

PHASE TRANSFORMATIONS IN STEEL DURING RAPID HEAT TREATMENT

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Received April 19, 1987

Abstract

Phase transformations in low-carbon steels during rapid heat treatment proceed very differently than under equilibrium conditions. The differences can successfully be utilized for improving the properties of the steels.

Introduction

During the past decades many efforts were made to increase productivity of technological operations, i.e. amount of product per unit time, simultaneously maintaining or improving the quality of the product. This economic-technological demand led to important results in the manufacture of metals and alloys, including acceleration of heat treatment processes: instead of traditional indirect heat transfer in furnaces, the metal is directly heated by the Joule heat of the electric current passed through it.

This technique allows to raise the heating rate from traditional 1—100 K/min by several orders of magnitude, to 10^3 — 10^5 K/s [1, 2], thus increasing productivity of the heat treatment operation in a similar extent.

The substantial increase of the heating rate largely changes the character of the structural transformations taking place in metals and alloys during heat treatment. This paper deals with the structural changes taking place in unalloyed carbon steels during rapid heating.

First of all, it should be considered that at such high heating rates, diffusion processes, i.e. place changes of atoms owing to structural changes will concern practically only atoms interstitially dissolved in the phases participating in the transformations. By way of example, let us mention that in dual-phase steels — even though their heat treatment time is much longer, in the order of minutes, than that of rapidly heated steels — phase change conditions differ so greatly from equilibrium conditions that the para-equilibrium concept has been introduced, indicating that when dual-phase steels are being heated in the γ region to the so-called intercritical temperature in order to attain the desired α/γ proportion, instead of aiming at thermo-

dynamical equilibrium, the aim is to reach the state where the appropriate α/γ phase proportion is realized and the carbon content in the phase reaches the value corresponding to the given conditions. During this time substitutionally dissolved atoms practically do not change their places, since their diffusion rate is lower by several orders of magnitude than that of interstitially dissolved atoms. In Table 1 the diffusion coefficients of some interstitially and

Table 1
Coefficient $D = D_0(\exp(-Q/RT))$

| Phase | Element | Q [kcal/mol] | D_0 [cm ² /s] | $D_{723^\circ\text{C}}$ [cm ² /s] | $D_{1000^\circ\text{C}}$ [cm ² /s] | $D_C : D_M$ 723 °C | $D_C : D_M$ 1000 °C |
|-------------|---------|-------------------|-------------------------------|---|--|-----------------------|------------------------|
| α Fe | C | 29.3 | 2.2 | $9 \cdot 10^{-7}$ | — | — | — |
| α Fe | Fe | 60.3 | 5.4 | $3.85 \cdot 10^{-13}$ | — | $2.3 \cdot 10^6$ | — |
| α Fe | Co | 62.2 | 7.19 | $1.98 \cdot 10^{-13}$ | — | $4.5 \cdot 10^6$ | — |
| α Fe | Cr | 57.5 | 2.53 | $7.36 \cdot 10^{-13}$ | — | $1.2 \cdot 10^6$ | — |
| α Fe | Mn | 52.5 | 0.35 | $1.25 \cdot 10^{-12}$ | — | $7.2 \cdot 10^5$ | — |
| α Fe | Ni | 56.0 | 1.3 | $8.03 \cdot 10^{-13}$ | — | $1.1 \cdot 10^6$ | — |
| α Fe | V | 55.4 | 1.43 | $1.19 \cdot 10^{-12}$ | — | $7.6 \cdot 10^5$ | — |
| α Fe | W | 55.1 | 0.29 | $2.82 \cdot 10^{-13}$ | — | $3.2 \cdot 10^6$ | — |
| γ Fe | C | 34.0 | 0.15 | $5.8 \cdot 10^{-9}$ | $1.5 \cdot 10^{-6}$ | — | — |
| γ Fe | Fe | 67.36 | 0.49 | $1.0 \cdot 10^{-15}$ | $3.23 \cdot 10^{-12}$ | $5.8 \cdot 10^6$ | $4.6 \cdot 10^5$ |
| γ Fe | Co | 72.9 | 1.25 | $1.6 \cdot 10^{-16}$ | $4.59 \cdot 10^{-13}$ | $3.6 \cdot 10^7$ | $2.7 \cdot 10^6$ |
| γ Fe | Cr | 69.7 | 10.8 | $6.9 \cdot 10^{-15}$ | $1.39 \cdot 10^{-11}$ | $8.4 \cdot 10^5$ | $1.1 \cdot 10^5$ |
| γ Fe | Mn | 62.5 | 0.16 | $3.8 \cdot 10^{-15}$ | $3.49 \cdot 10^{-12}$ | $1.5 \cdot 10^6$ | $4.3 \cdot 10^5$ |
| γ Fe | Ni | 67.6 | 0.77 | $1.4 \cdot 10^{-15}$ | $2.27 \cdot 10^{-12}$ | $4.1 \cdot 10^6$ | $6.6 \cdot 10^5$ |
| γ Fe | V | 69.3 | 0.28 | $2.2 \cdot 10^{-16}$ | $4.23 \cdot 10^{-13}$ | $2.6 \cdot 10^7$ | $3.5 \cdot 10^6$ |
| γ Fe | W | 90.0 | 1000.0 | $2.4 \cdot 10^{-17}$ | $4.45 \cdot 10^{-13}$ | $2.6 \cdot 10^8$ | $3.4 \cdot 10^6$ |

