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Grain boundary diffusion and segregation of Cr in α-Zr

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ABSTRACT

^{51}Cr diffusion along grain boundaries in polycrystalline α-Zr was measured by means of the radiotracer technique in the temperature range 449–680 K. The use of Harrisońs C and B kinetics provided direct data about grain boundary diffusivity (D_{gb}) and the apparent grain boundary diffusivity (P_{gb}) in the temperature range of power reactors service. The grain boundaries segregation factor s of Cr in α-Zr was determined at the limit of very dilute solute concentration.

1. Introduction

A large amount of metallurgical processes, such as plastic deformation and corrosion at high temperatures, solid-state transformations, surface treatments and the stability of precipitates in a matrix, depend on atomic transport along grain and interphase boundaries [1]. In this frame, solute and self-diffusion studies in the bulk and in those boundaries are relevant in order to predict the performance of structural components.

Zr-based alloys are extensively used in nuclear and chemical industries due to their excellent corrosion, mechanical and nuclear properties. They are usually employed in polycrystalline forms, exhibiting a high density of grain and interphase boundaries.

Cr is an impurity normally present in the so-called Zircaloy's. The bulk diffusion of Cr in α-Zr polycrystals shows values about 3–4 orders of magnitude larger than self-diffusion [2], as observed also for Fe, Co and Ni diffusion. In order to explain this behaviour, some models considered the possibility of a non-substitutional state as suitable for those so fast heterodiffusion diffusors. A detailed review can be found in [3]. Then, our aim was to investigate whether Zr grain boundaries act as short circuits for Cr diffusion and to elucidate the role that the segregation factor plays. The use of Harrison's kinetics type B and C [4] allowed us to measure the proper grain boundary diffusion coefficient and the segregation factor.

2. Experimental procedure

Stabilized pure α-Zr (purity better than 99.9 wt%) was cut in samples of 0.75 cm^2 of surface and 5 mm height. They were mechanically polished up to 1 μm diamond paste; some of them were employed to verify the correlation between the real morphology with the ideal one suitable for the application of the mathematical models of the s employed kinetics. The base material had the following chemical analysis, (all the values are in weight ppm): O, Fe and Hf are the main impurities. O has influence in the α → ß transformation temperature. Being an α-phase stabilizer, it does not segregate to the grain boundaries. Hf is normally present as Zr is extracted. It has total solubility with α-Zr, so no segregation to grain boundaries is expected. On the other hand, Fe, Co, Ni, Cr are a particular kind of impurities in pure Zr, Zry and Zr–Nb alloys; they have very low solubility in α-Zr and are ultra fast diffusors. Fe is the most important among them because can be present in quantities as high as 400 ppm and can hardly be lowered to less than 50 ppm in extremely pure materials.

The structure of the samples (Fig. 1) shows a small and randomly distributed grain pattern, suitable for grain boundary diffusion determinations. In fact, several hundreds of grain boundaries are involved in the experimental evaluation of the diffusion coefficients, so the results obtained in this work are average values for the grain boundaries.

^{51}Cr in a HCl solution was directly deposited onto the polished surface of the samples to get the diffusion pairs. The samples were wrapped in high purity tantalum foil and vacuum sealed in quartz tubes with a slight overpressure of high purity argon. The diffusion annealings were performed in Adamel electrical furnaces, provided with P + I + D electronic control, with a precision of ±1 K.

