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Abstract

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PHYSICS

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CALORIMETRIC DETERMINATION OF THE ENERGY OF FORMATION OF VACANCIES IN GOLD

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In a number of works devoted to the measurement of the energy of formation and the concentration of vacancies in metals, these quantities are determined, as a rule, from the change in electrical conductivity caused by the formation or disappearance of vacancies ([1-5]). Such a method makes it possible to determine with sufficient accuracy (to 2-3% ([1,2])) the energy required for the formation of one vacancy; the vacancy concentration, however, is estimated only to within an order of magnitude.

In some works ([2-4]) the concentration is determined from the results of dilatometric measurements. In this case it is assumed that the concentration is approximately equal to the relative change in volume caused by vacancies. Such measurements, however, must be treated with a certain caution, since there is no assurance that the indicated change in volume is, in magnitude, close to the total volume of vacancies in the metal.

In view of the foregoing, it is of interest to measure the concentration of vacancies by some other, independent method. In particular, this quantity can be determined from the amount of heat released during annealing of a metal saturated with vacancies by quenching. To determine the concentration it is necessary to relate this amount of heat, equal, as is readily seen, to the total energy of formation of the vacancies, to the energy of formation of one vacancy and to the number of atoms in the given volume of metal. The energy of formation of one vacancy can be determined both from the results of measurements of electrical conductivity and from the dependence of the total energy of formation of vacancies Q on the quenching temperature T. Indeed, since the number of vacancies in a metal, even at premelting temperatures, is relatively small, the total energy of their formation, as well as the magnitude of the increase in electrical resistance, may be considered proportional to the concentration. Consequently, in this case the energy of formation of one vacancy can be determined from the slope of the straight line $\ln Q = f\left(\frac{1}{T}\right)$.

Fig. 1

Figure 1: Fig. 1

The path indicated above for determining the concentration of vacancies is, however, associated with difficulties consisting in the fact that, when ordinary calorimetric methods are used, comparatively massive specimens are required, whereas quenching of vacancies can be successfully carried out only on specimens of sufficiently small mass. An attempt to perform such measurements on a massive specimen is described in a communication by De Sorbo ([6]). This work, as the author himself points out, is only preliminary in character: it gives a comparatively rough estimate of several values of the total energy of formation of vacancies, corresponding to approximately identical quenching temperatures. The author does not attempt to determine the energy of formation of one vacancy and, consequently, the concentration of vacancies from the results of his own measurements. Moreover, the absence of control over the quenching of the specimen makes it difficult to compare the results with data reported in other works.

The present work is also devoted to determining the total energy of vacancy formation. The difficulty indicated above is overcome by using a pulsed differential technique, which makes it possible to use thin wires as specimens. This method, developed by one of the authors ([7]), was previously applied to measurements of the stored energy of deformation of metals. In the present case the only difference is that, instead of a deformed specimen, a specimen containing an excess number of vacancies is included in the measuring circuit.

The specimens were gold wires (purity 99.99%) 0.1 mm in diameter and about 60 mm long. Quenching was carried out by rapidly immersing the electrically heated wire in distilled water. In parallel with the calorimetric measurements, the increase in electrical resistance was measured with a potentiometer.

Fig. 1

As a result of the experiment, values were obtained for the total energy of vacancy formation Q and for the relative increase in electrical resistance $\Delta R/R_{20^\circ}$, corresponding to various quenching temperatures (from 600 to 900°).

Figure 1 shows the straight line characterizing the relation between these two quantities. The coefficient of proportionality between them is

$$0.073 \pm 0.005 \frac{\text{cal}}{\text{g} \cdot \% \, \Delta R/R_{20^\circ}}.$$

From the slope of the straight lines $\ln Q = f\left(\frac{1}{T}\right)$ and $\ln \frac{\Delta R}{R_{20^\circ}} = \varphi\left(\frac{1}{T}\right)$, the energy of formation of one vacancy was determined. Within the experimental error ($\sim 6\%$) this quantity coincides with that given in the work of B. G. Lazarev and O. N. Ovcharenko ([1]) (19,000 cal/g-atom).

The data obtained made it possible to determine vacancy concentrations for different quenching temperatures. The largest value of this quantity reached in our experiments (corresponding to a quenching temperature of 890°, or to a 1% increase in electrical resistance) was $(7.6 \pm 1.0) \cdot 10^{-4}$. Extrapolation to the melting temperature gave the value $2.1 \cdot 10^{-3}$. This value is approximately 3 times greater than the value determined from the change in volume in quenched gold ([2], [3]), and almost $1\frac{1}{2}$ times greater than the value obtained from measurements of volume at high temperatures ([5]). Such a discrepancy, it seems to us, permits the conclusion that dilatometric measurements lead to somewhat underestimated results.

From the data obtained, the value of the pre-exponential factor in the well-known formula for the vacancy concentration

$$c = Ae^{-u/kT}$$

was also determined. According to our data, $A = 2.6$. The estimates of this coefficient available in the literature, given by various authors on the basis of both theoretical and experimental (dilatometric) investigations, lie in the range from 0.5 ([1], [5]) to 3.8 ([2], [3]).

It is also of interest to estimate the increase in electrical resistance per atomic percent of vacancies. According to our data, this quantity is equal to $0.30 \cdot 10^{-6}$ $\Omega \cdot$ cm/at. % vac.. It is close to the theoretical estimate in one of the early works ([8]) ($\Delta\rho/c = 0.4 \cdot 10^{-6}$ $\Omega \cdot$cm/at. % vac.), but differs appreciably from later estimates ([9], [10]) ($\Delta\rho/c = 1.5 \cdot 10^{-6}$ $\Omega \cdot$ cm/at. % vac.). It is interesting to note that the obtained value of $\Delta\rho/c$ is closer than the data given in other works to the change in resistance produced by 1 at.% of impurity elements closest in···

to gold (for a silver impurity, $0.38 \cdot 10^{-6}$ $\Omega \cdot$ cm/at. %; for a copper impurity, $0.48 \cdot 10^{-6}$ $\Omega \cdot$ cm/at. %).

In conclusion, the authors take this opportunity to express their gratitude to Academician of the Academy of Sciences of the Ukrainian SSR B. G. Lazarev and O. N. Ovcharenko for the discussion.

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