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Vacancy migration at high temperatures in Au studied by positron annihilation measurements in fast pulse-heating experiments

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Abstract. A novel method for investigating the time-dependent approach to the thermal equilibrium concentration of vacancies in metals at high temperatures has been developed. The time-dependent accumulation of thermal vacancies in the bulk after fast pulse-heating was studied in Au by isothermal measurements of the positron lifetime and the Doppler broadening of the annihilation γ-line. The experimental method is described and preliminary results are reported.

1. Introduction

Thermal equilibrium defects play an important role in the high-temperature properties of solids. The high-temperature equilibrium concentration of vacancies and the vacancy formation enthalpy, H_{1V}^{F}, have been extensively investigated in metals [1] by the technique of positron lifetime measurements. Recently, this technique was employed in the study of elemental semiconductors [2, 3] and metal oxides [4] at high temperatures. On the other hand, measurements of the vacancy migration enthalpy H_{1V}^{M} at high temperatures, which we attempt to investigate in the present paper, would be of great interest from two aspects. Firstly, the sum of the two independently determined quantities H_{1V}^{F} and H_{1V}^{M} could be compared to the activation enthalpy of self-diffusion Q^{SD} in order to detect contributions apart from vacancies to the self-diffusion processes, e.g., of self-interstitial atoms [5]. Secondly, the question of the temperature dependence of H_{1V}^{M}, having been discussed for many years [6], should be studied experimentally.

Former studies of the time-dependent approach to the thermal equilibrium concentration of defects ('equilibration process') were performed by pulse-heating with subsequent quenching [7–9] or interrupted quenching [10], and subsequent electrical resistivity measurements at low temperatures. However, in this method vacancy agglomeration, impurity contamination and additional formation of vacancies during quenching complicate the interpretation of the experimental data.

Three inherent features of the positron annihilation technique appear to be attractive for the investigation of high-temperature defect equilibration processes:

(i) It is sensitive to vacancy-type defects exclusively which may be discerned from other types of defects.

(ii) It can be employed at high temperatures because in many cases the positron–vacancy binding energy is sufficiently high for efficient trapping.

(iii) Due to the short lifetime of the positron of at most a few hundred picoseconds, fast time-dependent processes can be studied precisely.

In the following sections we shall first outline the principles of the diffusion-limited equilibration process of the thermal defect concentration. Then we will describe the fast pulse-heating technique with synchronised isothermal measurements of the positron annihilation characteristics. Finally we shall present some preliminary results [11].

2. Approach to thermal equilibrium

The equilibration process of the vacancy concentration in metals at high temperatures is considered to occur by vacancy formation at dislocation jogs and diffusion-limited accumulation in the bulk. Former studies indicate that external and internal surfaces, e.g. large-angle grain boundaries, can be neglected as vacancy sources [7, 8].

By using Ham's analysis of diffusion-limited precipitation [12] Seidmann and Balluffi [7] treated the problem of monovacancy formation at dislocations in a regular array and subsequent radial diffusion of these vacancies into the bulk. The mean fraction $f(t)$ of the time-dependent accumulation of vacancies in the bulk after a rapid temperature increase from T_1 to T_2 was deduced to follow the relationship [7]

$$f(t) = \frac{\bar{C}(t) - C_i}{C_{1V} - C_i} \simeq 1 - \exp(-\alpha_1^2 D_{1V} t) = 1 - \exp(-t/\tau_D). \tag{1}$$

Here C_i denotes the equilibrium vacancy concentration at the initial temperature T_1 and

$$C_{1V} = \exp(S_{1V}^F/k) \exp(-H_{1V}^F/kT_2) \tag{2}$$

the equilibrium vacancy concentration at the final temperature T_2 with the vacancy formation entropy S_{1V}^F. $\bar{C}(t)$ designates the time-dependent mean bulk concentration of vacancies and

$$D_{1V} = D_{1V}^0 \exp(-H_{1V}^M/kT_2) \tag{3}$$

the diffusivity of monovacancies. The quantity

$$\alpha_1^2 \simeq 2/R^2[\ln(R/r_0) - 0.6] \tag{4}$$

is given by the mean dislocation density

$$N_D = 1/4R^2 \tag{5}$$

and $r_0 \simeq 3$ Å is the effective source radius of a narrow cylinder around a dislocation within which the vacancy equilibrium concentration can be attained at all times [7]. At low initial temperatures T_1 the concentration C_i is negligible and equation (1) simplifies to

$$\bar{C}(t) \simeq C_{1V}[1 - \exp(-\alpha_1^2 D_{1V} t)] = C_{1V}[1 - \exp(-t/\tau_D)]. \tag{6}$$

From (6), (2) and (3) it is obvious that measurements of $\bar{C}(t)$ in fast pulse-heating experiments at various temperatures can yield both the migration enthalpy H_{1V}^M and the formation enthalpy H_{1V}^F simultaneously.

