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Nº 1 AÑO 1976

01.76.11

CNEA-NT 13/76

COMISION NACIONAL DE ENERGIA ATOMICA
DEPENDIENTE DE LA PRESIDENCIA DE LA NACION

HETERODIFFUSION OF Co AND Cr IN PURE α AND β HAFNIUM

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1976

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RESUMEN

Se han medido los coeficientes de heterodifusión de Cr y Co en Hf puro utilizando el método de seccionamiento directo.

El Cr se ha medido en las fases α y β del Hf, el Co en la fase α únicamente.

Los coeficientes de difusión obtenidos son varios órdenes de magnitud mayores que los de autodifusión debido, se sugiere, a que los solutos difunden por un mecanismo intersticial. La difusividad del Cr no muestra discontinuidad en su valor al pasar de la fase α a la β , lo cual avala el mecanismo propuesto.

HETERODIFFUSION OF Co AND Cr IN PURE α AND β HF

ABSTRACT

Using the serial sectioning method, the diffusion coefficients have been measured of Cr in α and β-Hf and of Co in α-Hf. Both coefficients are many orders of magnitude greater than that for α-Hf self-diffusion owing, it is suggested, to the solute diffusion being by an interstitial process. The Cr coefficients are notable in being continuous through the transformation temperature.

INTRODUCTION

It is well accepted that self-diffusion in most f. c. c. metals, as well as in many b. c. c. metals, operates predominantly by a vacancy mechanism. The transport of substitutional impurities in these same hosts also appears to be effected mainly by vacancies. At high dilutions the impurity diffusivities in these systems rarely differ from the self-diffusivities by a factor greater than 10 to 20.

However a number of systems have been recognized in which the impurity diffusivity is several orders of magnitude greater than that of the host, and far above the range considered normal for vacancy- controlled mechanisms. *

Among these are many impurities diffusing in the anomalous elements Ti and Zr in their b. c. c. β -phases; more recently such measurements have been extended down into their lower temperature h. c. p. α-phases. However, the transformation temperatures of both metals are rather low relative to their melting points ($T_F/T_M \simeq 0.59$ for Ti and 0.53 for Zr), so diffusion measurements in the α phase are practicable over only a comparatively restricted temperature range. For the very closely analogous metal Hf the transformation temperature is high ($T_F/T_M = 0.81$) so the temperature dependence of D in the α phase can be more thoroughly investigated.

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* Various aspects of this process of fast diffusion in metals have been discussed in reviews by several authors, the more recent ones being those of Warburton and Turnbull (1) and of Le Claire (2).

Measurements of the diffusion coefficients of Co and Cr in α-Hf and of Cr in β-Hf are reported in this paper.

EXPERIMENTAL PROCEDURES

The diffusion experiments were carried out by the serial sectioning method using Hf polycrystals of 99.99% purity, apart from the 2.7 wt % of Zr content. Each sample had only a few grains, so the contribution from grain boundary diffusion can be neglected. However, being few in number the measured D's might vary a little from sample to sample because of anisotropy.

The samples were prepared by the same techniques as reported elsewhere (3). The tracers, ^{60}Co and ^{51}Cr supplied as chloride in hydrochloric acid solutions, were electroplated using the method described by Santos and Dyment (4).

The diffusion-anneals were also made as described in ref (3), except that at temperatures greater than 1200°C they were made in a Brew furnace, in an Argon atmosphere.

The activity of the tracers was measured with a NaI (Tl) detector and a single channel sprectrometrer. Data were analysed by a least squares programme (5). For ^{51}Cr decay corrections were made since it has a 27.8 days half life. For the very short annealing times for ^{60}Co diffusion it was necessary to make the usual heat-up time corrections.

RESULTS

Tables I and II give the values of the diffusion coefficients obtained. These and the associated statistical errors were calculated by a least squares treatment of the experimental ln c versus x^2 data. It is considered that the total error in D is of $\pm$ 4%.

TABLE I

^{51}Cr diffusion coefficients

T(^{o}C)	t (sec)	D (cm^2/Sec)
910	2423160	$5,08 \times 10^{-11}$
960	2253780	$6,24 \times 10^{-11}$
980	1470360	$2,68 \times 10^{-10}$
992	1412100	$2,73 \times 10^{-10}$
1100	79320	$1,11 \times 10^{-09}$
1154	324000	$2,01 \times 10^{-09}$
1156	175980	$1,69 \times 10^{-09}$
1254	102960	$6,12 \times 10^{-09}$
1515	10320	$1,80 \times 10^{-07}$
1600	8700	$1,30 \times 10^{-07}$
1710	4500	$3,05 \times 10^{-07}$
1800	2700	$5,66 \times 10^{-07}$
1850	2100	$6,80 \times 10^{-07}$
1900	1080	$7,92 \times 10^{-07}$

TABLE II

^{60}Co diffusion coefficients

T (^{o}C)	t (sec)	D (cm^2/Sec)
833	17820	$1,60 \times 10^{-07}$
1200	1974	$2,42 \times 10^{-06}$
1335	804	$4,54 \times 10^{-06}$
1480	702	$7,27 \times 10^{-06}$
1510	546	$1,15 \times 10^{-05}$
1525	543	$7,70 \times 10^{-06}$

Fig. 1 shows typical penetration profiles and Fig. 2, the Arrhenius plots for ^{51}Cr and ^{60}Co diffusivity in Hf, and also the self-diffusivity of Hf in both phases.

