Computational Materials Science 82 (2014) 399-404

Contents lists available at ScienceDirect

Computational Materials Science

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

Molecular-dynamics study of the $\alpha \leftrightarrow \gamma$ phase transition in Fe–C

Binjun Wang, Emilia Sak-Saracino, Nina Gunkelmann¹, Herbert M. Urbassek*

Physics Department and Research Center OPTIMAS, University Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany

ARTICLE INFO

Article history: Received 24 July 2013 Received in revised form 23 August 2013 Accepted 14 September 2013

Keywords: Solid-solid phase transitions Molecular dynamics simulation Martensite Fe-C alloy Martensitic transformation

ABSTRACT

Using molecular dynamics simulation, we study the austenitic and the martensitic solid-solid phase transformation in the Fe–C system. Random alloys with C contents up to 1 at% are subjected to a heat-ing/cooling cycle. The martensite and austenite phase transition temperatures can be determined from the hysteresis of the system volume with temperature. The martensite temperature decreases with C content, as in experiment. The influence of the C atom position on the phase transformation and the pathways of the transition are analyzed. The transformed austenite phase shows strong twinning.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The mechanisms and kinetics of solid–solid phase transitions in iron form an important research field. Besides experiment [1–3], atomistic simulation investigated this topic in detail. Here most studies are devoted to pure Fe, and investigated the phase transition in the bulk [4–7], in thin films [8–11] and in nanoclusters and nanowires [12–15]. Studies of iron alloys concentrate on metallic alloying elements like Cu or Ni [16–18].

Among the iron-based alloys, the Fe–C system is of special importance as it forms the basis of steels. Many important issues have been investigated for this system, such as the position of the C atoms in the Fe lattice [19–21], the diffusivity of C atoms [22–25] or elastic properties [20,24,26]. Up to now, however, few atomistic studies have been published on the solid–solid phase transformations of the Fe–C system. In the present study, we investigate bulk Fe–C systems with different C concentrations to study the temperature induced α (bcc) $\leftrightarrow \gamma$ (fcc) phase transition.

The interatomic interaction potential plays a critical role in atomistic studies based on molecular-dynamics simulation and must be chosen with care. Six available potentials for iron in the embedded-atom model (EAM) class have been analyzed by Engin et al. [27]. The authors concluded that among the analyzed potentials, only the Meyer–Entel potential [28] can describe both the bcc and the fcc phase faithfully: The free energy curves of the fcc and

URL: http://www.physik.uni-kl.de/urbassek/ (H.M. Urbassek).

the bcc phase cross at a temperature of 550 ± 50 K. While this is smaller than the experimental value of 1184 K, this potential has been used widely to study the $\alpha \leftrightarrow \gamma$ phase transition in pure Fe [10–15,29–31].

Several empirical interatomic potentials have been published to describe the Fe–C interaction. Johnson et al. [32] developed a pair potential for Fe–C systems but excluded the C–C interaction. With this potential, the authors reproduced the migration energy of C in the Fe lattice, the activation volume of the migration and the binding energy of the C atom to a vacancy. Rosato [33] improved the Johnson potential by including the Finnis–Sinclair [34] potential for the bcc and the Rosato–Guillope–Legrand potential [35] for the fcc phase. More recently, several EAM-based Fe–C potentials have been published [21,24,36]. These, however, only describe the low-temperature α phase.

In the present paper, we study the $\alpha \leftrightarrow \gamma$ phase transition in Fe–C systems. Both the austenitic and martensitic phase transition will be analyzed. We focus on the dependence of the transition temperatures on the C content and analyze the transition pathway.

2. Simulation method

We use the method of classical atomistic simulation. The simulation volume is cubic and contains a bcc crystallite; all faces are oriented in $\langle 100 \rangle$ directions. The dimensions of the system amount to $43.05 \times 43.05 \times 43.05$ Å³; this corresponds to 15 bcc atom layers in each cartesian direction. The total number of Fe atoms amounts to 6750. C atoms are inserted randomly in octahedral interstitial sites. Note that due to this random insertion, the simulation volume shows no tetragonal distortion but remains cubic.