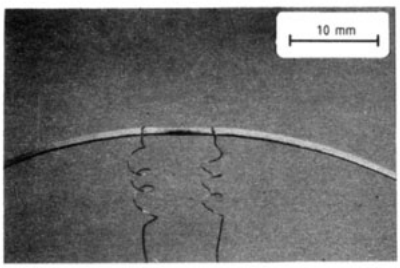

Figure 1. Gold specimen with gold potential leads (diameter 100 μm) for continuous monitoring of the measuring temperature. The specimen is mounted in water-cooled Cu current junctions. The positron source is located within the gauge length (8 mm) between the thin potential leads.

3. Experimental procedure

The present study of the vacancy equilibration process at high temperatures by positron annihilation was performed on Au, because in this material detailed information on vacancy properties is available [1, 13, 14]. Moreover the changes in the lifetime and of the trapping rate σC_{1V} of positrons due to vacancy formation are large [14] and gold is insensitive to impurity contamination. Here σ denotes the specific trapping rate of positrons at vacancies.

To prepare a specimen with a sealed source, the positron emitter (^{22}NaCl, 5.5×10^5 Bq) was deposited in the central part of a polycrystalline tube of high-purity gold (diameter 1.0 mm, wall thickness 0.15 mm, length 90 mm, residual resistivity ratio of 214) after etching and annealing. Then the tube was squeezed flat and the source was hermetically sealed within the gauge length (8 mm) by electron beam welding. Two 100 μm gold wires were fixed on the specimen as potential leads for continuous monitoring of the specimen temperature by resistance measurements over the gauge length (see figure 1). The temperature calibration of the resistance was performed on a dummy specimen by means of a NiCr–Ni thermocouple at the melting temperature of gold. For the pulse-heating experiments the sample was mounted in a He-filled housing with a fan for enhanced cooling. A fast–slow spectrometer with BaF_2 scintillators [15] and a time resolution (FWHM) of 198 ps was used for the positron lifetime measurements. The Doppler broadening of the annihilation γ-line was measured by means of a Ge(Li) detector with an energy resolution (FWHM) of 1.3 keV.

In the experiments the specimen was first heated to a constant temperature T_1 for a time t_1 (see figure 2) by an electrical current. Then a superimposed capacitor discharge

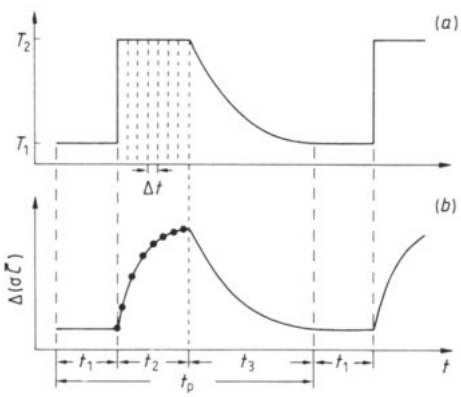

Figure 2. Diagrams showing the time variation of (*a*) the specimen temperature T, and (*b*) the positron trapping rate $\Delta(\sigma\bar{C})$, for the study of the vacancy equilibration process in a high-temperature pulse-heating experiment. The time intervals are defined in § 3 of the text.

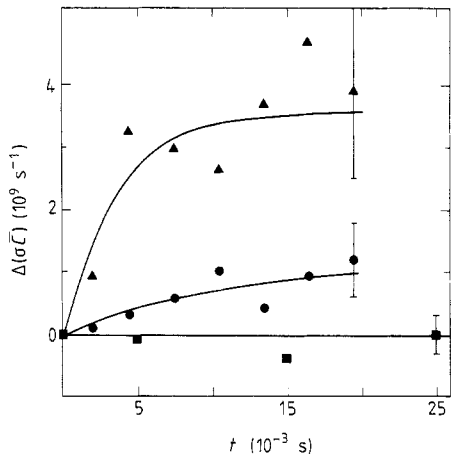

Figure 3. Isothermal variation of the positron trapping rate $\Delta(\sigma\bar{C})$ in Au with time. ▲, initial temperature $T_1 = 790$ K, measuring temperature $T_2 = 900$ K; ●, $T_1 = 680$ K, $T_2 = 800$ K; ■, $T_1 = 500$ K, $T_2 = 600$ K. The full curves denote exponential fits using the saturation values of $\bar{\tau}$ from thermal equilibrium experiments.

was used to raise the temperature rapidly to the temperature T_2 (rise time 0.5 ms), which was held constant for a time t_2. After that the sample was cooled to T_1 during t_3 until the vacancy equilibrium concentration at T_1 was attained. This temperature cycle was repeated about 10^6 times with a repetition rate of 2 s^{-1} in order to collect a sufficient number of annihilation events. After pulse-heating, the time-dependent variation of the positron lifetime and of the Doppler broadening were measured isothermally during the time t_2. This period of time was subdivided into seven intervals, Δt, which were typically in the range 1–20 ms in the present experiments. In each interval and during t_1, annihilation events were stored in different sections of a multichannel analyser in order to collect the spectra at various times. From these spectra the mean positron lifetime $\bar{\tau}$ and the Doppler broadening S-parameter were determined in order to derive the time variation of the positron trapping rate $\Delta(\sigma\bar{C})$ (see figure 2 and [16]).