The activation energies and frequency factors are listed in Table III.

TABLE III

Diffusion parameters for Co and Cr in Hf (present work)

and previous values for self-diffusion

	Q (cal/mol)	D (cm^2/sec)	Author
Co in α-Hf	22800^{+}_{-} 860	$5,3\ ^{+\ 1,8}_{-\ 1,3} \times 10^{-03}$	Present work
Cr in (α + β) Hf	51100^{+}_{-} 1300	$0,14\ ^{+\ 0,07}_{-\ 0,05}$	Present work
Self-diffusion in α-Hf	41600^{+}_{-} 2300	$7,3 \times 10^{-06}$	Dyment and Libanati (6)
" " // c	88400^{+}_{-} 3200	0,86	Davies and Mc Mullen (7)
" " $\perp$ c	83200^{+}_{-} 4800	0,28	Davies and Mc Mullen (7)
Self-diffusion in β-Hf	38700^{+}_{-} 1000	$1,2\ ^{+\ 0,7}_{-\ 0,5} \times 10^{-03}$	Winslow and Lundy (19)
"	43800^{+}_{-} 2200	$4,8 \times 10^{-03}$	Reca and Libanati (20)

Fig. 2 shows both the Dyment et al (6) and the Davies et al (7) data for self-diffusion in α-Hf. After a study of the detailed experimental results given in the thesis of Davies it is difficult to accept the reduced slopes that are claimed in the Arrhenius plots at low temperatures. Therefore, only the higher temperatures results of Davies and Mc Mullen are reproduced here. Many of their lower-temperature data are from penetration plots of only three or even two experimental points. There seems no explanation of the differences between the two sets of self-diffusion data.

DISCUSSION

Fig. 2 shows very large differences between D_2 (heterodiffusion coefficient) and D_0 (self-diffusion coefficient) for both ^{51}Cr and ^{60}Co, but especially for ^{60}Co. For this tracer, D_2/D_0 ratios are among the highest reported. ^{60}Co is also a very fast diffuser in Zr (8-10), Ti (3, 11), U (12) and Pr (13) and Cr is very fast in Zr (10).

An interesting observation, perhaps no more than fortuitous is that the Co diffusion rates in α-Hf in the temperature range 800° to 1600°C are nearly identical with those for Co in β-Zr at corresponding temperatures in the same range.

Taking into account the results shown in Fig. 2 and the Q values in Table III, Co appears to be an "anomalous" diffuser in the two respects of D_2/D_0 being very large and Q_2/Q_0 being very appreciably less than unity. Cr, however, while remaining "anomalous" in respect of D ($D_2/D_0 \sim 10^3$), has a very much larger Q_2 value and $Q_2/Q_0 > 1$ in the β phase. It is also > 1 in the α-phase with respect to the Dyment and Libanati data, although it is < 1 with respect to Davies data. A similar situation ($Q_2/Q_0 > 1$) prevails for Cr and for Zn in Zr (10).

The diffusion coefficients obtained for ^{51}Cr and ^{60}Co are well represented by linear Arrhenius expressions. There is no evidence of any curvature in spite of the wide temperature range of the measurements. The slight scatter of points may be due to anisotropy in the coarse polycrystal samples used, as well of course to the experimental errors.

^{60}Co diffusivity measurements did not completely cover the α phase and were not extended into the β range. This was because the extremely short anneal times (a few minutes) that would have been necessary, with the samples available, could not be measured sufficiently accurately because of the comparatively long times needed to reach the anneal temperature. The anneal times in the β phase would have been much shorter than the correction for heat-up time in the α phase !

With ^{51}Cr this problem did not exist and a complete study of both phases was possible. A perfect continuity of D_{Cr} through the transformation temperature was obtained, a phenomenon also found with Ag in Tl (14), Ni in Ti (8, 11), and Zn in Pr (15). In the present results, and also with Ni in Ti, the slopes are also the same.

