

## Very Short and Very Long Heat-Treatments in the Processing of Steel

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### ABSTRACT

It is conventionally assumed in the mass production of steels that the processing time must be reasonable and that the material must have uniform properties. The consequence is that short heat-treatments cannot be tolerated since the scale of engineered products may be so large that uniform temperatures cannot be achieved. Similarly, thermal treatments requiring several days or weeks are not considered practical because of productivity concerns.

In this paper I will show that these conservative ideas are a huge disadvantage to the creation of radically different steels whose manufacture could lead to an improvement in the quality of life. Indeed, such steels are capable of wiping out the competition from newcomers in the field of structural materials, such as the infamous carbon nanotubes and metal-matrix composites.

*Keywords : steel, rapid heat treatment, long heat treatment, processing*

### INTRODUCTION

The purpose of this paper is to discuss the time needed to generate the desired microstructure in steel, and what should make the time acceptable or otherwise in the context of industrial practice. There are commercial processes being developed which take milliseconds to some ten days [1-3].

### QUALITATIVE FUNDAMENTALS

We begin with a brief discussion of the atomic mechanisms which determine the time scales of phase transformations.

The microstructure is usually generated beginning with austenite as the parent phase. The transformation products can be classified into two categories, those which involve long-range diffusion and others in which the change in crystal structure is achieved by a macroscopically homogeneous deformation [4]. The former

mechanism is known as *reconstructive* and the latter *displacive* (Fig. 1).

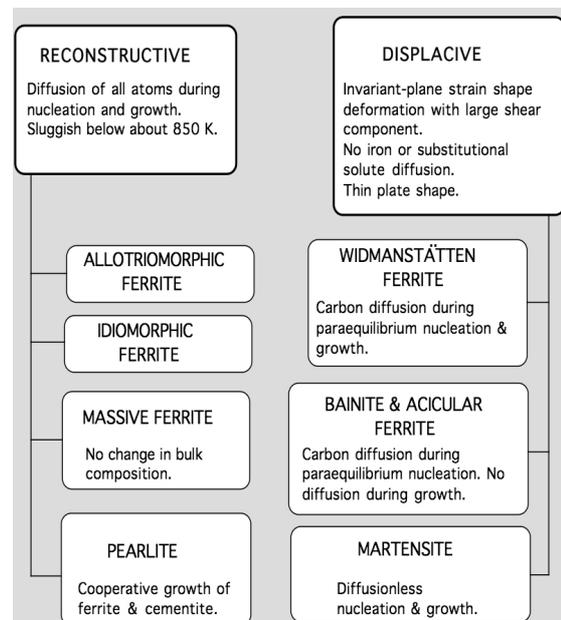


Fig. 1: Classification of transformation products as a function of the atomic mechanism of transformation.

The formation of allotropic, idiomorphic and massive ferrite, and of pearlite, requires the diffusion of all elements including iron [5,6]. The movement of iron or substitutional

solutes occurs by a vacancy mechanism and hence can be slow at low temperatures. As illustrated in Fig. 2, the scale of the microstructure must diminish as the transformation temperature is reduced [7], which is an advantage since both strength and toughness are improved when the microstructure is refined.

However, it is also evident that the time required to achieve a given scale increases dramatically as the temperature is reduced, making it impractical to design structures which are fine by reducing the transformation temperature. To summarise, rapid heat treatments are impossible with reconstructive transformations if the ultimate goal is to achieve fine microstructures.

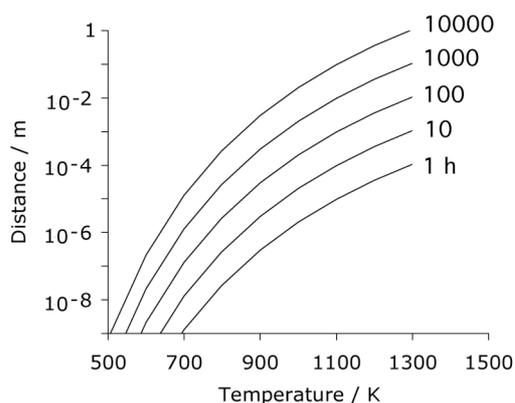


Fig. 2: Diffusion distance of an iron atom in austenite as a function of temperature and time. The estimate is made using  $2\sqrt{Dt}$  where  $D$  is the diffusion coefficient of iron in austenite [8] and  $t$  is the time.

