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THERMOPHYSICAL PROPERTIES OF IRON, NICKEL, AND ALLOYS BASED ON THESE METALS IN THE VICINITY OF PHASE TRANSFORMATIONS

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A method is proposed for obtaining undistorted values of the temperature dependence of the thermophysical properties of metals and alloys in the vicinity of of phase transformations, based on taking into account directly the thermal inertia of the system.

In studying phase transformations, calorimetric methods, based on their being modeled by independent sources of heat energy, including the method of scanning adiabatic calorimetry, are most often used. Together with the advantages (rapidity, possibility of realizing a wide dynamic range), this method has the disadvantage that the results of the measurements obtained with its help are greatly distorted due to the thermal inertia of the system.

In the present work, we propose a method for obtaining undistorted values of the temperature dependence of thermophysical properties of metals in the vicinity of phase transformations, based on taking into account the thermal inertia of the system in an operational manner. This method permits using the temperature dependence of thermophysical properties for identifying the types of processes occurring [1].

The actual investigations were carried out in a vacuum (10^{-5} mm Hg) using an adiabatic scanning calorimeter, developed at the Institute of Metal Physics of the Academy of Sciences of the Ukrainian SSR [2], using standardized cylindrical specimens, heated by internal microheaters with heating rates of 1-10 deg/min, scanning from 300 to 1500°K, and a precision of $(\Delta T)_{\max}/T = 0.1\%$, in maintaining the regular regime of the second kind relative to the maximum deviation of the temperature from the set value and of $(\Delta b/b)_{\max} = 0.1\%$ relative to the maximum deviation of the heating rate $b = dT/dt = \mathrm{const}$ from the given value. The limiting systematic error of the measurements not accounted for was $\delta C_p/C_p \leq 3.5\%$.

Let us examine a hollow cylindrical specimen with an internal heater, surrounded by a protective shell, the temperature of which was maintained equal to the temperature of the specimen surface programmed according to $T_p = T_i + b_p t$ (where $b_p = dT_p/dt$) in order to create quasiadiabatic conditions. Under these conditions, all of the heat power $P_p(t)$ input to the specimen goes into heating it.

When the regular regime is strictly observed, without taking into account thermal inertia, the temperature dependence of the heat capacity $C_p(T)$ is described by the expression

$$C_p(T) = P_p(t)/b_p. \tag{1}$$

In actuality, in order to transmit heat from the heater to the specimen, a finite time, which is determined by the thermal inertia of the specimen $\tau = C_p/\gamma$ (γ is the coefficient of

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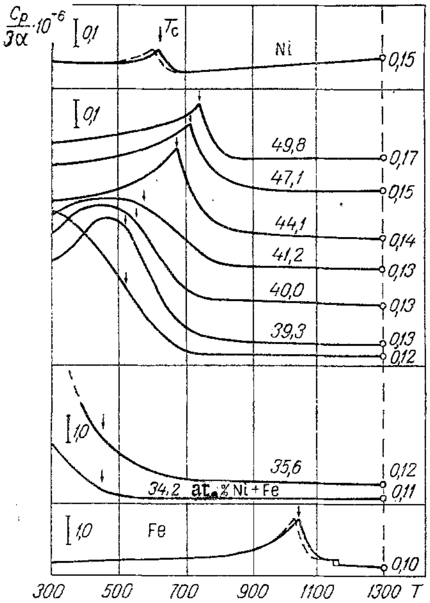

Fig. 1. Temperature dependence of the ratio of the heat capacity (cal/g-atom) to the coefficient of volume expansion for Fe, Ni, and Fe—Ni alloys: the dots indicate the values of $(C_p/3\alpha)\cdot 10^{-6}$ for Fe, Ni, and Fe—Ni alloys at $T = 1300$°K and represent the origin for each curve in the scale indicated on the figure; the dashed line shows the function $C_p/3\alpha = f(T)$ without taking into account thermal inertia.

heat transfer), is required. This leads to a lag in the temperature dependence of the heat capacity by an amount $b_p\tau$, which is taken into account in the recording system.

