

EFFECT OF HEATING RATE ON THE MARTENSITIC TRANSFORMATION OF CARBON STEELS

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The mechanical properties of temper grade steels widely employed in practice depend on the heat treatment parameters. Since the decomposition of the martensite is a diffusion process, the correct selection of temperature and of the duration of the heat treatment period can alter the strength characteristics within a wide range. GRANGE and BAUGHMANN [1] have studied the hardness variation of different carbon content hardened steels as a function of a parameter combining time and temperature. After 10 min to 24 h tempering processes performed at different temperatures, each steel had all its relevant points along a single curve. Studying the transformations under tempering conditions, when gradually heating hardened steels, ESSER and CORNELIUS [2] observed three heat effects fairly easy to distinguish along the differential heating curve. The first one occurred between 100 and 200°C, the second and most intensive one between 200 and 300°C, and the third above 300°C. These authors arrived at the conclusion that the three heat effects were due to the transformation of the hardened steel texture and, thus, tempering consisted of three phases.

According to KAUFMAN and COHEN [3], the electric resistance in iron-nickel alloys increased gradually up to 390°C, and then abruptly, during the decomposition of the martensite. This, however, seems to contradict the finding of ESSER and CORNELIUS [2] who claim that the decomposition of martensite in the function of increasing temperature would involve three stages. Owing to these contradictions in literature, no univocal conclusions can be arrived at on the structural changes taking place in the course of tempering.

The present paper intends to investigate the internal energy variation of martensitic steels at different heating rates. The energy released under heating can render information on the structural changes within the material, that is, by a direct measurement of the released energy the internal energy variations in the material can be readily determined.

The measurement method employed

There are several calorimetric techniques known to determine transformation heat. According to the measurement principle, these may be grouped in two main categories:

a) Methods to determine temperature difference, such as mixing calorimeter, bomb calorimeter, differential thermal analysis (DTA), etc.;

b) Methods to determine energy difference, for example differential micro-calorimeter.

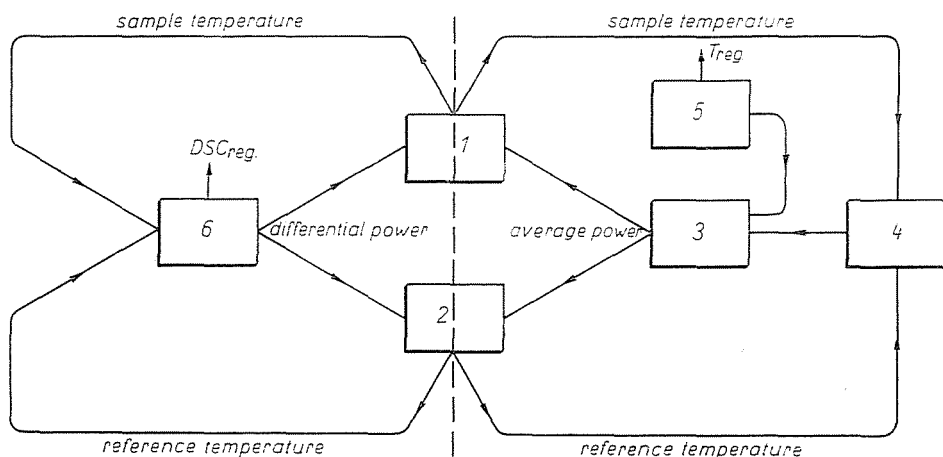


Fig. 1

Methods in the first group show temperature variations during transformation, as compared to the environment or some known material, in function of time. With the temperature difference, thermal capacity of the system, and the equipment constant known, the heat quantity taking part in the transformation is easy to calculate. The method requires exposure involving a calibration material. As a theoretical drawback, the process does never take place under defined temperature conditions.

Techniques in the second group maintain the sample at a programmed temperature identical to that of the inert material, and record the energy difference required for equilibrium. This features direct calory/time dimensions and is, therefore, not impaired by the above disadvantage, requiring no extra calibration, either.

