

Mechanisms of Volume Diffusion of Gold into Single Crystal Iridium

EVIDENCE THAT VOLUME DIFFUSION, INTRINSIC OR EXTRINSIC, DEPENDS ON THE ATMOSPHERIC COMPOSITION WHICH OCCURS DURING ANNEALING OF SINGLE CRYSTAL IRIDIUM

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Iridium crucibles, examined after being used in the extraction of gold and silver from residues remaining after zinc manufacture, showed an anomalously high permeability to substitutional components and impurities, such as gold. To discover the cause of this high permeability, the volume diffusion of gold into nominally pure single crystals of iridium (single-Ir), annealed under ultrahigh and technical grade vacuums, UHV and TGV, respectively, was studied at temperatures from 1300 to 2000 K. The coefficients of volume diffusion of gold into single-Ir were measured by secondary ion mass spectrometry. The activation enthalpies measured for volume diffusion of the gold were: $(Q_{Ir}^{Au})_{UHV} = (423 \pm 5) \text{ kJ mol}^{-1}$ and $(Q_{Ir}^{Au})_{TGV} = (193 \pm 27) \text{ kJ mol}^{-1}$ in UHV and TGV, respectively, for annealing single-Ir. On annealing in TGV, interstitial impurities formed vacancy-impurity complexes (VICs). The binding energy of the VIC components $(E_{VIC})_{Ir} = (116 \pm 16) \text{ kJ mol}^{-1}$. In TGV, the gold diffusion was determined by 'extrinsic' vacancies dissociating from the VICs. At typical working temperatures for iridium the concentration of the 'extrinsic' vacancies was several thousand times larger than the concentration of the equilibrium 'intrinsic' vacancies. The 'extrinsic' vacancies are responsible for the high coefficient of volume diffusion and the corresponding anomalously high mass transfer of gold into iridium during TGV annealing.

Iridium (Ir) is a noble metal with the highest melting point, 2719 K, of all the face centred cubic metals (1). It is a secondary fixed point on the International Temperature Scale (ITS-90) (2), and is used as a high-temperature and heat-resistant construction material (3–5). The working temperature of Ir is from ~ 1300 to 1800 K , ~ 0.48 to $\sim 0.67 T_m$ (T_m is the melting point of Ir). Over this temperature range, Ir crucibles are used in the extraction of gold (Au) from zinc scrap. At these temperatures, the 'impurity' mechanism of volume diffusion in metals can be seen more clearly, and the diffusion of impurities (in this case Au through Ir) has been found to be many orders of magnitude higher than estimates made by measuring the coefficients of volume self-diffusion in Ir (6).

Prior Work

Theoretical and experimental studies of the atomic mechanisms of diffusion and of typical features of volume diffusion indicate that atomic mechanisms are an efficient tool for analysing microscopic interactions between point defects (vacancies and impurities) participating in diffusion. The parameters of volume diffusion in solids are determined by mutual interactions between such point defects (6–13).

The effect of substitutional and interstitial impurities on the diffusion parameters of atoms used as atomic probes in metals has previously been studied (13–19). Work has also been done on the thermodynamics of formation of vacancy-impurity complexes (VICs) in interstitial solid

