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N. Filonenko[1,2], O. Babachenko[2], G. Kononenko[2], K Domina[2]

Solubility of Carbon, Manganese and Silicon in γ-Iron of Fe-Mn-Si-C alloys

[1]*State Institution "Dnipropetrovsk Medical Academy of the Ministry of Health of Ukraine", Dnipro, Ukraine,* natph2016@gmail.com
[2]*Iron and Steel Institute of Z.I. Nekrasov of the National Academy of Sciences of Ukraine, Dnipro, Ukraine,* A_Babachenko@i.ua

The study was performed on alloys with a carbon content of 0.37 - 0.57 % (wt.), silicon 0.23 - 0.29 % (wt.), manganese 0.7 - 0.86 % (wt.), the rest– iron. To determine the phase composition of alloys used microstructural, microanalysis and X-ray analysis. In addition, the physical characteristics of the alloys studied in this paper were determined, such as alloy chemical dependence of extension and contraction ratio, impact toughness and hardness. The results obtained in this paper showed that the iron-based alloy with the content of carbon of 0.57 % (wt.), silicon of 0.28 % (wt.) and manganese of 0.86 % (wt.)) had the superior microstructure and physical properties. It was determined that after a number of crystallization and phase transformation the alloy phase structure includes two phases: α-iron and cement magnesium doping $Fe_{2.7}Mn_{0,3}C$.

For the first time using the method quasichemistry received an expression of the free energy of a γ-iron alloyed with silicon and magnesium, and determined the solubility limit of carbon, manganese and silicon. The maximum content in γ-iron can reach: carbon 6.8 % (at.), manganese – 67.5 % (at.), silicon – 2.3 % (at.).

Keywords: Fe-Mn-Si-C alloys, solubility limit of carbon, manganese, silicon in γ-iron.

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Introduction

Currently, there is a particular interest in steels that have high strength and ductility. For the formation of these steels, there are three approaches - the two-phase steel (DP), steel with martensitic transformation conditioned plasticity (TRIP) and high manganese austenitic steel with double industrial plasticity (TWIP).All these types of steel are based on an iron-carbon-manganese system with the addition of ferrite formers such as flint and aluminum, whose content is much higher than other steels. For example, type TWIP steel with the composition of Fe-C-Si-Al-Mn often or without aluminum or with a high content of manganese up to 25 % (wt.) [1-3].Fe-Mn-Si-C alloys containing up to 0.6 % (wt) of carbon are used as structural steels for the manufacture of various parts, mechanisms and structures in mechanical engineering and construction.

In alloys of the Fe-Mn-Si-C system during crystallization by primary phase melting, there can be δ-iron , when carbon is contented up to 0.2 % (wt.);in the presence of carbonate up to 0.5 % (wt.), manganese up to 2 % (wt.) and force action up to 1% (wt.), during the crystallization, a cascade of transformation of the pretektics was observed: $L \rightarrow L + \delta \rightarrow \delta + \gamma \rightarrow \gamma$ [4-7].

It is known that the solubility of silicon system Mn-Si 3 % (at.), for the system Fe-Si – 3 % (wt.). In the alloy of the Mn-C system, the carbon solubility is 2 - 3 % (at.), and in the Fe-C system – 2.14 % (wt.) in γ-Fe [8-9].

The aim of this work was to determine the solubility limit of carbon, manganese, and silicon in austenite in Fe-Mn-Si-C alloys.

I. Materials and research methodology

The studies were carried out on samples of steels with the carbon content of 0.37 – 0.57 % (wt.), silicon 0,23-0,29% (wt.), manganese 0.7 – 0.86 % (wt.), the rest - iron. The alloys of the Fe-Mn-Si-C system were

smelted in an alundum crucibles in the furnace in an argon atmosphere. The average cooling rate of the alloys after casting was 10 K/s. Chemical and spectral analysis was used to determine the chemical composition of the alloy [10].The phase composition of the alloys was determined using a Neophot-21 optical microscope. The main results of micro-X-ray spectral analysis were obtained by JSM-6490 electron microscope with a scanner ASID-4D and the energy-dispersive X-ray microanalyzer "Link Systems 860" with software. The X-ray diffraction analysis was performed on a DRON-3 diffractometer in monochromatized Fe-Kα radiation. The energy of interaction between atoms was calculated in Gaussian 09W.

II. Results and discussion

The microstructure of the alloy with the carbon content of 0.37 % (wt.), silicon 0.23 % (wt.), manganese 0,86% (wt.) in the cast, state is represented by ferrite and perlite (Fig. 1a).

