SEGREGATION AND DIFFUSION

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Résumé - Le but de cet article est de montrer que l’étude simultanée de l’équilibre de ségrégation et de la diffusion intergranulaire conduit à des informations importantes sur la structure et les propriétés des joints de grains dans les solides non élémentaires. Les techniques expérimentales sont rappelées brièvement ainsi que les résultats obtenus dans des solutions solides binaires ou ternaires à base de Cu, Ag ou Fe (polycristaux ou bicristaux). De l’ensemble de ces données les conclusions essentielles suivantes sont déduites :

- selon que la perturbation introduite par la ségrégation est faible (C$_{y}$ ou $\alpha$ petit) ou forte (C$_{y}$ et $\alpha$ grands), les joints de grains peuvent être décrits correctement soit par un modèle "3D" de solution solide diluée (ex. Ag(Sn)) soit par un modèle "2D" analogue à ceux adoptés en surface (ex. Ag(S), Fe(Sb)) ; dans le cas de solutés peu tensioactifs, il faut admettre qu’une partie des atomes ségrégés n’occupe pas les sites de plus hautes énergies, responsables de la diffusion intergranulaire ; en présence de deux solutés une coségrégation notable peut se manifester et modifier structure et composition des joints.

Abstract. - This paper is devoted to the new data on structure and properties of grain boundaries, which can be deduced from a simultaneous study of the segregation equilibrium and intergranular diffusion, in non elemental solids. The experimental means are briefly described as well as the results obtained in binary and ternary solid solutions made with Cu, Ag or Fe (poly-or bi-crystals). From all the experimental data, the following main conclusions are drawn : according as segregation is associated to a little ($\alpha$ or C$_y$ small), or large ($\alpha$ and C$_y$ large) perturbation, the grain boundaries can be described either with a "3D"model of dilute solid solution (i.e Ag(Sn)) or with a "2D" model similar to those used for the surface (i.e Ag(S), Fe(Sb)) ; when the solute in not tensioactive, a part of the segregated atoms is not localized on sites of highest energies used for intergranular diffusion ; when another solute is added, a noticeable co-segregation can occur and change the structure and composition of the grain boundaries.

I. INTRODUCTION

Presently, it is quite well understood how the transfer of matter occurs in a "good" single crystal ; diffusion measurement accounts for the species and number of point defects in the bulk. Conversely, when a polycrystalline material is involved, the problem is not so well solved ; thus, grain boundaries (g.b.) were early recognized to be preferential paths for atomic diffusion (1), nevertheless recent (2,3) reviews show off some discipancy between experimental results according to the temperature field, the material purity or the concentration of alloying elements. Therefore, there is an actual difficulty to connect diffusion to grain boundary structure, even in simple solids.
The origin of this situation can be found in the nature of the grain boundary, which can be summarized as follows:

a) the existence of a g.b. is drastically connected to the simultaneous presence of two different crystals.

b) at the atomic scale, a g.b. behaves like a transition between two crystals, which takes place on some interatomic distances; it is intermediate between an actual 3D medium and a 2D one.

c) the ratio of g.b. to bulk atoms is always very tiny.

d) at last, difference in composition must generally be taken into account between the bulk and the g.b. (or equilibrium segregation); it allows to fulfill the condition of constant free enthalpy everywhere in the experimental solids which are rarely free of foreign atoms (impurities or/and alloying elements). Hence, transfer of matter is always related to segregation, except when intergranular self diffusion ($\text{M}^*/\text{M}$) is studied in elemental samples of ultra high purity.

The purpose of this paper is to present experimental results performed in conditions where both g.b. diffusion and segregation are investigated and the main conclusions drawn from this set of experimental data, on the structure and properties of grain boundaries.

II. STUDYING MEANS

II.1. Equilibrium segregation

Equilibrium segregation occurs when no new 3D phase is allowed to precipitate in the g.b.; the segregated amount is then of the same order of magnitude as an atomic monolayer. Hence there is only few technical means for such studies; some of them allow to carry out together segregation and diffusion experiments; we will lay some emphasis to these last ones which are specially used in our laboratory.

