EFFECT OF A MAGNETIC FIELD ON PHASE TRANSFORMATIONS IN AUSTENITIC STAINLESS STEELS

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Inzhenerno-Fizicheskii Zhurnal, Vol. 14, No. 4, pp. 620–625, 1968

UDC 532.785:538.12

A differential equation is obtained and solved for the entropy of transformation in first-order phase transformations with allowance for the effect of an external magnetic field. The effect of a constant magnetic field on phase transformations in an austenitic stainless steel is investigated. It is shown that the theoretical values for the magnetic δT effect are of the same order as the experimental values.

In [1] the δT effect was obtained in the general form

$$\delta T = -\left(\int \frac{\Delta\left(\frac{\partial \Phi}{\partial p}\right) dp}{\Delta S} + \int \frac{\Sigma\Delta\left(\frac{\partial \Phi}{\partial \alpha_i}\right) d\alpha_i}{\Delta S}\right). \tag{1}$$

As follows from (1), to compute δT it is necessary to know $\Delta S = f(p, \alpha_i)$. With this object in view, we will find the corresponding differential equation for determining the integrating factor $\mu = 1/\Delta S$. The necessary and sufficient conditions for the expression $\mu \Sigma X_i x_i = 0$ to be a total differential of some function $f(X_i)$ are constituted by $n(n-1)/2$ equations. For the case of three variables, which we will consider below, we accordingly obtain three equations:

$$\frac{\partial}{\partial x_2}(\mu X_1) - \frac{\partial}{\partial x_1}(\mu X_2) = 0\,, \text{ etc.} \tag{2}$$

From these we obtain three differential equations for the integrating multiplier

$$X_1 \frac{\partial \mu}{\partial x_2} - X_2 \frac{\partial \mu}{\partial x_1} + \mu\left(\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial x_1}\right) = 0, \text{ etc.} \tag{3}$$

Since $X_i = \Delta(\partial\Phi/\partial\alpha_i)$, we can write Eqs. (3) in the form

$$X_1 \frac{\partial \mu}{\partial x_2} - X_2 \frac{\partial \mu}{\partial x_1} = 0\,, \text{ etc.} \tag{4}$$

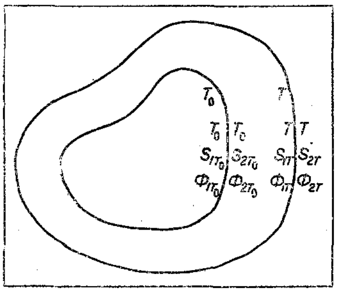

Fig. 1. The equithermal surfaces $T_0 = f(p_0, \alpha_{0i})$ and $T = f(p, \alpha_i)$.

Adding Eqs. (4), we obtain the differential equation for the integrating factor μ:

$$X_1\left(\frac{\partial \mu}{\partial x_2} - \frac{\partial \mu}{\partial x_3}\right) + X_2\left(\frac{\partial \mu}{\partial x_3} - \frac{\partial \mu}{\partial x_1}\right) + X_3\left(\frac{\partial \mu}{\partial x_1} - \frac{\partial \mu}{\partial x_2}\right) = 0. \tag{5}$$

Substituting into (5) the values $X_1 = \Delta(\partial\Phi/\partial p)$, $X_2 = \Delta(\partial\Phi/\partial\alpha_1)$, $X_3 = \Delta(\partial\Phi/\partial\alpha_2)$, $x_1 = p$, $x_2 = \alpha_1$, $x_3 = \alpha_2$, we obtain a differential equation for the entropy of transformation of first-order phase transformations in external fields in the form

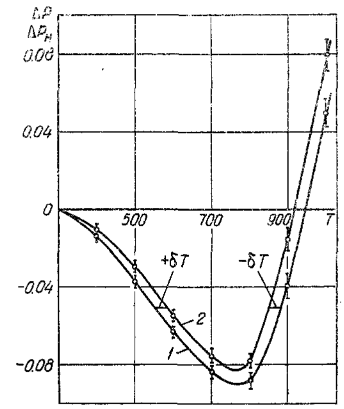

Fig. 2. Temperature dependence of the percentage content of ferritic phase in Cr18Ni10Ti steel: 1) without field; 2) with field, $H = 8.4 \cdot 10^5$ A/m.

