THE MELTING DIFFUSION CORRELATION IN THE PLUTONIUM ZIRCONIUM ALLOYS

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The activation volumes for self-diffusion of Pu in b.c.c. PuZr alloys (10 and 40 at % Zr) have been determined, so that we could check the validity of Nachtrieb's melting-diffusion correlation. Indeed, in the Pu-40 at % Zr alloy, which has a pressure temperature phase diagram whose liquidus has a positive slope, we found a positive activation volume, whereas in pure εPu where the slope is negative, the activation volume is negative. A self-diffusion mechanism in PuZr alloys is proposed.

I - INTRODUCTION

The study of self-diffusion under pressure of b.c.c. εPu, which was carried out by Cornet [1] in our laboratory, showed that the rate of self-diffusion increases with pressure. This acceleration corresponds to a negative activation volume equal to - 4.9 cm^3 (i.e. - 34 % of the molar volume). This value which is astonishing since it is the first time a negative activation volume is observed, corresponds very well with the one (- 5,2 cm^3) given by Nachtrieb's correlation [2] :

$$\Delta V = \frac{\Delta H}{T_m} \cdot \frac{dT_m}{dp} \qquad (1)$$

where ΔH is the activation enthalpy under atmospheric pressure and T_m is the melting point at the same pressure.

We undertook two series of experiments to check whether the slope (dT_m/dp) of the liquidus of the pressure-temperature phase diagram is really determinant to forecast the effect of pressure on the self-diffusion rate in a metal. Firstly Languille [3] showed that δ-cerium (the melting point of δ-cerium decreases under pressure like the one of ε-plutonium) has also a negative activation volume. Afterwards -it is the subject of the present paper - we intended to change the sign of the slope of the liquidus of the pressure - temperature phase diagram of ε-plutonium by adding zirconium and then, to study the self-diffusion of plutonium in these alloys.

Firstly this study involved the determination of the pressure-temperature phase diagram of some PuZr alloys to know the slope of their solidus. Then we evaluated the activation volume for self-diffusion of Pu in these alloys.

II - EXPERIMENTAL

The pressure-temperature phase diagrams of two PuZr alloys (containing 10 and 40 at % Zr) were determined by differential thermal analysis. This study, as well as the diffusion anneals under pressure was carried out in a single-stage piston-cylinder apparatus previously described [4] contained in a glove-box under purified argon. The electric system and the internal furnace have been presented in detail by Cornet [1].

Meanwhile, it was necessary to prevent our samples from oxidation

by the pyrophyllite which was used as pressure - transmitting medium . So that every sample was enclosed in a tantalum container.

Temperature was measured by two tantalum-sheathed chromel-alumel thermocouples. Whenever necessary, we took into account the effect of pressure on the thermocouple emf and made the temperature corrections as determined by Cheng, Allen and Lazarus [5].

The diffusion couple was formed by two alloy PuZr cylinders (5 mm diam by 3 mm long) with the same Zr concentration (10 or 40 at %) but with different Pu 240 (X emitter) percentages. The two sorts of plutonium that were used to prepare the alloys respectively contained 1 and 28 at % Pu 240. We observed the Pu 240 diffusion by counting its X activity (17 keV) with a scintillation counter and a 400 - channel analyzer (Intertechnique model SA40B).

The determination of the penetration profiles was performed by using the generalized Gruzin analysis [6].

III - DETERMINATION OF THE PRESSURE-TEMPERATURE PHASE DIAGRAM OF PuZr (10 AND 40 at %) ALLOYS

Since the aim of this study was to check whether a change of the sign of the slope of the liquidus of the p.T phase diagram of εPu due to Zr additions, also modifies the activation volume sign for self-diffusion in this phase, we investigated only the ε region, disregarding the low temperature phases (ζ , θ, ι). Liptai and Friddle [7] already noticed that Ti additions (1, 3, 6 at %) made the slope of the solidus less and less negative.

This investigation was made by differential thermal analysis.

The results are presented in fig. 1 for the 10 at % Zr alloy and in fig. 2 for the 40 at % Zr alloy. The transformation temperatures observed under atmospheric pressure corresponds fairly well with those of previous publications [8].