^{*} Corresponding author. Tel.: +49 631 205 3022; fax: +49 631 205 3907. *E-mail address: urbassek@rhrk.uni-kl.de* (H.M. Urbassek).

¹ Present address: Institute for Multiscale Simulations, Friedrich-Alexander-Universität, D-91052 Erlangen, Germany.

^{0927-0256/\$ -} see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.commatsci.2013.09.069

We investigate five different atomic C concentrations: 0, 0.2, 0.5, 0.8, and 1 at%. Periodic boundary conditions are employed in all three directions.

Fe atoms interact via the Meyer–Entel interaction potential [28] with each other. The C–Fe interaction is taken from the work of Johnson et al. [32]. Finally, C atoms interact via the Tersoff potential [37]. We recently calculated the free energy of the bcc and the fcc phase in this Fe–C system [38] and showed that the transition temperature decreases with increasing C content, in qualitative agreement with the phase diagram, see Fig. 3 below.

The systems are relaxed for 50 ps in an NPT ensemble at 50 K with pressure control (0 Pa) in all three directions. After equilibration, a heating/cooling cycle is performed: we increase the temperature from 50 K up to 1600 K with a heating rate of 1 K/ps. and then cool down from 1600 K to 50 K with the same rate. The total simulation time thus amounts to 3.1 ns. During this cycle the simulation is controlled via an NPT ensemble: The temperature is fixed to 0 through a barostat with pressure control in all three directions. By the solid–solid phase transformations, the initially cubic volume can deform to a parallelepiped. We monitor the evolution of the system volume. The austenite and martensite temperature are determined from the volume-temperature plots.

For each C concentration, five different simulations are run, which differ from each other by the initial C atom position. For each simulation, the austenite and martensite temperatures are determined. The average over these individual temperatures is taken as the final result.

To study the dependence on the heating/cooling rate, we investigate 5 cooling rates: 1, 2, 3, 4, 5 K/ps for the system with 0.5 at% C concentration. In this case the initial positions of the C atoms are exactly the same for these runs.

All calculations are performed with the open-source LAMMPS code [39]. The local atomic structure is analyzed using commonneighbor analysis (CNA) [40].

3. Results

3.1. Austenitic and martensitic phase transition

We first discuss the temperature-induced phase transition in our Fe–C systems. Fig. 1(a) displays the volume-temperature plot for the 0.2 at% system as an example. Upon heating the system expands until at around 1250 K, the volume suddenly jumps; this indicates the austenitic transformation to the fcc phase. Upon cooling, the system contracts until at around 380 K the volume jumps back, indicating the transformation to the bcc phase. The hysteresis observed here thus can be taken as an indicator of a first-order structural phase transition. Similar hystereses have been observed previously in metallic systems during the austenitic/martensitic phase transition [41–43].

Note that the volume changes occur abruptly, thus signaling that the transformations proceed in one step throughout our simulation volume. This is due to the fact that (i) we start from a single crystal; (ii) due to the high thermal rates strong superheating and - cooling is created and thus the driving force for the transition becomes strong; (iii) our system is small. In experiment, as a rule the transformation proceeds in several steps [44]; thus it is necessary to distinguish between a *martensite start* and a *martensite finish* temperature. This is not necessary in our simulations.

The volume change in the austenitic transformation is considerably smaller than that in the martensitic transformation. This is due to the local microstructure forming in the austenitic phase and will be discussed below, see Section 3.2, Fig. 6.



Fig. 1. Dependence of system volume on temperature during a heating/cooling cycle. C concentration 0.2 at%. Data normalized to the volume at 50 K immediately after relaxation. (a) Data for the entire heating/cooling cycle. Inset shows details of the austenitic transition. (b) Individual data for 5 different systems with identical C concentration (0.2 at%) but varying sites of the C atoms in the bcc Fe lattice.