The results of X-ray analysis in this alloy were discovered only two phases - ferrite and carbide (Fig. 1b). Carbide, as a structural component of perlite, was presented in these alloys of the Fe-Mn-Si-C phase $Fe_{2.7}Mn_{0,3}C$. It should be noted that perlite has two colors after ching the surface of the samples with sodium picrate – light and dark. In perlite light r color content of manganese – 0.37 % (wt.), silicon – 0.38 % (wt.). In perlite dark color high content of alloying elements: manganese – 0.79 % (wt.), silicon – 0,41 % (wt.). Thus, there sults make it possible ti assert that in alloys for med areas enriched manganese and silicon.

As Table 1 shows, the characteristics of strength and hardness for all the alloys are high, and for the alloy containing carbon – 0.57 % (wt.), silicon – 0.28 % (wt.) and manganese – 0.8 6% (wt.), plasticity and fracture toughness are higher as compared to those for the other alloys that are used in the manufacture of railway wheels.

The microstructure of alloys studied in this paper was represented by pearlite, whose bulk fraction was up to 95%. To clarify the structural components in this study was determined the solubility of carbon, manganese and silicon alloys in austenite Fe-C-Mn-Si.

Crystal cell fcc austenite is octahedral and tetrahedral pores (Fig. 2).The coordinate number for the fcc of the lattice is 12. The elemental cell of the fcc lattice has 4 atoms. In octahedral pores can be inscribed sphere with a radius 0,41 r. The carbon atom located in the octahedral pore has the nearest 6 adjacent atoms of iron, manganese or silicon. The iron atoms are at a distance a/2 from the carbon atoms. For tetrahedral pores, there are 4 atoms at a distance $a\sqrt{3}/4$, where a is the lattice parameter of the γ-iron. In the tetragonal pore, the carbon atom has 4 of the nearest metal atoms. In a tetragonal pore can fit a sphere with a radius of 0.22 r. Each octa atom has one octahedral and two tetragonal

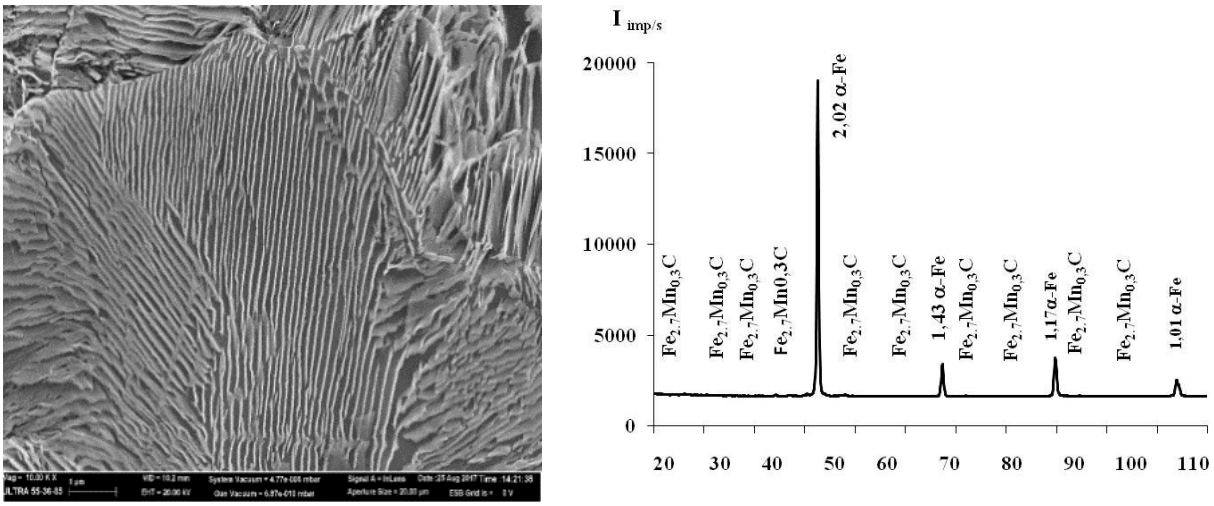

Fig. 1. Alloy based on iron with a carbon content of 0.37% (wt.), Silicon 0.23% (wt.), Manganese 0.86% (wt.) In the cast state: a) pearlite microstructure, b) diffractogram.

Table 1

Dependence of the extension and contraction ratio, impact toughness and hardness on the chemical composition

Content of chemical elements in alloys, % (wt.)	Relative extension n, δ, %	Relative contraction ψ,%	Impact toughness, KCU_{obed}, J/cm^2	Hardness, HB
C = 0.37;Si = 0.23; Mn = 0.75	8	17	34	324
C = 0.57; Si = 0.28; Mn = 0.86	11	25	40	341

pores [11]. A quasi-chemical method was used to determine the free energy of austenite [12].