The samples were turned radially to avoid lateral diffusion in order to consider unidirectional flux from the deposited face. The sectioning of the samples was made in a precision abrasion machine. The thickness of the removed layers was determined by difference of weight of the samples after each sectioning in a 10^{-5} g precision scale (both the density and the involved area of the slices are known). An INa(Tl) detector was employed to measure the activity (concentration) of the layers; this concentration

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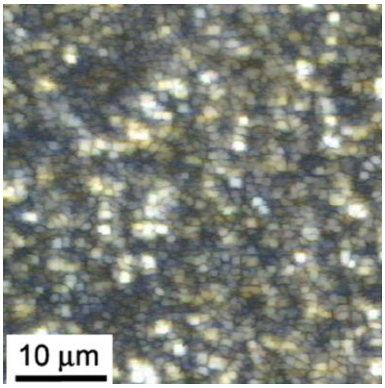


Al	B	C	Ca	Cd	Cl	Co
<20	<0.25	31	<10	<0.25	<5	<10

Cr	Cu	Fe	H	Hf	Mg	Mn	Mo
<50	<17	138	<3	74	<10	<25	<10

N	Na	Nb	Ni	O	P	Pb
<20	<5	<50	<36	423	<3	<25

Si	Sn	Ta	Ti	U	V	W
<10	<10	<50	<25	<1	<25	<25

Fig. 1. Morphology of the material employed and its chemical analysis.

divided by the mass of each slice provided the specific activity of each layer. The quoted errors were estimated to be around 15% and 20% for the GB diffusion parameter P_{gb} and the D_{gb}, respectively.

3. Results and discussion

As it is well known, diffusion in polycrystalline materials is a complex process that includes a series of elemental processes [1]:

- Bulk diffusion from the surface of the sample.
- Diffusion along the grain boundary.
- Bulk diffusion from the grain boundary.

According to the relative importance of these processes, different situations or kinetics could appear. The well known Harrison's classification [4] allows us to deal with three different kinetics: type A, B and C. In the case of the B and C kinetics, both used in this work, (Fig. 2) the principal characteristics could be summarized as follows.

3.1. Type B kinetics

Main processes: Diffusion along grain boundaries and lateral bulk diffusion from the grain boundaries.

$$100\delta < \text{bulk diffusion distance} = (D/\mathrm{t})^{1/2} < d/20,$$

where d is the mean grain size and δ is the grain boundary thickness. Then, the solutions for isolated grain boundary, e.g., Whipple [5] or Suzuoka [6] solutions based on Fisher [7] analysis, can be applied. In this framework, and in order to obtain the penetration profile, the following equations are applied:

$$\text{Constant source}\quad P_{gb} = \delta s D_{gb} = 1.322(D/\mathrm{t})^{1/2}(-\partial c/\partial x^{6/5})^{-5/3}, \quad (1)$$

$$\text{Instantaneous source}\quad P_{gb} = \delta s D_{gb} = 1.308(D/\mathrm{t})^{1/2}(-\partial c/\partial x^{6/5})^{-5/3}, \quad (2)$$

where s is the grain boundary segregation factor, D is the bulk diffusion coefficient, being $P_{gb} = \delta s D_{gb}$ the experimentally measurable parameter usually refered as the 'apparent grain boundary diffusion coefficient'. The B kinetics is the most used framework because it allows the employment of both: reasonable times and temperature ranges.

3.2. Type C kinetics

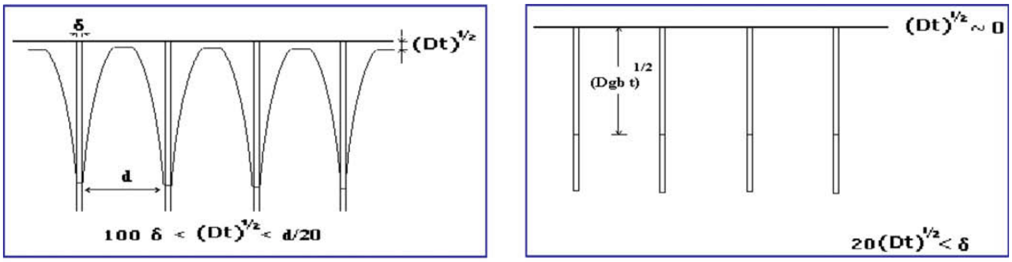
Main process: Diffusion along grain boundaries. Bulk diffusion from the surface and from the grain boundaries is neglegible. The penetration profile in this kinetics, equivalent to the bulk diffusion, is gaussian (instantaneous source) or an error function (constant source). D_{gb} is directly measured. For a Gaussian solution:

$$C(x,t) = C_o \exp(-x^2/4D_{gb}t), \quad (3)$$

where C_o is the initial diffusor concentration.

