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Figure 1

Figure 1: Figure 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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THERMODYNAMIC PROPERTIES OF SOLID ALLOYS OF THE IRON–TELLURIUM SYSTEM

Solid alloys of iron with tellurium (compositions of 0-50 at.% iron) were investigated by the electromotive-force (emf) method.

The emf of concentration chains (relative to the electrodes) was measured as a function of temperature:

$$(-)\ \mathrm{Fe} \mid \mathrm{FeCl_2(KCl + LiCl)} \mid \mathrm{Fe - Te}\ (+) \qquad \text{(I)}$$

melt solid alloy

The preparation of the alloys and the conduct of the experiment are described in work [1].

The literature gives the results of investigations of the phase diagram of the Fe–Te system [2,3]. The phase diagram constructed from the data of Grønvold, Haraldsen, and Vihovde [2] is given in the book by Hansen and Anderko [4]. In Fig. 1 the solid lines show the phase diagram according to the work of Chiba [3]; the dashed lines indicate the positions of the boundaries of the phase regions proposed by us.*

At temperatures of 360-650° we investigated iron-tellurium alloys of various compositions belonging to the phase regions $\beta + \mathrm{Te}$, β, $\beta + \gamma$, γ, $\gamma + \alpha$, and $\beta + \alpha$ (21 alloys in all). The data obtained for alloys belonging to the same two-phase region were treated as follows. By the method of least squares, from the entire set of experimental emf values for all alloys at all temperatures, an equation for the dependence of the emf (E) on the absolute temperature was found in the form of a straight-line equation. For homogeneous alloys of definite co-

Fig. 1. Phase diagram of the Fe–Te system: solid lines according to work [3], dashed lines—our data

Table 1

Atomic fraction of iron, at.%	Phase composition	Temperature interval, °K	emf, mV
0–0.323	$\beta + \mathrm{Te}$	630–700	$344.2 - 97.8 \cdot 10^{-3} T$
0.332	β	650–750	$343.9 - 110 \cdot 10^{-3} T$
0.338	β	740–880	$531.4 - 384 \cdot 10^{-3} T$
0.35–0.51	$\beta + \alpha$	690–786	$-109.5 + 220.6 \cdot 10^{-3} T$
0.35–0.40	$\beta + \gamma$	790–900	$-598.6 + 841 \cdot 10^{-3} T$
0.40–0.425	$\beta + \gamma$	variable—900	$-598.6 + 841 \cdot 10^{-3} T$
0.43–0.51	$\gamma + \alpha$	786–900	$80.3 - 21.9 \cdot 10^{-3} T$

* The names of the phases throughout the present work are taken to be the same as in the work of Chiba [3].

Table 2

Atomic fraction of iron, at. %	Phase composition	ΔG, kcal/g-at. (700° K)	ΔH, kcal/g-at. (700° K)	ΔS, e.u./g-at. (700° K)	Phase composition	ΔG, kcal/g-at. (800° K)	ΔH, kcal/g-at. (800° K)	ΔS, e.u./g-at. (800° K)
0.338	β	-4.32 ± 0.12	-5.42 ± 0.44	-1.57 ± 0.6	β	-4.13 ± 0.12	-5.40 ± 0.44	-1.57 ± 0.6
0.43	$\alpha + \beta$	-4.08 ± 0.16	-3.40 ± 0.55	-0.15 ± 0.8	γ	-4.07 ± 0.19	-4.33 ± 0.62	-3.4 ± 0.8
0.5	$\alpha + \beta$	-3.85 ± 0.16	-3.06 ± 0.54	$+1.1 \pm 0.8$	$\alpha + \gamma$	-3.92 ± 0.21	-1.83 ± 0.75	$+2.9 \pm 1.0$
0.53	α	-3.71 ± 0.16	-2.65 ± 0.54	$+1.7 \pm 0.8$	α	-3.86 ± 0.21	-1.75 ± 0.75	$+2.7 \pm 1.0$

The straight line $E = A + BT$ was drawn on the graph through the experimental points; the values of the coefficients A and B were found from the graph.

Table 1 gives the equations $E = A + BT$ for electrodes that are alloys of different compositions.

The magnitude of the change in the chemical potential of iron upon transfer of 1 g-atom of iron from the pure metal into an alloy of a definite composition is obtained from the known relation:

$$\Delta\mu_{\text{Fe}} = -zFE,$$

where z is the charge of the carrier ion ($z_{\text{Fe}^{++}} = 2$), F is the Faraday number ($F = 23064$ cal/V).