In Fig. 1(b) we compare data on the martensitic transition for the individual simulations performed for the system with 0.2 at% C concentration. 5 individual systems have been simulated which only varied in the initial random position of the C atoms. We see considerable changes between the individual systems. The maximum variation of the martensite temperature amounts up to 100 K. We note that the influence on the austenite temperature is much smaller. The results for systems with higher C concentration are similar. We attribute the strong influence of the random C positions to the local elastic stress generated by them. High local stresses will influence the phase transition.

We note that C atoms do not diffuse during our simulation; they remain at the position which they occupied initially. This means that C atoms will not equilibrate or homogenize their positions in the course of the simulation.

Fig. 2 shows the volume-temperature hystereses for varying C concentration. Here we display the absolute volumes of the systems to show the volume increase of our initially relaxed samples with increasing C content. The main result here is that both the austenite and martensite temperatures systematically decrease with C content.

These data are quantified in Fig. 3 which shows the austenite and martensite temperature in dependence of the C concentration. We compare our simulation results with the experimental values



Fig. 2. Dependence of system volume on temperature during a heating/cooling cycle. Data for several C concentrations are shown.



Fig. 3. The austenite and martensite temperature in dependence of the C concentration compared with experimental values [44] and the results from free energy calculations [38]. Error bars denote the average error of the mean values for the simulation data.

[44]; these have been obtained for the martensite start temperature. In addition we include recently obtained transition temperatures from free-energy calculations [38]. The simulation data for the martensite temperature are considerably smaller than the experimental data. This is a well-known feature of the Meyer– Entel potential used by us, which features the equilibrium bcc–fcc transition temperature at 550 ± 50 K [27]; in reality it is 1185 K. However, our data are in good agreement with our recent free-energy calculations.

Fig. 4 displays snapshots of the simulation system at 0.2 at% C concentration during the heating/ cooling cycle. The initial and final surface is a bcc {100} plane. Fig. 4(a) shows the status immediately after relaxation. The CNA detector identifies the local crystal structures around the Fe atoms as bcc, fcc, or hcp. Unidentified sites may be defects; in our case many unidentified structures are caused by the strain field of nearby C atoms, which distort the local atomistic arrangement of the Fe atoms.

At a temperature of about 1300 K, the austenitic phase transition takes place; Fig. 4(b) shows a snapshot just during this austenitic transition. Here the local crystal structures of many Fe atoms cannot be correctly identified by using the CNA. This is due to several reasons: (i) During the phase transition, the atoms leave their equilibrium positions. They may be located on intermediate positions between the fcc and bcc sites. (ii) The high



Fig. 4. Snapshots of the system with 0.2 at% C concentration during the heating [(a) and (b)] and cooling [(c)-(e)] cycle. Colors denote the local crystal structure as obtained by CNA. Yellow: bcc; dark blue: fcc; light blue: hcp; red: unknown; small blue spheres: C atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Diagonal components of the stress tensor in the three cartesian directions during the heating/cooling cycle for the system with 0.2 at% C concentration. Data have been smoothened to get rid of temperature-induced fluctuations.



Fig. 6. Twin structure developing during the austenitic phase transition for the system with 0.2 at% C concentration. The snapshot shows the original $(001)_{bcc}$ plane which has transformed to a $(\bar{2}11)_{fcc}$ plane. The axis orientation of the initial bcc phase is indicated at the lower right-hand side. The white rectangles show the symmetric fcc lattice at both sides of the twin planes. The formation of the twin structure is indicated schematically.



