

COVALENCE OF THE Fe-C INTERATOMIC BOND AND THE HARDNESS OF MARTENSITE OF CARBON AND ALLOYED STEELS

КОВАЛЕНТНОСТЬ МЕЖАТОМНОЙ СВЯЗИ Fe-C И ТВЕРДОСТЬ МАРТЕНСИТА УГЛЕРОДИСТЫХ И ЛЕГИРОВАННЫХ СТАЛЕЙ

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Abstract: A technique for determining the generalized degree of covalence of the interatomic Fe – C bond is proposed by the addition rule taking into account the fractions of Fe₂C, Fe₄C and Fe₆C clusters and cementite in steel. The correlation dependence of the generalized degree of covalence of the interatomic Fe – C bond with the hardness of microstructures observed in eutectoid carbon steel, as well as the hardness of ferrite and cementite, is revealed. A functional relationship between the generalized degree of covalence of the Fe-C interatomic bond and the martensite hardness at different mass content of carbon is established, which ensures the correspondence of the calculated and experimental data.

KEYWORDS: COVALENCE; INTERATOMIC BOND, MARTENSITE, CARBON STEEL, ALLOYED STEEL, MARTENSITE HARDNESS

1. Introduction

The fundamental problem of modern material's science is the search for new theoretical approaches to the task of developing the foundations of the synthesis of steels and alloys with a given set of physical and chemical properties of the metal in the finished product. This problem has a huge amount difficult factors to take into account, including the limits of the melt production and processing, technological redistribution between the liquid metal and the finished product, which makes it difficult to solve it. To simplify the tasks necessary to transition to a single system of reference for the evaluation of the effects of these factors. This may be a consideration of their influence on the structure of the atomic hierarchical level of the metal structure.

The atomic level is the initial in the hierarchical row of the metal structure: atomic → nanostructural → microstructural → mesostructural → macro-structural level.

The atomic level is usually characterized by the belonging of atoms to specific chemical elements, the spatial arrangement of atoms and vacancies in the crystal lattice and interatomic interaction. At the same time, the structure of the set of interatomic bonds in the alloy, characterized by generalized degrees of metallicity C_m^g , covalence C_k^g and ionicity C_i^g , ($C_m^g + C_k^g + C_i^g = 1$), is potentially able to reflect the chemical and phase composition, structure and mechanical properties of the metal. But the corresponding equations have not yet been obtained. This problem will be theoretically investigated and the results compared with experimental data on the example of carbon steel.

The problem can be formulated as: Development of a method for determining the generalized degree of covalence C_k^{gFe-C} , characterizing in general all interatomic bonds between iron and carbon atoms in all structural components of carbon steel and establishing a connection C_k^{gFe-C} with the type of microstructure, as well as with the hardness of martensite.

2. Results and Discussion

In the crystal lattice α -Fe the most energy-efficient placement of the carbon atom in the octahedral pore, located in the plane A, (Figure 1A). The Fe 1 and 2 atoms are shifted in the direction with a lower packing density of atoms. As a result, the atom C is placed at an equal distance from the nearest six Fe atoms. This configuration of 6 iron atoms and a carbon atom can be considered as a cluster Fe₆C. In the crystal lattice. As is known, there are Fe₂C clusters in ferrite [1, 2], and in martensite there are Fe₄C clusters along with Fe₂C clusters [2, 3]. One of the possible variants of the spatial arrangement of Fe₂C and Fe₄C clusters in the

formation of tetragonal distortion of the martensite crystal lattice is shown on the figure 1B.

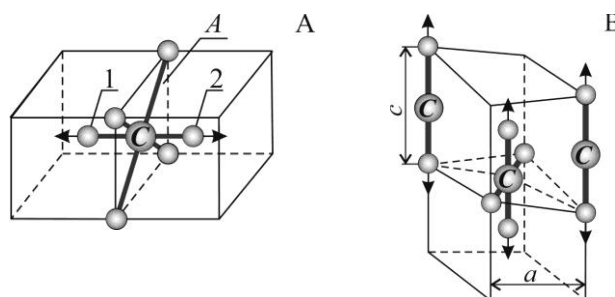


Fig. 1. Cluster Fe₆C (A) in the BCC lattice and clusters Fe₂C and Fe₄C (B) in the formation of tetragonal distortion of the martensite crystal lattice; 1, 2 – displaced Fe atoms

Table 1 shows the calculation data of the degree of covalence of Fe–C bonds in the Fe₂C, Fe₄C, Fe₆C and cementite Fe₃C clusters, where i corresponds to the number of Fe atoms forming a bond with the C atom.

i	2	3	4	6
$C_{k_i}^{Fe-C}$	0,3141	0,2654	0,2438	0,224

For ferrite, including ferrite, which is a part of pearlite, sorbitol, troostite and bainite, the generalized value of the degree of covalency of Fe–C bond, related to the solid solution is determined by the dependence:

$$C_k^F = \sum_i n_i C_{k_i}^{Fe-C} \quad (1)$$

where n_i is the fraction of C atoms in octahedral pores in ferrite; $i = 2, 6$.