The partial changes in entropy and enthalpy are found from the equations:

$$\Delta\overline{S}_{\text{Fe}} = -\,d\Delta\mu_{\text{Fe}}/dT = zF\,dE/dT,$$

$$\Delta\overline{H}_{\text{Fe}} = \Delta\mu_{\text{Fe}} + T\Delta\overline{S}_{\text{Fe}}.$$

The integral quantities for the formation of a gram-atom of alloy from pure iron and tellurium were found from the Gibbs–Duhem equation:

$$B = N_{\text{Te}} \int_0^{N_{\text{Fe}}} \overline{B}_{\text{Fe}}\, d\left(\frac{N_{\text{Fe}}}{N_{\text{Te}}}\right),$$

where B is the integral quantity ($\Delta G^*,\ \Delta H,\ \Delta S$), $\overline{B}_{\text{Fe}}$ is the corresponding partial quantity for iron, and N_i is the atomic fraction of the i-th component. The integration was carried out graphically over the interval $N_{\text{Fe}} = 0$–0.51 for temperatures of 700 and 800° K.

The results calculated per 1 g-at. of alloy are presented in Fig. 2 and in Table 2. In Fig. 2 the integral values of the thermodynamic functions for 800° K are plotted as functions of alloy composition. Table 2 gives these quantities for the β-, γ-, and α-phases of the system and for the heterogeneous alloy of composition $N_{\text{Fe}} = 0.5$. The data for $N_{\text{Fe}} = 0.53$ were obtained by extrapolating the dependences $B(N_{\text{Fe}})$ from $N_{\text{Fe}} = 0.51$ in the homogeneity region of the α-phase.

To obtain the integral quantities at 800° K, the dependences $E(T)$ obtained experimentally at lower temperatures for alloys of compositions $N_{\text{Fe}} = 0$–0.332, and given in Table 1, were extrapolated to this temperature.

Table 2 gives quantities referred to the standard state "solid iron and tellurium." For conversion to the standard state "solid iron and liquid tellurium," the quantities $\Delta H^{\text{pl}}_{\text{Te}} =$

[*] For the isobaric-isothermal potential we use the notation G, in accordance with that adopted in the international literature.

$$= 4.18 \text{ kcal/g-at.}, \qquad \Delta S_{\text{Te}}^{\text{melt}} = \Delta H_{\text{Te}}^{\text{melt}}/T_{\text{Te}}^{\text{melt}} = 5.78 \text{ e.u./g-at}$$

and

$$\Delta G_{\text{Te}}^{\text{melt}} = (4.18 - 5.78 \cdot 10^{-3} T) \text{ kcal/g-at.}$$

(neglecting the temperature dependence of $\Delta H_{\text{Te}}^{\text{melt}}$). The values of the melting temperature and heat of fusion of tellurium were taken from (^{5}).

Discussion of the results. From the data in Table 2 it is seen that the entropies of formation from the elements of the α- and γ-phases are positive, while the β-phase is formed with a decrease in entropy. The enthalpy of formation changes in a manner similar to the entropy, but remains negative over the entire concentration range (Fig. 2, Table 2). We observed the same behavior of the entropy and heat of formation with changing alloy composition in the Fe—Sb system (^{6}). This agreement appears not to be accidental if one considers the nature of analogous phases in the two systems.

The β-phase of the Fe—Te system has the marcasite structure; the range of existence of the phase includes the stoichiometric composition FeTe_2; FeSb_2 is a stoichiometric compound with the marcasite structure. The γ-phase Fe —Te and the ε-phase Fe—Sb are berthollide phases with a defective structure of the nickel arsenide type. Their regions of existence do not include the 1:1 composition, ideal for a lattice of the NiAs type. The region of existence of the γ-phase Fe—Te lies farther from the 1:1 composition and, at the same time, has a larger positive entropy of formation than the ε-phase Fe—Sb. This is in agreement with the assumption made by us in (^{6}) concerning the influence of defects in the NiAs-type lattice on the magnitude of the entropy of formation of the intermetallic phase.

Fig. 2. Dependence of the thermodynamic functions on alloy composition in the Fe—Te system at 800°K (extrapolation is indicated by dashed lines).
1—$\Delta G\left(\frac{\text{kcal}}{\text{g-at}}\right)$;
2—$\Delta H\left(\frac{\text{kcal}}{\text{g-at}}\right)$;
3—$\Delta S\left(\frac{\text{e.u.}}{\text{g-at}}\right)$.

Measurement of the e.m.f. of type-I cells as a function of temperature, in addition to determining the values of thermodynamic functions, makes it possible to draw conclusions about the boundaries of phase regions in the phase diagram. At the boundary of phase regions the dependence $E(T)$ undergoes a break. For all iron–tellurium alloys of compositions $N_{\text{Fe}} = 0.35$—0.51, at one and the same temperature (approximately 513°C) there is a break, which confirms the data (^{2,3}) on the eutectoid decomposition of the γ-phase into α- and β-phases (Fig.

1). In Fig. 1 the dashed lines indicate the probable boundaries of the phase regions of the Fe–Te system. The dashed line was drawn taking into account the e.m.f. data obtained by us and the literature data (^{2,3,7}).

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