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Abstract

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THERMODYNAMIC PROPERTIES OF IRON-SILICON ALLOYS

The phase diagram of the Fe–Si system is given in Fig. 1 according to the data of Hansen and Anderko' s handbook ([1]) and later works ([2], [3], [4]). We studied the thermodynamic properties of solid alloys of iron with silicon by the electromotive-force (e.m.f.) method in the range 600–800° C. The e.m.f. of the galvanic cell was measured:

$$\text{Fe(solid)} \mid \text{Fe}^{2+} \text{ in molten KJ} + \text{NaJ} \mid \text{Fe—Si (solid alloy)},$$

the potential-forming process of which is the transfer of iron from pure iron into the alloy under study. The thermodynamic functions of this process are the partial thermodynamic functions of alloy formation for iron and are related to the e.m.f. of the cell (E) by the following equations:

$$\Delta\mu_{\text{Fe}} = -zFE; \tag{1}$$

$$\Delta\overline{S}_{\text{Fe}} = zF\frac{dE}{dT}; \tag{2}$$

$$\Delta\overline{H}_{\text{Fe}} = \Delta\mu_{\text{Fe}} + T\Delta\overline{S}_{\text{Fe}} = -zFE - zFT\frac{dE}{dT}, \tag{3}$$

where $z = 2$ is the charge of the Fe^{2+} ion, and F is the Faraday constant.

The experimental procedure is described in ([4]). Iron–silicon alloys were prepared from carbonyl iron of special purity and silicon of 99.99% purity by powder metallurgy and were subjected to homogenizing annealing at 800° C for 200–500 h.

The phase composition of the alloys before the experiment and, selectively, after the experiment was checked by X-ray diffraction analysis. The phase composition of the specimens corresponded to that expected on the basis of the phase diagram.

Table 1

x^*_{Fe}	Phase region	$\Delta\mu_{\mathrm{Fe}}$ (cal/g-at Fe)	$\pm\delta(\Delta\mu_{\mathrm{Fe}})$, cal/g-at Fe
0–0.333	$FeSi_2 + Si$	$-21317 + 6.12T + \int_{1000}^{T} \Delta c_p\, dT - T\int_{1000}^{T} \frac{\Delta c_p}{T}\, dT$	280
0.333–0.495	$FeSi + FeSi_2$	$-15813+1.41T$	127
0.503–0.740	$Fe_3Si(\alpha') + FeSi$	$-3280 - 0.30T$	92
0.755	α'	$1335 - 2.07T$	65
0.770	α'	$1324 - 1.965T$	74
0.786	α'	$1291 - 1.880T$	60
0.81–0.88	$\alpha + \alpha'$	$630 - 1.167T$	55
0.914	α	$493 - 0.820T$	14
0.945	α	$163 - 0.268T$	32

* x_{Fe} is the atomic fraction of iron in the alloy (given according to the results of chemical analysis of the alloys after the experiment).

Equilibrium values of the emf (which did not change at a given temperature over 4-5 hours within 1 mV and were reproduced when passing through the temperature interval upward and downward) were plotted on graphs of the dependence E—T. In all cases this dependence proved to be linear within the errors of the experiment.

The coefficients of the equations

$$E = A + BT \tag{4}$$

were found by the method of least squares from the experimental data for each alloy. Data relating to alloys whose compositions belong to one and the same two-phase region of the phase diagram were treated jointly, since within a two-phase region the value of the emf does not depend on composition. Substitution of the equations (4) obtained into equation (1) yielded equations for the dependence of $\Delta\mu_{\mathrm{Fe}}$ on T, which are given in Table 1. For alloys in the region $FeSi_2 + Si$ (and only for this region)

$$\Delta\mu_{\mathrm{Fe}}(\text{cal/g-at Fe}) \equiv \Delta G(\text{formation of } FeSi_2,\ \text{cal/mol}),$$

which made it possible to take into account the temperature dependence of $\Delta\overline{H}_{\mathrm{Fe}} \equiv \Delta H(\text{formation of } FeSi_2)$ and $\Delta\overline{S}_{\mathrm{Fe}} \equiv \Delta S(\text{formation of } FeSi_2)$ using literature data on the heat capacities of Fe ([5]), Si ([6]), and $FeSi_2$ ([7]).

Fig. 1

Fig. 2

Fig. 1. Phase diagram of the iron–silicon system

Fig. 2. Dependence of integral thermodynamic quantities on composition in the iron–silicon system at 1000°K.

The maximum error (δ in Table 1) is determined as the confidence interval with probability 0.95 ([8]).

