Computational Materials Science 111 (2016) 503–512

Contents lists available at ScienceDirect

Computational Materials Science

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

Impurity and alloying elements on grain surface in iron: Periodic dependence of binding energy on atomic number and influence on wear resistance

Yuri F. Migal [a,*], Vladimir I. Kolesnikov [b], Igor V. Kolesnikov [b]

[a] Southern Scientific Center of Russian Academy of Sciences, Rostov-on-Don, Russia
[b] Rostov State Transport University, Rostov-on-Don, Russia

ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form 28 September 2015
Accepted 1 October 2015
Available online 18 October 2015

Keywords:
Iron
Grain boundary
Compatibility of elements
Wear resistance
DFT

ABSTRACT

A quantum chemical analysis of interaction of impurity and alloying elements with grain surface in iron is carried out. The elements of the first five periods (from hydrogen to xenon) are considered. The cluster and slab models are used. Within these models the boundary between grains is imitated by a multilayered system including atoms of two neighboring grains of iron and a layer of the impurity (alloying) atoms between them. Grain surfaces with the Miller indices (100) and (110) are considered. The energy needed for disintegration (decohesion) of the system into two parts is determined. It is shown that dependence of decohesion energy of the system on atomic number of the impurity (alloying) atoms is of the same type for different models. It testifies to opportunity of studying such dependence by means of simple models and carrying out on this basis a classification of elements based on their ability to strengthen grain boundaries. The produced estimates of compatibility of the elements with iron on grain boundaries in steel agree with the known experimental data and correspond to Mendeleev's periodic law. Possibilities of diffusion introduction of the strengthening elements into steel surface layers with a view to increase their wear resistance are discussed. The discovered dependences can be used for the prediction of wear resistance and strength properties of polycrystalline materials with various alloying additives.

1. Introduction

Wear resistance of steel and other polycrystalline materials is known to be determined to a large extent by the properties of boundaries between grains in surface layers. Although the structure of grains of these layers can essentially differ from the structure of grains in the inner domains of polycrystals, in either case the destruction mechanism is look-alike in general. One of the reasons for the destruction of polycrystals mentioned in literature is grain boundary segregation, during which atoms of alloying and impurity elements come out of the bulk of grains to their surface. As a result the bond between grains can weaken. This idea was put forward long ago, but in spite of numerous experimental studies of the grain boundary segregation, at the moment the relation between this phenomenon and the destruction mechanism of polycrystalline materials has not been completely ascertained yet.

There are different points of view on how segregated atoms affect the destruction (see, e.g., [1,2]). One of the hypotheses is based on the fact that in the course of grain boundary segregation the metal–metal bond is replaced by a weaker or stronger metal-segregated atom bond [1]. To confirm the hypothesis, the estimates of energy amount required to break the grain bond were carried out in [2]. It should be noted that the data connected only with the sublimation enthalpy and atom sizes of the substances under test were used in [2]. Fig. 1 represents a graph of grain boundary embrittlement, plotted in accordance with the data from [2] for the basic materials (matrix) and segregated elements. If iron is used as the matrix, then all the elements located above the dotted line on the graph (e.g., carbon and molybdenum) increase the grain bond strength, and the elements located below (e.g., phosphorus, copper and sulfur), on the contrary, reduce the bond strength (these elements also embrittle iron). The degree of this effect depends on the distance between the point of the respective element on the graph and the dotted line.

It is astonishing that results of these estimates, despite the simplicity of the approach, basically agree with the known experimental data related to steel embrittlement (see [1]). This fact makes it possible to suppose that the amount of energy of atom binding determines to a large extent the ability of segregated

* Corresponding author.
E-mail address: ymigal@mail.ru (Y.F. Migal).

http://dx.doi.org/10.1016/j.commatsci.2015.10.003
0927-0256/

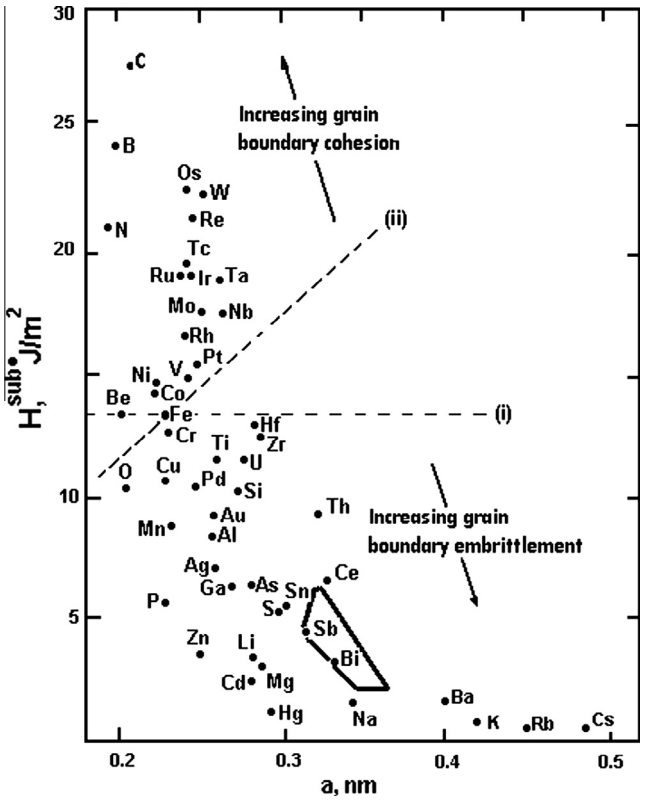

Fig. 1. A graph of grain boundary embrittlement, built according to the data from [2].

atoms to weaken or strengthen grain boundaries. However, in view of the assumptions made as the basis for the calculations, such conclusion needs an experimental confirmation and/or further study.