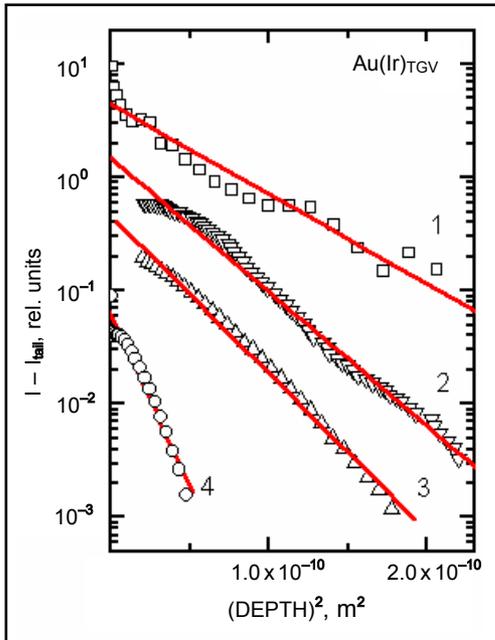


Fig. 1 Straightened gold profiles in single-Ir annealed in TGV and measured by secondary ion mass spectrometry (SIMS) using primary O^+ and Cs^+ beams. The straight lines were drawn using the least squares method. The depth scales of the given profiles were extended by applying the following coefficients: (1) $\times 85$; (2) $\times 50$; (3) $\times 20$; (4) $\times 1$

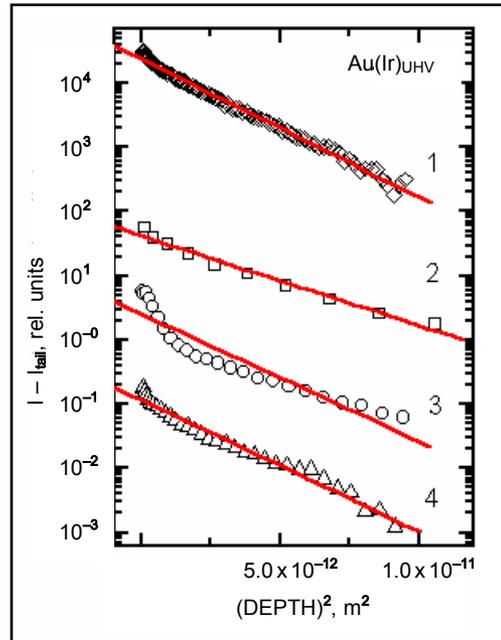


Fig. 2 Straightened gold profiles produced in single-Ir annealed in UHV and measured by the SIMS method using primary O^+ and Cs^+ beams. The straight lines were drawn using the least squares method. The depth scales of the profiles: 1, 2, 3 and 4, were extended by applying the following coefficients to them: (1) $\times 85$; (2) $\times 50$; (3) $\times 20$; (4) $\times 1$

solutions, and thermodynamics has been used to describe the diffusion of substitutional atomic probes in interstitial solid solutions of carbon in iron (C(Fe)) and carbon in palladium (C(Pd)) (15–18).

The formation of a VIC flow during carbon diffusion in platinum has been vividly demonstrated (18, 19). Pores formed in the diffusion zone, where carbon had diffused into the platinum, due to the condensation of ‘extrinsic’ vacancies released during thermal dissociation of the VICs. The binding energy of the VIC components in the platinum is: $|E_{VIC}| > 50 \text{ kJ mol}^{-1}$.

This paper presents results of a study of the volume diffusion of Au into single crystals of Ir (single-Ir) of 4N (99.99%) purity during annealing in an ultrahigh vacuum (UHV) and a technical grade vacuum (TGV). The single-Ir crystals were grown at the Ekaterinburg Non-Ferrous Metals Processing Plant. Single crystals do not have grain boundaries. Coefficients of volume diffusion in

TGV, $(D_{Ir}^{Au})_{TGV}$, were measured in single-Ir annealed in a TGV at the working temperatures of Ir. The values obtained were several thousand times larger than coefficients of volume diffusion, $(D_{Ir}^{Au})_{UHV}$, measured for the same samples in UHV. This is due to a new diffusion mechanism found during annealing in TGV. The mechanism involves ‘extrinsic’ vacancies which arise from dissociation of the VICs.

