue[8] to the structure of the β' phase. In view of the difficulty experienced in obtaining a quadratic form satisfying the $\sin^2 \Theta/2$ values of the β' phase, the authors consider it possible that the diffraction pattern is in reality due to a mixture of two phases. Opposed to this view, however, stands the fact that the relative intensities of the lines of the β' pattern remain practically the same whether the alloy contains 27, 39 or 48% Sn.

The Beta″ Phase

The powder photograms of alloys containing 27, 39 or 48% Sn and annealed at 860°, all contain the β'' phase (corresponds to Fe_2Sn of Edwards and Preece) among other phases. The phase is also present in the 27 and 48% alloys when quenched from 950°. A glance at the summary of results will show that the alloys quenched from this region of the temperature-composition diagram were usually not in equilibrium, *i. e.*, three and even four phases were present. Two explanations may be given for this: (1) liquation, or the formation of tin-rich liquid during the annealing, and

---

(8) Bjurström, *Z. Physik*, **69**, 346 (1931).

(2) the possibility that transformations took place in the time that elapsed between withdrawal from the annealing furnace and entrance into the quenching bath. The absence of equilibrium has made it difficult to single out the region of the equilibrium diagram in which the β'' phase will be stable. Tentatively it may be said that the phase can exist between 750 and 950°.

On all the photograms containing it, the β'' phase presents the same diffraction pattern, and there is therefore no variation in the dimensions of the unit cell. There exists, presumably, a very narrow homogeneity range for the phase. The latter crystallizes in the hexagonal system and the size of the unit cell may be calculated with the aid of the constants given in the quadratic forms below. The dimensions are: $a_1 = 5.449$ Å., $a_3 = 4.353$ Å., $a_3/a_1 = 0.799$. The volume of the unit cell is 111.9 Å^3. The alloy containing 48% tin (860°) comes nearest to containing only β''. The density of this alloy, 7.68 g./cc., gives by calculation 6.7 atoms per unit cell. It is likely that the number of atoms is six and that the slightly larger number found is to be attributed to having used a value for the density that was too high. The density measurements were made upon a piece of the alloy that was in low-temperature equilibrium, *i. e.*, contained the β and the relatively heavy α phase. The composition of the 48% alloy corresponds closely to Fe_2Sn (51%) and it is probable that the unit cell of β'' contains two groups of Fe_2Sn. The β'' phase differs only very little from the β phase in dimensions and volume of the unit of structure. Quadratic forms which will give the $\sin^2 \Theta/2$ values are

$$(K_{\alpha_1}) \qquad \sin^2\frac{\Theta}{2} = 0.0419(h_1^2 + h_1h_2 + h_2^2) + 0.04925h_3^2$$

$$(K_{\alpha_2}) \qquad \sin^2\frac{\Theta}{2} = 0.0421(h_1^2 + h_1h_2 + h_2^2) + 0.04945h_3^2$$

$$(K_{\beta}) \qquad \sin^2\frac{\Theta}{2} = 0.0345(h_1^2 + h_1h_2 + h_2^2) + 0.04055h_3^2$$

The Gamma Phase

According to V. M. Goldschmidt[9] the nickel arsenide type of crystal structure is to be looked for whenever we have the possibility of union between a transition element and an element whose atoms are large and easily polarized. Iron and tin furnish such a pair. In a large number of related systems, such as Fe–Sb, Fe–Se, Fe–S, Cu–Sn, Au–Sn, Ni–Sn, etc., a phase having the characteristic nickel arsenide structure exists. In the Fe–Sn system such a phase (γ) has been found in alloys containing 27, 39 and 81% Sn, when quenched from 750–900°. Although no homogeneous alloy was obtained, it is assumed that the composition range of the phase lies close to FeSn (68% Sn). It is possible, however, that the homogeneity range does not include this concentration. This was found to be the case

(9) Goldschmidt, *Ber.*, **60**, 1286 (1927); *Trans. Faraday Soc.*, **25**, 253 (1929).

