CONCERNING THE EFFECT OF NEUTRON IRRADIATION ON CERTAIN THERMOPHYSICAL CHARACTERISTICS OF METALS

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It is shown experimentally that in neutron irradiated metals the heat capacity and thermo-emf undergo changes because of the introduction of radiation effects. The feasibility of using these phenomena to determine the concentration of excess vacancies is discussed.

The introduction of crystal lattice defects into metals as a result of irradiation by nuclear particles causes changes in many of their structure-sensitive physical properties; it causes changes in isobaric-isothermal potentials of the crystals and the internal energy increases [1-5]. The investigation of these effects is of both direct practical importance and of theoretical interest from the point of view of explaining the nature, concentration, mobility and interaction of point defects and other kinds of defects which affect the physical and mechanical properties of metals.

I. Heat Capacity. Since lattice defects (vacancies, interstitial atoms, dislocations, etc) change the energy of the crystal lattice, i.e., its internal energy, it is reasonable to expect that the heat capacity will also change since the latter is the derivative of the internal energy with respect to the temperature.

Under thermodynamic equilibrium conditions, the concentration of point defects at T °K is given by

$$n = A \exp(-U_f/kT). \tag{1}$$

As the temperature increases, the concentration of point defects, which are obviously vacancies, increases rapidly, and the increase in the heat capacity associated with the formation of vacancies is proportional to the expression [8]

$$\Delta C \sim \frac{U_f^2}{kT^2} \exp(-U_f/kT). \tag{2}$$

An exponential growth of ΔC can be expected at high temperatures. This was indeed observed in a number of experimental studies of the heat capacity of metals [6-10], and the resulting values of ΔC were used by the authors to determine the formation energy and concentration of vacancies near the melting point. The results of these investigations showed that if the vacancy concentration in the metal is 1 at.%, the heat capacity can increase by 50%. It should, moreover, be noted that according to [9, 10], the vacancy concentration in a metal near its melting point lies between 1 to 2.7% which is an order of magnitude higher than the values computed from the data of other authors [2, 12, 13]. If we accept the point of view of the latter and assume that the vacancy concentration in most metals is about 0.1 to 0.2 at.% in the vicinity of the melting point, then the increase in the heat capacity can be 5 to 10 times larger, i.e., it would amount to 100 to 200% for 1 at.% vacancies.

When a metal is irradiated by neutrons, a nonequilibrium vacancy concentration is introduced into the latter. The atomic fraction of displaced atoms is given by the relation [2, 4].

$$B = \varphi \tau \sigma_d \bar{\nu}. \tag{3}$$

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For an integral flux of fast (E > 1 MeV) neutrons equal to $10^{20}/cm^2$, assuming that according to the cascade theory $\bar{\nu} = 380$ as given in [4] and that σ_d is 3.2 barns [14], we obtain for copper B = 0.12, i.e., 12% Frenkel pairs. Although this value is clearly too high because of the simplifying assumptions introduced into the cascade theory [15] (these assumptions are related in particular to neglecting collective processes, like displacement spikes and thermal spikes, focusing phenomena, the true energy spectra of neutrons in the reactor, etc.) the vacancy concentration in copper can reach values of 2 at %, according to more exact calculations [16]. According to experimental data [17], an integral dose of fast neutrons of $10^{20}/cm^2$ (for copper, $2.03 \cdot 10^{20}/cm^2$) is needed to generate 1% Frenkel pairs in most metals. Such a dose requires several weeks of irradiation in modern nuclear reactors. Consequently, it is relatively easy to attain concentrations of point defects sufficient to produce substantial changes in the heat capacity by neutron irradiation. In spite of its importance, there have been relatively few publications devoted to studies of the effects of irradiation on the heat capacity of materials [34]. One of these investigations is that published by Overhauser [18] who performed a theoretical calculation in which he showed that if the Frenkel pair concentration in an irradiated metal is 10^{-5} it is reasonable to expect that ΔC will increase by 1%. Another publication on this topic is [19] in which the increase of heat capacity of α-quartz irradiated by neutrons was investigated experimentally. In our opinion, experimental investigations of the effects of radiation on such fundamental properties of metals like the heat capacity have an independent interest and they can also serve as an important method for studying the kinetics of pile-up and annealing of radiation defects in irradiated metals. Accurate data on the behavior of the heat capacity in irradiated materials is especially necessary for studying subtle thermal effects like the release of stored energy on annealing [11, 20]. In the course of such investigations, we observed the difference in heating rates of an irradiated sample and a control sample which was tentatively attributed to increased heat capacity of the irradiated sample. Subsequent measurements demonstrated the existence of such an effect.