The second class of transformations does not require the diffusion of atoms (Fig. 1) in substitutional sites and hence can be much more rapid. The change in crystal structure is achieved by a physical deformation which can be detected experimentally as a permanent strain. Interstitial atoms may in certain cases be mobile, but their order or disorder does not influence the nature of the deformation.

The motion of the interface during displacive transformation is in principle only limited by the speed of sound in the metal, some thousands of  $\text{m s}^{-1}$ , which is in contrast to the highest solidification velocities in pure nickel at

some  $80 \text{ m s}^{-1}$ . In practice the growth velocity of, for example martensite, may not get as high as the speed of sound in the metal, being limited by damping due to the emission of dislocations or other dissipating phenomena.

Diffusion of solute, whether this is substitutional or interstitial must always slow the rate of transformation. Diffusional transformations will therefore tend to be faster in pure materials.

Rapid transformation of austenite, involving diffusion, can therefore only occur at elevated temperatures. There is one exception to this, as described below.

Many commercial processes cause the steel to revert into the austenitic condition. The transformation of low-temperature ferrite into high-temperature austenite differs from the case where the latter transforms during cooling. Transformation during cooling follows C-curve kinetics in which the overall transformation rate goes through a maximum as a function of the undercooling below the equilibrium temperature. This is because diffusion coefficients decrease but the magnitude of the driving force  $|\Delta G|$  increases as the temperature is reduced. In contrast, both the diffusivity and driving force for austenite formation increase as a ferritic microstructure is superheated. The rate of *diffusion-controlled* transformation increases indefinitely as the temperature is raised, Fig. 3 [9].

Since the transformation rate during heating accelerates indefinitely at the temperature is raised, the transformation times tend towards zero. One consequence of this is that in many steel diffusion is unavoidable during heating, so incredibly high heating rates are needed in order to induce displacive transformation during heating. Austenite formation

can be induced in incredibly small time periods using laser heating [10-13].

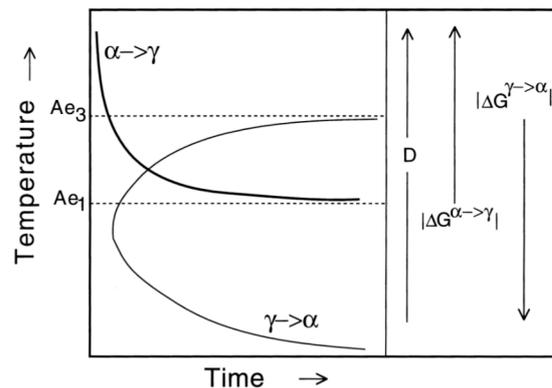


Fig. 3: The TTT (time temperature transformation) curves for the  $\gamma \rightarrow \alpha$  reaction, and for the  $\alpha \rightarrow \gamma$  reverse transformation. The  $Ae_3$  and  $Ae_1$  temperatures represent the temperatures at which austenite formation begins and ends respectively, under equilibrium heating conditions.

### LONG TRANSFORMATION TIMES

Slow reaction rates can be an advantage when dealing with strong steels which are destined for critical applications such as shafts. This is because the austenite does not need to be cooled rapidly, thus avoiding the development of quench stresses [9,10].

Temperature gradients naturally occur in large samples when they are cooling from the austenite phase field to an isothermal transformation temperature. The transformation then does not occur at the same instant in all locations within the component being heat-treated. A slow reaction rate would ensure that the steel reaches a uniform temperature before transformation begins, thus making the material resistant to the development of internal stresses due to a heterogeneous distribution of temperature.

Long transformation times also permit the manufacture of components which are large in all three dimensions; this is why processes such as the manufacture of metallic glasses by rapid quenching are limited to thin ribbons.

