INVESTIGATION OF THE PROCESS OF MARTENSITE TETRAHEDRAL DISTORTION FORMATION BY MOLECULAR DYNAMICS[*]

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Formation of tetragonal martensite in Fe–C system was studied. Parameters of thermodynamic ordering theory are calculated using energy minimization and molecular dynamic simulations with EAM potentials. It was found that carbon atoms in tetragonal martensite form plane-shaped groups.
Keywords: molecular dynamics, EAM potential, martensite tetragonality, order-disorder.

On rapid cooling of a *fcc* phase in Fe-C alloys specific low-temperature transformation occurs, named martensitic transformation. This transformation is the basis of quench steel hardening, since it is martensite formation that provides an abrupt hardness and strength increase which often forms a practical purpose of quenching. Investigations of the martensite crystal lattice carried out first by G.V. Kurdyumov et al. [1] showed that martensite has a tetragonal lattice that is to be considered as a *bcc* lattice of α iron slightly tensioned in one direction. Martensite lattice parameters *a* and *c* depend linearly on the carbon content. It should be noted that strict linearity is observed only with carbon contents more than 2.5 at. pct.

C. Zener [2] mentioned that iron atoms in a *bcc* iron lattice form a distorted octahedron where one space diagonal is shorter than others. When a carbon atom appears in an octahedral interstice of the α iron lattice, it moves apart the nearest iron atoms with a greater force than other four octahedron atoms. Thus, lattice tension occurs in one direction only. The *bcc* lattice contains octahedral interstices having a small diagonal oriented along *x*, *y* and *z* axes, so interstices of the *X*, *Y* and *Z* types should be distinguished. For instance, the carbon atom located in the *Z* type site tensions the lattice along the *z* axis, and in the *X* type site it tensions along the *x* axis and so on.

Thus, tetrahedral distortion of martensite is a consequence of the preferable location of carbon atoms in the course of martensitic structural transformation in interstices of one type. If carbon atoms remain randomly and uniformly distributed among interstices of three types, the structure stays cubic, the state is named a disordered state. If carbon atoms fill up only one type of sites, e.g. *Z*, then uniaxial lattice tension and tetragonality appear, the state is named an ordered state.

The statistical theory of carbon atom ordering in octahedral interstices was first developed by C. Zener [2]

and later by A.G. Khachaturyan [3]. Its main idea was that the excess number of carbon atoms in interstices of one type (compared to the chaotic one), e.g. *z*, yields an anisotropic strain of the cubic lattice or an "effective" stress making the elastic dipoles orient along *z* axis. According to this theory the free energy of the system at a given temperature and carbon concentration is

$$F(c, \eta) = F(c, 0) - \frac{1}{3} N c^2 \lambda_0 \eta^2 +$$
$$+ \frac{kT}{3} \Big[2(1-\eta)\ln(1-\eta) + (1+2\eta)\ln(1+2\eta) \Big], \quad (1)$$

where η is the order parameter reflecting the excess of carbon atoms in *z* type octahedral interstices compared to *x* and *y* types, N is the number of iron atoms, λ_0 is the strain interaction parameter, c is atomic fraction of carbon, T is temperature and k is Boltzmann constant.

Using the condition of minimum $F(c, \eta)$ with respect to η, one can find the dependence of the order parameter on temperature and carbon concentration:

$$\tau = \frac{kT}{\lambda_0 c} = \frac{\eta}{\ln\big[(1+2\eta)/(1-\eta)\big]}, \quad (2)$$

where τ is a generalized parameter characterizing external conditions of the ordering process. Fig. 1 shows the lattice parameter dependence on τ (for $\lambda_0 = 5.65$ eV/atom). If follows from this figure that order-disorder transition temperature T_c equals

$$T_c = 0{,}36 \frac{c\lambda_0}{k}. \quad (3)$$

As follows from eq. (2), a plot of η as a function of $1/c$ will be analogous to Fig. 1. Thus, if redistribution of carbon atoms in martensite is considered at a fixed temperature T, tetragonal transition will occur when carbon content exceeds
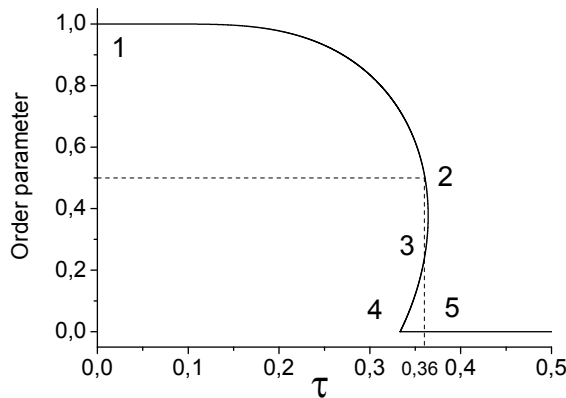
$$c_c = \frac{kT_0}{0{,}36\lambda_0}. \quad (4)$$

