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GRAIN BOUNDARY DIFFUSION AND FRACTAL INTERFACE CONCEPT

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Résumé - Cette étude porte sur une nouvelle approche de la description de la diffusion aux joints des grains s’appuyant sur le concept de surfaces fractales, à travers les résultats quantitatifs obtenus par radiotraces.

Le concept de surface fractale appliqué aux joints tient compte ici de l'influence des impuretés et des éléments d'alliage à haute température, qui participent directement aux modifications des sauts élementaires associés aux défauts intergranulaires.

Abstract - This study concerns a new way for a generalization concerning the movements of atoms along grain boundaries taking into account quantitative values of intergranular diffusion and bulk diffusion obtained by radiotracer techniques.

The concept of fractal interface applied to grain boundaries, particularly under the influence of impurity contents or alloying additions, gives a new description of these phenomena by the determination of fractal dimension of grain boundaries (GBs) at high temperatures.

I - INTRODUCTION

In previous papers, the author has suggested the possibility to introduce the new fractal surface concept in the description of the intergranular diffusion mechanism (1,2). However, no direct determination of fractal dimension of the grain boundaries was reported. This paper aims to apply the fractal concept to grain boundaries quantitative results from the literature.

Some years ago, Mandelbrot et al (3) have given interesting interpretation of the Mandelbrot model (4) to fracture surfaces of metals (maraging steel) under the influence of heat treatment at different temperatures. Here, we give a transposition of the surface roughness analyzed by the fractal concept, using the mobility of atoms in grain boundaries during high temperature treatments, taking into account the diffusion parameters measured by classical radiotracer methods.

2 - BRIEF RECALL OF GRAIN BOUNDARY DIFFUSION : DEFINITION OF THE DYNAMIC FRACTAL GB DIMENSION

In practice, the intergranular diffusion parameters studied by radiotracer techniques are defined by the magnitude of the parameter:

\[ P_{GB} = D_{GB} \cdot \mathcal{L} \cdot \alpha \]

where \( \mathcal{L} \) is the GB width and \( \alpha \) is the segregation term of the moving species.

In spite of an important work described in the literature (5) it is often difficult to analyze clearly the different parameters to know:

a) The mechanism of the mobility of defects in the boundary which concerns the interface zone dimension.

b) The mechanism of segregation in the boundaries (\( \alpha \)) which concerns reorganization on short distances in and near the GB.

We can consider \( \mathcal{L} \) and \( \alpha \) as consequences of the fractal properties of the GB during the migration and segregation of atoms at the same temperature, through the picture presented on Fig. 1. But, it is necessary to consider at the same time the bulk diffusion coefficient (\( D_B \)) which is an unavoidable term in the mathematical solutions of the models describing the GB diffusion. Recently SAPOVAL (6) have shown that the front of the bulk diffusion (by computing simulation) has fractal properties and have found a value of 1.75 for this dimension. This property is to be introduced in the grain boundary diffusion because the contribution of bulk diffusion from the GB is always present.

So, the fractal characteristic of a grain boundary may be used to analyze the change of the parameter \( P_{GB}/D_B \) versus concentrations concerning GB zone and bulk medium (\( C_{GB} \) and \( C_B \)).

To correlate these different factors, we use the relationship proposed by KIRKPATRICK (7) which defines the percolation threshold, necessary to obtain the diffusion in an alloy versus concentration.

If \( \alpha_{GB} \) is the GB dimension corresponding to \( D_{GB} \), the penetration parameter \( P_{GB} \) can be des-
The relative concentration \( \frac{C_{GB}}{C_B} \) concerns the moving element studied by radiotracers.

The relation (1) is equivalent to the definition of a measured length of a path \( N \) measured with a unit scale \( \kappa \) characterized by a fractal dimension \( \mathcal{D} \):

\[
\log N (\kappa) = \mathcal{D} \log \frac{1}{\kappa}
\]

The unit length \( \kappa \) has the same role as the effect of concentration acting on jumps of atoms through the lattice sites and the boundary defects.

**Remark**

The dimension of the diffusion in the GB can be considered with two approaches:

a) Taking into account the segregation factor \( \alpha \), we obtain directly the value \( \mathcal{D}_{GB} - \mathcal{D}_B \)

b) To characterize the diffusion only through the defects of GB without the factor \( \alpha \), we take:

\[
\frac{P_{GB}}{D_B} = \frac{D_{GB}}{D_B} \mathcal{D}_{GB} = \left( \frac{C_{GB}}{C_B} \right) \mathcal{D}_{GB} - \mathcal{D}_B
\]

which gives:

\[
\frac{D_{GB}}{D_B} = (\alpha) \mathcal{D}_{GB} - \mathcal{D}_B - 1
\]

\[
\log \frac{D_{GB}}{D_B} = \left( \mathcal{D}_{GB} - \mathcal{D}_B - 1 \right) \log (\alpha)
\]

3 - APPLICATION TO GB DIFFUSION IN PURE METALS NEAR THE MELTING POINT

We consider the singular case of pure metals near the melting point where \( D_B \) and \( P_{GB} \) are well defined by the literature (8,9,10), particularly for cubic metals.