substitutionally dissolved atoms at 723 °C and 1000 °C in the ferritic phase (α) and in the austenitic phase (γ) are listed [3]. These values can also be interpreted as the time required for the atom in question to cover unit path length in the steel. This is one of the reasons why the character of structural change will be different in rapid heating.

Some remarks should be made regarding Table 1. First, it should be noted that the diffusion coefficient of carbon is higher by 5—7 orders in both ferrite and austenite than that of substitutional atoms in the same phase. Second, it should be remarked that the diffusion coefficients of both interstitial and substitutional atoms are higher by several orders of magnitude in ferrite than the values or calculated values in austenite. This phenomenon is due to the much looser structure of ferrite, allowing easier place changes for both interstitial and substitutional atoms as well as for same-species atoms (cf. self-diffusion coefficients). The very low values for substitutional atoms also indicate that even homogenization of several hours will not be sufficient to achieve uniform distribution of these atoms in the alloy.

Figure 1 represents the part important for practice of the isothermal section at 740 °C of the state diagram of Fe—Mn—C steels [4, 5]. In the figure, the broken lines indicate the true thermodynamic equilibrium for a steel containing 0.06% C and 1.5% Mn. The figure demonstrates that the equilibrium phase contains more carbon and manganese than the para-equilibrium phase formed in rapid heating. The same statement is represented in Fig. 2, showing Mn distribution in ferrite and austenite after 1 hr heating to 740 °C in the above composition steel. According to Fig. 1, in the equilibrium state, at 0.06% C content, austenite will dissolve 3% Mn. This is confirmed in

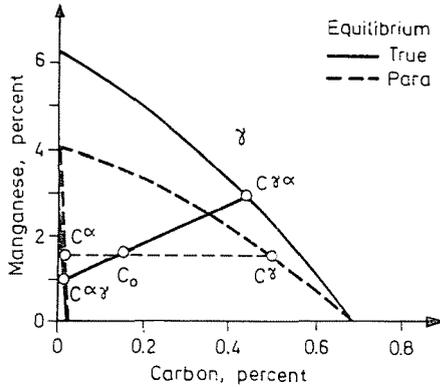


Fig. 1

Fig. 2. Ferrite, however, in the equilibrium state, dissolves around 1% Mn, whereas Fig. 2 indicates that ferrite, after 1 hr heat treatment at 740 °C, still contains about 1.3% Mn at the ferrite-austenite phase boundary. The figures confirm that heat treatment for 1 hr is insufficient for rearrangement of substitutional elements. The duration of heat treatment in modern technol-

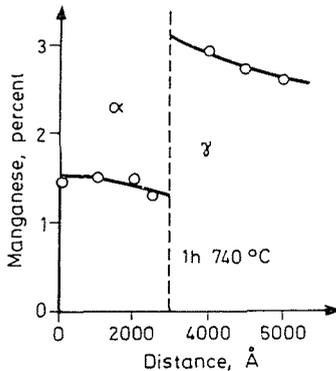


Fig. 2

ogies is in the order of seconds, that is, concentration distribution of substitutional elements will be retained practically unchanged.