Fig. 7. Dependence of relative system volume on temperature during a heating/ cooling cycle. (a) Data are shown for heating/cooling rates from 1 to 4 K/ps for the system with 0.5 at% C concentration. Inset shows details of the austenitic transition. (b) For a heating/cooling rate of 5 K/ps the hysteresis has vanished.

temperature leads to strong thermal fluctuations of the atoms, which negatively influence the operation of the CNA detector. (iii) As mentioned before, the C atoms disturb the local symmetry of the Fe lattice. Fig. 4(c) shows the completely transformed



Fig. 8. Dependence of the (a) austenite and (b) martensite temperature on the heating/cooling rate.

austenite phase at a temperature of 400 K (during the cooling phase). The transformed fcc phase shows a characteristic twin structure, which will be discussed in detail below. At a temperature of 320 K, Fig. 4(d), the martensitic phase transition takes place, and is terminated at 310 K, Fig. 4(e).

3.2. Mechanisms of the transition

In this subsection, we discuss the pathway followed by the phase transition. Our simulations show that in all systems the pathway of the transition is similar. We take the system with 0.2 at% C concentration as an example.

Fig. 5 displays the evolution of the stress during the heating/ cooling cycle. Due to the barostat, the pressure is well controlled and stays at zero during the cycle. Only at the austenitic and martensitic phase transitions considerable stresses are created in the system. While the stress in the austenitic transition is only around 0.1 GPa, stresses in the martensitic transition amount to >1 GPa.

This difference can be understood by monitoring the microstructure developing in the austenite phase, Fig. 6. Here the formation of a regular twin structure can be observed. The twin planes running diagonally through this figure are {111} planes, as it is common in fcc systems. The lattice shear accompanying twinning relieves the stress during the transformation and is thus responsible for the relatively small stresses showing up during the transformation.

Upon cooling, at the martensite temperature the twinned austenite structure back-transforms to bcc, and the twin structure is resolved. Without the stress-relieving effect of the twins, the martensitic transition causes about 12 times higher stress than the austenitic transition (Fig. 5) and the volume change is much bigger than the austenitic phase transition (Figs. 1 and 2).

3.3. Dependence on the heating/cooling rate

It is well known [45] that the difference of the austenite and martensite temperature (the width of the hysteresis) depends on the heating/cooling rate dT/dt: The hysteresis becomes wider for larger rate. We performed simulations of heating/cooling rates from 1 to 4 K/ps for an Fe–C system with 0.5 at% C concentration. Our simulation results, Fig. 7(a), show that indeed the width of the hysteresis increases with dT/dt; the austenite temperature increases and the martensite temperature decreases. Fig. 8 quantifies the dependence of the martensite (austenite) temperature on the heating (cooling) rate.

In addition, with increasing rate, the transformation needs more time. This is seen most clearly in the almost 100-K span of temperatures which the martensite transformation requires for completion in Fig. 7(a) for the highest cooling rate. The simulation data for dT/dt = 3 and = 4 K/ps are almost identical. When further increasing the rate to 5 K/ps, the thermal expansion and contraction follow the same pathway, see Fig. 7(b); the phase transitions are suppressed.

4. Conclusions

Using classical molecular-dynamics simulation, we study the austenitic and the martensitic solid-solid phase transformation in the Fe-C system as a function of the C content. We find the following.

- 1. When subjecting the Fe–C system to a heating/cooling cycle, the martensitic and the austenitic transformation occur at well defined temperatures and spontaneously transform the entire crystallite.
- 2. Both the martensite and austenite temperature decrease with increasing C content. These results are in agreement with the experimental finding that C stabilizes the fcc phase.
- 3. We find a strong dependence of the transition temperatures on the actual positions of the C interstitial atoms; this feature is due to the local stress exerted.
- 4. The stresses building up during the austenitic transition are an order of magnitude smaller than during the martensite transition. This is caused by the build-up of a regular twin structure in the austenite phase, which helps release the high transformation stress.
- 5. With increasing heating/cooling rate the phase transition is retarded; for extreme rates $(dT/dt \ge 5 \text{ K/ps})$ it is suppressed.