The experiments were based on the differential thermal analysis (DTA) technique and were performed in the vacuum chamber described in [21]. The samples were 99.99% pure copper, irradiated to moderate fluences ($8 \cdot 10^{17}$ to $6 \cdot 10^{18}$ fast neutrons/cm^2) at the ambient temperature in a VVR-M thermal reactor. Copper was chosen so that there would be no recovery of physical properties in the temperature interval 50 to 150°C; most of the change in electrical conductivity occurs as a result of annealing at room temperature, but the mechanical properties have not yet recovered and consequently, the stored energy should not be liberated; the observed thermal effect can be attributed to changes in heat capacity. On the other hand, moderate fluences were selected in order to ensure that the radiation induced defect concentration would be low; this would permit the results to be interpreted with the help of a simple model but large enough to obtain a readily measureable increase in heat capacity.

According to the DTA method [22], the following equations describe the annealing of the irradiated sample and the control

$$\left(\frac{dQ}{d\tau}\right)_1 = m_1 C_1 \frac{dT_1}{d\tau} + G_1 \Delta T_1, \tag{4}$$

$$\left(\frac{dQ}{d\tau}\right)_2 = m_2 C_2 \frac{dT_2}{d\tau} + G_2 \Delta T_2, \tag{5}$$

$$\delta = T_1 - T_2; \frac{d\delta}{d\tau} = \frac{dT_1}{d\tau} - \frac{dT_2}{d\tau}. \tag{6}$$

Assuming that $(dQ/d\tau)_1 \simeq (dQ/d\tau)_2$ and $G_1 \simeq G_2$ and combining (4), (5), and (6), we can write the following equation for the first anneal assuming that $C_1 = C_2 + \Delta C$:

$$\left(\frac{d\delta}{d\tau}\right)_I = \left(\frac{dT_2}{d\tau}\right)_I \left[\frac{m_2 C_2 - m_1 C_1 - m_1 \Delta C}{m_1 (C_2 + \Delta C)}\right] - \frac{G\delta_I}{m_1 (C_2 + \Delta C)}, \tag{7}$$

for the second anneal assuming that $C_1 = C_2$:

$$\left(\frac{d\delta}{d\tau}\right)_{II} = \left(\frac{dT_2}{d\tau}\right)_{II} \left[\frac{m_2}{m_1} - 1\right] - \frac{G\delta_{II}}{m_1 C_2}. \tag{8}$$

Subtraction of (8) and (7) and taking into account that the experiment is conducted so that $(dT_2/d\tau)_I = (dT_2/d\tau)_{II}$ we have:

$$\Delta = \left(\frac{d\delta}{d\tau}\right)_I - \left(\frac{d\delta}{d\tau}\right)_{II} = \frac{dT_2}{d\tau} \frac{m_2 \Delta C}{m_1 (C_2 + \Delta C)} - \frac{G\delta_I}{m_1 (C_2 + \Delta C)} + \frac{G\delta_{II}}{m_1 C_2}. \tag{9}$$

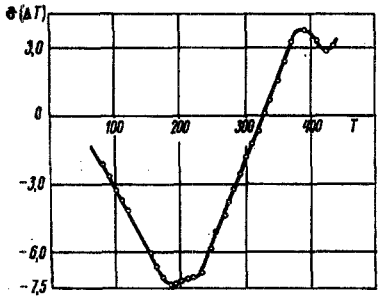

Fig. 1

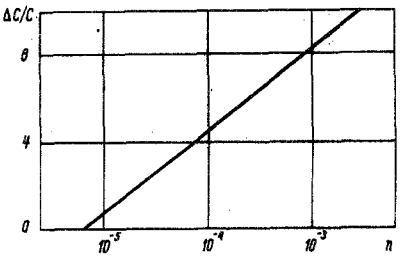

Fig. 2

Fig. 1. Difference between thermograms obtained for two successive heatings of an annealed and an irradiated copper sample (δ (ΔT), °C; T, °C).

Fig. 2. Increase in heat capacity of neutron irradiated copper as a function of the point defect concentration ($\Delta C/C$, %).