Theoretical Background

The profile of diffusing species (the diffusant) within a homogeneous sample is described by Expression (i) (6):

$$C(y,t) = C_0(t) \exp(-y^2/4Dt) \quad (i)$$

where $C(y,t)$ is the concentration of the diffusant (in this case gold) at depth y in the sample, and $C_0(t)$ is the concentration at the surface where $y = 0$; t is the diffusion annealing time, and D is the coefficient of volume diffusion. D is determined

Table I Values for Parameters: D_0 and Q of the Arrhenius Dependencies of Self Diffusion (7) and Volume Diffusion of Gold in Single Crystals of Iridium, and for the Binding Energy E_{VIC} between VIC Partners			
System	^{192}Ir (single-Ir)	Au (single-Ir) _{UHV}	Au (single-Ir) _{TGV}
Reference	(22)	(This work)	
Temperature, K	2020–2600 (0.74–0.96) T_m	1300–2000 (0.48–0.73) T_m	1300–2000 (0.48–0.73) T_m
D_0 , $\text{m}^2 \text{s}^{-1}$	3.5×10^{-5}	5.4×10^{-5}	1.7×10^{-10}
Q , kJ mol^{-1}	449.5 ± 0.3	424.3 ± 5.2	193 ± 27
Q_{Au}/Q_{Ir}	0.94		0.43
E_{VIC} , kJ mol^{-1}			$-(231 \pm 32)$

from the slope of the linear function in (ii):

$$\ln C = -y^2/4Dt \quad (\text{ii})$$

The activation enthalpy, Q , for volume diffusion is given by the relationship (iii):

$$\ln D = -Q/RT \quad (\text{iii})$$

where R is the gas constant and T is the annealing temperature.

The interaction energy (binding energy) E_{VIC} , of the components in the VICs is determined from Expression (iv) (12–14):

$$E_{VIC} = \frac{[Q_{VIC} - Q]}{2} \quad (\text{iv})$$

where Q_{VIC} is the activation enthalpy for diffusion by ‘extrinsic’ vacancies dissociating from VICs.

Results

Gold Profiles in Single-Ir after Annealing in UHV or TGV

The volume diffusion of Au in Ir was studied using single-Ir. The materials, their preparation and measurement by secondary ion mass spectrometry (SIMS) are described elsewhere (20, 21). The dependence of $\ln I_{Au}(y^2)$, where I_{Au} is the intensity of secondary Au ions, recorded during SIMS analysis of single-Ir annealed in TGV or UHV, and y^2 is the square of the depth (y) in the Ir, is shown in Figures 1 and 2 (see Expressions (i) and (ii)). The same samples were annealed alter-

nately in UHV or TGV in a random sequence of annealing temperatures.

The profiles of all the measured diffusion zones were characteristic of volume diffusion (7), that is, the dependencies, $\ln I_{Au}(y^2)$, were linear over a broad range of concentrations and remained linear up to the initial surface of the samples. In all cubic crystals the crystal orientation is not important for diffusion (6).

Temperature Effects of Diffusion Coefficients in Single-Ir Annealed in UHV or TGV

Diffusion in solids follows the Arrhenius equation, and the Arrhenius dependence of the coefficients of volume diffusion for Au in Ir, $(D_{Ir}^{Au})_{UHV}$ and $(D_{Ir}^{Au})_{TGV}$, are shown in Figure 3. At low temperatures ($1/T > 0.75$) it can be seen that coefficients $(D_{Ir}^{Au})_{TGV}$ are 3 to 4 orders of magnitude larger than coefficients $(D_{Ir}^{Au})_{UHV}$. The parameters D_0 and Q of the Arrhenius dependencies of the coefficients of self diffusion, D_{SD} , (3), and the coefficients of volume diffusion $(D_{Ir}^{Au})_{UHV}$ and $(D_{Ir}^{Au})_{TGV}$ are given in Table I.