The AUGER ELECTRON SPECTROSCOPY (A.E.S.) is the best known method whenever segregation involves intergranular brittleness. The surface analysis is performed after the sample has been fractured in the UHV apparatus; theoretically, it accounts for every foreign atom present on one side of the failure (e.g. Fe(Sn) (4)); the meaning of these data is very improved when the sample is simultaneously observed by Scanning Electron Microscopy (SEM) so as to only analyze the actual grain boundary fracture. (e.g. Fe(Sb), Fe(Sb,Ni) (5)).

Using RADIOELEMENTS is practically the only means to attain g.b. segregation when it does not involve g.b. brittleness. Two different methods were experienced in our laboratory and allowed to study sulfur segregation in Cu(6,7) and Ag(8) and nickel segregation in Ag(9,10).

The first one, known as "Flat Boundary Method" is schematically shown in fig. 1; a plate ($E \neq 2$ mm) and a thin platelet ($e \neq 50$ μm) of the same metal M (e.g. copper) are tightened each other, submitted to a small mechanical pressure and heated to high temperature so as to obtain a single sample by sintering; this treatment is performed either in the presence of pure hydrogen or in ultra high vacuum, to preserve the purity of the metal and the cleanliness of the interfaces. The synthetized boundary is made of a set of various grain boundaries very similar to grown-in boundaries, the surfaces of which are approximately parallel to the surface (6). A long diffusion treatment at constant temperature allows to introduce the radionative element $I^*$ in the neighborhood of the "flat boundary"; cutting the sample parallel to the surface, leads to the activity (A) - depth (y) graph (fig. 1b). It gives the bulk activity at any depth and the excess in activity due to segregation in the g.b. set ($A_{\text{max}} - A_{\text{p}}$).

The second method, represented in fig. 2, consists in a "Scanning Radioactive Analysis" at a constant depth (y). The sample is a bicrystal; the grain boundary and the external surface are roughly perpendicular and their intersection is very linear; the radionous element is
Fig 1: "Flat Boundary Method" for segregation measurement:
- preparation of the boundary,
- experimental activity (A) - depth (y) graph after a segregation treatment (S in Ag); A is expressed in arbitrary unit.

Fig 2: "Scanning Radioactive Analysis" for segregation measurement: a theoretical activity (A) - distance (x) profile for a segregated sample, when the slit moves from (1) to (3).

Introduced by diffusion at constant temperature. A very narrow slit (from 10 to 100 μm) is set parallel to the boundary and moves very slowly (about 1 μm/h) while the I* activity is measured past the slit. Recording this activity as a function of time, leads to the activity (A) - distance (x) graph; the activity increase near the boundary, generally takes into account both diffusion and segregation phenomena but when the diffusion treatment is long enough, this variation in activity only involves segregation (fig. 2b).

As far as these two methods are concerned, the measured activities are converted into I* concentration, owing to proper standardization. The bulk concentration is generally expressed in at.cm⁻³ (C_b). The grain boundary composition is either expressed in at.cm⁻² (C_g) or in at.cm⁻² (12) or in monolayer ratio (6); it amounts to approximating the g.b. medium to a 3D one (11) in the first case and to a 2D one in the last two cases. Thus, as far as segregation is concerned the g.b. properties can be compared either to the bulk or to the surface properties.

Note that a thickness of 5 Å is generally given to the g.b. when the concentration is expressed in at.cm⁻³.