Figs. 3 and 4 show typical penetration profiles for B and C kinetics, obtained in grain boundaries of α-Zr. In all cases, the average depths of penetration were about 30 μm.

The B kinetics allows the determination of the experimental P_{gb} values (see Table 1). In order to calculate P_{gb} it is necessary to know the bulk diffusion coefficient (D) at the same temperatures. The D



(1) (2)

Fig. 2. Schematic illustration of grain boundary diffusion. B (1) and C (2) kinetics.

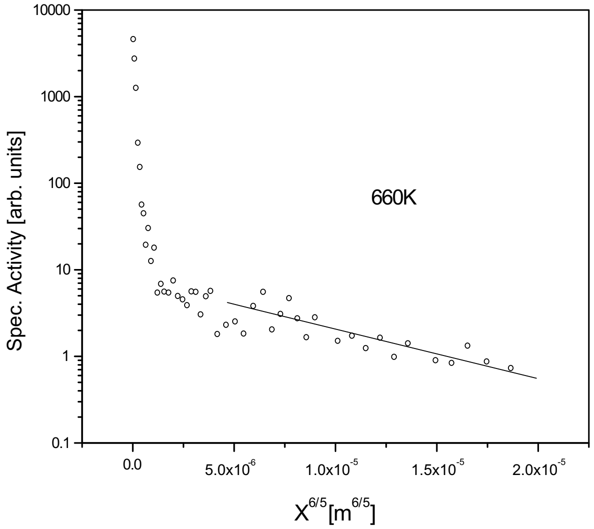


Fig. 3. Grain boundary diffusion in α-Zr. B kinetics.

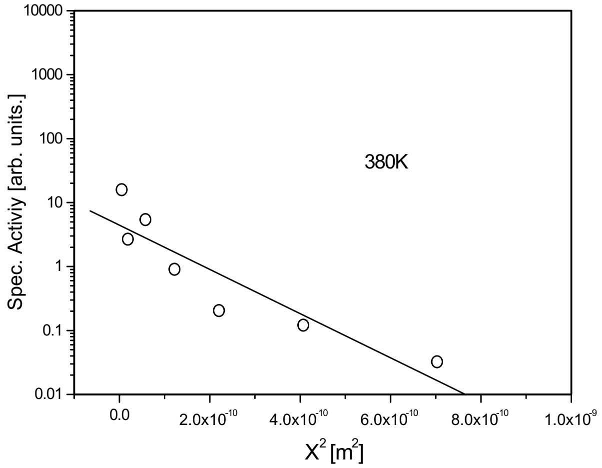


Fig. 4. Grain boundary diffusion in α-Zr. C kinetics.

values were obtained from data of Tendler and Varotto [2]. They measured ^{51}Cr bulk diffusion in the temperature range of 890–1080 K; the linear behaviour shown in the Arrhenius plot of [2] allows us to extrapolate the values to the range of temperature of the present work.

The C kinetics allows the determination of the experimental D_{gb} values (see Table 1). The Gaussian solution was employed in a similar way as in a bulk diffusion experiments. It is not necessary to consider the grain boundary segregation factor (s) and the width of grain boundary (δ).