$$\Delta\left(\frac{\partial \Phi}{\partial p}\right)\left(\frac{\partial \mu}{\partial \alpha_1} - \frac{\partial \mu}{\partial \alpha_2}\right) + \Delta\left(\frac{\partial \Phi}{\partial \alpha_1}\right)\left(\frac{\partial \mu}{\partial \alpha_2} - \frac{\partial \mu}{\partial p}\right) + \Delta\left(\frac{\partial \Phi}{\partial \alpha_2}\right)\left(\frac{\partial \mu}{\partial p} - \frac{\partial \mu}{\partial \alpha_1}\right) = 0. \tag{6}$$

The solution of Eq. (6) is

$$\mu = \mu_0(p_0, \alpha_{0i}) \exp\left(\pm \frac{\Delta \Phi(p, \alpha_i)}{\Theta}\right). \tag{7}$$

Accordingly, for the entropy of transformation in external fields we obtain

$$\Delta S = \frac{1}{\mu} = \Delta S_0 \exp\left(\mp \frac{\Delta \Phi(p, \alpha_i)}{\Theta}\right) = \frac{\Delta q_0}{T_0} \exp\left(\mp \frac{\Delta \Phi(p, \alpha_i)}{\Theta}\right). \tag{8}$$

The expression $\Delta S_0 = \Delta q_0/T_0$ represents the entropy of transformation of first-order phase transformations in the absence of external fields. The value ΔS_0 corresponds to $\Delta\Phi_0 = 0$, i. e., equality of the thermodynamic potentials of the two phases in equilibrium at the equithermal surface $T_0 = f(p_0, \alpha_{0i})$. We denote this as follows: $\Phi_{1T_0} = \Phi_{2T_0}$. A state of equilibrium will also exist on the equithermal surface $T = f(p, \alpha_i)$ and the thermodynamic potentials will be equal, i.e., $\Phi_{1T} = \Phi_{2T}$. However, in view of the effect of the external fields, the thermodynamic potentials Φ_{1T_0} and Φ_{1T} are not equal. Consequently, we have $\Phi_{1T} - \Phi_{1T_0} = \Delta\Phi(p, \alpha_i) \neq 0$. The same may also be said of the entropy of transformation. It is clear that $\Delta S(p, \alpha_i) \neq \Delta S_0(p_0, \alpha_{0i})$, and $\exp(\pm\Delta\Phi(p, \alpha_i)/\Theta)$ determines the effect of the external (magnetic, electric, gravitational, inertial, etc.) fields on the entropy of transformation. Let there be given the two equithermal surfaces $T_0 = f(p_0, \alpha_{0i})$ and $T = f(p, \alpha_i)$ (Fig. 1). In the case of first-order phase transformations on the zero equithermal surface $T_0 = f(p_0, \alpha_{0i})$ we have the relations: $\Delta T_0 = 0$; $S_{2T_0} - S_{1T_0} = \Delta S_0 \neq 0$; $\Phi_{2T_0} - \Phi_{1T_0} = \Delta\Phi_0 = 0$. On the T-th equithermal surface $T = f(p, \alpha_i)$: $\Delta T = 0$; $S_{2T} - S_{1T} = \Delta S \neq 0$; $\Phi_{2T} - \Phi_{1T} = \Delta\Phi_T = 0$. However, $T - T_0 = \delta T \neq 0$; $\Delta S \neq \Delta S_0$. Here we have: $\Delta S - \Delta S_0 = \Delta_1 S$ and $\Phi_{1T} - \Phi_{1T_0} = \Phi_{2T} - \Phi_{2T_0} = \Delta\Phi \neq 0$.

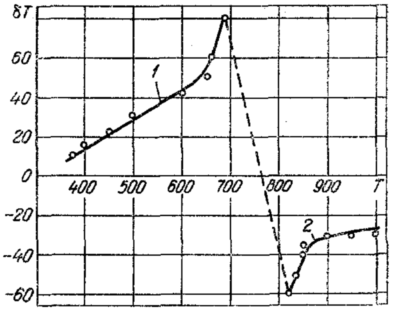

Fig. 3. δT effect in Cr18Ni10Ti steel as a function of temperature (°C) in a field $H = 8.4 \cdot 10^5$ A/m (1 and 2 for positive and negative δT effects, respectively).

Consequently, for any equithermal surface, i.e., for any equilibrium state of the thermodynamic system corresponding to the equithermal surface $T = f(p, \alpha_i)$, we will have an entropy of transformation $\Delta S = \Delta S_0 \pm \Delta_1 S$ due to the effect of the external fields and pressure, and a change of thermodynamic potential $\Delta\Phi \neq 0$ with the physical significance indicated above.