Since the experiment was conducted in vacuum at relatively low temperatues, the thermal losses are small so that it is possible to assume that terms with Gδ in (9) cancel each other. Then it is possible to obtain from (9), formulae for determining the increase in heat capacity of an irradiated (or deformed) sample

$$\Delta C/C = \frac{1}{\frac{m_2}{m_1}\frac{dT_2}{d\tau}\frac{1}{\Delta} - 1}. \qquad (10)$$

Figure 1 shows the difference in DTA thermograms obtained for two successive anneals of irradiated ($8 \cdot 10^{17}$ /cm^2) and annealed samples. Here for Δ = 0.137°C/min, ($dT_2/d\tau$) = 1.75°C/min, m_1 = 1.787 g, m_2 = 1.830 g and calculation based on (10) gives $\Delta C/C$ = 0.0825, i.e., around 8%. Thus, as a result of irradiating copper by neutrons to a fluence of $8 \cdot 10^{17}$ fast neutrons/cm^2, the heat capacity increases by 8%.

According to (3), the concentration of point defects for such an irradiation is equal to $9.7 \cdot 10^{-4}$, but if we take into account that between 50 and 60% of the radiation defects introduced into copper are annealed before reaching room temperature, it is reasonable to assume that the concentration was 0.05 at %. If it is assumed, in accordance with what we have previously pointed out, that $\Delta C/C$ = 100% for 1 at.% vacancies in a metal, then our value $\Delta C/C$ = 8% is clearly related to a concentration of 0.08 at.% which is in good agreement with cascade theory. Furthermore, it is interesting to note that the magnitude of n_V, calculated from the stored energy released in this experiment at temperatures above 200°C (~1 cal/g) amounts to $7 \cdot 10^{-4}$, i.e., it is in good agreement with the value obtained from ΔC and the cascade theory.

On the basis of our data [23], and also of the calculations in [18], the heat capacity of irradiated copper can increase as a function of the concentration of radiation point defects in metals, as shown by the plot of Fig. 2.

The resulting magnitude of ΔC in the irradiated metal is higher than the value which could have been expected by taking into account only changes in the frequency spectrum of lattice vibrations caused by the presence of defects [24, 25]. The value of ΔC is probably affected to a considerable extent by energy losses associated with "evaporation" of single vacancies from complexes of various configurations [26], as a result of their thermal activation in the course of heating the metal. This is definitely similar to experiments performed under equilibrium conditions when ΔC was obtained from (2) because of energy losses Uf associated with the formation of vacancies. In support of this hypothesis, we cite the fact that the result of evaluating n_V from ΔC by using data from equilibrium experiments [6-10] agrees with the values obtained for our nonequilibrium case by other means.

II. Thermo-emf. The phenomenon of the generation of a thermo-emf by a pair of deformed–undeformed metals has been known for a long time. Theoretical [27, 28] and experimental investigations showed that the cause of this phenomenon is the introduction of vacancies and dislocations in the deformed metal accompanied by change in the electron density and free path length of the electrons.

Since a characteristic of neutron irradiation of metals is the formation of point defects and other kinds of lattice defects, it is reasonable to expect that an emf will be generated by an irradiated–unirradiated metal

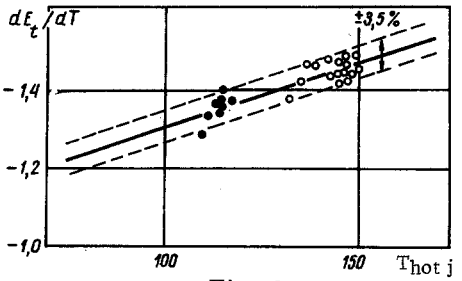

Fig. 3

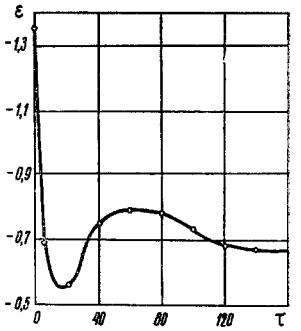

Fig. 4

Fig. 3. Thermo-emf generated by a pair consisting of an irradiated and an unirradiated sample of molybdenum (dE_t/dT, $\mu V/deg$; $T_{hot\ j}$, °C).

Fig. 4. Changes in the radiation induced thermo-emf in molybdenum for isothermal (T = 150°C) annealing (ε, $\mu V/deg$; τ, min).

pair. This effect has not been studied sufficiently. In [31] the results of an irradiation of iron and constantan by protons are published, and [32] presents similar results for thermal neutron irradiated molybdenum. On the basis of these experimental studies and of the available theoretical models, it is not possible to obtain information about the behavior of thermo-emf in metals,* especially with body centered cubic lattices, irradiated by fast neutrons.

