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LATTICE AND GRAIN-BOUNDARY DIFFUSION OF ^{121}Te IN SILVER AFTER RADIOISOTOPE IMPLANTATION AT THE ISOLDE

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ABSTRACT

Lattice and grain-boundary diffusion of ^{121}Te in Ag were measured over a wide temperature range after implanting the radioisotope into single- and polycrystalline Ag samples with the ISOLDE. The values of the preexponential factor ($0.21 \text{ cm}^2 \text{ s}^{-1}$) and the activation enthalpy (155 kJ mol^{-1}) for lattice diffusion are in line with previous measurements of impurity diffusion of Cd, In, Sn and Sb in Ag and correspond to a vacancy mechanism of diffusion. For polycrystalline samples the product $P=s\delta D_{\text{GB}}$ (D_{GB} =grain-boundary diffusivity, s =segregation coefficient, δ =grain-boundary width) was determined from the type B kinetics of grain-boundary diffusion for temperatures above 650 K. At lower temperatures due to the large segregation coefficient type C kinetics of grain-boundary diffusion was observed, which permits a determination of D_{GB} itself. By comparing D_{GB} with P the segregation coefficient of Te in Ag was estimated.

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The production and on-line implantation of radioisotopes in diffusion samples with the ISOLDE (Isotope Separator On-Line Detector) at CERN in Geneva enables studies of lattice and grain-boundary diffusion with absolutely carrier-free isotopes. This is a great advantage especially for systems with small solid solubility and/or high vapour pressure, like tellurium in silver. In systems with low solubility in the bulk one also expects strong grain-boundary segregation, which results in large values of the product $P \cdot s \cdot D_{GB}^*$. Thus, it should be possible to measure grain-boundary diffusion over a wide temperature range. The experimental problem in detecting grain-boundary diffusion profiles with sufficient accuracy in the very interesting low-temperature region stems from the extremely small flux of tracer material penetrating through the grain boundaries. A considerable improvement in grain-boundary diffusion measurements, however, was recently obtained by employing a large well-type intrinsic germanium detector [1]. A prerequisite for the determination of P from the usual type B grain-boundary diffusion kinetics is a knowledge of the lattice diffusion coefficients. The only study of Te lattice diffusion in Ag available in the literature [2] is limited to a very narrow temperature range near the melting point. In the present study therefore lattice and grain-boundary diffusion of ^{121}Te in Ag in single- and polycrystalline samples, respectively, were measured in a large temperature range.

EXPERIMENTAL METHOD AND PROCEDURE

After the production and on-line implantation of the radioisotope into the diffusion samples we followed the usual procedure of the radiotracer method. Serial sectioning combined with counting the activity of the individual sections was used as the most reliable technique for measuring diffusion profiles. Single- and polycrystalline cylindrical samples with a diameter of about 10 mm were prepared from silver of a nominal purity of 99.999%. An average grain size of 0.5 mm in diameter was stabilized by a recrystallization annealing at 1153K. Radioactive ^{121}Xe was obtained as spallation product in a lanthanum target irradiated with 600 MeV protons from the CERN synchrocyclotron. Mass-separated $^{121}\text{Xe}^+$ ions of 60 keV energy were produced in the ISOLDE facility (see e.g. [3]) and implanted into the Ag samples to doses up to $5 \cdot 10^{12}$ at.cm $^{-2}$. The projected range was about 10 nm. The implanted ^{121}Xe decays within a few hours via ^{121}I into the desired radioisotope ^{121}Te with a half-life of 16.8 d. This ^{121}Te has a radioactive purity of 100 % and a maximum specific activity of 3.3 GBq/ μg . The diffusion experiments were carried out in the laboratory at Münster. The samples were encapsulated under purified argon in silica tubes. The temperature was measured to an accuracy of ± 1 K. The annealing times in the grain boundary diffusion experiments were limited by the requirement that the mean lattice diffusion length, $(D^* t)^{1/2}$, had to be smaller than 20 % of the grain diameter. In spite of the high vapour pressure of tellurium of more than 10^5 Pa at the highest diffusion temperature (1169 K) evaporation losses of the tracer from the sample surface were negligible. After the annealing the samples were reduced in diameter and sectioned on a microtome. The sections were weighed and dissolved in dilute nitric acid. The specific count-rate of ^{121}Te was determined with a well-type intrinsic Ge detector and corrected for the half-life. Because of the extremely high specific activity of ^{121}Te , the good counting efficiency and the low background of the detector it was possible to follow the diffusion profiles over several orders of magnitude.

LATTICE DIFFUSION

The concentration of the radiotracer in a depth y after a diffusion anneal of time t may be given by the thin film solution of Fick's second law

$$c(y,t) = A_0 / (\pi D^* t)^{1/2} \exp[-y^2 / 4 D^* t] \quad (1)$$

where A_0 denotes the implanted concentration per unit area and D^* the diffusivity. Equation 1 is applicable if the lattice diffusion length, $(D^* t)^{1/2}$, is large as compared to the projected implantation range and if no solubility-limited diffu-

sion occurs. Figure 1 shows penetration profiles for diffusion of ^{121}Te in Ag single crystals plotted according to equation 1. Apart from a surface segregation effect the profiles are Gaussian over 4 to almost 7 orders in magnitude.