The more numerous the examples of continuity in D that are observed the less likely seems the suggestion, often made, that phase transformation might in - crease dislocation densities sufficiently to enhance diffusion rates. For if there is regularly such an enhancement, a continuity in D implies that it is just sufficient to compensate a difference between the diffusion coefficients on either side of the trans formation ---- but such a combination of circumstances is surely not likely to occur often !

The very fast diffusion of Co and Cr in Hf is presumably to be understood on the same hypothesis of interstitial solution and diffusion as has been advanced to explain anomalously fast diffusion in other systems, especially as it is usually con- sidered that an insensivity of D_2 to a phase transformation supports this hypothesis. Furthermore, the conditions established by Anthony and Turnbull (16, 17) for the occurrence of interstitial solution of one metal in another are indeed obeyed for Co and Cr in Hf. Thus (i) both Co and Cr ions have radii sufficiently small for them to occupy interstitial sites in α or β -Hf without core overlap; (ii) the solvent is poly valent (early transition elements like Hf behave in alloys with an effective high valen cy, $\geq$ 2) and (iii) the solutes are of low valency (the later transition elements gener ally behave as having effective valencies $\leq$ 2).

Tendler et al (10) noted that fast diffusers, at least in Zr, are all so- lutes with atomic radii smaller by more than 15% than that of the solvent and so are probably dissolved interstitially because of the Hume-Rothery rule that for substi- tutional solution the solute radius must be within 15% that of the solvent. On the basis also of this alternative criterion Co and Cr are expected to dissolve inter- stitially in Hf, because the atomic radii of both are more than 15% smaller than that of Hf.

Finally, if Co and Cr are indeed interstitially dissolved in Hf then, in view of the observation made by Turnbull (18), CoHf and CrHf alloys may be ex- pected to show propensity for existing in amorphous form.

ACKNOWLEDGMENTS

The author wish to thank Mr. A. Aristarain for his assistance with experimental techniques and to acknowledge helpful discussions with Dr. Le Claire. Special gratitude is due to Dr. Le Claire for his suggestions for improving the manuscript.

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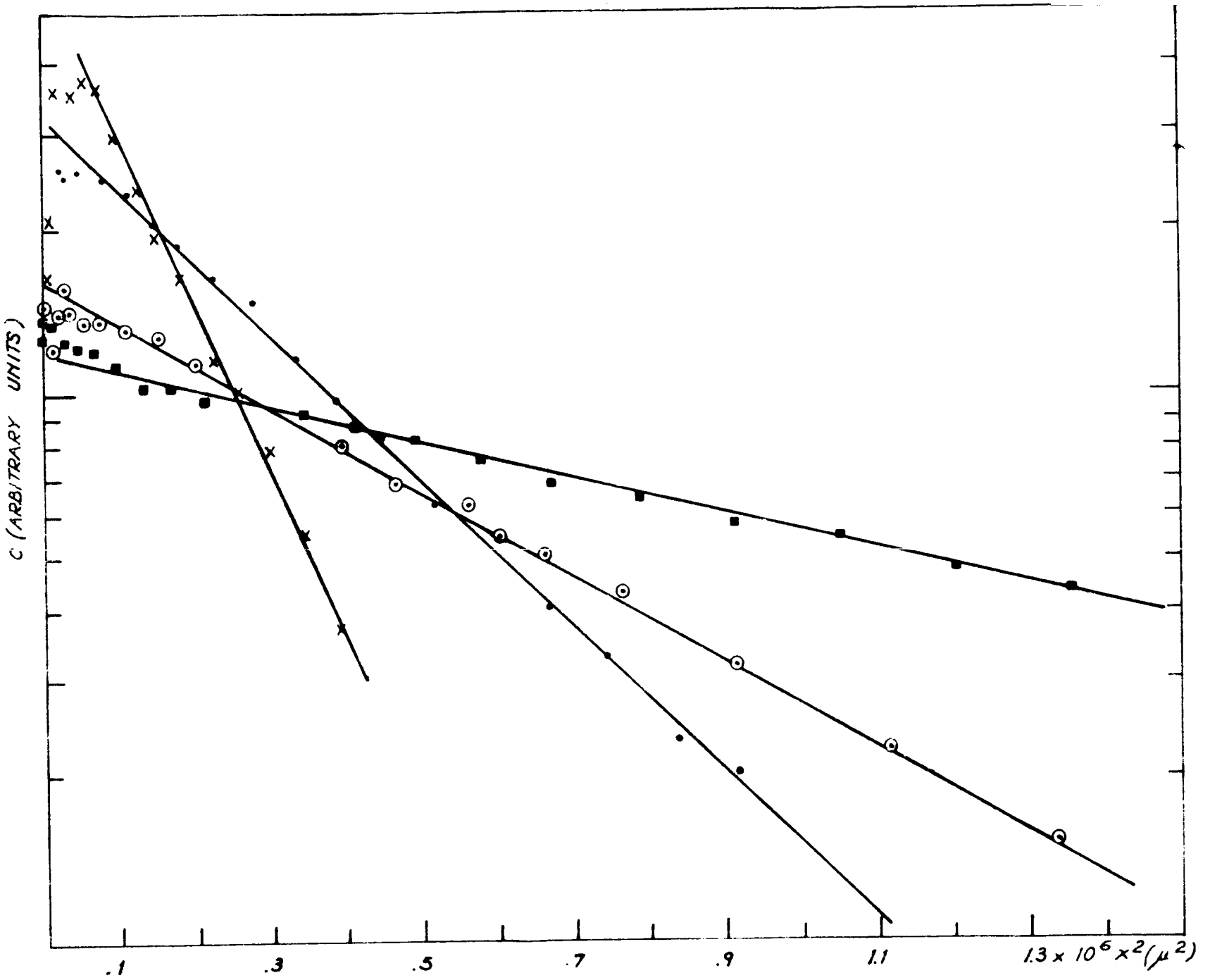

