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MATHEMATICAL FORMALISMS TO REPRESENT KNOWLEDGE CONCERNING THE PRODUCTION PROCESS OF AUSTEMPERED DUCTILE IRON

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The aim of this study is to develop computer tools for calculation of the Fe - Fe_3C phase equilibrium diagram. The phase equilibrium diagram is of fundamental importance in materials science and heat treatment processes of ferrous alloys. It enables prediction of carbon steel microstructure in the annealed condition, and facilitates selection of proper temperature for the heat treatment process. Choosing the right values of the heat treatment process parameters is essential in the production of Austempered Ductile Iron (ADI).

Key words: Fe - Fe_3C diagram, phase equilibrium diagram, ADI, CALPHAD method

INTRODUCTION

The process of ADI production from ductile iron comprises two steps: austenitising at a temperature above the A_{c1} point and subsequent austempering in the temperature range of bainite transformation. The properties of the resulting product depend on the quality of base materials (the structure of ductile iron - in particular) and on the technological parameters of heat treatment (time, temperature, and cooling rate). The purpose of the heat treatment is to obtain a material with the resultant properties superior to the properties of the starting product[1]. The most commonly considered are the mechanical properties such as the tensile strength R_m, yield strength $R_{p0,2}$, elongation A_5, hardness *HB* and toughness *KC*.

The production of ADI can be schematically represented as a five-step process, involving [2]:

• Step 1: making ductile iron castings characterised by high hardenability, usually achieved by adding Ni, Cu or Mo.

• Step 2: annealing (austenitising) of castings at a temperature of 850 ÷ 950 °C and for the time of 0,5 to 3 hours (depending on the casting weight and shape), to obtain maximum austenite saturation with carbon originating from the decomposition of pearlite and partly dissolved graphite.

• Step 3: cooling of castings, usually in a salt bath, to the austempering temperature in a range of 230 ÷ 400 °C at a rate sufficient to avoid pearlite formation.

• Step 4: austempering of castings for the time of 0,5 ÷ 5 hours, sufficient to form an ausferritic matrix. The primary γ austenite with an equilibrium carbon content at the temperature of austenitising is transformed during austempering into supersaturated ferrite plates and high-carbon γ_{HC} austenite. This process proceeds in two stages, with Stage II adversely affecting the properties of ADI: 1) primary austenite → stable (high-carbon) austenite + ferrite; 2) stable (high-carbon) austenite → ferrite + carbides.

• Step 5: Cooling of castings to room temperature.

When designing the process line, the technologist is forced to take a number of decisions regarding the individual process parameters. The task of computer-based decision support systems is to facilitate as much as possible the work of technologist at various stages of the design and production. For this purpose, various systems provided with the knowledge base are used, where the knowledge representation formalisms are dependent on the type of information processed. The authors in their previous works have already presented the possibility of using rough sets, ontologies, attribute tables and fuzzy logic. Formal knowledge representation is the key element of modern knowledge integration processes [3]. In the problem under consideration, the mathematical formalisms in the form of equations and graphs have been used. Each of them contains a finite amount of knowledge and is applicable in the processes of inference. Mathematical formalism is the most versatile, unambiguous and best recyclable tool. Whenever it is possible to describe knowledge with mathematical models, this option is the best choice. This paper presents the problem of creating a knowledge representation system for the heat treatment process, with particular emphasis put on the role of charts, knowing how important in the task of optimising the structure and

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properties of iron alloys are the methods of computer modelling of phase transformations occurring during heating and cooling.

The choice of heat treatment parameters is based on graphs describing the state of thermodynamic equilibrium (Fe - Fe_3C diagram – the choice of austenitising temperature) and on graphs describing the kinetics of the decomposition of undercooled austenite under the conditions of isothermal holding temperature (TTT diagrams – the choice of time and temperature of holding the cast iron subjected to preliminary austenitising treatment). The Fe - Fe_3C phase diagram was developed using the results of experimental studies made by Chipman [4]. Progress in the thermodynamics of solutions allowed developing a model and an algorithm for calculation of this diagram, knowing the free energy function of phases present in the Fe - Fe3C system.