II.2. Grain Boundary diffusion

When there is a radioelement of the diffusing species an usual method consists in following it in a polycrystalline sample or in a bicrystal after a diffusion anneal at a constant temperature. Cutting the sample into thin slices perpendicular to the diffusion direction gives the activity-depth (y) graph, similar to the mean concentration (C) - depth graph. To the extent that diffusion is not very different from an isotopic exchange, the penetration curve can be analyzed as follows:

- for small depths, only bulk diffusion from the surface is involved; it is characterized by the diffusion coefficient D_b and the concentration C_b.
- for large depths, an g.b. diffusion and a bulk diffusion from the g.b. are involved together; the first one is characterized by D_g > D_b.
and \( C_g^b = a c^b \); the second one by \( D^b \), \( C_g^b \) and \( c^b \). Applying Fick's law, allows to deduce from the penetration curve \( C = f(y) \) a parameter \( P \), characteristic of the mean transport, the expression of which depends on the g.b. model:

\[
P = \frac{(C_g^b/c^b)}{D_g^b} = \frac{D_g^b}{a^b} \quad \text{in the 3D model (13,14)}
\]

\[
P = \frac{r/c^b}{D_g^b} \quad \text{in the 2D model (15)}.
\]

In these relations the experimental parameter \( P \) involves the true g.b. coefficient and the segregation equilibrium. Isothermal curves \( P = f(c^b) \) are obtained when \( C^b \) is allowed to vary at constant temperature; but only the comparison between these curves and the segregation isotherms \( C_g^b = f(c^b) \) can lead to valid data relative to the g.b. diffusion coefficient \( D_g^b \), which is connected to the diffusion mechanism.

We will now review some diffusion and segregation studies recently carried out in high purity materials. Firstly the typical results will be given according to the studying means, then they will be analyzed as a whole in order to draw some conclusions as to the behaviour of grain boundaries.

### III. SEGREGATION AND DIFFUSION : EXPERIMENTAL RESULTS

#### III.1. Materials

Segregation and diffusion measurement was made in the following solid solutions:

- a) \( \text{Ag}^*(\text{Sn}^*) \), \( \text{Fe}^*(\text{Sn}^*) \), \( \text{Fe}(\text{Sb}^*) \), \( \text{Fe}(\text{Sb}^*,\text{Ni}) \)
- b) \( \text{Ag}^*(\text{S}^*) \), \( \text{Cu}^*(\text{S}^*) \), \( \text{Cu}(\text{Fe},\text{S}^*) \), \( \text{Cu}(\text{Ni},\text{S}^*) \)
- c) \( \text{Ag}^*(\text{Pb}) \), \( \text{Ag}(\text{Ni}^*) \)

Note that a star means that \( P \) was determined for this element; a subline means that interfacial segregation was studied. Except for Sn in Ag, the solubility limits are less than 2 at\% and sometimes very low (\( \approx 10^{-2} \) at\%) which is a suitable condition for segregation to occur (16).

In a) and b) alloys, the solubility is limited either by the formation of an intermetallic phase or by a sulfide (17); it roughly means that the attraction between different atoms is stronger than between atoms of the same kind. Conversely in c) alloys a demixtion takes place at the solubility limit, which roughly implies stronger mean interactions between atoms of the same kind than between different atoms.

#### III.2. Segregation and diffusion in brittle alloys : \( \text{Fe}(\text{Sn}) \) (4), \( \text{Fe}(\text{Sb}) \) and \( \text{Fe}(\text{Ni},\text{Sb}) \) (5).

Segregation and diffusion were studied in the same alloys; typical results are shown in Fig. 3. In all these alloys, the segregation equilibrium was followed by A.E.S. in "random" g.b.

In the binary solid solutions, segregation is characterized as follows:

- at low bulk concentration, the segregation coefficients are about 200,
- the g.b. is saturated for solute amounts of about a monolayer,
- the shape of the isotherms (Foxler) accounts for attractive interactions between atoms in the g.b.

Add some nickel (1 or 2 \%at.) in \( \text{Fe}(\text{Sb}) \) alloys, considerably steepened the isotherms; the saturation of the g.b. takes place at lower bulk concentration and Ni coverage linearly increases with Sb coverage, when the Ni bulk concentration is kept constant. It means that a cosegregation Sb-Ni takes place in the boundary.