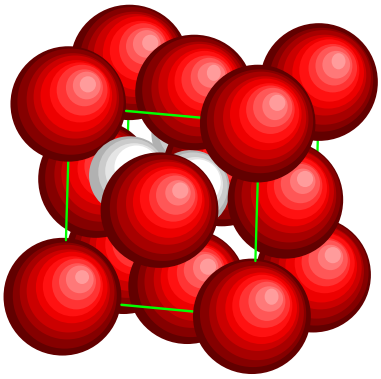

Fig. 2. Crystal latticeof γ-Fe.

In this work, we consider the case where carbon atoms penetrate the octahedral pores of the γ-iron lattice. The choice of this approach was due to the fact that the tetrahedral pores in the γ-iron lattice are small in size and the number of carbon atoms located in these pores will be quite small. Denote the number of atoms in the octahedral pore of iron –N_{Fe}, manganese – N_{Mn}, silicon – N_{Si}, carbon - N_C, vacancies - N_V. The interaction of atoms can be considered as follows: for atoms of the octahedral pore energy of the interaction of pairs of atoms Fe-C, Mn-C, Si-C, Fe-V, Mn-V, Si-V – $\nu_{FeC}, \nu_{FeV}, \nu_{MnC}, \nu_{MnV}, \nu_{SiC}, \nu_{SiV}$.

In this work, the energy of interaction between atoms in the Gaussian 09W program was calculated using the method [13]. The results of the calculation showed that the highest energy of interaction in the γ-iron between the atoms of manganese and iron. The interaction energies are almost the same between iron and carbon atoms, manganese atoms and carbon. The interaction energy between atoms of iron, manganese and silicon was used from work [14].

The free energy of the phase was determined by the formula:

$$F = -6\left(N_{Fe}N_C\nu_{FeC} + N_{Mn}N_C\nu_{MnC} + N_{Si}N_C\nu_{SiC} + N_{Fe}N_V\nu_{FeV} + N_{Mn}N_V\nu_{MnV} + N_{Si}N_V\nu_{SiV}\right) -$$
$$-kT(6(N_{Fe}+N_{Mn}+N_{Si})(\ln(N_{Fe}+N_{Mn}+N_{Si})-1) - 6N_{Fe}(\ln N_{Fe}-1) - 6N_{Mn}(\ln N_{Mn}-1) - \quad (1)$$
$$-6N_{Si}(\ln N_{Si}-1) + (N_C+N_V)(\ln(N_C+N_V)-1) - N_C(\ln N_C-1) - N_V(\ln N_V-1)$$

To calculate the solubility of carbon, manganese, and silicon in γ-iron, we need to find the solution of the equation with the free energy of γ-iron (1):

$$\frac{\partial F}{\partial N_C}=0,\ \frac{\partial F}{\partial N_V}=0,\ \frac{\partial F}{\partial N_{Si}}=0,\ \frac{\partial F}{\partial N_{Mn}}=0,\ \frac{\partial F}{\partial N_{Fe}}=0. \quad (2)$$

The resulting system of equations (2) is transcendental. Usually solutions of such equations can be obtained graphically or numerically. But as part of this task, it is advisable to consider an asymptotic solution of the equations. For this present logarithm, part of each system of equations (2) as a Taylor series (this is permissible under the terms of its convergence):

$$\frac{\partial F}{\partial N_C} = -6N_{Fe}\nu_{FeC} - 6N_{Mn}\nu_{MnC} - 6N_{Si}\nu_{SiC} - kT\left(\ln N_V + \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\left[\frac{N_C^n}{N_V^n} - (N_C-1)^n\right]\right) = 0$$

$$\frac{\partial F}{\partial N_V} = -6N_{Fe}\nu_{FeV} - 6N_{Mn}\nu_{MnV} - 6N_{Si}\nu_{SiV} - 6kT\left(\ln N_C + \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\left[\frac{N_V^n}{N_C^n} - (N_V-1)^n\right]\right) = 0$$

$$\frac{\partial F}{\partial N_{Fe}} = -6N_C\nu_{FeC} - 6N_V\nu_{FeV} - 6kT\left(\ln(N_{Mn}+N_{Si}) + \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\left[\frac{N_{Fe}^n}{(N_{Mn}+N_{Si})^n} - (N_{Fe}-1)^n\right]\right) = 0 \quad (3)$$

$$\frac{\partial F}{\partial N_{Mn}} = -6N_C\nu_{MnC} - 6N_V\nu_{MnV} - 6kT\left(\ln(N_{Fe}+N_{Si}) + \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\left[\frac{N_{Mn}^n}{(N_{Fe}+N_{Si})^n} - (N_{Mn}-1)^n\right]\right) = 0$$

$$\frac{\partial F}{\partial N_{Si}} = -6N_C\nu_{SiC} - 6N_V\nu_{SiV} - 6kT\left(\ln(N_{Mn}+N_{Fe}) + \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\left[\frac{N_{Si}^n}{(N_{Mn}+N_{Fe})^n} - (N_{Si}-1)^n\right]\right) = 0$$

To obtain an asymptotic estimate of system (3) solution it is sufficient to consider the first two terms of expansion in the logarithm expanding.