Fig. 1 Typical penetration plots
X 992°C, ⊙ 1880°C, • 1900°C ^{51}Cr; Δ 1415°C ^{60}Co

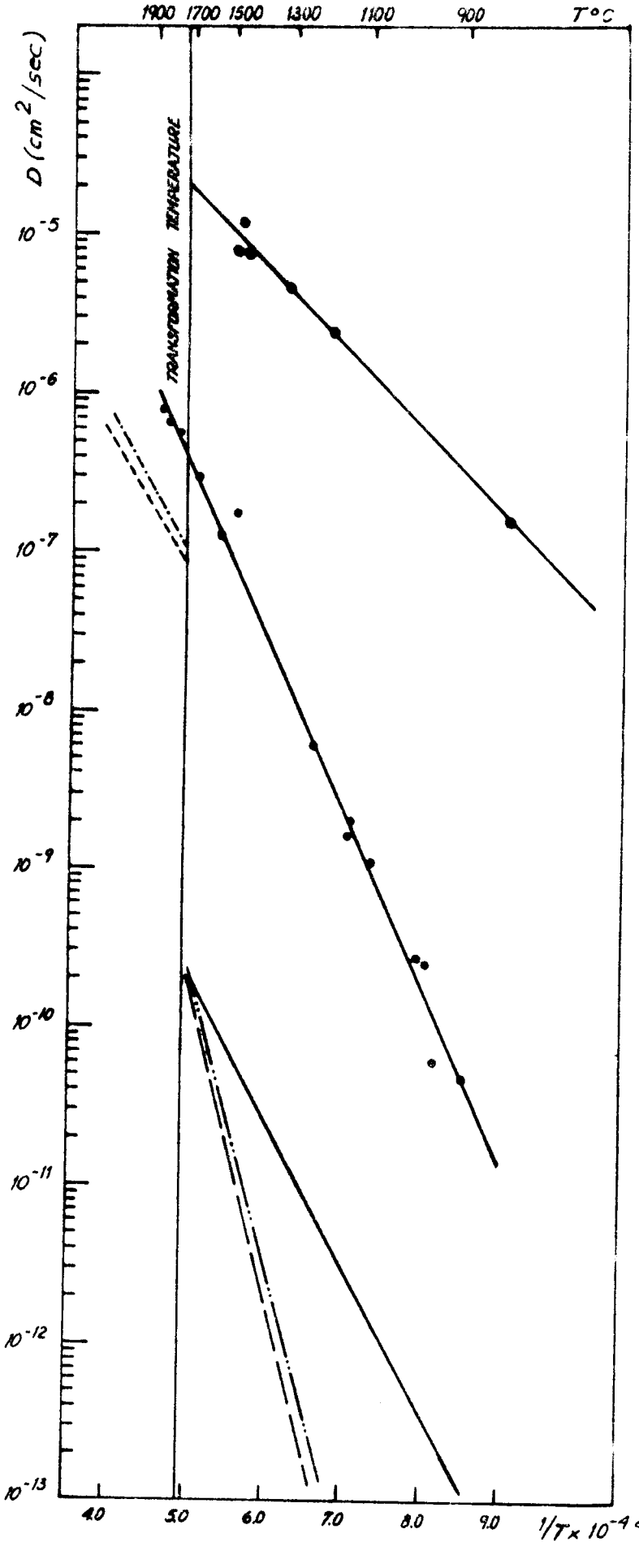

Fig. 2

Arrhenius plots

⊙ ^{60}Co
• ^{51}Cr
} present work

——— α-Hf self-diffusion (6)
—·—·— ⊥ c " " " (7)
— — —// c " " " (7)
- - - - - β-Hf self-diffusion (19)
—·—·— " " " (20)