A slow rate can be achieved either by increasing the hardenability of the steel or by transforming at a temperature where solid-state transformations become sluggish. We present here an example where both hardenability and suppressed-transformation temperatures are exploited in order to reduce the rate of transformation.

It would be nice to have a strong material which can be used for making components which are large in all their dimensions, and which does not require mechanical processing or rapid cooling to reach the desired properties. The following conditions are required to achieve this:

- The material must not rely on perfection to achieve its properties. Strength can be generated by incorporating a large number density of defects such as grain boundaries and dislocations, but the defects must not be introduced by deformation if the shape of the material is not to be limited.
- Defects can be introduced by phase transformation, but to disperse them on a sufficiently fine scale requires the phase change to occur at large undercoolings (large free energy changes). Transformation at low temperatures also has the advantage that the microstructure becomes refined.
- A strong material must be able to fail in a safe manner. It should be tough.
- Recalescence limits the undercooling that can be achieved. Therefore, the product phase must be such that it has a small latent heat of formation and grows at a rate which allows the ready dissipation of heat.

Recent discoveries have shown that carbide-free bainite can satisfy these criteria [2]. Bainite and martensite are generated from austenite without diffusion by a displacive mechanism. Not only does this lead to solute-trapping but also a huge strain energy term [14,15], both of which reduce the heat of transformation. The growth of individual plates in both of these transformations is fast, but unlike martensite, the *overall rate* of reaction is much smaller for bainite. This is because the transformation propagates by a sub-unit mechanism in which the rate is controlled by nucleation rather than growth [16,17]. This mitigates recalescence [7].

The theory of the bainite transformation allows the estimation of the lowest temperature at which bainite can be induced to grow. Such calculations are illustrated in Fig. 4a, which shows how the bainite-start ( $B_S$ ) and martensite-start ( $M_S$ ) temperatures vary as a function of the carbon concentration, in a particular alloy system. There is in principle no lower limit to the temperature at which bainite can be generated. On the other hand, the rate at which bainite forms slows down dramatically as the transformation temperature is reduced (Fig. 4b). It may take hundreds or thousands of years to generate bainite at room temperature. For practical purposes, the carbon concentration has to be limited to about 1 wt% for the case illustrated.

An alloy has been designed in this way, with the approximate composition Fe-1C-1.5Si-1.9Mn-0.25Mo-1.3Cr-0.1V wt%, which on transformation at 200°C, leads to bainite plates which are only 20-40 nm thick. The slender plates of bainite are dispersed in stable carbon-enriched austenite which, with its face-centred cubic lattice, buffers the propagation of cracks (Fig. 5).

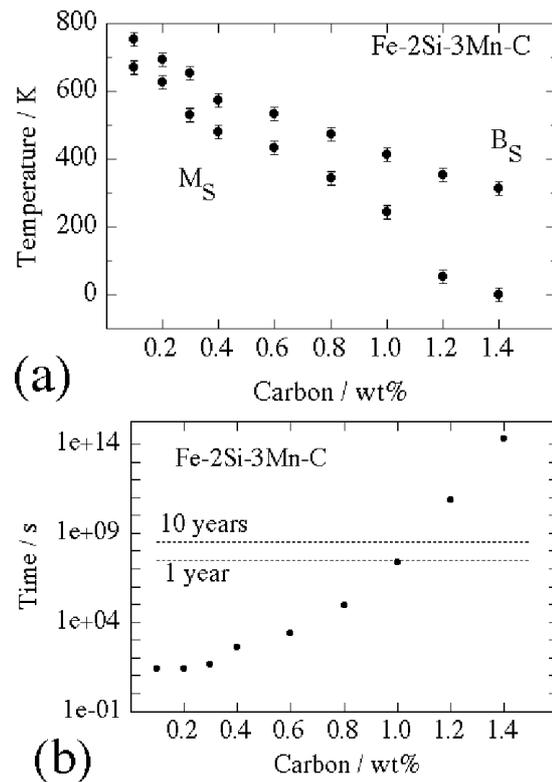


Fig. 4: (a) Calculated transformation start temperatures in Fe-2Si-3Mn wt% steel as a function of the carbon concentration. (b) The calculated time required to initiate bainite at the  $B_S$  temperature.