In this case, we substitute the chemical terms by the vacancy concentrations, \( \Box \), at the melting point:

\[
(\Box)_B \approx 10^{-2}
\]

\[
(\Box)_{GB} \approx 10^2 \quad \text{(liquid structure with clusters)}
\]

so,

\[
\log_{10} \left( \frac{C_{GB}}{C_B} \right) = 4
\]
If we take the diffusion parameters at the same temperature, we have:

- \( P_{\text{GB}} \approx 5 \times 10^{-18} \text{ m}^3 \text{ s}^{-1} \) with \( \delta = 5 \times 10^{-10} \text{ m} \), \( \alpha = 1 \) and \( D_{\text{GB}} = 10^{-8} \text{ m}^2 \text{ s}^{-1} \)
- \( D_B \approx 10^{-12} \text{ m}^2 \text{ s}^{-1} \)

so

\[
\delta_{\text{GB}} - \delta_B = \log \frac{P_{\text{GB}}}{D_B} \left/ \log \left( \frac{\alpha}{\alpha} \right)_{\text{GB}} \right. = 1.17
\]

Taking for \( \delta_B \) the value of 1.75 given by SAPOVAL et al \((6)\), we note that \( \delta_{\text{GB}} \) is 2.92 at the melting point. This means that the movements of atoms along grain boundaries, at the melting point, concern widely a tridimensionnal space \( \delta = 3 \)

Now, it is interesting to see what happens at lower temperatures with impurities or chemical effects at grain boundaries.

4 - FRACTAL DIMENSION OF GRAIN BOUNDARIES IN ORDINARY METALS AND ALLOYS

We present some cases concerning polycrystals and high angle grain boundaries, limited to rare experimental cases where the terms

- \( P_{\text{GB}} \), \( D_B \), \( C_{\text{GB}} \) and \( C_B \)

have been correctly measured by different workers. \((\text{or the present author})\)

**First example**: GB diffusion of iron in Fe-S alloys \((11, 12)\)

The GB segregation of sulfur has been determined at 1123 K for different bulk concentrations and at the same time, \( D_B \) and \( P_{\text{GB}} \) have been measured with iron tracer \((\text{Fe}59)\). Table I gives, for the self-diffusion of iron, the dimensionality \( \delta_{\text{GB}} - \delta_B \).

For low sulfur content, \( \delta_{\text{GB}} \) is similar to a pure metal \( (1 + 1.75 = 2.75) \). For greater sulfur concentrations, we note a high value for \( \delta_{\text{GB}} \) concerning iron movements along grain boundaries and near the GB \( (\delta_{\text{GB}} = 3.55, 3.35) \). These high values for \( \delta_{\text{GB}} \) mean that the iron diffusion concerns a wider GB, without any reorganization of iron and sulfur atoms.

**Second example**: GB diffusion of sulfur in Cu alloys \((13)\)

AUFRAY has studied two different systems: Cu (Fe,S) and Cu (Ni,S). Diffusion coefficients and segregation of sulfur have been measured at 873 K.

The representation of \( \frac{P_{\text{GB}}}{D_B} \) versus \( \frac{C_{\text{GB}}}{C_B} \) shows an important difference of the two systems (Fig. 2):

For Cu (Fe,S) alloys, \( \delta_{\text{GB}} - \delta_B \approx 0.3 \), which gives for \( \delta_{\text{GB}} = 2.05 \)

For Cu (Ni,S) alloys, \( \delta_{\text{GB}} - \delta_B \) is unrealistic because \( \alpha = \frac{C_{\text{GB}}}{C_B} \) has a quasi-constant value, and cannot be taken as a correct parameter.

It may be concluded that the self-diffusion of S in \((\text{Cu-Fe-S})\) system concerns all the sites in the space of the grain boundaries, because \( \delta_{\text{GB}} = 2 \). In other words, moving atoms have used paths without no directive ways in the plane and with an important interaction between sulfur and iron particles during diffusion and cosegregation.

5 - CONCLUDING REMARKS

The description of the grain boundary diffusion by the fractal concept is a new approach in the study of elementary mechanism. It gives a characterization of the space in which moving atoms are present. Particularly, segregation effects which play an important role in diffusion kinetics can be used to describe a dynamic fractal dimension of grain boundaries at high temperatures. In future, it remains to analyse by this way the GB diffusion in bicrystals with selected crystallographic orientations under the influence of typical impurities interactions.

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TABLE I

GRAIN BOUNDARY DIFFUSION OF Iron in (Fe-S) alloys (11)(12)

<table>
<thead>
<tr>
<th>C_B(wt. ppm sulfur)</th>
<th>C_GB wt. ppm sulfur</th>
<th>C_GB (% iron)</th>
<th>P_GB(m^3/s^-1)</th>
<th>D_B (m^2/s^-1)</th>
<th>( \eta )<em>{GB} - ( \eta )</em>{B}</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>99</td>
<td>( 2 \times 10^{-19} )</td>
<td>( 1.5 \times 10^{-5} )</td>
<td>1</td>
</tr>
<tr>
<td>35</td>
<td>3</td>
<td>97</td>
<td>( 5 \times 10^{-20} )</td>
<td>( 1 \times 10^{-15} )</td>
<td>1.8</td>
</tr>
<tr>
<td>51</td>
<td>8</td>
<td>92</td>
<td>( 1.5 \times 10^{-20} )</td>
<td>( 1 \times 10^{-15} )</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Fig. 1: Picture of the grain boundary diffusion front of radiotracers with different mobility of atoms in the G.B. plane and in the bulk.
Fig. 2: Example of the variation of $\frac{P_{GB}}{D_B}$ versus $\frac{C_{GB}}{C_B}$ for sulfur in Cu-Fe-S and Cu-Ni-S alloys (13).