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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Local Atomic Mechanism for the Diffusion Jump of Carbon Atom in Austenite

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(received data, accepted data)

Abstract

A carbon atom diffusion jump in iron austenite was considered as a subsequence of transformations between the cementite structure and the regular FCC packing. A model of this transformation was based on a 2D model of the elemental act of a polymorph transformation in metals. The energy threshold of this transformation has been calculated using the Morse pair potential. It occurs that the estimated enthalpy of the transformation is equal to 149±20 kJ/mole which is in satisfactory agreement with experimental data.

Keywords

iron austenite, carbon, diffusion jump, atomic model, Morse potential

1. Introduction

It is well known that the diameter of carbon atom is too large for the arrangement of carbon atom into the octahedral or tetrahedral cavity of iron austenite. The radii of octahedral and tetrahedral voids are equal respectively to 53 and 29 pm [1]. The covalent radius of carbon is equal to 77 pm. The radii of C^{+1} and C^{+2} ions are equal respectively to 67 and 60 pm [2].

On the other hand, the free volume in the prismatic packing of the cementite structure stated in [3] is larger than the volume of the octahedral cavity in the FCC austenite packing. We are suggesting that the soluted carbon atom in the austenite lattice could be arranged in the prismatic cavity, and this prismatic cavity in the initial austenite lattice is created itself by introducing the interstitial carbon atom.

Consequently, the single diffusion jump of the carbon atom presumes overcoming the energetic barrier which is corresponding to the local transformation of a regular FCC structure of the iron austenite into the local prismatic configuration similar to the cementite structure. As appeared, the magnitude of this energetic barrier could be estimated by the atomistic modelling of such local transformation, and the obtained estimations of the energetic barrier for such transformation must be juxtaposed to the published experimental values for the enthalpy of the carbon diffusion in iron austenite.

Bearing in mind the said above this paper is aiming to the formulation of the non-contradictory self-consistent model for the diffusion of the interstitial impurities in iron.

2. Methods of Modeling

In our model the diffusion jump of the carbon atom in the austenite lattice is considered as a succession of two transformations. The local prismatic configuration centered by carbon atom is reconstructed into the ordinary rhombohedral cavity (i.e., a regular octahedron plus regular tetrahedron) of the FCC packing (Fig. 1, *a*). Correspondingly, carbon atom jumps into the new position in which the local iron rhombohedron is reconstructed once more into the triangular prism (Fig. 1, *b*), which is similar to the carbon atom arrangement in the Fe_3C cementite structure [3]. This transformation takes place due to distortions resulted from the placement of carbon atom in this position. Therefore, the energy threshold for the diffusion jump must be equal to the energy threshold for the transformation of rhombohedral cavity into the prismatic cavity.

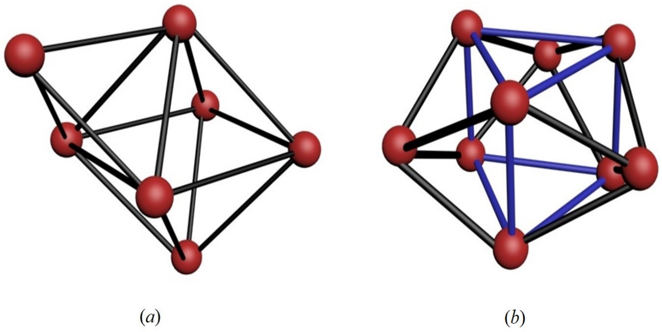
(*a*) (*b*)

Fig. 1: By introducing the carbon atom into the local dense atom packing (FCC) of octahedra and tetrahedra (a) the local prismatic packing of the cementite type (b) is arising [3]. Carbon atom is not shown; the edges of prism are shown by blue color.

Bearing in mind the simplification of calculations, the local reconstruction of the regular FCC packing into the prism was described by a 2D model: the elementary act of a polymorph transformation in metals is considered as the mutual substitution of a short by long diagonal belonging to the atomic rhombus (from position (a) up to position (e) in Fig. 2) [4]. Atoms arranged in the rhombus vertices 1 and 3 are moving apart, while atoms arranged in the vertices 2 and 4 are draw together. In the saddle point (d) diagonal lengths became equal to each other [4].

