



## CALCULATION OF THE Fe-Fe<sub>3</sub>C PHASE EQUILIBRIUM DIAGRAM

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### Abstract

In heat treatment processes of steel the very important role plays the Fe-Fe<sub>3</sub>C phase equilibrium diagram. It enables the selection of the temperature of austenitisation in respect to carbon content in steel as well as to predict the microstructure composition of annealed steel. For numerical calculation of the phase equilibrium diagrams the CALPHAD method is applied, based on the knowledge of Gibbs energy of phases existing in alloy as functions of temperature and chemical composition of alloy,  $G=f(T,C)$ . The existing phases in Fe-Fe<sub>3</sub>C system are: liquid, austenite, ferrite and cementite. The functions of Gibbs free energy,  $G(T,C)$ , for these phases were published elsewhere. The basic rule for the phase equilibrium diagrams calculations is to calculate the minimum free energy,  $G$ , conditions in system for actual parameters: temperature,  $T$ , pressure,  $p$ , and chemical composition of alloy.

In presented paper the algorithm for Fe-Fe<sub>3</sub>C phase diagram calculation and developed computer program, PD\_Fe\_Fe<sub>3</sub>C are presented. Results of calculations using this program were compared with data obtained using commercial program, Thermo-Calc and both results were identical.

Developed computer program is open and can take into account the alloy elements applied in steel in order to improve their physical properties. The data base for the effect of alloying elements on the free energy of system was prepared, enabling to calculate the effect of common alloying elements, such as Mn, Cr, Si or Ni, on critical temperatures,  $A_1$ ,  $A_3$ ,  $A_{cm}$ . The program may be used for calculation the driving force for phase transformations which occur during heat treatment of steel process as well as in modeling the image of microstructure formed during heat treatment using such numerical methods as cellular automata, CA, or phase field method, PFM.

**Key words:** equilibrium phase diagram, Fe-Fe<sub>3</sub>C diagram, Gibbs free energy

### 1. INTRODUCTION

The phase diagrams are very important tools in study of alloys for solving problems in practical metallurgy. These diagrams define the regions of phases stability that can exist in an alloy system under the condition of constant atmospheric pressure. For binary system the coordinates of these diagrams are temperature and composition. The interrelationships between the phases, the temperature and composition in an alloy system are presented by phase diagram only under equilibrium conditions. Such conditions occur during slow

heating and cooling rates of alloys, when the kinetics of transformations do not play important role.

The phase diagrams are developed using different technical methods: metallographic, dilatometry, magnetics, rentgenographic and – most frequently – the thermal analysis. It is necessary to emphasize that increasing role plays the computer methods of phase diagrams calculations, based on the knowledge of the parameters of free energies for different phases.

The iron-carbon phase diagram plays the very important role in technology of carbon steels because it enables to predict their microstructure

after annealing as well as their mechanical properties. It also enables to select the temperature for heat treatment processes. Currently as the standard iron-carbon the Chipman (1972) diagram is accepted.

Thermodynamic calculation of Fe-Fe<sub>3</sub>C phase diagram was carried out by Gustafson (1985). In literature there are several works for evaluation of complex systems containing Fe, C and alloying elements (Andersson, 1988; Beyong-Joo, 2001; Hillert & Qiu, 1991, 1992; Huang, 1987; Lacaze & Sundman, 1991). In these works there are thermodynamic data used for calculation Fe-Fe<sub>3</sub>C diagram with taking into account additions of alloying elements on the critical temperatures of transformations in this system.

The aim of present work was to develop the computer program for calculation of Fe-Fe<sub>3</sub>C phase diagram.