Discussion

Mechanism of Gold Diffusion in Single-Ir during Annealing in UHV and TGV

The activation enthalpy for self diffusion, Q_{SD} , (22) and the activation enthalpy for volume diffusion $(Q_{Ir}^{Au})_{UHV}$ of Au in single-Ir under UHV conditions (see Table I) are related as Expression (v):

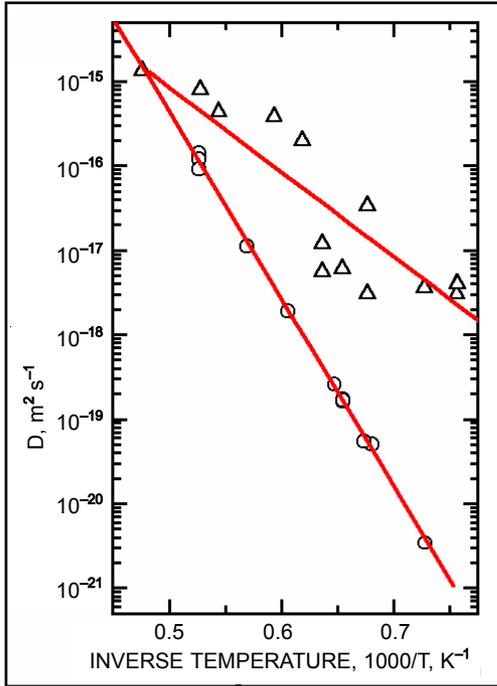


Fig. 3 Arrhenius dependencies of the coefficients of diffusion, D_{Ir}^{Au} , in single-Ir annealed under UHV (O) and TGV (Δ) conditions. The straight lines were drawn using the least squares method

$$(Q_{Ir}^{Au})_{UHV}/Q_{SD} = 0.94 \quad (v)$$

Expression (v) is characteristic of the volume diffusion of substitutional impurities assisted by equilibrium, 'intrinsic' vacancies in pure metals (6). The 'intrinsic' vacancies arise from thermal effects. However, for annealing Ir in a TGV we obtained:

$$(Q_{Ir}^{Au})_{TGV}/Q_{SD} = 0.43 \quad (vi)$$

It follows from Expressions (v) and (vi) that volume diffusion occurs by 'extrinsic' vacancies rather than by equilibrium 'intrinsic' vacancies during TGV annealing at temperatures below 2000 K ($\sim 0.73 T_m$). Using Expression (iv) and the measured activation enthalpies for Au diffusion, the binding energy, E_{VIC} , of the interaction between the components in the VICs can be determined from Expression (iv):

$$\begin{aligned} E_{VIC} &= 0.5[(Q_{Ir}^{Au})_{TGV} - (Q_{Ir}^{Au})_{UHV}] \\ &= 0.5[(193 \pm 27) - (424 \pm 5)] \\ &= - (116 \pm 16) \text{ kJ mol}^{-1} \end{aligned} \quad (vii)$$

The negative value indicates that stable VICs are formed during TGV annealing. The large value of $|E_{VIC}|$ is important for determining the stability of point defect complexes. Stable VICs form in Ir during TGV annealing when $T < 0.73 T_m$.

Concentration of Interstitial Impurities and Excess Vacancies

Excess vacancies are induced by interstitial impurities in single-Ir during TGV annealing. The concentration, $C_{interst}$, of the interstitial impurities which form VICs in single-Ir during TGV annealing is determined from the relationship of pre-exponential factors, D_0 , in the Arrhenius dependencies of the corresponding diffusion coefficients:

$$C_{interst} = \frac{(D_{VIC})_0}{D_0} = \frac{1.7 \times 10^{-10}}{5.4 \times 10^{-5}} \cong 3 \times 10^{-6} \text{ at. parts} \quad (viii)$$

