Scripta Materialia 120 (2016) 90–93

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular Article

A methodology for the measurement of the interfacial excess of solute at a grain boundary

P. Maugis *, K. Hoummada

Aix-Marseille University, Toulon University, CNRS, IM2NP UMR 7334, Av. Escadrille Normandie Niemen, Case 142, 13397 Marseille, France

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form 21 March 2016
Accepted 4 April 2016
Available online xxxx

Keywords:
Interface segregation
Atom probe tomography
Dual phase steel

ABSTRACT

Segregation of solutes on grain boundaries is usually quantified by the peak value of the concentration profile measured across the grain boundary. This procedure is inadequate both from the theoretical and from the practical point of view. Instead, we put forward the concept of interfacial excess of solute, as having a thermodynamic background and being of operative efficiency. Our analyses reveal carbon and boron co-segregation at a martensite lath boundary of a Dual Phase steel.

Segregation of solute atoms on structural defects such as grain boundaries is known to have various impacts on the properties of solids. A well-known example is temper embrittlement by phosphorous segregation at the grain boundaries of ferrite [1]. Also, through the decrease in the interfacial energy, segregation may reduce the rate of subsequent heterogeneous precipitation at grain boundaries, as boron does in austenite [2]. The amount of segregation is usually quantified experimentally by measuring a concentration profile across the boundary by means of a local probe [3,4,5,6]. The peak value of this profile is claimed to be representative of the amount of interface segregation. This procedure has been proven to be inadequate (i) because the value of the peak concentration depends on the spatial resolution of the characterization process and (ii) because the peak concentration is not a proper thermodynamic variable [7]. To overcome those drawbacks, we recommend measuring the interfacial excess of solute from a concentration profile instead. The concept is of simple implementation via the integral profile and has a firm thermodynamic background. Krakauer [8] determined by APFIM the excess number of solutes from integral profiles in the case of grain boundaries in a Fe(Si) alloy. Their theoretical approach is presented in the general case of a heterophase interface, where the mathematical derivation is complex. In order to promote the use of excess number of solute by the community, we present in this paper the simpler case of adjacent grains sharing the same composition. The method is applied to a lath boundary in the martensite of a Dual Phase steel, revealing carbon and boron co-segregation.

In the paper, we will consider the case of a grain boundary, although the analysis is general to homophase boundaries such as sub-grain boundaries, stacking faults or twin boundaries. Also, for clarity, we restrict this presentation to a unique solute, since generalization to several solutes is straightforward. Equilibrium segregation of a solute is manifested as a non-uniform concentration distribution in the immediate vicinity of the interface, presenting a surplus of solute atoms. For simplicity, let us consider first a rectangular concentration profile $C(z)$ (in atoms per unit volume) normal to the boundary, and consisting of a flat peak at C^{max} over a short distance l, neighbored by uniform concentrations C^{∞} in the adjacent grains. That profile will be called the "real concentration profile" (Fig. 1a). Measurement of this profile usually involves a local probe analysis, limited in spatial resolution both longitudinally (along z) and laterally (along the interface plane). Unless atomic-scale resolution is achieved, e.g. by High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) [9], the real profile cannot be retrieved experimentally, and the measured profile is dampened and spread out along the z-axis. In addition, at the scale of the lateral resolution of the technique, the boundary is not necessarily flat, so that its roughness creates additional blunt. Consequently, the original rectangular profile will appear through the chemical analysis as a diffuse distribution of solutes. The width of the distribution will be larger when the resolution is poorer, and its height will be smaller, as illustrated in Fig. 1a. From this example, it is apparent that the measured peak concentration is dependent on the spatial resolution of the characterization technique. Therefore, the peak concentration cannot be considered as a physical parameter representative of the real profile. It cannot be compared between different characterization techniques, having different spatial resolutions. However, and this is

---

* Corresponding author.
E-mail address: philippe.maugis@im2np.fr (P. Maugis).

http://dx.doi.org/10.1016/j.scriptamat.2016.04.005
1359-6462/

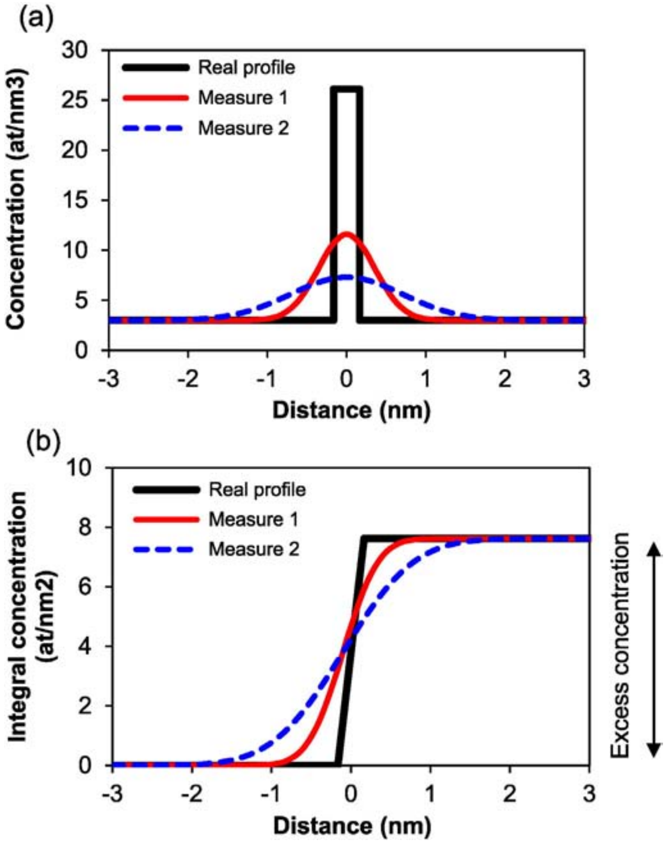

Fig. 1. Principle for calculating the excess concentration of a solute. (a) When analyzing the real profile, measure 2 has a poorer resolution than measure 1, resulting in a smaller peak concentration. (b) The excess concentration calculated from the integral concentration profiles is however identical in both cases to the real one. The origin of the distance axis is arbitrary.