## 2. DESCRIPTION OF THE THERMODYNAMIC EQUILIBRIUM IN Fe-M-Fe<sub>3</sub>C SYSTEM

The method of equilibrium phase diagram calculations is based on the knowledge of Gibbs free energy functions,  $G$ , for phases existing in analyzed system. Principle thermodynamic properties of  $\varphi$  phase which are used in calculations are free energy of pure  $i$  elements,  ${}^{\circ}G_i^{\varphi}$  and interaction parameters,  $L_{ij}^{\varphi}$  of  $i, j$  elements dissolved in  $\varphi$  phase. In Fe-Fe<sub>3</sub>C system exist four phases: liquid solution, existing above liquidus temperature, austenite,  $\gamma$ , ferrite,  $\alpha$ , and carbide, Fe<sub>3</sub>C. Functions  $G$  for austenite and ferrite in Fe-M-C system, containing alloy element,  $M$ , are described using Hillert and Staffansson (1971) two sublattice model, (Fe,M)<sub>b</sub>(C,V<sub>a</sub>)<sub>c</sub> with substitution elements, Fe, M in one sublattice and carbon, C, with vacancies, V<sub>a</sub>, in second sublattice. The  $b$  and  $c$  parameters denote the number of sites in each sublattice. For austenite  $b=c=1$  and for ferrite  $b=1, c=3$ .

The Gibbs free energy,  $G_m^{\varphi}$ , for one mole of austenite,  $\gamma$ , and ferrite,  $\alpha$ , are given by formulas:

$$\begin{aligned} G_m^{\gamma} = & y_{Fe}y_C {}^{\circ}G_{FeC}^{\gamma} + y_{Fe}y_{Va} {}^{\circ}G_{FeVa}^{\gamma} + \\ & y_My_C {}^{\circ}G_{M:C}^{\gamma} + y_My_{Va} {}^{\circ}G_{M:Va}^{\gamma} + \\ & bRT(y_{Fe} \ln y_{Fe} + y_M \ln y_M) + \\ & cRT(y_C \ln y_C + y_{Va} \ln y_{Va}) + {}^E G_m^{\gamma} + {}^{mg} G_m^{\gamma} \end{aligned} \quad (1)$$

$$\begin{aligned} G_m^{\alpha} = & y_{Fe}y_C {}^{\circ}G_{FeC}^{\alpha} + y_{Fe}y_{Va} {}^{\circ}G_{FeVa}^{\alpha} + y_My_C {}^{\circ}G_{M:C}^{\alpha} + \\ & y_My_{Va} {}^{\circ}G_{M:Va}^{\alpha} + bRT(y_{Fe} \ln y_{Fe} + y_M \ln y_M) + \\ & cRT(y_C \ln y_C + y_{Va} \ln y_{Va}) + {}^E G_m^{\alpha} + {}^{mg} G_m^{\alpha} \end{aligned} \quad (2)$$

where excess free energies,  ${}^E G_m^{\varphi}$  are:

$${}^E G_m^{\gamma} = y_{Fe}y_M (y_C L_{Fe,M:C}^{\gamma} + y_{Va} L_{Fe,M:Va}^{\gamma}) + y_C y_{Va} (y_{Fe} L_{Fe:C,Va}^{\gamma} + y_M L_{M:C,Va}^{\gamma}) \quad (3)$$

$${}^E G_m^{\alpha} = y_{Fe}y_M (y_C L_{Fe,M:C}^{\alpha} + y_{Va} L_{Fe,M:Va}^{\alpha}) + y_C y_{Va} (y_{Fe} L_{Fe:C,Va}^{\alpha} + y_M L_{M:C,Va}^{\alpha}) \quad (4)$$

The term  ${}^{\circ}G_{i:Va}^{\varphi}$  is the Gibbs energy of component  $i$  with structure  $\varphi$  in a hypothetical nonmagnetic state and  ${}^{\circ}G_{i:C}^{\varphi}$  is the Gibbs energy of a hypothetical state, where all interstitial sites are filled with carbon atoms,  $C$ . The  $L$  parameters can be composition dependant according to a Redlich-Kister polynomial.