The problem outlined by the introduction was studied by using the latter method. A Perkin—Elmer DSC-1B micro-calorimeter was selected as a measuring apparatus. Its theoretical operation is illustrated in Fig. 1. The sample (1) and reference (2) holders are located in the head under identical

geometric conditions. Both have separate heaters and sensors. The two holders are heated to an identical temperature by the supply unit (3) via the temperature signals from the holders and the proportioner (4). The supply unit (3) is supplemented with a program control (5) to realize the different rate heating, cool-off, and holding programs. The sensor signals control the difference amplifier (6) employed to maintain the relative thermal equilibrium of the two holders by providing for the required heat excess. The abscissa of the record indicates the temperature expressed by the signals of the programming unit (5), whereas the ordinate displays the compensation energy fed by the difference amplifier (6).

Since both the employed measurement technique and the equipment may be considered as new, it seems justified to briefly describe the measurement methodology as well as the evaluation process.

Experimental substances

For the experimental purposes a plain carbon steel type of 0.45 per cent carbon content was made use of, in the form of 6 mm diameter and 0.1 mm thick discs. Prior to testing, the surface was cleaned, then heated under argon shield for 1 hour at a temperature of 850°C, finally hardened in water. The large surface and small cross section of the samples ensured the formation of a pure martensitic structure, and provided for the thermal equilibrium within a few tenths of a second under test conditions. One of the samples prepared in the above manner was heated to 800°C, then slowly cooled off to room temperature, to represent the inert material, whereby the complete transformation of the martensite could be taken care of.

Experimental conditions

The equipment employed made possible the adjustment of the heating rate, heat flow measurement, and recording velocity in well-defined proportional steps. The different heating rates applied in the experiments and the associated adjustment data are presented in Table 1.

Table 1

Heating rate °C/min	Paper velocity in/h	Thermal sensitivity mcal/sec
64	120	32
32	60	32
16	30	32
8	12	32
4	6	32

In order to avoid sample oxidation, the measurements were made in a nitrogen atmosphere flow of 30 ml/min velocity. Measurement accuracy was increased by refusing the reference line of the instrument proper, and exposing the sample once tested to another heating, and considering the resulting approximately horizontal line the reference line. This reference line was then used to control the actual completion of the transformation during the measurement.

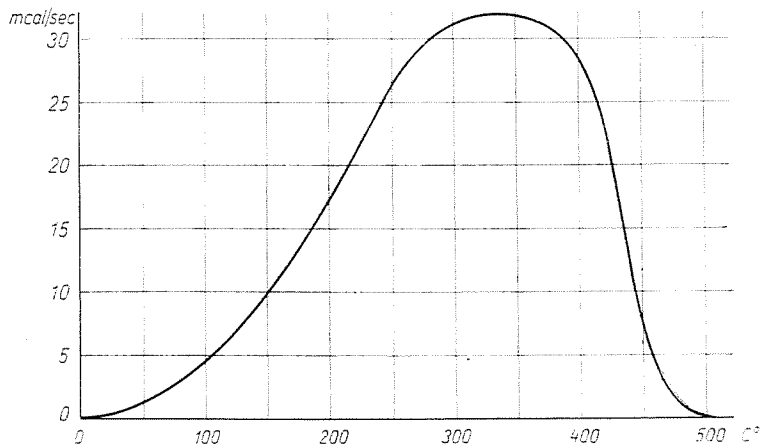


Fig. 2

The evaluation process is illustrated in Fig. 2. The horizontal axis indicates the momentary temperature, while the vertical one displays the heat flow required to maintain the balance between sample and inert material, as expressed in mcal/sec. Since the temperature axis is, at the same time, the time axis, as any heating rate is proportional to the period of the measurement, it follows that the integral of the area below the curve directly represents the heat quantity sought for. The heat quantity proportional to the unit area can be calculated by proportioning the 32 mcal pertaining to the 1 sec transit of the heat flow required for full deviation (in the given case: 32 mcal/sec) to the paper area obtained as the product of full deviation and 1 sec paper travel. This was calibrated by plotting the melting curve of a known weight of pure indium. This multiplication factor was measured and calculated for each heating rate. The areas concerned were determined by planimetry, and three parallel measurements were made with each heating rate accordingly. Since these parallel measurements were relatively in good agreement, the diagrams and Table 2 were to show their arithmetic mean results only.