It is well known that all alloying elements have a strong influence on the α - γ transition temperature of Fe; elements have therefore been classified into those that stabilize the α -phase (' γ -loop forming elements') and those that destabilize it (' γ -openers'). For substitutional alloys, the number of electrons introduced by the alloying element plays the central role, as it influences the magnetism in the alloy and hence the relative stability of the α - and γ -phase [46]. Phase stability of interstitial alloys, in contrast, depends on the interstitial volume present in the different phases. Here, for simple geometric reasons, the γ -phase provides more space: The radius of the octahedral void in the Fe fcc lattice, r = 0.517 Å, is larger than both the tetrahedral (r = 0.360 Å) and the octahedral (r = 0.191 Å) void in the bcc lattice. This feature explains both the higher solubility in the fcc phase and the destabilization of the bcc lattice with increasing alloy concentration; it holds similarly for C, N, and B interstitials.

This simple geometrical concept is corroborated by an analysis of the influence of C interstitials on the bonding and the elastic constants in Fe-C alloys. A recent combined experimental and theoretical study has observed that C atoms weaken the Fe-Fe bonds in the α -phase, since Fe atoms neighboring an interstitial are shifted apart [26]. Similarly the elastic constants are weakened. In particular the elastic anisotropy - characterized by the ratio of the maximum and minimum shear modulus - increases with C content in the α -phase; this feature is thus directly connected with the tetragonal distortion building up. As Zener [47] showed the increased anisotropy destabilizes the bcc lattice structure.

Acknowledgment

We acknowledge support by the Deutsche Forschungsgemeinschaft via the Sonderforschungsbereich 926.