$y_i$  are the site fractions in sublattices and related to ordinary mole fractions,  $x_i$  by formulae:

$$y_C = \frac{b}{c} \frac{x_C}{1 - x_C} \quad (5)$$

$$y_{Va} = 1 - y_C \quad (6)$$

$$y_{Fe} = \frac{x_{Fe}}{x_{Fe} + x_M} \quad (7)$$

$$y_M = \frac{x_M}{x_{Fe} + x_M} \quad (8)$$

The magnetic term,  ${}^{mg}G_m^{\varphi}$  is magnetic contribution to the Gibbs free energy in  $\gamma$  and  $\alpha$  phases:

$${}^{mg}G_m^{\varphi} = RT \ln(\beta + 1) f(\tau) \quad (9)$$

where  $\tau = T/T_c$  ( $T_c$  – temperature Curie) and  $\beta$  resembles magnetic moment. For ferrite the parameters  $\beta = 2.22 y_{Fe}$ ,  $T_c = 1043 y_{Fe}$  and for austenite:  $\beta = -2.1 y_{Fe}$ ,  $T_c = -201 y_{Fe}$ .

For  $\tau < 1$ :

$$\begin{aligned} f(\tau) = & 1 - \\ & \left[ \frac{79\tau^{-1}}{140p} + \frac{474}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right] / A \end{aligned} \quad (10)$$

and for  $\tau > 1$ :

$$f(\tau) = - \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right) / A \quad (11)$$



where:

$$A = \frac{518}{1125} + \frac{11692}{15975} \left[ \frac{1}{p} - 1 \right] \quad (12)$$

Parameter  $p$  depends on the phase structure,  $p=0,4$  for ferrite and  $p=0,28$  for austenite.

For liquid phase is assumed that liquid can be described as a mixture between Fe, M and C on a single sublattice. Therefore the Gibbs free energy is described by formula:

$$G_m^{liq} = x_{Fe}^o G_{Fe}^{liq} + x_C^o G_C^{liq} + x_M^o G_M^{liq} + RT(x_{Fe} \ln x_{Fe} + x_M \ln x_M + x_C \ln x_C) + {}^E G_m^{liq} \quad (13)$$

where

$${}^E G_m^{liq} = x_{Fe} x_M L_{Fe,M}^{liq} + x_C x_{Fe} L_{Fe,C}^{liq} + x_C x_M L_{M,C}^{liq} \quad (14)$$

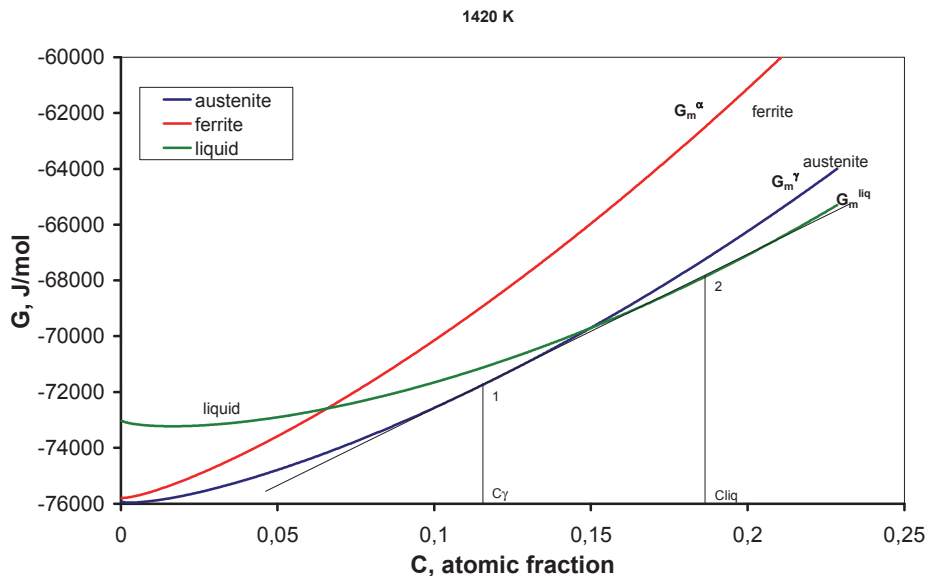
Cementite has orthorhombic structure and is stoichiometric with respect to C,  $(Fe,M)_3C$ . This phase is described by two-sublattice model. The Gibbs free energy for one mole of cementite is given by following expression:

$$G_m^{cem} = y_{Fe}^o G_{Fe,C}^{cem} + y_M^o G_{M,C}^{cem} + 3RT(y_{Fe} \ln y_{Fe} + y_M \ln y_M) + y_{Fe} y_M L_{Fe,M:C}^{cem} \quad (15)$$

a comprehensive data base of these parameters is presented by Adrian (2011).

### 3. METHOD OF Fe-Fe<sub>3</sub>C DIAGRAM CALCULATION

In Fe-Fe<sub>3</sub>C phase diagram there is 11 different areas, where exist one or two phases: 4 one-phase areas (liquid,  $L$ , ferrite high temperature,  $\delta$ , (above  $A_4$ ), ferrite low temperature,  $\alpha$ , (below  $A_3$ ) and austenite,  $\gamma$ ) and 7 two-phase areas ( $L+\delta$ ,  $L+\gamma$ ,  $L+Fe_3C$ ,  $\delta+\gamma$ ,  $\gamma+Fe_3C$ ,  $\alpha+\gamma$ ,  $\alpha+Fe_3C$ ). Characteristic temperatures are:  $T_l$  – melting point for Fe,  $T_{icem}$  – melting point for cementite,  $A_4$  – temperature of allotropic transformation,  $Fe_\gamma \rightarrow Fe_\delta$ ,  $A_3$  – temperature of allotropic transformation,  $Fe_\alpha \rightarrow Fe_\gamma Fe_\delta$ ,  $T_{peritectic}$  – temperature of peritectic transformation,  $L+\delta \rightarrow \gamma$ ,  $T_{eutectic}$  – temperature of eutectic transformation,  $L \rightarrow \gamma + Fe_3C$ , and  $A_1$  – temperature of eutectoid transformation,  $\gamma \rightarrow \alpha + Fe_3C$ . Temperatures of transformations (peritectic, eutectic, eutectoid) depends on the chemical composition of iron alloy and addition of M alloying element may change these temperatures. Calculation of Fe-Fe<sub>3</sub>C phase diagram involves the calculation of two-phase areas boundaries as functions of temperature. In these areas in any temperature there is constant chemical composition of existing phases resulting from



**Fig. 1.** Relationships between Gibbs free energy and carbon content for ferrite, austenite and liquid at 1420 K. Tangent line to  $G_m^{liq}$  and  $G_m^\gamma$  determines the chemical composition of austenite,  $C_\gamma$  and liquid,  $C_{liq}$  in two-phase ( $\gamma$ +liquid) area.

Thermodynamic properties of Fe-M-C system are published elsewhere (e.g. Huang, 1987),

minimum Gibbs free energy of the system. The chemical composition of these phases is defined by coordinates points of tangent line to both Gibbs free



energy functions of phases  $\varphi$  and  $\Phi$ . Therefore in order to calculate the carbon contents in equilibrium phases,  $c_\varphi$  and  $c_\Phi$  it is necessary to solve following non-linear equations system:

$$G_m^\varphi(c_\varphi) - G_m^\Phi(c_\Phi) - \frac{\partial G_m^\varphi(c_\varphi)}{\partial c} \cdot (c_\varphi - c_\Phi) = 0 \quad (16)$$

$$G_m^\Phi(c_\Phi) - G_m^\varphi(c_\varphi) - \frac{\partial G_m^\Phi(c_\Phi)}{\partial c} \cdot (c_\Phi - c_\varphi) = 0 \quad (17)$$

Graphical illustration of the method is shown in figure 1, which presents the relationships between Gibbs free energy,  $G$ , and carbon content,  $C$ , for liquid, austenite and ferrite at 1420 K. At this temperature exist two phases: austenite with composition  $C_\gamma$  and liquid with composition  $C_{liq}$ .