According to the calculations performed in this work, the maximum carbon content of γ-iron can reach 7.3 % (at.) (1.76 % (wt.)), manganese 64.5 % (at.) (64.3 % (wt.).)) and silicon 2.1 % (at.) (0.93 % (wt.)).

Thus, alloying silicon-manganese iron-based alloys

reduces the solubility of carbon in Fe-C-Mn-Si alloys.

Conclusions

The analysis of the phase composition in the investigated Fe-C-Mn-Si alloys with carbon content of 0.37 – 0.57 % (wt.), silicon 0.23 – 0.29 % (wt.), manganese 0.7 - 0.86 % (by mass), the rest - iron. For the first time it was shown experimentally that the alloys of the Fe-Mn-Si-C system containing carbon (0.57 % (wt.), silicon (0.28 % (wt.)), manganese (0.86 % (wt.)) have better mechanical characteristics, namely, higher numerical value of strength and hardness, as well as of plasticity and fracture toughness, as compared to the alloys with a different content of carbon, manganese and silicon. Thus, the results obtained in this paper show that to improve the mechanical properties of the wheels to be used in the railway transport, the alloys containing carbon (0.57 % (wt.), silicon (0.28 % (wt.)), manganese (0.86 % (wt.)) can be used. The microstructure of this alloy contains up to 95 % of the bulk fraction of pearlite, whose constituent is cementite.

For the first time using the quasichemistry method received free energy dependence of γ-iron with silicon iron and manganese and determined the solubility limit of carbon, manganese and silicon. The maximum carbon content of austenite can reach 7.3 % (at.), manganese 67.5 % (at.) and silicon at 2,3 % (at.).

It was determined that after crystallization and a number of phase transformations the microstructure of the alloy containing 0.37 % (wt.), silicon 0.23 % (wt.), manganese 0.86 % (wt.), consists of α-ferrite and doped cementite $Fe_{2.7}Mn_{0.3}C$.

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Filonenko N.Yu. - Ph.D., Head of the Department of Medical and Biological Physics and Informatics, Senior Researcher of the Department of Deformation and Thermal Treatment of Structural Steels;
Babachenko O.I. - doctor of technical sciences, senior researcher, head of the department of problems of deformation-thermal processing of structural steels;
Kononenko G.A. - Ph.D., Senior Research;
Domina K.G. - Ph.D., Senior Research.

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Н.Ю. Філоненко[1,2], О.І. Бабаченко[2], Г.А. Кононенко[2], К.Г. Дьоміна[2]

Розчинність карбону, мангану та силіцію в γ-залізі сплавів системи Fe-Mn-Si-C

[1]*ДЗ «Дніпропетровська державна медична академія МОЗ України», м. Дніпро, Україна, natph2016@gmail.com*
[2]*Інститут чорної металургії ім. З. І. Некрасова НАН України (ІЧМ НАНУ), м. Дніпро, Україна, A_Babachenko@i.ua.*

Дослідження проводили на сплавах з вмістом карбону 0,37 - 0,57 % (мас.), силіцію 0,23 - 0,29 % (мас.), мангану 0,7 - 0,86 % (мас.), решта – залізо. Для визначення фазового складу сплавів використовували мікроструктурний, мікрорентгеноспектральний та рентгеноструктурний аналізи. В роботі були визначені фізичні характеристики сплавів, що досліджували в даній роботі, а саме, залежність відносного видовження, відносного звуження, ударної в'язкості та твердості від хімічного складу сплаву. Отримані в даній роботі результати показали, що найкращі мікроструктурні та фізичні характеристики має сплав на основі заліза з вмістом карбону 0,57 % (мас.), силіцію 0,28 % (мас.), мангану 0,88 % (мас.). Визначено, що після кристалізації та низки фазових перетворень фазовий склад сплаву представлений двома фазами: α-залізом та легованим манганом цементитом $Fe_{2.7}Mn_{0,3}C$.

Вперше за допомогою методу квазіхімічного методу отримали рівняння вільної енергії твердого розчину γ-заліза, легованого силіцієм і манганом, і визначили межу розчинності карбону, мангану і силіцію. Максимальний вміст карбону в γ-залізі може досягати 6,8 % (ат.), мангану 67,5 % (ат.) та силіцію 2,3 % (ат.).

Ключові слова: сплави Fe-Mn-Si-C, межа розчинності карбону, мангану, силіцію в γ-залізі.