CALPHAD METHOD

The CALPHAD method currently used for the calculation of phase equilibrium systems is based on the Gibbs free energy function, *G*, of phases present in the system, where the value of the function depends on the temperature and chemical composition. In the Fe - Fe_3C system, four phases are present, i.e. a liquid solution of carbon in iron - *L*, solid solutions of carbon in Fe_α (ferrite) and Fe_γ (austenite), and iron carbide - Fe_3C (cementite). The basic thermodynamic properties of any φ phase used in the calculations are free energies of pure components - ${}^oGi^\varphi$ and impact parameters – $L_{i.j}^{\ \varphi}$ of elements dissolved in the φ phase. The functions of the free energy *G* of austenite and ferrite in the Fe - Fe_3C system, which also contains a small amount of an alloying additive X, are described with the Hillert and Staffansson two-sublattice model $(Fe, X)_b\,(C, V_a)_c$ with substitution solution present in one sublattice, and carbon atoms - C and vacancies - V_a in the other. For austenite b = c = 1, while for the ferrite b = 1, c = 3. The free energy of one mole of austenite $G_m^{\ \gamma}$ and ferrite $G_m^{\ \alpha}$ is described by the following equations:

$$\begin{aligned} G_m^\gamma &= y_{Fe}y_C\,{}^\circ G_{Fe:C}^\gamma + y_{Fe}y_{Va}\,{}^\circ G_{Fe:Va}^\gamma + \\ &+ y_X y_C\,{}^\circ G_{X:C}^\lambda + y_X y_{Va}\,{}^\circ G_{X:Va}^\lambda + \\ &+ bRT(y_{Fe}\ln y_{Fe} + y_X \ln y_X) + \\ &cRT(y_C \ln y_C + y_{Va}\ln y_{Va}) + {}^E G_m^\gamma + {}^{mg} G_m^\lambda \end{aligned} \tag{1}$$

$$\begin{aligned} G_m^\alpha &= y_{Fe}y_C\,{}^\circ G_{Fe:C}^\alpha + y_{Fe}y_{Va}\,{}^\circ G_{Fe:Va}^\alpha + \\ &+ y_X y_C\,{}^\circ G_{X:C}^\alpha + y_X y_{Va}\,{}^\circ G_{X:Va}^\alpha + \\ &+ bRT(y_{Fe}\ln y_{Fe} + y_X \ln y_X) + \\ &cRT(y_C \ln y_C + y_{Va}\ln y_{Va}) + {}^E G_m^\alpha + {}^{mg} G_m^\alpha \end{aligned} \tag{2}$$

where: ${}^E G_m^{\ \varphi}$ is the residual free energy, and ${}^{mg}G_m^{\ \varphi}$ is the contribution of a magnetic effect to the free energy of the φ phase.

The residual free energy of austenite ${}^E G_m^{\ \gamma}$ is described by the equation:

$$\begin{aligned} {}^E G_m^\gamma &= y_{Fe}y_X(y_C L_{Fe,X:C}^\gamma + y_{Va}L_{Fe,X:Va}^\gamma) + \\ &+ y_C y_{Va}(y_{Fe}L_{Fe:C,Va}^\gamma + y_X L_{X:C,Va}^\gamma) \end{aligned} \tag{3}$$

The residual free energy of ferrite ${}^E G_m^{\ \alpha}$ is described by the equation:

$$\begin{aligned} {}^E G_m^\alpha &= y_{Fe}y_X(y_C L_{Fe,X:C}^\alpha + y_{Va}L_{Fe,X:Va}^\alpha) + \\ &+ y_C y_{Va}(y_{Fe}L_{Fe:C,Va}^\alpha + y_X L_{X:C,Va}^\alpha) \end{aligned} \tag{4}$$

In equations (1), (2), (3) and (4), the symbol y_i represents the proportional fraction of the *i* element (or of vacancies V_a) in one sublattice referred to the atomic fraction x_i of this element in steel:

$$y_C = \frac{a}{c}\frac{x_C}{1-x_C} \tag{5}$$

$$y_{Va} = 1 - y_C \tag{6}$$

$$y_{Fe} = \frac{x_{Fe}}{x_{Fe}+x_X} \tag{7}$$

$$y_X = \frac{x_X}{x_{Fe}+x_X} \tag{8}$$

The symbol ${}^oG_{i:Va}^{\ \phi}$ denotes the Gibbs free energy of the *i* element in ϕ structure, and ${}^oG_{i:C}^{\ \phi}$ - the free energy of the state in which all interstitial positions are filled with C atoms. *L* is the parameter of interaction between elements dissolved in the ϕ phase.