in the related systems Fe–Sb,[10] Cu–Sn[11] and Ni–Bi,[12] in each of which the nickel arsenide type of phase contains an excess of the atoms of the transition element. The γ phase is apparently homogeneous over a small range of concentrations since its unit cell dimensions vary from $a_1 = 4.179$ Å., $a_3 = 5.201$ Å., $a_3/a_1 = 1.245$ on the iron-rich side of the homogeneity interval to $a_1 = 4.231$ Å., $a_3 = 5.211$ Å., $a_3/a_1 = 1.232$ on the tin-rich side. The volume of the unit cell varies from 78.63 to 80.75 Å^3. Since the γ phase was not obtained homogeneous, any calculation of the number of atoms per unit cell will necessarily give only approximate results. Using a density value obtained by extrapolation from the densities of the 59.4 and 81.7% Sn alloys, we arrive at 4.15 atoms per unit cell. This is quite close to 4, which is the value to be expected in the nickel arsenide structure. There are, then, two iron and two tin atoms in each elementary parallelopiped. The following quadratic forms serve to calculate the values of $\sin^2 \Theta/2$.

$$(K_{\alpha_1}) \qquad \sin^2 \frac{\Theta}{2} = 0.06964(h_1^2 + h_1h_2 + h_2^2) + 0.0345h_3^2$$

$$(K_{\alpha_2}) \qquad \sin^2 \frac{\Theta}{2} = 0.06985(h_1^2 + h_1h_2 + h_2^2) + 0.03465h_3^2$$

The Tin Phase

On all the photograms in which this phase appeared, the diffraction lines occupied positions identical with those of pure tin. Iron and the intermetallic phases already mentioned are, therefore, practically insoluble in tin.

Correlation of the Results with Previous Work

A number of references have already been made to the interrelation of our results and those obtained by other workers. The latest thermal diagram for this system, that by Edwards and Preece, agrees on the whole with the x-ray analysis, but some phases (β' and γ) present at higher temperatures have been overlooked by these investigators. The complete accord existing at lower temperatures leads us to the conclusion that the diagram of Edwards and Preece may be taken as substantially correct below 496°. The fact that an alloy containing 82% Sn, when tempered at 600° for two days and then quenched, consists almost entirely of the β and Sn phases, substantiates the conclusion of Edwards and Preece, *i. e.*, that $FeSn_2$ decomposes into FeSn and Sn when heated to *ca.* 496°. Our analysis shows that the solubility of tin in iron falls off more rapidly with temperature than is indicated on the aforementioned diagram or that of Wever and Reinecken. The solubility (Fig. 3) is about 10% at 680° instead of 15% as shown by the previous authors. Figure 3 indicates that the phases

---

(10) Hägg, *Z. Krist.*, **68**, 470 (1928).

(11) Westgren and Phragmén, *Z. anorg. allgem. Chem.*, **175**, 80 (1928).

(12) Hägg and Funke, *Z. physik. Chem.*, **B6**, 272 (1930).

β and β' are formed through transformations in the solid state whereas the $FeSn_2$ is probably formed by reaction of the β phase with the melt. For reasons already stated, the homogeneity ranges of the phases stable at elevated temperatures have not been fixed. It is clear, however, that there are at least four intermetallic phases (α, β', β'', γ) stable in the temperature interval 650–950°. Because of the possibility that β' represents more than one phase, there may be five phases in this interval. The authors are of the opinion that the question of the constitution of Fe–Sn alloys, in the range 10–100% Sn and at temperatures above 496°, is far from settled and that much additional work will be necessary before this portion of the diagram is completed.

Summary

A number of alloys in the system Fe–Sn have been examined by means of the powder method of crystal analysis. The following phases were found.

Alpha Phase.—A solid solution of tin in alpha iron. The solubility at 680° is 9.8% Sn. At 900° it is 18.8%. The length of the cube edge in the body-centered α-Fe lattice increases linearly with the concentration of tin.