The diffusion parameters obtained for type B and C kinetics can be expressed as:

$$P_{gb}(T) = (4.4 \pm 2.2) \times 10^{-9} \cdot \exp\left(\frac{-(126.0 \pm 19)\ \text{kJ/mol}}{RT}\right)\ (\text{m}^3/\text{s})$$

$$D_{gb}(T) = (727 \pm 364) \cdot \exp\left(\frac{-(138 \pm 27)\ \text{kJ/mol}}{RT}\right)\ (\text{m}^2/\text{s}).$$

The grain boundary segregation enthalpy of Cr in α-Zr was obtained from the direct comparison of the activation energies given above:

$$H_s = Q_{ap} - Q_{gb} = -12\ \text{kJ/mol},$$

Table 1
Cr grain boundary diffusion in α–Zr

Type	T (K)	P_{gb} (m^3/s)	D_{gb} (m^2/s)	δD_{gb} (m^3/s)
B	680	$(5.8 \pm 0.9) \times 10^{-19}$	–	–
B	660	$(5.7 \pm 0.8) \times 10^{-19}$	–	–
B	621	$(1.5 \pm 0.2) \times 10^{-19}$	–	–
B	590	$(3.7 \pm 0.6) \times 10^{-20}$	–	–
B	550	$(3.5 \pm 0.5) \times 10^{-21}$	–	–
C	449	9.4×10^{-24} [a]	$(7.7 \pm 1.5) \times 10^{-14}$	3.8×10^{-23}
C	423	1.1×10^{-24} [a]	$(9.8 \pm 2.0) \times 10^{-15}$	4.9×10^{-24}
C	400	1.5×10^{-25} [a]	$(2.7 \pm 0.5) \times 10^{-16}$	1.4×10^{-25}
C	380	2.0×10^{-26} [a]	$(1.4 \pm 0.3) \times 10^{-16}$	7.2×10^{-26}

[a] Extrapolated from high temperatures.

where Q_{ap} and Q_{gb} are the measured activation energies for type B and C kinetics, respectively.

The low value of H_s is consistent with the solubility of Cr in α-Zr: 0.49 at.% Cr at 1109 K.

The grain boundary is a bidimensional defect as it is the surface of the material. It is valid to assume that the enthalpy of surface segregation is similar to the one corresponding to segregation in grain boundary. Nevertheless, as the grain boundary is a defect between two crystalline regions while the surface is a limit of one crystalline zone, it is possible to expect a surface segregation enthalpy slightly larger. This assumption was experimentally confirmed in [8]. Then, assuming that the relationship between both segregation enthalpies is around 0.6 [8], a value of 19–20 kJ/mol can be assigned to the absolute value of the surface segregation enthalpy, lower than the one corresponding to Fe: 71.8 kJ/mol [9].

Besides, the values in Table 1 allow us to calculate the segregation factor, s, with the use of the expression (4) and the assumption that $\delta = 5 \times 10^{-10}$ m [1,10].

$$s = P_{gb}/(\delta \cdot D_{gb}), \tag{4}$$

where the P_{gb} values were extrapolated from high temperatures (see Table 1).

The very low concentration of the radiotracer used in our experiments lets us suppose that the atomic segregation follows a Henry-type behaviour; so, the grain boundaries are far from the saturation zone. Similar cases can be seen in [11–12]. Although the amount of Fe present in our samples is low, it can segregate to the grain boundaries. The effect of Fe segregation on the grain boundary diffusion of other solutes deserves further investigations.

When extrapolating the P_{gb} values from the range of temperatures measured to the lower one corresponding to the

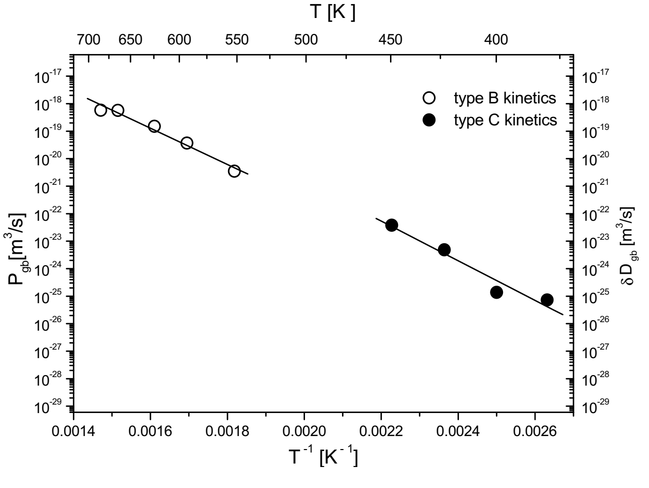


Fig. 5. Cr diffusion along α-Zr grain boundaries. B and C kinetics.