It results from the correlation between the segregation and diffusion isotherms that the same sites are probably concerned by these two phenomena, which usually enables to calculate \( D_g^b \) from experimental \( P \).
and g values. However, accurate values of \( D_{gb} \) cannot be calculated; indeed, several assumptions must be made to deduce the g.b. composition from the A.E.S. measures: one of them concerns the g.b. model and another the sharing of the segregated amount, when the sample is fractured. Nevertheless, the analysis of \( P_{Fe} \) and \( P_{Sn(Sb)} \) variations shows off the following points:

- In pure iron, the Sn or Sb diffusion coefficients are less than the self diffusion ones:
  \[ D_{gb,Fe}^{Sn(Sb)} < D_{gb,Fe} \]

- In binary alloys, both the coefficients \( D_{Fe}^{gb} \) and \( D_{Sn}^{gb} \) decrease a lot as the segregated amount increases.

- In ternary alloys, the Sb g.b. coefficient decreases with the addition of Nickel, when the Sb bulk concentration is kept constant; it does not change when the g.b. Sb coverage remains constant.

This set of g.b. segregation and diffusion results, implies strong interactions between the g.b. atoms; thus segregation cannot simply consist in a random substitution of solvant atoms to solute ones, at least when the segregated amount is greater than some % of a monolayer; it seems necessary to assume that segregation involves structure modification so that solvent and solute atoms are strongly bound and have similar roles in the g.b. (10).

III.3. Sulfur diffusion and segregation in copper and silver

\[ \text{Cu(S)} \ (6,7), \text{Ag(S)} \ (8), \text{Cu(Fe,S)} \ (9,18), \text{Cu(Ni,S)} \text{ and Ag(Ni,S)} \ (19) \]

It was never shown any embrittlement due to sulfur dissolved in high purity copper and silver; however a comparison between the grain boundaries and the surface enables us to think to very large g.b. segregation (20,21).

Segregation and diffusion were studied under conditions such as sulfur is introduced through the gaseous phase; this experienced device (20) allows to perfectly control the sulfur chemical potential and to preserve or even improve the cleanliness of the samples; moreover it allows to realize diffusion experiments which consist in an isotopic substitution of inactive atoms by radioactive ones, whithout any other change.

The first experimental isotherm for equilibrium segregation at g.b. in a non brittle alloy, was realized in Ag polycrystals (8); it is represented in Fig. 4 and compared to the superficial one, deduced from (21):

- g.b. segregation occurs in the same range of bulk concentration as surface adsorption, that is to say, very far below the solubility
**Fig 4**: Equilibrium sulfur segregation in silver: surface and grain boundary isotherms at 550°C.

**Fig 5**: Grain boundary sulfur diffusion in silver: variation of $\alpha D_{gb}$ with the bulk concentration.

**Fig 6**: Bulk and grain boundary diffusion in silver: variation with $1/T$. 
limit. It is related to a great stability for segregated sulfur compared to sulfur in silver sulfide; this excess of stability is about - 27 \text{kJ mole}^{-1} \text{ at 550°C.}

- at very low concentration the segregation coefficient remains constant and is about 10000 at 500°C. In this field, the segregation enthalpy is found about 65 \text{kJ mole}^{-1} \text{ in silver (8) as well as in copper (6).}

- the g.b. segregated amount reaches half a surface monolayer that is about one sulfur atom for five silver atoms.

- the shape of the isotherm (Langmuir) is consistent with small interactions in the boundary. Note however that in a "random" bicrystal (18), the segregation is far more greater than in a polycrystalline sample; conversely, in a twin crystal, \( \alpha \) is very small (7):

\[ \alpha \text{twin cryst.} < \alpha \text{polycryst.} < \alpha \text{rand. bicryst.} \]

Thus the shape of the isotherm only reflects a mean behaviour of a set of various g.b.