The melting of the alloys was very difficult to observe, especially in the case of the 40 at % Zr alloy. Furthermore this alloy melts at high temperatures (950°C under atmospheric pressure and about 1000°C at 10 kbar) which produces a fast deterioration of the thermocouples. Owing to the latter reason, the solidus points of each alloy were determined at the first heating run. The difficulty of the experimental conditions shown above explains the scattering of the solidus points obtained here.

Meanwhile we clearly see (fig. 2) that the slope of the solidus of the 40 at % Zr alloy is positive. This slope lies between 3 and 5.2 °C/kbar. In the case of the 10 at % Zr alloy, we cannot make any statement about the sign of the slope of the solidus. All we can say is that it lies between - 1.5 and 1°C/kbar, that is to say near zero.

The main result of this investigation is that 40 at % Zr make the slope of the solidus of εPu positive. We are going to see in the next chapter whether the activation volume for the self-diffusion of Pu too in this alloy has become positive.

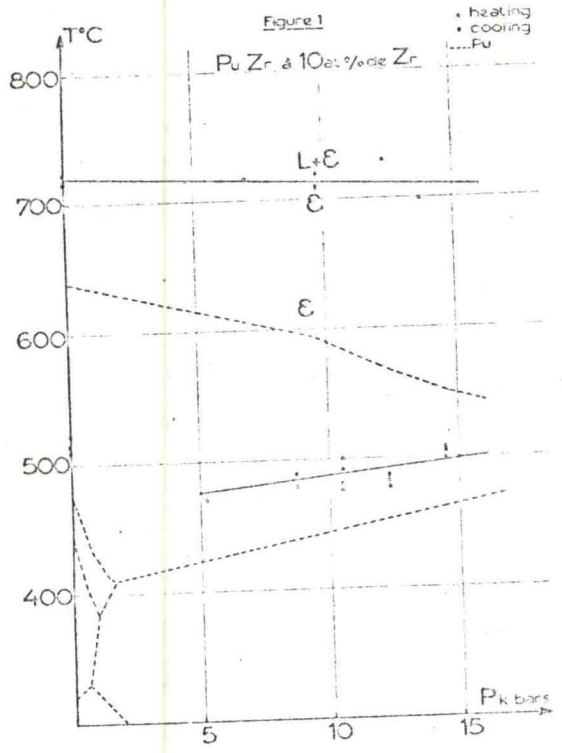


Fig. 1 - Pressure-temperature phase diagram of a Pu - 10 at % Zr alloy

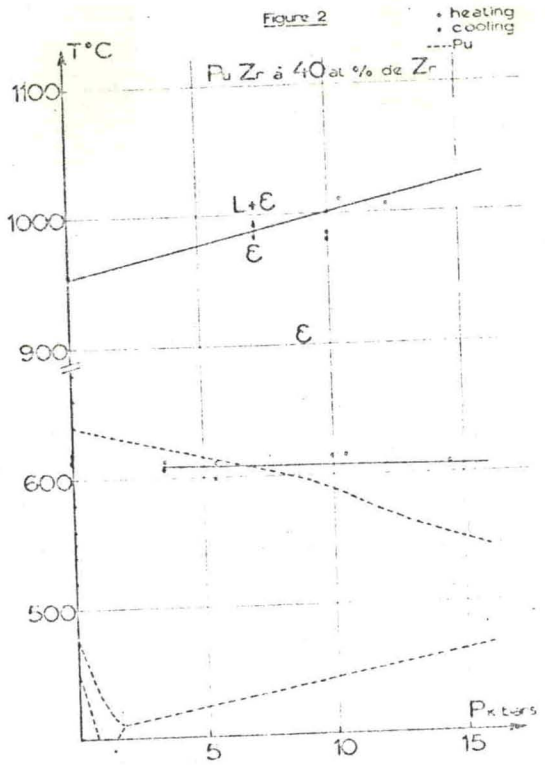


Fig. 2 - Pressure-temperature phase diagram of a Pu - 40 at % Zr alloy

IV - SELF-DIFFUSION UNDER HYDROSTATIC PRESSURE OF Pu IN THE PuZr ALLOYS (10 AND 40 at % Zr)

IV.1 - Results

Owing to the small difference between the X activity of the two sorts of plutonium used, the uncertainty due to the counting statistics is the largest, if we compare it with those introduced by the penetration measuring and by the lack of parallelism between the abrasion plane and the welding plane.

