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Diffusion behavior in Nickel–Aluminum and Aluminum–Uranium diluted alloys

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ABSTRACT

Impurity diffusion coefficients are entirely obtained from a low cost classical molecular statics technique (CMST). In particular, we show how CMST is appropriate in order to describe the impurity diffusion behavior mediated by a vacancy mechanism. In the context of the five-frequency model, CMST allows to calculate all the microscopic parameters, namely: the free energy of vacancy formation, the vacancy-solute binding energy and the involved jump frequencies, from them, we obtain the macroscopic transport magnitudes such as: correlation factor, solvent-enhancement factor, Onsager and diffusion coefficients. Specifically, we perform our calculations in f.c.c. diluted *Ni–Al* and *Al–U* alloys. Results for the tracer diffusion coefficients of solvent and solute species are in agreement with available experimental data for both systems. We conclude that in *Ni–Al* and *Al–U* systems solute atoms migrate by direct interchange with vacancies in all the temperature range where there are available experimental data. In the *Al–U* case, a vacancy drag mechanism could occur at temperatures below 550 K.

1. Introduction

The low enrichment of *U*–Mo alloy dispersed in an *Al* matrix is a prototype for new experimental nuclear fuels [1]. When these metals are brought into contact, diffusion in the $Al/U{-}Mo$ interface gives rise to interaction phases. Also, when subjected to temperature and neutron radiation, phase transformation from γU to αU occurs and intermetallic phases develop in the U–Mo/Al interaction zone. Fission gas pores nucleate in these new phases during service producing swelling and deteriorating the alloy properties [1,2]. An important technological goal is to delay or directly avoid undesirable phase formation by inhibiting interdiffusion of *Al* and *U* components. Some of these compounds are believed to be responsible for degradation of properties [3].

Housseau et al. [4], based on the effective diffusion coefficients values calculated from their experimental permeation tests, have demonstrated that these undesirable phases have not influence on the mobility of *U* in *Al*. On the other hand, Bierlin and Green [5] have reported the activation energy values of *U* mobility in *Al*, based on the maximum rate of penetration of *U* into *Al*.

On the other hand, Brossa et al. [6], have produced couples and triplets structures using deposition methods to study the efficient diffusion barriers that should have simultaneously, a good bonding effect and a good thermal conductivity. The practical interest of a *Ni* barrier is shown by several publications concerning with the diffusion in the systems $Al{-}Ni, Ni{-}U$ and $Al{-}Ni{-}U$. The study of the $Ni{-}Al$ binary system was, limited to solid samples of the sandwich-type, clamped together by a titanium screw and diffusion treatments have been carried out. Results from this work [6], have inspired present calculations.

Therefore it is important to study carefully and with special attention the initial microscopic processes that originate these intermetallic phases. In order to deal with this problem we started studying numerically the static and dynamic properties of vacancies and interstitials defects in the $Al(U)$ bulk and in the neighborhood of a $(111)Al/(001)\alpha U$ interface using molecular dynamics calculations [7,8]. Here, we review our previous works [7,8], performing calculation of the tracer diffusion coefficients in binary $Ni{-}Al$ and $Al{-}U$ alloys, using analytical expressions of the diffusion parameters in terms of microscopical magnitudes.

We have summarized the theoretical tools needed to express the diffusion coefficients in terms of microscopic magnitudes such as, the jump frequencies, the free vacancy formation energy and the vacancy-solute binding energy. Then we start with non-equilibrium thermodynamics in order to relate the diffusion coefficients with the phenomenological Onsager *L*-coefficients. The microscopic kinetic theory, allows us to write the Onsager

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coefficients in term of the jump frequency rates [9,10], which are evaluated from the migration barriers and the phonon frequencies under the harmonic approximation. The lattice vibrations are treated within the conventional framework of Vineyard [11] that corresponds to the classical limit.

The jump frequencies are identified by the model developed further by Le Claire in Ref. [12], known as the five-frequency model for f.c.c lattices. The method includes the jump frequency associated with the migration of the host atom in the presence of an impurity at a first nearest neighbor position. All this concepts need to be put together in order to correctly describe the diffusion mechanism. Hence, in the context of the shell approximation, we follow the technique developed by Allnatt in Refs. [9,10] to obtain the corresponding transport coefficients, which are related to the diffusion coefficients through the flux equations.

A similar procedure for f.c.c. structures was performed by Mantina et al. [13,14] for *Mg*, *Si* and *Cu* diluted in *Al* but using density functional theory (DFT). Also, using DFT calculations for b.c.c. structures, Choudhury et al. [15] have calculated the tracer self-diffusion and solute diffusion coefficients in diluted *Fe—Ni* and *Fe—Cr* alloys including an extensive analysis of the Onsager *L*-coefficients.

In the present work, we do not employ DFT, instead we use a classical molecular statics technique coupled to the Monomer method [16]. This much less computationally expensive method allows us to compute at low cost a bunch of jump frequencies from which we can perform averages in order to obtain more accurate effective frequencies. Although we use classical methods, we have also reproduced the migration barriers for *Ni—Al* with DFT calculations coupled to the Monomer method [17].

We proceed as follows, first of all we validate the five-frequency model using the *Ni—Al* system as a reference case for which there is a large amount of experimental data and numerical calculations [18]. Since, the *Al—U* and *Ni—Al* systems share the same crystallographic f.c.c. structure, the presented description is analogous for both alloys. The full set of frequencies are evaluated employing the economic Monomer method [16]. The Monomer is used to compute the saddle points configurations from which we obtain the jumps frequencies defined in the five-frequency model.