Fig. 2. Penetration profiles for ^{121}Te in Ag single crystals plotted according to equation 2 (above)

Fig. 1. Penetration profiles for ^{121}Te in Ag single crystals plotted according to equation 1 (left)

At temperatures lower than 830 K the solute solubility of Te in Ag was exceeded. Penetration profiles for solubility-limited diffusion are described by

$$c(y,t) = c_0 \{1 - \text{erf}[y/2(D^*t)^{1/2}]\} \quad (2)$$

The measurements below 830 K are plotted according to equation 2 in figure 2.

Table 1. Diffusion parameters of lattice diffusion (D_0, Q) and of P in grain-boundary diffusion (D'_0, Q') for various diffusants in silver

	Ag	Cd	In	Sn	Sb	Te
$D_0/\text{cm}^2\text{s}^{-1}$	0.041	0.44	0.36	0.25	0.23	0.21
$Q/\text{kJ mol}^{-1}$	169.8	174.6	168.8	164.5	163.6	154.7
$D'_0/\text{cm}^2\text{s}^{-1}$	$8.6 \cdot 10^{-10}$	-	$3.9 \cdot 10^{-10}$	$6.0 \cdot 10^{-10}$	$6.7 \cdot 10^{-10}$	$1.7 \cdot 10^{-9}$
$Q'/\text{kJ mol}^{-1}$	74.5	-	63.6	59.9	57.2	42.0

In figure 3 the present results for lattice diffusion of Te in Ag are shown in an Arrhenius diagram together with self-[4] and impurity diffusion data of Cd [5], In [6], Sn [5] and Sb [7], available from literature. The frequency factor D_0 and the activation enthalpy Q of the present study and of the above mentioned diffusants are listed in table 1. The results for Te are in line with the values for other polyvalent impurities in Ag. They indicate that Te like Cd, In, Sn and Sb diffuses predominantly by a vacancy mechanism.

Fig. 3. Arrhenius plot of lattice diffusion of Te in Ag (full circles: present results; open circles [2]) in comparison with Ag, Cd, In, Sn and Sb diffusion in Ag

GRAIN-BOUNDARY DIFFUSION

In polycrystalline materials diffusion in the grain boundary can be the dominating process of mass transport especially for penetration depths which are large as compared to the lattice diffusion length.

Starting from the solutions of Suzuoka [8] (instantaneous source) and of Whipple [9] (constant source) to the problem of simultaneous diffusion in the lattice and isolated grain boundaries, LeClaire [10] has derived an equation, which is suitable to determine the grain-boundary diffusion parameter P according to

$$P = s \delta D_{GB}^* = - \left(\frac{\partial \ln \bar{c}}{\partial y^{5/3}} \right)^{-5/3} \left(\frac{4D^*}{t} \right)^{1/2} 0.63 \quad (3)$$

Here s denotes the equilibrium segregation coefficient, δ the grain-boundary width and D_{GB}^* the diffusivity in the boundary. $\bar{c}$ is the mean tracer concentration per section in depth y parallel to the sample surface. Using equations 3 the product P can be calculated from the slope of the plot of $\ln \bar{c}$ versus $y^{5/3}$ provided that D^* is known. This analysis is applicable if the experimental conditions fulfill the following requirements:

$$s \delta \ll 2(D^* t)^{1/2} < 0.5 d \quad (4)$$

d is the average grain diameter. The two inequalities of equation 4 define what is usually denoted as type B kinetics of grain-boundary diffusion [11,12,13]. In the present experiments on polycrystals care always has been taken that the lattice diffusion length was small as compared to the grain diameter. The fulfillment or violation of the left hand side inequality of equation 4 is more difficult to judge since s was not known when we started the experiments.

Fig. 5. Penetration profile for ^{121}Te in a Ag polycrystal at 456 K plotted according to type B kinetics (lower-scale) and plotted according to type C kinetics (upper scale) (above)

Fig. 4. Penetration profiles for ^{121}Te in Ag polycrystals plotted according to equation 3 (left)

Figure 4 shows penetration profiles for diffusion of ^{121}Te in Ag polycrystals at higher temperatures as $\ln \bar{c}$ versus $y^{6/5}$ plots. In the region dominated by grain-boundary diffusion the plots are indeed straight lines as required by type B kinetics. The values of P determined from the slopes of figure 4 are listed in table 2 and plotted in the Arrhenius diagram of figure 6. If an Arrhenius equation is fitted to the $s\delta D_{\text{GB}}^*$ values above 650 K (full circles in figure 6) a preexponential factor and an activation enthalpy of

$$D_0' = (1.7 \pm 0.8) 10^{-9} \text{ cm}^3 \text{ s}^{-1} \quad ; \quad Q' = (42 \pm 4) \text{ kJ mol}^{-1}$$