In the study of the self-diffusion of Pu in the 40 at % Zr alloy, two isotherms were made : one at 641°C and the other at 682°C. The diffusion coefficients are given in Table I. The self-diffusion activation enthalpy and the frequency factor under atmospheric pressure were computed from measurements at five different temperatures. We found out :

$$Q = 29650 \pm 3100 \text{ cal/mole}$$

$$\text{and} \quad D_o = 0.04 \begin{matrix} + 0.15 \\ - 0.03 \end{matrix} \text{ cm}^2/\text{s}$$

The Arrhenius plot at atmospheric pressure Log D = f(1/T) is presented in fig. 3. On fig. 4 we give the two straight lines : Log D=f(p).

By the method of least squares we calculated the following average value of the activation volume :

$$\Delta V = 3 \begin{matrix} + 1.6 \\ - 1.1 \end{matrix} \text{ cm}^3$$

T K	p kbars	D $cm^2 xs^{-1}$ x 10^9	t s	$\frac{\Delta D}{D}$ %	$-RT \frac{\partial Log\ D}{\partial p}$ cm^3
913	0	3.3	21600	11	
955	0	6.45	18000	9.5	$2.3 \begin{matrix} + 2.2 \\ - 1.3 \end{matrix}$
	5.25	5.31	21600	12.1	
	7	5.14	22800	11.8	
	12.25	4.48	25200	9.9	
1013	0	21.0	18000	12	
1075	0	35.4	18000	9.1	
1114	0	62.5	11100	6.3	3.8 ± 1
	7	41.1	12900	10.1	
	12.25	38.0	14400	10.4	

Table I

Self-diffusion under pressure of Pu in a Pu 40 at % Zr alloy

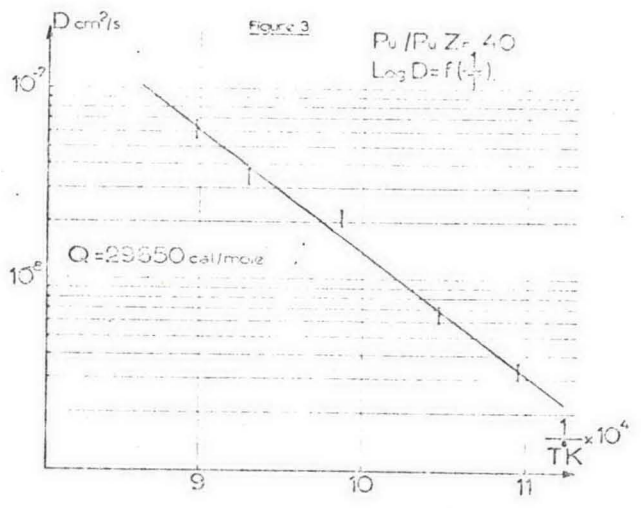


Fig. 3 - Arrhenius plot Log D = f(1/T) for the self-diffusion of Pu in a Pu - 40 at % Zr alloy

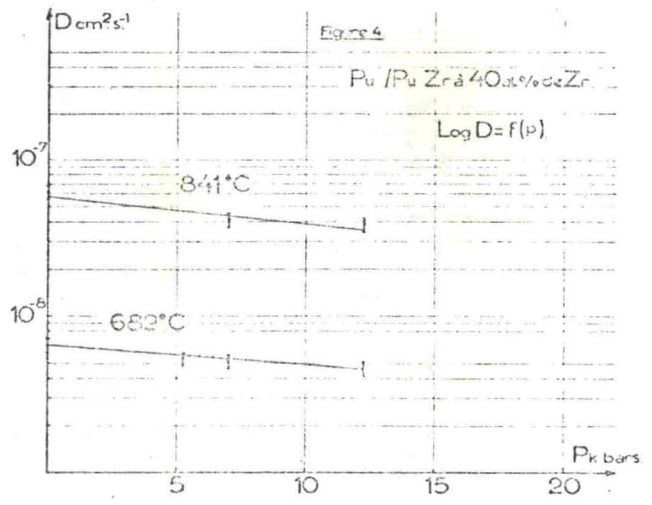


Fig. 4 - Self-diffusion coefficients under pressure of Pu in a Pu 40 at % Zr alloy

or with the molar volume calculated from the lattice parameters measured by Marples [9].