In the presence of a magnetic field we can set $\Delta\Phi = \Delta MH$. Consequently, the expression for the entropy of transformation (8) can be written as

$$\Delta S = \frac{\Delta q_0}{T_0} \exp\left(-\frac{\Delta MH}{\Theta}\right). \qquad (9)$$

We have investigated the effect of a constant magnetic field on the $\alpha \rightleftarrows \gamma$ transformations in austenitic stainless steel. The difference between this work and that reported in [2–8] is that we investigated the effect of a constant magnetic field on the phase transformations at temperatures above as well as below the Curie temperatures, i.e., in regions where the α phase, like austenite, is not a ferromagnetic. For purposes of investigation we selected industrial steel Cr18Ni10Ti in the form of a pipe blank 150 mm in diameter with the following chemical composition in %: C–0.08; Mn–1.32; Si–0.42; P–0.025; S–0.07; Cr–17.50; Ni–10.40; Cu–0.15; W–0.11; Mo–0.08; Ti–0.45; N_2–0.018.

The cylindrical or cubical specimens, measuring ~2 × 2 mm, were cut cold. They contained 0.1–0.2% ferritic phase. In order to eliminate the effect of surface working, the specimens were subjected to chemical etching or electropolishing before the magnetic measurements were made. The percentage content of ferritic phase and its variations under the influence of the magnetic field were determined by the magnetodifferential method developed by the authors, which makes it possible to determine the content of α phase correct to $10^{-3} - 10^{-4}\%$.

The effect of temperature on the variation of α phase in the specimens $\Delta P = f(T)$ was investigated as follows. The percentage content of α phase P_0 in the specimen was measured before heating on a magnetometric balance [9]. Then the specimen was heated to a certain temperature, at which it was kept for 3 min, and cooled together with the tube furnace (at approximately 200 deg/min). After the specimen had cooled to room temperature, the percentage content of ferritic phase was again determined. Similar experiments were conducted with other specimens but at different temperatures. The results are presented in Fig. 2, curve 1.

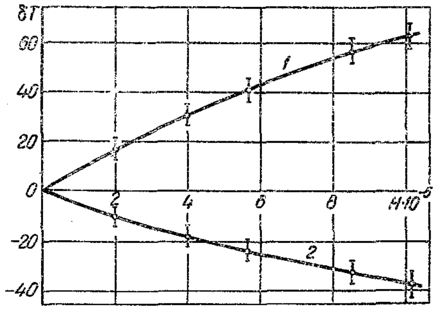

Fig. 4. Dependence of positive (curve 1, T = 873° K) and negative (curve 2, T = 1273° K) δT effects on the constant magnetic field.

The effect of a magnetic field on the phase transformations $\alpha \rightleftarrows \gamma$ at various temperatures was determined by heating the specimens, holding them at a given temperature, and cooling them in a constant magnetic field. Curve 2 (Fig. 2) shows how the field affected the α phase content $\Delta P_H = f(T)$. It is clear from Fig. 2 that up to the region where curves 1 and 2 have a minimum the δT effect is positive. This means that a constant magnetic field increases the equilibrium temperature of the α and γ phases. Conversely, above the temperatures corresponding to the minima of curves 1 and 2 the magnetic field reduces the phase equilibrium temperature. According to our measurements the minimum on curves 1 and 2 corresponds approximately to the Curie point α – Fe(~ 770° C). As may be seen from Fig. 2, the δT effect changes sign on passing through the minimum on curves 1 and 2. The temperature dependence of the δT effect is presented in Fig. 3, which shows that in the region of transition temperatures the δT effect does, in fact, have a discontinuity with change of sign. We also determined the dependence of the positive and negative δT effect on the applied external magnetic field. The results are presented in Fig. 4.

It is known that for metals the parameter p has only a very weak influence on phase transformations. Therefore the first term in (1) can be neglected. Considering only the effect of the magnetic field and using (9), we write the following expression for δT:

$$\delta T = -\frac{T_0}{\Delta q_0}\int \Delta\left(\frac{\partial \Phi}{\partial H}\right)\exp\frac{\Delta MH}{\Theta}dH. \tag{10}$$

Bearing in mind the fact that the δT effect is being calculated for high fields ($H > 5 \cdot 10^3$ Oe), and integrating (10), we obtain

$$\delta T = \frac{T_0\Theta}{\Delta q_0}\left(1-\exp\frac{H\Delta M}{\Theta}\right). \tag{11}$$