Table 2

Heating rate °C/min	Temperature °C	Calory/g first measurement	Total
64	500	149	281
	400	88	162
	300	34	71
	200	10	21
	100	2	3
32	500	241	497
	400	112	332
	300	57	128
	200	14	34
	100	1	4
16	500	953	953
	400	694	694
	300	361	361
	200	76	76
	100	8	8
8	500	1802	1802
	400	1230	1230
	300	515	515
	200	140	140
	100	17	17
4	500	2517	2617
	400	2138	2138
	300	927	927
	200	264	264
	100	27	27

Experimental results and discussion

Exposures were made with the setting data presented in Table 1, then, after integration and averaging the parallel exposure results, the heat quantities were plotted in function of the heating rate. As an example, Fig. 3 presents the exposure illustrating the results of a 4°C/min heating rate experiment, wherefrom two important phenomena can be detected.

On the one hand, transformation of the martensite will begin as early as at room temperature, in agreement with the previous findings. On the other hand, the release of energy in the function of temperature is continuous, that is, the curve does not exhibit distinctly separable sections. This statement contradicts the observations of ESSER and CORNELIUS referred to in the introduction, although these authors have drawn conclusions from resistance variations on the structural changes of the material.

Fig. 4 reveals that the heat quantity will continuously decrease with an increasing rate of heating. According to the exposures, at the rates of 32 and 64°C/min some qualitative differences can be observed as compared to the preceding results, as the transformation is not completed during the test period. This is confirmed by the experimental finding that the reference line

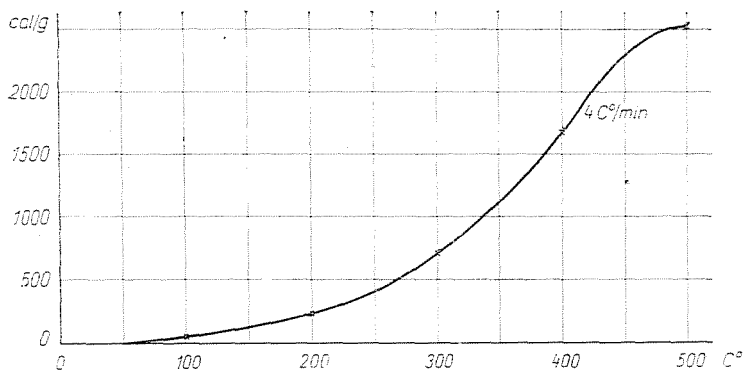


Fig. 3

indicating complete transformation was obtained in these cases after repeated heating. Fig. 4 presents the total heat energy values thus calculated. In the first approximation, however, variation of the thermal energy inversely to the rate of heating could not be explained for. This relation is illustrated by Fig. 5 where, at an identical paper velocity, exposures made with different heating rates are combined.

The measurement principle of the apparatus employed as well as the fact that the peaks of the curves did not vary at different heating rates have led to the conclusion that the transformation of the martensite would be of a completely different character than, for example, the melting of a pure metal, since the apparatus would show a deviation as soon as the heat conductivity of the sample differed from that of the inert material. If this value is integrated in the function of time, a virtual energy is obtained which, when added to the actual change, would make the result depending on the measurement period.

