PHYSICAL PROPERTIES OF MARTENSITE AND BAINITE

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Military transformations: an introductory survey

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SYNOPSIS

The features common to different types of phase transformation are considered in relation to crystallography, morphology, substructure, and kinetics. 'Military' transformations are characterized by the existence of a lattice correspondence, and the importance of interface structure is emphasized. Recent work on the difference between acicular and massive martensite, the fine structure of martensite and bainite, the influence of stacking fault energy in parent and product phases, and the strength of martensite is discussed, and some current problems are surveyed. 2604

INTRODUCTION

AMONG the more interesting and dramatic metallurgical advances of recent years has been the development of new high-strength alloys by imaginative combinations of martensitic transformation with other thermal or mechanical treatments. These technological successes have followed a decade of considerable scientific interest in the mechanism of martensitic transformations, during which a very successful theory of the crystallography of martensite was evolved and its main features subsequently confirmed by electron microscopy. Although this theory is based on very simple ideas, it is usually presented in a rather abstruse mathematical form, and it has seemed to many metallurgists to be far removed from the practical world of the steelworks. It should now be clear that this is not so, and that a detailed picture of the mechanism of martensite formation and of the fine structure of martensite is required if the strengthening effects are to be properly understood.

At the Scarborough conference last year, Dr Kelly pointed out that man has known about the strength of ordinary martensite for about 3 000 years, and he added the challenging comment that the transformation which leads to the hard brittle phase in steels is even more remarkable than are its mechanical properties. This year we are dealing with both the transformation mechanism and the properties of the product, but the emphasis is perhaps on the mechanism. This seems logical since the mode of transformation establishes the substructure of the product, and the properties may be very sensitive to this substructure.

We now recognize different kinds of martensitic transformation, which may be distinguished from one another by kinetics, morphology, crystallography, or internal structure. There are also transformations which are generally distinguished from martensite formation but which are mechanistically related; these include the formation of bainite in steels, some ordering reactions, and some of the transformations which have been described as 'massive'. The common feature of these changes is that the formal theory of martensite crystallography seems to be applicable to all of them, and this provides some information about the way in which the new phase grows from the parent phase. In this introductory survey an attempt is made to summarize the present position that has been reached in understanding these transformations and the properties of their products. The term 'military' transformation has been borrowed from Professor Frank.[1] It is not suggested that it be adopted in the literature, but it conveys an immediate picture of the basic postulate of the theory of martensite; and it is used here as a convenient sustained metaphor.

Military transformations are reactions in which the rearrangement of the atomic configuration takes place in an orderly, disciplined manner. Complete regimentation is found only in martensite itself, where (in principle) none of the atoms changes place with its neighbours. The other extreme is a nucleation and growth transformation in which the atoms behave as civilians, that is they move independently of each other and in an apparently random manner. Bainitic transformations are mixed in character, inasmuch as some of the atomic movements are highly disciplined while other atoms (of a different kind) move through much greater distances in a civilian fashion. An orderly rearrangement of the atoms is much more likely at low temperatures, so that the lower the transformation temperature in relation to the melting point the greater is the probability that the transformation is predominantly of the military type. An attempt will be made to formulate these rather vaguely expressed concepts in a more precise form.

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GENERAL CLASSIFICATION OF TRANSFORMATIONS

Attempts to define transformations of different kinds by reference to particular characteristics become increasingly difficult as more and more intermediate categories are discovered. The aim is, of course, to understand what happens in all cases, and the nomenclature used can only serve as a very approximate guide to the often subtle distinctions between individual modes of reaction. Nevertheless, a discussion of terminology cannot be entirely avoided, since different authors occasionally use the same word to denote quite different types of transformation, and this may cause considerable confusion. In recent years this has been especially true of the so-called massive transformations. It is generally agreed that in such reactions there is no change of composition, that the new phase grows from the parent phase at a rapid rate (often during moderately fast quenching), and that the morphology is non-acicular. Unfortunately these characteristics can be found with two very dissimilar growth mechanisms, one involving an incoherent boundary and the other a martensitic type interface. There is also some confusion over the use of the word bainitic to denote a type of transformation. Since the bainite reaction in steels is not yet fully understood, it is not surprising that individuals may differ in their estimates of the characteristics which are fundamental to this mode of transformation.

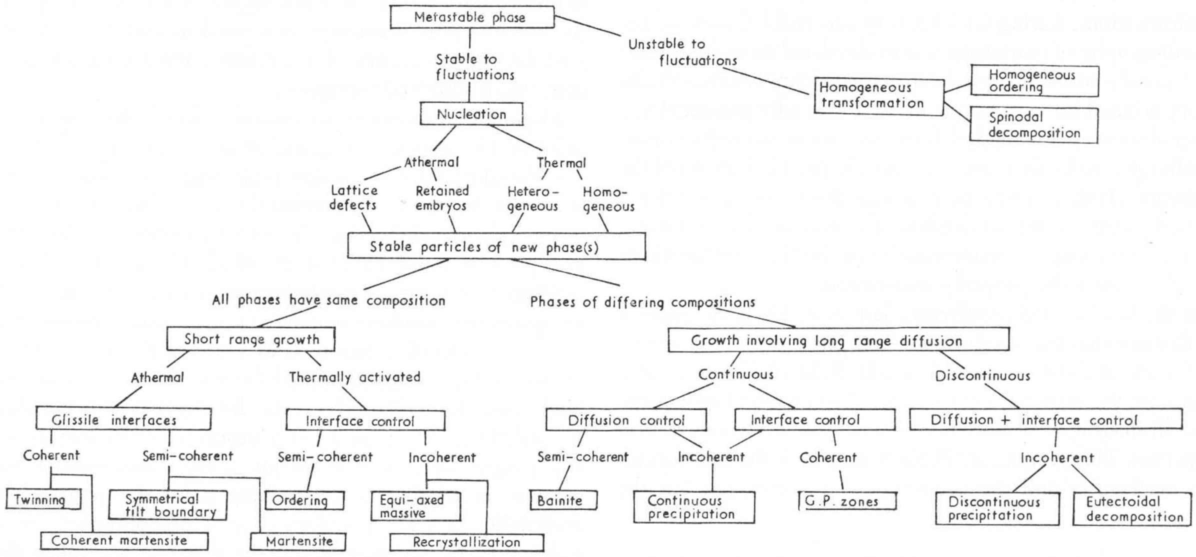
In view of these difficulties, it may be useful to draw attention to the similarities and differences in the atomic processes involved in various solid state transformations. Figure 1 is an attempt to produce a synthesis in diagrammatic form of all the relevant kinetic and crystallographic features used to differentiate transformations from one another. The figure is not restricted to the military transformations to be discussed here, but is rather intended to show these transformations in relation to nucleation and growth type reactions. For simplicity, however, the diagram excludes conditions in which the growth rate is determined primarily by the transport of energy towards or away from the moving interface. Growth controlled by heat flow is frequently encountered in liquid–solid transformations, but seldom in the normal conditions of solid state reactions.

Figure 1 shows that there are a few special solid state reactions which are quasi-homogeneous, and do not involve nucleation in the usual sense since the parent phase is unstable to fluctuations, except for the activation energy barrier to atomic migration. Most reactions must be nucleated, so that interfaces are present in the partially transformed assembly, irrespective of whether the initial and final states are single-phase or multiphase. In a military type transformation the structures are necessarily coherent or semi-coherent, and the structure of the interface is of great significance. It should be noted that the basis of most methods of classifying transformations is the mechanism of growth, which is generally more readily related to observable features than the mechanism of nucleation. The overall kinetics, however, may be controlled by either the nucleation rate or the growth rate. The experimental criterion which best separates military from other transformations is the observation of whether or not there is a change of shape, as distinct from a change of volume, in the transformed region.[2-3]

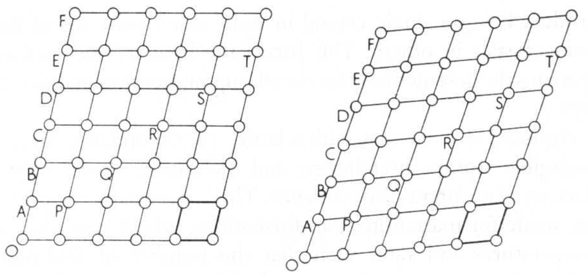
CRYSTALLOGRAPHY

Lattice correspondence

The theoretical concept which links the various military transformations is the existence of a lattice correspondence. Consider a transition from one solid phase to another, and suppose for simplicity that the primitive unit cells of the two phases each contain only one atom. For purposes of illustration, it is imagined that the atoms in the parent phase can be labelled and recognized in the product phase. A lattice correspondence then implies that a vector of the parent defined by a particular set of labelled atoms becomes a vector in the product with the atoms following the same sequence, although they will be differently spaced. In the same way, a labelled plane in the parent becomes a similarly labelled plane in the product. A relationship of this



1 *Schematic relations between transformations*



labelled atoms define corresponding lattice vectors; corresponding unit cells are indicated by heavy lines

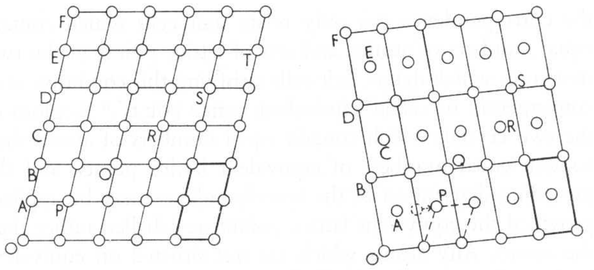
2 *Simple illustration of lattice correspondence*

kind in which straight lines transform to straight lines and planes to planes is described mathematically as an affine transformation. Physically, it may be considered as a homogeneous deformation of one lattice into the other. The correspondence associates each vector, plane, and unit cell of the parent with a *corresponding* vector, plane, or unit cell of the product.

Figure 2 illustrates the simplest type of lattice correspondence described above. In general, corresponding lattice vectors and the spacings of corresponding lattice planes are not equal in the two structures, and angular relations are also not preserved. Although the angle between any pair of vectors (or planes) in the parent and the corresponding vectors (or planes) in the product is changed by the transformation, it may readily be shown that there are three mutually perpendicular vectors (and planes) in the parent which remain mutually perpendicular after the transformation. These directions are called the principal axes of the deformation in the physical representation, and the whole change may be resolved into component displacements parallel to these axes. A deformation of this type is called a pure strain; the ratios of the final to the original lengths of vectors parallel to the principal axes are called the principal deformations, and the changes in length per unit length in these directions are called the principal strains.

An important point to note is that the lattice correspondence does not itself imply any orientation relationship between the phases, since the two structures shown in Figure 2 may be imagined to be given any rigid body rotation relative to each other. There is, in principle, an infinite number of correspondences which could be used to relate the two structures, but most of these are physically implausible because they involve large principal strains or large changes in angular relations. The correct correspondence can usually be chosen by inspection; in difficult cases, systematic procedures are available for computing the principal strains, and correspondences for which these exceed (say) 20% may then be rejected.[4] Alternatively, the experimental orientation relations may be used as a guide, since the relative rigid body rotation will generally be such that corresponding vectors in the two structures are inclined at small angles to each other.

In the above description it has been assumed that the lattice correspondence defines the positions of each atom in the product structure relative to the parent structure. As with mechanical twinning, it is also possible to choose a correspondence which defines the positions only of some integral fraction of the whole number of atoms. The smallest corresponding unit cells are now not primitive cells, and vectors defined by sequences of labelled atoms will remain straight lines only if the atoms all lie on the corners of these larger cells. A homogeneous deformation applied to the parent structure will not now produce the correct product structure, and additional localized displacements have to be envisaged. The atomic sites are now regarded as sets of interpenetrating lattice points, and the additional movements are equivalent to relative translations of these interpenetrating lattices; they are called 'shuffles'. Figure 3 illustrates this possibility. The structural transformation is identical with that in Figure 2, but by choosing a different correspondence it is found that atomic shuffles as indicated are also necessary.

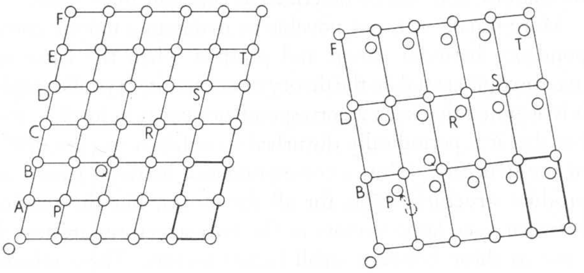


corresponding (non-primitive) unit cells are indicated by heavy lines; broken lines indicate the primitive unit cell of the product, and the 'shuffle' of atoms A,P,C,R, etc. is shown

3 *The same structural change as Figure 2, but a different lattice correspondence*

The advantage of using a non-primitive cell as the smallest unit that is homogeneously deformed into the product cell may be that the principal strains are thereby reduced. Clearly larger and larger cells could be used to accomplish this end, but only at the expense of more and more complex shuffles. When the cell becomes very large, the description of the correspondence ceases to have much significance and the transformation is no longer of the 'military' type. An examination of the opposing factors of small principal strains and simple shuffles has been made by Crocker and Bilby[5] for the case of mechanical twinning. For martensitic type transformations between structures with one atom per unit cell, the correspondence seems to relate primitive unit cells in all known cases.

Turning now to the more complex case where the primitive unit cell of at least one of the structures contains more than one atom, it is obvious that some shuffling is unavoidable. Clearly



heavy lines outline corresponding unit cells: that in the product is a primitive cell; the 'shuffle' of atoms A,P,C,R, etc. is indicated

4 *The same lattice correspondence as Figure 3, but a different structural change*

the correspondence can only relate unit cells which contain equal numbers of atoms, and sets of lattice points in the two structures which define unit cells satisfying this condition may conveniently be called 'equivalent lattice points'.[6] Regions of the two crystals which contain equal numbers of atoms then contain equal numbers of equivalent lattice points, and the preceding description of the correspondence may be applied, provided the equivalent lattice points are labelled rather than the atoms. Any atoms which are not situated on equivalent lattice points must be 'shuffled' to accomplish the transformation. Figure 4 illustrates a case in which the parent structure of Figures 2 and 3 is given the same pure deformation as in Figure 3 but different shuffles so as to produce a different product structure. The correspondence shown in Figure 2 is now unable to give the product structure directly, since the primitive cell of the new product contains two atoms.

Partial destruction of the correspondence

A civilian transformation is one in which there is no lattice correspondence; the labelled atoms of Figure 2*a* will be distributed more or less randomly over the atomic sites in Figure 2*b*, illustrating the well-known civilian principle of each atom for itself. The opposite limit, in which the correspondence is preserved over the whole volume of the crystal, seems to be possible only in two extreme cases. The first of these is when the new phase is a very small crystal enclosed in the surrounding matrix, so small that the disturbances arising from the change of volume and shape accompanying its formation can be accommodated by elastic displacements. This leads to the formation of fully coherent crystals in the very early stages of a reaction, but is not of interest in the present discussion, since the correspondence and its associated change of shape must disappear before the crystal can grow appreciably. The second possibility is that the two lattices are able to fit together exactly over a common surface, so that the product can grow from the parent without destroying the correspondence. This condition is a restriction on the pure lattice deformation and cannot generally be satisfied. When there is a matching surface this must be planar, and the deformation is described as an invariant plane strain. There is one important structural transformation of this type, that between close-packed phases (generally fcc and hcp) which have common close-packed atomic planes. Important examples are the transformations in cobalt and its alloys, and the formation of ε-phase in iron–manganese alloys and certain alloy steels. This is the most disciplined of all transformations, and will be described as coherent martensite.

More usually it is not possible to maintain a unique correspondence between parent and product when the latter is a macroscopic crystal. In the theory of martensite crystallography, it is assumed that such a correspondence exists in local regions, but that it is periodically disturbed to obtain a macroscopic fit of the structures. Thus a correspondence between parent and product structures exists for all the atoms, but the relations between very large vectors in the two structures are not the same as those between small lattice vectors. These relations between large vectors define the shape or macroscopic deformation associated with the formation of a plate of martensite. The different ways in which the correspondence is periodically interrupted lead to martensites of different fine structures, the product being a single crystal in some cases and a set of fine twin crystals in others. This forms the basis of one method (perhaps the best method) for classifying martensites of different types.

Figures 2–4 show that with a lattice correspondence there is negligible atomic interchange, and each atom moves only a fraction of an interatomic distance. This is essentially the postulate made for martensitic transformations, which take place at temperatures and rates such that the number of thermally activated atomic migrations is negligible. However, individual atoms cannot really be labelled, so that the existence of a correspondence has to be inferred from more macroscopic observations, such as the change of shape produced in a transformed region of the parent. A small number of atomic interchanges during the period of transformation would not be incompatible with these macroscopic observations, so that the preservation of a strict correspondence is not essential for the observance of martensite crystallography. In particular it has been found in some alloys that the formation of a superlattice from a disordered solid solution is accompanied by a change of shape and has the crystallography expected of a martensitic reaction. It is obvious that some atomic mobility is required for the ordering, but we might describe the situation approximately by stating that there is a correspondence of atomic sites, although migrations of individual atoms over a few interatomic distances on these sites can take place.

The question which next arises is how far this process can go. Clearly, as atoms become more mobile, the transformation becomes increasingly undisciplined, and there is movement towards a situation where the correspondence has been completely destroyed. It seems that this will happen at least when the average distance moved by a diffusing atom during the transformation is of the order of magnitude of the dimensions of the product crystal. This would enable any hypothetical correspondence of sites to be eliminated by atoms creating new sites in some parts of the assembly and destroying old sites in other parts, so as to eliminate the shape change of the correspondence. Moreover, the strain energy of the shape change would provide a driving force for this net flow.[6]

The conclusion is thus formed that in some quasi-military transformations the atoms may migrate over small distances but not over distances of the order of the dimensions of the product crystals. However, there is one other way of envisaging a transformation with a partial correspondence. Considering an alloy in which the two components occupy different sets of sites, as for example in an interstitial solid solution, it may happen that, at the transformation temperature, one component is sufficiently mobile for long range diffusion to take place, while the other is relatively immobile. The whole transformation may then consist in the diffusion of the mobile component to form phases of different composition, combined with a rearrangement of the atomic configuration of the other component by a martensitic type transformation. There will then be a lattice correspondence for the slow-moving component, and the transformation will have 'military' features, even though phases of different composition have been produced. This is the type of reaction which is thought to produce bainite in steels, and it seems to the present author that only reactions corresponding to these general criteria should be described as bainitic.

There remains the question of whether bainitic type transformations are possible when the components occupy a common set of sites, as in a substitutional solid solution. There are obvious difficulties in assigning orders of magnitude differences to the mobilities of the components, and this would lead to accumulations of large numbers of vacancies. On the other hand, if both components diffuse comparable distances of the order of size of the new crystals, it is very difficult to see how a correspondence could be produced and maintained.

Interface structures

The discussion of the lattice correspondence shows the importance of the structure of the interface in military transformations. A correspondence clearly implies some continuity across the interface, so that incoherent interfaces are not compatible with the types of transformation under discussion. It may be noted in passing that the non-martensitic type of massive transformation involves rapid growth through the thermally activated motion of an incoherent interface, as illustrated by the absence of a shape change and by the motion of the interface across pre-existing grain boundaries. This type of massive transformation occurs in copper–gallium and similar alloys,[7] and in iron alloys, where it has also been termed equiaxed ferrite.[8] It is quite distinct from the 'massive martensite' transformation in iron alloys.[8]

In the special case of fcc ⇌ hcp transformations, a fully coherent planar interface is possible. Such a boundary is completely analogous to a coherent twin boundary, and should have a similar low energy. Rows and planes of atoms are continuous across this interface, which in principle contains no dislocations or other discontinuities. The main problem with such an interface, as with a twin boundary, is in explaining its mobility.

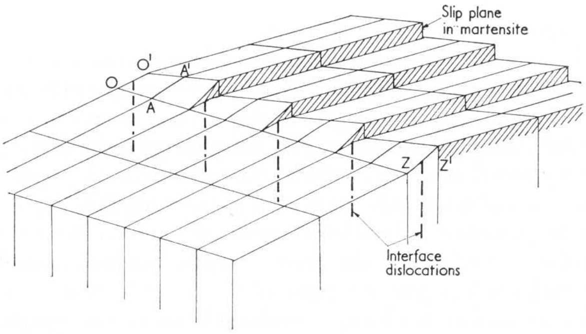
A semi-coherent boundary may be regarded as an interface in which regions of coherence are separated by regions of discontinuity. The structures do not really fit at the interface, and the mismatch would accumulate unless periodically corrected. Two main types of semi-coherent interface have been discussed. In one of them, the two structures have nearly identical atomic configurations in planes parallel to the interface, but the planar densities of atoms in the two structures are unequal. The slight differences in interatomic spacings can be accommodated by interface dislocations with Burgers vectors in the interface, and these dislocations must climb as the interface moves. The motion is thus non-conservative and requires the diffusion of vacancies and atoms to or from the boundary region. Boundaries of this type might form when small fully coherent particles grow to a size at which formed elastic coherence can no longer be maintained.

We are interested in the other type of semi-coherent boundary, which is characteristic of martensite. The basic postulate of the formal theory of martensite crystallography is that the deformation implied by the lattice correspondence is combined with a 'lattice invariant deformation' which does not affect the unit cell. The shape deformation is thus adjusted so that there is an undistorted plane, and a suitable rotation enables the two structures to fit together on this plane. These stages are distinguished only in the mathematical analysis, and no physical separation of the actual atomic movements is implied. This theory has been reviewed several times[3,9–13] and will not be discussed in detail here. The lattice invariant shear may be accomplished by the glide motion of a set of parallel dislocations lying in the interface and moving with it. The slip planes of these dislocations are corresponding planes in the two structures and meet edge to edge at a small angle in the interface. The dislocations along the line of intersection of the slip planes define an invariant line of the lattice deformation.

A schematic picture of a martensitic interface of the above type is shown in Figure 5. The dislocations have been represented as pure screws only in order to simplify the figure, which becomes very complex in the general three-dimensional case. The habit plane is also irrational in the general case so that it must be regarded as stepped or interlocking on an atomic scale.

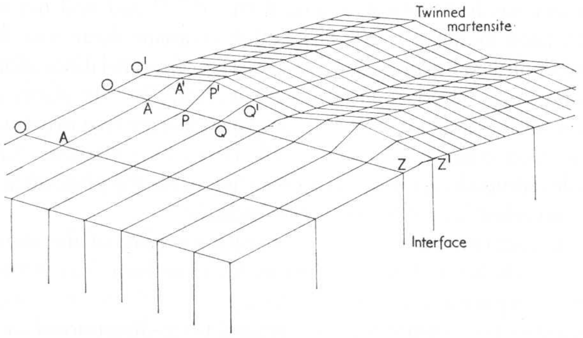
The crystallographic theory also envisages another possibility, namely that instead of a dislocation interface the invariant plane of the shape deformation is obtained by alternating two different lattice deformations. The two lattice deformations must give twin-related regions of product so that the energy of the many interfaces shall be reasonably low. The theory predicts the volume ratio of the two twinned regions, but not their absolute widths; the corresponding prediction for the dislocation interface is strictly the product of the Burgers vector and the reciprocal of the dislocation separation, but the assumption that the Burgers vector is a unit lattice vector in the direction of the lattice invariant shear leads to an absolute prediction of the mean dislocation spacing.

Figure 6 shows a schematic picture of a martensite interface when the product is twinned, and may be compared directly with Figure 5. Obviously this type of structure will only be expected when the energy of a twin boundary is small. The first evidence that the products of martensitic reactions may consist of stacks of fine parallel twins was obtained by optical microscopy for the transformations in indium–thallium[14–15] and gold–cadmium alloys.[16] The twins in these products are relatively coarse, but there are indications that very fine twins are formed at the interface and broaden in the region immediately behind the interface. The most striking confirmation of the theory came when very fine twins were observed by electron microscopy, first by Pitsch in transformed thin films[17, 18] and soon after by Kelly and Niutting[19, 20] and Nshiyama and Shimizu [21, 22] in films prepared from previously transformed bulk material. The assumptions made in the crystallographic



OA and O′A′ are corresponding lattice vectors, OZ and O′Z′ are matching macroscopic vectors

5 *Schematic picture of martensite interface of dislocation type*



OA and O′A′ are corresponding lattice vectors in parent and first product orientation; PQ and P′Q′ are corresponding lattice vectors in parent and second product orientation; OZ and O′Z′ are matching macroscopic vectors

6 *Schematic picture of martensite interface when product is twinned*

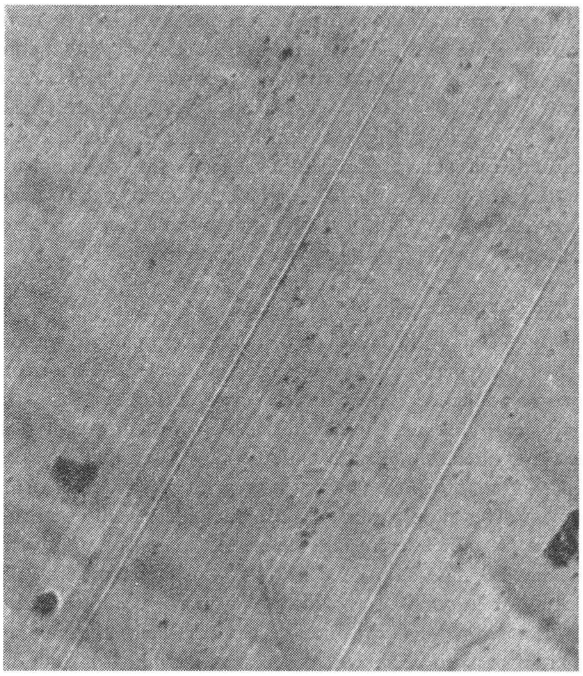
theory have been confirmed for martensite in steels with both {259} and {225} type habits, and the widths and relative volumes of the twins are generally those expected.

Twinned martensite structures have also been found in several non-ferrous alloys, but not all martensite plates are twinned. Single crystal martensites have been observed in stainless steels, where α-martensite forms in conjunction with ε-martensite, and also in very low-carbon iron–carbon alloys. Massive martensite, as formed in iron–nickel alloys with less than 30% nickel, is also of this type.

We must now mention a third type of fine structure in the product of a martensitic transformation, first found by Nishiyama and Kajiwara[23] and by Swann and Warlimont[24] in copper–aluminium alloys. The dislocation interface of Figure 5 leaves a single crystal product only if the Burgers vector of the interface dislocations is a lattice repeat vector of one structure which becomes a corresponding lattice vector of the other structure. It is also possible to envisage a dislocation interface in which the individual dislocations correspond to allowed partial dislocations of the product structure. As the product grows, the interface dislocations then leave parallel stacking faults along the slip planes of Figure 5. As in the case of twinned martensite, this type of structure will only be possible when the stacking faults have low energy. The condition is satisfied in copper–aluminium alloys, where both twinned and faulted products may be formed.[24]

Morphology

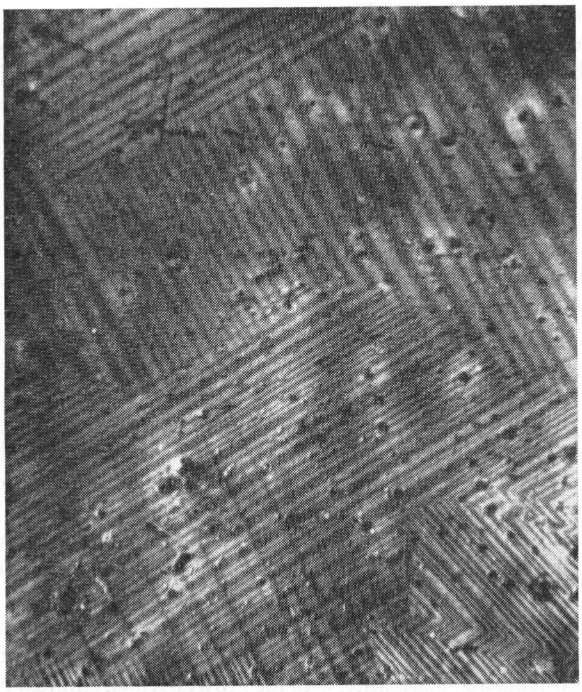
The most familiar martensitic product formed in steels consists of irregular plates which in three dimensions are approximately lens-shaped, and which give highly typical microstructures usually described as acicular. This morphology is also found in many non-ferrous alloys which undergo martensitic transformation, and it is mainly attributable to the constraints imposed on the growth of a plate by the surrounding matrix. These constraints are relaxed if the product region traverses a single crystal, and it is generally expected that the habit plane interface would then be planar, as predicted by the crystallographic theory. A very few alloys have been made to transform by the motion of a single habit plane interface normal to itself,[14–16,25] and this boundary is then accurately planar, as in the analogous case of deformation twinning. Unfortunately, the experiment has only been possible with alloys in which the polycrystalline morphology is banded rather than acicular (see below). Planar interfaces crossing single crystals have also been observed for the special case of the coherent martensitic transformation in cobalt and its alloys.[26–28] In this case, the transformation occurs by the repeated formation of parallel narrow shear bands (Figure 7), each with a planar habit. The bands represent regions in which the correspondence varies among three equivalent possibilities, all of which give the same product orientation. The product is thus a single crystal, but the shape deformation is zero (apart from a small component normal to the habit plane) when averaged over several bands.



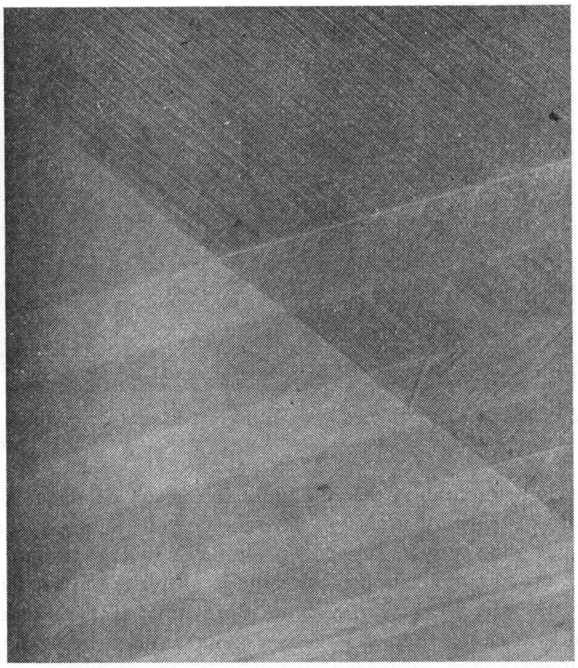
7 *Transformation markings produced on polished surface of single crystal of pure cobalt* ×200

The microstructures of transformed indium–thallium,[14,15] manganese–copper,[29] and certain uranium alloys[30] show a banded appearance (Figures 8–10) which is very different from acicular martensite in steels. The parallel-sided 'main bands' are able to form because the shape deformation is small, and because the crystallography is degenerate in the sense that opposite shape deformations may share a common habit plane, thus forming a self-accommodating system. The 'sub-bands' within a main band are twinned regions of product and are discussed below. The whole transition occurs over a comparatively small temperature range, and coherence is presumably not destroyed since the transformation is completely reversible by opposite motion of the interfaces. This is not true of acicular martensites where the reverse transformation has usually to be re-nucleated.

The remaining martensitic morphology to be described is that typical of the massive martensites. Greninger[31] used the term 'massive α' to describe the product of a fast reaction in copper–aluminium alloys, and the similar transformation in copper–zinc alloys was studied by Hull and Garwood.[32] The



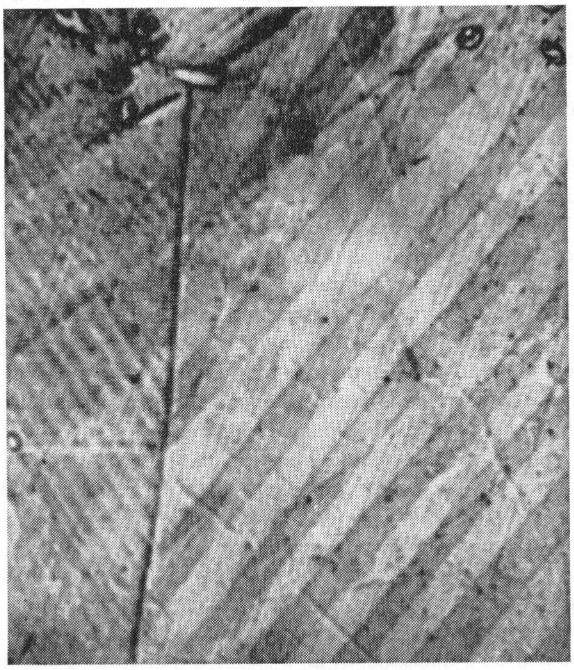
8 *Banded pattern produced by transformation in Mn–6·5%Cu alloy*[29]*; oblique illumination* ×150



fine markings are twin boundaries; electropolished and etched specimen, polarized light

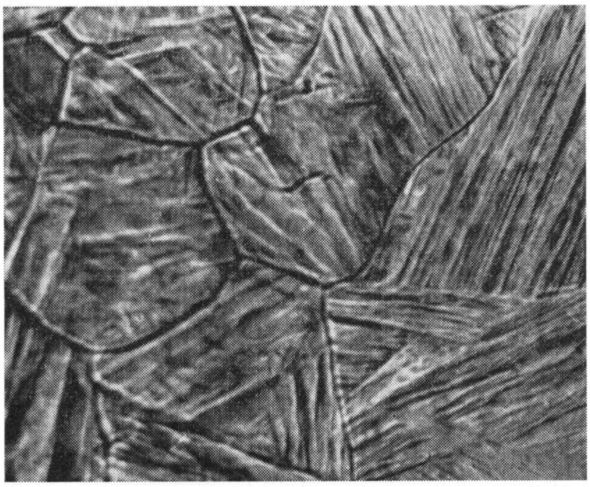
10 *Single main band crossing set of main bands in transformed indium–thallium alloy* ×45

product consists of large irregular grains with jagged, straight-edge boundaries, and in the case of copper–zinc there are many narrow twin bands within these large grains. At the time of Hull and Garwood's work, it was believed that these transformations could not be described as martensitic because of their non-acicular morphology, but it is now clear that this view is incorrect. Examination of pre-polished specimens of iron–nickel alloys which undergo a massive transformation on cooling has recently shown that the transformation is accompanied by a shape change.[33,43] As may be seen from Figure 11, each product volume consists of groups of parallel shear plates, and the straight edges of the product grain boundaries represent regions where different packets of plates impinge on one another.

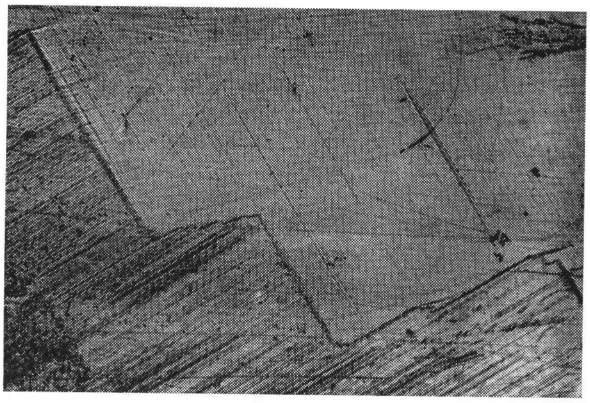


9 *Banded pattern produced by transformation during rapid cooling of a uranium–titanium alloy*

The explanation of the structure of massive martensite in steels is far from clear at present, but Figure 11 carries the



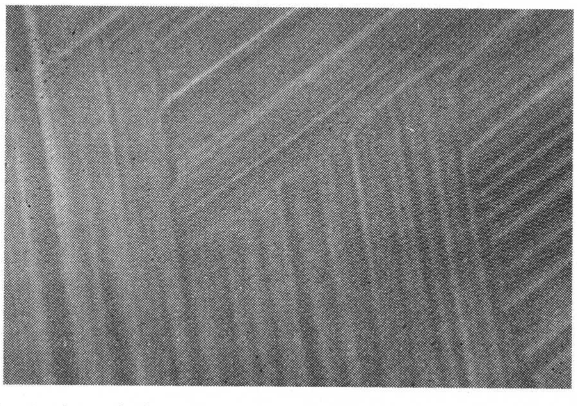
11 *Surface relief markings produced by massive martensitic transformation in Fe–15 at-%Ni alloy*[8] ×875



12 *Boundary between two hexagonal orientations in a transformed Co–30·3%Ni alloy* ×65

obvious implication that the individual plates constitute the units of transformation, to which the crystallographic theory applies, and that the larger units can be single crystals only if the product orientation is the same in all plates of a parallel group. The connexion with the formation of the banded microstructures discussed above is interesting; both morphologies seem to depend essentially on the mutual accommodation of adjacent plates, although this accommodation is presumably more perfect when parallel-sided bands are formed. The cobalt transformation is also self-accommodating, and very similar morphologies can arise. Figure 12 shows a jagged interface between two 'grains' of hexagonal product formed from a cubic single crystal of a cobalt–nickel alloy, and Figure 13 illustrates how this arises from the interaction of groups of plates. Indeed, it now appears that in a classification based on morphology, many other transformations which have long been recognized as martensitic are essentially of the type which is now being described as massive martensite. Figure 14, for example, shows the hexagonal α-phase formed by martensitic transformation from pure β-titanium,[34] and it can be seen that here also groups of parallel plates combine to give the irregular grains of α-titanium. The morphology of zirconium is similar.[35]

As mentioned above, transformations which produce equiaxed grains by the rapid motion of an incoherent interface have also been described as massive. Although such transformations would not be expected to develop plane boundaries, it is not certain that morphological features enable a distinction between the two kinds of massive transformation to be made in all circumstances. The observation of a change of shape in the transforming region still seems to be the most definitive way of establishing that a transformation is martensitic (or rather military) in character.



13 *Surface relief markings produced by transformation of a cubic single crystal of a Co–30·3%Ni alloy, to illustrate formation of agged interface*[28] ×1600

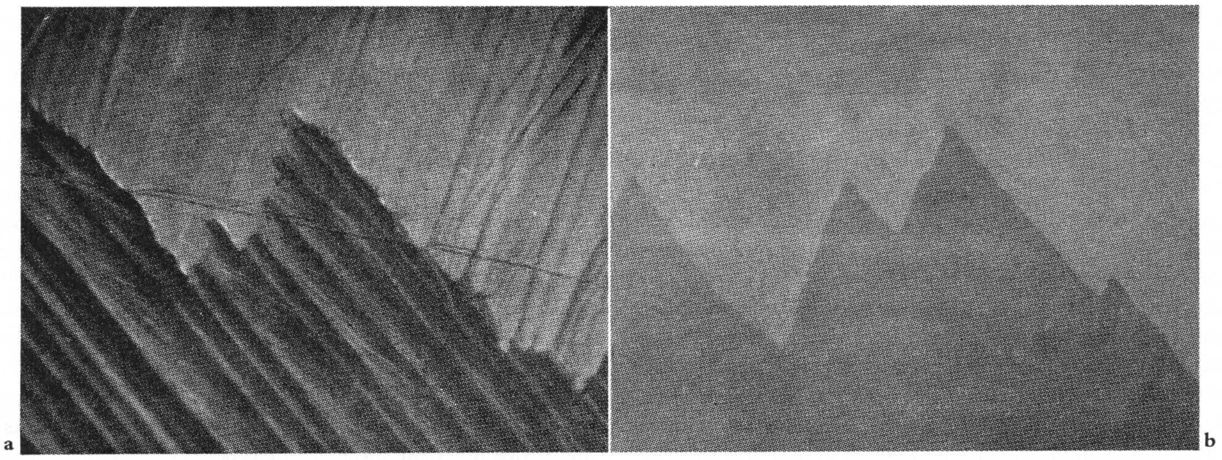
Two kinds of bainite in steels are usually distinguished by reference to morphology or kinetics. The morphological change from upper to lower bainite is not always apparent under the optical microscope, but it now seems to be generally recognized from electron microscope studies that lower bainite resembles tempered martensite, with carbides precipitated inside the ferrite plates.[20,36–38] In upper bainite, the cementite is usually precipitated at the boundaries of the ferrite, but some precipitation within the ferrite has also been observed.[38] A shape change is associated with the formation of the ferrite plates in both upper and lower bainite regions.[37,39,40] Figure 15 shows a micrograph and a two-beam interferogram of the same area, and proves directly that the shape change (in lower bainite at least) is an invariant plane strain.

The simple interpretation of the lower bainitic transformations is that the product structure is essentially equivalent to auto-tempered martensite, with the growth velocity limited by the diffusion of carbon, since carbide precipitation is needed to provide an adequate driving force for the boundary motion.[39,40] An alternative possibility is that the isothermal growth is interface controlled,[41] as reported for iron–nickel massive martensite[42,43] (see below), and the carbide precipitation is then not rate-controlling. The corresponding process in upper bainite would be the prior diffusion of carbon in austenite ahead of the ferrite boundary, until concentrations of carbon become sufficient for cementite to be formed. This description implies that the crystallography of lower bainite should resemble that of martensite formed in steel of the same composition, whereas that of upper bainite should resemble that of martensite formed in steel of lower carbon content.[13] Experimental results for bainite show a wide scatter, and hence do not well fit the predictions of the crystallographic theories of martensite,[44] but the general trend is in the sense expected from the results on martensite.

Plates of pro-eutectoidal ferrite have also been observed to be formed with an associated shape change,[45,46] and the above description of upper bainite might also apply to this reaction. If the process is regarded as typical of bainitic reactions in general, diffusion ahead of the interface (or prior segregation) must also be involved in the non-ferrous transformations which have been described as bainitic. However, as already mentioned, it is not clear why the structural change need be martensitic in character if the temperature is sufficiently high for long-range transport by diffusion of components in substitutional solution.

Fine structure of martensite products

As already described, some martensites form in bands containing parallel arrays of relatively wide twins, whereas many acicular martensites in both ferrous and non-ferrous alloys are twinned on a fine scale. With a twinned martensite plate, the coherency strains at the interface are reduced if the twins are very narrow, probably of the order of the dislocation spacing in

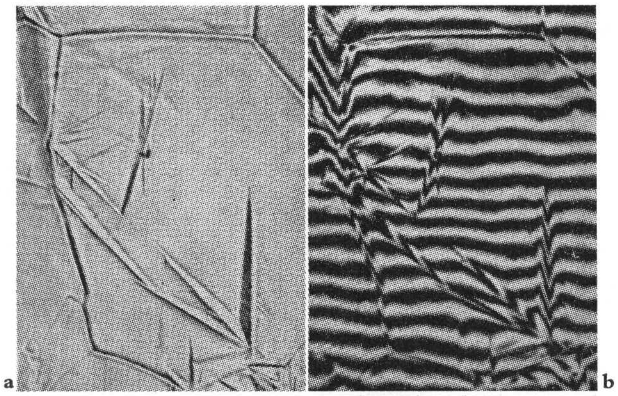


a as received, polarized light ×300 **b** same area after deep polishing, polarized light ×300

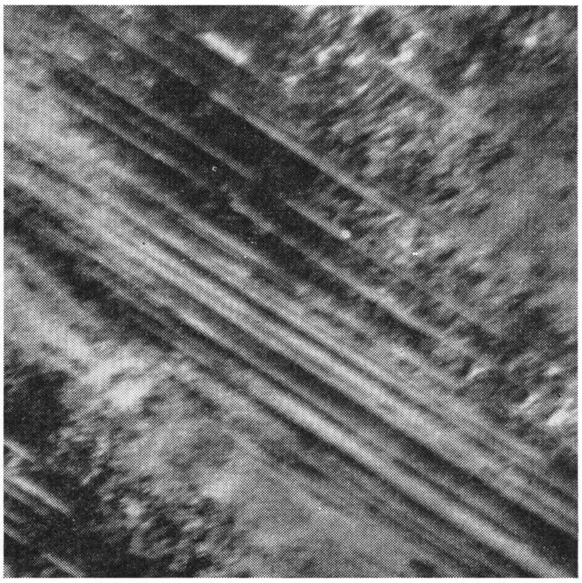
14 *Grains of α-titanium formed by martensitic transformation of iodide bar on cooling*[34]; *note similarity to Figures 11 and 13*

the alternative model of the interface. This may represent the situation in steels, where widths of ~20Å have been observed, and it is to be expected when the transformation strain is large. Figure 16 shows the twinned structure of martensite in a carbon steel. With small lattice deformations, the energy of the coherent twin boundaries may become important, and the equilibrium width increases. The energy can probably be minimized by having narrow twins at the interface, broadening into much wider twins behind the interface, and this configuration has been inferred from optical micrographs of interfaces in transforming single crystals of indium–thallium alloys.[15] The twin markings are often not visible immediately adjacent to the interface, and the apparent gap is believed to represent a region in which the twins become narrower. On an atomic scale, the tapering of the twins could be accomplished by steps (twinning dislocations) in the coherent twin interfaces.

Quite recently, evidence has been obtained that the very fine twins which are characteristic of many martensitic products may also not extend to the interface. Warlimont[47] has reported that twins in an Fe–30·9%Ni alloy are often restricted to a band along the centre of each sectioned martensite plate, and that outside this band the plate contains dislocations of increasing density. He suggests that the twin band delineates the 'mid-rib' frequently observed in optical micrographs, and represents the part of the plate which forms first. Subsequently the plate may thicken by a different mechanism involving a dislocation interface. An alternative possibility might be that the interface is always of the dislocation type, and that twinning occurs after transformation, but this seems less probable. Warlimont compares the dislocation distribution with that observed in iron deformed at low temperatures and high strain rates, and regards the similarity as evidence for a lattice invariant shear produced by a dislocation interface. In the usual theoretical model, there would be no accumulation of dislocations behind this interface, but Warlimont (private communication) has emphasized that real transformations show many deviations from idealized behaviour. Warlimont's pictures show remarkably straight



15 *Optical micrograph of relief markings* **a** *and corresponding two beam interferogram* **b** *to illustrate the shape change accompanying the formation of bainite in an Fe–3%Cr–0·7%C alloy*[37] ×350



16 *Electron micrograph of twins in martensite found in a 1·0%C steel*[20] ×80 000 dislocations of at least two types, whereas the simple model of the interface contains only one type of dislocation; further evidence for a complex dislocation structure is given in this report by Wayman.

Twin plates crowded in the region of the mid-rib have also been reported by Shimizu,[22] using an alloy (Fe–30·64%Ni) of almost identical composition (Figure 17). Shimizu found that the twins were in the form of thin ribbons elongated in the η_1 direction, and that the plane of the twin plates deviates from the $\{112\}$ twinning plane by an angle of 3–21°, the angle being almost constant in any one martensite crystal. It is suggested that this deviation is due to periodic slipping within the twin plates, and some fine striations along $\langle 111 \rangle$ in the twins were visible. The thickness of the twin plates was estimated at 30–70Å. These observations show that the substructure may be much more complex than is indicated by the simple theory.

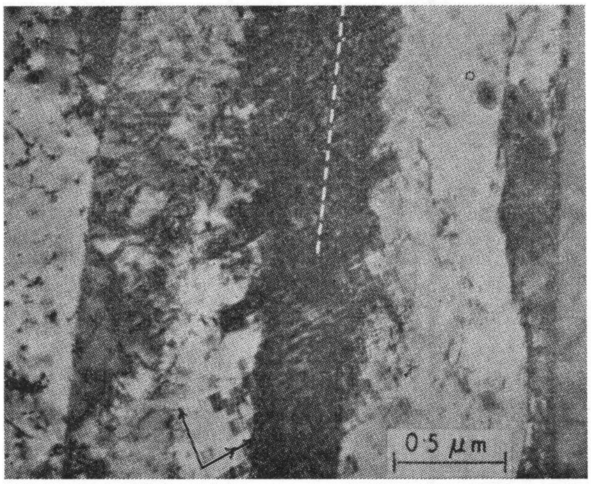
An opposite effect to a band of twins along the mid-rib is a structure in which very wide twins appear to extend to the interface. This seems to be the situation in gold–cadmium alloys, and in indium–thallium alloys when the interface is made to move towards the twinned region, although the observation has been made only under the optical microscope. The structure seems to require dislocations either in the interface or possibly ahead of the interface (in the parent phase) to accommodate the misfit which is not cancelled on a sufficiently fine scale by the twinning. Accommodation tilts are indeed sometimes visible in the parent phase.[15]

Martensites which are not internally twinned have been found in low-carbon alloys and in stainless steels, where they occur in conjunction with the hexagonal ε-martensite. The fine structure of massive martensite is of this form[33] and apparently consists of parallel plates containing a high density of random dislocations. The plates are presumably the same as those visible in relief, though this is not known with certainty, and they are separated by sub-boundary regions containing a high density of tangled dislocations. Adjacent plates are misorientated with respect to one another, but are not twins of each other.[8,33]

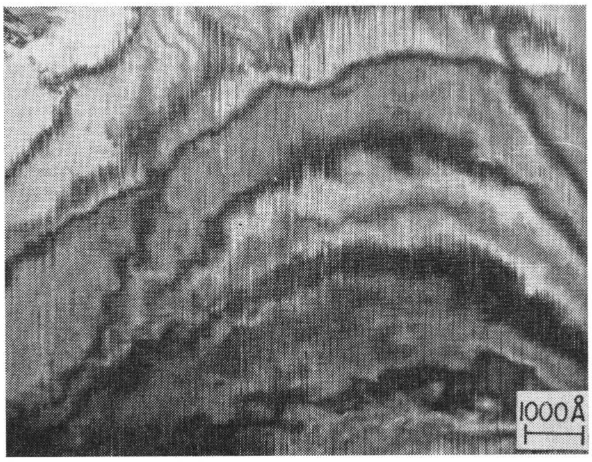
The structure of martensite in high-alloy steels can often be investigated more conveniently than in other systems because of the presence of retained austenite which enables the complications caused by impinging martensite plates to be avoided. In high-nickel alloys, acicular martensites with twinned substructures are formed, but in steels containing chromium or manganese the martensite is not internally twinned. Earlier suggestions that martensite in low-carbon alloys and in stainless steels forms as needles rather than plates[20] now seem to have been discarded, and it is believed instead that elongated plates (laths) are grouped into sheets bounded by $\{111\}$ planes.[48,49] This may obviously be related to the morphology of the massive transformation, although one difference is that adjacent laths or needles are often twin related in stainless steel. Kelly[49] has made an analysis of the crystallography of the α-martensite formed in stainless steels, and has concluded that the elements of the lattice invariant shear are of type $\{111\}\langle 1\bar{2}1 \rangle$ in austenite or $\{101\}\langle 10\bar{1} \rangle$ in martensite. These elements are different from those generally assumed for steels, i.e. $\{110\}$ $\langle 1\bar{1}0 \rangle$ in austenite equivalent to $\{112\}\langle 11\bar{1} \rangle$ martensite, giving twinned products.

Kelly associates the difference in structure and morphology with the stacking fault energy of the parent austenite. The high-alloy steels in which untwinned martensites are observed are also those in which hexagonal ε-martensite forms, and in which the stacking fault energy is low. There has been much controversy about whether the ε-phase helps to nucleate the α-phase or vice versa, since the electron micrographs show clearly that the two are associated.[20,50,51] The majority view seems to be that the ε-phase forms first and subsequently nucleates the α-phase,[48–50,52] although the opposite opinion is expressed by Dash and Otte.[51] The lath morphology may be explained if the α-plates always form in clustered stacking fault regions of the austenite or in plate-shaped crystals of ε-phase.[49]

It is not known at present whether the crystallography of low-carbon alloys, and specifically of massive martensites, is equivalent to that in stainless steels. The morphology and absence of internal twinning support this conclusion, but ε-martensite does not form, and there is no evidence that the



17 *Transmission electron micrograph showing short twins concentrated along mid-rib region of martensite plate in an Fe–30·64%Ni alloy*[22]



18 *Transmission electron micrograph showing stacking faults in the β′ product of martensitic transformation in a Cu–12·2%Al alloy quenched from 1 000°C*[24] stacking fault energy is low, particularly in iron–nickel alloys. Kelly[49] points out that if the two types of martensite are distinguished by stacking fault energy, the implication would be that carbon appreciably increases the fault energy of austenite.

The final type of martensite is characteristic of a low stacking fault energy in the product rather than in the parent phase. This results in a substructure in which there is a regular array of stacking faults, presumably produced by a dislocation interface containing partial dislocations. Figure 18 shows an example of this kind of structure in copper–aluminium alloys.[24] If the stacking faults are very regularly spaced, the martensite plate may be regarded as an unfaulted single crystal of larger unit cell.[53,54]

KINETICS

Nucleation

Much less is known about the nucleation of martensite or bainite than about their growth. The schematic classification in Figure 1 indicates that martensite may be nucleated either thermally or athermally, and in a formal sense this is well established experimentally. Most martensitic transformations exhibit athermal characteristics, the amount of transformation product being a function of temperature and the transformation rate independent of temperature. Some steels transform isothermally in suitable temperature ranges,[55–58] and the rate-limiting step usually appears to be the formation of nuclei, each nucleus growing to its final size in a very short time. The few transformations in which slow isothermal growth of martensite has been reported will be considered separately below. When isothermal transformation is preceded by athermal transformation, its rate is considerably increased. This autocatalytic phenomenon has recently been included in a formal theory of transformation kinetics.[59]

Simple calculations[3,60–62] indicate that nuclei of martensite could not be formed by random fluctuations in a defect-free region of solid solution, at least in transformations (e.g. steel) where the shape deformation is reasonably large. Thermal nucleation must thus be catalysed in some way, making use of existing defects, heterogenities, or internal stress fields. There is some difficulty in formulating a nucleation theory if the growth of embryos is thermally activated while that of stable plates is not. The maximum free energy associated with the formation of a nucleus is now of significance only in showing that homogeneous nucleation is impossible. The critical growth condition is presumably that the embryo attains a size, larger than that corresponding to the maximum free energy, at which the driving force is sufficient to move the glissile interface. Attempts have been made by Knapp and Dehlinger[63] and Kaufman and Cohen[61] to formulate such a theory. The postulates require that rather large embryos (exceeding the critical size of the classical theory) be present in the assembly above M_s, either as a result of structural defects or because they are inherited from the earlier heat treatment. No convincing evidence of such defects has been found; one experimental difficulty is that a metastable phase just above M_s tends to transform spontaneously when samples are thinned for examination in the electron microscope.[64–66]

Athermal nucleation of martensite may be envisaged as beginning from structural defects or from embryos formed at a higher temperature when a critical driving force is exceeded, or it may be treated as rapid thermal nucleation, the M_s temperature being determined by the condition that the nucleation time is small.[67] The possibility of the parent phase in the vicinity of a defect becoming unstable at M_s is attractive, since it avoids the necessity for nucleation in the classical sense. This is quite feasible in the formation of fully coherent hexagonal martensite from the fcc phase where single stacking faults could probably initiate the transformation.[68–70] Similar suggestions have been made for martensite in steels, but remain highly speculative.

In the original form of the theory,[67] the treatment of apparent athermal characteristics as produced by thermal nucleation was difficult to sustain.[61] However, it appears possible that insufficient attention has been paid to the autocatalytic effects of previously formed martensitic plates in promoting new nuclei. The formal theory developed by Entwisle and Raghavan[59] seems to offer the possibility of rationalizing the observations on athermal and isothermal martensite in this way.

Brief mention has already been made of the controversy over whether ε-martensite nucleates α-martensite in stainless steels, or vice versa. According to one point of view, the hexagonal ε-martensite forms first when the stacking fault energy is sufficiently low, and plates of α are then nucleated within ε-martensite, or at the junction of two ε-plates.[50] The opposite view[51] is that accommodation of the α produces stacking faults in the surrounding matrix, and this leads to ε. The evidence on balance favours the first theory, as provisionally concluded by Kelly,[49] but it is clear that further work is needed. It is possible that ε-martensite forms first when the stacking fault energy is very low, and α forms first when it is moderately low.

Interface mobility

Martensite plates and mechanical twins form very rapidly, even at low temperatures. It is difficult to estimate the actual growth velocity, but measurements of the time taken for individual plates to form using fast response apparatus to follow the change in electrical resistance[71] indicate that it may be of the order of one-third of the velocity of sound. It is clear that the growth is not thermally activated since the velocity is not temperature dependent, and rapid growth can be observed near 0°K.

The rapid growth of a martensite plate with a semi-coherent dislocation type interface is readily understood. According to the postulates of the crystallographic theory in its simplest form, the lattice invariant deformation is a simple shear and is obtained by the motion of an array of parallel dislocations in the interface, all dislocations having the same Burgers vector. As the interface moves into either lattice the dislocations glide in the appropriate glide planes. The interface could move in response to a chemical driving force or a mechanical stress, and its motion may be regarded as a mode of plastic deformation. As indicated in Figure 1, a symmetrical low angle tilt boundary is essentially a special case of a semi-coherent martensite boundary in which the parent and product structures are identical, and the dislocations are pure edge in character.

In the formal theory of surface dislocations developed by Bilby *et al.*[13,72–74] the habit plane interface of a martensite plate is regarded as a glissile surface dislocation. By allowing the number of dislocations in the interface to increase towards infinity while the Burgers vector of each simultaneously tends to zero in such a way that the product of these two quantities remains constant, a transition may be made to a mathematical model in which there is a continuous distribution of dislocations. The net Burgers vector of the dislocations crossing any unit vector in the interface is then specified by a surface dislocation tensor β_{ij}. A twin may be obtained formally by placing a twinning dislocation on each of a succession of lattice twinning planes of the parent structure, and the corresponding continuous distribution for twinned martensite is then the same as that given by the dislocation model. This is necessary, of course, from the equivalence of the two situations in the formal theory of crystallography, but it may be helpful to think of the twin model in this way. It can then be understood that a twinned martensite plate should also have a habit plane interface which is able to move normal to itself without thermal activation.

When there is a change in twin thickness behind the boundary, as in indium–thallium, the motion of the boundary must also involve the movement of the arrays of twinning dislocations which represent the tapering twins behind the boundary. There is experimental evidence that these arrays are not as mobile as the boundary itself. Rapid motion of a single interface boundary in indium–thallium alloys, for example, leaves a region in which no twins are immediately visible under an optical microscope, although the twins reappear in a short time.

The above discussion refers specifically to the motion of the habit plane interface normal to itself, and is thus most appropriate to the growth of a martensite region which traverses a single crystal. A lenticular plate within the matrix may be regarded as having parallel sections of habit plane interface separated by steps. These steps have similar characteristics to twinning dislocations, and may be called transformation dislocations[75]; they have Burgers vectors equal to the displacement vector of the invariant plane strain shape deformation multiplied by the step height. Lengthwise extension of the plate is equivalent to expansion of loops of transformation dislocation in their own planes, and should take place very readily. The problem is analogous to the growth of a lenticular twin, and the stresses near the edge reach high values because of the large shape shear. An additional complication with a martensite plate is that as it extends in the direction in the habit plane which is normal to the interface dislocations or twin boundaries, new dislocations or boundaries have to be nucleated. This should be a spontaneous process because of the high stress concentration.[76]

The motion of the habit plane interface normal to itself in coherent martensite raises special problems, analogous to those encountered in the theory of crystal growth and mechanical twinning. In the pole mechanism,[69,70,75,77,78] transformation dislocations accomplish this growth by rotating about suitable pole dislocations which thread through the surface of the plate. Some indirect evidence for this growth mechanism is provided by the observation of a shape change in transformed hexagonal regions,[26–28,79] since the shape change could otherwise be reduced to zero by random averaging over the three shear directions in the habit plane. Observations of this type have been mainly confined to cobalt and its alloys, but Nishiyama and Shimizu[80,81] have detected thin shear plates of ε-martensite during an electron microscopic investigation of the structure of high-manganese (Hadfield) steel.

Isothermal growth of martensite

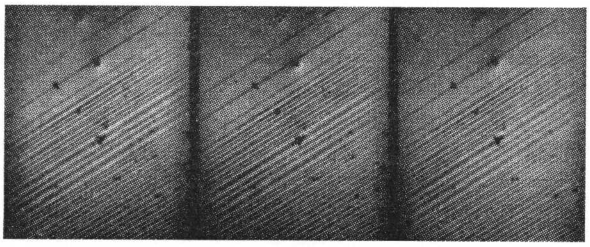
In some circumstances, martensite plates grow slowly at a rate which may be observed under an optical microscope and photographed with a ciné-camera. Slow growth is generally observed only when the transformation begins at small values of the chemical driving force, but there appear to be several possible rate-controlling processes. Some slowly moving plates are in thermo-elastic equilibrium with the surrounding matrix, and may be made to grow or to shrink as either the temperature or the externally applied stress is changed.[82–83] This behaviour is analogous to mechanical twinning, and is comparatively well understood; it involves no modifications in the description of the martensite interface as a glissile surface dislocation. When the growth of a plate is constrained by a surrounding matrix, the net change in free energy may include negative terms from the chemical driving force and the potential of any applied stresses, and positive terms from the strains needed to accommodate the shape deformation of the enclosed plate. Thermo-elastic martensite will result if a size and shape at which the free energy is a minimum is attained without appreciable plastic deformation, which would cause the plate to lose coherency. There is then a balance between driving stress and opposing stress acting on the interface, and any variation in external conditions will allow it to move. The velocity depends only on the rate at which the external constraint is varied, the plate remaining essentially in equilibrium at all times. Thermo-elastic martensite is likely only when the shape deformation is small and the parent phase has a high yield strength.

Slow growth has also been observed in the transformations in indium–thallium and gold–cadmium alloys, under conditions where single interfaces traverse single crystals so that thermo-elastic equilibrium is precluded. The interface moves in a jerky manner, and the temperature has to be changed continuously to maintain its motion. However, there is considerable evidence that the interface may be able to move very rapidly between obstacles or when it moves into a region of increasing driving force. The results have been interpreted in terms of some kind of relaxation process, proportional to the volume transformed. A similar effect has been observed in the motion of a symmetrical low-angle tilt boundary. At low temperatures, an increasing stress is needed to maintain this motion,[84] possibly because the boundary accumulates debris.

Förster and Scheil[85] divided martensite in steels into 'schiebung' and 'umklapp' types, and other authors[86,87] have accepted the kinetic distinction between slow and fast growing plates as indicative of fundamental differences in interface structure and growth mechanism. The opposite view, based on the above examples, is that the martensitic interface is always glissile, and that slow growth is attributable to secondary factors. The distinguishing feature of slow growth is often that it is athermal, i.e. that it corresponds to increase of driving force, and this is clearly not inconsistent with the existence of a glissile interface. Most measurements on isothermal martensite also indicate that the growth is athermal,[8] only the nucleation being thermally activated. Evidence for the slow isothermal growth of martensite plates in an Fe–28·8%Ni alloy has, however, been presented by Yeo.[42,43] His pictures show lengthwise extension of plates in a manner rather similar to that previously noted for indium–thallium alloys[15] (see Figure 19), although it was not believed in the latter case that the growth was truly isothermal. The growth velocity measured by Yeo is about 10 million times slower than that estimated for athermal or rapid isothermal growth,[71] but is still some 30 000 times faster than the expected growth rate for bainite extrapolated from the high-temperature results of Goodenow *et al.*[41] It thus seems difficult to attribute the growth to thermally activated atomic migration. It may be tentatively suggested that the growth velocity is limited by the rate at which obstacles which stop the plate can be overcome by the aid of thermal energy. This would then be a type of interface controlled motion, analogous to logarithmic creep, and at a sufficiently high driving force the velocity would no longer be limited in this way.

An interesting variant of the interface control theory has been suggested by Owen *et al.*[8] They point out the possibility that massive martensite in steels implies a cubic product, and suggest that this may be produced by Zener disordering[88] of the interstitial atoms immediately behind the interface. The rate of disordering, which depends on interstitial atom jumps in the otherwise tetragonal product, will then control the interface velocity. Yeo also observed that martensite plates nucleate preferentially on austenitic $\{111\}$ twin boundaries, and grow in a one-sided manner from these boundaries. This may be related to the arrangement of the martensite laths in sheets on $\{111\}$ planes, described above. The kinetic observations have not yet been repeated successfully by other workers, and more information on this mode of transformation is desirable.

The other well established example of slow isothermal growth in a martensite is the transformation from β to α-uranium, which has been most studied in dilute uranium–chromium alloys.[89–92] The structure of β-uranium is complex, with thirty atoms in the unit cell, so that it is remarkable that the change has any military characteristics. The majority of the atomic displacements during the transformation must involve rather complex shuffles, which may well be thermally activated. The transformation is more rapid in pure uranium than in a uranium–chromium alloy, and this might indicate that the chromium atoms occupy preferred sites in the cell. Another factor is the difficulty of deforming the complex β-structure. This may mean that the growth rate is limited by the rate at which accommodation stresses in the matrix can be thermally relaxed.



19 *Growth of a main band at the front of an extending set of main bands in an In–18·5% Tl alloy*[15]*; oblique illumination* ×70*; intervals between ciné frames* $\frac{1}{16}$ *s*

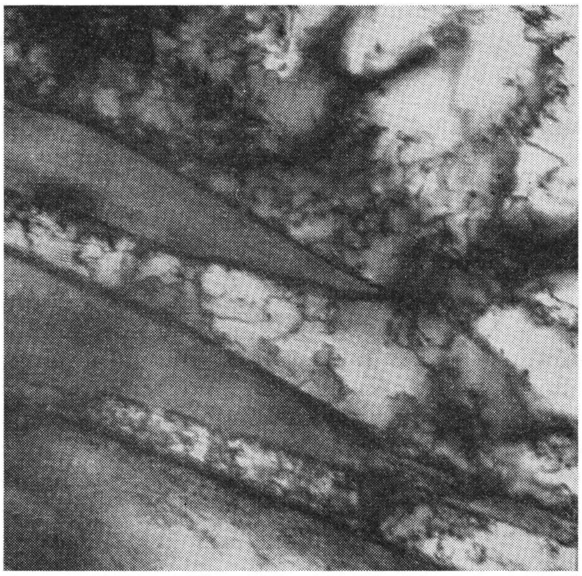
The edgewise growth rates of individual phases in bainite have been measured by several workers.[37,41,93] Both edgewise and lengthwise growth occur at constant linear rates, and have been attributed to the diffusion of carbon in austenite using the Zener–Hillert model.[93,94] There are, however, many difficulties in accepting this model, and the present theoretical description of the growth is unsatisfactory.

Cessation of growth: stabilization

There has been little systematic work on the effects of substructure, inclusions, precipitates, etc. on the growth of martensite. When acicular martensite forms, edgewise growth of the plates often continues until a grain boundary or another plate is encountered, but the plate does not then thicken substantially. The first plates formed partition the grains of the matrix, so that the average plate size decreases as the amount of martensite increases. The partitioning effect is important in the formal kinetics of both isothermal and athermal martensite.[95]

Acicular plates which form rapidly do not usually increase in size when the chemical driving force is increased by changing the temperature, or when the mechanical driving force is increased by varying the stress. This contrasts with the behaviour of thermo-elastic plates, already described, and the difference is further pointed by the opposite transformation. Whereas the growth of a thermo-elastic plate is reversed on heating, and the whole transformation is crystallographically reversible, an acicular plate usually disappears only when heated to a temperature appreciably above M_S. The heating transformation is often separately nucleated, and is thus not completely reversible; surface tilts, for example, may remain after a complete transformation cycle.

The shape deformation of a constrained acicular plate will normally lead to plastic deformation in the surrounding matrix unless a thermo-elastic equilibrium is attained. Such deformation



20 *Dislocations surrounding martensite plates in an Fe–Ni–C steel*[20] ×30 000 may be severe and very dense accumulations of dislocations around the plates are visible in thin-film electron micrographs (*see* Figure 20). This must lead to at least partial loss of coherence at the boundary, so that the interface is no longer glissile. The plate is then stabilized, and further motion of the interface in either direction is not possible. Because of the deformation, it may be difficult to transform the last parts of the parent phase, which are trapped between previously formed plates. The cooling transformation then usually takes place over a relatively wide range of temperature, and in some cases complete transformation cannot be obtained unless mechanical stresses are applied.

Observations on systems which form parallel-sided plates or bands of martensite show that the transformation behaviour is quite different. Since the shape deformation is small and the plates are self-accommodating, there is little deformation of the surrounding matrix, and coherency is not lost at the interfaces. Complete transformation on cooling is then possible, and is usually attained in a small interval of temperature. Individual plates thicken until they meet one another along their habit plane interfaces, so that the boundaries remaining after transformation separate different regions of product, rather than product and parent phases. Nuclei must be retained or re-formed at the boundaries, since the reverse transformation is obtained by motion of these same boundaries. This type of transformation can be completely reversible, the original surface tilts disappearing again on heating. There is generally little hysteresis between cooling and heating transformations.

The massive martensite transformation found in low-carbon iron–nickel and other iron alloys has some of the characteristics of the banded martensites. There is little if any retained austenite, and the transformation begins at a smaller driving force than that required for acicular martensite. The transformations in titanium and zirconium also go readily to completion, and in some circumstances are completely reversible on reheating. The internal structure of massive martensite differs from the banded structures inasmuch as it is not internally twinned, but there is the obvious possibility that it is also self accommodating in the sense that adjacent parallel plates of a cluster have opposite shape shears. This has not yet been proved directly.

The accommodation stresses around an isolated martensite plate, which ultimately stop it growing, may also assist the formation of another plate on a crystallographically equivalent variant of the habit plane. This is an autocatalytic effect which is important in nucleation as well as in growth, since it has been observed to have a considerable influence on the course of an isothermal reaction.[58] The plates formed in this way must have shape deformations which are partially self accommodating, but complete accommodation will not be possible if each variant of the habit plane has a unique shape deformation associated with it. In some cases, the autocatalytic effect occurs catastrophically, the first plate initiating a kind of chain reaction in which a large number of plates form in a characteristic zig-zag pattern during a very short time interval. Machlin and Cohen[96] found that about 25% of the whole transformation in an iron–nickel alloy occurred in a single 'burst' of this kind; the effect is now called the burst phenomenon. Plates formed in this way are appreciably thicker than normal acicular plates, in conformity with the above discussion.

A martensitic transformation may be inhibited by either mechanical or thermal stabilization. Mechanical stressing above M_s frequently promotes transformation since the shape deformation reduces the potential of applied stresses, but a temperature M_d exists above which transformation will not occur. Stressing above M_d results in plastic deformation, and the M_s temperature on subsequent cooling is then often found to be lowered. This mechanical stabilization presumably results from the obstruction to growth offered by defects introduced during deformation, and possibly from the destruction of coherency in small nuclei. Deformation produced internally by accommodation stresses can also have the same effect; thus the M_s temperature in cobalt–nickel alloys may be drastically reduced by thermal cycling through the transformation range.[28]

An opposite effect is that small deformations of the parent phase above M_d may sometimes promote transformation by raising M_s.[97,98] The stresses here must produce defects which aid the nucleation of martensite or must help small nuclei to grow. Kelly[49] has pointed out that the stimulation effect in austenite appears to occur only in alloys of low stacking fault energy, and he has therefore associated it with the production of ε-martensite or of stacking faults by stress.

In addition to mechanical stabilization, there is a well established thermal stabilization effect in steels. This is often called simply stabilization and has a voluminous literature. The effect is most pronounced if the specimen is held for some time at a fixed temperature in the transformation range of an athermal transformation. When cooling is resumed, the transformation does not begin at once, but only after a finite fall in temperature. When transformation does resume, it often does so at an enhanced rate, and some martensite is formed in bursts.[99] Stabilization is not observed in steels unless carbon or nitrogen is present,[100] but experimental activation energies for the process are much lower than those for diffusion of interstitials in austenite.[100,101] Although there have been several theories, we shall mention only two, both of which have been discussed in recent literature. One possibility is that interstitial solute atoms migrate to the interface and lock it in position[101]; direct evidence for an effect of this type is available for single interface transformations in indium–thallium alloys.[15] The other theory is that stabilization arises from the destruction of the autocatalytic effect of previously formed plates.[99] Glover[102] has suggested that this is the main effect in most investigations of thermal stabilization.

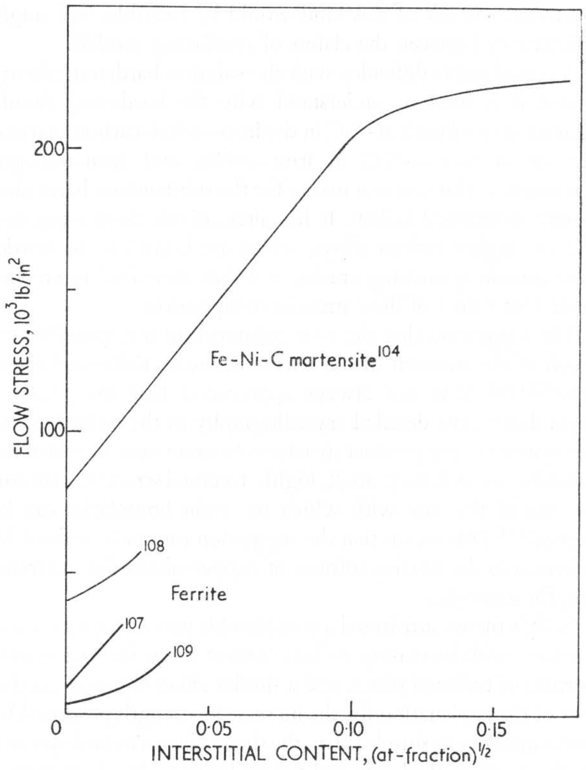
STRENGTH OF MARTENSITE

Martensite in steels is very strong and also often very brittle; martensitic products in other alloy systems (including carbon-free iron alloys) do not necessarily possess these characteristics. The strength of martensite thus cannot be attributed solely to factors inherent in the transformation mechanism, such as, for example, the fine structure of the product. Equally, however, we cannot dismiss the fine structure as a strengthening mechanism simply by comparing different alloys with similar fine structures. The fine structure might be effective only in products of particular crystal structure, for example, or in solid solutions of a particular type. Much progress in understanding the strength of martensite, and of high-strength steels which utilize a martensitic reaction, has been made in recent years by carefully designed experiments, but the overall position is still rather confused.

The main controversy has arisen from theories which attribute the strength of martensite in steels (*a*) to carbon atoms in solution and (*b*) to the fine twinning in the product. The evidence in favour of solid solution strengthening by carbon atoms is that the strength of nearly carbon-free martensite is not very high, but that it increases rapidly with increasing carbon content. The most convincing experiments are those made on iron–nickel–carbon alloys by Winchell and Cohen,[103–106] the compositions being adjusted to give a roughly constant sub-zero M_S temperature of -35°C so that complications due to autotempering could be minimized. Flow stress measurements in compression (and in tension for the low-carbon alloys) were made at various sub-zero temperatures and at various martensite contents to eliminate the effects of retained austenite. All of the martensites were internally twinned, and Cohen[106] has quoted electron microscope observations by Richman which show that the twin thickness and volume ratio is constant across the whole composition range.

The flow stress was found to be a strong function of carbon content, and the carbon strengthening was independent of the test temperature except for aging effects at higher temperatures. In the low-carbon region, the increase in flow stress was measured as $\sim 2{\cdot}3\times 10^6$ lb/in^2/wt-%C, which compares with values of $\sim 1{\cdot}9\times 10^6$ lb/in^2/wt-%C determined by Wert[107] and $0{\cdot}6$–$0{\cdot}75\times 10^6$ lb/in^2/wt-%C determined by three other groups of workers[108–110] for the strengthening effects of carbon in ferrite.

Stephenson[108] and Cracknell and Petch[109] found the flow stress of ferrite to increase linearly with carbon content, but other workers have reported that the stress increases less rapidly than this. Winchell and Cohen[103] plotted the flow stress against the cube root of the carbon concentration and obtained a straight line relation. Their theory is based on the Mott–Nabarro model of hardening by centres of internal stress, but seems to require the dislocations to bend in three dimensions, i.e. out of their slip planes. In an alternative treatment of the Mott–Nabarro theory, Cracknell and Petch[109] have predicted a nearly linear dependence of stress on concentration for small concentrations. More recent models[113] assume that dislocations interact appreciably only with solute atoms close to the core. Mordike and Haasen[111] suggested a (concentration)$^{1/3}$ dependence of stress when considering the effect of interstitials on pure iron, but this requires three dimensional bending which is very improbable.[8,112] If the dislocations are confined to slip planes and interaction is short range, the stress should vary with the square root of the atomic fraction. When plotted in this way (see Figure 21), Winchell and Cohen's results give a straight line of slope slightly greater than that obtained from Wert's results for ferrite. This slope is $\sim\mu/9$, where μ is the shear modulus, and corresponds to a slope of $\sim\mu/18$ for the corresponding shear stress relation; the equivalent value for ferrite is $\mu/20$.[113] This is a high rate of hardening, but is nevertheless appreciably smaller than the theoretical value of $0{\cdot}4\mu$ obtained from Fleischer's model[113] of solid solution hardening.



21 *Comparison of hardening effects of interstitials (carbon and nitrogen) in solution in ferrite and in iron–nickel–carbon martensite*

Short resting at 0°C produced appreciable increases of flow stress in the iron–nickel–carbon martensites, and some aging was found at all temperatures above -60°C. For this reason there are no experimental results on martensite in plain carbon steels which can be compared directly with those of Winchell and Cohen. The variation of flow stress with carbon content in iron–carbon martensite is indeed difficult to measure because of the very brittle nature of the martensite. Hardness measurements have been made on both iron–carbon and iron–nitrogen alloys, but are only of limited value since it is certain that autotempering must have taken place during the quench. Qualitatively, however, the curves show a rapid increase of hardness up to a maximum value at ~ 3 at-%C, followed by a slight decrease which is probably due to increasing retained austenite. The maximum value corresponds approximately to the transition from massive to acicular martensite, but in view of other results this seems likely to be coincidental.

The considerable discrepancy between Fleischer's theoretical prediction of the hardening expected from carbon in solid solution and the highest measured hardening has been attributed partially to the effects of thermal activation. Unfortunately, however, the available evidence at present is that, while interstitials in bcc metals produce marked increases in yield stress, the temperature and strain rate dependence of the yield stress is not greatly changed[114–117] except possibly at extremely low carbon levels.[118] Recent work by T. L. Altshuler[119] at Oxford has indicated that even the very purest iron so far produced has a temperature dependence at low temperatures equal to that of other irons. In contrast to the volume of work on nominally pure bcc metals, however, there have been few experiments on the temperature and strain rate sensitivity of the flow stress in martensite. Work of this kind would be valuable, and might differentiate between the claims of conflicting models.

A considerable difficulty with the solution hardening theory is that it is hard to understand why the hardening should saturate at less than 2 at-%C in the iron–nickel–carbon martensite, or at ~3 at-%C in iron–carbon and iron–nitrogen martensites. This was one reason for the substructure hardening theory mentioned below. It has alternatively been suggested that the higher carbon alloys, which are known to be brittle, may contain quenching cracks, and that these lead to erroneously low values of flow stress in compression.

The suggestion that the twin substructure is responsible for much of the strength of martensite is due to Kelly and Nutting.[19,20,120] It is not always appreciated that the proposal depended on the detailed crystallography of the twinning and slip systems in the product structure. In some cases in which the twinning shear is very small, highly twinned structures are soft because of the ease with which the twin boundaries can be moved.[121] This means that the suggestion cannot be refuted by referring to the relative softness of copper–aluminium martensite, for example.

Kelly's theory attributed a considerable part of the increase in hardness with increasing carbon content to an increasing proportion of twinned plates, and a similar effect was suggested as part of the explanation for the increase in strength produced by ausforming. In its simple form, the theory seems to be disproved by the work of Radcliffe and Schatz,[122] who simply measured the hardness of cubic martensite in a series of iron–nickel alloys. This increases with nickel content up to ~5%Ni and then remains nearly constant; the results have subsequently been confirmed by Roberts at Liverpool.[8] Since the transition from massive to acicular (twinned) martensite occurs at about 30%Ni, it seems that the substructure has relatively little effect. However, the reservation must be made that results obtained from cubic, carbon-free martensite are not necessarily applicable to tetragonal martensite in steels.

The good agreement between hardening rates produced by carbon additions in ferrite and martensite (Figure 21), together with the absence of a detectable substructure effect on the strength, seem to show that the hardening is predominantly due to carbon in solution. Nevertheless, the correct explanation of this hardening is not yet evident, and it is clear that further work is needed in this field. The aging experiments of Winchell and Cohen have shown that low-temperature tempering makes an appreciable contribution to strength, and it is not inconceivable that some of the strength depends on carbon segregation, perhaps to twin boundaries, even when the M_s is below zero. The main evidence that the carbon is in solution and not clustered comes from Wert's and Stephenson's comparable results on ferrite,[107–108] where internal friction methods were used, but the possibility of some precipitation even here has been raised.[123]

SUMMARY: CURRENT PROBLEMS

In concluding this brief survey of the whole field of military transformations, attention will be drawn to some of the outstanding problems, and the possible roads to their solution. The following kinds of military transformations have been distinguished:

(i) fully coherent martensite; the transition is always between close-packed structures, and is to be expected in fcc alloys of low stacking fault energy; examples are the transformations in cobalt and its alloys and the formation of ε-martensite in steels

(ii) thermo-elastic martensite; this sub-division is not based on fundamentals of crystallography or growth mechanism, but only on the attainment of an equilibrium between isolated lenticular plates and the opposing elastic stresses of a constraining matrix

(iii) banded martensites; the crystallography is degenerate, so that plates can be self accommodating, and the transformation can proceed to completion without loss of coherency

(iv) acicular martensite; in steels this is internally twinned, although there is no obvious connexion between the internal structure and the morphology; the crystallography indeed can vary; both {225} and {259} type habits are observed in acicular martensites of similar substructures

(v) massive martensite; this is untwinned in steels, although again the connexion of internal structure and morphology may be only coincidental; this may be an imperfectly developed form of (iii), in which clusters of plates are not completely self accommodating because of the larger shape change

(vi) lower bainite; this is probably a self-tempered martensite, the growth velocity being limited by the tempering rate behind the interface

(vii) upper bainite; this may be a military transformation in which segregation in the parent phase precedes the structural change

(viii) military type order–disorder changes.

The above distinctions are made for reasons of convenience and depend on a mixture of crystallographic, morphological, and kinetic criteria. It is obvious that the classification could be made in other ways, for example mainly on the basis of the type of substructure. However, attention can now be drawn to some of the problems with which this report is concerned.

Relationship between massive martensite and acicular martensite

The morphological change in steels is associated with a change in substructure; acicular martensite is twinned and massive martensite is not. The crystallography of acicular martensite is generally well understood, although difficulties are still caused by the scatter of habit planes,[9] and by certain experimental results for {225} habits.[124,125] The recent suggestion by Kelly[49] that the elements of the lattice invariant deformation are different for massive martensite helps to rationalize many of the observations, although a detailed comparison of theory and experiment will not be possible until more complete experimental data are available. This still leaves unanswered, of course, the question of what determines the elements of the lattice invariant deformation. Dr Kelly has tentatively suggested the stacking fault energy of the austenite, but has himself recognized that there are certain difficulties in this assumption, which is further discussed below.

Professor Owen and his collaborators[8] have emphasized that massive martensite in iron alloys is almost always associated with a cubic product phase, whereas acicular or twinned martensite is tetragonal. (The major exception to this rule is cubic acicular martensite in high-nickel iron–nickel alloys.) According to this view, massive martensite in low-carbon iron–carbon alloys or low-nitrogen iron–nitrogen alloys is cubic because of Zener-disordering of the interstitial atoms as the martensite forms, rather than because of a subsequent auto-tempering process. Zener-disordering of the traces of interstitial impurity in iron–nickel alloys with $>30\%$Ni might be difficult because of the low transformation temperature, although the tetragonality which results is too small to be detected and the authors admit that it could scarcely be expected to affect the crystallographic mechanism of transformation. This is, indeed, the difficulty with this suggestion; there is no discontinuity in the predictions of the crystallographic theory when c/a becomes unity, and twinned structures are equally possible for cubic and tetragonal products. A discontinuity would be expected, of course, if the tetragonal twinning plane were a mirror plane of the cubic structure, but that is not the case here.

Another question which arises is how gradual is the transition from one form of martensite to another. The evidence is that it is moderately sharp in iron–nickel alloys, but in iron–carbon alloys it is often suggested that there is an increasing proportion of twinned plates as the carbon content increases. The form of the product can also be changed in some steels simply by increasing the quenching rate.[126]

Finally there is the question of the more general significance of the massive morphology. It has been suggested above that it is dependent on an assembly of parallel, self-accommodating martensite plates, and that this is quite unrelated to the question of whether or not these plates are internally twinned.

Effect of low stacking fault energy in the parent phase

Low stacking fault energy in steels is known to lead to the metastable product ε-martensite, and also seems to favour massive rather than acicular martensite (although it would be more correct to say untwinned rather than twinned martensite). Two transformation sequences have been suggested for steels in which α and ε products are associated, namely:

austenite → ε-martensite → α-martensite
austenite → α-martensite → ε-martensite or stacking faults

It is probable that both sequences operate in alloys of different fault energy. They could even operate in the same alloy if the α and ε-phases help to accommodate each other, no matter which is found first.

A difficulty in the stacking fault theory arises from the effects of alloying elements such as nickel and manganese on the toughness of martensite. Manganese lowers the fault energy of austenite, and should thus favour massive rather than twinned martensite according to Kelly's description, while nickel has the opposite effect.[127,128] The available evidence is that twinned martensite is more brittle than massive martensite, so that in general manganese might be expected to increase ductility, and nickel to reduce it. As Nutting[129] has remarked, the observed effects are opposite to those predicted.

Effect of low stacking fault energy in the product

In transitions between close-packed phases this is implied above and as expected the product phase is also highly faulted. X-ray data for cobalt[130,131] show that the predominant type of faulting changes from 1∇ in the naturally formed hexagonal phase to 2∇ when the transformation is completed by external stress. It is not known whether this is also true for ε-martensite in steels, nor has a detailed mechanism been suggested.

The more interesting effects arise when the fault energy is low only in the product, as in copper–aluminium and similar alloys.[24,132] The highly faulted product then seems to be produced at the interface by the lattice invariant deformation. It is interesting to note that for the bcc → (faulted) fcc transformation, the lattice invariant deformation must have the same elements as those postulated by Kelly for massive martensite in steels. This is relevant to the suggestion that massive martensite comes from austenite of low fault energy, and at least provides confirmation that this type of lattice invariant deformation is feasible. The martensitic product in lithium and lithium–magnesium alloys is also heavily faulted.[133–135] If the faults are obtained at the interface because the lattice invariant deformation is accomplished by partial dislocations in the interface, the elements of the lattice invariant deformation can be similarly deduced. It is difficult to use electron microscopy to investigate these elements because of the low transformation temperature, but the current crystallographic theory of this transformation[136] does not correspond to this assumption.

Nucleation of martensite

Little progress has been made in this topic in recent years, except for the special case of ε and α-martensites forming together. It is clear that martensite nuclei in steels may be thermally activated at an early stage in their growth, and that internal stresses from previously formed plates play a large role in the nucleation process. We do not know what is the critical stage in the formation of the nuclei, whether large embryos are present in the metastable parent phase above the M_s temperature, and whether embryos are formed from structural imperfections or composition fluctuations.

Slow growth in military transformation

When slow growth is athermal it may readily be explained, as indicated above; slow isothermal growth is considered here. The rate-controlling mechanism is presumably one of two general types. In martensites, some kind of interface process must be rate controlling. Possible examples include the overcoming of obstacles to interface motion, relaxation processes such as Zener-disordering in steels or ordering in copper–gold alloys, and thermally activated shuffling of the atoms. There may also be thermally-activated relaxation of the opposing stresses in the matrix.

In bainites, the growth is controlled by some kind of long-range diffusion, leading ultimately to precipitation and increase of chemical driving stress on the glissile interface. The diffusion process may be mainly in the product (lower bainite?) or the parent phase (upper bainite?).

All of these ideas are expressed qualitatively, and critical experimental tests of the hypotheses have not been devised.

Properties of the product

The factors affecting the physical and mechanical properties of any phase interact in a complex manner, and this is especially true of martensite. Much more work is needed before final assessment can be made of the importance of type and distribution of alloying element, substructure, temperature of formation, etc. on the properties of martensite. This is perhaps the stage of greatest practical interest, where theoretical concepts begin to lead to design data. It is already clear that the usefulness of a martensitic transformation is primarily that it provides a means of obtaining solutions with degrees of supersaturation which are otherwise inaccessible. These solutions may themselves be very strong, and the classical problem (still only partially solved) is whether the strength should be attributed solely to the alloying element or to its interaction with the substructure. The strongest alloys, however, are those which are hardened by precipitates, and the important factors in processes such as ausforming and maraging seem to be that the treatments provide novel ways of controlling the size and distribution of the ultimate precipitates. The physical metallurgist interested in the theory of martensitic transformations is still a long way from making predictions of immediate utility to the producers and consumers of steel, but at least he can feel that this is a possibility that is no longer remote.

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Discussion I

Chairman: Mr J. E. Russell (English Steel Corporation Ltd)

Mr J. A. Klostermann (Stichting voor Fundamenteel Onderzoek der Materie, Delft, Holland) said that he agreed with the suggestion of Dr Christian that more information about slow isothermal growth of martensite was desirable. This subject had been studied by Yeo[1] and by Professor Burgers and himself.[3] Yeo had spoken of growth of plates from the interior of the specimen. Perhaps he was not fully aware of the fact that he was observing surface martensite. Yeo also mistook boundaries of mechanically polished surface martensite needles for coherent twin boundaries of austenite. Speaking also on behalf of Professor W. G. Burgers, he would like to give further information. A film had been made of the growth of surface martensite.

The film was then shown.

The surface martensite formed spontaneously at room temperature after electropolishing on single crystals of iron with about 30%Ni (Figure *A*). It could also be nucleated by scratching. The condition controlling the orientation of these needles appeared to be that they must lie in $\{112\}\gamma$ planes. The needles often branched. They grew fast in the length direction and then thickened sideways on one side only, so that they had one straight boundary. The other boundaries were in most cases rather ill defined but seemed to strive to approach also a $\{112\}\gamma$ plane. Figure *B* showed a surface martensite crystal with boundaries which lay in $\{112\}\gamma$ planes. That meant that in this case there was one martensite crystal with three different habit variants. This crystal seemed to have thickened layer by layer. Obstacles were not simply included.

When one supposed that the martensite and austenite lattices would fit together in such a way that close-packed atom rows in both lattices were parallel,[4] then it followed that the $\{112\}$ austenite plane was the only lattice plane with low indices that fitted together with a martensite lattice plane, in fact, the $\{123\}$ plane (see Table 1).

The particular orientation relation associated with a particular habit variant had also been determined. This resulted in an orientation relation lying between that of Kurdyumov and Sachs, and Nishiyama. The particular variant was the 'standard variant' (Wayman *et al.*[2] also found the standard variant for martensite with a $\{449\}$ habit).

The orientation relation was such that the $\{112\}\gamma$ lattice plane transformed without rotation to the corresponding $\{123\}\alpha$ plane. Thus it appeared that the habit plane in this case was an austenite lattice plane which fitted on an atomic scale to the martensite plane into which it transformed by the correspondence matrix for planes; secondly it was a lattice plane that was not rotated by the transformation.

Perhaps fitting on an atomic scale also played an important role in the $\{225\}$ habit for martensite in steel. Fitting on an atomic scale was not considered in the Bowles – Mackenzie and Wechsler – Lieberman – Read theory.

An attempt had been made to get an impression of the shape deformation of the surface martensite. Figure *C* (i) showed a surface martensite needle which grew after the specimen was scratched. Figure *C* (ii) showed the related interferogram.

The displacements of the scratches showed that the shape deformation was not a simple invariant plane strain. The shape deformation on the Figure *C* (i) was in fact exaggerated by the interference contrast microscope. Actually the shape deformation was not only complicated but also very small. The depth and breadth of the needles was 25 μm. The maximum deviation of the bands of the interferogram corresponded to a distance of $\frac{1}{3}$ μm, so that the deformation was of the order of 1%. Thus the lattice deformation was practically fully compensated by the lattice invariant deformation which therefore could not be an invariant plane strain. Of course, the 112 plane was an invariant plane, but the equation $F = S\ R\ P$ could not be solved by postulating a lattice invariant deformation. (In this equation F was the shape deformation, S the lattice invariant deformation, which must be an invariant plane strain, and $R\ P$ the lattice deformation written as the product of the 'Bain strain' P and a rotation R.)

On the other hand, the problem could be solved, considering only a narrow zone of the needle, by introducing the experimentally found orientation relation. The distribution of the cube reflections in space of one particular variant of the surface martensite relative to the austenite was measured with precision with a texture goniometer. A very eccentric choice with low intensity out of this distribution had to be taken for the orientation of this zone, to satisfy the invariant plane strain theory.

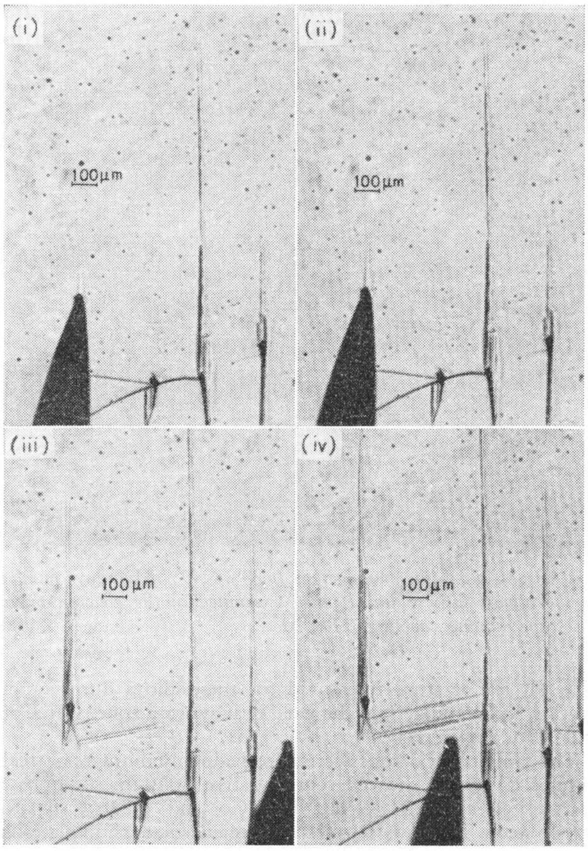
Another point that he wished to bring forward was that the growth mechanism in the plane of a plate or in the direction of a needle was essentially different from the growth normal to the plate (needle).

Figure *D* showed plate martensite with a $\{259\}$ habit, which formed after surface martensite with a $\{112\}$ habit had formed on the surface.

The micrograph suggested that the thickening of the $\{259\}$ plates took place with a mechanism like the lengthwise growth of the surface martensite. The branches of the plate lay also in $\{112\}\gamma$ planes.

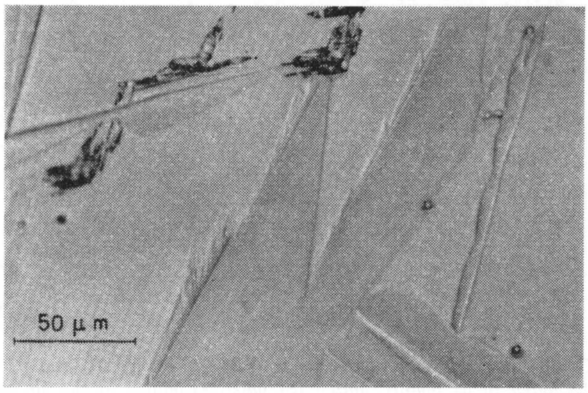
For $\{259\}$ martensite with a midrib, a twinned region, and an untwinned region, one could perhaps suppose three different mechanisms of growth. It was thought that more attention should be directed to these growth mechanisms.

Dr T. Boniszewski (BWRA) said that he wished to make a few comments in relation to the morphology of martensite discussed by Dr Christian. Confusing terminology appeared to result from the comparison of different martensites on the basis of geometry of their crystals on one hand, and the fine, internal structure of the crystals on the other hand. It had been assumed so



A *Nucleation of (slow growing) surface martensite by scratching*
(i) $t=0$ s (ii) $t=\frac{1}{64}$ s
(iii) $t=\frac{1}{3}$s (iv) $t=\frac{1}{2}$ s

far that the acicular, plate-like, martensite was always twinned while the 'massive' martensite or lath martensite was slipped. Hence, in the confrontation of the different martensites, 'twinned' and 'lath' had been used as the distinguishing adjectives. Such terminology was faulty because it was based on different criteria: the internal structure on one hand, and the crystal geometry on the other. Furthermore, this terminology was contrary to facts.



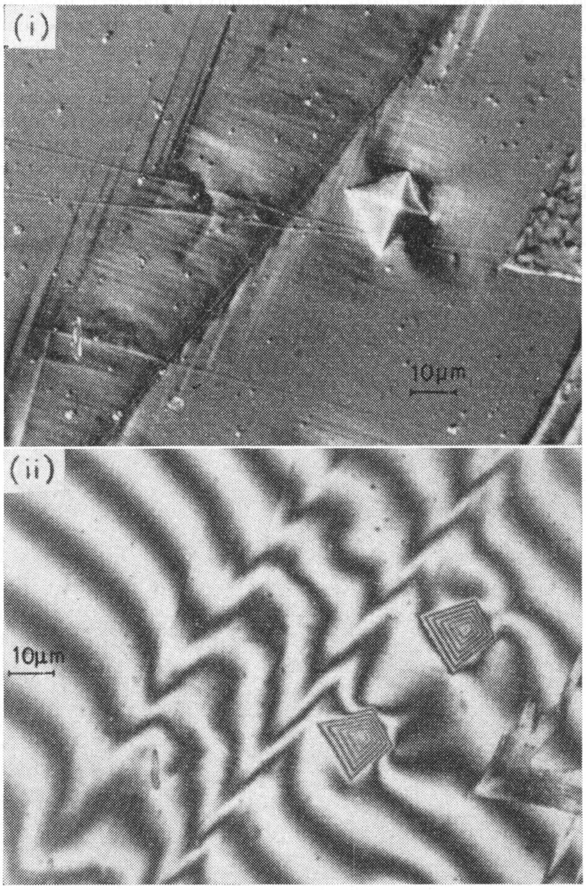
B *Surface martensite crystal with boundaries which lie in {112} planes of the austenite*

TABLE 1 Austenite and martensite lattice planes

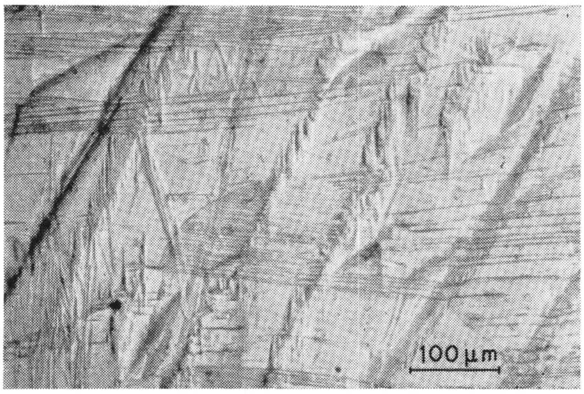
Plane which contains the [110] direction in the austenite	Distance of closest packed [110] rows in the austenite, Å	Plane which contains the [111] direction in the martensite	Distance of closest packed [111] rows in the martensite, Å
$(1\bar{1}0)$	3·58	$(1\bar{1}0)$	2·86
$(1\bar{1}1)$	2·19		
$(1\bar{1}2)$	6·20	$(11\bar{2})$	4·04
$(2\bar{2}1)$	8·39★		
		$(\bar{3}21)$	6·16
		$(\bar{4}31)$	8·38

★$(2\bar{2}1)_\gamma$ and $(\bar{4}31)_\alpha$ are not corresponding planes

There were a number of commercial structural steels whose microstructures would demonstrate the inadequacy of the above terminology. Such steels were used as quenched (normalized) and tempered. Their carbon content varied between 0·10 and 0·20%, but higher carbon contents were used when welding was not the critical factor. With carbon content limited to about 0·20%, such steels were known as QT series in the UK and HY series in the USA. These steels might contain 3–10% total amount of alloying elements such as manganese, chromium, nickel, molybdenum, vanadium, and titanium, the alloy type and quantity depending on strength and other properties required in various



C *Shape deformation of surface martensite; the interferogram was made with monochromatic light with a wave length 0·6µm; thanks are due to Mr P. F. Colijn for his help in obtaining this photograph*

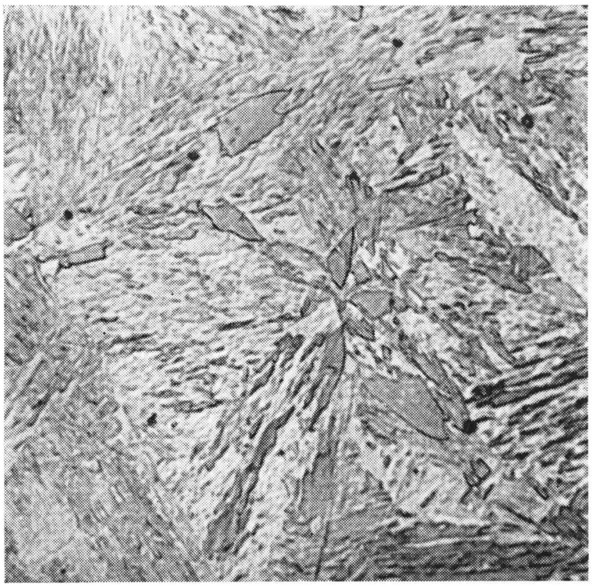


D *Plate martensite in Fe–30%Ni with a {259} habit that seems to be built up of {112} formations*

thicknesses. 9%Ni steel also belonged to this group of steels. During quenching, giving full hardening, these steels transformed to acicular microstructures. Within the prior austenite grains of these steels, martensite in plate-like form could be found, but this plate-like martensite was often *not* twinned.

The acicular plate-like martensite could be both slipped and twinned. The examples shown referred to the following heat treatment: 0·100in thick specimens were austenitized at 950°C for $\frac{1}{2}$ h and quenched in an argon stream with a rate comparable with oil quenching. The indication of the quenching rate was important, because after quenching in water the same martensite plates, which were slipped after quenching in oil, might show twinning.

Figures *E* and *F* showed representative light micrographs of martensites in 0·21%C–2%Mn and 0·20%C–7%Mn experimental alloys respectively. The incidence of the plate-like martensite morphology was similar on the microsections of both the alloys. However, electron microscopic examination revealed that the martensite in 0·21%C–2%Mn alloy was mainly untwinned, while that in 0·20%C–7%Mn alloy was nearly fully twinned.

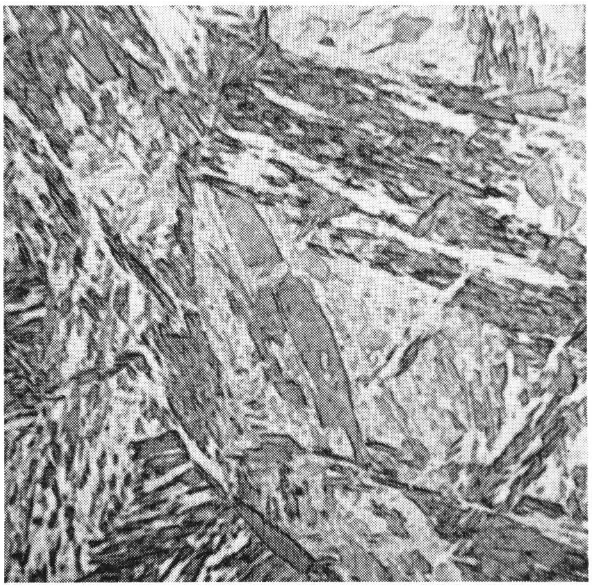


F *Acicular plate-like martensite in 0·20%C–7%Mn alloy; found to be almost fully twinned when examined in the electron microscope; hardness about 550 HV10* ×1000

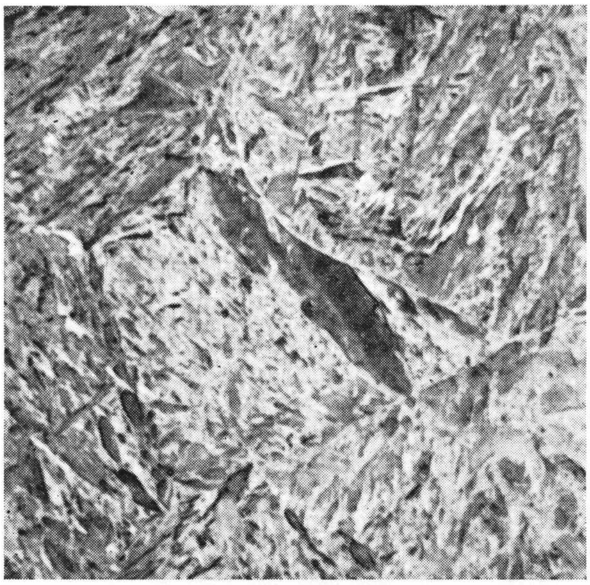
The M_s temperatures measured for these alloys during rapid heating and cooling, as in the weld heat affected zone, were 350° and 200°C respectively.

The same observations were also made on commercial steels. Figures *G* and *H* showed representative light micrographs of martensites in 0·23%C–9%Ni–4%Co and 0·38%C–9%Ni–4%Co steels. These martensites were again acicular and plate-like but the one in 0·23%C–9%Ni–4%Co steel was mainly untwinned, while that in 0·38%C–9%Ni–4%Co steel was twinned. The M_s temperatures measured for these steels, in the same manner as for the two Fe–Cr–Mn alloys, were 290° and 240°C respectively.

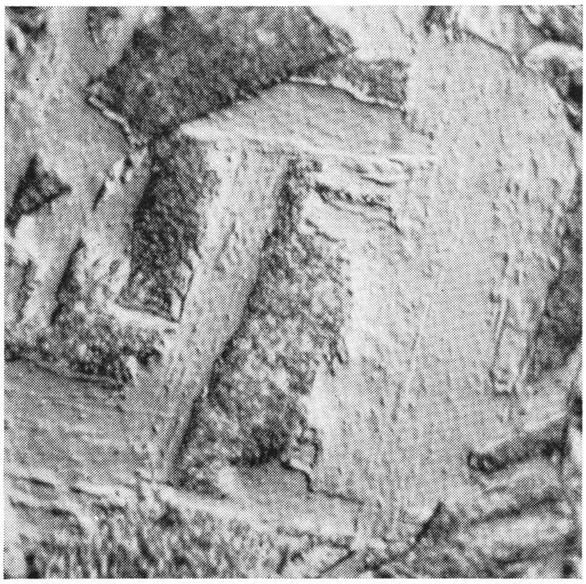
E *Acicular plate-like martensite in 0·21%C–2%Mn alloy; found to be practically untwinned when examined in the electron microscope; hardness about 450 HV10* ×1000



G *Acicular plate-like martensite in 0·23%C–9%Ni–4%Co steel; found to be mainly untwinned when examined in the electron microscope; hardness about 520 HV10* ×1000



H *Acicular plate-like martensite in 0·38%C–9%Ni–4%Co steel found to be almost fully twinned when examined in the electromicroscope; hardness about 700 HV10* ×1 000



J *Substructure within massive blocks in 18%Ni–Co–Mo steel; Nomarski contrast* ×930

This evidence indicated that martensite plates might form when the inhomogeneous shear was either by slip or twinning. Therefore, when reference was made to the geometry of martensite crystals (plates, laths, needles), one should not assume tacitly that the term 'plate martensite' was equivalent to 'twinned martensite'.

Referring the terminology to the internal structure of martensite might be more relevant, because the experience obtained so far indicated that the internal structure dominated the properties of martensite. It was, therefore, proposed to divide the acicular martensite into two groups:

(i) twinned martensite
(ii) slipped martensite (alternatively other adjectives might be used: dislocated, plain, untwinned).

This division was important in everyday metallurgical practice.

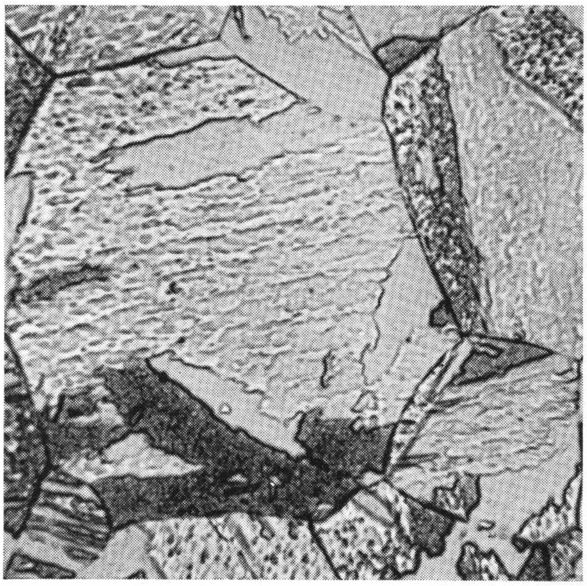
In the so-called 'massive' martensite, it was possible to reveal an elongated substructure within the blocks with the straight but jagged boundaries, at least in 18%Ni–Co–Mo steel, by etching in a reagent made of 10 g $FeCl_3$, 100 ml conc. HCl, and 100 ml alcohol. Figures *I* and *J* showed this substructure within the blocks as seen under ordinary illumination and the Nomarski contrast respectively. The 18%Ni–Co–Mo steel was austenitized at 1100°C for 15 min and quenched as indicated for the other materials.

Since the elements of the substructure in the massive blocks were elongated, they might also be referred to as acicular. Therefore, the term 'acicular' could not be used unambiguously to differentiate between the martensites in Figures *E–H* on one hand and the martensite in Figures *I* and *J* on the other hand, if the latter structures were eventually shown to be martensitic. The inadequacy of metallographic technique could not be an excuse for the term 'massive' when the acicular elements within the blocks happened to be difficult to resolve. One should, thus, consider the way the martensite crystals were arranged within the prior austenite grain. This was again quite a different criterion and, irrespective of the martensite crystal geometry or the fine internal structure, one could refer to:

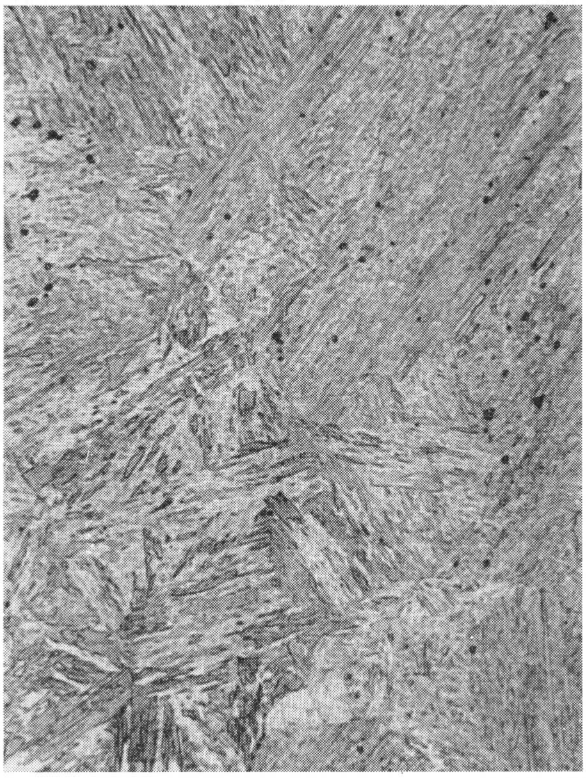
(i) multidirectional martensite colonies
(ii) unidirectional martensite colonies (crystals grown side-by-side).

It was not impossible that both plates and laths might form either multidirectional or unidirectional aggregates, and it was also not impossible that both slipped and twinned plates would be found in the two different arrangements. The real possibilities would be shown by the future research.

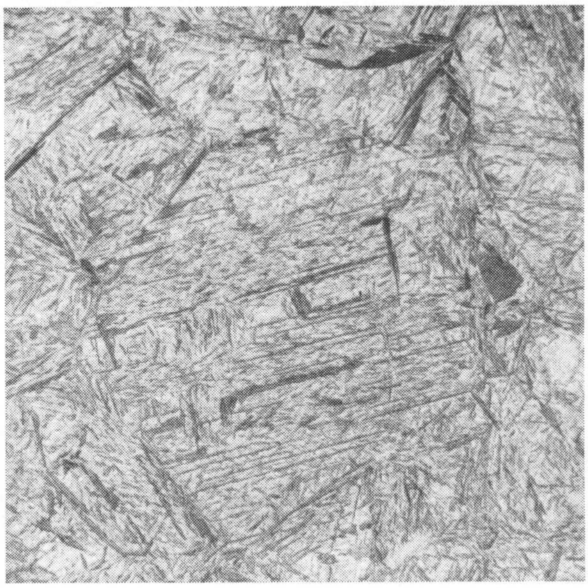
Dr Christian referred also in his paper to the toughness of martensite. This was a topic generally neglected by the academic metallurgists, while the mass of data produced by the industrial physical metallurgists was difficult to use in comprehensive generalizations. In the military transformations, kinetics, growth habit of individual crystals, and crystallographic relations between phases had been considered. But one thing which was



I *Substructure within massive blocks in 18%Ni–Co–Mo steel; ordinary illumination* ×800



K *Martensite in 0·20%C–7%Mn alloy; 0·100in thick specimen austenitized 950°C for ½ h and quenched as in oil* ×500



L *Martensite in 0·38%C–9%Ni–4%Co steel; 0·020in thick specimen heated to 1 325°C in 6 s and quenched as in oil* ×250

missed completely was what he would call, on the spur of the moment, the 'intragranular texture' of the transformation products within the prior austenite grain. To illustrate what he meant by this expression, Figure *K* showed martensite (twinned) in 0·20%C–7%Mn alloy; in the upper right hand part of the micrograph, the martensite crystals formed a large side-by-side or unidirectional colony. In the lower left hand part of the micrograph multidirectional growth could be seen. Thus, prior austenite grains could transform to martensite, the crystals of which could be arranged in various ways. It appeared that the higher the austenitizing temperature, the more unidirectional growth there was within the prior austenite grains (Figure *L*). The austenitizing temperature might affect the 'texture' of martensite within a prior austenite grain because of dissolution of various particles and annealing of dislocations. It was also possible that alloying elements would exert their effect. It was almost certain that this texture of martensite would affect its toughness because it would affect the crack propagation from one crystal to another.

One could not assess the effects of alloying elements on the toughness of martensite while disregarding the fine, internal structure of martensites. The slipped martensite was tough as-quenched, while twinned martensite was very brittle. Therefore, to examine the effect of alloying elements on martensite toughness one should work either with slipped martensites or with twinned martensites properly tempered. It would be meaningless to compare slipped martensite with twinned martensite, both in the as-quenched condition.

Dr Christian mentioned that there appeared to be some discrepancy between the effect of manganese and nickel on the stacking fault energy of austenite, and hence the type of martensite favoured, and their effects on the toughness of steel. This discrepancy could be resolved by studying martensites with similar internal structures and similar M_s temperatures. For example, in 0·21%C–2%Mn and 0·20%C–9%Ni alloys slipped martensites would form during quenching in oil, their respective M_s temperatures being 350° and 300°C. Perhaps, by adjusting the M_s temperatures more closely, the effects of manganese and nickel on the toughness of the as-quenched slipped martensites could be obtained. However, 0·20%C–7%Mn alloy, quenched as those above, transformed to twinned martensite, the M_s temperature of which was 200°C. Therefore, the comparison with the nickel-containing alloy would no longer be valid.

The information on the effect of alloying elements on the stacking fault energy in austenite had been obtained on high-alloy austenite. The application of such information to the effect of the fault energy on the type of martensite in low-alloy structural steels was dubious. It appeared that the M_s temperature might be a more critical factor in determining the internal structure of martensite crystals than the stacking fault energy of austenite.

Professor C. M. Wayman (University of Illinois) congratulated Dr Christian for doing a good job in getting the ball rolling. He said that in going over the various papers which had gone in to the make-up of the conference, he felt that perhaps a worthwhile point to make was one on morphology. That was, if possible, to establish some definitive means of distinguishing the various morphologies (i.e., 'massive' martensite v. 'ordinary' martensite in iron alloys). He did not think that calling something which was obviously a lenticular plate an acicular structure was a step in the right direction. There were clearly bona fide lenticular plates of martensite, whereas the morphology of the so-called 'massive' martensite was not yet resolved. The complicating effects of surface martensite were also not resolved, and this might add to the present confusion.

Dr L. Kaufman (ManLabs Inc.) said that he would like to comment in agreement with Dr Klostermann. Several years ago when Yeo first presented his work on 'isothermal' martensite,[1] his experiments were repeated at MIT, using resistivity measurements which measured bulk and not surface transformation. Several iron–nickel alloys were heat treated for 400 h in hydrogen (to reduce carbon to the level reported by Yeo) and then cooled. The transformations observed were bursts *and no isothermal martensite was obtained.* The feeling at that time was that Yeo's observation[1] was strongly controlled by the formation of surface martensite. The observations contributed by Dr. Klostermann to this discussion also pointed in that direction. He thought Dr Christian's point on the manganese *v.* nickel was well taken, since there was a significant difference between the effect of nickel and manganese on the stacking fault energy of iron. Thus the nature of the transformation might indeed be conditioned by the propensity of the transformation to go either to hexagonal phase first or directly to body-centred phase. At present one could not predict the path for all alloy systems. However, the day when such predictions could be made might not be very far off. He thought that the fault energy was an important variable, and could control the morphology of the daughter phases.

Dr J. W. Christian (University of Oxford), in reply, said that he had been thinking primarily of Dr Klostermann's work when he talked about surface observations. He was sure that everyone had been very impressed by the film, and he would like a chance to study the more detailed observations at leisure.

He agreed with what Dr Boniszewski said. He had realised, after reading Professor Wayman's paper, that some of the things in his general review were incorrect, and he had now been put right on one or two others. He hoped he had not confused morphology and internal structure too much. He had tried to point out that the apparent association which he had thought existed might only have been coincidental. Perhaps the best thing he could say was that he might have compared the gentleman with brown eyes with the gentleman with red hair, but at least he had not compared him with a lady with red hair. He agreed also with what Professor Wayman said, but it was rather a difficult matter. If one looked at the microstructure it was difficult to be sure without a lot of work whether crystals were acicular or lenticular. Acicular seemed to be well established in the literature as a descriptive term, without implication that the three-dimensional shape was needle-like. He would like to satisfy himself also that anything which was a three-dimensional needle was genuinely martensite, because there was some difficulty about this. Finally he wished to make a disclaimer in a general sense. Most of the things he had talked about were not his own work, and the comment on the effect of nickel and manganese on stacking fault energy was a direct quotation from something Professor Nutting had said the year before.

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Martensite transformation in terms of elastic moduli

W. D. Robertson

SYNOPSIS
A comprehensive theory of the martensite transformation would be capable of predicting the relative stability of different arrangements of atoms and the characteristics of the transformation process as a function of temperature, composition, and pressure. Needless to say, no such comprehensive theory is available at the present time. However, it is also true that some of the relevant information is not available either. It is the purpose of this paper to point out that more extensive use could be made of elastic constants in developing a more detailed theory from which predictions could be derived 2609

INTRODUCTION

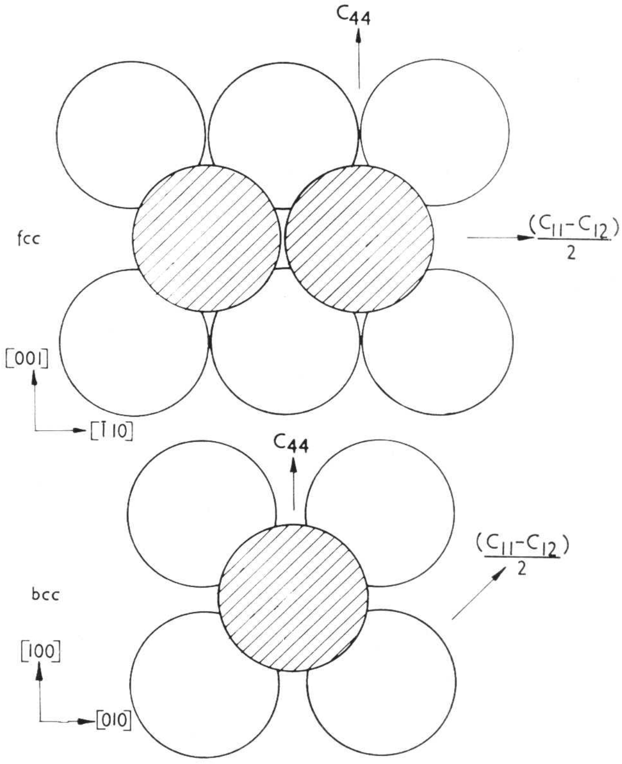
THE ELASTIC CONSTANTS of the *unstable* phase enter the problem in two ways. Firstly, they may be used as a measure of lattice instability, as Zener[1] pointed out in 1948 with respect to the bcc lattice. Secondly, they may be used to evaluate the restraint imposed on the transformation by the surrounding matrix, and thereby provide a measure of the supercooling required for the transformation to occur.[2]

ELASTIC SHEAR MODULI

The two primary moduli characterizing resistance to shear in a cubic crystal, C_{44} and $(C_{11}-C_{12})/2$, are shown schematically in Figure 1 for the fcc and bcc lattices. For both lattices it is clear that $C' = (C_{11}-C_{12})/2$ will be small relative to $C = C_{44}$, and that the ratio of the two constants C/C' is a measure of the anisotropy of the lattice. The magnitude of the constants will define the vibration amplitude in each direction and therefore the vibrational entropy which contributes to stabilizing the lattice at high temperatures.[1]

All the data that are available for unstable cubic lattices that transform spontaneously to another lattice as the temperature decreases are collected in Table I. The elastic constants are given for the temperature of the transformation, or as close to that temperature as measurements have been made. Considering the significance of the constants with respect to the mechanism of the transformation, the amount of information available seems to be remarkably small. No example has been found of a transformation for which the constants have been measured for both phases.

The values in Table I for γ-iron (fcc) have been obtained by extrapolation of the data for iron–nickel alloys,[16] as shown in Figure 2. The data refer to room temperature, and accordingly



1 *Schematic diagram of shear constants C_{44} and $(C_{11}-C_{12})/2$ for the bcc and fcc lattices*

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