are obtained. These values are compared in table 1 with the preexponential factors and activation enthalpies of various diffusants in Ag grain boundaries available from literature [2,7,14,15]. The corresponding Arrhenius relations are also shown in figure 6. It appears that the present activation enthalpy is in line with self-diffusion and the available data on other polyvalent impurities from the same row of the periodic table like Te. The high values of $s\delta D_{\text{GB}}^*$ may be attributed to high values of the segregation coefficient (see below). Grain-boundary diffusion coefficients resulting in a strongly downward curved Arrhenius plot, however, were found, when analyzing the diffusion profiles obtained at temperatures below 650K. In impurity grain-boundary diffusion a curvature in the Arrhenius plot may result from different reasons as was recently

discussed [16]. Inspection of the results of P in table 2 shows that with decreasing temperature the lattice diffusion length is becoming so small that the condition $s\delta \ll 2(D^*t)^{1/2}$, guaranteeing pure type B diffusion kinetics, has to be questioned, if s adopts large values as can be expected for Te in Ag. Though most of the diffusion profiles showed linear portions in the plots of $\ln \bar{c}$ versus $y^{6/5}$, we have to suspect that the experiments below 650 K were performed in a transition range between type B and type C kinetics. Under such conditions a forced fit of equation 3 of the diffusion profiles leads to a considerable underestimation of P [12,13] with the consequence that the observed curvature of the Arrhenius plot is an apparent feature of the analysis only.

Fig. 6. Arrhenius plots of $s\delta D_{GB}^*$ for ^{121}Te in Ag (full and open circles; see text) in comparison with data from literature for Ag [14], In [15], Sn [2] and Sb [7] in Ag polycrystals

If the condition for type C kinetics in grain-boundary diffusion [12,13]

$$s\delta > 2(D^*t)^{1/2} \quad (5)$$

is fulfilled, the average concentration $\bar{c}$ in a section parallel to the surface is given by

$$\bar{c} \sim \exp(-y^2/4D_{GB}^*t) \quad (6)$$

Figure 5 shows the penetration profile measured at 456 K plotted either as a $\ln \bar{c}$ versus $y^{6/5}$ plot (lower scale) or as a $\ln \bar{c}$ versus y^2 plot (upper scale). Obviously the profile obeys type C kinetics rather than type B kinetics. The profile at 429 K is also compatible with type C kinetics. The grain-boundary diffusivities determined according to equation 6 for the two lowest temperatures are listed in table 3 together with the values of P obtained by extrapolation from the results above 650 K. If we make the usual assumption for the grain-boundary width ($5 \cdot 10^{-8}$ cm) the segregation coefficients listed in table 3 are obtained. A very tentative fit of an Arrhenius relation to these two values yields an activation enthalpy of 72 kJ mol^{-1} and a preexponential factor of $0.015 \text{ cm}^2 \text{ s}^{-1}$ for the grain-boundary diffusivity and a segregation enthalpy of 30 kJ mol^{-1} . As a conclusion we get the quite remarkable result that the true grain-boundary diffusion coefficient D_{GB}^* of Te in Ag is almost the same as that for self-diffusion in the boundary (see table 1), if one accounts for δ in the same way. This indicates that the difference between P_{self} and P_{imp} is mainly due to the segregation coefficient, while D_{GB}^* is predominantly characterized by the grain-boundary properties of the host material rather than by the impurity itself. These conclusions have of course to be verified by further experiments and should at present be regarded as a hypothesis.

Table 2. Grain-boundary diffusion data for ^{121}Te in Ag polycrystals. Analysis according to type B kinetics

T [K]	t [s]	$P=s\delta D_{\text{GB}}^*$ [cm ³ /s]	$(D^* t)^{1/2}$ [cm]
970	900	$9.84 \cdot 10^{-12}$	$9.4 \cdot 10^{-4}$
883	13320	$5.33 \cdot 10^{-12}$	$1.4 \cdot 10^{-3}$
793	157380	$2.42 \cdot 10^{-12}$	$1.5 \cdot 10^{-3}$
721	685860	$1.98 \cdot 10^{-12}$	$9.4 \cdot 10^{-4}$
650	853980	$6.49 \cdot 10^{-13}$	$2.6 \cdot 10^{-4}$
578	1960920	$(1.39 \cdot 10^{-13})$	$6.6 \cdot 10^{-5}$
538	1011900	$(4.34 \cdot 10^{-14})$	$1.4 \cdot 10^{-5}$
506	2847480	$(3.23 \cdot 10^{-15})$	$8.0 \cdot 10^{-6}$
456	1295700	$(1.64 \cdot 10^{-16})$	$7.2 \cdot 10^{-7}$
429	1402860	$(1.18 \cdot 10^{-17})$	$2.1 \cdot 10^{-7}$

Table 3. Grain-boundary diffusivities obtained from type C kinetics and segregation coefficients

T [K]	D_{GB}^* [cm ² /s]	$P=s\delta D_{\text{GB}}^*$ [cm ³ /s]	s
429	$2.8 \cdot 10^{-11}$	$1.3 \cdot 10^{-14}$	9500
456	$9.2 \cdot 10^{-11}$	$2.6 \cdot 10^{-14}$	5600

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