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DIFFUSION OF IMPLANTED Te AND Se IN NOBLE METALS

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Abstract

Diffusion of Se and Te into single crystals of Cu, Ag and Au was studied by the radiotracer technique. To overcome difficulties with the low solubility of these elements in noble metals ^{75}Br and ^{121}Xe available in radioactive ion beams at the ISOLDE facility of CERN were implanted in a mass-separated form into the samples with an energy of 60 keV. The projected ranges of the implanted ions are about 30 nm. The short-lived implants decay within several hours into their long-lived daughters/granddaughters $^{75}\text{Se}/^{121}\text{Te}$. These were utilized as 'thin film' sources for radiotracer experiments. After heat-treatments and microtome sectioning Gaussian penetration profiles were observed. The lattice diffusion coefficients can be represented by ARRHENIUS relations with the following preexponential factors and activation enthalpies:

Se in Cu:	$1.0 \cdot 10^{-4} \text{m}^2 \text{s}^{-1}$,	180.5 kJ mole $^{-1}$
Te in Cu:	$0.97 \cdot 10^{-4} \text{m}^2 \text{s}^{-1}$,	180.5 kJ mole $^{-1}$
Se in Ag:	$0.285 \cdot 10^{-4} \text{m}^2 \text{s}^{-1}$,	157.4 kJ mole $^{-1}$
Te in Au:	$0.063 \cdot 10^{-4} \text{m}^2 \text{s}^{-1}$,	140.9 kJ mole $^{-1}$

The present results on Te and Se together with literature data on the diffusion of other electropositive foreign atoms in noble metals show that the diffusivity of foreign atoms increases with increasing valence difference between foreign atom and solvent.

1 Introduction

The on-line implantation of radioisotopes produced at the ISOLDE facility of CERN in Geneva as a novel source deposition technique for diffusion studies in solids was developed recently in our group [1]. This elegant technique supplements conventional methods of radiotracer deposition like evaporation or electrodeposition. The new method is very clean, surface oxides can be penetrated and because the implantation is done in a mass-separator a carrier-free deposit is obtained.

We were mainly prompted by the latter advantage to use the implantation method in the present work. The solubility of Se and Te in noble metals is very low. Therefore, carrier-free deposits are highly welcome if the diffusion of these elements in noble metals is investigated. We report such measurements in the present paper.

2 Experimental Procedure

Single crystalline cylindrical samples with a diameter of about 6 mm were grown by the BRIDGMAN technique from copper, silver and gold of a nominal purity of 99.9998 %. The crystals were cut into short lengths by spark erosion and etched to remove contaminants. One flat surface was prepared on each sample by standard metallographic procedures. After the production and on-line implantation of the radioisotopes into the diffusion samples, details of which are described in section 3, we followed the usual procedure of the radiotracer method. These experiments were carried out in our laboratory at Münster. The samples were encapsulated under purified argon in quartz ampoules. Diffusion anneals were carried out in resistance furnaces and the temperature was measured with an accuracy of ± 1 K. Warming-up and cooling-down corrections were performed when necessary. After the annealing the samples were reduced in diameter to avoid possible effects of surface diffusion and sectioned on a microtome. The sections were weighed and dissolved in dilute nitric acid in the case of Cu and Ag and in aqua regia in the case of gold. The specific activity of ^{75}Se and ^{121}Te in each section was determined with a liquid scintillation counter. The thickness of each section was determined from section weight, diameter and the density of the material.

3 Implantation of Radioisotopes with the ISOLDE

The ISOLDE facility produces intense radioactive ion beams of more than 60 elements by bombarding certain targets with 600 MeV protons or ^3He ions. By spallation, fragmentation and fission processes a wide range of both neutron-deficient and neutron-rich nuclear reaction products are obtained. These products are usually separated from the target by heating low pressure target material to high temperatures. The reaction products are then released by diffusion and desorption processes. Afterwards they are transferred to the ion source which is combined with the target and where the nuclear reaction products are converted into 60 keV singly charged radioactive ion beams which are continuously injected into the mass separator of ISOLDE. In the present work the isotopes ^{75}Br and ^{121}Xe were produced with targets of niobium powder and molten lanthanum respectively. The yields were 10^8 ^{121}Xe -atoms per second and 10^9 ^{75}Br -atoms per second. The ^{121}Xe decays in a few hours to the granddaughter nuclide ^{121}Te (half life 17 days), the ^{75}Br decays to the daughter nuclide ^{75}Se (half life 120 days). About 15 diffusion samples mounted on an implantation flange were simultaneously implanted within a few hours. Typically $5 \cdot 10^5 \text{ Bq } ^{121}\text{Te}$ and $8 \cdot 10^4 \text{ Bq } ^{75}\text{Se}$ were deposited in each diffusion sample during such an implantation run.

4 Results and Discussion

Diffusion temperatures and times were chosen in such a way that the lattice diffusion length $\sqrt{D_2 t}$ was always much larger than the projected range of the implanted atoms, which was typically about 30 nm. Under these conditions and provided that solubility problems could be avoided the concentration of the radiotracer in depth x after a diffusion anneal of time t is given by the thin film solution of FICK's second law

$$c(x, t) = \frac{c_0}{\sqrt{\pi D_2 t}} \cdot \exp\left(-\frac{x^2}{4 D_2 t}\right), \quad (1)$$

where c_0 denotes the implanted concentration per unit area and D_2 the diffusivity. As an example figure 1 shows penetration profiles for diffusion of ^{75}Se in single crystals of copper plotted according to equation 1. Apart from a slightly enhanced activity at the surface the profiles are indeed

Gaussian. Penetration profiles of similar quality were obtained for ^{75}Se in Ag and ^{121}Te in Cu. Extremely low concentrations down to 10^9cm^{-3} in the case of ^{121}Te and 10^{10}cm^{-3} in the case of ^{75}Se could be detected.