Table 2

Formula	$\Delta\mu_{\mathrm{Fe}}$, $\frac{\text{kcal}}{\text{g-at Fe}}$	$\Delta\overline{H}_{\mathrm{Fe}}$, $\frac{\text{kcal}}{\text{g-at Fe}}$	$\Delta\overline{S}_{\mathrm{Fe}}$, $\frac{\text{cal}}{\text{deg}\cdot\text{g-at Fe}}$	ΔG, $\frac{\text{kcal}}{\text{mol}}$	ΔH, $\frac{\text{kcal}}{\text{mol}}$	ΔS, $\frac{\text{cal}}{\text{deg}\cdot\text{mol}}$
$FeSi_2$	$-15,20\pm 0,28$	$-21,3\pm 1,8$	$-6,1\pm 1,8$	$-15,20\pm 0,28$	$-21,3\pm 1,8$	$-6,1\pm 1,8$
FeSi	$-14,41\pm 0,13$	$-15,8\pm 0,5$	$-1,4\pm 0,5$	$-14,70\pm 0,15$	$-18,4\pm 0,9$	$-3,7\pm 1,0$
Fe_3Si	$-3,58\pm 0,10$	$-3,28\pm 0,20$	$+0,3\pm 0,2$	$-21,6\pm 0,2$	$-24,4\pm 1,0$	$-2,8\pm 1,1$

The integral ΔG, ΔH, and ΔS of formation of alloys from the components at 1000° K were found from the Gibbs–Duhem equation:

$$\Delta G\ (\text{cal/g-at}) = x_{\mathrm{Si}} \int_0^{x_{\mathrm{Fe}}/x_{\mathrm{Si}}} \Delta\mu_{\mathrm{Fe}}\, d(x_{\mathrm{Fe}}/x_{\mathrm{Si}}) \tag{5}$$

(and analogously for ΔH and ΔS) from the data of Table 1.

Table 2 gives these values for the iron silicides, multiplied by the total number of gram-atoms in a mole of the compound.

The dependence of the integral thermodynamic quantities on composition at 1000° K is shown in Fig. 2.

Using literature data on the temperature dependences of the heat capacities of the iron silicides ([7,9,10]) and of pure iron ([5]) and silicon ([6]), our data obtained for 1000° K were recalculated to 298, 1798, and 1188° K (the temperature of the eutectoid transformation):

$$FeSi_{2.33}(\zeta_\alpha) \rightleftarrows FeSi_2(\zeta_\beta) + 0.33\mathrm{Si}. \tag{6}$$

The calculated values of ΔH_{298}, ΔS_{298}, and ΔH_{1798} (liquid) are given in Table 3.

Table 3

Phase	ΔH_{298}, kcal/mole	ΔH_{298}, kcal/mole	ΔS_{298}, cal/deg·mole	ΔS_{298}, cal/deg·mole	ΔH (liquid), kcal/g-at	ΔH (liquid), kcal/g-at	ΔH (liquid), kcal/g-at
Phase	Present work	([11])	Present work	([7,9,10])	Present work, 1798°	([11]), 1873° K	([12]), 1798° K
$FeSi_2(\zeta_\beta)$	−19.4± 1.8	−16.9± 2	−3.3 ± 1.8	−2.2			
$FeSi_{2.33}(\zeta_\alpha)$	−15.7*			−0.4	−6.6	−7.0	−7.0
$FeSi(\varepsilon)$	−17.6± 0.9	−19.2± 2	−2.6 ± 1.0	0	−8.6	−9.0	−10.7
$Fe_3Si(\alpha')$	−22.4± 1.0	−19.2± 2	−1.2 ± 1.1	+0.7	−6.7	−6.6	−6.7

* The value was obtained by calculation.

At 1188° K, ΔG of reaction (6) $= \Delta G(FeSi_2) - \Delta G(FeSi_{2.33}) = 0$; consequently,

$$\Delta H(FeSi_2) - 1188\Delta S(FeSi_2) = \Delta H(FeSi_{2.33}) - 1188\Delta S(FeSi_{2.33}). \quad (7)$$

Substituting in (7) our data for $\Delta H(FeSi_2)$ and $\Delta S(FeSi_2)$, recalculated to 1188° K, and the value of $\Delta S(FeSi_{2.33})$ from ([7]), we obtain:
$\Delta H_{1188}(FeSi_{2.33}) = -17.9$ kcal/mole.