For perlite, sorbitol, troostite, and bainite, the generalized value of the degree of covalence of the Fe–C bond with respect to the mechanical mixture as a whole is given by the equation:

$$C_k^{gFe-C} = m_F C_k^F + m_{cem} C_{k_3}^{Fe-C} \quad (2)$$

where m_F , m_{cem} are the mass fraction of ferrite and cementite in the phase mixture, respectively; $C_{k_3}^{Fe-C}$ – degree of covalence of Fe–C bond in cementite (table 1). In the table 2 shows the m_F and m_{cem} values of the various mixtures formed

in eutectoid carbon steel calculated on the basis of the mass conservation law.

Table 2

m_F and m_{cem} values for various microstructural components of eutectoid steel

Type of structural component	Carbon content of ferrite, %	m_F	m_{cem}
Pearlite, sorbite, troostite	0,022	0,883	0,117
Bainite upper	0,1 [5]	0,894	0,106
Bainite lower	0,16 [5]	0,902	0,098

Table 3 summarizes the Fe–C bond covalency for ferrite, cementite, and various possible types of microstructural components of eutectoid steel, their respective hardness, and estimates of the fraction of carbon atoms Q_{Fe_iC} , where $i = 2, 4, 6$, octahedral pores in the formation of clusters, respectively, Fe_2C , Fe_4C and Fe_6C . The values Q_{Fe_2C} on table 3 obtained based on assumptions about the defining and the proportional contribution of Fe_2C clusters in the hardening of the ferrite included in the mechanical mixture.

Table 3

Generalized degrees of Fe–C bond covalency C_k^{gFe-C} for ferrite, cementite and various possible types of structural components of eutectoid steel, their hardness and Q_{Fe_iC} [6]

Structural component	HB, MPa (HB in kg/mm ² or HRC)	C_k^{gFe-C}	Estimation of the possible fraction of carbon atoms in octahedral pores for Fe_iC clusters at $i = 2, 4, 6$
Ferrite	588 (HB≈60)	0,224 (Table 1)	$Q_{Fe_2C} = 0$; $Q_{Fe_6C} = 1$
Pearlite	2000 (HRC≈15)	0,23156 (2)	$Q_{Fe_2C} = 0,034$; $Q_{Fe_6C} = 0,966$
Sorbite	2800 (HRC≈30)	0,23564 (2)	$Q_{Fe_2C} = 0,085$; $Q_{Fe_6C} = 0,915$
Troostite	3640 (HRC≈40)	0,24045 (2)	$Q_{Fe_2C} = 0,146$; $Q_{Fe_6C} = 0,854$
Bainite upper	4125 (HRC≈45)	0,2429 (2)	$Q_{Fe_2C} = 0,18$; $Q_{Fe_6C} = 0,82$
Bainite lower	5075 (HRC≈55)	0,24821 (2)	$Q_{Fe_2C} = 0,248$; $Q_{Fe_6C} = 0,752$
Martensite	7350	0,26 (8)	Q_{Fe_2C} for (4); Q_{Fe_4C} for (5); Q_{Fe_6C} for (6) to $C = 0,8\%$
Cementite	8330 (HB≈850)	0,2654 (Table 1)	-

Note: conversion between different hardness units was performed according to ISO 18265.

The data on table 3 are presented in figure 2.

Equation 1 on figure 4 is determined by the dependence of $HB = -41301,08 + 187004,83C_k^{gFe-C}$ with $R = 0,999$, which in terms of hardness HRC at $HRC \geq 12$ with $R = 0,997$ takes the form:

$$HRC = -17040,87 + 193296,32C_k^{gFe-C} - 730579,208(C_k^{gFe-C})^2 + 923819,288(C_k^{gFe-C})^3 \quad (3)$$

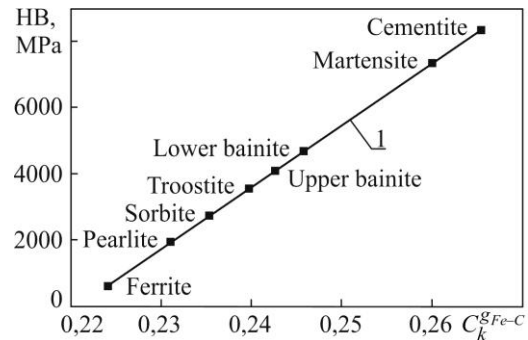


Fig. 2. Hardness of ferrite, cementite and different types of possible structural components of eutectoid steel (table 3), depending on the generalized degree of covalence of Fe–C structural component: 1 – regression equation

Martensitic transformation hasn't diffusion character and is carried out by the corporate movement of atoms. The proportion of carbon atoms in octahedral voids $Q_{Fe_2C}(C)$ on the edges with the formation of clusters Fe_2C (Figure 1B) can be considered proportional to the known angular coefficient of the concentration dependence of the lattice period martensite, in which the processes of redistribution of carbon atoms between the internodes, $\alpha = 0,118$ [5, 7]. That is:

$$Q_{Fe_2C}(C) = a_1 + 0,118C \quad (4)$$

where C is mass concentration of carbon in steel; a_1 – coefficient; $l = 1, 2$.