The bainite obtained by transformation at very low temperatures is the hardest ever (700~HV, 2500 MPa), has considerable ductility, is tough (30-40 MPa  $m^{1/2}$ ) and does not require mechanical processing or rapid cooling. The steel after heat-treatment therefore does not have long-range residual stresses, it is very cheap to produce and has uniform properties in very large sections. In effect, the hard bainite has achieved all of the essential objectives of structural nanomaterials which are the subject of so much research, but in large dimensions.

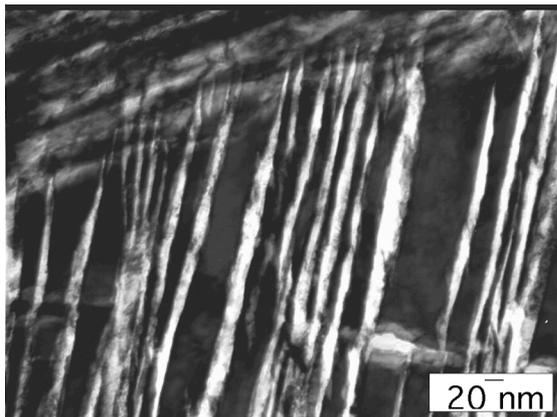
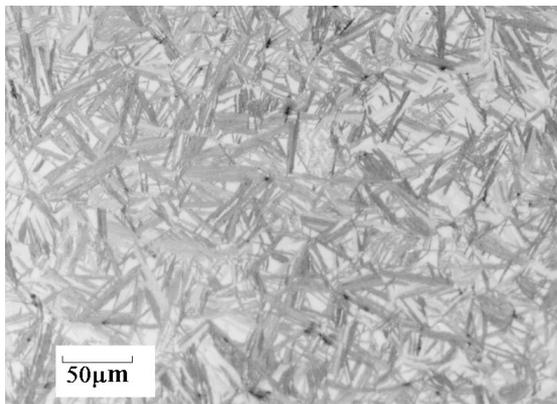


Fig. 5: Bainite obtained by transformation at 200°C. (a) Optical micrograph. (b) Transmission electron micrograph (Mateo and Bhadeshia).

### SHORT TRANSFORMATION TIMES

Rapid transformation is conducive to high productivity and can be exploited to minimise the alloy content of the steel. Hence the tremendous success of the process of accelerated cooling which is used in the manufacture of large quantities of steel for structural engineering [18,19].

A major advantage of using a leanly alloyed steel in combination with rapid cooling is to mitigate the effects of solidification-induced chemical segregation.

Control-rolled steels are cast continuously so they contain pronounced chemical segregation along the mid-thickness of the plate. For example, the manganese concentration at the centre can reach twice the average value. Ferrite naturally forms first in the manganese-depleted regions; the carbon partitioned as the ferrite grows ends up

in the manganese-rich regions of austenite. This exaggerates the hardenability of the manganese-rich regions which transform into bands of hard microstructure.

These bands are susceptible to hydrogen cracking. Hydrogen can be infused into the steel through corrosion reactions or other phenomena. An advantage of the accelerated cooled steels is that they are more microstructurally homogeneous (Fig. 6); this is because the ferrite and bainite form at a larger undercooling during accelerated cooling (Fig. 7), so transformation occurs everywhere, even in the manganese-rich regions. The gross banding characteristic of ferrite-pearlite microstructures is therefore minimised or avoided altogether [18,20]. The resulting lower hardness in the segregated zone makes the steel less susceptible to hydrogen-induced cracking.

Cracking ceases to be a problem because the hardness in all regions becomes less than about 250 HV [18,19].

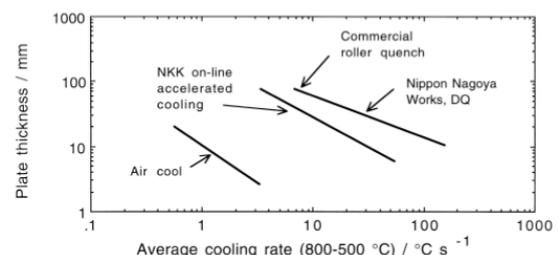


Fig. 7: Cooling rates that can typically be achieved in commercial circumstances.

