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Interfacial segregation and grain boundary embrittlement: An overview and critical assessment of experimental data and calculated results

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ABSTRACT

One of the most dangerous technical failures of materials is intergranular brittle fracture (temper embrittlement) as it proceeds very quickly and its appearance is often hardly predictable. It is known that this phenomenon is closely related to the chemistry of grain boundaries and to the difference of the segregation energies of the grain boundaries and the free surfaces (Rice–Wang model). To elucidate the effect of individual solutes on embrittlement of various materials such as steels and nickel-base superalloys, grain boundary and surface segregation was extensively studied in many laboratories. As a result, numerous data on surface and grain boundary segregation have been gathered in literature. They were obtained in two main ways, by computer simulations and from experiments. Consequently, these results are frequently applied to quantify the embrittling potency of individual solutes. Unfortunately, the values of the segregation energy of a solute at grain boundaries as well as at the surfaces obtained by various authors sometimes differ by more than one order of magnitude: such a difference is unacceptable as it cannot provide us with representative view on the problem of material temper embrittlement. In some cases it seems that these values do not properly reflect physical reality or are incorrectly interpreted. Due to the above mentioned large scatter of the segregation and embrittlement data a critical assessment of the literature results is highly needed which would enable the reader to avoid both the well known and less well known pitfalls in this field. Here we summarize the available data on interfacial segregation and embrittlement of various solutes in nickel and bcc iron and critically discuss their reliability, assessing also limitations of individual approaches employed to determine the values of segregation and strengthening/embrittling energies, such as density functional theory, Monte Carlo method, molecular statics and dynamics and tight binding on the theoretical side, and Auger electron spectroscopy, 3D tomographic atom probe, and electron microscopy techniques on the experimental side. We show that experimental methods have serious limitations which can be overcome by accepting reasonable assumptions and models. On the other hand, the theoretical approaches are limited by the size of the computational repeat cell used for the calculations of the segregation energy. In both cases, a careful critical analysis of the available segregation energy and/or enthalpy reflecting physical reality allows to assess the reliability of these values and their applicability in analysis of intergranular brittle fracture in steels and nickel-base alloys.

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Contents

1. Introduction

Solute segregation at grain boundaries and free surfaces which is characterized by changed chemical composition at nanoscale [1] is a very important phenomenon because it affects the behavior of polycrystalline materials used in technical applications. For example, the grain boundary segregation often causes loss of cohesion resulting in brittle intergranular fracture under loading what consequently limits practical use of the materials. It may also be detrimental for corrosive properties, strongly affects grain growth and thus recrystallization. On the other hand, grain boundary segregation can stabilize the grain size in nanocrystalline materials (e.g. [2]) and may be used for design of interfaces (e.g. [3]). The surface segregation improves catalytic ability and, therefore, chemical reactions in a wide spectrum of systems [1,4].

Early efforts to study the surface and grain boundary segregation were experimental. They were focused mainly on measurements of averaged composition at a given temperature for a variety of grain boundaries or surfaces in polycrystals of selected materials (for a review see e.g. [5]). However, such data represent a specific case related to a material of a given composition and its thermal treatment (i.e. annealing temperature) without crystallographic specification of the interfaces [1]. Later the attempts were made to determine the thermodynamic parameters of segregation: free energy or enthalpy, and entropy, which represent the most general data. In the case of grain boundaries, a vast majority of these values were obtained for bcc iron since ferritic steels are basic construction materials [1,4]. Only rarely such data were obtained for other hosts despite the fact that, for example, application of aluminum or nickel base alloys has been rapidly increasing in the last decades. The absence of such studies for other materials may be a consequence of the fact that grain boundary segregation was not considered to cause such extensive embrittlement as in the case of iron and steels. Recently, the values of the segregation enthalpy and entropy have been systematically determined for individual grain boundaries in bicrystals (for a review see [1]) which represent the data of clear physical meaning [6].

Let us note that in the case of the grain boundary segregation, the choice of the studied systems was oriented rather to brittle materials because majority of experimental techniques used to detect grain boundary segregation (so called *surface analysis techniques*, for example Auger electron spectroscopy (AES) as the most frequently used technique to study grain boundary chemistry) need to open the boundary by intergranular brittle fracture [1]. Therefore, non-brittle systems were principally omitted in these studies. Only recently the application of "non-destructive" techniques such as 3-dimensional atom probe tomography (3D APT) [7] or high-resolution transmission electron microscopy (HRTEM) equipped with a chemical analyzer, e.g. on the basis of electron energy loss spectroscope (EELS) [8], offers a possibility to study solute segregation in specific non-brittle systems [1].

In the last decades the surface and grain boundary compositions have also been investigated theoretically (see e.g. [1]). Similarly to experimental approaches, these calculations are also limited by the possibilities of the computing techniques. Very