the clue to our problem, the total amount of solute in surplus in the vicinity of the interface as reference to the neighboring grains is resolution-independent. That quantity is precisely the excess interfacial concentration of the solute C^{ex} and can be calculated from the concentration profile: it is the integral of $C(z) - C^{\infty}$, where C^{∞} is the concentration far from the interface (Eq. (1)),

$$C^{ex} = \int_{-L/2}^{+L/2} (C(z) - C^{\infty}) dz. \tag{1}$$

C^{ex} is independent on the integration range as long as L is large enough to embed the whole region of non-homogeneity. As C(z) is in atoms per unit volume, the unit of C^{ex} is atoms per unit area of the interface. Graphically, it is the area situated between the concentration profile and the horizontal line at $C = C^{\infty}$. Notice that for the rectangular profile considered above, $C^{ex} = (C^{max} - C^{\infty})l$. In practice, C^{ex} is easily determined by plotting the integral concentration curve, i.e. the integral of $C(z) - C^{\infty}$ from $-L/2$ up to z. Then the excess concentration is the asymptotic value of the integral when z is large enough (Fig. 1b).

The excess concentration has the advantages of being independent on the apparatus spatial resolution and can thus be compared between different characterization techniques. One can check easily that it is also independent on surface roughness, alignment of the z-axis relative to the interface normal, sampling of the points of measure, numerical smoothing (at least conservative) and other operative details. Finely, it is worth noting that in the case of grain boundaries, the excess concentration as defined by Eq. (1) does not need reference to any precise interface position.

In his theory of capillarity [10], J. W. Gibbs introduced the variable Γ denoted “superficial density of a component” at a dividing interface. When transposed to a homophase boundary, Γ is the surplus of solutes per unit area of the defect at equilibrium, with reference to the material without the defect. Wagner [11] cited in [12] gives an equivalent interpretation that can be summarized as follows: Γ is the number of solute atoms per unit area that have been brought from the grains (as a reservoir) to the interface to ensure equilibrium during the creation of the interface. Therefore, Γ is the excess concentration of solute introduced in Eq. (1) [13,14,15]. The Gibbs adsorption isotherm (Eq. (2)) expresses how the excess concentration of component i is related to the variation in the interface energy γ accompanying a variation in the chemical potential μ_i of the component:

$$\Gamma_i = -\left(\frac{\partial \gamma}{\partial \mu_i}\right)_{T, \mu_{j \neq i}} = C_i^{ex}. \tag{2}$$

The excess concentration is positive for solutes that induce a decrease in the interface energy. In that case, the solutes have a tendency to segregate in the interfacial region. C^{ex} is negative in the opposite case, for solutes that have the tendency to deplete the interfacial region. Eq. (2) proves that Γ is independent of a precise position of the interface. This is of importance, since a grain boundary is impossible to locate in common situations: (i) when the interface is revealed only by the segregated elements through a diffuse concentration profile (e.g. with APT [16] or nanoSIMS) (ii) when the interface is rough at the scale of the probe, or (iii) when segregation is multilayered or diffuse.

Depending on the characterization technique in use and the choice of the subsequent data analysis, the excess of solute can be quantified by alternative variables, all related to Γ. If atom fraction X is used, the excess fraction (in length unit) can be computed from Eq. (3), provided that the atomic volume V_{at} is uniform along the profile:

$$V_{at}\Gamma = \int_{-L/2}^{+L/2} (X(z) - X^{\infty}) dz = X^{ex}. \tag{3}$$

From Eq. (3), X^{ex} is the area under the profile $X(z) - X^{\infty}$. Notice that, when expressed in nanometers, this quantity can be seen as the excess of solute arising from an ideal rectangular profile: (i) solutes of fraction X^{ex} uniformly distributed over a distance of 1 nm, or equivalently (ii) solutes of fraction 1 over the distance X^{ex}.

With the Atom Probe Tomography technique (APT), the numbers of solute and solvent atoms are directly accessible from a reconstructed volume. It is also the case for numerical simulations at the atomic scale such as Atomic-scale Monte Carlo (AMC), and Molecular Dynamics (MD). In those cases, it is useful to express the excess concentration as a finite summation (Eq. (4)) [7]:

$$C^{ex} = \frac{1}{A} \sum\nolimits_p (N^p - N^{\infty}) \tag{4}$$

where N^p is the number of solute atoms contained in slice p of a measuring box, N^{∞} is the number of solute atoms in a similar slice far from the defect, and A is the base area of the measuring box. Notice that ΣN^{∞} is simply the number of solute atoms contained in an identical box located in one of the adjacent grains. Both summations can be calculated from an integral profile plotted versus the cumulated number of atoms. Then AC^{ex} is the asymptotic value of the sum in Eq. (4) when p is large. This procedure is at slight variance of that proposed by Krakauer [8], but yields identical results.

Γ is a physical parameter entering various equations of theoretical interest and practical use. For example, the interfacial energy – which is also an excess variable – is related to Γ via the adsorption equation [13]:

$$d\gamma = -SdT + \sum\nolimits_i \Gamma_i d\mu_i. \tag{5}$$