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Carbon Diffusion in Austenite: Computer Simulation and Theoretical Analysis

Alexander V. Evteev, Elena V. Levchenko, Irina V. Belova and Graeme E. Murch

Diffusion in Solids Group, Centre for Geotechnical and Materials Modelling,
School of Engineering, The University of Newcastle, NSW 2308 Callaghan, Australia,
E-Mail: Alexander.Evteev@newcastle.edu.au

1. Introduction

Carbon interstitial diffusion in austenite (γ-Fe) has been studied experimentally and analytically for many years. Two experimental studies have been made of carbon diffusion in austenite at low carbon contents. One is a measurement of the carbon chemical or intrinsic diffusion coefficient at 1075 K, 1124 K and 1273 K, and as a function of carbon content [1]; the other is a measurement of the tracer carbon diffusion coefficient at the single temperature 1273 K as a function of carbon content [2]. These data demonstrate that both the carbon tracer and chemical diffusion coefficients increase with carbon content. The data have been analyzed on many occasions with two different diffusion models.

The first is the well-known interacting lattice gas model in which nearest neighbour pair interactions are supposed between the carbon atoms and an inter–site transition rate based on those interactions is formulated; see, for example, [3]. Repulsive interactions between the carbon atoms are required in order to make quantitative contact with the diffusion data. A difficulty with the lattice gas model is one of uniquely describing 'rotational jumps' (a second atom making a rotational jump from one nearest neighbour site to another of a given atom) in the f.c.c. lattice when simple inter–site transition probabilities are used.

In the second model [4] (which is appropriate only at very low carbon content) it is supposed that the interstitials can diffuse only as isolated atoms or as bound nearest neighbour pairs. Because this model is based on a specification of fundamental jump frequencies it is a more general starting point for a diffusion kinetics analysis than the first, which started with effective interactions from which jump frequencies can be derived. In this second model, four atom – vacant site exchange frequencies are explicitly specified. These are: an atom – vacant site exchange frequency for jumps of isolated interstitial atoms, a rotational atom – vacant site frequency of one atom about the other when the pair of interstitial atoms are first nearest neighbours, a dissociative exchange frequency of a first nearest neighbour pair and the frequency of the reverse jump (associative) to form a pair. All other interstitial jumps are assumed in this model to occur with the same frequency as for jumps of isolated interstitial atoms. The increase in diffusion with carbon content could be ascribed to a higher mobility of pairs than isolated carbon atoms. The most important assumption of the 4–frequency model for interstitial diffusion is that the frequencies of dissociation and association of the first nearest neighbour pairs do not depend on whether dissociation occurs to the second, third or fourth nearest neighbour sites or whether association takes place from any of these sites.

2. Model

In the present work, a kinetic 10–frequency model for interstitial diffusion by octahedral voids in f.c.c. lattice, which considers the specific role of the transition probabilities during association and dissociation of the first nearest neighbour interstitial pairs through the second nearest neighbour sites, was developed. Next, we performed molecular dynamics simulations to investigate carbon interstitial diffusion in austenite at low carbon contents. The assumption that carbon atoms can interact with each other only indirectly (via neighbouring iron atoms) has been used. We have determined the Arrhenius parameters of the interstitial carbon jump frequencies as identified by the 10–frequency model and have also implemented Monte Carlo calculations of correlation factors.

3. Results and discussion

Comparison of the molecular dynamics and Monte-Carlo results with the experimental data at 1273 K in the context of the 10–frequency model is then made. It is shown that direct repulsion between the carbon atoms at the first nearest neighbour pairs in dilute austenite is undoubtedly present. Jump frequency ratios at 1273 K for the carbon first nearest neighbour pairs have been adjusted according to the experimental data.

It was established that direct repulsive interaction between the first nearest neighbour carbon atoms and indirect repulsive interaction via neighbouring iron atoms between the second nearest neighbour carbon atoms lead to significantly lower values (by ~ 42 % and by ~ 24 %) of both concentrations of the first and second nearest neighbour carbon pairs respectively near 1273 K in comparison with a random distribution. At the same time, the concentrations of the third and the fourth nearest neighbour carbon pairs are very close to a random distribution. At 1273 K the initial increase of both the tracer and the chemical diffusion coefficients with increasing carbon content can be explained as increased rates of dissociation of the carbon first and second nearest neighbour pairs to the third nearest neighbour sites.

4. Conclusions

A kinetic 10–frequency model for interstitial diffusion via octahedral interstices in the f.c.c. lattice was developed. In this model, the specific role of the transition probabilities during association and dissociation of the first nearest neighbour interstitial pairs through the second nearest neighbour sites is considered. Molecular dynamics was used to investigate carbon interstitial diffusion in austenite at low carbon contents with the assumption that carbon atoms can interact with each other only indirectly (via neighbouring iron atoms). The Arrhenius parameters of interstitial carbon jump frequencies were determined and compared with experimental data at 1273 K in the context of the 10–frequency model. It was shown that a small direct repulsion between carbon atoms at first nearest neighbours should be included. It was found that the initial increase (with increasing carbon content) in both the tracer and the chemical diffusion coefficients is shown to be a result of increased rates of dissociation of carbon from first and second nearest neighbour pairs to third nearest neighbour sites.

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