The general conclusion is that microstructures which are homogeneous, and which contain less carbon, are less susceptible to both hydrogen-induced cracking and sulphide stress-corrosion cracking. In low-carbon pipeline steels, a bainitic microstructure is found to be more resistant to these problems than one containing allotriomorphic ferrite [21].

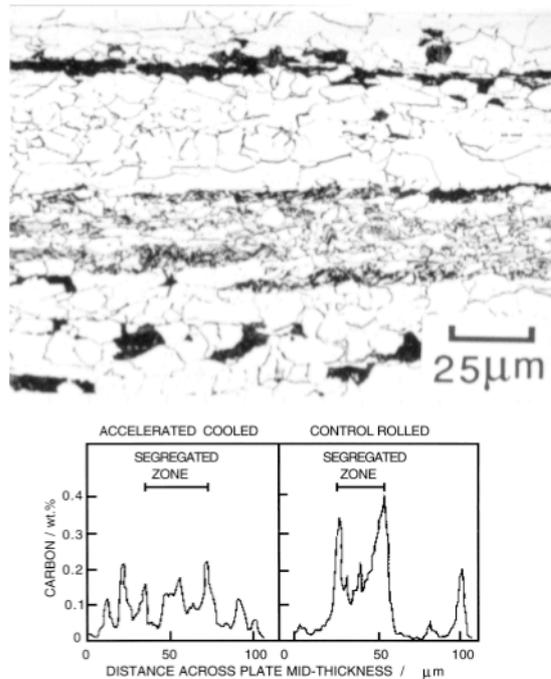


Fig. 6: (a) A light micrograph illustrating the effect of chemical segregation along the mid-thickness of heavy gauge plate. (b) Distribution of carbon concentration in the segregated zone for conventional control-rolled and rapidly cooled steel plates [18,19].

### “FLASH PROCESSING”

In recent work, Cola Jr. [1] has claimed to have produced bainitic steel in tens of milliseconds using a process designated *flash processing*.

In this, a strip shaped sample of steel of typical composition 0.2C-0.3Si-0.7Mn-0.5Cr-0.5Ni-0.2Mo-0.2Cu wt% is passed through an oxygen-propane fired system which applies heat directly to the steel strip as it passes through the equipment. The rapidly heated 1.5 mm thick strip is then directly water quenched.

This is a high productivity process which results in steel with a yield strength in the range 786-1269 MPa and elongation in the range 3-7%, depending largely on the chemical composition. There may be significant applications of the process in the manufacture of components in the automobile industry, particularly those which are currently hot-press formed.

### ACCELERATING REACTIONS

All of the major transformations in steels, including martensite, involve the stages of nucleation and growth. Anything which enhances the nucleation rate will accelerate transformation, and the most common way of doing this is by refining the austenite grain size. The number density of nucleation sites increases with inversely with the austenite grain size.

A further method is to increase the amount of austenite grain boundary area per unit volume by pancaking the austenite; the increase in grain surface can be predicted quantitatively [22].

If the austenite is left in the deformed state then other defects such as shear bands and dislocations may also contribute to the nucleation rate. However, such defects can, in the case of displacive transformations, retard kinetics by a phenomenon known as mechanical stabilisation [23].

Another technique is to increase the magnitude of the free energy change accompanying the transformation of austenite. This can be done by reducing elements such as manganese or carbon, or by adding cobalt or aluminium, both of which have the desired effect.