For known ferromagnetics up to $H \sim 10^6$ Oe the expression $H\Delta M/\Theta \sim 0.01$. Expanding (11) we obtain

$$\delta T = -\frac{T_0}{\Delta q_0}\Delta MH, \tag{12}$$

which coincides with the formulas of [1, 2]. In the case of equilibrium of the ferromagnetic and paramagnetic phases $\Delta M = M_2 - M_1 = I_2V_2 - I_1V_1$. In view of the fact that $I_1V_1 \gg I_2V_2$ in the region up to the minimum on curves 1 and 2 (Fig. 2), in accordance with (12), the δT effect will be positive and we can write

$$\delta T = \frac{T_0}{\Delta q_0}I_1V_1H. \tag{13}$$

In our experiments at $T_0 = 873°$ K

$$\Delta q_0 \approx 150\frac{\text{cal}}{\text{g-mole}},\quad I_1 \approx 1.5\cdot 10^3\ \text{G},$$

$$V_1 = 7\frac{\text{cm}}{\text{g-mole}},\quad H = 1.3\cdot 10^4\ \text{Oe}.$$

Substituting these data in (13) for δT we obtain the value $\delta T \approx 20°$ K. As may be seen from Fig. 2, for the same temperature experiment gives $\delta T \approx 60°$ K.

For phase transitions in the high-temperature region (above the Curie point) integration of (10) leads to the formula

$$\delta T = \frac{T_0\Theta}{2\Delta q_0}\left(1-\exp\frac{\Delta(\varkappa V)H^2}{\Theta}\right). \tag{14}$$

As in the case of (11), (14) can also be expanded in series and we obtain

$$\delta T = -\frac{T_0}{2\Delta q_0}(\varkappa_1V_1 - \varkappa_2V_2)H^2. \tag{15}$$

Substituting the values $\varkappa_1 \approx 5\cdot 10^{-3}$, $\varkappa_2 \approx 3\cdot 10^{-5}$, $V_1 \approx 7.27$ cm^3/g-mole, $V_2 \approx 7.19$ cm^3/g-mole, $H = 1.3\cdot 10^4$ Oe, $T_0 = 1300°$ K, and $\Delta q_0 \approx 150$ cal/g-mole, for the δT effect we obtain $\delta T \approx -1°$ K. For this case experiment gives $\delta T \approx -40°$ K.

If we now use the experimental data given in [2], namely, $T_0 = 300°$ K, $\Delta q_0 \approx 700$ cal/g-mole, $I_1 \approx 1.5\cdot 10^3$ G, $V_1 \approx 7$ cm^3/g-mole, $H = 3.5\cdot 10^5$ Oe, and substitute them into (13), then for δT we obtain $\delta T \approx 40°$ K, while experiment gives $\delta T \approx 50°$ K.

We note that the lower the phase transition temperature, the closer the calculated data to the experimental values, and conversely. The above data from [2] relate to martensitic transformations in steels at $T_0 = 300°$ K. In these transformations the diffusion processes are weak, and the thermodynamic calculations for the δT effect approach the experimental values. As the temperature rises, however, the diffusion processes, neglected in the thermodynamic calculations, intensify, and apparently for this reason the higher the temperature of the diffusion phase transformations taking place in austenitic steels, the greater the discrepancy between the thermodynamic and experimental values of the δT effect.

Formulas (11) and (14) give the dependence of the δT effect on the magnetic field strength. Clearly, the graphs of (11) and (14) are a quite good reflection of the $\delta T = f(H)$ curves presented in Fig. 4.

In conclusion a few words concerning the physical nature of the magnetic δT effect. When a magnetic is introduced into a magnetic field, its energy falls. A magnetic in the ferromagnetic state has an especially large negative energy. In the steels investigated the α phase is ferromagnetic and the γ phase paramagnetic. Accordingly in the $\alpha \rightarrow \gamma$ transition, since the energy of the former is lower in the magnetic field than outside it, the field should inhibit the process. Conversely, in the $\gamma \rightarrow \alpha$ transition the magnetic field should assist the transformation. Consequently, in all cases a magnetic field should expand the region of existence of the α phase in austenitic steels, which is in fact confirmed by experiment and agrees with the conclusions of [2].

NOTATION

Φ is the thermodynamic potential; p is the pressure; α_i are external fields; H is the magnetic field; $\mu = 1/\Delta S$ is the integrating factor; ΔS and ΔS_0 denote the entropy of transformation with and without allowance for the magnetic field; x_i are generalized forces; x_i are generalized coordinates; Θ is a parameter with the dimension of energy; M_1 and M_2 are magnetic moments of the α and γ phases, respectively; I_1 and I_2 are the magnetization of α and γ phases; V_1 and V_2 are the gram-molecular volumes of α and γ phases; T_0 is the phase transition temperature; Δq_0 is the heat of phase transition; $\varkappa_1$ and $\varkappa_2$ are the magnetic susceptibilities of α and γ phases.

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26 July 1967

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