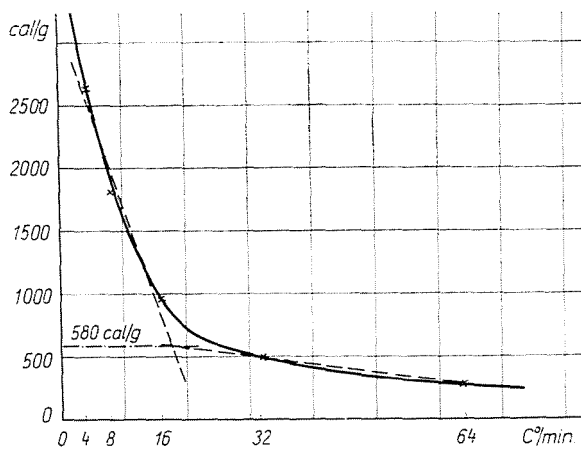


Fig. 4

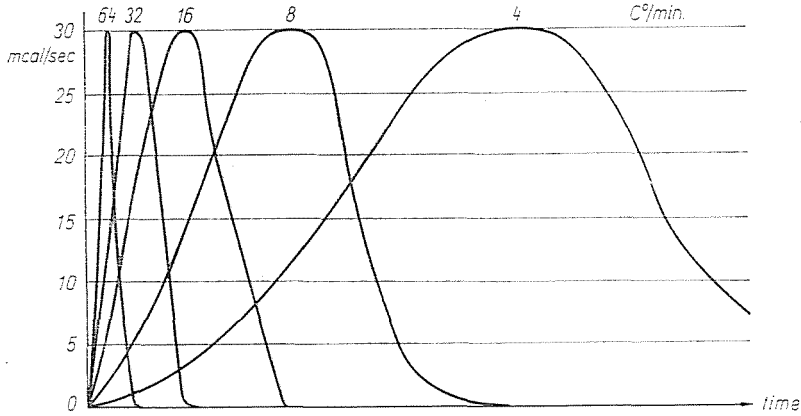


Fig. 5

In order to support our assumption, exposures were made with heating interrupted at 100, 200, 300 and 400°C. As revealed by Fig. 6, the current passing through the sample did not vary in the course of holding at 100, 200, or 300°C.

This means that, up to 400°C, each temperature value has a specific equilibrium condition, which represents a predetermined martensite content and, in this connection, requires a similarly predetermined heat flux during measurement, while the equilibrium is restored within a very short period of time. On the other hand, at 400°C, somewhat over the transformation temperature of the martensite, the process will take place spontaneously, whereby an exponentially decreasing heat flux curve in function of time will be obtained. This exact experimental result verifies the earlier assumptions found in literature.

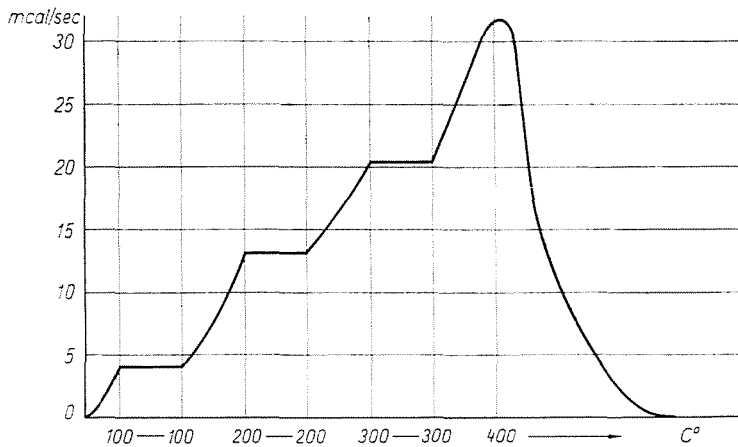


Fig. 6

With the above statements taken into consideration, Fig. 7 illustrates the integral curves obtained during the first heating. The coincidence of the values for the first three heating rates, and the sloping curves obtained for

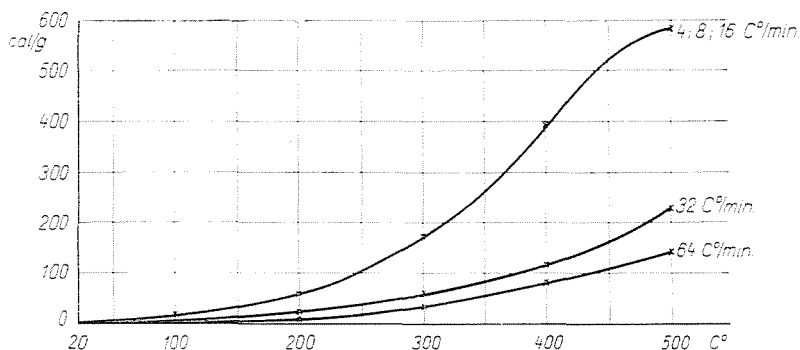


Fig. 7

32 and 64°C/min, respectively, prove that the transformation of the martensite is time and temperature dependent. This critical transient point was plotted in Fig. 4, whereby the energy requirement of the transformation was determined to amount to 580 cal/g.

A detailed kinetic examination of the transformation will be performed below.

The experimental data used for plotting the figures are summarized in Table 2.

Summary

The transformation of the martensite content of unalloyed carbon steels was studied in the function of temperature.

The transformation was found to start at room temperature and become continuous with increasing temperature.

Up to the temperature of martensite transformation, the process will pass through a series of equilibria taking place at a rapid rate, whereas above about 390°C it will be completed spontaneously. Decomposition depends on the rate of heating; under continuous heating conditions the critical value will vary between 16 and 32°C.

The total released energy associated with the total decomposition of martensite is always identical, regardless of the heating rate employed.

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