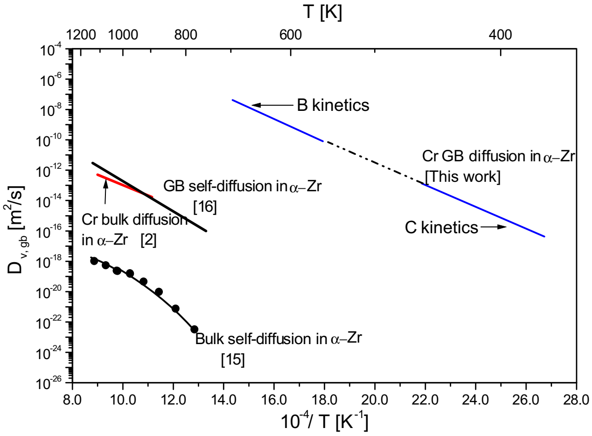


Fig. 6. Cr and self diffusion in α-Zr.

Table 2
Bulk diffusion coefficients D^i and grain boundary diffusion D_{gb} in α-Zr at 900 K

Element	D^i (m^2/s)	D^i_{gb} (m^3/s)	D^i/D^{Zr}	D^i_{gb} / D^{Zr}_{gb}
Zr	2.2×10^{-20}	1.8×10^{-14}	1	1
Cr	2.3×10^{-14}	4.2×10^{-7}	1×10^6	2.3×10^7

measurements in the C regime, the values obtained are very similar to the product $\delta \cdot D_{gb}$ which means that all the calculated segregation factor values in the temperatures range 380–449 K are around 1 (see Table 1). Cr segregation in grain boundaries of α-Zr shows a very different behaviour as compared to Co, where high segregation factors were obtained in a similar temperature range [13].

Fig. 5 shows an Arrhenius plot for the P_{gb} values (B kinetics) and the product $\delta \cdot D_{gb}$, (C kinetics).

In Fig. 6 a direct comparison of bulk and grain boundary diffusion was possible on the basis of the diffusion measurements performed in the present work in C kinetics. The Cr diffusion in the bulk of α-Zr single crystals is anisotropic [14], with $D_{\parallel} > D_{\perp}$ (diffusion coefficients parallel and perpendicular to *C-axis* in α-Zr structure) and the experiments in α-Zr polycrystals show a lineal behaviour with a straight line between $D_{\parallel}$ and $D_{\perp}$ (Table 2).

The ratios of impurity to self-diffusion in both bulk and grain boundary diffusion [15,16] indicate that Cr is an ultra-fast diffuser also in α-Zr grain boundary. This suggests that a partially interstitial-type mechanism could operate in the diffusion of Cr along the grain boundary as it is believed to act in the bulk of α-Zr.

4. Conclusions

This work presents results of the diffusion of Cr in grain boundaries of pure α-Zr in the range of temperatures 449–680 K. These are the first results where the Harrison's kinetics type C is applied in this system.

The results show that Cr is a fast diffuser in grain boundaries of pure α-Zr as it is in the bulk of α-Zr. A relation of 10^7 is obtained by comparing Cr to Zr self grain boundary diffusion at 900 K. The Arrhenius plot is straight, indicating the operation of a unique diffusion mechanism.

The comparison between B and C kinetics allowed us to obtain a direct evaluation of the Cr segregation factor, *s*, in the grain boundaries of α-Zr, as well as the diffusion coefficient D_{gb}. The parameter *s* does not show an important variation with the temperature in a range of 70 K and remains near to 1.

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