With sharp changes in the heat capacity in the vicinity of phase transformations, the temperature and rate of heating of the specimen deviate from the programmed value in view of the inertia of the control systems. Two methods can be used to correct for these distortions.

In the first method, the programmed rate (introduced in the measurements as a constant of the apparatus) is corrected by an amount $d\Delta T/dt$ (where $\Delta T = T - T_p$ is the deviation of the measured temperature T from the program value) and, in order to obtain the heat capacity, the instantaneous value of P(t) is operationally divided by the true heating rate $b = b_p + d\Delta T/dt$.

Taking this into account, we obtain

$$C_p(T + b_p\tau) = P(t)\Big/\left(b_p + \frac{d\Delta T}{dt}\right). \tag{2}$$

If the operational determination of the derivative $d\Delta T/dt$ is difficult, then partial correction can be achieved by an additional shift in the temperature dependence of C_p by the amount ΔT:

$$C_p(T + \Delta T + b_p\tau) = P(t)/b_p \tag{3}$$

Let us consider the origin of this correction. Let the instantaneous value of the power input to the specimen P(t) differ from the programmed value $P_p(t)$. For definiteness, we assume that $P(t) > P_p(t)$, which means that $b > b_p$. The shift in time, required in order that the recorded power coincide with the programmed value, will be denoted as Δt, so that $P(t) = P_p(t + \Delta t)$. From here, it is evident that the controlled quantity $P(t)/b_0$ describes the heat capacity of the specimen relative to the temperature that differs from the program value by some quantity δT.

Thus,

$$P(t)/b_p = P_p(t + \Delta t)/b_p = C(T_{pr} + \delta T). \tag{4}$$

On the other hand, the quantity P(t)/b describes the heat capacity relative to the instantaneous measured temperature T of the specimen: $C_p(T) = P(t)/b$. Therefore,

$$\frac{P(t)}{b_p} = \frac{P(t)}{b}\,\frac{b}{b_p} = C(T)\frac{b}{b_p}. \tag{5}$$

From (4) and (5) follows the equation

$$C(T_p + \delta T) = C(T)\frac{b}{b_p}. \tag{6}$$

In order to determine δT, we introduce a system of coordinates T'–t' with origin at the points T_0–t_0', where the program temperature coincides with the measured value. Assuming the temperature varies linearly over a small interval, we write in this system of coordinates

$$T_p' = T_p - T_0 = b_p t', \; T = T - T_0 = bt'. \tag{7}$$

For a small change in temperature, the heat capacity also changes linearly with temperature:

$$C = C_0 (1 + \beta t), \tag{8}$$

where the temperature coefficient is approximately determined from the instantaneous value of the power:

$$\beta = \frac{1}{C} \frac{dC}{dT} \simeq \frac{1}{b_p P} \frac{dP}{dt}. \tag{9}$$

From (6)-(9), we find in the first approximation with respect to $\Delta T = (b - b_p)t'$ that

$$\delta T = 2\Delta T + \frac{1}{\beta b_p} \frac{d\Delta T}{dt}. \tag{10}$$

If the heating rate is maintained with a precision $\Delta b/b = b^{-1} d\Delta T/dt \simeq 0.1\%$, then the second term in (10) is comparable with the first term or less than it. Thus, taking into account only the first term, we find that the partial correction to the temperature dependence is given by $\delta T = 2\Delta T$ relative to the program temperature or by ΔT relative to the measured value, as described in (3).

It should be noted that the correction for the nonuniformity in the heating rate over the extent of the specimen was not made due to the fact that for the high thermal conductivity of metallic specimens the error contributed is significantly less than that caused by the inaccuracy in maintaining the regime and the thermal inertia of the specimen.

In connection with the fact that in a vacuum heat transfer occurs mainly by radiation, in order to take into account the temperature dependence of τ we used the formula

$$\tau = \tau_0 \left(1 + \frac{T - T_i}{b_p P} \frac{dP}{dt}\right) \left(\frac{T_{ni}}{T}\right)^3. \tag{11}$$

Quantities measured in determining the heat effects by a differential method relative to a standard specimen, the temperature of which is maintained equal to the temperature of the specimen studied, are corrected in a similar manner. The heat power q input to the specimen, for example, as a result of a phase transformation is described by the additional heating power ΔP of one of the specimens.