Add a metallic solute, changes the surface and g.b. segregation in the same way (19); in copper for instance, 1% of nickel only increases \( \alpha \) from 10000 to 15000 while 2% of iron increases \( \alpha \) from 10000 to 72000 (18); hence it is concluded that cosegregation in \( \text{M(Ni,S)} \) solutions is favored by a large chemical activity of \( \text{M'} \) and \( \text{M}^4\text{S} \) chemical bonds stronger than \( \text{M-S} \) ones.

Sulfur diffusion experiments give two kinds of informations: variation of the diffusion parameter \( \alpha \text{Dg}^b \) with the bulk concentration (fig. 5) and temperature dependance of the g.b. diffusion. Note that in silver the experiments were performed at constant amount of segregated sulfur from 500 to 700°C so that the actual variation of \( \text{Dg}^b \) is reached (fig. 6).

Within the frame of this paper the most interesting conclusions are the following ones:

- it comes from the comparison of the segregation isotherm to the diffusion one that the same sites are certainly involved in the two cases.

- the very small diffusion coefficients \( \text{Dg}^b \ll \text{Dg}^b \) must be related to very strong Ag-S interactions in the g.b., similar to those involved on the surface. It is emphasized when diffusion occurs in cosegregated \( \text{Cu(Fe,S)} \) alloys (19).

Thus, generally speaking, a comparison of g.b. segregation to the surface adsorption is very fruitful: hence some resemblance of the g.b. segregated phase to a 2D sulfide is more credible than to a 3D solid solution.

### III.4. Grain boundary diffusion in \( \text{Ag(Sn)} \) alloys (22)

These alloys are not brittle and the segregation not large enough to use a radiochemical technique. Diffusion is the only means to reach segregation to the extent that the diffusion parameter \( P \) depends on the g.b. composition.

Sn and Ag diffusion was studied in series of alloys (0-6% at.Sn), at different temperatures. Typical variation of \( P_{\text{Sn}} \) and \( P_{\text{Ag}} \) are represented in Fig. 7:

- tin diffusivity is always greater than silver one.
- the variations of \( P_{\text{Sn}} \) and \( P_{\text{Ag}} \) with \( C^b \) show off two different domains with the same limit (\( C^b \) for solute) for the solvate and the solute
  - when \( C^b_{\text{Sn}} < (C^b_{\text{Sn}})_{\text{lim}} \), \( P_{\text{Ag}} \) and \( P_{\text{Sn}} \) linearly increase; when
  - \( C^b_{\text{Sn}} > (C^b_{\text{Sn}})_{\text{lim}} \), \( P_{\text{Ag}} \) remains constant while \( P_{\text{Sn}} \) varies in inverse proportion to \( C^b_{\text{Sn}} \).
A careful analysis of these data leads to the conclusion that only a small tin segregation coefficient, evaluated to $a \approx 30$, explains all the results; a g.b. saturation takes place at bulk concentrations far below the solubility limit. Comparing the g.b. to a 3D solid solution leads, on one hand, to attractive tin - vacancy interactions and on the other hand, to Ag-Sn interactions stronger in the g.b. than in the bulk; it takes into account all the experimental results.

III.5. Grain boundary diffusion and segregation in Ag(Ni) alloys (10)

A large g.b. Ni segregation was found ($a \approx 3000$), but the g.b. diffusion was only little influenced by this segregation. This result was explained by assuming that a fraction of the segregated nickel is not involved in diffusion; it is in good agreement with a recent study of Ni segregation on silver surfaces (23), which leads to a particular model to account for large segregation of low tensioactive solute (24) such as nickel. There, a lot of the segregated element is localized just below the surface plane in order to allow large segregation without a noticeable increase of the surface tension.

IV. CONCLUSIONS

It seems difficult to simply relate segregation, diffusion and g.b. properties from these different experimental studies; for instance, a large nickel segregation less influences the grain boundary diffusion in silver than a small tin segregation; sulfur segregation does not produce embrittlement of copper while antimony does in iron when the segregated amount is of the same order of magnitude.