4. Experimental results and discussion

Initially, positron lifetime measurements at high-temperature thermal equilibrium were performed without pulsing in order to test the experimental set-up. In these experiments, former results [14] of the temperature variation of the positron trapping rate σC_{1V} in Au at high temperatures were quantitatively confirmed. The time variation $\Delta(\sigma\bar{C})$ of the positron trapping rate was derived from the Doppler broadening data of the pulse-heating experiment and the results of the thermal equilibrium measurements (see figure 3). The variations $\Delta(\sigma\bar{C})$ of the trapping rate with time are clearly visible at the final temperatures $T_2 = 800$ K and 900 K whereas no variation is visible at $T_2 = 600$ K. From the latter result we conclude that any dislocations generated during pulse-heating do not contribute to the trapping rate. This should be visible at $T_2 = 600$ K, where no positron trapping by thermal vacancies is detected in thermal equilibrium measurements [14].

Exponentials were fitted to the time variations of the positron trapping rates $\Delta(\sigma\bar{C})$ measured at $T_2 = 800$ K and 900 K using equation (6), yielding the characteristic equilibration times τ_D of 11.7 and 3.6 ms, respectively. From their temperature variation an activation enthalpy of $H = (0.73 \pm 0.2)$ eV can be estimated which is attributed to vacancy migration.

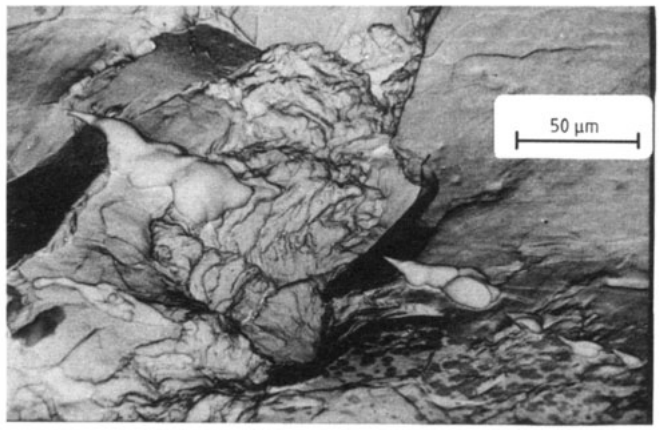

Figure 4. Scanning electron micrograph of the specimen surface close to the gauge length after 10^6 pulse-heating cycles. The surface shows a structure typical for cyclic deformation of a polycrystalline material.

Taking into consideration the statistical accuracy of the data, this is in reasonable agreement with the value $H_{1V}^{M} = 0.85$ eV deduced from self-diffusion, vacancy formation, and quenching studies [13, 17] asssuming that only vacancy-type defects contribute to self-diffusion.

Making use of the (3)–(6) and the values $H_{1V}^{F} = 0.84$ eV and $D_{1V}^{0} = 0.028 \times 10^{-4}\,m^2\,s^{-1}$ [17], the density $N_D \simeq 4 \times 10^{12}\,m^{-2}$ of dislocations acting as vacancy sources can be estimated from the above values of τ_D. This is in rough agreement with a first estimate of the mean dislocation density of about $8 \times 10^{12}\,m^{-2}$ derived from transmission electron microscopy near the gauge area after 10^6 heating pulses.

Values of τ_D can be derived from the results in [7], these being higher than in the present work by a factor of 50 over the same temperature range. This can chiefly be explained by the lower dislocation density of $6 \times 10^{11}\,m^{-2}$ observed in the specimens in [7]. This lower value may originate from the application of only a few fast temperature pulses [7], and therefore less plastic deformation, than in the present experiments. The fast heating pulses in the present experiments obviously give rise to mechanical stresses. This leads to a macroscopic plastic deformation and an extrusion-type surface topology. The surface contours of single grains are revealed by scanning electron microscopy (SEM), after the pulsing experiment (see figure 4). TEM inspection shows a dislocation density of some $10^{12}\,m^{-2}$ in the main fraction of the specimen volume and only a few small areas with a very dense dislocation network, as occurs in fatigue experiments. The latter areas are not expected to influence the equilibration process substantially.

Finally, it should be emphasised that the statistical precision of the measurement described here can be substantially improved by optimising the γ-detection efficiency and by using a positron source of higher activity. The initial increase of the vacancy concentration at short equilibration times may then be studied, in order to obtain information on the vacancy–source geometry (see [8]). In addition, the available temperature range may be extended to higher temperatures by investigating shorter equilibration times τ_D. Moreover, the study of vacancy migration may be extended to lower temperatures by cooling the specimen rapidly from high temperatures and investigating the decay of the vacancy concentration to the thermal equilibrium concentration at lower temperatures.

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