A lot of experimental (see, e.g., [3–6]) and the theoretical [7–13] works devoted to the problem of segregation has been published in the last two decades. They have made significant progress in the study of grain boundary properties. The authors of theoretical studies examined the segregation of H, B, C, S, P, Mn and some other elements. In these works, in particular, the strengthening or weakening influence of the elements on boundaries at various arrangements of atoms of these elements on boundaries has been studied. The received results are coordinated generally with empirical information on properties of the studied elements, in particular, in steel. However, now there are no works in which data on separate elements would be generalized and a classification of a big group of elements based on their ability to influence the boundary strength would be carried out by means of the theoretical principles. Obviously, such a problem posing is admissible because in practice some approximate classification of elements exists and is quite widely used. For example, it is known that vanadium strengthens iron, and sulfur weakens. Evidently, the task of theoretical research is the clarification of reasons of similar properties and the systematization of all elements of the periodic table based on their ability to influence the boundary strength.

In our previous works [14–17] we have attempted to carry out the systematic analysis of the strengthening properties of a big group of elements (from hydrogen to krypton). We used two simple models (cluster and slab models), and with their help it was shown that the studied effect is rather strong, and already such models allow us to predict on the semi-quantitative level influence of the elements on strength of boundaries in steel. The main result consists in the fact that the dependence of strength of bonds between impurity atoms and iron surface on atomic number of impurity is similar for different approximations and different positions of atoms relative to a grain surface. In particular, such dependence is similar in case of two essentially different situations, for adsorbed and segregated atoms. This fact correlates with Seah's argumentation as he estimated the grain boundary embrittlement by means of sublimation data.

It is known that grain boundaries are destroyed at surfaces of grains. The whole complex of the above-stated facts allows us to assume that pair interactions Fe–X on grain surfaces are defining in estimating boundary strength. (The symbol X here and further means an impurity or alloying element.) The analysis of these interactions by using simple models showed that there is a possibility to carry out the classification of chemical elements by considering their ability to strengthen grain boundaries. Of course, it is a question of the chemical component of such strengthening because the strengthening is a multifactor problem (see below).

In this work we continue the systematic research of interaction of atoms of various elements with a grain surface of iron. Firstly, the number of objects studied is significantly increased, calculations are carried out for the fifth period whose elements are used often as alloying elements in steel. Secondly, the comparison of two various positions of impurity atoms on boundary surfaces with the Miller indices (011) and (001) in steel is carried out. Thirdly, the obtained data are compared with experimental facts known from literature.

We suppose that received results can be used for the prediction of wear resistance and strength properties of polycrystalline materials with various alloying additives.

2. Binding energy of clusters containing adsorbed and segregated atoms

Let us consider grain boundaries in ferritic steel with the body-centered crystal lattice, typical for steel at regular temperatures. In the capacity of a boundary model we consider the thin layer of impurity atoms located between two parallel flat grain surfaces. Of course, such a construction is not a model of a boundary in a strict sense. A boundary, as is known, has very complex structure (see, e.g., [18]). In our model we do not try to take into account the variety of conditions that are significant for segregation and wear resistance (including, e.g., crystallite surface irregularities, the non-parallel nature of surfaces, dislocations, etc.). The main purpose of the model proposed is, firstly, to evaluate the effect of the closest atomic surrounding on the chemical bond between segregated atoms and matrix atoms on the grain boundary, and, secondly, to determine how the bond affects the strength of microscopic domains and surface layers of polycrystals. As it was already noted above, interaction of impurity atoms with grain surfaces is defining in estimating boundary strength. In the capacity of grain surfaces on which impurity atoms are located we choose surfaces (100) and (110) of the bcc structure having the greatest density of Fe atoms. It is natural to expect that interaction of impurity atoms with configurations of Fe atoms, characteristic for such surfaces, makes the greatest contribution to bond strength.

At the beginning we consider grains with bcc (100) surface and use the cluster model. A 30-atom cluster $Fe_{13}X_4Fe_{13}$ which imitates in our calculations the grain boundary between two such surfaces is shown in the left-hand section of Fig. 2. The cluster includes five horizontal layers. Two top and two bottom layers are composed of iron atoms, and the middle layer contain atoms of the elements *X* which appear on the boundary due to the phenomena of grain boundary segregation and intergranular diffusion. We shall call it a segregation cluster.