However, the fact that the distribution of substitutional elements will remain practically unchanged will — to a certain extent — affect the distribution of interstitial elements, too. This is clearly shown by Fig. 1, demonstrating that in the given alloy, austenite contains about 0.5% C in the para-equilibrium state, while in the equilibrium state C content is 0.43%.

Phase transformations are of greater importance than concentration distribution of the components. Before discussing these phenomena, let us have a look at the recrystallization processes in plastic steel deformation. Diffusion will play no important role here, since the transformation which as to its characteristics belongs to recrystallization processes without concentration changes in the alloy will proceed differently under the effect of rapid heating than in the case of slow heating.

Recrystallization

To describe recrystallization exactly, the frequency of nucleus formation, i.e. the number of nuclei capable of growth formed in unit time and unit volume N

$$N = N_0 \exp(-Q_N/RT) \quad (1)$$

(where N_0 and Q_N are assumed to be constant values for the given material) and linear growth rate of the nuclei G

$$G = G_0 \exp(-Q_G/RT) \quad (2)$$

(where G_0 and Q_G are materialspecific constants) should be combined with the Avrami—Mehl equations. However, the required data N_0 , G_0 , Q_N , Q_G are not at disposal for the majority of metals and alloys used in practice. Therefore, the relationship for recrystallization rate which has proved a very good approach for practice will be made use of:

$$v = \frac{dV}{dt} = A \exp(-Q/RT) \quad (3)$$

where A is a constant characteristic for the material and its deformation, Q is well approached by the self-diffusion coefficient of the material and dV is the volume transformed during the interval dt .

It follows from Eq. (3) that if a given material recrystallizes at the temperature T_1 during the time t_1 , a time interval t will be required for recrystallization at the temperature T , i.e.

$$t = t_1 \exp Q/R(1/T - 1/T_1) \quad (4)$$

Making use of Eq. (4), we listed, in Table 2, the time intervals required for recrystallization of three metals: Al, Cu and Fe, assuming that at the homologous temperature 0.5, recrystallization time is 0.5 hr. The data indicate that time requirement for Al recrystallization is reduced to 1.5 s by raising recrystallization temperature by 110 °C. To attain similar reduction in recrystallization time for copper, a temperature increase of 160 °C is necessary.

The temperature increase necessary for steel does not exceed 220 °C. However, such an increase will raise the temperature of steel above the temperature A_1 : it is more than 100 °C higher than the temperature of perlite-austenite transformation. None the less, one may disregard this transformation, since — as will be shown in the following — the transformation cannot proceed at the given temperature in such a short time.

Drastically reduced recrystallization time results not alone in important time saving of the heat treatment process, but also in average crystallite size far below the value attained with traditional heat treatment methods. For instance, a value of 8 to 9 by the ASTM standard is considered a good result for steels recrystallized in furnaces. With rapid heating, during fractions of a second, an ASTM value of 11—12 can readily be obtained.

Table 2

| $\frac{T}{T}$ m.p. | Al | | | Cu | | | Fe | | |
|--------------------|---------|-----------|---------|---------|-----------|---------|---------|-----------|---------|
| | T [K] | T' [°C] | t [s] | T [K] | T' [°C] | t [s] | T [K] | T' [°C] | t [s] |
| 0.5 | 466 | 193 | 1800 | 678 | 405 | 1800 | 904 | 631 | 1800 |
| 0.52 | 485 | 212 | 431 | 705 | 432 | 432 | 941 | 668 | 485 |
| 0.54 | 504 | 231 | 115 | 732 | 459 | 115 | 977 | 704 | 149 |
| 0.56 | 522 | 249 | 35.9 | 759 | 486 | 33.8 | 1013 | 740 | 49.7 |
| 0.58 | 541 | 268 | 11.4 | 786 | 513 | 10.8 | 1049 | 776 | 17.9 |
| 0.60 | 560 | 287 | 3.94 | 814 | 541 | 3.57 | 1085 | 812 | 6.9 |
| 0.62 | 578 | 305 | 1.53 | 841 | 568 | 1.32 | 1121 | 849 | 2.8 |
| 0.64 | 597 | 324 | 0.66 | 868 | 595 | 0.52 | 1158 | 885 | 1.19 |
| 0.66 | 616 | 343 | 0.25 | 895 | 622 | 0.22 | 1193 | 920 | 0.56 |

The above data are equivalent to average crystallite sizes of 0.022—0.016 mm for traditional heat treatment and 0.008—0.006 mm for rapid heat treatment. According to the Hall—Petch equation, strength values of the steel will increase importantly, for the above numerical values by at least 50%, as a result of smaller crystallites.