**Fig. 1. Order parameter η
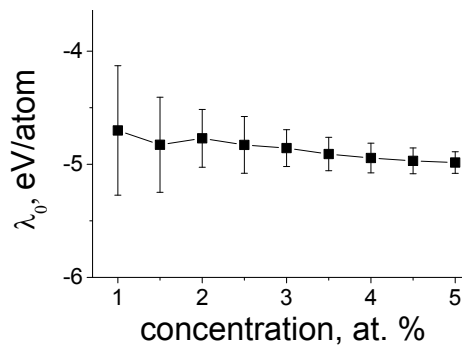as a function of τ as provided by (2)**

**Fig. 2. Concentration dependency
of carbon interaction parameter λ_0**

It should be noted that the key parameter of the Zener–Khachaturyan theory is λ_0. However, different works give a great discrepancy in estimates of this parameter ranging from –2.73 to –10.77 eV/atom due to different methods and calculation parameters used.

To eliminate these difficulties we propose to use atomistic modeling for the calculation of the interaction parameter and martensite tetragonality. Another advantage of this method is that homogeneous formation of iron carbide is actually suppressed in atomistic modeling. This permits to study the process of carbon redistribution on the lattice in a wide range of temperatures, while in real experiments when carbide precipitation begins at above 370 K it becomes difficult.

All calculations were performed by LAMMPS [6] simulation package using an EAM potential for Fe–C [7]. It was shown earlier [8] that this potential describes adequately the interaction of C atoms in *bcc* iron. Structure relaxation by the energy minimization method (molecular statics, MS) and molecular dynamics (MD) at constant temperature and zero external pressure were used.

Using the former method, the λ_0 parameter can be evaluated from (1):

$$\lambda_0 = 3\frac{E_z - E_{xyz}}{Nc^2},$$

where E_{xyz} is internal energy of cubic martensite (disordered state) when carbon atoms are uniformly distributed among different interstices, and E_z is energy of the ordered state when all C atoms are located in Z type interstices.

E_{xyz} and E_z have been calculated by the energy minimization method. The supercell contained $30 \times 30 \times 30$ unit cells. Carbon atoms were randomly distributed on octahedral sites, the minimum distance between the nearest carbon atoms being equal to the lattice parameter $a_0 = 2,866$ Å, as carbon atoms repulse at small distances according to *ab initio* results [9]. Energies E_{xyz} and E_z were averaged on 100 random configurations. The λ_0 parameter at different concen-

trations is shown in Fig. 2. The results show weak dependence of the λ_0 parameter on carbon content and this agrees with the Zener–Khachaturyan theory where this value is constant.

Second, we used direct calculation of the λ_0 parameter by molecular dynamics in an isobaric-isothermal (*NPT*) ensemble. The following procedures were performed to obtain equilibrium configurations of martensite:

• initial configurations consisted of 16000 Fe atoms, carbon atoms were randomly distributed on Z sites as described above,

• then structure relaxation by MS was performed, and tetragonal distortion appeared,

• the next step was performing MD in the *NPT* ensemble; the time simulated being 500 ns.

On the last stage the system comes to equilibrium and diffusive redistribution of carbon atoms between octahedral sites takes place. Concentration dependence of lattice parameters of martensite at $T = 750$ K is shown in Fig. 3. Cubic lattice exists up to 3 at. % and in this case carbon atoms occupy uniformly octahedral interstices. At 3.2 at. % a jump in lattice parameters occurs, and Z type octahedral interstices become preferable, which indicates an order-disorder transition.

We should note that when tetragonal distortion arises, carbon atoms located in Z sites form parallel planes with (102) indicies. This structure is presented in Fig. 4 at $T = 750$ K and 4.5 at. % C. The iron lattice and 8 % of carbon atoms occupying X and Y type interstices are not shown in Fig. 4.