In making the correction by determining the adjustment of the programmed heating rate, we obtain

$$q\left(T_0 + \frac{P_0}{P_s} b_p \tau\right) = \Delta P(t) \left(1 - \frac{\tau}{P_s} \frac{dP_s}{dt}\right) + \frac{1}{b_p} \frac{d(P_s \Delta T)}{dt}, \tag{12}$$

where $\Delta P = P_s - P_0$; $\Delta T = T_0 - T_s$, while T_0, T_s, P_0, and P_s are the temperature of the specimen and the standard, and the power input to them, respectively.

Thus, the recorded quantity ΔP is corrected by the expressions $1 - (\tau/P_s) dP_s/dt$; $(1/b_p) \cdot d(P_s \Delta T)/dt$, and the temperature dependence $(P_0/P_s) b_p \tau$.

If a partial correction is made without determining the derivative $d\Delta T/dt$, then

$$q\left(T_0 + \Delta T + \frac{P_0}{P_s} b_p \tau\right) = \Delta P \left(1 - \frac{\tau}{P_s} \frac{dP_s}{dt}\right) + 2 \frac{\Delta T}{b_s} \frac{dP_s}{dt}, \tag{13}$$

where $\Delta T_0 = T_0 - T_p$, $\Delta T_s = T_s - T_p$, and $\Delta T = \Delta T_0 - \Delta T_s = T_0 - T_s$.

In the absence of transformations in the standard, $\Delta T_s \ll \Delta T_0$ and $\Delta T_0 \simeq \Delta T$. A quantitative analysis shows that the corrections introduced have a significant effect on the results of the measurements in the scanning regime. For example, for nickel $\tau_0^n = 6 \cdot 10^3 C_p$ (with $T = 300$°K), $b_p = 5$ deg/min, the error in determining the temperature dependence is $b\tau_0^n = 54°$. For iron $\tau_0 = 7 \cdot 10^3 C_p$, $b_p \tau_0 = 70°$. In view of the high thermal conductivity, the error caused by the nonuniformity of the temperature field in the specimen constitutes 10^{-1}-10^{-2} deg for metals (for the indicated heating rates this is significantly less than the error caused by thermal inertia). For low temperatures, relative to nickel, the error caused by the inaccuracy in maintaining the program temperature is $\Delta T = 10^{-3}T \sim 0.3°$, but for high temperatures it increases by several degrees.

Since the vacuum in the calorimeter is 10^{-5} torr and the heat transfer from the heater to the specimen occurs primarily by radiation, we can assume approximately that with increasing temperature the error in determining the temperature dependence stemming from thermal inertia according to (11) decreases and becomes comparable with the error stemming from the inaccuracy in maintaining the temperature. Thus, for $T = 1500°K$, $b\tau \simeq 1°$, while $\Delta T \simeq 1.5°$. In the absence of anomalies, the main contribution to the total error in determining the magnitude of the heat capacity $\frac{\Delta C_p}{C_p} = \frac{\Delta T + b\tau}{C_p}\frac{dC_p}{dT} + \frac{\Delta b}{b}$ comes from a deviation of the heating rate from the program value, in view of the smallness of $\frac{1}{C_p}\frac{dC_p}{dT}$ ($\sim 10^{-4}$ for nickel and $\sim 10^{-3}$ for iron). However, in the anomalous region, with increasing dC_p/C_p, these errors become comparable. Thus, for a phase transition of the second kind (magnetic transition) for nickel $\frac{1}{C_p}\frac{dC_p}{dT}b\tau = 9\%$, and for iron 6%. At the same time, in the region of these transformations, $b\tau^n = 12°$ for nickel and 6° for iron.

Thus, the proposed optimization of the method eliminates a series of significant errors, which is especially significant for identifying the physical processes in materials from measurements of thermal properties and for determining the critical points.