In order to use the well known classical dependence of the absolute thermo-emf

$$E_t = \frac{kT}{e} \ln (N_1/N_2) \tag{11}$$

or the more exact relation [29]

$$E_t = \frac{\pi^2 k^2 T^2}{2e \frac{h^2}{8m} \left(\frac{3N}{\pi}\right)^{1/3}}, \tag{12}$$

from which we obtain

$$\Delta\varepsilon/\varepsilon = \left(\frac{2\Delta N}{N}\right)^{1/3}, \tag{13}$$

where $\varepsilon = dE_t/dT$; it is necessary to know how the effective number of free electrons per unit volume changes in the metal as a result of irradiation. No such data are available from the literature [1-5], and there is little basis for setting $\Delta N/N$ equal to $\Delta v/v$, as was proposed in [29] for deformed metals.

Experiments performed on wire samples (d ≃ 0.5 mm) of molybdenum, tungsten and other metals of standard technical purity showed [23] that a measurable thermo-emf exists for the irradiated – unirradiated metal pair.

The sample irradiation conditions were similar to I above; the fluence of fast (E ≥ 1 MeV) neutrons was $4 \cdot 10^{18}/cm^2$. The measurement circuit based on a sensitive mirror galvanometer type M17/2 ($1.5 \cdot 10^{-7}$ V/mm/m) and the low resistance P-306 potentiometer; the cables were carefully shielded.

The results for Mo are shown in Fig. 3. For a temperature of the hot junction $T_{hot\ j}$ = 100°C and of the cold junction $T_{cold\ j}$ = 25°C, the thermo-emf developed was $\varepsilon = dE_t/dT = 1.3\ \mu V/deg$. This value increases with increased $T_{hot\ j}$ and its rate of growth was related to the Thompson emf so that changes in the latter was equal to $\Delta\sigma = (d^2E/dT^2)\ T = 1.27\ \mu V/deg$. As is well known from [33], the Thompson emf is related to the electronic heat capacity of a metal through the relation

$$\Delta\sigma/\sigma = \Delta C_p/C_p. \tag{14}$$

* This situation may be somewhat improved by the recent appearance of publications [35] and [36].

It was assumed in [33] that $\sigma = 10$ μV/deg for Mo, determined from $\Delta C_p/C_p = 0.127$, i.e., 13%. Thus, as a result of neutron irradiation of the metal, its electronic heat capacity changes also.

Parallel measurements of the electrical resistivity ρ in these Mo samples show that the increase of $\Delta\rho$ amounts to 13.5%. From these data, assuming that 1 at.% vacancies in Mo lead to an increase of about 10 $\mu\Omega \cdot$ cm it is possible to determine the magnitude of $n_v = 0.075\%$ and to obtain the value $\Delta\varepsilon$ for 1 at %. The latter amounts to 20 μV/deg. On the other hand, by using the experimentally determined value of ε and taking into account the data [29] on $\Delta\varepsilon$ for a single vacancy, it is possible to compute their concentration; for this case, it was equal to 0.06%. Here $\Delta\varepsilon$ for a single vacancy was assumed to be equal to the value appropriate to silver, since this parameter has not yet been evaluated for body-centered metals. This can be partly explained by the difference in concentrations computed from ρ and ε.

Isothermal anneal of irradiated Mo leads to a lowering of the induced thermo-emf because of the annihilation of radiation defects. Figure 4 shows measurements of ε as a function of time for T = 150°C. After long annealing time, a correlation is observed in the behavior of ε and ρ.

NOTATION

T	is the temperature;
τ	is the time;
n	is the concentration of point defects;
n_v	is the concentration of vacancies;
U_f	is the energy of defect formation;
C, ΔC	are the heat capacity of metal and its increment;
C_p, ΔC_p	are the electronic heat capacity of metal and its increment;
k, h	are the Boltzmann and Planck constants;
$\varphi\tau$	is the integral flux of neutrons;
σ_d	is the cross section of neutron collision;
$\bar{\nu}$	is the theoretical value of the mean number of displaced atoms per one primary collision;
$(dQ/d\tau)_1$, $(dQ/d\tau)_2$	are the heat powers supplied to irradiated and standard samples;
$dT_1/d\tau$, $dT_2/d\tau$	are the rate of increase in the temperature of irradiated and standard samples;
m_1, C_1, m_2, C_2	are the masses and heat capacities of irradiated and standard samples;
$G\Delta T$	are the heat losses;
δ	is the temperature difference between irradiated and standard samples;
E_t	is the absolute thermal emf;
e, m	are the charge and mass of electron;
N_1, N_2	are the effective number of free electrons per unit volume of irradiated and unirradiated metals;
$\Delta v/v$	is the relative change in volume of irradiated metal;
ε	is the absolute differential thermal emf;
σ	is the Thomson emf;
ρ, $\Delta\rho$	are the specific electric resistance and its increment;
A	is the preexponential factor taking into account entropy factor.

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