We have performed analogous calculations for different temperatures in the range of carbon contents and tetrahedral distortions shown in Fig. 5a. These graphs allow to define the concentration of order-disorder phase transition at a given temperature. Ordering temperatures defined in our MD calculations, in MS calculations by eq. (2) at $\lambda_0 = -4.95$ eV/atom and for $\lambda_0 = -6.38$ eV/atom according to [6] are shown in Fig. 5b. Linear approximation of MD calculation results shows that λ_0 equals –5.55 eV/atom.
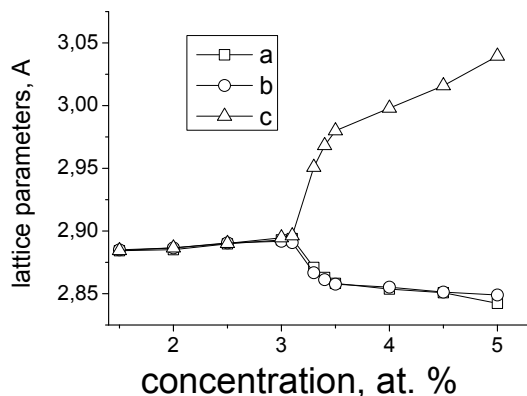
**Fig. 3. Concentration dependence
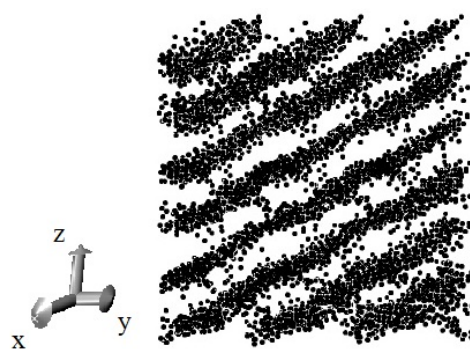of lattice parameters at *T* = 750 K**

Fig. 4. Appearance of ordered plane fields of C atoms located in *Z* sites of *bcc* iron lattice at *T* = 750 K and 4.5 at. % C
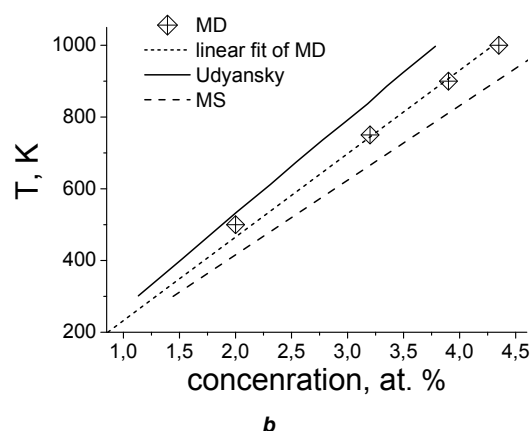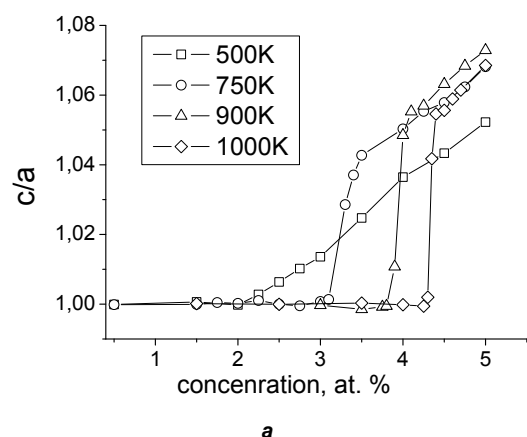

a

b

Рис. 5. Concentration dependence of tetragonal distortion (*a*) and ordering temperature (*b*)

Discussion

Simulation results confirm the Zener – Khachaturyan theory. When carbon concentration c increases, transition from cubic to tetragonal lattice occurs. At temperatures above 500 K both the order parameter and c/a ratio increase very rapidly showing behaviour similar to Kurdjumov's straight line (Fig. 5, *a*, *b*). Therefore, the theory of continuous decrease of the order parameter η with the temperature increase suggested by Khachaturyan is not implemented.

Attention is also to be drawn to the rearrangement character of carbon atoms obtained in modeling. The Zener – Khachaturyan theory does not take into account the possibility of appearence of a short-range order inside *X*, *Y* and *Z* interstice sublattices. However, experimental investigations [11] of high carbon steel ageing at 300…500 K showed that carbon atoms clusterization occurred in planes with (103) indices. In this work a similar process was observed in planes with similar indices, namely (102).

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ИССЛЕДОВАНИЕ ПРОЦЕССА ВОЗНИКНОВЕНИЯ ТЕТРАГОНАЛЬНОСТИ МАРТЕНСИТА МЕТОДОМ МОЛЕКУЛЯРНОЙ ДИНАМИКИ

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Исследовалось образование тетрагональности мартенсита в сплавах Fe–C. Получены параметры термодинамической теории упорядочения методом минимизации энергии и методом молекулярной динамики с использованием потенциала погруженного атома. Обнаружено, что в тетрагональной структуре атомы углерода группируются в плоскости.

Ключевые слова: метод молекулярной динамики, ЕАМ потенциал, тетрагональность мартенсита, порядок-беспорядок.

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