Recalculation to 298° K gives $\Delta H_{298}(FeSi_{2.33}) = -15.7$ kcal/mole. It should be noted that in work ([7]) the entropy of $FeSi_{2.33}$ was determined from the results of heat-capacity measurements from 54° K on quenched specimens. The value obtained in work ([7]) represents $S - S_0$, where $S_0 > 0$ because of the partial disorder of the specimen. In this connection, the value of $\Delta H(FeSi_{2.33})$ calculated by us contains an error equal to $-1188S_0(FeSi_{2.33})$.

In Table 3, literature data ([7,9–12]) are presented together with our results for comparison.

As is seen from the data of Table 3, the values of $\Delta S(FeSi_2)$ obtained in the present work and in work ([7]) agree within the errors of our experiment. For FeSi and Fe_3Si, our data are approximately 2 cal/deg·mole lower than the data of Grønvold and Westrum ([9,10]). The reason for the discrepancy is not clear to us.

It is of interest to compare our value of ΔS(FeSi) with the value of ΔS obtained by Eremenko and co-workers ([13]) for MnSi (structure of the FeSi type). ΔS (MnSi, cal/deg · mole) $= -3.2 \pm 1.0$ at 1023° K, which is very close to the value ΔS_{1000}(FeSi, cal/deg · mole) $= -3.7 \pm 1.0$ obtained in the present work.

The value we obtained, $-\Delta H_{298}(FeSi_2)$, is higher than the value of Körber and Oelsen (11) by 2.5 kcal/mol. In our opinion, the results of Körber and Oelsen are too low because, when liquid metals are mixed in their calorimeter and the alloy crystallizes rapidly, a nonequilibrium mixture of phases may form. It should be noted that the value of Körber and Oelsen for $FeSi_2$ lies between the values obtained by us from experiment and by calculation for $FeSi_2$ and $FeSi_{2.33}$. This is consistent with the assumption that a mixture of phases formed in the calorimeter of Körber and Oelsen. The possibility that Körber and Oelsen obtained values that were too low has already been discussed in the literature (for example, (14)). From the same point of view, one can explain the discrepancy between the values of $\Delta H(Fe_3Si)$ obtained by us and in (11). For the congruently melting FeSi, our data on ΔH agree with the data of (11) within the experimental error.

The values of the enthalpies of mixing for liquid FeSi alloys calculated from our data agree well with the data of Körber and Oelsen (11), but differ appreciably from the data of Gertman and Geld (12) for compositions close to equiatomic.

The results obtained by us for disordered and ordered solid solutions of silicon in iron (α- and α'-phases, Table 1) were discussed briefly in (4) and will be discussed in greater detail subsequently.

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CITED LITERATURE

1. M. Hansen, K. Anderko, *Structures of Binary Alloys*, 2, 1963, p. 753.

2. F. A. Sidorenko, P. V. Geld, L. V. Dubrovskaya, *Fiz. met. i metalloved.*, **8**, No. 5, 735 (1959).

3. F. A. Sidorenko, P. V. Geld, *Izv. vyssh. uchebn. zaved., Chernaya metallurgiya*, No. 7, 110 (1963).

4. Ya. I. Gerasimov, R. A. Vecher, V. A. Geiderikh, *ZhFKh*, **39**, No. 5 (1965).

5. L. D. Darken, R. P. Smith, *Ind. and Eng. Chem.*, **43**, 1815 (1951).

6. L. N. Serebrennikov, P. V. Geld, *DAN*, **87**, 1021 (1952).

7. R. P. Krentsis, P. V. Geld, G. I. Kalishevich, *Izv. vyssh. uchebn. zaved., Chernaya metallurgiya*, No. 11, 146 (1963).

8. V. V. Nalimov, *The Application of Mathematical Statistics in the Analysis of Substances*, Moscow, 1960.

9. R. P. Krentsis, P. V. Geld, G. I. Kalishevich, *Izv. vyssh. uchebn. zaved., Chernaya metallurgiya*, No. 9, 161 (1963).

10. R. P. Krentsis, P. V. Geld, ibid., No. 11, 12 (1962).

11. F. Körber, W. Oelsen, *Mitt. Kaiser Wilhelm Inst. Eisenforsch., Düsseldorf*, **18**, 109 (1936), cited after F. Weibke, O. Kubaschewski, *Thermochemie der Legierungen*, 1943, p. 241.

12. Yu. M. Gertman, P. V. Geld, *ZhFKh*, **36**, No. 7, 1477 (1962).

13. E. M. Eremenko, T. M. Lukashenko, *Poroshkovaya metallurgiya*, No. 5 (23), 49 (1964).

14. V. A. Geiderikh, Ya. I. Gerasimov, A. A. Vecher, *DAN*, **120**, No. 6, 274 (1958).

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