The reason why such fine crystallites are formed in rapid heat treatment is that despite very high crystallization rate, the frequency of nucleus formation also greatly increases, and the short meeting intervals will hinder growth. Owing to the short time there is no opportunity either for the crystallites to grow at the expense of one another.

Phase transformations in low-carbon steels during rapid heat treatment

During rapid heat treatment phase transformations will differ very much from equilibrium, since there is not enough time at disposal to proceed in the manner as accustomed in traditional heat treatment. For simplicity's sake let us follow the changes of two ferrite crystallites and a cementite crystallite in between (Fig. 3), since phase transformation proceeds similarly in the whole bulk. Above the $x-x$ line, perpendicularly to it we plotted the C concentration of the phases. The corresponding part of the Fe—FeC state diagram is shown in Fig. 4.

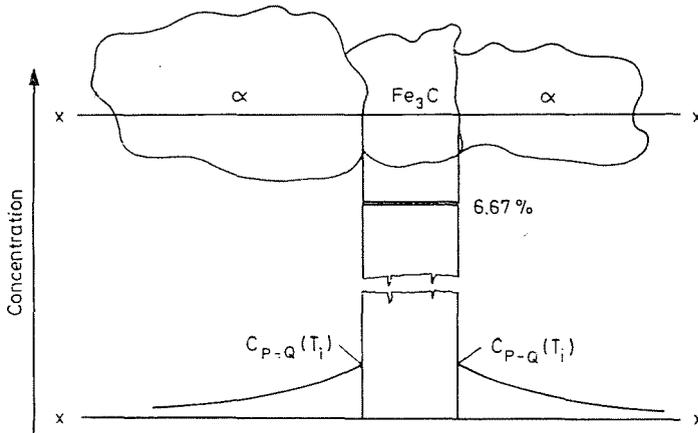


Fig. 3

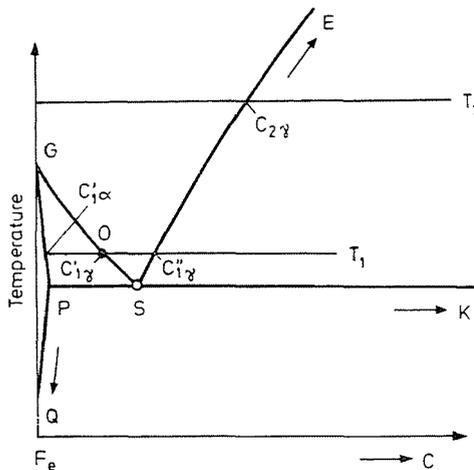


Fig. 4

During rapid heat treatment heating rate is such that the specimen reaches the temperature of 1000°C in 1 s. Let the temperature-time function of the heating process be $T = K\sqrt{t}$. The specimen will then reach the eutectoid temperature in 0.88 s. During this time the amount of carbon defined by the $P-Q$ line should go into solution from the tertiary cementite. Owing to the short time at disposal, this cannot take place, and if the steel was in equilibrium at the start of heating, only the carbon content of the ferrite layers in direct vicinity to the cementite crystallites will grow according to the $P-Q$ line, but nothing will change in the interior of the ferrite particle.

Equilibrium conditions change when the temperature A_1 is reached. When heating rate is traditionally low, austenite will appear. At rapid heating, however, the short time at disposal does not allow it. Both ferrite and cementite are stable, ferrite, depending on its C content, up to 910°C , and cementite up to even higher temperatures. In the momentary state only the conditions of austenite newly formed must be considered. In this situation phase change is caused by the fact that ferrite and cementite cannot co-exist at this temperature under equilibrium conditions. Separately, however, both of them would be in equilibrium. Free enthalpy is high only on the ferrite-cementite phase boundaries; such phase boundaries should disappear and be replaced by cementite-austenite and austenite-ferrite phase boundaries. However, the precondition for such boundaries is that beside cementite an austenite nucleus to be formed and grow. For such a nucleus to be formed it is necessary that in the cementite phase and in the ferrite phase, in a region corresponding to the critical nucleus size, carbon concentration of 0.8% should be established at 723°C . This needs time, since the C concentration of the existing two phases is rather far from it, one being 6.67%, the other 0%.