$$\Delta V/V_M = 0.2 \begin{matrix} + 0.11 \\ - 0.07 \end{matrix}$$

We did not include the correction term : $\Delta V_c = RT\ \chi_T\ \gamma_G$ (χ_T is the isothermal compressibility, γ_G the Grüneisen constant and R is the gas constant) in calculating ΔV.

We do not know either χ_T or γ_G for our alloy, but we can estimate ΔV_c for pure εPu at 700°C (with $\chi_T = 1.7 \times 10^{-11}$ cm²/dyne, $\gamma_G = 0.15$ [1] and $R = 8.32 \times 10^7$ erg). We come to : $\Delta V_c \simeq 0.2$ cm³ which represents 6 % of $\Delta V = - RT\ \partial \text{Log } D / \partial p$. So we can neglect ΔV_c, firstly because the uncertainty on ΔV value is approximately 50 % and secondly because the ΔV_c value that we calculated above is certainly a maximum value for our alloy because Zr additions are likely to decrease the εPu compressibility ($\chi_T = 2.13 \times 10^{-12}$ cm²/dyne for βZr at 900°C [11]).

In the case of the 10 at % Zr alloy, we studied only one isotherm at 650°C. The diffusion coefficients are presented in Table II and the straight line Log D = f(p) is given in fig. 5. We calculated :

$$\Delta V = - 0.9 \begin{matrix} + 1.3 \\ - 1.1 \end{matrix} \text{ cm}^3$$

T K	p kbars	D cm²xs⁻¹ x 10⁷	$\frac{\Delta D}{D}$ %	t s	$-RT\frac{\partial \text{Log } D}{\partial p}$ cm³
923	0	1.05	9.4	10800	$- 0.9^{+1.3}_{-1.1}$
	5.25	1.09	11.3	11400	
	8.8	1.2	10.7	10800	
	12.25	1.19	12	11100	

Table II - Self-diffusion under pressure of Pu in a Pu-10at% Zr alloy

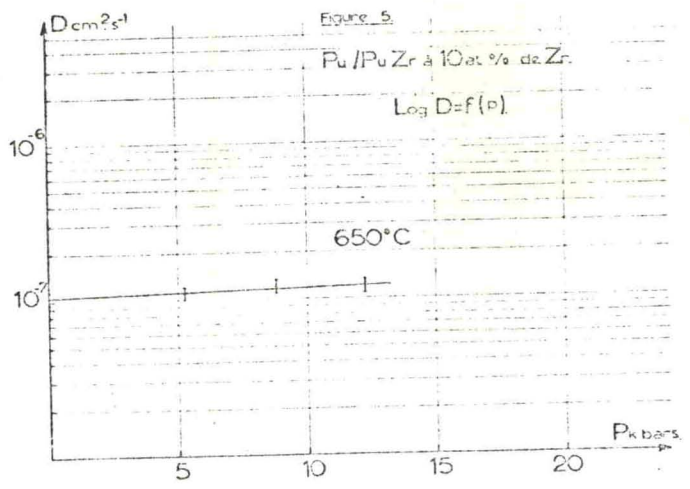


Fig. 5 - Self-diffusion coefficients under pressure of Pu in a Pu - 10 at % Zr alloy

or with the molar volume derived from the lattice parameters of Marples [9] :

$$\Delta V / V_M = - 0.06 \begin{matrix} + 0.09 \\ - 0.08 \end{matrix}$$

For this plutonium-rich alloy, the correction term ΔV_c is probably not very different from the one of pure εPu calculated above ($\Delta V_c \simeq 0.2$ cm^3). It tends to make ΔV less negative :