Fig. 7 illustrates how low-temperature bainite, which normally takes many days in order to achieve the required degree of transformation, has been accelerated by alloying with Co and Al; detailed compositions (wt%) below:

| Alloy | C    | Si   | Mn   | Mo   | Cr   | V    | Co   | Al   |
|-------|------|------|------|------|------|------|------|------|
| 1     | 0.98 | 1.46 | 1.89 | 0.26 | 1.26 | 0.09 |      |      |
| 2     | 0.83 | 1.57 | 1.98 | 0.24 | 1.02 |      | 1.54 |      |
| 3     | 0.78 | 1.49 | 1.95 | 0.24 | 0.97 |      | 1.60 | 0.99 |

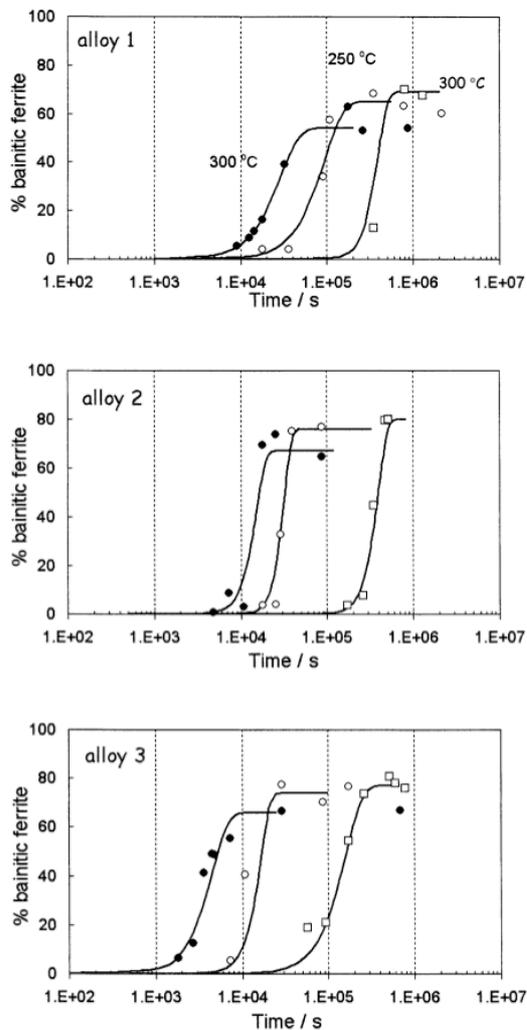
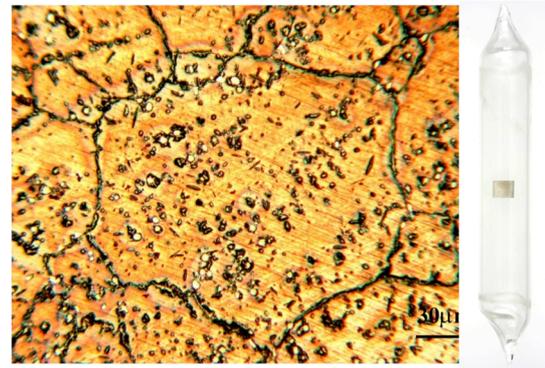


Fig. 7: Isothermal transformation curves. The filled circles, open circles and open squares correspond to the transformation temperatures of 300, 250 and 200°C respectively [24].

## 100 YEAR EXPERIMENT

An examination of Fig. 4 shows that it should be possible to obtain bainite at room temperature, but that the transformation time would be approximately 100 years. An appropriate alloy was made in 2004 to test this theory. Its starting microstructure, illustrated in Fig. 8, is austenite and carbides, but no bainite. Two samples have been archived, one at Cambridge University and the other at the Science Museum in London. The samples are sealed in quartz tubes containing pure argon. The tubes will be broken in 2104 to see whether bainite has formed and to conduct detailed characterisation. The samples have been polished to a mirror finish so any phase change will

be evident in the mean time, through surface rumples caused by transformation.



Fe-1.75C-Si-Mn wt% [Chatterjee & Bhadeshia, 2004](#)

Fig. 8: Experiment started in 2004, to stimulate bainite to form by 2104.

## SUMMARY

Transformation times of tens of milliseconds to ten days are no longer regarded as impossible by industry. Indeed, there are leading-edge products under development and at an advanced stage of application where these transformation times are deemed acceptable.

This is because the steels resulting from these unusual heat treatments also have interesting properties.

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