If the total time of heating up to 1000°C is only 1 s, it is practically impossible for austenite to be formed during this interval. It becomes possible only when temperature will exceed the intersection of the GOS line and the vertical line characterizing the C content of ferrite in the steel. In this moment the free enthalpy state of the system will change to a state that will force this transformation. Up to reaching the GOS line, the two phases beside one another, ferrite and cementite, are to be considered stable, owing to what has been said. Only the phase boundary layer is labile, having a free enthalpy value much higher than the equilibrium value. The difference in free enthalpy will further increase with temperature and will reach a fairly high value at 900°C . The difference will decrease only above 900°C , where austenite can be formed at carbon concentrations as low as 0.1%. It must be underlined, however, that austenite with such low C concentrations can be in equilibrium with ferrite only; the phase boundary ferrite-austenite corresponds to equilibrium conditions. In contrast, the phase boundary cementite-austenite can, at 900°C , be in equilibrium only with austenite containing close to 1.6%

carbon. (This is why the temperature A_1 can be disregarded in recrystallization at rapid heat treatment.)

If austenite is formed in the rapidly heated steel in the temperature interval $A_1 - A_3$, in the equilibrium state its carbon concentration on the phase boundary with ferrite will be given by the section of the GOS line, while its carbon concentration on its boundary with cementite will be given by the section of the SE line valid for the given temperature. These conditions and the critical nucleus size will define the formation of austenite in that interval.

Fig. 5 shows carbon distribution at the temperatures T_1 and T_2 , resp., along the $x-x$ line for the case where austenite crystallites are formed between ferrite and cementite.

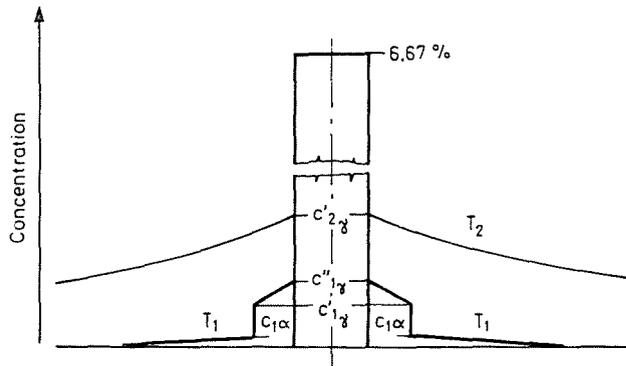


Fig. 5

As soon as the temperature reaches the intersection of the GOS line and the vertical line corresponding to the carbon content of ferrite, a critical thermodynamic situation fully novel in its character and related to the total ferrite amount will arise. Austenite can be formed at any point of the ferrite phase, if the critical nucleus size is attained. It is not limited by any concentration requirement, since the C content of the ferrite and the austenite being formed is identical. From this moment on, transformation proceeds rapidly; it is further promoted by the fact that with increasing temperature critical nucleus size decreases, and ferrite must disappear very swiftly from the whole structure.

In this stage of rapid heating we have arrived to a point where the structure consists of austenite and of the remaining cementite crystallites of the perlite. In this moment, the carbon content of the austenite is still largely inhomogenous. Maximum carbon content will be at the cementite boundaries corresponding to the $C'_{2\gamma}$ value in Fig. 5. Minimum C content, i.e. practically zero, will be where the ferrite-austenite transformation has only just taken

place. The microphotograph of an unalloyed carbon steel with 0.08 C content tempered in water from the transition stage is represented in Fig. 6. The structure is very similar to that of dual-phase steels. In austenite the diffusion of C atoms proceeds very rapidly and the carbon concentration gradually equalizes. In the meanwhile, however, the boundaries of austenite in contact with cementite will progressively be extended in the direction of cementite, consuming the cementite amount. This process will continue till the size of