Beta Phase.—This phase has a hexagonal structure and a very narrow homogeneity range. The cell constants are: $a_1 = 5.292$ Å., $a_3 = 4.440$ Å., $a_3/a_1 = 0.839$. It is probable that the composition corresponds to FeSn and that the unit cell contains six atoms (three groups of FeSn).

Beta′ Phase.—Alloys containing 27, 39, 48 and 59% Sn all show the presence of the β' phase after annealing at 680°. With the usual methods, the authors have not been able to discover the symmetry and dimensions of the unit cell of this phase. It is considered possible that the so-called β' phase is in reality a mixture of two or more phases.

Beta″ Phase.—Alloys containing 27, 39 or 48% Sn and annealed at 860°, contain the β'' phase. The exact stability range of this as well as the other high temperature phases in the system could not be determined because of the difficulty of obtaining equilibrium in the alloys. The diffraction patterns indicate a very narrow homogeneity interval. The phase is hexagonal and has the following unit cell dimensions: $a_1 = 5.449$ Å., $a_3 = 4.353$ Å., $a_3/a_1 = 0.799$. Density measurements indicate the presence of six atoms in the cell, which makes it probable that there are two groups of Fe_2Sn.

Gamma Phase.—This phase was found in alloys quenched from 750–900° and containing 27, 39 and 81% Sn. It has the nickel arsenide structure and it is assumed that the composition is close to that indicated by the formula FeSn. The dimensions of the unit cell vary from $a_1 = 4.231$ Å., $a_3 = 5.211$ Å., $a_3/a_1 = 1.232$ to $a_1 = 4.179$ Å., $a_3 = 5.201$ Å., $a_3/a_1 = 1.245$ and the phase is probably homogeneous over a small range of concentrations.

$FeSn_2$ Phase.—The photograms of this phase indicate a very narrow homogeneity interval, corresponding almost exactly with the composition $FeSn_2$. The unit cell is probably hexagonal, having the following dimensions: a_1 = 5.317 Å., a_3 = 9.236 Å., a_3/a_1 = 1.737. It is likely that the cell contains twelve atoms, *i. e.*, 4 $FeSn_2$.

Sn Phase.—The diffraction pattern of this phase, as found in a number of our alloys, does not differ from that of pure tin. It follows from this that iron and the other phases in the system are insoluble in tin.

The discrepancies existing between the results of the x-ray analysis and the thermal diagram for the system as set up by Edwards and Preece, have been indicated and discussed.

NEW YORK CITY
STOCKHOLM, SWEDEN

RECEIVED SEPTEMBER 14. 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES AT PITTSBURGH]

Thermodynamic Functions of Hydrocarbon Gases from Spectroscopic Data[1]

BY LOUIS S. KASSEL[2]

Methods

Within the last few years spectroscopic data for numerous diatomic molecules have been used to give very accurate values for those thermodynamic functions which do not involve the absolute value of *H*. The same methods may be applied to polyatomic molecules; here the spectroscopic data are usually both less accurate and less complete; nevertheless, there seem to be a number of cases in which such calculations may be usefully made. In the present article, methane, ethylene and acetylene will be considered.

The method used has been given in principle by Giauque,[3] but since there are a number of short cuts which may be used when making approximate calculations, the procedure to be followed will be described briefly.

For molecules with energy levels 0, ϵ_1, ϵ_2 . . . and associated quantum weights p_0, p_1, p_2 . . . the Maxwell–Boltzmann distribution law may be written in the form

$$H = -N\,(\mathrm{d}\log Q/\mathrm{d}\Theta) \qquad (1)$$

where

$$Q = \sum_i p_i\, e^{-\epsilon_i \sigma} \qquad (2)$$

and

$$\Theta = 1/kT \qquad (3)$$

---

(1) Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

(2) Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh. Pa.

(3) Giauque, THIS JOURNAL, **52**, 4808 (1930).