The contribution of a magnetic transformation to the Gibbs free energy of austenite and ferrite is described by the equation:

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

where $\tau = T/T_c$ (T_c – Curie temperature). For $\tau<1$:

$$f(\tau) = 1 - \frac{\frac{79\tau^{-1}}{140p} + \frac{474}{497}\left(\frac{1}{p}-1\right)\left(\frac{\tau^3}{6}+\frac{\tau^9}{135}+\frac{\tau^{15}}{600}\right)}{A} \tag{10}$$

for $\tau>1$:

$$f(\tau) = -\left(\frac{\tau^{-5}}{10}+\frac{\tau^{-15}}{315}+\frac{\tau^{25}}{1\,500}\right)/A \tag{11}$$

where:

$$A = \frac{518}{1\,125} + \frac{11\,692}{15\,975}\left(\frac{1}{p}-1\right) \tag{12}$$

The parameter *p* depends on the type of lattice and is equal to 0,4 and 0,28 for the ferrite and austenite, respectively.

The free energy of the liquid $G_m^{\ liq}$ is described with a one-sublattice model (Fe, X, C) and for one mole is equal to:

$$\begin{aligned} G_m^{liq} &= x_{Fe}\,{}^O G_{Fe}^{liq} + x_C\,{}^O G_C^{liq} + x_X\,{}^O G_X^{liq} + \\ &+ bRT(x_{Fe}\ln x_{Fe} + x_X \ln x_X + x_C \ln x_C) + \\ &+ {}^E G_m^{liq} \end{aligned} \tag{13}$$

where:

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

The cementite occurring in the system is described by a model composed of two sublattices, $(Fe,X)_bC_c$, allowing for the stoichiometry of the compound:

$$G_m^{Fe3C} = y_{Fe}\,{}^{O}G_{Fe:C}^{Fe_3C} + y_X\,{}^{O}G_{Fe:C}^{Fe_3C} + \\ + bRT(y_{Fe}\ln y_{Fe} + y_X \ln y_X) + \\ + cRTy_{Fe}y_X L_{Fe,X:C}^{Fe_3C} \quad (15)$$

All parameters used in the calculation of the Fe - Fe3C equilibrium diagram are given in [2].

METHOD TO CALCULATE THE Fe - Fe_3C PHASE EQUILIBRIUM DIAGRAM

To calculate the chemical composition of phases coexisting in the two-phase region at a temperature *T*, it is necessary to calculate the points tangent to the curves of the free energy G_m^{φ} of the coexisting phases. The diagram shown in Figure 1 is an example of the calculation of the chemical composition of the austenite and liquid at a temperature of 1 420 °C.

The coordinates of an independent variable for points 1 and 2 lying on a tangent to the free energy curves G_m^{γ} and G_m^{liq} define the composition of austenite (c_γ) and liquid (C_{liq}). The values of c_γ and c_{liq} are the solution of two equations:

$$G_m^{\gamma}(c_\gamma) - G_m^{liq}(c_{liq}) - \frac{\partial G_m^{liq}}{\partial c}\left(c_{liq}\right)\cdot\left(c_\lambda - c_{liq}\right) = 0 \quad (16)$$

$$G_m^{liq}(c_{liq}) - G_m^{\gamma}(c_\gamma) - \frac{\partial G_m^{\gamma}}{\partial c}\left(c_\gamma\right)\cdot\left(c_{liq} - c_\gamma\right) = 0 \quad (17)$$

It should be noted that parameters present in functions *G* and *L* must be multiplied by (1 - xc).

COMPUTER SUPPORT

A computer programme has been developed to aid the calculation of phase equilibrium state in an iron alloy containing alloying elements (Mn, Cr, Ni, Mo, Si, V, Nb). The programme allows for the effect of alloying elements present in steel on the Gibbs free energy of phases in the steel of a given chemical composition at a given temperature *T*. Using this programme, one can calculate the basic input data for the modelling of phase transformations occurring in the examined material: (1) the difference in the free energy of ferrite and austenite, which is the driving force for the austenite-ferrite transformation, (2) the basic critical temperatures: A_{c3}, A_{cm}, A_{c1}.