For solution the non-linear equations system the steepest descent method was used, described in Burden (1985). Advantage of this method, in comparison to others (e.g. Newton method) is, that it does not require an accurate initial approximation to the solution in order to ensure convergence.

descent method was used (Burden, 1985). General scheme of calculation is as follows:

1. Input chemical composition of alloy
2. Calculate  $T_b$ ,  $T_{icem}$ ,  $A_3$  and  $A_4$
3. Define temperature limits for areas 1 to 7,
4. For  $i=1$  to 7 repeat steps 5 to 11
  5.  $T_a = T_g(i)$
  6.  $j=1$ ,
  7. Repeat steps 8 to 11 until  $T_a < T_d(i)$
  8. calculate  $C^\varphi(T_a)$ ,  $C^\Phi(T_a)$
  9. store calculated data in Fe\_C table
  10.  $j:=j+1$
  11.  $T_a = T_a - \Delta T$
12. Calculate the transformation temperatures –  $T_{peritectic}$ ,  $T_{eutectic}$ ,  $A_1$
13. Draw Fe-Fe<sub>3</sub>C phase diagram.

where  $T_g(i)$ ,  $T_d(i)$  – assumed temperature range for  $i$  – line. Except of pure Fe-Fe<sub>3</sub>C phase diagram calculation the program enables to calculate modified diagram taking into account different alloying elements, such as Mn, Si, Cr but in low

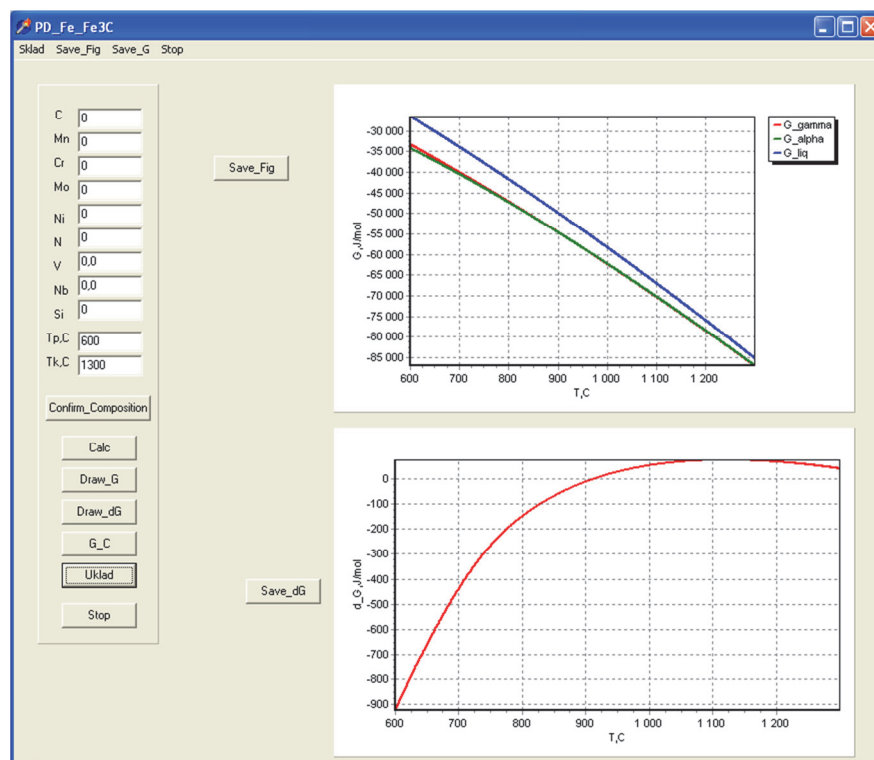


Fig. 2. Input data window of PD\_Fe\_Fe3C program.