In low-carbon steel at the initial stage of formation of tetragonal lattice distortion $\alpha-Fe$ can be considered that:

– the probability of placing an atom C in any of the 18 octahedral pores of the elementary lattice $\alpha-Fe$ is $P_{p.o.} = 1/18$;

– the probability of the joint occurrence of two independent events of the placement of atoms of C in 12 octahedral pores on the edges with the formation of the Fe_2C cluster is $P_{pair} = 1/(12 \cdot 12)$.

In the joint appearance of these cases $a_1 = P_{p.o.} + P_{pair} - P_{p.o.} \cdot P_{pair} = 0,0621$. At $C \geq 0,16\%$ $Q_{Fe_2C}(C)$ in the equation (4) corresponds to the probability of placing one of the two atoms on the edges of C with the formation of the cluster Fe_2C as joint events and the coefficient a_2 in the equation (4) corresponds to the probability of co-location of pairs of atoms on the edges and is 0,1597 (table 4).

The placement of carbon atoms in octahedral voids with the formation of a cluster Fe_4C is a random process and for its description the most suitable logarithmically normal distribution. The proportion of carbon atoms in octahedral voids forming Fe_4C clusters is the same:

$$Q_{Fe_4C}(C) = \frac{1}{C\sigma_1\sqrt{2\pi}} \exp\left[-\frac{(\ln C)^2}{2\sigma_1^2}\right] \quad (5)$$

where σ_1 is the standard deviation. The values of σ_1 in (5), providing the closest correspondence of the calculated martensite hardness values to the experimental data, are given in table 4.

Table 4

The coefficients a_j and σ_1 with different contents of carbon in the martensite

Coefficient	$C < 0,16\%$	$C \geq 0,16\%$
a	$a_1 = \frac{1}{18} + \frac{1}{12 \cdot 12} - \frac{1}{18 \cdot 12 \cdot 12} = 0.0621$	$a_2 = \frac{1}{12} + \frac{1}{12} - \frac{1}{12 \cdot 12} = 0.1597$
σ	$\sigma_1 = \ln 2,96$	$\sigma_2 = \ln 2$

The fraction of carbon atoms forming Fe_6C clusters is:

$$Q_{Fe_6C}(C) = 1 - [Q_{Fe_2C}(C) + Q_{Fe_4C}(C)] \quad (6)$$

Generalized value of the degree of covalency of $Fe-C$ coupling in martensite:

$$C_k^{gFe-C}(C) = C_{k_6} Q_{Fe_6C}(C) + C_{k_2} Q_{Fe_2C}(C) + C_{k_4} Q_{Fe_4C}(C) \quad (7)$$

where $C_{k_2}, C_{k_4}, C_{k_6}$ – is the degree of covalency of the $Fe-C$ bond at i , equal, respectively, 2, 4 and 6 (table 1).

The solution of equations (3) – (7) with respect to the concentration of C is given on figure 3.

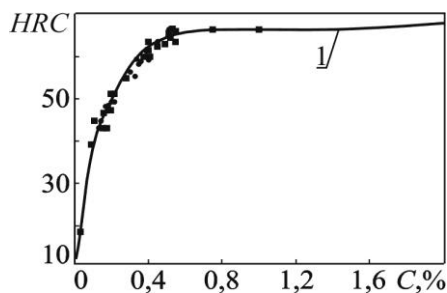


Fig. 3. Martensite hardness depending on the mass content of carbon: 1 – solution of equations (3) – (7); experimental data [8]: ■ – carbon steel, ● – alloy steel

3. Conclusion

It is shown that the generalized degree of covalently describing in general all inter-atomic bonding between atoms of iron and carbon in all the structural components of carbon steel, reflects the chemical and phase composition of the steel, the structure and functionally determines the hardness of martensite.

This shows the fruitfulness of the proposed path to the creation of a new approach to the synthesis of steels and alloys with the given physical and chemical properties of the metal in the finished product, in which the entire set of factors, including the parameters of the production and processing of the melt, technological redistribution between the liquid metal and the finished product, will be considered in a single reference system, taking into account their influence on the structure of the atomic hierarchical level of the metal structure, that is the influence on the generalized degree of metallicity and covalency, characterizing the whole

set of all interatomic bonds in all structural components of the alloy.

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