For the *Ni—Al* system case, our results of the tracer solute and self-diffusion coefficients are in good agreement with the experimental data. In this case we found that *Al* in *Ni*, at diluted concentrations, migrates as a free specie in the full range of temperatures here considered. In the case of *Al—U*, present calculations show that both, the tracer and self-diffusion coefficients agree very well with the available experimental data in Ref. [4], although a vacancy drag mechanism could occur at temperatures below 500 K, while, for at high temperatures the solute *U* migrates by direct interchange with the vacancy.

The paper is organized as follows: In Section 2 we briefly introduce a summary of the macroscopic equations of atomic transport that are provided by non-equilibrium thermodynamics [19–21]. In this way analytical expressions of the intrinsic diffusion coefficients in binary alloys in terms of Onsager coefficients are presented. Section 3, is devoted to give the way to evaluate the Onsager phenomenological coefficients following the procedure of Allnatt [9,10] in terms of the jumps frequencies in the context of the five-frequency model. In Section 4 we show the methodology used to evaluate the tracer diffusion coefficients for the solvent and solute atoms, as well as, the so called solvent enhancement factor. Finally, in Section 5 we present our numerical results using the theoretical procedure here summarized, which show a perfect accuracy with available experimental data, also we give an expression for the vacancy wind parameter which gives essential information about the flux of solute atoms induced by vacancy flow. The last section briefly presents some conclusions.

2. Theory summary: the flux equations

Isothermal atomic diffusion in binary *A—S* alloys can be described through a linear expression between the fluxes $\boldsymbol{J}_k$ and the driving forces related by the Onsager coefficients L_{ij} as,

$$\boldsymbol{J}_k = \sum_i^N L_{ki}\boldsymbol{X}_i, \tag{1}$$

where N is the number of components in the system, $\boldsymbol{J}_k$ describes the flux vector density of component k, while $\boldsymbol{X}_k$ is the driving force acting on component k. The second range tensor L_{ij} is symmetric ($L_{ij} = L_{ji}$) and depends on pressure and temperature, but is independent of the driving forces $\boldsymbol{X}_k$. From (1) the 1st Fick's law, which describes the atomic jump process on a macroscopic scale, can be recovered. On the other hand, for each k component, the driving forces may be expressed, in absence of external force, in terms of the chemical potential μ_k, so that [19],

$$\boldsymbol{X}_k = -T\nabla\left(\frac{\mu_k}{T}\right). \tag{2}$$

In (2) T is the absolute temperature, and the chemical potential μ_k is the partial derivative of the Gibbs free energy with respect to the number of atoms of specie k that is,

$$\mu_k = \left(\frac{\partial G}{\partial N_k}\right)_{T,P,N_{j\neq k}} = \mu^{\circ}{}_k(T,P) + k_BT\ln(c_k\gamma_k), \tag{3}$$

where γ_k, is the activity coefficients, which is defined in terms of the activity $a_k = \gamma_k c_k$ and c_k, is the molar concentration of specie k.

For the particular case of a binary diluted alloy (A,S) with N available lattice sites per unit volume, containing molar concentrations c_A for host atoms, c_S of solute atoms (impurities) and c_V vacancies, the fluxes in terms of the Onsager coefficients are expressed as,

$$\boldsymbol{J}_A = -\frac{k_BT}{N}\left(\frac{L_{AA}}{c_A} - \frac{L_{AS}}{c_S}\right)\left(1 + \frac{\partial \ln\gamma_A}{\partial \ln c_A}\right)\nabla c_A, \tag{4}$$

$$\boldsymbol{J}_S = -\frac{k_BT}{N}\left(\frac{L_{SS}}{c_S} - \frac{L_{AS}}{c_A}\right)\left(1 + \frac{\partial \ln\gamma_S}{\partial \ln c_S}\right)\nabla c_S, \tag{5}$$

and

$$\boldsymbol{J}_V = -(\boldsymbol{J}_A + \boldsymbol{J}_S). \tag{6}$$

From (4) and (5), we define

$$D_A = \frac{k_BT}{N}\left(\frac{L_{AA}}{c_A} - \frac{L_{AS}}{c_S}\right)\phi_A, \tag{7}$$

$$D_S = \frac{k_BT}{N}\left(\frac{L_{SS}}{c_S} - \frac{L_{SA}}{c_A}\right)\phi_S. \tag{8}$$

In the case of $c_A, c_S \gg c_V$, the diffusion coefficient for the vacancy is given by,

$$D_V = \frac{k_BT}{c_V}(L_{AA} + L_{SS} + 2L_{AS}). \tag{9}$$

In (7) and (8), D_A and D_S are the intrinsic diffusion coefficients for solvent A and solute S respectively, while D_V is the vacancy diffusion coefficient [22]. In (7) and (8) the quantities ϕ_A, ϕ_S are the thermodynamic factors,

$$\phi_A = \left(1 + \frac{\partial \ln\gamma_A}{\partial \ln c_A}\right) = \phi_S = \left(1 + \frac{\partial \ln\gamma_S}{\partial \ln c_S}\right). \tag{10}$$

Murch and Qin [21] have shown that the standard intrinsic diffusion coefficients in (7) and (8) can be expressed in terms of the tracer diffusion coefficients $D^{\star}_A, D^{\star}_S$ which are measurable quantities, and the collective correlation factor f_{ij} $(i,j = A,S)$ as: