MECHANICAL PROPERTIES OF MARTENSITE IN HEAT–RESISTANT STEELS

H. K. D. H. Bhadeshia
University of Cambridge, U.K.

ABSTRACT

It is interesting that martensite is the key microstructure in the most modern of creep resistant steels. This may be an accidental consequence of alloy design, or it may be a fortunate outcome. For the energy generation industries, the temperatures are such that creep occurs with the climb of dislocations over obstacles. It is argued that in these circumstances, it is favourable to have a fine martensite plate microstructure. Factors controlling the size of martensite plates are discussed and novel experiments are proposed to identify the role of the martensite plate boundaries. At the same time, there are some detrimental consequences of a martensitic or bainitic microstructure which need to be controlled for optimum properties.

INTRODUCTION

The most exciting ferritic creep–resistant steels start with a microstructure which is martensitic [1,2]. On the other hand, the best established steels of this kind rely on allotriomorphic ferrite or bainite as the starting microstructure. It is therefore pertinent to ask:

(a) Why are modern heat–resistant steels based on martensite?
(b) What makes martensite desirable for heat–resistant steels?
(c) Can the martensite itself be altered to better fit the application?

WHY MARTENSITE?

Low–chromium steels, such as the classical $2\frac{1}{4}$Cr1Mo or 1CrMoV alloys have formed the backbone of the power generation and petrochemical industries for at least five decades, for operating temperatures of 565 °C or less. The $2\frac{1}{4}$Cr1Mo is essentially bainitic, whereas the 9Cr1Mo type alloys developed much later, for higher temperatures and greater corrosion/oxidation resistance, are martensitic. They undoubtedly have better creep strength (Fig. 1a, b), but why are they martensitic?

The probable answer to this has little to do with microstructure. A greater chromium concentration is needed to obtain the oxidation and corrosion resistance necessary for higher service temperatures. The chromium must then be balanced by other solutes to avoid an excessive fraction of δ–ferrite. The net solute content then becomes so large that the steels cannot transform to bainite and hence the martensitic microstructure. This is illustrated by the time–temperature transformation diagrams for 2.3, 4.3 and 9.3 wt% chromium steels shown in Fig. 1c.

Could it be that the martensitic microstructure, which has a very high number density of defects, encourages the precipitation of more numerous and finer carbide particles which resist creep deformation? Baker and Nutting [4] conducted a transmission electron microscope study of carbide precipitation reactions during the isothermal tempering of a $2\frac{1}{4}$Cr1Mo steel in two starting microstructural conditions, bainite and martensite. Fig. 2 shows that whereas the kinetics of precipitation are not identical in the two cases, the differences are very small over the temperature range of interest (500–650 °C). This is to be expected since both microstructures contain similar defect densities (dislocations, plate boundaries, austenite grain boundaries); the slightly smaller defect density expected in bainite does not seem to have any significant effect on the precipitation kinetics. A martensitic microstructure is not therefore necessary

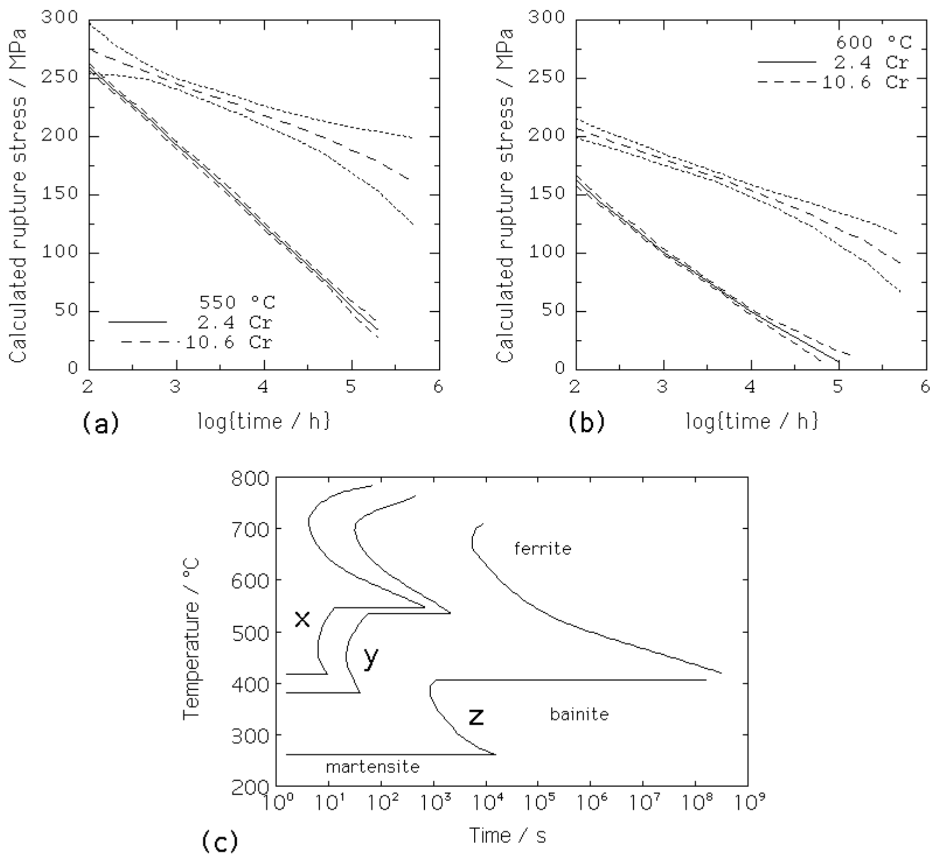

Fig. 1: (a,b) Calculated rupture strength as a function of time for a bainitic (low Cr) and martensitic (high Cr) steel. The details can be found in [3]. (c) Calculated time–temperature transformation diagrams for steels x (0.15C–0.25Si–0.5Mn–1Mo–2.3Cr wt%), y (4.3Cr) and z (9.3Cr). The transformation curves refer to zero percent reaction. In each case the upper curve represents diffusional transformation whereas the lower curve represents bainite.

in heat–resistant steels; bainite is adequate. The modern trend towards martensitic creep–resistant steels is associated with the need to improve the environmental resistance of the alloys rather than microstructural considerations. Indeed, there are well known disadvantages to high hardenability martensitic steels when it comes to weldability.

DESIREABLE FEATURES OF MARTENSITE

Extremely fine dispersions of carbides can be achieved during the transformation of ferrite to austenite. "Interphase precipitation" is a term used to describe the precipitation of a third phase at the α/γ interface during the transformation of austenite to ferrite. The phase may be cementite, alloy carbides or other particles such as those of copper or gold which have limited solubility in iron [5]. The scenario is one of ferrite grains on the scale of tens of microns containing the fine dispersions of precipitates.

It is surprising therefore that these coarse grained microstructures have not been developed for creep resistant applications. The martensitic or bainitic steels have the advantage that the

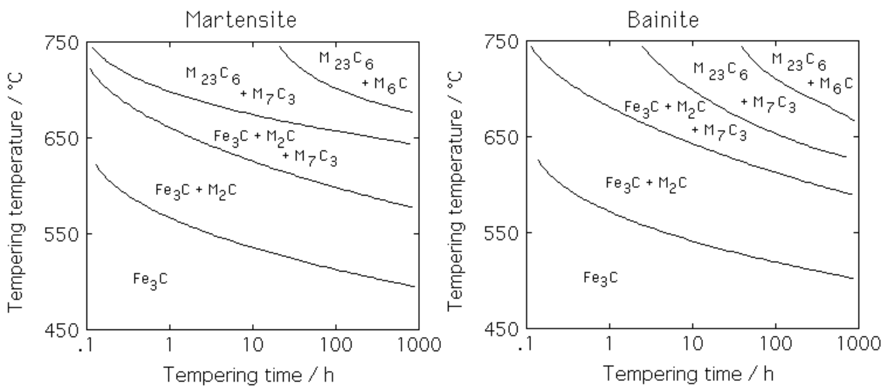

Fig. 2: Measured isothermal transformation diagrams for carbide precipitation reactions in $2\frac{1}{4}Cr1Mo$ steel. (a) Martensitic starting microstructure; (b) bainitic starting microstructure. Adapted from Baker and Nutting [4].

plate size is very small, of the order of a quarter of a micron. The mean free path for dislocations is only about twice the thickness of the plate [6]. This must provide additional hinderance to the passage of dislocations during creep, over and above the barriers due to precipitates. Indeed, dislocation cell structures develop within the martensite boundaries. Anything that can be done to refine these plates must therefore lead to an improvement in the creep resistance.

> *It is proposed here that when the mechanism of creep is one controlled by the climb of dislocations over precipitates, there is an advantage to refining the matrix grain size.*

We shall return to this proposal when considering oxide–dispersion strengthened iron alloys. But for the moment, what determines the thickness of martensite or bainite plates and how can that be refined? This can be dealt with using a quantitative model developed for bainite [7], but similar criteria should apply also to martensite, bearing in mind that the transformations are both displacive in character.

THICKNESS OF PLATES

If the shape deformation associated with martensitic or bainitic transformation is elastically accommodated then the plates may be expected to maintain an elastic equilibrium with the matrix; they may continue to thicken until the strain energy balances the available free energy. It follows that if the plates are allowed to grow freely (*i.e.* without impingement), they would be expected to be thicker at lower temperatures, where the driving force is the greatest. Not surprisingly, this contradicts the experimental data which repeatedly indicate finer plates at lower temperatures. This is because in steels of the type considered here the shape deformation is not elastically accommodated. The dislocation debris associated with the plastic accommodation resists the advance of the bainite/austenite interface, the resistance being greatest with strong austenite. The strength of austenite must therefore feature in any assessment of plate size; indeed, this effect has been known for some time [8]. The plates are expected to become thicker at high temperatures, where the austenite has a lower yield strength. Dynamic recovery at high temperatures should further weaken the austenite and lead to coarser plates.

The thickness must also be influenced by impingement between adjacent plates; a large nucleation rate must naturally refine the microstructure.

The observed effect of temperature could easily be indirect since both the austenite strength and the nucleation rates are strongly dependent on temperature and the composition of the steel. A quantitative analysis of the bainite plate thickness as a function of the strength of the austenite, the chemical free energy change accompanying transformation and the transformation temperature has shown that the latter has only a small independent effect on the thickness (Fig. 3). Strong austenite and high driving forces lead to a finer microstructure.

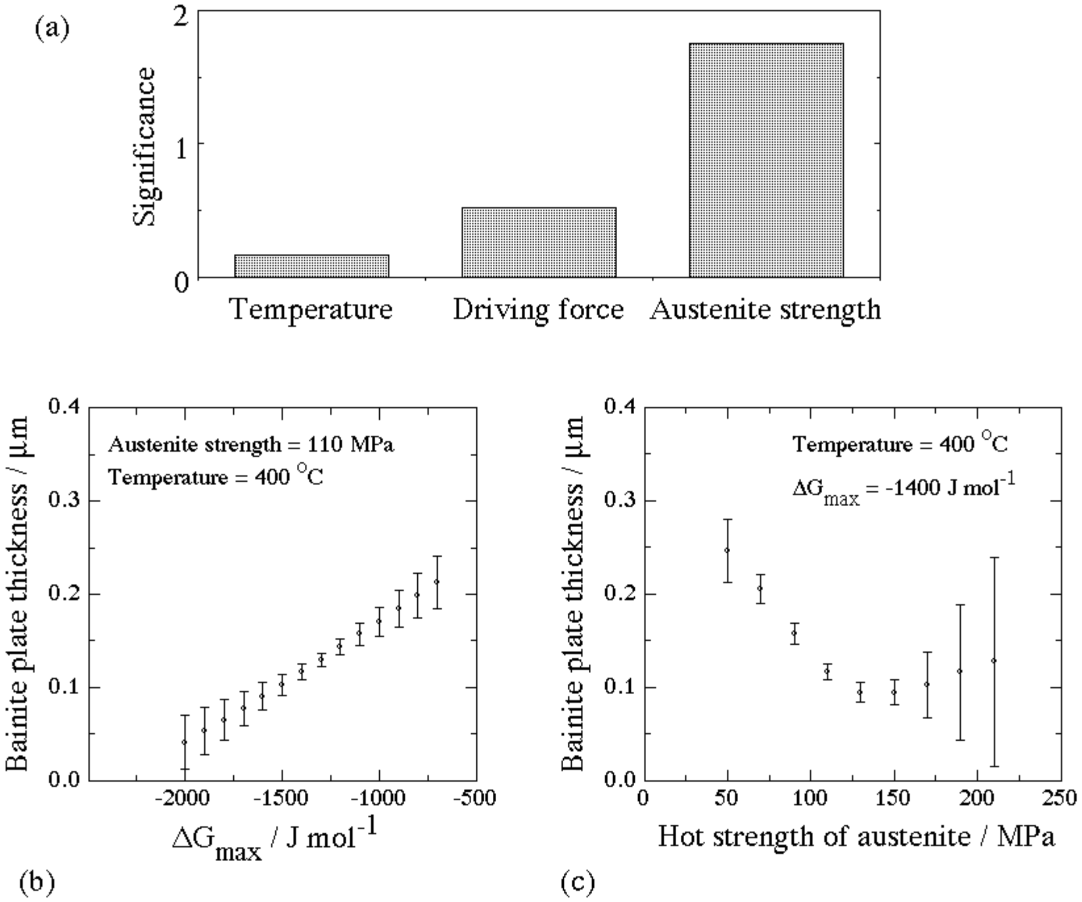

Fig. 3: (a) The model perceived significance of each of the variables plotted on the horizontal axis, in influencing the thickness of bainite plates. The vertical scale represents the ability of the variable to explain variations in plate thickness. (b) Variation in thickness with the chemical driving force. (c) Variation in thickness with the strength of the austenite. After Singh and Bhadeshia [7].

Controlled experiments are needed to discover whether the creep resistance of steels increases as the plate thickness is reduced. Obviously, any refinement of the microstructure should not be so large that the mechanism of creep changes, from one controlled by the climb of dislocations over obstacles, to one dominated by diffusion along martensite boundaries. However, this is unlikely to be an issue because the boundaries between martensite plates in a given austenite grain tend to have a high degree of coherence.

This naturally brings us to a consideration of the crystallography of martensite. Davies and Magee in 1970 [9] reported some fascinating experiments in which the *crystallography* of martensite was studied as a function of the magnetic state of the austenite, and when the austenite was solid–solution strengthened using either substitutional or interstitial solutes. I am not aware of any work relating martensite crystallography to the creep properties of steels.

OXIDE DISPERSION STRENGTHENED MARTENSITE

Mechanical alloying [10–13] is a process in which an alloy is created by the intense mechanical deformation of mixtures of elemental or master–alloy powders (Fig. 4). The powders are then consolidated by various combinations of hot–isostatic pressing and extrusion; the alloys in this condition are usually too hard to use. They are therefore heat–treated, either isothermally or in a temperature gradient to induce recrystallisation. Mechanical alloying permits the usual limits of solubility imposed by solidification to be exceeded, but in addition, dispersoid particles (such as oxides) can be introduced uniformly into bulk materials.

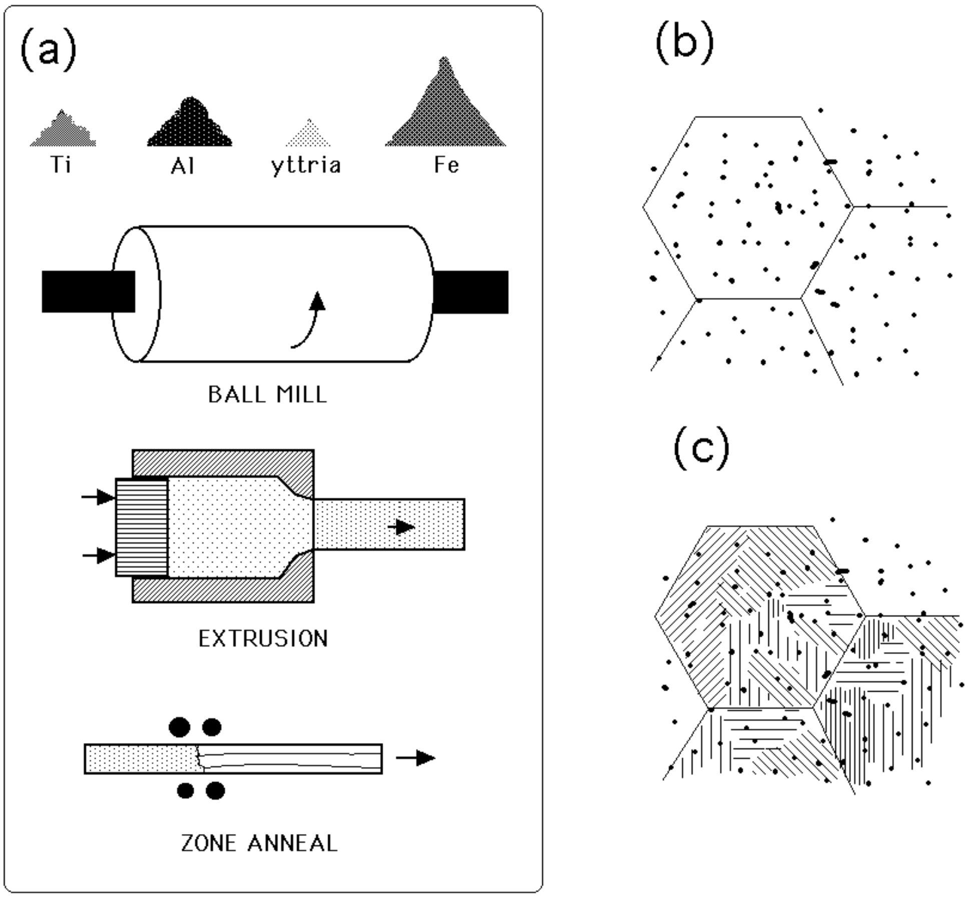

Fig. 4: (a) A schematic illustration of a common method of manufacturing large quantities of mechanically alloyed metals for engineering applications. The elemental powders/master–alloys/oxides are milled together to produce solid solutions with oxide dispersoids. This powder is then consolidated and the resulting bulk alloy heat–treated to achieve a coarse, directional grain structure. (b) An ODS alloy with coarse matrix grains. (b) A martensitic ODS alloy.

Mechanically alloyed iron–base materials are used in a recrystallised condition with extremely coarse grain structures [14]. This is because the are destined to operate in environments where the temperature is very high, about 1000 °C, where creep by diffusion along boundaries is an important contribution to the overall creep strain.

Typical commercial alloys are ferritic at all temperatures. A critical esperiment to test the role of martensite boundaries in creep resistant steels could involve the manufacture of heat treatable ODS alloys [15]. This would allow the testing of a dispersion–strengthened martensite (Fig. 4b,c) which can be compared using low temperature (600 °C) creep measurements in two states, the first a recrystallised grain structure and the second with an identical oxide dispersion but in a martensitic matrix. The experiment would reveal directly the role of the martensite boundaries in a creep process controlled by dislocation climb over obstacles.

UNDESIREABLE FEATURES OF MARTENSITE

Grain Boundary Embrittlement

During diffusional growth, grains of ferrite grow freely across the austenite grain boundaries, which are destroyed in the process. By contrast, displacive transformations occur with the disciplined motion of atoms. Such movements cannot be sustained across grain boundaries. It follows that a vestige of the austenite grain boundary remains when the transformation is displacive. These prior boundaries become susceptible to impurity segregation and embrittlement, liquid zinc embrittlement, and any phenomenon able to exploit the disorder associated with these boundaries [16–19].

The disorder at the prior austenite grain boundaries is larger than that associated with martensite–martensite boundaries. This is because adjacent martensite plates have coherence with the parent austenite grain and hence a good fit with each other, whereas the orientation relationships between austenite grains can be random. There are considerable practical consequences of this difference. Thus, the extent of segregation is smaller at martensite lath boundaries. Carbides nucleate preferentially at the prior austenite grain boundaries during the tempering of martensite or bainite [20,21]. The boundaries can be revealed by etching [22], often with great clarity even though the original grain is no longer present.

The problem of austenite grain boundary embrittlement in martensitic or bainitic steels is not exclusive to high strength steels used at ambient temperature. It is well established that the fracture toughness of many power plant steels deteriorates during service at elevated temperatures for two reasons. Firstly, the carbide particles, particularly those located at at the prior boundaries, coarsen and hence provide easier sites for crack or void nucleation. Secondly, the elevated temperatures permit the impurities to diffuse relatively rapidly and saturate the boundaries. Fig. 5 shows the impact transition curves for both the virgin steel (*i.e.* at implementation into service) and for an ex–service sample which had experienced 88,000 h at 813 K [23].

Avoiding Grain Boundary Embrittlement

The traditional routes for avioiding temper embrittlement involve a reduction in the impurity concentration and the addition of substitutional solutes which getter the impurities [24].

A solute causes embrittlement by reducing the cohesion across the boundary plane. On the other hand, those solutes which enhance covalent bonding normal to the boundary must reduce embrittlement. *Ab–initio* calculations of the bonding at grain boundaries in iron suggest this mechanism and confirm that phosphorus should embrittle and boron should toughen [25].

Boron additions must therefore be useful in commercial, martensitic power plant steels, which can be made clean but not free of impurities. The difficulty, however, is that much of the boron enters the $M_{23}C_6$ phase [26] and hence less is available to segregate to the austenite grain boundaries. Much further work is needed on this topic.

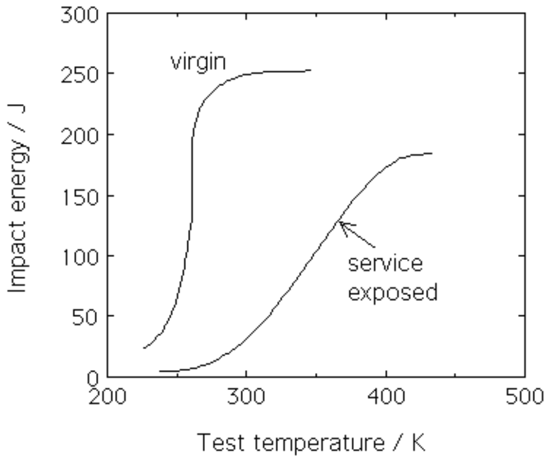

Fig. 5: Impact test data on $2\frac{1}{4}$Cr1Mo steel. (a) Comparison of the impact energies of the steel in its virgin condition, after service exposure at 813 K for 88,000 h and for a service–simulated sample (873 K for 10,000 h). After Wignarajah *et al.* [23].

Another possibility, which has never been investigated, would be to reduce the energy of the prior austenite grain boundaries. This could be done by making the austenite grain structure strongly crystallographically textured. The resulting austenite grain boundaries would have a high degree of fit and hence be less prone to impurity segregation.

DOUBLE AGEING HEAT TREATMENTS

There is a tendency during the tempering of martensite for precipitation to occur preferentially at the prior austenite grain boundaries and at the martensite plate boundaries, because these represent defects where the activation energy for nucleation is smallest. A given material will contain nucleation sites with different activation energies. However, the relative nucleation rates do not necessarily increase in the same order as the activation energies because the number density of high activation–energy sites may be much larger [27]. Hence, more uniform microstructures are possible if heat treatments are conducted at large driving forces, which in the context of martensitic steels corresponds to lower temperatures.

The important precipitates in heat–resistant martensitic steels are rich in substitutional solutes and hence cannot grow at low temperatures. Furthermore, many heat–treatments have the dual purpose of relieving residual stresses and undesirable local microstructures arising during fabrication operations such as welding. The minimum temperature at which substitutional atoms in iron are mobile over reasonable time scales is around 500 °C (Fig. 6a), whereas commercial heat treatments are conducted at temperatures in excess of 700 °C. It may be possible to produce a better dispersion of precipitates by employing a dual heat treatment procedure in which the initial anneal is at 500 °C followed by an elevated temperature treatment at 720 °C.

Heat–treatment at the lower temperature (larger driving force) should lead to more uniform precipitation and a larger number density of precipitates, whereas the subsequent higher temperature treatment allows the precipitates to grow, and for appropriate diffusion to anneal residual stresses and brittle microstructures such as those induced in the heat–affected zone of a weld.