References

- [1] G.P. Krielaart, C.M. Brakman, S. Van der Zwaag, J. Mater. Sci. 31 (1996) 1501.
- [2] J.P. Rueff, M. Krisch, Y.Q. Cai, A. Kaprolat, M. Hanfland, M. Lorenzen, C. Masciovecchio, R. Verbeni, F. Sette, Phys. Rev. B 60 (1999) 14510.
- [3] C.-M. Liu, H.-C. Cheng, C.-Y. Chao, K.-L. Ou, J. Alloys Compds. 488 (2009) 52.
- [4] S. Tateyama, Y. Shibuta, T. Suzuki, Scr. Mater. 59 (2008) 971.
- [5] C.W. Sinclair, R.G. Hoagland, Acta Mater. 56 (2008) 4160.
- [6] E. Pereloma, D.V. Edmonds (Eds.), Phase transformations in steels. Diffusionless Transformations, High Strength Steels, Modelling and Advanced Analytical Techniques, Vol. 2, Woodhead Publishing Limited, Cambridge, UK, 2012
- [7] B. Wang, H.M. Urbassek, Phys. Rev. B 87 (2013) 104108.
- [8] Z.Q. Qiu, J. Pearson, S.D. Bader, Phys. Rev. Lett. 67 (1991) 1646.
- [9] W. Dürr, M. Taborelli, O. Paul, R. Germar, W. Gudat, D. Pescia, M. Landolt, Phys. Rev. Lett. 62 (1989) 206.
- [10] K. Kadau, R. Meyer, P. Entel, Surf. Rev. Lett. 6 (1999) 35.
- [11] K. Kadau, P. Entel, J. Magn. Magn. Mater. 198–199 (1999) 531.
- [12] P. Entel, M. Kreth, R. Meyer, and K. Kadau, in Modeling and simulating materials nanoworld, edited by P. Vincenzini and F. Zerbetto (Techna Group, Faenza, Italy, 2004), vol. 44 of Advances in Science and Technology, p. 101.
- [13] L. Sandoval, H.M. Urbassek, Nano Lett. 9 (2009) 2290.
- [14] L. Sandoval, H.M. Urbassek, Nanotechnology 20 (2009) 325704.
- [15] L. Sandoval, H.M. Urbassek, Appl. Phys. Lett. 95 (2009) 191909.
- [16] J.J. Blackstock, G.J. Ackland, Philos. Mag. A 81 (2001) 2127.
- [17] K. Kadau, P. Entel, P.S. Lomdahl, Comput. Phys. Commun. 147 (2002) 126.
- [18] L.E. Kar'kina, I.N. Kar'kin, Y.N. Gornostyrev, Phys. Met. Metallogr. 101 (2006) 130.
- [19] K.F. Laneri, J. Desimoni, G.J. Zarragoicoechea, A. Fernández-Guillermet, Phys. Rev. B 66 (2002) 134201.
- [20] N.N. Rammo, O.G. Abdulah, J. Alloys Compds. 420 (2006) 117.
- [21] M. Ruda, D. Farkas, G. Garcia, Comput. Mater. Sci. 45 (2009) 550.
- [22] D.E. Jiang, E.A. Carter, Phys. Rev. B 67 (2003) 214103.
- [23] D.E. Jiang, E.A. Carter, Phys. Rev. B 71 (2005) 045402
- [24] C.S. Becquart, J.M. Raulot, G. Bencteux, C. Domain, M. Perez, S. Garruchet, H. Nguyen, Comput. Mater. Sci. 40 (2007) 119.
- [25] A. Ishii, S. Ogata, H. Kimizuka, J. Li, Phys. Rev. B 85 (2012) 064303.
- [26] N. Gunkelmann, H. Ledbetter, H.M. Urbassek, Acta Mater. 60 (2012) 4901. [27] C. Engin, L. Sandoval, H.M. Urbassek, Model. Simul. Mater. Sci. Eng. 16 (2008) 035005.
- [28] R. Meyer, P. Entel, Phys. Rev. B 57 (1998) 5140.
- [29] P. Entel, R. Meyer, K. Kadau, H.C. Herper, E. Hoffmann, Eur. Phys. J.B 5 (1998) 379
- [30] P. Entel, R. Meyer, K. Kadau, Philos. Mag. B 80 (2000) 183.
- [31] L. Sandoval, H.M. Urbassek, P. Entel, Phys. Rev. B 80 (2009) 214108.
- [32] R.A. Johnson, G.J. Dienes, A.C. Damask, Acta Metall. 12 (1964) 1215.
- [33] V. Rosato, Acta Mater. 37 (1989) 2759.
- [34] M.W. Finnis, J.E. Sinclair, Philos. Mag. A 50 (1984) 45;
 - M.W. Finnis, J.E. Sinclair, Philos. Mag. A 53 (1986) 161.
- [35] V. Rosato, M. Guillope, B. Legrand, Philos. Mag. A 59 (1989) 321.
- [36] D.J. Hepburn, G.J. Ackland, Phys. Rev. B 78 (2008) 165115.
- [37] J. Tersoff, Phys. Rev. B 39 (1989) 5566.
- [38] E. Sak-Saracino, H.M. Urbassek, 2013, in preparation.
- [39] S. Plimpton, J. Comput. Phys. 117 (1995) 1. http://lammps.sandia.gov/.
- [40] D. Faken, H. Jonsson, Comput. Mater. Sci. 2 (1994) 279.
- [41] T. Krenke, M. Acet, E.F. Wassermann, X. Moya, L. Mañosa, A. Planes, Phys. Rev. B 72 (2005) 014412.

- [42] N.P. Lazarev, C. Abromeit, R. Schäublin, R. Gotthardt, J. Appl. Phys. 100 (2006) 63520.
- [43] V.G. Sathe, S. Banik, A. Dubey, S.R. Barman, A.M. Awasthi, L. Olivi, Adv. Mater. Res. 52 (2008) 175.
- [44] G. Krauss, Principles of heat treatment of steel, American Society for Metals, Metals Park, Ohio, 1980.
- [45] J.L. Dossett, H.E. Boyer, Practical Heat Treating (ASM International, Materials Park, OH, USA, 2006), second ed.
 [46] W. Pepperhoff, M. Acet, Constitution and Magnetism of Iron and its Alloys,
- [47] C. Zener, Elasticity and Anelasticity of Metals (U. Chicago, Chicago, 1948), pp. 16 ff.