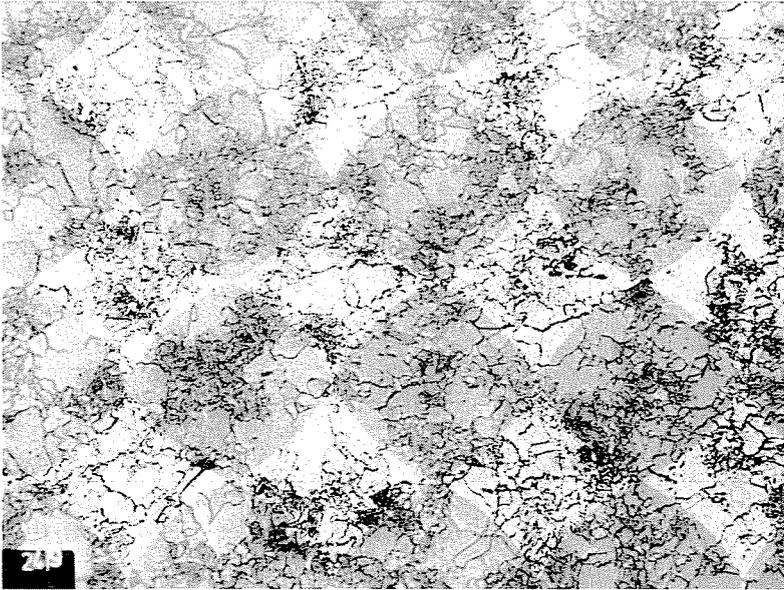


Fig. 6

the cementite crystallites does not finally reach the critical nucleus size for the given temperature. This is again a critical point of the transformation, since when this size or a smaller size is attained, the cementite crystallites must immediately disappear. Their disappearance can only proceed by their transformation into austenite or eventually into some other phase with a smaller r^* nucleus size. This latter possibility is, however, very improbable. Austenite formed in this manner would, at the place of critical nucleus size, have a carbon concentration of 6.67%, which — evidently — cannot be kept up. For the same reasons which led to the carbon concentration corresponding to cementite in austenite during cooling within the critical nucleus size under the effect of thermal fluctuation, now this small region must disappear very rapidly. Under such conditions, the carbon content will equalize rapidly. In Fig. 7, a steel with the above-mentioned C content, heated for 5 s only and tempered in water is shown. These phase transformations differing from

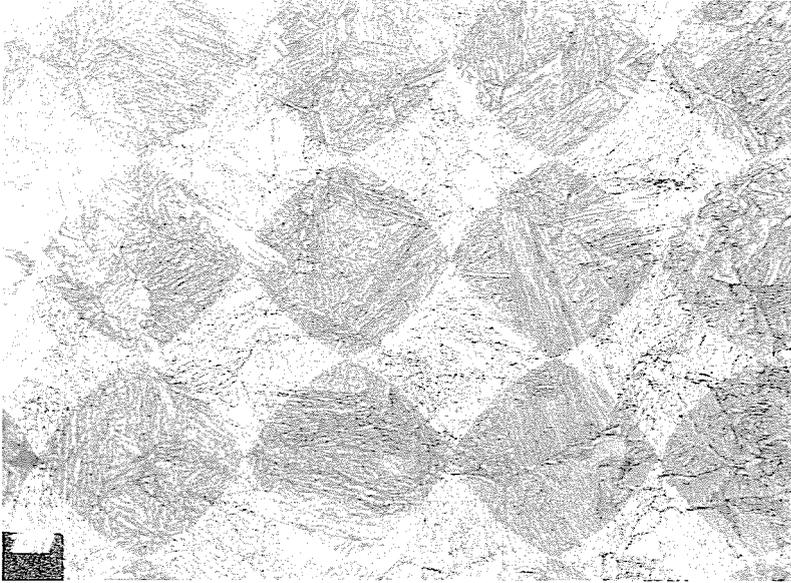


Fig. 7

the traditional can readily be utilized for changing mechanical properties [2]. The microstructure shown in Fig. 6 (also obtained after 5 s heating and tempering) corresponds to 700 MPa tensile strength and $A_5 = 15\%$ elongation, whereas the microstructure represented in Fig. 7 corresponds to 1000 MPa tensile strength and an elongation of 7% .

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