Data on the heat capacity of liquid gadolinium, holmium, and lutecium confirm and refine the parallel behavior of the heat capacity of liquid REM and the specific Gibbs free energy found in [7]. The results for yttrium lead to the conclusion that the smallness of the jumps in the thermal diffusivity and thermal conductivity on melting are general properties of all group IIIA elements in the periodic system.

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EXPERIMENTAL INVESTIGATION OF VACANCY EFFECTS IN PURE METALS

I. I. Novikov, V. V. Roshchupkin, N. A. Semashko, and L. K. Fordeeva

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The energy for the formation of vacancies in copper ($2.1 \cdot 10^{-19}$ J (1.3 eV)), platinum ($2.56 \cdot 10^{-19}$ J (1.6 eV)), and titanium ($1.9 \cdot 10^{-19}$ J (1.2 eV)) are determined from the results of measurements of the enthalpy and heat capacity of the latter in deformed and annealed states.

The study of the thermodynamic properties of nonequilibrium states of metals permits determining the energy characteristics of defects in the crystalline structure. In what follows, we describe experiments for determining the energy of vacancy formation, based on the measurement of enthalpy and heat capacity of metals in equilibrium and nonequilibrium states.

Measurements of the enthalpy and the heat capacity of a deformed metal in the recrystallization region yield the values of the enthalpy and heat capacity of the given metal in the nonequilibrium state; measurements of the undeformed, carefully annealed metal yield values of the enthalpy and heat capacity in the equilibrium state. Comparison of the values of the enthalpy and heat capacity obtained for the same range of temperatures establishes reliably the magnitude of the energy of vacancy formation. Indeed, the equilibrium concentration of vacancies is given by

$$c = A \exp\left\{-\frac{E}{kT}\right\}. \quad (1)$$

In the nonequilibrium state, the vacancy concentration c' is not equal to the vacancy concentration in the equilibrium state and can be found from the following considerations. Assume that the formation of excess vacancies has occurred as a result of deforming the metal, which is characterized by the stress appearing in the metal on deformation. Its

A. A. Baikov Institute of Metallurgy, Academy of Sciences of the USSR, Moscow.

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Gibbs energy per atom increases by the amount $(\sigma^2/2\mu)v_a$ (in the case of balanced cubic compression the increase in the free energy equals σv_a). The activation volume v_a is proportional, under the simplest assumptions, to the third power of the interatomic distance b, i.e., b^3.

The energy of vacancy formation is determined by the values of the Gibbs energy of a free atom (located outside the crystal) and an atom at a lattice site [1]. In the deformed metal, the Gibbs energy per atom G is greater in comparison to the undeformed metal by the amount $(\sigma^2/2\mu)v_a$, and the energy of vacancy formation is smaller and equals

$$E' = E - \frac{\sigma^2}{2\mu} v_a.$$

The Gibbs energy of a vacancy always equals zero; viewing the vacancy as a quasiparticle dissolved in the metal and using thermodynamic relations for solutions, we find that the Gibbs energy of a vacancy equals

$$G_v = E' + kT \ln c.$$

From the condition $G_V = 0$, taking into account the fact that $E' = E - (\sigma^2/2\mu)v_a$, we find from here that

$$c' = \exp\left\{-\frac{E - \frac{\sigma^2}{2\mu} v_a}{kT}\right\}. \tag{2}$$

If we take into account the entropy factor A, then the formula takes the form

$$c' = A \exp\left\{-\frac{E - \frac{\sigma^2}{2\mu} v_a}{kT}\right\}. \tag{3}$$

For an undeformed metal, when $\sigma = 0$, formula (3) assumes the form (1).

Each vacancy is associated with a definite value of the enthalpy i_V, equal to E'; the enthalpy of all vacancies in the metal equals E'c' (Ec in the undeformed metal). The quantity E'c' is the contribution of the vacancies to the enthalpy of the metal, so that

$$i_d = i_{V=0} + i_V, \tag{4}$$

where $i_{V=0} = i$ is the enthalpy in the absence of vacancies.

At the initial stage of recrystallization, all changes in the structure of defects in the prestressed metal reduce primarily to changes in the vacancy concentration (i.e., to a decrease in the degree of saturation by vacancies and a decrease of their concentration from the nonequilibrium value c' to the equilibrium value c); changes in the dislocation structure (annihilation of a significant part of dislocations with increasing temperature) can be assumed to occur at the second stage, i.e., after the vacancy concentration approaches the equilibrium value.

According to what was said above, for temperatures corresponding to the initial stage of recrystallization, in a prestressed metal the contribution of excess vacancies (c' — c) vanishes, which leads to the liberation of heat c'E' — cE inside the metal, as a result of which a given temperature increase for p = const requires an amount of heat that is less by c'E' — cE in comparison with the unstressed metal. Then

$$i_d = i - (c'E' - cE) = i - (c' - c)E + c' \frac{\sigma^2}{2\mu} v_a.$$

The third term is small in comparison with the first, so that $(\sigma^2/2\mu)v_a \ll E'$, and therefore,

$$i_d = i - (c' - c)E. \tag{5}$$

The saturation vacancy concentration is, as already noted, a function of the energy E', and in addition, the difference (c' — c) is comparatively small so that c' can be represented in the form of an expansion in powers of [E' — E], using only the first two terms of the series. Then