Taking into account the perturbation due to segregation, enables us to better understand the g.b. behaviour:
when segregation is associated to a little perturbation (α or \( \sigma_{gb} \) small), the grain boundary can be compared to a substitutional dilute solution; the g.b. properties are not very influenced by segregation; a 3D usual model correctly describes what happens in the g.b. .

when segregation is associated to a large perturbation (α and \( \sigma_{gb} \) large), it is no longer valid to consider a random distribution of the solute in the grain boundary and to analyze the variation of diffusivity with a model related to a pure metal. A comparison with the 2D structures observed (Ag(S), Cu(S), Ag(Ni), Ag(Pb)) or proposed on the surface, is then more credible. These ones are much more connected to the structures of 3D ordered phases limiting the solubility than to dilute solid solutions. The decrease of the intergranular diffusion coefficients which accompanies segregation in different alloys (Ag(S), Cu(S), Cu(Fe,S), Fe(Sn), Fe(Sb), Ag(Pb)), can then be explained by the presence in the grain boundary of small 2D-like islands, where solvant and solute atoms are strongly tied and hardly move. In Ag(Ni) alloys, a little influence on diffusion of the large segregation is explained by the fact that a part of the segregated atoms is not localized on sites of highest energies used for intergranular diffusion. Observations with a scanning electron microscopes, have been made after some mechanical tests; they are in good agreement with this comprehensive view on the grain boundaries in dilute solid solutions.

In this case the g.b. properties depends on the amount of the segregated element(s) and on the nature of the chemical bound in the grain boundaries.

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DISCUSSION

N.L. PETERSON: Can you comment on the value of $\alpha$ for different types of boundaries; tilt boundaries, twist boundaries, boundaries with different $\theta$?

F. CABANE-BROUTY: We had only recently, a method available for bicrystal (Scanning Radioactive Analysis), and it is somewhat difficult to have very linear grain boundaries in metals; thus we only performed few experiments in the bicrystals which the assumption previously made, that segregation is very small in twin boundary and very high in large angle boundaries; moreover, when 2at% of iron is added to copper, (Fe-S) cosegregation occurs in the twin boundary as well as in the large angle boundaries (7).

V. VITEK: You mentioned you need a fracture model in order to determine the diffusion coefficient. Could you elaborate on this point?

F. CABANE-BROUTY: When A.E.S. is used to determine the segregated amount, the measure is only performed on one side of the fracture; the question is, what happens to the segregated amount when fracture occurs: is it equally divided into the two new surfaces or not? The answer to this question amounts to taking a fracture model. In fact, some informations (from our work and other ones), seem in agreement with a "half and half" distribution; for instance, the A.E.S. signal is not very different from one g.b. to the other for Sb in Fe (Sb) alloys. Thus we use this assumption to calculate the segregation coefficient from A.E.S. measures.

C.L. BRIANT: This comment is in regard to the fracture path down a segregated grain boundary. We have found in our laboratory that when both sides of a fracture surface are analyzed, the splitting in the amount of solute is very close to 50% in each side. Therefore doubling the value obtained from one side appears to be a good approximation.
P. GUIRALDENQ : Avez-vous eu l'occasion d'observer au microscope électronique si, lors des expériences de "diffusion — segregation", il apparaît de nouveaux défauts au voisinage des joints de grains (Kirkendall effect) lorsque le système choisi pourrait favoriser une telle évolution de la structure?

F. CABANE-BROUTY : We only had microscopic observations with a Scanning Electron Microscope, so as to look at the aspect of the grain boundaries either in the "flat boundary" or in polycrystals; we had not satisfying conditions to observe new kind of defects, or change in the defect concentration due to segregation; nevertheless, we would like to observe controlled segregated grain boundaries under conditions where changes in the structure due to segregation could be seen.