	D_2^0	Q_2	Temperature range
	$10^{-4}\text{m}^2\text{s}^{-1}$	kJ mole^{-1}	K
Se in Cu	1.0	180.5	887–1150
Te in Cu	0.97	180.5	822–1214
Se in Ag	0.285	157.4	759–1109
Te in Au	0.063	140.9	908–1145

Table 1: Preexponential factors and activation enthalpies for the diffusion of Se and Te in noble metals

	T	D^0	Q
	K	$10^{-4}\text{m}^2\text{s}^{-1}$	kJ mole^{-1}
Cu	1000	0.50	206.9
Ag	900	0.173	178.5
Au	1000	0.047	168.5

Table 2: Self diffusion parameter for copper, silver and gold (see text)

Fig. 1: Penetration profiles of ^{75}Se in single crystals of copper

Fig. 2: ARRHENIUS-diagram of diffusion coefficients of ^{75}Se in Cu from this work (circles) and of Cu [2], Zn (in the lower temperature range [3], in the higher one [4]), Ga [5], Ge (in the lower temperature range [6], in the higher one [5]) and As [7] in Cu from literature

Fig. 3: ARRHENIUS-diagram of diffusion coefficients of ^{121}Te in Cu from this work (circles) and of Cu [2], Cd [8], In [9], Zn [10] and Sb [11] in Cu from literature

Fig. 4: ARRHENIUS-diagram of diffusion coefficients of ^{75}Se in Ag from this work (circles) and of Ag [2], Zn [12], Ge [13] and As [14] in Ag from literature

The D_2 values deduced from the penetration profiles for the various systems are shown in figures 2 to 5 in semilogarithmic plots as functions of reciprocal absolute temperature. If ARRHENIUS equations

$$D_2 = D_2^0 \cdot \exp\left(-\frac{Q_2}{kT}\right) \quad (2)$$

with D_2^0 denoting the preexponential factors and Q_2 the activation enthalpies are fitted to the present data the values listed in table 1 are obtained.

In the figures 2 to 5 self-diffusion in the base metal as well as the diffusion of electropositive foreign atoms according to literature data have been also included for reasons of comparison. Usually the diffusivity of the foreign atom increases with increasing valence difference between foreign atom and base metal. The present data for Se and Te are in line with this tendency.

It is interesting to compare diffusion of foreign atoms with self-diffusion in the base metals. For Cu, Ag, and Au where self-diffusion has been measured over wide temperature ranges the data show slight upward curvatures in ARRHENIUS diagrams which may be described by sums of two exponentials pertaining to mono- and divacancy contributions. The most recent analysis along this line was performed by NEUMANN and TÖLLE [2]. However, for the present purpose of comparison with impurity diffusion which is usually measured over a not too wide temperature

Fig. 5: ARRHENIUS-diagram of diffusion coefficients of ^{121}Te in Au from this work (circles) and of Au [2], In [15], Zn [15] and Sb [16] in Au from literature

Fig. 6: Comparison of theoretical and experimental values of ΔQ with Cu as the solvent metal

range, self-diffusion may be conveniently described within the experimental scatter by

$$D = D^0 \cdot \exp\left(-\frac{Q}{kT}\right) \quad , \quad (3)$$

provided that effective preexponential factors D^0 and activation enthalpies Q are used, which have to be chosen appropriate to the temperature ranges under consideration. In table 2 we have listed values of D^0 and Q for Cu, Ag, Au. These effective values have been obtained from the two-exponentials analysis of [2], for the mean temperatures $\bar{T}$ listed also in table 2.

For a monovacancy mechanism of diffusion the well-known relation (see, e.g., [17])

$$\Delta Q = Q_2 - Q = -H^B + \Delta H_2^M - C \quad (4)$$

holds for the difference between the activation enthalpies. H^B in equation 4 denotes the binding enthalpy between vacancy and foreign atom and ΔH_2^M the difference between heights of the activation barriers for atom-vacancy exchanges of foreign atoms and of solvent atoms. The term C accounts for the temperature dependence of the correlation factor of foreign atom diffusion. For simple metals the quantities on the right-hand side of equation 4 can be calculated within the framework of a free electron model proposed by LECLAIRE [18]. According to this electrostatic model the vacancy in a monovalent metal behaves like a negative elementary charge and a solute

atom is regarded as an additional charge $+Ze$ where Z denotes the valence difference between solute and solvent. Within LECCLAIRE's model we have calculated theoretical values for ΔQ_{theor} (for details, see [19]). As an example we show in figure 6 a comparison between theoretical and experimental values of ΔQ for Cu as the solvent metal. At a first glance the agreement is not bad. However, there are deviations which are beyond the experimental scatter. Such deviations can have several origins:

1. Instead of using a THOMAS-FERMI potential as is done in LECCLAIRE's model rather a self-consistent perturbation potential should be used for a calculation of the electrostatic contribution of the vacancy-solute interaction.
2. The electrostatic model completely neglects interactions which are due to size effects of atoms.

On the other hand Se and Te are quite different in atomic size. Nevertheless the ΔQ values for Se and Te almost coincide. This is also true if Ag is chosen as solvent metal. Perhaps this is a hint that in these cases it is not the size effect but rather the inappropriate screening potential which accounts for the deviations.

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