$$c' = c + \frac{\partial c'}{\partial E'_{E'=E}} [E' - E].$$

Substituting here the value of $\partial c'/\partial E'$ from relation (3), for the case $\sigma = 0$ we will have

$$c' = c - A \frac{1}{kT} \exp\left\{-\frac{E}{kT}\right\} [E' - E],$$

which leads with the help of Eq. (5) to the following expression for the enthalpy of a deformed metal:

$$i_d = i + A \frac{E}{kT} \exp\left\{-\frac{E}{kT}\right\} [E' - E] \tag{6}$$

or, taking into account the fact that $E' - E = -(\sigma^2/2\mu)v_a$:

$$i_d = i - \frac{AE[E - E']}{kT} \exp\left\{-\frac{E}{kT}\right\}. \tag{6a}$$

It follows from Eq. (6a) that

$$\ln[(i - i_d)T] = \ln \frac{AE(E - E')}{k} - \frac{E}{kT},$$

i.e., in semilogarithmic coordinates $\ln[(i - i_d)T]$, $1/T$ the experimental values of the enthalpy for the deformed and annealed metal must form a linear function, and in addition, the tangent of the slope angle of this line, equal to $-E/k$, determines the energy of vacancy formation.

For the heat capacity, differentiating expression (6) with respect to T, we obtain (neglecting the dependence of E and E' on T)

$$\frac{\partial i_d}{\partial T} = \frac{\partial i}{\partial T} + \frac{AE(E' - E)}{kT^2} \exp\left\{-\frac{E}{kT}\right\} \left[\frac{E}{kT} - 1\right].$$

Since $E/kT \gg 1$, the number 1 in the square brackets can be neglected. Then

$$c_p^d = c_p + \frac{AE^2(E' - E)}{k^2T^3} \exp\left\{-\frac{E}{kT}\right\} \tag{7}$$

or, taking into account the fact that $(E' - E) = -(\sigma^2/2\mu)v_a$, i.e., less than zero:

$$c_p^d = c_p - \frac{AE^2(E - E')}{k^2T^3} \exp\left\{-\frac{E}{kT}\right\}. \tag{7a}$$

It follows from Eq. (7a) that

$$\ln[(c_p - c_p^d)T^3] = \ln \frac{AE^2(E - E')}{k^2} - \frac{E}{kT},$$

i.e., as in the case of enthalpy, in semilogarithmic coordinates $\ln[(c_p - c_p^d)T^3]$, $1/T$ the experimental values of the heat capacity of the deformed and annealed metal must lead to a linear function, and the angle of inclination of this straight line determines the energy of vacancy formation E.

The enthalpy of the deformed and annealed copper in the temperature range 373-673°K was measured by the mixing method with the use of an ice calorimeter [2] (the error of the measurement of enthalpy for the given temperature range was 0.4%). The specimen studied was made out of electrolytic brand OSCh-11-4 copper (99.996% purity). Cleaned and degassed plates were resmelted twice in an electron beam furnace in a vacuum with an ingot diameter of 50 mm. The latter were annealed in a vacuum at a temperature of 923°K and pressed into a diameter of 25 mm. Then, by cooling, a sample with mass 35 g was prepared. First, the enthalpy of the deformed specimen was measured, and then the specimen was annealed and the enthalpy of the annealed specimen was measured in the same temperature range. The maximum difference in the enthalpy of the deformed and annealed copper was about 1%. The results of the enthalpy measurements of the deformed and annealed copper, presented in semilogarithmic coordinates $\ln[(i - i_d)T]$, $1/T$, lie on a straight line, and the vacancy formation energy E, determined from the slope angle, constituted $2.1 \cdot 10^{-19}$ J (1.3 eV) in copper, which agrees satisfactorily with the data obtained by other workers [3, 4]. The error in determining the vacancy formation energy in copper from the results of the measurement of the enthalpy in deformed and annealed copper is estimated as 40-60%.

The vacancy formation energy in pure platinum (99.96%) and titanium (99.997%) was determined by measuring the heat capacity of plastically deformed (by 20% platinum and 89.80% titanium) and annealed wire specimens with the help of an adiabatic calorimeter [5]. The measurements were carried out in the temperature range 300-1200°K, and the maximum difference in the heat capacities of the deformed and annealed metals was about 5-6% with a measurement error in the given temperature range of 0.5-0.8%. In semilogarithmic coordinates $\ln[(c_p - c_p^d)T^3]$, $1/T$, the experimental results form a straight line, while the vacancy formation energy for platinum was $2.6 \cdot 10^{-19}$ J (1.6 eV) and $1.9 \cdot 10^{-19}$ J (1.2 eV) for titanium. The error in determining the vacancy formation energy in platinum and titanium from the results of measurements of the heat capacity of the deformed and annealed platinum and titanium is estimated to be 20-30%.

NOTATION

c, equilibrium vacancy concentration; A, entropy factor; E, vacancy formation energy; k, Boltzmann's constant; T, absolute temperature; σ, deformation stress; μ, modulus of elasticity; G, Gibbs energy of an atom in a lattice site of the crystal lattice; E', vacancy formation energy in the deformed metal; c', nonequilibrium vacancy concentration; G_v, Gibbs energy of a vacancy; i_v, total enthalpy of vacancies; i_d, enthalpy of the deformed metal; $i_{v=0}$, enthalpy in the absence of vacancies; c_p^d, heat capacity of the deformed metal; c_p, heat capacity of the annealed metal.

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