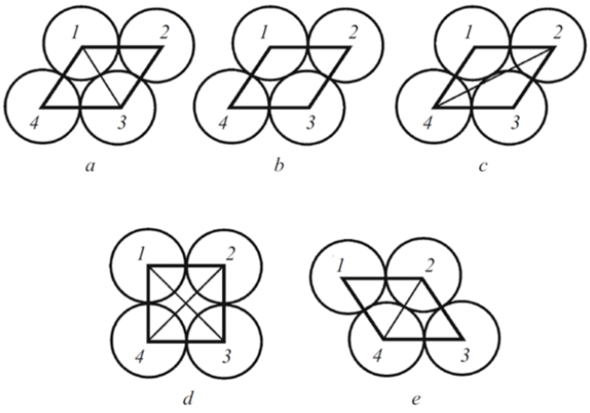

Fig. 2: A 2D model of the elementary act of the polymorph transformation in metals [4].

The energy threshold for change of interatomic distances in the rhombus is determined by the potential of the interatomic interaction using the pair Morse potential, which is seemed as the most effective potential to solve this problem in transition metals.

The value of the energy threshold *E* has been determined in the frameworks of the Morse pair interatomic potential:

$$U = U_{bond} + U_{rep} = -\alpha \exp\left(-\frac{\lambda d}{2}\right) + \beta \exp\left(-\lambda d\right), \tag{1}$$

where U_{bond} is the attraction energy, U_{rep} is the repulsion energy, α, β are constants, λ is the atomic compressibility, d is the interatomic distance. In accordance to [5] the atomic compressibility for iron was taken as equal to 3,2882 Å^{-1}.

In the point of the energy minimum at $d = d_0 = 256$ pm with d_0 as the equilibrium interatomic distance, the first derivative of the energy U by the interatomic distance is equal to zero, hence:

$$\alpha = \frac{2U_0}{\exp(-\frac{\lambda d_0}{2})} \text{ and } \beta = \frac{U_0}{\exp(-\lambda d_0)}. \tag{2}$$

where U_0 – is the U value of the modulus at the point of the energy minimum.

At thus:

$$U_0 = -U_{sub}, \tag{3}$$

where U_{sub} is the sublimation energy for iron at the temperature of the polymorphic transformation.

The sublimation energy for a given temperature iron was found as:

$$U_{sub} = H_{sub} + S_{sub} T, \tag{4}$$

here $H_{sub} = 415$ kJ/mole [6] is the sublimation energy at 298 K; S_{sub} is the sublimation entropy at 450-1250 К; T is the temperature.

S_{sub} was determined by the temperature dependence of the shear modulus according to [7]:

$$S_{sub} = \frac{H_{sub}}{G_0} \cdot \frac{\partial G}{\partial T}, \tag{5}$$

where G is the shear modulus, and G_0 is the shear modulus at $T = 0$ К.

Bearing in mind the data in [8] we have obtained:

$$G = -0,0492T + 98,96. \tag{6}$$

At that time:

$U_{sub} = 415 - 0{,}2063\ T.$ (7)

The calculated energy threshold for the polymorph transformation in pure iron has been calculated in [3] as equal to 160 kJ/mole at 1193 K. This calculated value is in good agreement with experimental data: the activation energy for the $\gamma \rightarrow \alpha$ transformation in Fe was determined as 147 kJ/mole in [9].

The energy threshold for the rearrangement has been taken as equal to the total activation energy for the carbon diffusion minus the product of temperature by the entropy of diffusion as was estimated by C. Zener approach [10].

3. Results and Discussion

The activation enthalpy for the carbon diffusion in iron austenite has been calculated as equal to 149±20 kJ/mole.

This value of the carbon activation enthalpy in γ-Fe is in good accordance to the experimental data of 148-157 kJ/mole [11].

So, the elementary act of the diffusional jump of the interstitial impurity atoms has been considered as local atomic reconstruction, i.e. as the diagonal throwing over in the atomic rhombus. By introducing the interstitial impurity atom, the local dense atom packing of octahedra and tetrahedra (face centered cubic packing or hexagonal close packing) is reconstructed into the local prismatic packing of the cementite type.

Bearing in mind the said above the diffusional jump of the interstitial atom is corresponding to the local transforming of the cubic packing in the nearby unit cell, and the former prism at the previous position of the interstitial atom is reconstructed into the ordinary interstitial void (an octahedron plus tetrahedron).

4. Conclusions

The calculations of the activation enthalpy for the carbon diffusion in iron austenite have been fulfilled in accordance to the proposed mechanism of the diffusion of the interstitial atoms. The obtained values are in satisfactory compliance with experimental values.

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