$$\Delta V \simeq - 0.7 \begin{matrix} + 1.3 \\ - 1.1 \end{matrix} \text{ cm}^3$$

or

$$\Delta V/V_M \simeq - 0.05 \begin{matrix} + 0.09 \\ - 0.08 \end{matrix}$$

IV.2 - Discussion

The main result of this investigation is that the activation volume for the self-diffusion of plutonium in PuZr alloys containing 40 at % Zr is positive, as could be infered from the positive slope of the solidus. Therefore the melting-diffusion correlation (equation 1) is qualitatively true. A quantitative correspondence is more difficult to establish. On the one hand because the pressure temperature phase diagram is not known with accuracy and on the other hand because we do not know what temperature must be taken for T_M in the equation 1 : the solidus, the liquidus or an intermediate temperature ? In the study of the self-diffusion in the Ag-Pd alloys Nachtrieb et al [11, 12] chose the solidus temperature. If we take the same temperature too, that is to say T_M = 955°C under atmospheric pressure, with ΔH = 29650 cal/mole and 3 < dT_m/dp < 5.2°C/kbar, we obtain : 3.04 cm^3 < $\Delta V \leq$ 5.26 cm^3 which corresponds fairly well to the ΔV value ($\Delta V = 3 \begin{matrix} +1.6 \\ -1.1 \end{matrix}$ cm^3) as determined from self-diffusion measurements.

In the case of the 10 at % Zr alloy, the correlation is also qualitatively verified, because dT_m/dp and ΔV are both nearly zero.

Therefore the melting-diffusion correlation is satisfied, at least qualitatively. It sounds logical to think that the peculiar properties of Pu which gives rise to the negative slope of the δPu liquidus, and also to the sign inversion of this slope when adding Zr, gives

rise too to the negative activation volume for self-diffusion and to its variation with Zr additions. We think that this physical property is the weak localization of the 5f electrons.

It is generally assumed that a contraction at melting (liquidus with a negative slope) can only be accounted for by an electronic transition which is for εPu an electronic promotion from the 5f to the 6d band. In the same way, Cornet [1] explained the negative activation volume for self-diffusion in εPu by assuming that self-diffusion takes place by an interstitial mechanism with interstitial atoms reducing their size by a promotion of two electrons from the 5f to the 6d band.

As we did already to explain our results on self-irradiation of the PuSc alloys, it is possible to develop Cornet's model. We think that the interstitial atom can minimize its distortion energy by creating bonds (comparable with those found in αPu) with its neighbours and by bringing forth the formation of bonds between these neighbours, by a localized enhancement of the d-f hybridization due to the weak localization of the 5f electrons. Thus the formation enthalpy of the interstitial atom will be decreased and its formation volume will be able to be negative. It is clear that the presence of Zr atoms will decrease this possibility. Consequently there is an increase of the formation volume ΔV_f which was negative and which becomes gradually positive and so it is for the activation volume ΔV since ΔV_f represents the most part of ΔV.

The formation enthalpy of the interstitial atom increases with Zr additions, like ΔV_f and then it is possible that the vacancy mechanism becomes energetically more probable than the interstitial mechanism.

Therefore the self-diffusion mechanism that we propose in εPu and in PuZr alloys is :

- The self-diffusion in εPu takes place by means of interstitial atoms and probably by a very correlated interstitialcy mechanism to explain the very low frequency factor.

- The formation enthalpy of an interstitial atom (and so it is for the activation enthalpy for self-diffusion) increases with Zr additionsand the self-diffusion of Pu in the 10 at % Zr alloy can be accounted for by a vacancy mechanism by means of very relaxed vacancies.

Consequently this investigation showed once more that the melting-diffusion correlation is verified at least qualitatively in all the observed cases, especially in the case of these very "anomalous" metals which present a negative activation volume for self-diffusion.

Furthermore it was specified in the case of εPu that these two exceptional phenomena which are a contraction at melting and a negative activation volume have probably the same origin which is the weak localization of the 5f electrons.

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