On the other hand, the situation may not be as clear as implied here; research on plain carbon steels indicates that particles at lath boundaries stabilise the lath microstructure. The microstructures of both tempered martensite and bainite contain two kinds of cementite par-

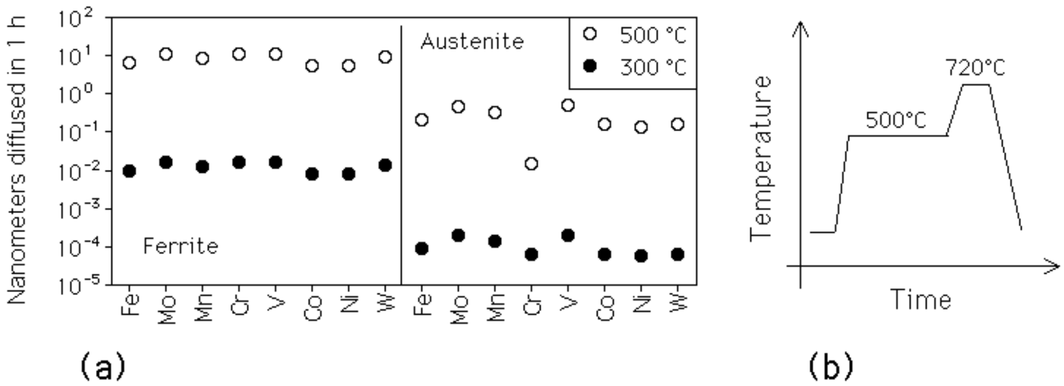

Fig. 6: (a) The random walk diffusion distance (in nanometers) of elements in ferritic or austenitic iron, at 500 °C and 300 °C. (b) Dual heat treatment.

ticles, those located at the lath boundaries and a finer distribution within the laths. In upper bainite the cementite is only located at the lath boundaries. Fig. 7 shows experimental data on the coarsening of cementite during the tempering of a medium carbon steel. The upper bound of each shaded region represents the lath–boundary cementite, the lower bound the intra–lath cementite. The bainitic microstructure is coarse to begin with because of the tempering inherent in the formation of bainite. With martensite the tempering induces the precipitation of cementite, with considerable intra–lath cementite and a larger overall number density of particles. Therefore, the coarsening rate is much larger for martensite; the bainitic starting microstructure shows considerable stability to tempering. A consequence is that the martix microstructure remains refined over a longer time period for bainite than for martensite.

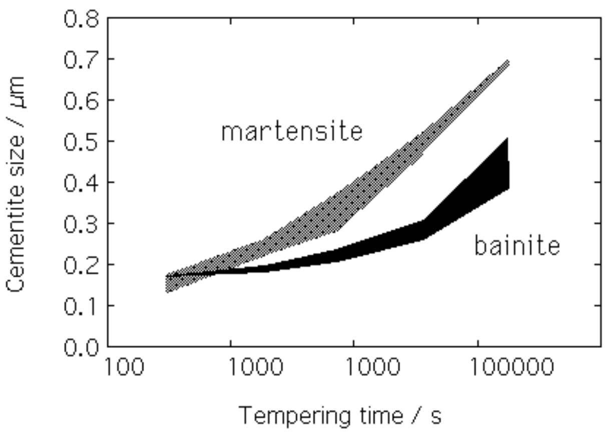

Fig. 7: Changes in the size of cementite particles as a function of the tempering time at 700 °C, with different starting microstructures. The upper bound of each shaded region represents the mean size of particles located at lath boundaries. The lower bound corresponds to particles within the laths. The data are for a Fe–0.45C–0.22Si–0.62Mn wt% steel; the bainite was prduced by isothermal transformation at 380 °C. After Nam [28].

CONCLUSIONS

The fact that modern creep resistant steels have a predominantly martensitic microstructure may be a fortuitous consequence of efforts to improve the corrosion resistance. It is nevertheless likely that such a microstructure had advantages, for example, the plate boundaries may provide additional barriers to dislocation creep. However, this hypothesis is not proven so some interesting experiments are suggested as critical tests. It is only when the hypothesis is established would it be reasonable to attempt modifications to the size, shape and crystallography of martensite as a means towards better creep resistance.

The high sensitivity of martensitic microstructures to impurity embrittlement can be controlled by minimising the deleterious elements in the steel. However, alternative approaches, such as the modification of the crystallographic texture of austenite in order to improve the fit at the prior austenite grain boundaries, could prove worthwhile.

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