#### 4. PD\_Fe\_Fe<sub>3</sub>C COMPUTER PROGRAM

The computer program PD\_Fe\_Fe3C was developed. The code was written in Delphi programming system. For solution of non-linear equation systems in two-phase areas, the steepest

contents, common for low alloy steel, where these elements are dissolved in Fe containing phases and do not form separated phases, because the formation of compounds formed by these elements is not include in the algorithm of program. Program enables also to calculate the Gibbs free energy,  $G=f(T)$  for different phases at given temperature





range (for definite chemical composition of alloy) - upper chart in figure 2, or  $G=f(C)$  functions (for given temperature,  $T$ , figure 3). Calculated functions  $G=f(C)$  for liquid, austenite and ferrite were compared with results of calculations using ThermCalc program and good agreement was observed.

One of the options of program is the calculation of difference Gibbs free energy for ferrite and austenite as a function of undercooling. This difference,  $\Delta G$ , is driving force for  $\gamma \rightarrow \alpha$  transformation (figure 2 – lower chart).

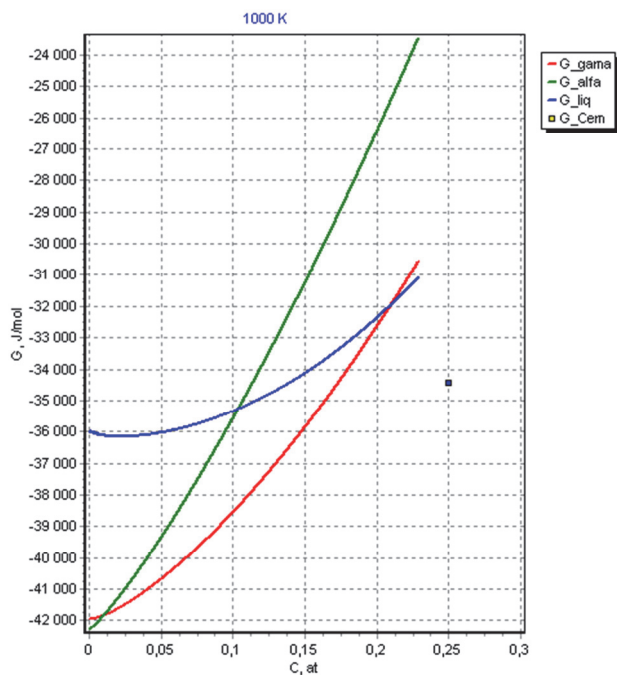


Fig. 3. The relationships between Gibbs energy,  $G$ , and carbon content,  $C$ , at 1000 K.

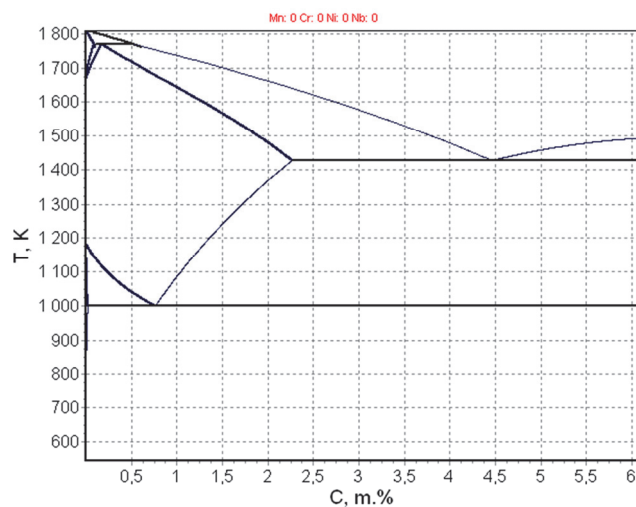


Fig. 4. Calculated Fe-Fe<sub>3</sub>C phase diagram.

Calculated Fe-Fe<sub>3</sub>C phase diagram is presented in figure 4.