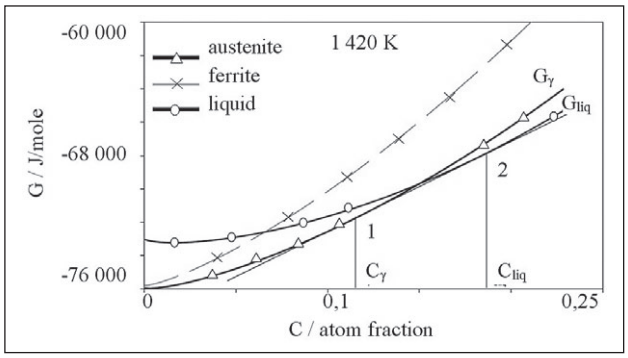

Figure 1 ree energy curves of austenite, ferrite and liquid at a temperature of 1 420 °C

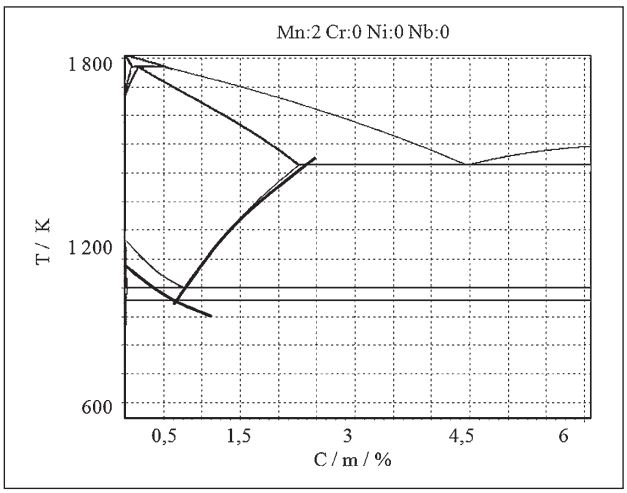

Figure 2 The calculated Fe - Fe3C phase equilibrium diagram allowing for 2 % Mn content (bold lines)

An example of the phase equilibrium diagram calculated for the Fe - Fe_3C system with 2 % Mn content is shown in Figure 2.

After entering the chemical composition, the following parameters are calculated: (1) the Gibbs free energy of austenite, ferrite, liquid and cementite for a given range of temperatures T_p, T_k, (2) the difference in the free energy of ferrite and austenite as a function of temperature $\Delta G^{\gamma\to\alpha}=f(T)$. The calculated data can be presented in the form of graphs or saved to files for further use.

This form of representation of the diagram describing the state of thermodynamic equilibrium can be easily implemented in a computer programme to model the heat treatment process of ADI [5]. The TTT graphs describing the kinetics of phase transformations taking place in the undercooled austenite under isothermal conditions are derived from experimental studies, although they could be equally well calculated with the help of Avrami equation [6]:

$$y = 1 - \exp\left(-\frac{\pi}{3}V_z V_w \tau^4\right) \quad (18)$$

where: *y* – the fraction of transformed austenite, V_z, V_w - the rate of nucleation and growth, respectively, of phases formed at a temperature *T* and holding time τ. The numerical calculation of TTT diagram is much more difficult because the values of V_z, and V_w depend not only on the temperature but also on the point of nucleation of a new phase. Therefore, the calculated TTT diagrams are generally less compatible with the empirical graphs.

CONCLUSIONS

Studies described in this article use mathematical formalisms of knowledge representation concerning the manufacture of ADI, discussing also possible use of these formalisms in the process of inference. Generating digitised graphs is an important tool supporting the task of optimisation of the structure and properties of ferrous alloys by a computer-aided method for the modelling of phase transformations that occur during heating and cooling. The choice of the heat treatment parameters is based on the diagrams describing the state of thermodynamic equilibrium.

The Fe - Fe_3C phase equilibrium diagram for the examined grade of cast iron, digitised with the above described application, is a useful tool in the design of the ductile iron austempering process.

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Note: The responsible translator for English language is K. Bany, Cracow, Poland