One of the promising methods for studying phase transformations in metals and alloys is the study of the temperature dependence of thermophysical characteristics, e.g., C_p and α, simultaneously. This method yields the most complete information on the object being studied. The method is based on the following experimentally observed behavior: each of the elementary thermodynamic processes corresponds to a narrow interval of ratios of thermal ΔQ and volume ΔV effects or rates of change of heat content to the rate of change of volume [3]. In addition, these intervals do not overlap for most processes.

Figure 1 shows the results of the studies of phase transitions in Fe, Ni, and Fe—Ni alloys according to the change in the ratio $C_p/3\alpha = f(T)$. It is easy to show that for $dT/dt =$ const, $\frac{C_p}{3\alpha} = K\frac{\dot{H}}{\dot{V}}$. The limiting error, unaccounted for, is $\frac{\delta(C_p/\beta)}{C_p/\beta} \leqslant 6\%$.

It is evident that for a phase transformation of the first kind, e.g., for an $\alpha \to \gamma$ transformation, in pure Fe, a discontinuity is observed in the curve $C_p/3\alpha$. For phase transformations of the second kind, a singularity of the λ-peak type, the apex of which can approximately be identified with the Curie temperature, occurs in the curves $C_p/3\alpha = f(T)$. In addition, it is evident that in Fe $C_p/3\alpha$ is an order of magnitude greater than in Ni. This is explained by the fact that in Fe the rate of change of heat content and the rate of change of volume have different signs.

In the temperature range where there are no phase transformations, the ratio $C_p/3\alpha$ remains constant within established limits. In alloys with 49.8 and 47.1 at.% Ni for $T = T_c$, as well as in Ni and Fe, λ-peak type singularities are observed. In the alloys 44.2, 40.0, and 39.3 at.% Ni, the ratio $C_p/3\alpha$ increases with increasing temperature and reaches a maximum for $T \sim 473°K$, after which it sharply decreases and for $T \sim 900°K$ remains approximately constant. Singularities of the λ-peak type are absent for $T = T_c$. In alloys with 37.4, 35.6, and 34.2 at.% Ni, the nature of the change in the ratio $C_p/3\alpha$ changes qualitatively: it decreases sharply in the interval 300-700°K; above 700°K it remains approximately constant; for $T = T_c$ there are no singularities of the λ-peak type. Discontinuities in the curves $C_p/3\alpha = f(T)$ for Fe—Ni alloys indicate the absence of phase transformations of the first kind in these alloys. In Fe—Ni alloys with a nickel content less than 44 at.%, the behavior of the curves $C_p/3\alpha = f(T)$ for $T = T_c$ does not correspond to a phase transformation of the second kind. From the nature of the change in the ratio $C_p/3\alpha$ in these alloys, it is evident that the magnetic transformation in them occurs gradually over a wide temperature interval. This stretching out of the temperature interval, in which the magnetic transformation is realized, becomes possible if with increasing temperature, the spin order—disorder or spin order—partial disorder transition does not occur simultaneously over the entire volume of the specimen, but gradually in some discrete regions of the volume, which are more predisposed to this type of transition for one reason or another (e.g., as a result of static fluctuations and antiferromagnetic interactions of the Fe atoms). The existence of paramagnetic regions in the ferromagnetic matrix Fe—Ni alloys below T_c [4] confirms the possibility of the existence of a similar mechanism for a magnetic transformation in these alloys.

NOTATION

T, temperature, in °K; $b = dT/dt$, rate of heating of the specimen; T_p, program temperature of the specimen surface; T_i, initial temperature; $P_p(t)$, programmed power liberated in heating the specimens; C_p, heat capacity at constant pressure; γ, coefficient of heat transfer; $\tau = C_p/\gamma$, thermal inertia parameter for the specimen; $\beta = (1/C)dC/dT$, temperature coefficient of the heat capacity; q, power liberated in the specimen as a result of a phase transformation; $3\alpha = 3/l(dl/dT)$, coefficient of volume expansion of the specimen.

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