The effect of addition of 1,5 %Mn on  $A_3$ ,  $A_{cm}$  and  $A_1$  temperatures in Fe-Fe<sub>3</sub>C diagram is presented in figure 5. This addition mainly decreases the  $A_3$  and  $A_1$  temperatures as well as decreases the carbon content in eutectoid point.

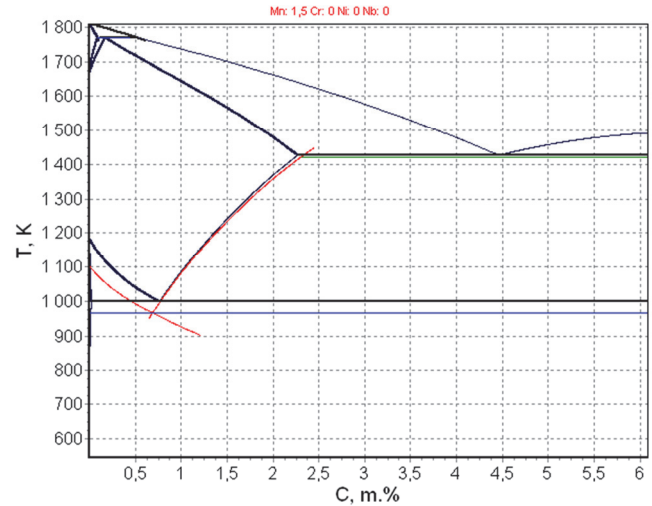


Fig. 5. Fe-Fe<sub>3</sub>C phase diagram with shifted  $A_3$  and  $A_{cm}$  lines as 1,5 m.% of Mn addition.

## 5. CONCLUDING REMARKS

For selection the optimum parameters for heat treatment of steels the useful tool is the quasi-equilibrium phase diagram, Fe-Fe<sub>3</sub>C. This diagram enables also to predict the microstructure of annealed steel on the knowledge of carbon content. Developed computer program PD\_Fe\_Fe<sub>3</sub>C enables to calculate this diagram. Additionally it enable to calculate the effect of alloying elements, commonly used in quenched and tempered steels, on the critical temperatures:  $A_3$ ,  $A_{cm}$ , and  $A_1$ . For calculation the microstructure image of heated treated steel different numerical models and methods are used (e.g. Adrian & Spiradek-Hahn, 2009; Marynowski et al., 2013). The input data used for such calculations are Gibbs free energies of phases existing in considered system and data obtained using PD\_Fe\_Fe<sub>3</sub>C program can be applied.

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## OBLICZANIE WYKRESU RÓWNOWAGI FAZOWEJ Fe-Fe<sub>3</sub>C

### Streszczenie

W obróbce cieplnej stopów żelaza ważnym narzędziem pomocniczym jest wykres równowagi fazowej Fe-Fe<sub>3</sub>C. Umożliwia dobór parametrów obróbki cieplnej stali węglowych, jak również pozwala określić skład strukturalny stali po obróbce cieplnej. Obliczanie wykresów równowagi fazowej metodą CALPHAD jest oparte na znajomości energii swobodnej Gibbsa jako funkcji temperatury i składu chemicznego,  $G=f(T,C)$  faz istniejących w układzie: austenit, ferryt, cementyt, ciecz. Obliczanie wykresu równowagi fazowej polega na obliczaniu minimum energii swobodnej układu metodami numerycznymi. W prezentowanej pracy przedstawiono program komputerowy PD\_Fe\_Fe<sub>3</sub>C do obliczania wykresu Fe-Fe<sub>3</sub>C. Program umożliwia również obliczanie wpływu pierwiastków stopowych na temperatury krytyczne wykresu w stali niskostopowej. Pozwala również obliczać siłę pędzą przemian fazowych zachodzących podczas obróbki cieplnej stali, co może być przydatne przy obliczaniu obrazu mikrostruktury metodami np. automatów komórkowych czy pola fazowego.

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