This concentration of interstitial impurities that form VICs in single-Ir, $C_{interst} \cong (1-10) \times 10^{-6}$ at. parts, is natural. The coefficients (D_i) of diffusion D_{UHV} and D_{TGV} of gold in Ir are related to the concentrations $C_{vac,i}$ of intrinsic or extrinsic types of vacancies and their diffusion coefficients D_{vac} (6):

$$D_i = D_{vac} \times C_{vac,i} \quad (ix)$$

D_i represents the gold diffusion coefficient in either UHV or TGV, D_{vac} is the diffusion coefficient of vacancies which is the same for both D_i . It follows from (ix) that the concentration $(C_{vac})_{VIC} \equiv (C_{vac})_{extr}$ of 'extrinsic' vacancies formed in TGV annealing is related to the concentration of equilibrium vacancies $C_{vac} \equiv (C_{vac})_{intr}$ formed in UHV annealing at each annealing temperature by the relationship between the corresponding diffusion coefficients D_{TGV} and D_{UHV} , respectively. For example, at the annealing temperature of 1300 K:

$$\begin{aligned} \{(C_{vac})_{extr} / (C_{vac})_{intr}\}_{1300 \text{ K}} &= \{D_{TGV} / D_{UHV}\}_{1300 \text{ K}} \\ &\cong 2 \times 10^{-18} / 4 \times 10^{-22} = 5 \times 10^3 \end{aligned} \quad (x)$$

Effects of VIC Participation in Mass Transfer of Impurities in Iridium

The industrial use of Ir for crucibles and sheathings that are heated in air at temperatures from 1300 to 1800 K, leads to the Ir being loaded

with interstitial impurities, such as carbon, oxygen, hydrogen and nitrogen, from the ambient atmosphere or from the processed contents of the crucibles. Under these conditions, alloying of the iridium which contains these interstitial impurities causes, besides Ir embrittlement, saturation of the Ir volume with VICs and these, as described, supply excess ‘extrinsic’ vacancies that dissociate from the VICs.

Consequently, all substitutional impurities become capable of diffusing from the body of the Ir crucible through the walls. Their diffusion coefficients are several orders of magnitude higher than the diffusion coefficients for the same impurities in VIC-free Ir, see Figure 3. This explains the high permeability of Ir walls to impurities such as gold. In addition, the accumulation of VICs and pores adjacent to internal interfaces, including grain boundaries, causes fast creep in the Ir sheath (3) and intercrystalline fracture, which appears as a specific intercrystalline embrittlement (23).

In order to prevent the appearance and growth of VICs in Ir used at high temperatures in air, it is necessary to alloy the Ir with components that have a larger affinity for interstitial impurities than Ir, and form VICs with the impurities. Such VICs must possess the highest binding energies, E_{VIC} .

Typical components that will bind all interstitial impurities (oxygen, carbon and nitrogen) are hafnium or thorium, etc. Their melting points and their binding energy with the interstitial impurities are much higher than those of Ir. With this method of preventing VIC formation, the lifetime

of products made from Ir-based alloy is determined by the components of the complexes formed in the Ir.

When electrodes of Ir alloys containing several weight percent of rhenium and ruthenium were used to weld vessels made of Ir rolled stock, the permeability of Au into Ir was considerably inhibited in walls near the weld seams. This result confirms our conclusion concerning the positive outlook for alloying Ir with elements that have a larger affinity for interstitial impurities than Ir.

Conclusions

The activation enthalpy of volume diffusion of Au in single crystals of Ir annealed in TGV is almost half the value of the activation enthalpy of the volume diffusion of Au into single crystals of Ir annealed in UHV. This difference is explained by the decisive contribution from ‘extrinsic’ vacancies that dissociate from the VICs, and is the cause of the large diffusivity of substitutional Au during TGV annealing.

The large negative binding energy of the VIC components, $-(116 \pm 16)$ kJ mol⁻¹, indicates that VICs are formed by vacancies with interstitial impurities (oxygen, hydrogen, nitrogen), that alloyed with single-Ir during TGV diffusion. When products manufactured from Ir are heated to high temperatures in air, Ir alloys are doped with the interstitial impurities, which form the basis of the VICs and thus determine the ‘extrinsic’ mechanism of the volume diffusion of substitutional components in Ir.

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